

# ECTP 21<sup>st</sup>

European Conference on Thermophysical Properties

September 3 - 8, 2017 Graz University of Technology, Graz, Austria

# **Book of Abstracts**

& Program

### Impressum

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### **ABOUT THE CONFERENCE**

The European Conference on Thermophysical Properties is held in a three-year cycle that includes the Asian Thermophysical Properties Conference and the American Symposium on Thermophysical Properties. All the European conferences are listed in the table below:

1	ECTP	1986	Nov. 11-13	Baden-Baden	Germany	E. Fitzer
2	ECTP	1970	Apr. 7-10	Salford	UK	A. Stuckes
3	ECTP	1972	Jun. 20-23	Turin	Italy	G. Ruffino
4	ECTP	1974	Sep. 4-6	Orleans	France	F. Cabannes
5	ECTP	1976	May 18-21	Moscow	USSR	A.E. Sheindlin
6	ECTP	1978	Jul. 26-30	Dubrovnik	Yugoslavia	K. Maglic
7	ECTP	1980	Jun. 30-Jul. 4	Antwerpen	Belgium	R. de Coninck
8	ECTP	1982	Sep. 27-Oct. 1	Baden-Baden	Germany	HE. Schmidt
9	ECTP	1984	Sep. 17-21	Manchester	UK	R. Taylor
10	ECTP	1986	Sep. 22-26	Rome	Italy	G. Ruffino
11	ECTP	1988	Jun. 13-16	Umea	Sweden	G. Backstrom
12	ECTP	1990	Sep. 24-28	Vienna	Austria	W. Neumann
13	ECTP	1993	Aug. 30-Sep. 3	Lisbon	Portugal	C.A. Nieto de Castro
14	ECTP	1996	Sep. 16-19	Lyon	France	J.F. Sacadura
15	ECTP	1999	Sep. 5-9	Würzburg	Germany	J. Fricke
16	ECTP	2002	Sep. 1-4	London	UK	W.A. Wakeham
17	ECTP	2005	Sep. 5-8	Bratislava	Slovakia	L. Kubicar
18	ECTP	2008	Aug. 31-Sep. 4	Pau	France	JL. Daridon
19	ECTP	2011	Aug. 28-Sep. 1	Thessaloniki	Greece	M.J. Assael
20	ECTP	2014	Aug. 31-Sep. 4	Porto	Portugal	L.Santos, J. Coutinho
21	ECTP	2017	Sep. 3-8	Graz	Austria	G. Pottlacher
22	ECTP	2020	Sep. 14-17	Venice	Italy	A. Muscio

For more information please visit:

http://www.thermophysicalpropertiesconferences.com/
european-conference-on-thermophysical-properties/

The 21<sup>st</sup> European Conference is organized by the Group of Thermophysics and Metal Physics of the Institute of Experimental Physics at Graz University of Technology, with the help of ÖGI Leoben and of AIT, Vienna.

The objective of the conference is to provide a forum for academic and industrial researchers to meet and exchange valuable experiences in the field of thermophysical properties for a wide variety of systems covering fluids and solids. The conference will concentrate mainly on measurement, theory and modeling of the following properties and materials.

**Properties:** thermal conductivity, diffusivity, electrical conductivity, viscosity and non-Newtonian properties, mass-diffusion and thermo-diffusion, optical and radiative properties including emissivity, reflectivity and absorptivity, solubility, phase equilibrium including liquid - solid, calorimetric and volumetric properties, speed of sound, interfacial properties including solid-solid and wettability....

**Materials:** metals and alloys, ceramics, glasses, composites, multi-functional materials, superconductors, insulation materials, porous materials, granular and thin-film materials, foams, gels, emulsions, soft materials, nano-materials, near critical and super-critical fluids, polymers, food and biomaterials, environmentally friendly fluids, aqueous systems, petroleum fluids, ionic liquids, molten salts,...

**Special focus on:** measuring techniques (including methodology of data evaluation and prediction) and engineering applications (polymerization, casting, sintering, plasma spraying, distillation, refrigerant techniques, thermoelectric cooling, insulation structures in civil engineering), standard data and standard substances.

This conference will include plenary and invited lectures, oral presentations, poster sessions and discussion sessions on specialized topics. Both the ECTP Award for Lifetime Achievements and the NETZSCH Young Scientist Award will be presented during this event.

### COMMITTEES

### International Organizing Committee

Prof. Marc J. Assael, Prof. Jean-Luc Daridon Prof. Josefa Fernandez Prof. Jochen Fricke Dr. Wolfgang Hohenauer Dr. Igor Medved Prof. Alberto Muscio Prof. Carlos Nieto de Castro Dr. Francesco Righini Prof. Luis Santos Prof. Zhang Xing Prof. Jean Christophe **Batsale** Dr. Hans-Peter **Ebert** Prof. V. E. **Fortov** Prof. Hiroyuki **Fukuyama** Prof. Andreas **Mandelis** Dr. Nenad **Milosevic** Prof. Akira **Nagashima** Prof. Gernot **Pottlacher** Prof. Jean-Francois **Sacadura** Prof. Sir William A. **Wakeham** 

### Local Organizing Committee

Prof. Gernot **Pottlacher** (Chair) Reinhard **Dämon** Alexandra **Frei** Bettina **Gsöls-Bedenik** Dr. Wolfgang **Hohenauer** Ass. Prof. Markus **Koch** Matthias **Leitner** Dr. Joe W. **Magee** Josef **Pichler** Dr. Alexander **Schmon** 

Alexander Gruber Andreas Jeindl Sebastian Riepl Marco Wieser Sandra **Brunner** Prof. Wolfgang E. **Ernst** Josef **Friedrich** Ass. Prof. Andreas **Hauser**, Dr. Erhard **Kaschnitz** Dr. Roland **Lammegger** Thomas **Leitner** Prof. Theo **Neger** Peter **Pichler Uwe Seidl** 

Moritz Hackhofer Florian Kametriser David Sorger

### **CONFERENCE INFORMATION**

### **Conference site**

Graz University of Technology, Petersgasse 16, 8010 Graz, Austria ("Physics Building")



Figure 1. Conference site.

### 4-day ticket for public transportation

Upon registration at the conference website, you will get a 4 day ticket for public transport. It will be valid for 4 days after the first use. On your first travel you will have **to validate this new ticket**. Please note that **parking space is very limited** at the campus and therefore we encourage you to use public transportation.

https://ectp2017.tugraz.at/files/transport%20network%20graz.pdf

### **Registration and Welcome reception**

Sunday, 3<sup>rd</sup> September, 17-21 h. Location: ground floor of the physics building. There will be signs to take you to the registration desk.

### **Conference office/Registration**

Located on the ground floor, to be accessed through the entrance of the Institute of Experimental Physics. The conference office is open on Sunday, September 3, from 17 - 19 h, Monday to Thursday (September 3 - 7) from 8 - 11 h. Please note that at the registration desk only a cash payment is possible.

You will get at registration the usual conference giveaways such as a fabric bag, pen and paper block. Further you nametag, an USB stick including the Book of Abstracts, a paperback copy of the Book of Abstracts and advertising material. For all activities please have your nametag well visible with you!

Outside these hours, help by the conference team is available at the secretarial office of the institute opposite the conference office.

### **Preliminary program**

A tentative program is given at https://ectp2017.tugraz.at/files/ECTP-schedule.pdf. Please always check the most recent version.

### Locations for lectures

Lectures are held in the phyics building of Graz University of Technology in Petersgasse 16 (HS P1, HS P2 and HS PHG016) and in HS BMT and HS BE01 in the neighboring buildings (see Figure 1). Due to the large number of proposed oral presentations, there are 5 parallel sessions.

### Guidelines for oral lectures and poster contributions

### **Oral lectures**

For the different categories of lectures the available times are given below.

Plenary:	40 minutes + 5 minutes discussion.
Invited:	25 minutes + 5 minutes discussion.
Young scientist award:	20 minutes + 5 minutes discussion.
Oral contribution:	15 minutes + 5 minutes discussion.

The time for oral contributions will be strictly limited to 15 minutes for the presentation and 5 minutes for discussion!

Please note that all speakers are responsible to use only such slides where they have the copyright. Also note that other attendees might take pictures of your presentation.

As we want to encourage discussion, we ask you to keep to the allotted time. In relation to the large number of parallel presentations, Session Chairs will strictly enforce timing. Chairpersons are asked to be seated not later than 5 minutes before their session starts. We ask the chairpersons to ensure that all presentations start and finish punctually as scheduled. The conference staff will assist with timing.

Please upload your talk (PowerPoint presentation) from an USB-stick before the session to the computer in the lecture hall. All the lecture halls are equipped with a projector, computer and a pointer. Our staff will be there to assist you. In case you want to present with your own computer, especially with apple computers, please assure that you have all the appropriate connections with you. Our projectors have VGA and HDMI input (see Figure 2). If you plan to present videos within you presentation, please assure that it will be "Windows Media Video" format (wmv - format - \*.wmv datei) and embedded within your PowerPoint presentation.



Figure 2. Power outlet in Austria, VGA IN and HDMI IN (from left.)

### Poster sessions

Posters must be mounted at the beginning of the conference and taken off at the end of the conference. All the posters will be displayed within the three story atrium with a glass roof (a map for the location of posters will be provided). Attendees will be encouraged to look at the posters during two specific poster sessions, one on Monday and the other on Tuesday. Material to fix your poster like adhesive tape or pins will be provided by the organizers.

The poster format has to be A1 (594 mm width  $\times$  841 mm height) !

### Further important informations

### Lunch and coffee

Lunch will be organized buffet style in the foyer of HS P2 and in a tent in front of the physics building. Coffee will be served on the first floor in front of the lecture hall HS P1.

### Exhibition

It will be held every day in front of lecture hall HS P1.

#### Internet access

Wlan-based internet access is available in all areas of the physics building. User IDs and passwords will be provided. At TU-Graz EURODAM is available.

### **Book of Abstracts**

Upon registration you will get the Book of Abstracts stored on an USB-stick together with the nametag, as well as a paperback hardcopy.

### City Walk and Castle Eggenberg

Wednesday afternoon guided city tours and guided tours to Castle Eggenberg are offered. Use the conference provided public transport card to reach the different locations. Please register for the different tours in the conference office.

### Conference dinner on Wednesday evening

Everyone is welcome at the conference dinner in the Grazer Congress Stephaniensaal (Sparkassenplatz 1, 8010 Graz) on Wednesday evening at 19:00 hours. The Lifetime Award presentation will take place during the dinner. Do not miss it!

### Publication of your presented papers

Following ECTP21<sup>st</sup>, authors of all papers are encouraged to submit their contribution for publication in special proceeding issues of the following mainstream journals:

### **International Journal of Thermophysics**

### **High Temperatures - High Pressures**

### Journal of Chemical and Engineering Data

It is up to the authors, to choose to which journal they want to submit their contribution. However, in order to have coherent and consistent special issues, the Organizing Committee will advise the authors that some specific sessions ask authors to submit preferably to one or the other journal with respect to the upcoming program.

When sending your manuscript to a journal please mention that it has been presented at ECTP21<sup>st</sup>, as agreed with the respective journal editors. The manuscript will undergo the normal peer review and this process is quite separate from presenting your paper at ECTP21<sup>st</sup>. It is the author's responsibility to submit his or her manuscript directly to the journal and this can be done as soon as possible after the conference and no later than 15<sup>th</sup> October 2017. When submitting your manuscript please ensure that:

The subject matter is within the scope of the respective journal and that the manuscript contains a sufficient amount of new (unpublished) results. Make sure to comply with the style of the journal to which you submit your manuscript.

The guide for authors for the respective journals is obtainable from the following websites:

### International Journal of Thermophysics

http://www.springer.com/materials/journal/10765

### High Temperatures - High Pressures

http://www.oldcitypublishing.com/journals/hthp-home/ hthp-notes-for-contributors/

### Journal of Chemical and Engineering Data

http://pubs.acs.org/page/jceaax/submission/index.html

## FLOOR PLANS AND LOCATIONS OF LECTURE HALLS







## TIMETABLES

Saturday 02	2.09.							
Room: HS PHEG016								
09:00 - 16:00	Satellite Meetings							
Sunday 02								
sunday 03.0	09.							
	Room: HS PHEG016							
09:00 - 17:00	IAPT Meeting (members only)							
	Room: PHEG108							
17:00	Registration Desk opens							
	Room: Ground Floor							
18:00 - 21:00	Welcome Reception							

## Monday 04.09.

			Room	: PHEG108		
08:00 - 09:00	Registration					
			Roo	m: HS P1		
09:00 - 09:30			Openin	g Ceremony	/	
			Roo	m: HS P1		
09:30 - 10:15		Plen	ary Lectu	re: Christof	Gaiser	
			( M.	Chair: Assael		
	D				Poom: US P	)
	Invi	ted Speaker			Invited Speal	<u>·</u> <er< td=""></er<>
10:15 - 10:45	Mi	chal Fulem			Hiroyuki Shibo	ata
	J	Chair: J. L. Daridon			Chair: E. Kaschnitz	
10.45 11.05						
10:45 - 11:05			C	offee		
	Room: HS P1	Room: HS P2	Room	: HS BEO1	Room: HS PHEG016	Room: HS BMT
	Oral Session 1	Oral Session 1	Oral S	Session 1	Oral Session 1	Oral Session 1
11.05 13.05	Nanofluids and Liquid Metals	Solids and Properties Solids	Theo Mo	ory and delling	Thermal Insulation	Standarddata and Standard Materials
11.03 - 13.03						
	<u>Oh sin</u>	Obain			Chair	Chair
	W. Wakeham	M. Fulem	Chair: D. Laaer		J. R. Filtz	B. Wilthan
	C. N. de Castro G. Pottlacher P. Burgholzer K. Kroenlein					K. Kroenlein
13:00 - 14:15	Lunch Buffet					
		R	oom: Thre	e Storey Atri	Jm	
14:15 - 15:30			Posters	and Coffee		

	Room: HS P1	Room: HS P2	Room: HS BE01	Room: HS PHEG016	Room: HS BMT
15:30 - 18:10	Oral Session 2 Fluids Systems - Measurement and Models	Oral Session 2 Properties for Materials Science at High Temperatures I	Oral Session 2 Theory and Modelling II	Oral Session 2 Phase Equilibria I	Oral Session 2 Ionic Liquids and Properties of Ionic Liquids I
	Chair: M. Richter V. Vesovic	Chair: D. Matson G. Pottlacher	Chair: N. Milošević R. Kovacs	Chair: M. Monte	Chair: L. Santos M. Shiflett

## Tuesday 05.09.

	Room: PHEG108					
08:00 - 09:00	Registration					
	R	oom: HS P1			Room: HS P2	2
09:00 - 09:30	Invi Manı	ted Speaker J <b>el J. S. Monte</b>			Invited Spea Douglas M. Ma	ker a <b>tson</b>
		Chair: M. Huber			Chair: I. Egry	
	R	oom: HS P1			Room: HS P2	2
09:30 -10:00	Invi <b>Ma</b>	ted Speaker I <b>rk B. Shiflett</b>			Invited Spea Boris Wiltha	ker n
		Chair: M. Huber	Chair: I. Egry			
10:00 - 10:20	Coffee					
	Room: HS P1	Room: HS P2	Room:	HS BE01	Room: HS PHEG016	Room: HS BMT
	Oral Session 3	Oral Session 3	Oral Se	ession 3	Oral Session 3	Oral Session 3
	Energy and Fuels	Properties for	Instrumer	ntation and	Phase Equilibria	lonic Liquids and
10:20 - 13:00		at High	Mea Tech	suring niques	Ш	Properties of Ionic Liquids
		Temperatures				
		Ш				
L	Chair: S. Lago E. Hassel	Chair: H. Shibata G. Pottlacher	Chair: H. P. Ebert G. Lohöfer		Chair: A. Bazyleva M. McLinden	Chair: L. Santos M. Shiflett
		·	·			·
13:00 - 14:15	Lunch Buffet					

	Room: Three Storey Atrium
14:15 - 15:30	Posters and Coffee

	Room: HS P1	Room: HS P2	Room: HS BE01	Room: HS PHEG016	Room: HS BMT
15:30 - 18:10	Oral Session 4 Aqueous Systems	Oral Session 4 Properties for Materials Science at High Temperatures III	Oral Session 4 Instrumentation and Measuring Techniques II	Oral Session 4 Phase Equilibria III	Oral Session 4 Materials
	Chair: A. Ribeiro G. Hefter	Chair: H. Fukuyama G. Pottlacher	Chair: C. Gaiser C. Glorieux	Chair: C. Rathgeber J. Oliveira	Chair: M. Rohde H. Mehling

## Wednesday 06.09



09:45 - 10:05

Coffee

	Room: HS P1	Room: HS P2	Room: HS BE01	Room: HS PHEG016	Room: HS BMT
10:05 - 13:05	Oral Session 5 Transport Phenomena	Oral Session 5 Emittance, Emissivity	Oral Session 5 Instrumentation and Measuring Techniques III	Oral Session 5 Engeneering Applications	Oral Session 5 Nanomaterials
	Chair: A. Fröba V. Shevtsova	Chair: J. Hartmann K. Boboridis	Chair: S. Vidi K. Anhalt	Chair: L. Mitterhuber R. Černý	Chair: W. Sprengel

13:00 - 14:15
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14:15 -17:00	Citywalk, Castle Eggenberg, see the Clocktower before the Conference Dinner (Please register for the different tours in the conference office)
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	Room: Stefaniensaal
19:00 - 22:00	Conference Dinner & Lifetime Award

Thursday 07	.09.				
	Room: PHEG108				
08:00 - 09:00	Registration				
09:00 - 09:45	Room: HS PI Plenary Lecture: <b>Wolfgang Schützenhöfer</b>				
	Chair: A. Muscio				
	Room: HS P1				
09:45 - 10:10	Young Scientist Award				
	Chair: G. Pottlacher				
10:10 - 10:30			Coffee		
	Room: HS P1	Room: HS P2	Room: HS BE01	Room: HS PHECO16	Room: HS BMT
	Oral Session 6		Oral Session 6	Oral Session 6	
10:30 - 12:50	Alternative Refrigerants	New Measuring Techniques	Equation of State	Optical and Thermal Radiative Properties	Photothermal and Photoacoustics Thermophysical Properties
	Chair: S. Bobbo Y. Kano	Chair: J. Blumm	Chair: W. Schröer	Chair: K. Boboridis B. Wilthan	Chair: A. Mandelis
	Room: HS P1				

	Room: HS P1
12:50 - 13:15	Closing Ceremony
	Chair: A. Muscio G. Pottlacher

13:15 -14:30	Lunch Buffet			
	Room: HS PHEG016			
14:15 - 18:00	Satellite Meetings			

## Friday 08.09.

	Room: HS PHEG016
09:00 -12:00	Satellite Meetings

### LIST OF EXHIBITORS

### Erich NETZSCH GmbH & Co. Holding KG Gebrüder-Netzsch-Straße 19 95100 Selb

### **LINSEIS Messgeräte GmbH** Vielitzerstr. 43 95100 Selb Germany

### Ing. Prager Elektronik HandelsGmbH.

Traunstrasse 21 2120 Wolkersdorf Austria

Germany

### **TA Instruments Corporate Headquarters**

159 Lukens Drive New Castle, DE 19720 USA

### L+H Vakuumtechnik Vertriebsges.m.b.H.

Zetschegasse 21 1230 Wien Austria

### **Hot Disk AB** Sven Hultins gata 9A 412 58 Göteborg Sweden

### Firma Herwitec

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### Anton Paar GmbH

Anton-Paar-Str. 20 8054 Graz Austria

Germany

AIT Austrian Institute of Technology GmbH Donau-City-Straße 1 1220 Vienna Austria

### **Springer Customer Service Center GmbH** Tiergartenstrasse 15-17 69121 Heidelberg

### **PLENARY LECTURES**

### **Christof Gaiser**

Physikalisch-Technische Bundesanstalt, Institut Berlin, Germany



Christof Gaiser received his diploma degree in physics at the "Humboldt-Universität zu Berlin" in the field of optical and electrical properties of semiconductors in 2003. Since 2004 he is with the Physikalisch-Technische Bundesanstalt (PTB) in Berlin and received his doctor degree in 2008 in physics in the field of thermophysical properties of helium at low temperatures and gas thermometry. Since 2007 he has been leading the project dedicated to the determination of the Boltzmann constant as basis for redefining the base unit kelvin. The so called dielectric-constant gas thermometry was used for this determination. This method combines different disciplines in physics ranging from properties of solids to gas properties and from pressure measurement to measurement of electrical units. All

of these properties have to be measured together on the metrological top level, which made this work a challenge. The successful end of the project allows now for a new definition of the kelvin in 2018. The fields of his future work are thermophysical properties of gases and noise thermometry for the realization of the new kelvin.

#### Plenary Lecture – 1 9:30 - 10:15 Monday

Room HS P1

Chair: M. Assael

### THE "NEW SI" – TEMPERATURE AND THE BOLTZMANN CONSTANT

C. Gaiser

*Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany* christof.gaiser@ptb.de

The International System of Units, the SI, is a coherent system of units for use through-out science and technology. Since the establishment of the SI in 1960, extraordinary advances have been made in linking SI units to invariant quantities such as fundamental constants of physics and properties of atoms. Recognizing the importance of such linking, in the "New SI", which will come into force in 2019, further four of the base units - namely the kilogram, the ampere, the mole and the kelvin - will be redefined in terms of fundamental constants. The new definitions will be based on fixed numerical values of the Planck constant h, the elementary charge e, the Avogadro constant  $N_A$ , and the Boltzmann constant k. The effect of the new definition of the kelvin is that one kelvin is equal to the change of thermodynamic temperature T resulting in a change of thermal energy kT by  $1.3806XXX \times 10^{23}$  J. It implies the equivalence of mechanical and thermal energy. Thus, k is simply the conversion factor between energy and temperature. As basis for fixing the value of k, since several years projects have been underway to measure independently k developing acoustic and

dielectric-constant gas thermometry, Doppler-broadening spectroscopy, and Johnson noise thermometry.<sup>1</sup> The progress achieved and the consequences of the new definition of the kelvin will be discussed. Special emphasis will be given to dielectric-constant gas thermometry performed at PTB and the astonishing relation to Ludwig Boltzmann's experimental work.

### References

[1] B. Fellmuth, C.Gaiser, J.Fischer., Meas. Sci. Technol. 17, R145 (2006)

### **Andreas Mandelis**

Center for Advanced Diffusion-Wave and Photoacoustic Technologies (CADIPT), Department of Mechanical and Industrial Engineering, University of Toronto, Toronto Canada



Andreas Mandelis is a Full Professor of Mechanical and Industrial Engineering; Electrical and Computer Engineering; and the Institute of Biomaterials and Biomedical Engineering, University of Toronto. He is the Canada Research Chair in Diffusion-Wave and Photoacoustic Sciences and Technologies and Director of the Center for Advanced Diffusion-Wave Technologies (CADIFT) at the University of Toronto. He received his BS degree (Magna cum Laude) in physics from Yale University, and MA, MSE, and Ph.D. degrees from the Applied Physics and Materials Laboratory, Princeton University. He is the author and co-author of more than 380 scientific papers in refereed journals and 190 scientific and technical proceedings papers. He is Editor-in-Chief of the Springer International Journal of Thermophysics, an Associate Editor of the AIP Journals Review of Scientific Instruments, Journal of Applied

Physics, Topical Editor of the OSA Journal Optics Letters, and he is on the editorial board of the SPIE Journal of Biomedical Optics. He is Consulting Editor of the AIP flagship magazine Physics Today. He has several inventions, 38 patents and patents pending in the areas of photothermal tomographic imaging, signal processing and measurement, hydrogen sensors, dental laser diagnostics (biothermophotonics), semiconductor laser infrared photothermal radiometry, laser photo-carrier radiometry and laser biophotoacoustic tissue imaging. He holds the Canada Research Chair (Tier 1) in Diffusion-Wave and Photoacoustic Sciences and Technologies at the University of Toronto. He is also a National 1000-Talents Professor at the University of Electronic Science and Technology of China in Chengdu.

Professor Mandelis has received numerous national and international prizes and awards including the APS Keithley Award in Instrumentation Science, the Discovery Award in Science and Engineering (the Ontario Premier's Innovation Award), the ASME 2009 Yeram Touloukian Award (and Medal) in Thermophysics, the Senior Prize of the International Photoacoustic and Photothermal Association, the Canadian Association of Physicists (CAP) Medal for Outstanding Achievement in Industrial and Applied Physics and the CAP-INO Medal for Outstanding Achievement in Applied Photonics. In 2014 he was elected Killam laureate, recipient of the Killam Prize in Engineering, Canada's highest academic prize awarded annually by the Governor General of Canada. Chair: W. Wakeham

### PHOTOTHERMAL COHERENCE TOMOGRAPHY: PRINCIPLES AND APPLICATIONS OF A NEW THERMOPHYSICS-BASED THREE-DIMENSIONAL IMAGING METHODOLOGY

Andreas Mandelis

*Center for Advanced Diffusion-Wave and Photoacoustic Technologies (CADIPT), Dept. of Mechanical and Industrial Engineering, Univ. of Toronto, Toronto M5S3G8, Canada* 

Energy transport in diffusion-wave fields is gradient driven and therefore diffuse, yielding depth-integrated responses with poor axial resolution. Traditional diffusion-wave techniques, controlled by the physics of parabolic diffusion and depth-limited by the thermal diffusivity, can only produce depth-integrated planar images as they are unable to generate depth-resolved three-dimensional subsurface imaging. This talk will present a new imaging method developed in the CADIPT for enabling parabolic thermal-wave fields to exhibit energy localization akin to propagating hyperbolic wave-fields like ultrasound. This approach when used with a mid-IR camera results in *depth-selective* (or depth-resolved) photothermal imaging that not only improves axial resolution allowing for deconvolution of individual responses to superposed axial source distributions (tomography), but also greatly enhances depth range thereby opening a new dynamic imaging field of subsurface Photothermal Coherence Tomography (PCT) using thermal waves. The talk will present the physical principles of Truncated-Correlation Photothermal Coherence Tomography (TC-PCT) and examples of applications to engineering materials non-destructive imaging, dental caries diagnosis, and biomedical imaging of tissues.

### Wolfgang Schützenhöfer

Department testing laboratories, BÖHLER Edelstahl GmbH & Co KG, Kapfenberg, Austria



Wolfgang Schuetzenhoefer is manager of ISO 17025 accreditated laboratories at Böhler Edelstahl GmbH & Co KG in Kapfenberg, Austria. He received his master degree in metallurgy from University of Leoben, his Ph.D. degree from steel metallurgy from University of Leoben. He is the author and co-author of approx. 90 scientific papers in refereed journals and scientific and technical proceedings papers. He is a free peer reviewer for Metallurgical and Materials Transactions B and invited peer reviewer for International Journal of Thermophysics. Formerly he was University Assistant at the Chair of Ferrous Metallurgy at the University of Leoben. At Böhler Edelstahl he started with numerical simulation of different production processes such as heat treatment, remelting technologies and casting processes. He has been innovation manager for more than 4 years. Additionally he is lecturer at the University for Applied Sciences Upper Austria for "Heat

Treatment Simulation" and ISO 17025-Auditor for metal testing for the Austrian Federal Ministry of Science, Research and Economy.

Dr. Schützenhöfer has received the international awards for the best paper at the "International Conference on Liquid Metals Processing and Casting" and the "Hans Malzacher Prize" for outstanding activities in the metallurgy of ASMET (Austrian Society for Metallurgy and Materials).

Plenary Lecture – 3 9:00 - 9:45 Thursday

Room HS P1

Chair: A. Muscio

## NUMERICAL SIMULATION AS AN OPTIMIZATION TOOL AT A SPECIAL STEEL PRODUCER (BÖHLER EDELSTAHL)

W. Schützenhöfer, V. Wieser, M. Magritzer, A. Bruggraber, B. Tian and M. Hafok

Böhler Edelstahl GmbH & Co KG, Kapfenberg, Austria Wolfgang.Schuetzenhoefer@bohler-edelstahl.at

Böhler Edelstahl is a leading special steel producer in the world. The keys to this are excellent products on one side and technology leadership on the other side. To reach this, newest production facilities, process development and permanent process optimizations are important requirements.

The keynote presentation shows processes for the production of special steel and nickel base alloys. The processes consist of melting, casting, remelting, powder production, hot forming, heat treatment and testing. The process development, a branch of the R&D department, works with physical and numerical/mathematical simulation to establish new processes and to improve conventional ones.

The overview of the whole production processes is followed by some examples of numerical/mathematical simulation using finite element methods, finite difference methods, thermodynamic models and models based on computational fluid dynamics. Answers to following question are given:

- What should be optimised in different processes?
- Which material data are used for the simulation models?
- How precise are the measured data and which significant influence do they have on the results?
- How precise are the results of the simulation models compared to results of experiments?

The presentation sum up with conclusions and an outlook to further projects.

### **INVITED LECTURES**

#### **Michal Fulem**

Department of Physical Chemistry, University of Chemistry and Technology, Prague, Czech Republic



Michal Fulem is an Associated Professor at the Department of Physical Chemistry at the Faculty of Chemical Engineering at the University of Chemistry and Technology, Prague (UCT Prague). He received his MS degree in Analytical and Physical Chemistry in 2000 and Ph.D. degree in Physical Chemistry in 2004 from UCT Prague. He then went on to do postdoctoral studies at the University of Porto, Portugal (with Prof. M. J. S. Monte and Prof. L. M. N. B. F. Santos, 2005-2006) and the University of Alberta, Canada (with Prof. John M. Shaw, 2006-2008) and for short-term stays at NIST, USA as a guest researcher (with Dr. Robert F. Berg, 2010-2012). He is the author and co-author of more than 60 scientific papers in refereed journals. His research interests focus mainly on the study of phase behavior and thermophysical properties of organic and organometallic compounds by both experimental and theoretical methods (using electronic structure and statistical thermo-

dynamics calculations), development of experimental set-ups and methodologies, and chemical thermodynamics. Michal Fulem has received several national and international awards among which the IACT Doctorate Award for excellence in thermodynamics (2006) and the Award of Ministry of Education, Youth and Physical Education of the Czech Republic (2004) can be mentioned.

 Invited Lecture – 1
 10:15 - 10:45
 Monday

 Chair: J. L. Daridon
 10:15 - 10:45
 Monday

Room HS P1

## THERMODYNAMIC PROPERTIES AND PHASE BEHAVIOR OF MOLECULAR CRYSTALS - THEORY AND EXPERIMENT HAND IN HAND

M. Fulem

Department of Physical Chemistry, University of Chemistry and Technology, Prague, Technickáa 5, 166 28 Prague 6, Czech Republic fulemm@vscht.cz

A knowledge of thermodynamic properties and phase stability of molecular crystals is indispensable in many applications including crystal engineering, polymorph screening in pharmaceutical research, environmental modeling, etc. As experimental determinations can never keep pace with data demand in these areas (for example, the number of compounds with available data on sublimation equilibrium is estimated to be around 1000), the ability to reliably predict thermodynamic data and phase stability of molecular crystals is of utmost importance. In addition, the theoretical methodologies may find use in cases when experimental

determinations are extremely difficult or even not feasible, as for example the measurements of sublimation pressure and enthalpy of extremely low volatile compounds.

In this contribution, an overview of the current possibilities of first-principles approaches to predict thermodynamic data as a function of temperature and phase diagrams for molecular crystals with a special focus on the sublimation equilibrium is given. The performance of computational methodologies is demonstrated based on several benchmark studies performed in our laboratory. An inherent part of such studies is the development of reference experimental data with low uncertainties as they set the error bars of the theoretical calculations and play thus an important role in testing and evaluating the performance of various computational approaches. Therefore, recent activities of our research group in the development of critically assessed reference thermodynamic data for molecular crystals are also presented.

### Hiroyuki Shibata

IMRAM, Tohoku University, Sendai, Japan



Hiroyuki Shibata is a Full Professor of the Institute of Multidisciplinary Research for Advanced Materials, Tohoku University. He received his BS degree in material science and engineering from Tohoku University, and Master and Dr.Eng. degrees from Tohoku University. He is the author and co-author of more than 120 scientific papers in refereed journals. He is an Associate Editor of High temperature materials and processes and he is on the editorial board of ISIJ International, the iron and steel institute of Japan. Professor Shibata has received several national and international prizes and awards including the best paper prizes in the iron and steel institute of Japan and John-Chipman Award (Iron and Steel Society in U.S.A).

Invited Lecture – 210:15 - 10:45MondayChair: E. Kaschnitz

Room HS P2

## THERMAL DIFFUSIVITY MEASUREMENT FOR METALIC AND OXIDE GLASSES USING A LASER FLASH METHOD

H. Shibata<sup>1</sup>, S. Sukenaga<sup>1</sup>, T. Nishi<sup>2</sup>, and H. Ohta<sup>2</sup>

<sup>1</sup>*Institute of Multidisciplinary Research for Advanced Materials, Tohoku University, Sendai, Japan* <sup>2</sup>*Department of Mater. Sci. and Eng., Ibaraki University, Hitachi, Japan* shibata@tagen.tohoku.ac.jp

Thermal diffusivity and conductivity values of molten materials at elevated temperatures are required to elucidate the metal production processes, such as continuous casting, welding, and refining by developing computer simulation models. In such numerical simulation, the thermal diffusivity and thermal conductivity values of molten materials are essentially required. However, the available thermal transport properties of materials in the molten state are very limited because of the experimental difficulties at high temperature, within the best knowledge of the present authors.

A laser flash method is recognized as a versatile technique for measuring thermal diffusivity of various materials. This laser flash method was originally developed for measuring thermal diffusivity of solid sample. A front surface of a disk shaped sample is instantaneously irradiated by a laser pulse. The resultant temperature response of the back surface of the disk is measured as a function of time. The measured temperature response curve is used to estimate thermal diffusivity of the sample. We have proposed novel techniques to measure thermal diffusivity of molten metals and oxides based on the laser flash technique. The unique sample cell was developed for measurement of the molten metals, and a front heating-front detection laser flash technique was also developed to measure thermal diffusivity of molten oxides. The main purpose of the present paper is to introduce the developed techniques and the obtained results for the molten materials, metallic glasses and oxide glasses such as Pd based alloys, Zr based alloys and silicate glasses. Then, the heat transfer mechanism will be discussed of the materials in the molten state.

### Manuel J. Monte

Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Porto, Portugal



Manuel J. S. Monte is Associate Professor of Department of Chemistry and Biochemistry of the Faculty of Science of University of Porto (FCUP). He was member of the first General Board of the University (2009-2013), Head of the Department of Chemistry (2006-2007) member of the Scientific Board of FCUP since 2006, and he is Vice-Chairman of the Representatives Council of this Faculty. He received his PhD degree (Magna cum Lauda) in Chemistry (Physical-Chemistry) in 1990 from University of Porto under the super-vision of Prof. Ribeiro da Silva. Part of his PhD work was done in the Thermodynamic Group of the University of Utrecht under the supervision of Prof. C. G. de Kruif and colleagues. He was the godfather of the Honoris Causa Doctorate of Professor Carl Djerassi by the University of Porto (2011) and has translated into Portuguese two science-in-fiction books from this author, edited by the University of Porto (Oxygen and Phallacy). He has authored a book

chapter (NATO ASI Series, 1999) and has co-authored nearly 100 scientific articles published in peer reviewed journals. He was co-Editor of a special issue of Journal of Chemical Thermodynamics (2014) and he is member of the Editorial Advisory Board of this Journal.

Invited Lecture – 3 9:00 - 9:30 Tuesday Room Hs P1

Chair: M. Huber

### ESTIMATION OF PHASE TRANSITION PROPERTIES OF HALOGENATED BENZENES

M. J. S. Monte, A. R. R. P. Almeida

Centro de Investigação em Química, CIQ-UP, Department of Chemistry and Biochemistry, Faculty of Science, University of Porto, Portugal

mjmonte@fc.up.pt

There are, virtually, ca. 1500 distinct benzene compounds where one or more hydrogen atoms are replaced by halogens (fluorine, chlorine, bromine, and iodine). Halogenated benzenes form a class of recognized pollutants and some of them are produced in large amounts since they find several industrial uses. Their physicochemical properties are strongly influenced by the halogen substituents.

For the prediction of the fate and transport of these contaminants in the environment accurate data of vapor pressures and of other transport properties, as the solubility in water, and partition and distribution coefficients, are needed. Some of these properties are difficult to determine experimentally for the existing compounds and are obviously impossible for those that were not synthesized yet.

This talk will address user friendly methods for accurate prediction, at the temperature 298.15 K, of standard Gibbs energies of sublimation and of vaporization (and then vapor pressures), Gibbs energies of hydration, solubility in water, and also a reasonable prediction of the temperature of fusion, for mono to hexa halogenated benzenes. Due to the weak interactions between the halogen atoms, the predictive equations of the properties referred to above don't need to take into account the relative positions of these substituents in the respective benzene derivatives.

### Acknowledgments

Thanks are due to FCT, Lisbon, Portugal, for the financial support to Project UID/QUI/0081/2013 and to FEDER (COMPETE 2020) for the financial support to Project NORTE-01-0145-FEDER-000028. A.R.R.P.A also thanks FCT, Operational Program and European Union for the award of the postdoctoral fellowship (SFRH/BPD/97046/2013).

### **Douglas M. Matson**

Mechanical Engineering Department, Tufts University, Medford MA, USA



Douglas Matson is an Associate Professor and the Program Director of the Mechanical Engineering Department at Tufts University and an Adjunct Associate Professor of the Tisch College of Citizenship and Public Service. He received his BS degrees in Chemical Engineering from Cornell University and Mechanical Engineering from California State University - Sacramento, his MS in Materials Science from UC-Davis, and his Ph.D. degree in Materials Engineering from MIT. He is a registered Professional Engineer in Chemical Engineering in California. He is the editor of a book on rapid solidification and is author or co-author of more than 35 scientific papers in refereed journals and 50 scientific and technical proceedings papers. He has coorganized 13 symposiums relating to space physical science, thermophysical property measurement and solidification phenomena. Professor Matson was an Erskine Fellow at the University of Canterbury, Christchurch NZ and visiting scientist at

both the NASA Marshall Space Flight Center in Huntsville AL USA and the German Space Agency (DLR) in Köln Germany. He has numerous reduced-gravity space science opportunities including parabolic aircraft missions on the KC-135 vomit comet in Johnson Space Center in Houston Texas and the Novespace A300 Zero-G in Bordeaux-Mérignac France, drop tube experiments at Vanderbilt and at NASA, the TEXUS-49 DLR sounding rocket experiment from ESRANGE Space Center outside Kiruna Sweden, and three space experiments as TEMPUS lead scientist on the NASA shuttle Columbia. He has two ongoing space collaborations on the ISS; a thermophysical property measurement program using the JAXA Electrostatic Levitator ELF and the ESA electromagnetic levitator MSL-EML collaboration for which he serves as Speaker of the International Working Group and NASA Facility Scientist.

Invited Lecture – 4 9:00 - 9:30 Tuesday

Room HS P2

Chair: I. Egry

### IN-SITU PROPERTY MEASUREMENT FOR SELECTION AND CONTROL OF CONVECTION IN EML SPACE EXPERIMENTS

D. M. Matson

Tufts University, Medford MA, USA douglas.matson@tufts.edu

Measurement of accurate thermophysical properties is a major concern of the materials science community because these results will be used to optimize performance modelling across a wide variety of engineering applications. The precision of these measurements also impacts the quality of numerical modelling predictions, especially for process control. One such application is the characterization of melt stirring of molten metal during electromagnetic levitation (EML).

Of particular interest is the temperature dependence of density and viscosity for the melt.

These quantities are used to characterize flow patterns and system Reynolds Number from laminar, through transitional, to turbulent flow conditions. Electrical resistivity may also be evaluated and the results are used to determine how induced internal fluid flows are produced by sample interaction with applied levitation and heating electromagnetic fields - and how the flows evolve over time. Magnetohydrodynamic (MHD) modelling thus provides the operator with a guide to select and control melt convection during space experiments on the International Space Station (ISS).

In-situ measurement of properties is critical. Thermophysical properties are measured for a given sample, under given conditions, in a unique facility operating in an environment where an experiment cannot be reset or a sample exchanged. If we know the properties for a given experiment we can have high confidence that the predictions on fluid flow during the experiment are known and controlled.

This is particularly important for understanding the influence of convection on phase selection during rapid solidification of steel alloys during recent space experiments. A new nucleation model has been proposed to explain how a metastable phase transforms to the stable phase based on an understanding of how liquid shear influences the microstructure formed during primary recalescence. Understanding this application requires *in-situ* measurement of thermophysical properties to predict the applied shear.

#### Mark B. Shiflett

*Chemical and Petroleum Engineering Center for Environmentally Beneficial Catalysis, Life Sciences Research Laboratory, University of Kansas, Lawrence KA, USA* 



Mark B. Shiflett is a Distinguished Foundation Professor in the School of Engineering at the University of Kansas. Professor Shiflett has a joint appointment in the Department of Chemical and Petroleum Engineering and the Center for Environmentally Beneficial Catalysis. Professor Shiflett recently joined the University of Kansas as the final Foundation Professor in August 2016. Professor Shiflett received his Ph.D. and M.S. degrees in chemical engineering from the University of Delaware in 2001 and 1998. He received his B.S. degree (Magna cum laude) in chemical engineering from N.C. State University in 1989. Dr. Shiflett recently retired from the DuPont Company after 28 years of service. He was a Technical Fellow in the Central Research and Development organization which is located at the Experimental Station in Wilmington, Delaware. Professor Shiflett was also an adjunct professor at the University of Delaware in the Department of Chemical and Biomolecular En-

gineering. Professor Shiflett is an inventor on 40 U.S. patents and has published over 70 articles on his research at DuPont. He was awarded the DuPont Bolton Carothers award in 2005, the ACS Hero of Chemistry award in 2006 and the University of Delaware presidential citation in 2007 for his development of hydrofluorocarbon refrigerant mixtures to replace chlorofluorocarbons which were linked to the depletion of the Earth's ozone layer. Three of these refrigerant mixtures were commercialized by the DuPont Company and have generated over \$1 Billion in revenue for the company. Professor Shiflett was elected in 2014 to be a Fellow in the American Institute of Chemical Engineers and in 2016 to be a Division Fellow in the American Chemical Society for his significant professional accomplishments and contributions to the chemical engineering profession. Professor Shiflett received the American Institute of Chemical Engineers Institute award for Industrial Research in 2016 for the development of non-ozone-depleting refrigerants which have led to the healing of the Earth?s ozone layer, new applications using ionic liquids, an environmentally friendly TiO<sub>2</sub> process and mentoring and educating chemical engineers. Professor Shiflett is a licensed professional engineer and his research at KU focuses on environmentally friendly, energy efficient processes and products for the chemical industry.

### Invited Lecture – 5 9:30 - 10:00 Tuesday

Chair: M. Huber

#### **IONIC LIQUIDS - PHASE BEHAVIOR TO APPLICATIONS**

Mark B. Shiflett

*The University of Kansas, Chemical and Petroleum Engineering, Center for Environmentally Beneficial Catalysis Life Sciences Research Laboratory, Building A, Office 110-F 1501 Wakarusa Drive Lawrence, Kansas 66047* 

The history of ionic liquids (ILs) effectively started in 1914, when the physical properties of

Room HS P1
ethylammonium nitrate ( $[CH_3CH_2NH_3^+][NO_3^-]$ , m.p. 13-14 °C) were first reported. ILs are generally defined as salts composed of discrete cations and anions with melting points below 100 °C, and many are liquid at ambient temperature. IL research has grown rapidly over the past two decades due to the realization that these materials have many unique properties such as negligible vapor pressure and outstanding solvation potential. Ionic liquids have been further emphasized by the fact that their physical and chemical properties can be finely tuned by varying both the cation and anion.

Our research has focused on accurately measuring vapor-liquid equilibria (VLE) and vaporliquid-liquid equilibria (VLLE) and using thermodynamic models to understand the phase behavior of binary gas mixtures in ILs. This presentation will focus on the importance of characterizing the global phase behavior of gases in ionic liquids and how this can provide insight into new applications. Solubility measurements of several gases in ILs will be discussed and important experimental details regarding VLE measurements using a gravimetric microbalance and VLLE measurements using a mass-volume technique will be highlighted. VLE data have been successfully correlated with a modified Redlich-Kwong equation of state (EOS), and in certain cases (*e.g.* hydrofluorocarbons) the EOS predicts partial immiscibilities (LLE) with lower critical solution temperatures (LCSTs) in the fluorocarbon-rich side solutions. We have also found that gases such as  $CO_2$  can exhibit different solubility behaviors in ILs (*i.e.* physical and chemical absorption) and that these behaviors can be analyzed with the EOS using a simple association model and excess thermodynamic functions.

Knowledge of gas and IL phase behavior has led to several practical applications including separation of azeotropic gas mixtures, removal of  $CO_2$  from flue gas and new fluid pairs for absorption cooling. These along with other interesting examples from the literature will be discussed.

### **Boris Wilthan**

Thermodynamics Research Center, Material Measurement Laboratory, Protiro @ National Institute of Standards and Technology, Boulder, CO, USA



Boris Wilthan is a Physicist working at the Thermodynamic Research Center (TRC) at the National Institute of Standards and Technology (NIST) in Boulder, USA. He received his MS and Ph.D. in Experimental Physics from Graz University of Technology (TUG) in 2005. After working on the characterization of thermophysical properties of metals in the liquid state with a  $\mu$ s-pulse heating technique and Differential Scanning Calorimetry, he focused on infrared radiometric characterization of sources and materials, in particular reflectance and emittance, during his time as a Postdoc at the Optical Technology Division at NIST Gaithersburg, USA. A researcher excellence grant from EURAMET funded his work "Improvement and validation of techniques and methods for accurate measurements of specific heat capacities up to 2600 K" at TUG and PTB in Braunschweig, Germany. In a staff position at PTB Berlin, he also worked on the determination of definitive thermody-

namic temperatures for the melting points of high temperature fixpoints from carbon eutectics by radiometric methods for the next international temperature scale. Since 2014 he is with TRC at NIST Boulder and is dedicated to his work to create improved, dynamically evaluated resources for thermophysical property data of metals and alloys. His work includes the design, implementation and enhancement of data capture procedures, abstraction and assessment of published properties data in this field, assessments of data quality, and predictive technologies derived primarily from original sources published in scientific literature. He is author or co-author of more than 40 scientific peer reviewed papers and in 2011, Dr. Wilthan has received the Charles Lucks Award for significant contributions to the field of thermophysics by a young researcher from the International Thermal Conductivity Conference.

Invited Lecture – 6 9:30 - 10:00 Tuesday Chair: I. Egry Room HS P2

Chuir: I. Egry

## A FREE ONLINE NIST/TRC RECOURCE FOR THERMOPHYSICAL PROPERTY DATA OF METALS AND ALLOYS

B. Wilthan, V. Diky, A. Kazakov, E. Pfeif, S. Townsend, K. Kroenlein

*National Institute of Standards and Technology, Broadway 325, CO 80305 Boulder, USA* boris.wilthan@nist.gov

The increased adoption of Integrated Computational Materials Engineering (ICME) and advancements in materials simulation tools allow researchers to rapidly model and characterize new materials but require improved data reliability and interoperability. The Thermodynamics Research Center (TRC) within NIST is actively engaged in addressing this bottleneck for the thermophysical property data for metals and alloys that are needed to feed those algorithms.

Beginning in 2013, TRC began expanding its focus to include metals and alloys in support of

the Materials Genome Initiative, a multi-agency effort to support the discovery, manufacturing, and deployment of advanced materials twice as fast, at a fraction of the cost. The presented first product of this effort is a data service that provides free access to an online resource of well-characterized experimental thermophysical property data with documented provenance and with quantified reliabilities expressed as uncertainty. This tool is publicly accessible at http://trc.nist.gov/metals\_data. This talk covers the overall methodologies required to efficiently and effectively convert information from data as presented in the open literature into structured, well-vetted datasets that can be then used as inputs for very large scale efforts in modelling, property-based literature searches or improving the quality of published information and preventing the propagation of erroneous data. It will furthermore include our progress in developing an XML standard to disseminate and share these data with the broader community.

## YOUNG SCIENTIST AWARD LECTURE

## Andriy Yakymovych

Department of Inorganic Chemistry Functional Materials, University of Vienna, Vienna, Austria



Award Lecture9:45 - 10:15ThursdayChair: G. Pottlacher

Room HS P1

## CALORIMETRIC OBSERVATION OF THE NANOEFFECT

## A. Yakymovych

Department of Inorganic Chemistry Functional Materials, University of Vienna, Vienna, Austria andriy.yakymovych@univie.ac.at

Over the last years, considerable attention has been drawn to materials with reduced dimensions. The nanoscale effects give rise to unique properties of nano-structured and nano-sized materials compared to their bulk counterparts. For instance, it was shown that thermodynamic properties of materials in nano-sized form may differ significantly from those in bulk form, leading to noticeable differences in phase stability. Furthermore, these effects are strongly depended on size and shape of nanomaterials.

At the same time, experimental measurements of nanosized materials, particularly metals, are challenging due to their higher chemical reactivity and reduced chemical stability compared with the corresponding bulk materials. This extra reactivity of nanomaterials is caused by a notable surface-to volume ratio and the excess surface energy stored in such materials. Due to this reason, a major number of experimental thermodynamic studies was performed dealing with nanosized materials, in particular with ceramic nanoparticles, using solution calorimetry.

Here we present some recent progress in thermodynamic investigations of metal nanoparticles using the drop calorimetry. For instance, experimental results will be shown of the mixing enthalpies on addition of some 3-d transitions metals in nano-sized form to liquid Sn-based

alloys. Furthermore, the size dependence of the excess enthalpy of metal nanoparticles will be discussed based on theoretical considerations related to the surface term of the Gibbs energy.

## **ORAL CONTRIBUTIONS**

## Fluids and Properties Fluids (FPF)

## Oral Session 1: Nanofluids and liquid metals

11:05 - 13:05 Monday HS P1

Chairs: W. A. Wakeham, C. N. Castro

Room HS P1

## FPF – O1 11:05 - 11:25 Monday

# HAMILTON-CROSSER THEORY CONFIRMED FOR APPARENT THERMAL CONDUCTIVITY OF NANOFLUIDS

G. J. Tertsinidou<sup>1</sup>, M. J. Assael<sup>1</sup>, W. A. Wakeham<sup>2</sup>

<sup>1</sup>*Chemical Engineering Department, Aristotle University, Thessaloniki 54636, Greece* <sup>2</sup>*Chemical Engineering Department, Imperial College London, London SW7 2BY, U.K.* assael@auth.gr

Enhancing the apparent thermal conductivity of a base fluid by the addition of solid particles of a different material has been an attractive idea for more than a century. For the last two decades many measurements have been reported in literature, which have claimed significant enhancements well above what had been expected<sup>1</sup>. In a very recent review by Tertsinidou *et al.*<sup>1</sup>, many of the large enhancements reported and, indeed, the large scatter of the results of different studies have been attributed to ill-characterization of the thermodynamic system studied and/or the application of experimental techniques of unproven validity. It was consequently shown1 that if only experimental techniques of proven validity implemented properly are considered, the enormous scatter in the experimental results is very significantly reduced. In subsequent work Tertsinidou *et al.*<sup>2</sup>, measured the enhancement of the apparent thermal conductivity of a selection of nanofluids, in a transient hot-wire instrument built and operated according to strict criteria imposed by the full theory<sup>3</sup>. The results obtained with this instrument were claimed to be the most accurate available for the thermal conductivity of nanofluids with an overall uncertainty of  $\pm 2\%$  at the 95% confidence level.

Armed then for the first time with accurate results for the thermal conductivity of nano-fluids, we examine in this paper the models appearing in literature, aiming to describe the enhancement of the thermal conductivity of a fluid when nanoparticles are added. Almost all models attempt to predict an enhancement of the thermal conductivity that is much greater than

that predicted by the Hamilton-Crosser model based on conduction through a system of one solid with embedded regions of another solid. Here we show that, that the Hamilton-Crosser model predicts the thermal conductivity of ethylene glycol-based nanofluids containing CuO,  $Al_2O_3$  and  $TiO_2$  nanoparticles within 2%; that is within the experimental uncertainty. For nanofluids based upon water containing the same nanoparticles the enhancement of the thermal conductivity is in fact lower than that predicted by Hamilton-Crosser by about 5%.

A recent theoretical scheme by Shukla *et al.*<sup>4</sup>, that considered convective heat transfer associated with the Brownian motion of the particles, was also examined. This scheme was found to predict the thermal conductivity of water based nanofluids within 2% but underestimated the thermal conductivity of ethylene glycol based nanofluids by 5%. It is concluded that the Hamilton-Crosser theory is adequate for evaluation of the apparent thermal conductivity of nanofluids for engineering applications, while the modification of Shukla *et al.*<sup>4</sup> offers a reasonable qualitative description for an additional convective heat transfer mechanism but may not be quantitatively accurate.

## References

[1] G.J. Tertsinidou, M.J. Assael, W.A. Wakeham, Int. J. Thermophys. 36:1367-1395 (2015).

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[3] K.D. Antoniadis, G.J. Tertsinidou, M.J. Assael, W.A. Wakeham, Int. J. Thermophys. **37**:78-100 (2016).

[4] K.N. Shukla, T.M. Koller, M.H. Rausch, A.P. Froba, Int. J. Heat Mass Transf. **99**:532-540 (2016).

## FPF – O2 11:25 - 11:45 Monday

### Room HS P1

## UNDERSTANDING THE INFLUENCE OF NANOPARTICLES INTERACTIONS WITH LIQUID SOLVENTS ON HEAT TRANSFER

Carlos A. Nieto de Castro, Salomé I. C. Vieira, Maria J. Lourenço, S. M. Sohel Murshed

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The development of nanofluids in the last 20 years led to many attempts to apply efficiently the discovered enhancements in thermal conductivity caused by the presence of nanoparticles in the common heat transfer liquids, from low to moderate temperatures. However, the need to obtain data for several systems led the authors to many artificial conclusions that differ from laboratory to laboratory and, sometimes, in the same laboratory.

The main problems are the preparation of the nanofluids, the characterization of the nanomaterials particles employed, and the instrumentation used to measure thermal conductivity. In addition, the understanding of the structure of nanofluid, namely the interaction of the nanoparticle with the bulk base fluid is fundamental, the interface size (extension in space), as the most significant theories of heat transfer in nanofluids are strongly dependent on it.

It is the purpose of this paper to analyse the current status of our knowledge of nanofluids

preparation, behaviour and properties, with specially emphasis in the heteromolecular interactions and its influence on the thermal conductivity of nanofluids. A detailed analysis of the most adequate methods for the measurement of this property in nanofluids will also be presented.

## FPF – O3 11:45 - 12:05 Monday

#### Room HS P1

### ARE MOLTEN METALS NEWTONIAN FLUIDS? SOME MORE EVIDENCE?

R Ritwik, P N Quested

Brunel University Uxbridge Middlesex UB8 3PH United Kingdom peter@quested.net

Historically molten metals are assumed to behave as Newtonian Fluids. This is largely based on their monoatomic structure. [1] Remarkably, historically there were few experiments to support this assumption but recent experimental studies, [2, 3] have questioned the validity of Newtonian behaviour. Recent work at this laboratory in conjunction with an instrument manufacturer, Ravenfield Designs, has developed two high shear viscometers with different working principles. One rotating the inner cylinder - referred to as a Searle type previously described in reference [2], whereas the other new design rotates the outer cylinder - referred to as a Couette type. The shear effects on the viscosity of molten metal, tin and lead were measured with both types of viscometer. Sn doped with Ge was also measured, where the dopant is expected to modify the surface tension of the Sn.

Two distinct zones were observed in the "apparent" viscosity against shear rate curves for the two viscometers. At lower shear rates (less than  $200 \text{ s}^{-1}$  Zone 1): a reduction of "apparent" viscosity with shear rate was observed with both viscometers. This is similar qualitatively [3] and quantitatively [3] to previous observations. This behaviour is discussed in terms of measurement technique and the observed onset of Zone 2 behaviour at a lower shear rate for Sn doped with Germanium compared with un-doped Sn.

At higher shear rates (Zone 2): a shear independent behaviour of "apparent" viscosity with shear rate in the Couette viscometer (maximum shear rate  $600 \text{ s}^{-1}$ ) was observed. This compares to a steady increase in "apparent" viscosity with shear rate in the Searle viscometer (maximum shear rate of 2600 s<sup>-1</sup>). These latter results are in agreement with previous measurements [2]. The apparent viscosity measured at high shear rates with the Couette Type viscometer are similar though not identical to accepted values of viscosity of tin and lead, mainly measured with oscillating cup type viscometers.

These observations of fluid behaviour are compared with the experiments by Taylor [4] and others [5] with Newtonian fluids. They demonstrate that the rheological behaviour of molten tin and lead is consistent with Newtonian behaviour. Suggestions for future experiments are given, and the implications of these results to the simulation of metal processes is discussed.

## References

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## FPF – O4 12:05 - 12:25 Monday

## Room HS P1

## DYNAMIC VISCOSITY OF LIQUID Sn-3.0Ag-0.5Cu ALLOY WITH Ni NANOPARTICLES

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In the present work, the temperature dependence of the dynamic viscosity of the liquid Sn 3.0Ag 0.5Cu alloy (SAC305) with up to 2 wt.% nano-Ni additions was investigated. The measurements were performed in the temperature range from the melting temperature up to 1023 K using an oscillating-crucible viscometer.

The nanocomposite samples were prepared by manually mixing the SAC305 powder (Kester, U.S.A.) with Ni nanopowder (IoLiTec, Germany) at a nominal content of 0, 0.5, 1.0 and 2.0 wt.% for at least 30 min to achieve a homogeneous distribution of the nanoparticles in the solder powder. The nanocomposite powder was cold pressed, afterwards. All operations were performed in a glove box in an atmosphere of purified Ar (O<sub>2</sub> and H<sub>2</sub>O < 5 ppm each) to avoid possible oxidation of the nanoparticles. After the viscosity measurements, the samples were investigated by scanning electron microscopy (SEM) and X-ray diffraction (XRD).

The viscosity values were obtained in two runs on heating and subsequent cooling. The obtained results suggest that during the first heating the viscosity of the samples was measured in two different states:

- at temperatures not too far above the melting temperature of the SAC305 alloy, the investigated sample was a suspension of Ni nanoparticles in the SAC305 melt;

- the following heating led to the dissolution of the Ni nanoparticles in the liquid matrix, resulting in a transformation of the investigated sample into a quaternary Ag-Cu-Ni-Sn liquid alloy. From this point, the viscosity of liquid (SAC305)<sub>100-x</sub>Ni<sub>x</sub> alloy was measured. The viscosity values measured during the first cooling are in a good agreement with the data obtained in the second heating/cooling run. The temperature dependence of the viscosity is well fitted by an Arrhenius equation.

The structure analysis of the samples after the viscosity measurements indicated formation of tin oxide although the viscosity measurements were performed under a vacuum better than  $10^5$  mbar. Further investigations suggested that the employed SAC305 powder had already initially a tin oxide shell.

## Acknowledgments

This study has been financially supported by the Austrian Science Fund (FWF) under Project

No. P 27049. The viscosity measurements were performed at the Institute for Complex Materials at the Leibniz Institute for Solid State and Materials Research (IFW Dresden), Germany.

### FPF – O5 12:25 - 12:45 Monday

Room HS P1

## A KINETIC STUDY OF HEAT TRANSFER IN NANOFLUIDS

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The performance of single phase heat transfer fluids is crucial to a broad application from cooling devices for miniaturized computer processors to chemical and thermal power plants. Recent studies have demonstrated that fluids laden with nanoparticles can enhance heat transfer significantly. Many works has been done in the past decades accordingly, and the major factor that accounts for the enhancement is attributed to the high thermal conductivity of nanoparticles. However, more and more studies show that this is rather questionable since the enhancement is still evident even when the concentration of nanoparticles is negligible and the overall conductivity of the nanofluids is almost the same as that of the pure fluid. In this work, we develop a model for heat transfer in nanofluids based on kinetic theory. It is shown that the enhancement of heat transfer in nanofluids is mainly caused by the nontrivial interactions between fluid molecules and nanoparticles at small scales, which was not included or clearly addressed in previous studies. The rotational and translational movements of nanoparticles are investigated and found to strongly affect the behaviours of their surrounding base fluid molecules, which can effectively enhance the energy transfer process via nanofluids. Furthermore, the size, shape and hydrophobicity effects of nanoparticles on the interactions with fluid molecules are investigated. Theoretical results have been confirmed by MD simulations and agree well with experiments.

## FPF – O6 12:45 - 13:05 Monday

### Room HS P1

## **VOLUMETRIC PROPERTIES OF RUBIDIUM-BISMUTH MELTS**

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The density and thermal expansion of liquid rubidium and a number of liquid rubidiumbismuth alloys have been investigated by using the gamma-ray attenuation technique over the temperature range from the liquidus line to 1000 K. The position of the liquidus curve in the Rb-Bi phase diagram has been clarified. The composition dependence of molar volume and volumetric thermal expansion coefficient (VTEC) in the liquid state have been constructed. As an example, the figure below shows the concentration dependence of the VTEC for the Rb-Bi melts at 950 K. It has been found that both concentration dependencies deviate strongly from the corresponding dependencies for an ideal solution. The maximum deviation of molar volume from ideality (35.4% at 950 K) is observed near 30 at.% Bi. Moreover, it has been found a quite sharp maximum on the concentration dependence of the thermal expansion coefficient of the Rb-Bi liquid alloys in the vicinity of 25 at.% Bi. It has been shown, that the large volume contraction of Rb-Bi melts and the peak in the concentration dependence of VTEC of this system suggest the existence of a chemical short-range order in these liquid alloys, which gradually breaks down with increasing temperature.



**Figure 1**. The concentration dependence of the volumetric thermal expansion coefficient for Rb-Bi liquid system at 950 K. The points are the data of this work.

## Acknowledgements

We gratefully thank the Russian Science Foundation (Grant No. 16-19-10023) for providing financial support for this research.

### **Oral Session 2: Fluid systems - Measurements and Models**

15:30 - 17:50 Monday HS P1

Chairs: M. Richter, V. Vesovic

#### FPF – O7 15:30 - 15:50 Monday

#### Room HS P1

# DETERMINATION OF DIELECTRIC- AND DENSITY VIRIAL COEFFICIENTS OF ARGON

C Guenz<sup>1</sup>, C. Gaiser<sup>1</sup>, M. Richter<sup>2</sup>

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For the determination of real gas properties, a new apparatus combining dielectric-constant gas thermometry (DCGT) and expansion methods has been built up and extensively tested at PTB [1]. With DCGT, electric polarizabilities and combinations of dielectric- and density virial coefficients are determined. To extract the virial coefficients separately, expansion methods based on either pressure or capacitance ratios are used. By combining these two methods, cross validated measurements with low uncertainties can be carried out in the temperature range (-40 - 90) °C for pressures up to 7 MPa. The main design features of the new apparatus will be presented. It contains four measurement cells and an innovative high-purity gas handling system that allows each chamber to be filled and evacuated independently. Furthermore, the main components of the uncertainty budget will be discussed. The budget includes components connected with thermal time constants and temperature gradients, influence of dead volumes, deformation of the measurement cells and compression of the measuring capacitors under gas pressure. The complex measurement procedure and data treatment will be exemplified and validated by isothermal measurements with argon. The measured second density virial coefficient of argon will be compared with literature values. For the second dielectric virial coefficient, such a comparison is difficult since experimental values are widely scattered and calculations differ by almost 20%. With relative uncertainties of only a few percent, the extracted dielectric virial coefficients may help to resolve these discrepancies.

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### FPF – O8 15:50 - 16:10 Monday

## MEASUREMENTS OF THE SPEED OF SOUND AND DERIVED THERMODYNAMIC PROPERTIES FOR LIQUID N-PENTANE

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Comprehensive and accurate measurements of the speed of sound in liquid n-pentane were carried out by a double-path-length pulse-echo technique. The measured data cover the temperature range between 200 K and 420 K with pressures up to 100 MPa. The expanded uncertainties (at the 95% confidence level) are 2.1 mK for temperature, 0.007% for pressure, and 0.04% for speed of sound. The high quality of the speed of sound data is validated by comparisons with several literature data sets and different fundamental equations of state.

Our experimental results for the speed of sound in combination with initial values for the density and isobaric heat capacity at a low pressure liquid isobar, which were calculated with the equation of state of Span and Wagner [Int. J. Thermophys., 24, 41, 2003], were used to determine values for the density and specific isobaric heat capacity in the range of our measurements by the method of thermodynamic integration. For this purpose, the speed of sound data were correlated as a function of temperature and pressure. The correlation equation was developed with the linear structural optimization technique of Wagner [Fortschr.-Ber. VDI-Z., Reihe 3, Nr. 39, 1974]. With our accurate speed of sound data and the calculated densities, the Helmholtz energy formulation for *n*-pentane can be improved significantly.

### FPF – O9 16:10 - 16:30 Monday

#### Room HS P1

## SPEED OF SOUND AND DENSITY IN CARBON DIOXIDE + n-HEPTANE BINARY MIXTURE

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Enhanced oil recovery by carbon dioxide miscible flooding is among the most effective non-thermal improved oil recovery methods. In that method,  $CO_2$  is injected into reservoir under high pressure, then it migrates in oil phase via convective dispersion processes and molecular diffusion causing a significant reduction in oil viscosity. In addition,  $CO_2$  dissolution makes the oil swell which results in an easier displacement of crude oil due to gravity. Both oil swelling and viscosity reduction improve crude oil mobility and thereby provide opportunities to recover oils that would not otherwise be produced. The process is applicable to a wide range of oil types as supercritical  $CO_2$  is mutually soluble with many hydrocarbons. To model recovery processes and to evaluate their real efficiency volumetric and transport properties are essential thermophysical properties. Accurate density as well as its derivatives with respect to pressure and temperature as a function of  $CO_2$  content in reservoir conditions is also

required to perform reservoir simulation during  $CO_2$  injection. The knowledge of viscosity as a function of  $CO_2$  composition, temperature and pressure is needed to predict diluted oil flow properties in porous media. With this aim in mind, an investigation of volumetric properties and viscosity of binary systems containing  $CO_2$  and a hydrocarbon has been initiated in our laboratory. At the initial phase of this program, it was chosen to investigate the carbon dioxide + n-heptane binary mixture.

The present work aims at reporting experimental data of density and its derivative with respect to pressures of carbon dioxide + n-heptane system in the liquid state. For that purpose, density and speed of sound measurements were carried out in six mixtures ranging from 0 to 90% of  $CO_2$  at pressure up to 70 MPa for two temperatures close to the critical temperature of  $CO_2$  (303.15 and 313.15) K. Speed of sound was measured with a pulse echo technique working at 3 MHz whereas density was obtained from a U-tube densimeter.

## FPF - O10 16:30 - 16:50 Monday

## Room HS P1

## NEW FORMULATION FOR THE VISCOSITY OF NORMAL BUTANE

S. Herrmann<sup>1</sup>, H.-J. Kretzschmar<sup>1</sup>, E. Vogel<sup>2</sup>

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The exact knowledge of thermophysical properties of fluids with industrial importance is required for a more accurate basic design of compressors, gas turbines, and gas pipelines as well as cooling cycles and chemical processes. In contrast to the thermodynamic properties, the transport properties of normal butane, particularly in the region near to the critical point, are not sufficiently well-known. The current NIST standard database REFPROP 9.1 of Lemmon et al. (2013) recommends the viscosity correlation of Vogel et al. (1999), which is characterized by standard uncertainties of up to 3% in its range of validity applying an outdated equation of state of Younglove and Ely from 1987. Due to the fact that REFPROP 9.1 approves the reference equation of state of Bücker and Wagner (2006) for the thermodynamic properties of normal butane, there is a basic necessity for developing a new viscosity formulation for this working fluid.

Recently, very accurate viscosity measurements were performed by Herrmann and Vogel (2015) using a vibrating-wire viscometer in combination with a single-sinker densimeter. The standard uncertainty of these data was conservatively estimated to be 0.3%. Hence, they are considered to be primary data. In addition, viscosity measurements by Küchenmeister and Vogel (1998), whose results have already been used by Vogel et al. (1999) when generating their correlation, were re-evaluated (2017), so that they are qualified for being primary data, too.

Applying the new reference equation of state of Bücker and Wagner (2006) together with the improved data situation in the dense-gas region, a new viscosity formulation for normal butane was generated using the structure-optimisation method by Setzmann and Wagner (1989). The new formulation concept incorporates four contributions concerning the zero-density viscosity, the initial-density dependence, the near-critical region, and the higher-density terms of the

residual viscosity. The first two contributions are completely treated separately using little support of the kinetic theory. The critical-enhancement terms related to the near-critical region were slightly pre-treated with respect to the choice of some parameters. At the end, the bank of terms needed in the optimization procedure comprises only terms for the near-critical region and for the higher-density contribution. The latter terms are composed of a combination of double polynomials in the reduced density and reciprocal reduced temperature, some of them combined with a negative exponential function of the reduced density. The validity range of the new formulation extends from the melting line to temperatures of 650 K and to pressures of 100 MPa. The extrapolation and consistency behaviours of the formulation were investigated. Values calculated for the new viscosity formulation were compared with the primary data, used when developing the formulation, and with values resulting from the earlier viscosity correlations of Vogel et al. (1999) and of Quiñones-Cisneros and Deiters (2006).

## FPF – O11 16:50 - 17:10 Monday

Room HS P1

## PREDICTING THE VISCOSITY OF MULTICOMPONENT LIQUID MIXTURES USING AN MOLECULAR APPROACH

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In numerous industrial applications that involve the flow of fluids, knowledge of viscosity of the mixtures is an essential pre-requisite for good design and optimal operations. The present talk will focus on the mixtures containing *n*-alkane and aromatic species, as a precursor for developing molecular based methods [1-3] for predicting the viscosity of petroleum fluids; a rather challenging task, due in part to compositional complexity. For practical purposes the petroleum fluids are commonly described by a limited number of pseudo-components and there are many approaches to establish both the number and the characteristics of pseudo-components [4].

In this work, we present a simple molecular model, based on the extended hard-sphere approach [2,5-6], that relies on representing the viscosity of the multicomponent mixture by a viscosity of a single pseudo-component, which is characterized by an appropriate molecular weight. The initial validation of the predictive capability of the developed model is performed on compositionally well-defined liquid mixtures consisting of *n*-alkane and aromatic species, taking advantage of large number of experimental measurements available in literature. The results obtained indicate that the single pseudo-component representation works best for multicomponent mixtures composed of species with not too different molecular weight, as is the case in petroleum fluids. The model is capable of generating viscosities within 5% of the experimental value.

The observed good agreement with experimental data indicates that the proposed approach offers a tangible way forward in developing the molecular based model for predicting the viscosity of real crudes.

## Acknowledgment

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## FPF – O12 17:10 - 17:30 Monday

## Room HS P1

## ADSORPTION OF THE YUKAWA MIXTURES: AS PRECURSORS TO THE ELECTRIC DOUBLE LAYERS

L. L. Lee, T. K. Nguyen, F. S. Ramos, A. M. Ramos, M. Redko, C. J. Faraj

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We examine the adsorption of binary Yukawa fluids on a solid wall. It is well-known that the Yukawa potential approaches the Coulomb potential when the screening parameter  $\lambda$  vanishes. Thus the study of the mixtures of repulsive Yukawa and attractive Yukawa molecules can mimic the ionic fluid behavior. One of the advantages of using the Yukawa detour is to mitigate the long-range complications of the Coulomb potential.

We developed a third-order Ornstein-Zernike relation<sup>1</sup> (OZ3) earlier and have adapted it to the adsorption of general fluids on solid walls. Specifically, a new generation of closures was developed for use in the Euler-Lagrange equations of the density functional theory (DFT) for determining the non-uniform densities of various types: the Lennard-Jones bulk fluid, as well as the regular Yukawa bulk fluid at an inhomogeneous substrate. In this work, we examine the applicability of the OZ3-inspired bridge functions to the adsorption of the "near-zero- $\lambda$ " Yukawa fluids at a structureless hard wall, simulating the electrical double layers: an important chemical-physical subject in physics, biochemistry, colloidal chemistry, and electrochemical engineering.

The bulk fluid is composed of a binary mixture of two types of Yukawa particles: (A) the (pseudo)-cations and (B) the (pseudo)-anions. The like-particles (A-A and B-B) interact with the repulsive Yukawa potential and the unlike particles (A-B) interact with the attractive Yukawa potential. The Yukawa potentials have a hard core with diameters  $d_{AA}$ ,  $d_{AB}$ , and  $d_{BB}$ , respectively. Both symmetric mixtures ( $d_{AA} = d_{AB} = d_{BB}$ ) and asymmetrical mixtures ( $d_{AA} \neq d_{BB}$ ) will be considered.

The Euler-Lagrange equation is solved with the new OZ3 closures. Two types of closures are investigated: one derived from the Jackson-Feenberg approximation, and the other derived from the linear cavity approximation. The results are compared with the Monta-Carlo results on symmetric ions and asymmetric ions at a hard wall. Satisfactory agreements are obtained.

This work represents for the first time this new type of DFT based on the OZ3 theory is applied to the adsorption of ionic species on non-uniform walls. Its success represents a major advance of the *closure-based* density functional theory as a useful theory in the gamut of other powerful approaches.

## References

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## **Oral Session 3: Energy and Fuels**

10:20 - 13:00 Tuesday HS P1

Chairs: S. Lago, E. Hassel

## FPF – O15 10:20 - 10:40 Tuesday

Room HS P1

## THERMAL CONDUCTIVITY OF GASEOUS MIXTURES OF METHANE, PROPANE AND HEPTANE AT PRESSURES TO 31 MPA

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Thermal conductivity measurements of two gaseous mixtures, a binary (0.95  $CH_4 + 0.05 C_3H_8$ ), and a ternary (0.85  $CH_4 + 0.1 C_3H_8 + 0.05 C_7H_{16}$ ), are presented. The measurements were performed from (200 to 423) K for pressures up to 31 MPa using the transient hot-wire technique which involves the application of multiple corrections to the data so that they may be analysed using the ideal model for the transient temperature rise. The transient hot-wire device was used to obtain high quality data for the thermal conductivity of these important fluid mixtures to help the gas processing industry to improve the design and operating costs of equipment items such as heat exchangers.

The transient hot-wire sensor used in this work is a modified version of a previous device and consists of two thin, parallel, 10  $\mu$ m-diameter platinum wires with lengths 15 and 4 cm, placed on different arms of a Wheatstone bridge. To demonstrate that the new sensor operates according to the theoretical model, thermal conductivity measurements of methane and argon were carried out in the same temperature and pressure range.

The experimental thermal conductivities obtained in the current work were compared with published data and results calculated from models implemented in REFPROP 9.1; this software package uses the extended corresponding states (ECS) correlation for calculating transport properties, the reference equations of state (EOS) of Setzmann and Wagner and Tegeler et al. for the densities of pure methane and argon, respectively; and the GERG 2008 EOS for mixture densities. The percentage deviations of the pure methane and argon data from thermal conductivities calculated using the ECS correlation were within  $\pm 2\%$ , which is within the uncertainty of the current measurements. Higher percentage deviations from the ECS model were found for the available literature data over this range of conditions, at up to 50% for methane and 5% for argon. For the binary (0.95 CH<sub>4</sub> + 0.05 C<sub>3</sub>H<sub>8</sub>), and ternary (0.85 CH<sub>4</sub> + 0.1 C<sub>3</sub>H<sub>8</sub> + 0.05 C<sub>7</sub>H<sub>16</sub>) mixtures, the percentage deviations from those calculated using ECS model were found to span between 3% and -3%, depending on the mixture densities. This work presents novel and accurate thermal conductivity data for mixtures never studied experimentally before and at temperature and pressure ranges relevant to those encountered in LNG production.

### THE CALORIFIC VALUE MEASUREMENT OF METHANE BY METAL BURNER

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As the origins and the contents of the natural gas diversify, the calorific value determination of natural gas has become very important issue in the natural gas trade. In KRISS, a gas calorimeter measuring gross calorific value of gas based on the isoperibolic principle has been developed and the reference gas of methane is measured. In the developed calorimeter, a burner made of stainless steel was utilized to enhance strength, precise manufacturing and standardization. The burner is immersed in the calorimeter vessel filled with water and the vessel is placed in the constant temperature bath. The methane, oxygen, argon gases are injected in the burner and the gas is ignited. The optimum flow rates of oxygen and argon gases are chosen by varying each gas flow rate and searching the minimum CO concentration in the reaction products. During approximately 20 minutes of combustion, the temperature rise of the water in the calorimeter vessel is recorded with Pt25 thermometer. Water vapour is produced during the combustion process and absorbed by absorption tube containing magnesium perchlorate. Liquid water produced during the combustion is collected in the water trap of the burner and the amount of water is determined by purging the burner after the combustion and measuring the weight increase of the absorption tube. The weight of combusted methane gas is measured by measuring weight of methane cylinder using electric balance before and after the combustion. Electrical heater coils around the heater and the heat capacity of the whole calorimeter is determined by simulating combustion process. By conducting data analysis, the gross calorific value of methane is measured and shows within 0.4% difference compared to the reference value.

## FPF – O17 11:00 - 11:20 Tuesday

## Room HS P1

## DEVELOPMENT AND CHARACTERIZATION OF SURROGATE DIESEL FUELS

T. J. Fortin, T. J. Bruno, J. L. Burger, M. E. Harries, and M. L. Huber *National Institute of Standards and Technology, Boulder, Colorado, U.S.A.* tara.fortin@nist.gov

Coordinated efforts in engine optimization and fuel development have the potential to increase efficiency and reduce costs and emissions. However, when trying to model thermophysical properties or chemical-kinetic behavior for example, the vastly complex composition of a typical commercial diesel fuel can make it impossible to do so explicitly. In such cases, it is desirable to create a surrogate fuel composed of a more manageable number of components, which are selected with the goal of reproducing specific compositional characteristics and key properties of the target fuel. This work focuses on four surrogate ultralow sulfur diesel fuels developed and characterized under projects AVFL-18 and AVFL-18a of the Coordinating Research Council (CRC) Fuels for Advanced Combustion Engines (FACE) working group. The four fuel samples, designated V0a, V0b, V1, and V2, differ in the number and identity of components in an effort to explore the inherent tradeoffs associated with formulating a surrogate fuel. NIST contri-

butions to the larger program will be presented. Specifically, modeling work relevant to both the formulation of the surrogate fuels and to the prediction of thermodynamic properties of the resulting mixtures will be discussed. Additionally, the results of experiments performed to characterize the composition and enthalpy of combustion as a function of distillate volume fraction via the advanced distillation curve (ADC) method, and of density and speed of sound measurements at atmospheric pressure for the four surrogate diesel fuels, will be presented, including how results compare to the target diesel fuel.

## FPF – O18 11:20 - 11:40 Tuesday

Room HS P1

### PRESSURE, DENSITY, TEMPERATURE AND DERIVED THERMOPHYSICAL PROPERTIES OF ETHANOL AND 1-BUTANOL - DIESEL BLENDS

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In modern IC Diesel engines common rail injection systems with rail pressures of more than 100 MPa pressure are standard. It is expected that this injection pressure will be going up in future in order to increase fuel vaporization for cleaner combustion, e.g. soot and  $NO_x$  emission reduction. For optimal engine operation so called injection rate shaping is controlled by the engine management system realized in many modern vehicles. Nowadays political and public pressures demand the reduction of  $CO_2$  emissions from engines, that is reduction of green house gases emission like  $CO_2$ . One means to do this is to mix fossil diesel fuel with renewable fuels like bio-ethanol or bio-butanol. For the design of the common rail engine injection systems it is important to have reliable knowledge of the thermophysical properties of the fuel under high pressures, such as density, vapor pressure, viscosity, speed of sound, heat capacity etc. which allows modeling, understanding, and optimizing the injection processes in an internal combustion engine.

This work presents the  $(p, \rho, T)$  properties at T = (263.15to468.15) K and pressures up to p = 200 MPa, vapor pressure at T = (274.15 to 468.15) K, heat capacity at T = (253.15 to 468.15) K at ambient and saturated pressures of these blends, also pure diesel, ethanol and 1-butanol which measured experimentally. An equation of state for fitting of the  $(p, \rho, T)$  data of investigated systems has been developed as a function of pressure, temperature and concentration. The various thermophysical properties of these fuel blends, such as isothermal compressibility, isobaric thermal expansibility, thermal pressure coefficient, internal pressure, specific heat capacities at constant pressure and volume, speed of sound, isothermal exponent were calculated at high pressures up to 200 MPa and temperatures, in which the  $(p, \rho, T)$  properties were studied experimentally. The excess molar volumes  $V_m^E$  of ethanol or 1-butanol and diesel binary mixtures at T = (263.15 to 468.15) K, pressures up to p = 200 MPa were calculated using the experimental  $(p, \rho, T)$  data values of fuel blends, pure diesel, ethanol and 1-butanol.

## EXPERIMENTAL SPEED OF SOUND MEASUREMENTS IN LIQUID METHANE AT CRYOGENIC TEMPERATURE

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The density of liquefied natural gas (LNG) is usually being calculated based on the composition and an equation of state. In the absence of an accurate composition measurement, the density is also commonly, but roughly, determined by the Coriolis or Ultrasonic Flow Meter (USM) used for the flow rate measurements. The calculation of density has a rather large uncertainty (between 0.2% - 0.5%, not including the uncertainty of the composition measurement), because the applied Equations of State are not yet validated at a sufficient low level of uncertainty.

As a part of an on-going European research project (called "Metrology for LNG III - Metrological support for LNG and LBG as a transport fuel") to promote the large scale use of LNG and liquefied biogas (LBG) as a transport fuel, the Italian Metrological Institute (INRiM) has developed a new on-line density and speed of sound ultrasonic sensor. The novel sensors, having the aim to improve the accuracy and reduce the measurement uncertainty of LNG density and speed of sound measurements, can work both in laboratory controlled conditions and in-field, it will be used for disseminating traceable density measurement when it is mounted on the same industrial circuits where commercial sensors are installed.

Calibration tests have been carried out both at ambient temperature, using water, and at cryogenic temperature in a closed-loop cryostat, using methane.

In this paper accurate speed of sound measurements in liquid-phase methane in the temperature range of (100 and 150) K and for pressures up to 10 MPa are reported. These results, with an associated uncertainty in the order of 0.1%, were compared with literature values and with predictions of the dedicated equation of state.

## FPF - O21 12:20 - 12:40 Tuesday

## Room HS P1

## VISCOSITIES AND DENSITIES OF METHYL LAURATE AND ETHYL LAURATE UNDER HIGH PRESSURE

## Xiangyang Liu, Tianwang Lai, Maogang He

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Biodiesels is composed of fatty acids alkyl esters, which are considered as promising renewable energy to substitute for fossil fuels due to their advantages, such as low or no sulfur content, high flash point, miscible with conventional fossil fuels. In addition, they can be obtained from vegetable oils and animal fats. The viscosities and densities of biodiesels are necessary for designing the injection process in diesel engine, which is up to the viscosities and densities of fatty acid alkyl esters in them. Although lots of experimental data have been reported for the viscosities and densities of fatty acid alkyl esters, but most of them are at atmospheric pressure.

In this work, new experimental data for the viscosities and densities of methyl laurate and ethyl laurate were presented at temperatures ranging from 303 K to 353 K and under pressures up to 20 MPa. Tai equation and Andrade-Tait equation were used to correlate the density and viscosity data. The isobaric expansivity coefficients of methyl laurate and ethyl laurate were also calculated based on the density data. The viscosities and densities of methyl laurate and ethyl laurate and ethyl laurate were found to decrease with the increasing temperature and increase with increasing pressure. The viscosities and densities of fatty acid alkyl esters with different carbon number were compared to investigate the influence of the molecular structure on the viscosity and density of fatty acid alkyl ester.

### Acknowledgements

This work was supported by the National Science Fund for Distinguished Young Scholars of China (No. 51525604)

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## FPF – O22 12:40 - 13:00 Tuesday

Room HS P1

## DENSITY, SPEED OF SOUND AND OTHER DERIVED PROPERTIES FOR A $\mathrm{CO}_2$ RICH NATURAL GAS MIXTURE

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The speed of sound (SOS) and density were measured simultaneously for a  $CO_2$  rich natural gas mixture (70 mol%  $CO_2$ ) for five isotherms from 323 K to 415 K in a range of pressure up to 60 MPa. In this work, density and speed of sound were measured employing a vibrating tube densitometer, and a high-pressure acoustic cell equipped with two ultrasonic transducers respectively. Both setups were calibrated using reference components, and validity of results was checked by doing measurements for components of well-known density and sound velocity in the investigated P-T range.

Then, the SBWR equation of state was tuned by adjusting the acentric factor to match the predicted density with measured density at each pressure and temperature. Then using calculated parameters, the speed of sound and other derived properties of the fluid (i.g. compressibility factor, isochoric and isobaric heat capacity) were calculated. To check the validity of the method, the measured and calculated sound velocities were compared. The average absolute percentage deviation between measured and calculated velocities was found to be 0.69%.

Moreover, other derived properties were compared against the GERG-2008 EoS. The average absolute percentage deviations of all points for isobaric heat capacity, isochoric heat capacity and Joule-Thomson coefficient were calculated to be 1.04%, 1.18% and 10.92% respectively. However, for the calculated Joule-Thomson coefficients exclusion of the Joule-Thomson values in the vicinity of inversion point (i.e., -0.1 < Joule-Thomson coefficient (K/MPa) < 0.1) lowers the average absolute percentage deviation from 10.92% to 5.74%.

## **Oral Session 4: Aqueous Systems**

15:30 - 17:50 Tuesday HS P1

Chairs: A. Ribeiro, G. Hefter

## FPF - O24 15:30 - 15:50 Tuesday

### Room HS P1

## MOLAR VOLUMES OF LITHIUM SALTS IN AQUEOUS SOLUTION TO 300 $\,^\circ C$

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The thermodynamic properties of lithium salts in aqueous solution are in general much less well-characterized than the corresponding values for the other alkali metal salts. This talk will summarize our recent measurements on the densities, and the molar volumes derived from them, for a number of lithium salts of scientific and industrial interest up to high concentrations. Densities up to 70 °C were determined using a commercial vibrating tube densimeter (Anton Paar), while those up to 300 °C were measured in a purpose-built flow densimeter. The apparent molar volumes calculated from these data were mostly well-behaved but also show some interesting variations with concentration and temperature. Similarities and differences between the volumetric properties of lithium salts and their alkali metal congeners will be highlighted.

### DIFFUSIVITIES OF TERNARY MIXTURES OF N-ALKANES WITH DISSOLVED GASES BY DYNAMIC LIGHT SCATTERING

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Theoretical approaches suggest that dynamic light scattering (DLS) signals from low-molecular weight ternary mixtures are governed by fluctuations in temperature as well as two individual contributions from fluctuations in concentration that are related to the eigenvalues of the Fick diffusion matrix. Until now, this could not be proven experimentally in a conclusive way. In the present study, a detailed analysis of DLS signals in ternary mixtures consisting of *n*-dodecane  $(n-C_{12}H_{26})$  and *n*-octacosane  $(n-C_{28}H_{58})$  with dissolved hydrogen (H<sub>2</sub>), carbon monoxide (CO), or water (H<sub>2</sub>O) as well as of n-C<sub>12</sub>H<sub>26</sub> or n-C<sub>28</sub>H<sub>58</sub> with dissolved H<sub>2</sub> and CO is given for temperatures up to 523 K and pressures up to 4.1 MPa. Thermal diffusivities of pure n-C<sub>12</sub>H<sub>26</sub> and *n*-C<sub>28</sub>H<sub>58</sub> as well as thermal and mutual diffusivities of their binary mixtures being the basis for the ternary mixtures with dissolved gas were studied for comparison purposes. For the investigated ternary mixtures, three individual signals could be distinguished in the time-resolved analysis of scattered light intensity by using photon correlation spectroscopy (PCS). For the first time, it could be evidenced that these signals are clearly associated with hydrodynamic modes. In most cases, the fastest mode observable for ternary mixtures is associated with the thermal diffusivity. The two further modes obviously related to the molecular mass transport are observable on different time scales and comparable to the modes associated with the concentration fluctuations in the respective binary mixtures. Comparison of the experimental data with results from molecular dynamics simulations revealed very good agreement.

#### FPF – O26 16:10 - 16:30 Tuesday

#### Room HS P1

## MULTICOMPONENT DIFFUSION OF PHARMACEUTICAL COMPOUNDS IN AQUEOUS SOLUTIONS

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We are studying the diffusion properties of up to three components in model pharmaceutical

formulations to help develop guidelines for the rational design of controlled-release systems. Such systems are of major importance for the reliable and safe delivery of precise dosages of drugs, and important insights have been obtained by manipulating the rates of diffusion of the carrier-drug complexes and the thermodynamic binding constants. However, for quantitative applications, detailed information is needed on the transport behaviour of these systems. Our purpose is a comprehensive experimental study of the diffusion of drugs and carriers alone, and drugs in combination with carrier molecules (including cyclodextrins (CDs) and block copolymer micelles) for enhanced solubility and facilitated transport.

The Taylor dispersion technique [1] has been used for measuring mutual diffusion coefficients, for aqueous systems containing different drugs (e.g., ethambutol dihydrochloride [2], which is used in treatment of tuberculosis, and the anti-Parkinson drug L-Dopa [3],) at 25 °C and 37 °C, respectively.

From these results, and by using the appropriate models (Stokes-Einstein and Hartley), we have estimated some structural, thermodynamic and transport parameters, such as the hydrodynamic radius, thermodynamic factors and limiting diffusion coefficients, as well as, in ternary systems, the number of moles of each component transported per mole of the other component driven by its own concentration gradient.

These studies have provided a comprehensive information - both kinetic and thermodynamic - for the design and operation of these systems and consequently, a better understanding of the physical chemistry of carrier-mediated transport phenomena in multicomponent systems of controlled drug releasing.

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## FPF – O27 16:30 - 16:50 Tuesday

### Room HS P1

## THERMODYNAMIC PROPERTIES OF AN AMINOMETHYLATED C-METHYLRESORCIN[4]ARENE IN AQUEOUS SOLUTIONS

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The structure of Resorcin[4]arenes in solution is of special interest because it can form well defined supramolecular structures, host-guest complexes or aggregates. The determination of thermodynamic properties in solution is useful to elucidate the interactions between the species involved in these processes. In this work the densities and speed-of-sound of aqueous solutions of an ionic C-methylresorcin[4]arene, functionalized on the upper ring with the

residue (-CH<sub>2</sub>NH(CH<sub>3</sub>)Cl), were measured in the concentration range of  $0.01 < m/mol kg^{-1} < 0.1$  and in the temperature range 278.15 < T/K < 308.15. The measurements permitted to calculate apparent molar volumes and isentropic compressibilities. Analysis of the former using the extended Redlich-Rosenfeld-Mayer equation yields the standard partial molar volume and partial molar expansibility, while the latter was used to calculate partial molar isentropic compressibilities and hydration numbers. The results show that the ionic standard partial molar volumes increase with temperature with a positive constant expansibility. Further discussion of the results is done in terms of structureness of the solution and ionic solvation.

## Acknowledgements

The authors wish to thank the Faculty of Science of the Universidad de los Andes for financial support.

## FPF – O28 16:50 - 17:10 Tuesday

## Room HS P1

## VOLUMES AND HEAT CAPACITIES OF DMPU/WATER MIXTURES AND OF ELECTROLYTES IN DMPU

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The organic compound DMPU (1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone) is of interest as a very strong electron-donor solvent that is much less toxic than similar solvents such as the more widely studied HMPA (hexamethylphosphorictriamide). Volumes and heat capacities of mixtures of DMPU with water have been measured over the whole composition range by vibrating-tube densimetry and flow calorimetry, respectively. The densities are rather sensitive to traces of water in the organic-rich region but the heat capacities are not. These mixtures are far from ideal, with negative excess molar volumes. Apparent molar volumes of selected electrolytes have also been measured in neat DMPU. Differences and similarities with their behaviour in water will be discussed. Ionic volumes were calculated based on the TPTB extra-thermodynamic assumption.

## Acknowledgements

This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, POCI-01-0145-FEDER-007679 (FCT Ref. UID /CTM /50011/2013), financed by national funds through the FCT/MEC and when appropriate co-financed by FEDER under the PT2020 Partnership Agreement.

## NUCLEATION RATES OF CARBON-DIOXIDE GASHYDRATES

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The formation of gas hydrates is one of the challenges in plant operation under conditions of elevated pressures, humidity and low temperatures. Furthermore, applications like the sequestration of carbon-dioxide, the basic understanding of processes in oil industry and natural gas processing are the most prominent applications, which urgently require a profound knowledge of the physico-chemical aspects of the underlying mechanisms. Unfortunately, basic research on the kinetics of hydrate formation taking into account the different aspects of equilibrium thermodynamics and the kinetics of phase transitions are scarce.

With the present study we contribute to the understanding of the basics of hydrate formation, therefore, we have been characterized onset-conditions of the formation of gas hydrates from carbon-dioxide saturated water and have been determined characteristic times and nucleation for different degrees of supersaturation.

For this purpose a set of experiments has been performed using a high pressure apparatus suitable up to pressures of p = 700 bar. The set-up consists of two independent parts, which allow for a preparation of binary mixtures under defined conditions and rapid kinetic studies of phase transitions induced by fast pressure changes, respectively. This concept allows for an independent control of temperature and pressure without a change of the composition of a sample.

First results indicate a strong variation of induction times or even nucleation rates of hydrate formation at different degrees of supersaturation and are discussed in terms of classical nucleation theories.

### **Oral Session 5: Transport Phenomena**

10:05 - 12:45 Wednesday HS P1

Chairs: A. Friba, V. Shevtsova

#### FPF – O30 10:05 - 10:25 Wednesday

#### Room HS P1

## VISCOSITY MEASUREMENTS OF PURE $\rm N_2, \rm CO_2$ AND THEIR MIXTURES OVER WIDE DENSITY AND TEMPERATURE RANGES

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The viscosity of pure  $N_2$  and  $(N_2 + CO_2)$  mixtures was measured over the temperature range from (253.15 to 473.15) K with pressures up to 2 MPa utilizing a rotating-body viscometer. Herewith, the viscosity is determined relative to helium on the basis of the decay rate of a slender cylindrical body, which rotates inside the measuring cell and which is vertically levitated by a magnetic-suspension coupling. The same instrument was recently used in our group to accurately measure the viscosity of pure  $CO_2$  with pressures up to 1.2 MPa [1]. Three gravimetrically prepared mixtures with compositions of approximately 0.25, 0.50, and 0.75 mole fraction  $N_2$  in  $CO_2$  were investigated. The relative expanded combined uncertainty (k = 2) was estimated to be between (0.15 and 0.20)% for  $N_2$ . For the binary mixtures, uncertainties ranged between (0.20 and 0.39)%. The new experimental data for  $N_2$  show very good agreement with current experimental data and recent ab initio calculations. The experimental data for the binary mixtures were compared to an Extended Corresponding States model as implemented in the NIST REFPROP 9.1 database. For the N<sub>2</sub>-rich mixture, comparisons show relative deviations to the calculated values which increase with density up to -2.1%. For the equimolar mixture, relative deviations to the calculated values are almost constant over density for each isotherm with a maximum deviation of ?0.51%. For the CO<sub>2</sub>-rich mixture, relative deviations for all isotherms have a positive trend with increasing density and vary from ?0.42% to 0.34%.

Furthermore, simultaneous viscosity and density measurements for pure N<sub>2</sub>, CO<sub>2</sub>, and their mixtures (0.25, 0.50, and 0.75 mole fraction N<sub>2</sub>) were carried out with a combined viscometer-densimeter. For this purpose, several modifications were made to the apparatus that was described by Evers et al. [2]. The principle of viscosity measurement is also based on a rotating-body viscometer incorporating a magnetic-suspension coupling. To measure density, the rotating body can be moved upwards to a second stable suspension position in order to pick up a sinker, thus, applying the single-sinker density measurement method [3]. Measurements cover the temperature range from (253.15 to 473.15) K with pressures up to 20 MPa. The relative expanded combined uncertainties (k = 2) were estimated to be between (0.5 and 1.0)% for viscosity and about 0.1% for density. For the viscometer-densimeter, larger uncertainties in viscosity result from difficulties in the characterization of the fluid (disc) flow on top of the cylindrical body at higher Reynolds numbers. In summary, we provide a comprehensive data set that is an accurate basis to effectively improve the performance of

pure fluid and fluid mixture viscosity models.

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## FPF - 031 10:25 - 10:45 Wednesday

Room HS P1

## MEASUREMENT OF THERMODIFFUSION IN CAB/STYRENE/ 2-BUTANONE BY SORET FORCED RAYLEIGH SCATTERING

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We have examined experimentally the thermodiffusion (or the Soret effect) in the ternary polymer solutions composed of cellulose acetate butyrate (CAB), styrene, and 2-butanone. CAB is generally used polymer for the functional films. The understanding of the mass transport including the thermodiffusion in CAB/styrene/2-butanone is important to optimize the solution casting process, because the temperature gradient as well as the concentration gradient exists in the cast solutions in the drying process.

In the present study, the Soret coefficient, themodiffusion coefficient, and the diffusion eigenvalues of CAB/styrene/2-butanone have been measured by the holographic grating technique which we call the Soret forced Rayleigh scattering (SFRS) method. In the SFRS technique, the themodiffusion is induced by the temperature distribution with the interference pattern of the heating laser. The probing laser enters the sample at the Bragg angle and the mass transport is detected by the diffracted beam. For the measurement of the ternary systems, the two probing lasers of the different wavelengths ( $\lambda = 403$  nm and  $\lambda = 639$  nm) are employed, which enables the evaluation of the mass transport of the two independent components in ternary systems.

The measurement has been carried out on several compositions of CAB/styrene/2-butanone with the mass fraction of CAB  $c_{CAB} = 0.10$  at the temperature T = 298.2 K. The change of the sign of the Soret coefficient with the composition has been evaluated, which indicates that the thermophobic components turn into themophilic.

## Acknowledgment

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## LIQUID VISCOSITY AND SURFACE TENSION OF FISCHER-TROPSCH SYSTEMS USING SURFACE LIGHT SCATTERING (SLS)

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The Fischer-Tropsch process used to produce high valued petroleum products from synthesis gas has experienced revitalized interest in the last years. For product design and modeling, reliable information on viscosity and surface tension of representative fluid systems involved in the process is required. While the viscosity affects heat as well as mass transfer and determines power requirements for mixers and pumps, the surface tension is important in connection with mass transfer rates at the contacting gas-liquid interfaces and the wetting behavior at the catalytic nanopores.

The present contribution aims to provide accurate experimental data for the liquid viscosity and surface tension of Fischer-Tropsch related model systems at process-relevant conditions with temperatures above 473 K. Such investigations can improve the data situation for hydrocarbon systems in the high temperature range where no measurement results are available in literature so far. The fundamental advantage of the used surface light scattering (SLS) method lies in its application to samples in thermodynamic equilibrium. In addition, while most conventional methods determine viscosity and surface tension in a relative manner with two completely different sets of experimental equipment, both properties can be determined simultaneously without calibration in a contactless way by SLS.

The investigated systems comprise the pure fluids n-dodecane  $(n-C_{12}H_{26})$  and n-octacosane  $(n-C_{28}H_{58})$ , their binary mixture at a  $n-C_{12}H_{26}$  mole fraction of about 0.3, and the commercially available hydrocarbon wax SX-70 representing a multicomponent mixture of *n*-alkanes with a broad chain length distribution. It could be demonstrated that the SLS method can access the liquid viscosity and surface tension of such medium- to long-chained *n*-alkane systems close to saturation conditions over a broad temperature range from (323 to 573) K with a typical measurement uncertainty (k = 2) of 2%. Over the entire temperature range, a simple polynomial equation for the viscosity and a modified van-der-Waals equation for the surface tension represent the measured data of the pure and binary systems well. The larger values for viscosity and surface tensions and structural entanglement in  $n-C_{28}H_{58}$ . While the values for both properties of the binary mixture approximately follow a mass-weighted mixing rule based on the pure data, the measured viscosities and surface tensions of the wax system cannot be predicted by simple structure-property relationships.

#### FPF – O33 11:05 - 11:25 Wednesday

## DEPENDENCE OF THE FICK DIFFUSION COEFFICIENTS OF TERNARY BENZENE-ACETONE-ALCOHOL MIXTURES ON THE NUMBER OF METHYLENE GROUPS IN THE ALCOHOL

V. Shevtsova<sup>1</sup>, Y. Gaponenko<sup>1</sup>, T. Janzen<sup>2</sup>, G. Guevara-Carrion<sup>2</sup>, J. Vrabec<sup>2</sup>

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Liquids appearing in nature and industrial applications are essentially multicomponent. However, only data on binary diffusion coefficients are relatively abundant because the description of ternary mixtures is significantly more complex. Instead of a single diffusion coefficient, there is a  $2 \times 2$  diffusion matrix D with four independent Fick diffusion coefficients. The presence of cross-diffusion elements makes measurements in ternary systems more complicated because four Fick diffusion coefficients have to be determined from a signal for two components. Thus a very limited number of measurements [1-2] is available, and hardly any that are accompanied by molecular dynamics simulations [3].



**Fig.1a**. State points along the concentration path which Fick diffusion coefficients were studied.

Fig.1b. Studied alcohols.

We report the results of a study on diffusion in ternary mixtures of benzene-acetone and three different alcohols, i.e. methanol, ethanol and 2-propanol, which are investigated on microscopic and macroscopic scales by means of molecular simulation and Taylor dispersion experiments. The analysed state points are located along a concentration path traversing the centre of Gibbs triangle, cf. Fig.1a. The structure of alcohols is indicated in Fig.1b.

The role of the third component in diffusion processes appears to be surprising. It is found experimentally and confirmed numerically that one of the main elements of the diffusion matrix, i.e.  $D_{11}$ , and one of the eigenvalues do not depend on the type of alcohol.

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### FPF – O34 11:25 - 11:45 Wednesday

#### Room HS P1

## THERMAL PROPERTIES OF INORGANIC PCM SYSTEMS: THERMODYNAMIC MODELING AND EXPERIMENTAL METHODS

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Application of thermal energy storage systems facilitates a better load adjustment of systems for building air conditioning as well as an energetic optimization of the operating regimes. Phase change materials (PCM) for latent heat storage in which the reversible melting and crystallization process is utilized are well suited for such applications. Inorganic salts and salt hydrates prove advantageous particularly as PCM due to their high heat of fusion, their low prizes, the non-toxicity, and the non-inflammability.

Nevertheless, there are some restrictions in thermochemical behavior, that require effortful thermal measurements for identification and characterization of applicability of potential PCM [1]. Thus, inorganic salts show characteristic types of thermal behavior as glass formation, semi-crystallization, a large temperature hysteresis, and incongruent melting behavior (peritectic melt). The experimental search for optimum conditions for reversible melting and crystallization behavior is hence unrewarding.

Furthermore, the selection of pure substances with a suitable melting temperature for the respective application temperature range is very limited. However, the formation of eutectic mixtures from two or more components - which have a sharp melting point similar to those of the pure substances - can significantly increase the amount of potential PCMs for the pertinent temperature range.

Since there are currently no suitable concepts for the rational planning of PCM systems, procedures for the efficient screening of these systems have to be established. A new approach is presented to get extended insights into the phase equilibria of eutectic systems by means of thermochemical calculation methods (CalPhaD method) [2] and specified calorimetric measurements. Thus, time-consuming 'trail-and-error' procedures can be avoided.



**Figure 1**. Formation of ternary eutectic systems of inorganic salt hydrates and its experimental proof.

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## FPF – O35 11:45 - 12:05 Wednesday

### Room HS P1

## VISCOSITY AND DENSITY MEASUREMENTS ON COMPRESSED LIQUID *n*-TETRADECANE

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Paraffins and their mixtures are one of systems that are suitable to be phase change materials (PCM) for thermal energy storage. Normal tetradecane (n- $C_{14}$ ), has a melting point near 6 °C, which makes it a promising PCM for "low temperature" applications, like for instance, cold water storage tanks.

Models to describe energy charge and discharge of PCMs, in particular when contained in capsules, require the knowledge of thermophysical properties of both their solid and liquid phases. The development of two-phase moving boundary models, may require accurate data on the thermophysical properties of the PCM's, at pressures slightly above atmospheric pressure.

The main aim of the present communication is to discuss the measurements of the viscosity of compressed normal tetradecane  $(n-C_{14})$  in the region of moderately high pressures, eventually more important for paraffin energy storage applications, where the available literature data are scarce.

Aiming to compare the viscosity with literature data, the measurement range extended to a pressure up to about 70 MPa, covering the temperature range (283-358) K. The measurements have been performed using the vibrating wire technique in the forced oscillation mode of operation.

Complementary density data have also been measured, by means of an Anton Paar U-tube DMA HP apparatus, using a DMA 5000 densimeter as a reading unit, in the temperature range from (283 to 373) K and pressures from (0.1 to 70) MPa. As far as the authors are aware, these results extend the range of published data from (323 to 373) K and pressures from (60 to 70) MPa.

The viscosity results were correlated with density, using a heuristic modified hard-spheres scheme, based on the van der Waals model of a fluid. The RMSD of the data from the correlation is less than 0.43% and the maximum absolute percent deviation is less than 1.0%. The expanded uncertainty of the present viscosity measurements is estimated to be  $\pm 0.9\%$  at a 95% confidence level.

The density results were correlated with the temperature and pressure using a modified Taittype equation. The expanded uncertainty of the present density data is estimated as  $\pm 0.2\%$ at a 95% confidence level. The isothermal compressibility and the isobaric thermal expansion coefficients were calculated by differentiation of the correlation equation. Their uncertainties are estimated to be less than  $\pm 1.7\%$  and  $\pm 1.1\%$ , respectively, at a 95% confidence level.

## FPF - 037 12:05 - 12:25 Wednesday

### Room HS P1

## MEASUREMENTS OF DIFFUSION OF HYDROCARBON FLUIDS IN SUPERCRITICAL CO<sub>2</sub> AT HIGH PRESSURES

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The subject of  $CO_2$  storage and utilisation is a widely known problematic in the global climate change discussion. One promising technique for long-term storage is the sequestration of  $CO_2$  in depleted oil & gas reservoirs. Under these conditions, the carbon dioxide will be in its supercritical state. Another active utilisation of  $CO_2$  is its use for enhanced oil recovery (EOR) ? injecting it into oil & gas reservoirs at high pressure in order to push the hydrocarbons out. Supercritical carbon dioxide is also used as an extraction solvent, and a natural refrigerant. All of these applications are impacted and even governed by the diffusion process.

Our objective is to investigate the diffusive properties of hydrocarbon impurities in  $CO_2$ , and how they depend on pressure, temperature and the nature of hydrocarbon. A particular focus

is therein set onto the supercritical condition of  $CO_2$ . To conduct the investigation, a dedicated experimental setup has been developed, comprising a Taylor dispersion instrument working at high pressure.

As a first step, the diffusion coefficients of benzene in supercritical  $CO_2$  have been measured to allow for an extensive benchmarking; and the results have been favourably compared with the available literature data. This serves as a confirmation of the experimental installation, the method of measurement, and the quality of data/ results. Following that, detailed measurements have been carried out on the mixture Methane/ $CO_2$  (20/80 mol%) in sub- and supercritical  $CO_2$ . The results have been extensively studied and compared to the few works available on this subject. A number of other fluids have then been investigated on their diffusion inside  $CO_2$  for the first time in scientific practice: such as hexane, dodecane, IBB and THN.

Among the key-findings is the observation that the dependence of the diffusion coefficient on the density of  $CO_2$  exhibits a local maximum, in the so-called Widom region around the supercritical density. The phenomenon seems to occur for all the tested fluids. This intriguing point calls for further investigation. Presently, the research is continuing on multiple other fluids.

## FPF - O38 12:25 - 12:45 Wednesday

Room HS P1

## MEASUREMENTS OF MASS DIFFUSION APPROACHING CRITICAL POINT

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Immiscible liquids find a wide application in such a field of chemical technology as the liquid-liquid batch extraction, with mass diffusion remaining always a limiting factor in the process. While the extraction itself is essentially multicomponent process, knowledge of binary diffusion coefficients forms a good starting point for estimations. The problem is that while the binary diffusion coefficients for ordinary liquid mixtures are easily accessible, the mixtures featuring a demixing zone are essentially more difficult to measure.

As an example, the binary mixture of methanol-cyclohexane is a challenge for experimental investigation of mass diffusion as it exhibits a wide demixing zone at normal conditions and being strongly non-ideal shows a rapid variation of the coefficient with concentration.

To assess the diffusion coefficients at these tough conditions we have developed a dedicated set-up. A special design of the diffusion cell, based on the counter-flow injection, allows creating of steep interface between two solutions of slightly different concentration that diminishes an impact of initial transient. Very sensitive interferometric probing resolves small concentration differences which in turn allows to minimize an effect of concentration on the measured diffusion coefficient. The full instrument (including all fluidic lines) is packed into an isolated and thermostabilised enclosure which enables experiments in a required temperature range avoiding the danger of demixing.

Using the developed set-up we have conducted careful measurements of the diffusion coefficients in the mixture Meth-Ch on both sides of the miscibility gap keeping the temperature constant. Such sets of measurements were performed for a few different temperatures. Our experiments have not been performed at a fixed composition but rather at a fixed temperature, and the distance to the spinodal changes by variation of the composition. The diffusion coefficients in the mixture Meth-Ch close to the miscibility gap have revealed a characteristic slowing down near the binodal. We have interpreted this in the spirit of the pseudospinodal concept, where scaling laws can also be observed for off-critical mixtures on approach of the spinodal, which is hidden under the binodal and not directly accessible.

## **Oral Session 6: Alternative Refrigerants**

10:30 - 12:50 Thursday HS P1

Chairs: S. Bobo, Y. Kano

Room HS P1

## FPF – O39 10:30 - 10:50 Thursday

## MEASUREMENT AND CORRELATION OF THE THERMAL CONDUCTIVITY OF 1,1,2,2,4,5,5,5-NONAFLUORO-4-(TRIFLUOROMETHYL)-3-PENTANONE

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Due to concerns about both ozone-depletion potential and global-warming potential, there is active research into finding alternative fluids that are environmentally friendly to replace existing CFC's and HCFC's. 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone (CAS 756-13-8), a fluorinated ketone, has been investigated as a potential working fluid for organic Rankine cycle applications, and also as a gaseous fire suppression agent. It is more commonly known by the trade names Novec 649 and Novec 1230. In this work, we report thermal conductivity measurements of 1,1,1,2,2,4,5,5,5-nonafluoro-4-(trifluoromethyl)-3-pentanone at temperatures from approximately 180 K to 500 K with pressures up to 70 MPa. The measurements were made with two hot-wire apparatus with platinum wires of 12.7 mm diameter. The measurements were made with the steady-state technique for gas at pressures below 1 MPa, while the transient technique was used for liquid and supercritical gas at pressures above 1 MPa. The low-temperature apparatus was used at temperatures from 180 K to 330 K, while the hightemperature apparatus was used at temperatures above 330 K. The experimental data were used to develop a wide-ranging correlation for the thermal conductivity valid over liquid, gas, and supercritical states that includes an enhancement in the critical region. The correlation is presented in terms of temperature and density, with a recent Helmholtz-formulation equation of state used to provide densities and other properties needed for data analysis and theory in the critical region.
#### LIQUID AND VAPOR PHASE DENSITY MEASUREMENTS FOR TRANS-1,3,3,3-TETRAFLUOROPROPENE (R1233ZD(E))

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Many of the most promising synthetic compounds being considered as potential substitutes for the present high-GWP refrigerants are halogenated olefins (HCFOs and HFOs), i.e. unsaturated hydrochlorofluorocarbons and hydrofluorocarbons containing one carbon-carbon double bond characterized by GWP values similar to that of natural refrigerants. Within this group, trans-1-chloro-3,3,3-trifluoroprop-1-ene (R1233zd(E)) is one of the most interesting working fluids for chiller applications, high temperature heat pumps, and organic Rankine cycles (ORC) due to its relatively high NBP (291.14 K).

In this paper, compressed liquid density and vapour phase density data for the refrigerant R1233zd(E) will be presented in a wide range of pressures and temperatures. Only one set of data [Mondejar et al. (2015)] is available in the open literature for densities in the single-phase regions for a total of 155 data for temperatures between 215.0 K and 443.9 K and pressures between 255 kPa and 24078 kPa. Hulse et al. (2012) measured 13 saturated liquid density data in the range between 243.3 K and 298.2 K.

Compressed liquid density was measured at CNR-ITC with a vibrating tube densimeter (Anton Paar DMA 512), calibrated by measuring the oscillation period of the U-tube under vacuum and filled with a fluid of known density (water). The overall estimated uncertainty for the density data is within 0.1%. A total of 93 data were measured along 9 isotherms between 283.15 K and 363.15 K for pressures up to 35 MPa.

Vapor phase p-v-T data were measured at UnivPM using a constant volume apparatus based on a stainless steel sphere with calibrated volume. The uncertainty for the specific volume measurements is estimated to be 0.005 m<sup>3</sup> · kg<sup>-1</sup>. A total of 72 data were measured along 8 isochores between 308 K and 373K for pressures up to 0.693 MPa.

The results obtained for both compressed liquid density and vapour density are shown and discussed through a comparison with literature data. The paper also presents a saturated liquid density correlation, a Tait correlation for the compressed liquid density data, and a Martin-Hou equation of state for the vapour phase p-v-T data.

#### SURFACE TENSION AND KINEMATIC VISCOSITY OF 2-METHYL-3-PENTANONE AND TRANS-1-CHLORO-3,3,3-TRIFLUOROPROPENE

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2-Methyl-3-pentanone (Novec 1230), with zero ozone depletion potential (ODP) and global warming potential (GWP) of less than 1 (100 years), has been proposed as Fire Protection with Greater margin of safety and lower environmental impact. Trans-1-chloro-3,3,3trifluoropropene (R1233zd(E)) has an GWP of 7 and ODP of 0.00024 to 0.00034. But its ODP can be neglected due to its relatively short atmospheric lifetime of 26 days. R1233zd(E) was widely used in organic Rankine cycles, and expected as working alternatives to 1,1,1,3,3-Pentafluoropropane (R245fa). Surface light scattering (SLS) represents a non-invasive optical technique for measuring surface tension and liquid viscosity. In contrast to conventional method, SLS has the advantage of not requiring a thermal gradient for measurements so there is no driving force for natural convection, making it particularly suitable for measurements near the gas-liquid critical point. In the present study, SLS method was applied to investigate the surface tension and liquid viscosity of Novec 1230 and R1233zd(E) with a temperature range from 303K to 433K and 303K to 403K, respectively. For determination of the liquid viscosity, the expanded uncertainties on a confidence level of more than 95 % (k = 2) are estimated to be 2% for reduced temperatures  $T_r(=T/T_c) \leq 0.95$ , and 6% for  $T_r$  close to 0.99. For the surface tension, the expanded uncertainties are less than 1.5% (k = 2) in the whole temperature range. A corresponding states method with two reference fluids were used to predict the surface tension of Novec 1230 and R1233zd(E). The results agree well with the experiment data. The absolute average deviations are  $0.14 \text{ mN} \cdot \text{m}^{-1}$  and  $0.37 \text{mN} \cdot \text{m}^{-1}$ , respectively.

#### FPF – O42 11:30 - 11:50 Thursday

#### Room HS P1

# U-TUBE DENSITY MEASUREMENTS OF FOUR LUBRICANTS AND HOW CALIBRATION CHOICES MAY AFFECT RESULTS

#### S. L. Outcalt

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Compressed-liquid densities of four lubricants have been measured from 270 K to 470 K at pressures from 0.5 MPa to 50 MPa. The fluids included pentaerythritol tetrapentanoate (PEC5), pentaerythritol tetraheptanoate (PEC7), pentaerythritol tetranonanoate(PEC9), and Royco 899 a commercially produced lubricant. Measurement results for each of the lubricants will be presented and compared to existing literature data.

The compressed-liquid densities of the lubricants studied cover a density range from  $828 \text{ kg/m}^3$  to  $1062 \text{ kg/m}^3$ . While the densities of the four lubricants are similar to that of water, none of them have a density range that is completely bounded by that of water over the same range

of temperature and pressure. Additionally, the viscosities of the lubricants are significantly greater than water, in some instances as much as one hundred times greater. As such, water alone may not be the best calibration fluid to most accurately determine the densities of these lubricants. Analysis of the lubricant data with various calibration fluids and different calibration equations will be presented to explore how these parameters effect the resulting densities.

#### FPF – O43 11:50 - 12:10 Thursday

#### Room HS P1

## SPEED OF SOUND AND DIELECTRIC CONSTANT MEASUREMENTS FOR LOW-GWP REFRIGERANTS IN THE GAS PHASE

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Hydrofluoroolefins (HFOs) are expected to be used for refrigerants with much lower global warming potential (GWP) than the existing hydrofluorocarbons (HFCs). It is important to know thermophysical properties of these new refrigerants so as to evaluate the performance in a practical thermal cycle system.

We measured speed of sound and dielectric constant in the gas phase for some refrigerants of HFOs. These properties were simultaneously measured by using a cylindrical acousticmicrowave cavity resonator. Two condenser microphones were used for a sound transmitter and receiver. The transmitter microphone generates audio frequency sound wave in the sample gas filled resonator. The sound wave propagating through the sample gas is detected by the receiver microphone, and its amplifier and phase-shift are measured with a frequency response analyser. In addition, two antennae, which were made from a copper semi-rigid cable, were put onto the each side end-plate of the resonator. Microwave is transmitted and detected by antennae in the gas filled resonator, and its resonance frequency curve is measured with a vector network analyser. Speed of sound was obtained from the acoustic resonant frequency in longitudinal mode, meanwhile dielectric constant was obtained from the microwave resonant frequency in transverse magnetic (TM) mode. The cavity dimensions of the cylindrical resonator, which are about 50 mm of length and 24 mm of diameter, were determined by measuring microwave resonant frequency under vacuum on each isotherm. No calibration using a reference gas is therefore needed to determine the cavity dimensions.

The measured speed of sound data was fitted to the acoustic virial equation so as to derive the ideal gas heat capacity at constant pressure from extrapolation to zero pressure. Similarly, the measured dielectric constant data was fitted to the dielectric virial equation which is an expanded function of Clausius-Mossoti equation related to the molar polarizability. Combined with Debye equation, dipole moment can be obtained by investigating temperature dependence of the molar polarizability in the ideal gas state.

## THERMAL CONDUCTIVITY OF R1234ZE(E) + R32 MIXTURES FROM 283 TO 363 K AT PRESSURES UP TO 20 MPA

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The Montreal Protocol and its subsequent amendments have created a schedule to replace ozone-depleting substances, such as chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), with chlorine-free molecules in several industrial applications. Trans-1,3,3,3tetrafluoropropene (R1234ze(E)) is a new synthetic working fluid expected as an alternative to conventional refrigerants R410A, R32 and R134a due to its zero ozone depletion potential (ODP) and low global warming potential (GWP). However, because of its low evaporating pressure and small latent heat, R1234ze(E) presented with low cooling capacity, low heat transfer performance and low coefficient of performance(COP) than R134a and R32. Comparing with the single component, R1234ze(E) mixtures have better adaptability in COP and heat transfer characteristic. Thermophysical properties of these mixtures are essential to the optimum design of energy conversion systems and the investigation of their performance in refrigeration or heat pump cycles. In this work, the thermal conductivity of difluoromethane (R32, CAS No. 75-10-5) + trans-1,3,3,3-tetrafluoropropene (R1234ze(E), CAS NO. 29118-24-9) binary system were measured over the temperature range from 283 to 363 K and at pressures up to 20 MPa with difluoromethane mass fractions of 0.10, 0.30, 0.50, 0.70 and 0.90, respectively. The expriment was conducted using the transient hot-wire method with single oxidized tantalum hot wire. The performance of the apparatus was tested by measuring the thermal conductivity of saturated liquid toluene from (283 to 363) K, which agreed with recommended values with a maximum deviation of 0.91%. The uncertainty of the thermal conductivity data was less than  $\pm 2.0\%$  with the coverage factor k = 2.

#### FPF – O45 12:30 - 12:50 Thursday

#### Room HS P1

# VAPOR PRESSURE AND CRITICAL PRESSURE MEAUREMENTS OF R1233zd(E) AND R356mmz

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Measurements of the vapor pressures and critical pressures for R1233zd(E) (trans-1-chloro-

3,3,3-trifluoropropene) and R356mmz (1,1,1,3,3,3-hexafluoro-2-methoxypropane) were carried out by the isochoric method. Twenty-eight vapor pressure data for R1233zd(E) were obtained in the temperature range between 291 K and 425 K and in the pressures 99 kPa and 2823 kPa. Thirty vapor pressure data for R356mmz are also obtained in the temperature range between 295 K and 415 K and in the pressures 37 kPa and 1174 kPa. These new refrigerants are expecting as the working fluids of organic Rankine cycles and of high-temperature heat pump system.

In the measurements for high temperature region, pressure transducer was calibrated taking consideration of temperature dependence at evacuated state. On the basis of the present data, vapor pressure correlations are newly formulated. In addition, the critical pressures of two refrigerants were determined from these correlations.

### Acknowledgments

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## **Thermal Insulation (TI)**

**Oral Session 1: Thermal Insulation** 

11:05 - 12:05 Monday HS PHEG016

### TI – O1 11:05 - 11:25 Monday

Room HS PHEG016

Chair: J.-R. Filtz

# THERMAL CONDUCTIVITY MEASUREMENT OF INSULATING MATERIALS WITHIN PROJECT EURA-THERMAL

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Within the frame of one objective of the European Metrology Programme for Innovation and Research (EMPIR) dedicated to capacity building, the project Eura-Thermal aims at strengthening in the field of thermal metrology, the traceability between National Metrology Institutes (NMIs) and Designated Institutes (DIs) in central and south east of Europe [1]. Based on experience acquired by the major NMIs in Europe, therefore, this collaborative project has a particular objective to implement and improve the metrological infrastructure in the field of thermo-physical properties in order to ensure reliable and traceable thermal conductivity measurements on materials.

The thermal characterization of materials is crucial for the building industry and thermal conductivity is the essential characteristic of insulating materials. Practically, the guarded hot plate (GHP) is a standard method for measuring this property. It has been largely developed and validated during the last decade within the main NMIs in Europe. The validation of this method is usually performed by using reference materials and through international inter-laboratory comparisons, enabling to insure the traceability of thermal conductivity measurements to the SI [2].

Considering the operating range of facilities of the laboratories involved in this project, measurements will be performed over a temperature range from 10 °C to 60 °C using two different widely available insulation materials. The inter-laboratory comparison was designed taking into account the diversity of the different GHPs. Specimens of selected materials have been machined in order to conform to dimensions of heater plates and especially, geometries

of metering sections [3].

This paper provides an overview of the Guarded Hot Plate and Heat Flow Meter facilities, their temperature ranges and uncertainties, which are available with respect to inter-laboratory comparison for the thermal conductivity measurement of insulating materials within Eura-Thermal project. This work will also give highlights in the context of the European Roadmap for Thermo-physical Properties Metrology [4].

This work was funded through the European Metrology Programme for Innovation and Research (EMPIR). The EMPIR initiative is co-funded by the European Union?s Horizon 2020 research and innovation programme and the EMPIR Participating States.

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## TI – O2 11:25 - 11:45 Monday

### **Room HS PHEG016**

# EFFECTIVE THERMAL CONDUCTIVITY OF INHOMOGENEOUS MULTIPHASE SYSTEMS

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The effective thermal conductivity of multiphase systems consisting of a matrix structure and a homogeneously distributed filling phase such as foams can be predicted by various analytical expressions. One example for this is effective medium theory. These analytical expressions are of great importance since the functional correlations between physical parameters are shown and the understanding of physics is improved. However, up to now all of these expressions do not account for the local distribution of the filling phase but assume a representative volume that can be approximated to be homogeneous. Changes in the local distribution of the filling phase lead to changes in the effective thermal conductivity. The impact of such inhomogeneities on the effective thermal conductivity is not accounted for and is therefore not described by these expressions.

In this work, the effective thermal conductivity of a insulation foam containing macroscopic inhomogeneities meaning homogeneous approximation is not possible is experimentally

investigated by means of guarded hot plate (GHP) technique (ISO 8302) an especially by means of numerical simulations, in this case finite element method and the analysis of the heat flow which determines the effective thermal conductivity. The relevant physical properties and their correlation are identified by a parameter study where the size, form, volume fraction and position of the inhomogeneities are varied. It can be shown that the effective thermal conductivity depends on the thermal conductivities of the components and also the distribution and coupling between the macroscopic inhomogeneities such that there are non-trivial minima for certain configurations. This again helps to understand, to modify and to optimize the effective thermal conductivity of any specimen.



**Figure 1**. The plot shows the simulated local heat flow in a PU foam specimen versus the position on the GHP. The rectangle shows the simulated temperature field in the homogeneous specimen ( $\lambda = 0.040 \,\mathrm{Wm^{-1}K^{-1}}$ ) with two inhomogeneities ( $\lambda = 0.100 \,\mathrm{Wm^{-1}K^{-1}}$ ). The effective thermal conductivity is  $\lambda_{\mathrm{eff}} = 0.042 \,\mathrm{Wm^{-1}K^{-1}}$ .

#### TI – O3 11:45 - 12:05 Monday

#### Room HS PHEG016

## THERMAL CONDUCTIVITY INVESTIGATION ON ZEOLITE POROUS COMPOSITES WITH A COMBINED APPROACH

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Thermalphysical properties of zeolite play essential roles on the heat transfer efficiency in catalytic and adsorption applications. Due to the lack of knowledge of solid's true thermalphysical properties as database for evaluating heterogeneous heat transfer in porous materials, an approach consists in a combination of experimental and theoretical methods is introduced in this research, in order to determine the apparent and true thermal conductivity of zeolite-based porous materials.

Experiments were carried out with transient method by Laser Flash. Zeolite Y (FAU) and

SAPO-34 (CHA) with pseudoboehmite (binder) were chosen as model systems. Pellet-shaped samples made of either type of zeolite with different wt.% compositions of binder and different levels of porosity were prepared, which were achieved by tuning the proportion of peptizing agent added during slurry preparation, as well as using different pelletizing pressures. Characterization results from TG, XRD and nitrogen-sorption indicated that zeolite crystal remained its crystallinity after pelletizing.

Sample's apparent thermal conductivity  $(\lambda_{app})$  was calculated by equation  $\lambda(T) = \alpha(T) \cdot \rho(T) \cdot c_p(T)$ . Apparent thermal diffusivity  $(\alpha_{app})$  was measured by Laser Flash method firstly at 20 °C under atmospheric pressure, then until 300 °C with vacuum condition, while bulk density  $(\rho)$  was calculated from its geometry and heat capacity  $(c_p)$  was determined by DSC. Pellet's solid density was also characterized by helium pycnometer in order to define its porosity  $(\epsilon)$ . Results of apparent thermal conductivity showed that binder has a positive effect on heat transfer properties, and the calculated apparent thermal conductivity decreased with increasing porosity in a linear function, while increased with increasing temperature.

Therefore, solid thermal conductivity ( $\lambda_s$ ) of each composition was found by extrapolating the measured thermal conductivity vs. porosity relationship to zero volume pore fraction. Followed by extrapolating solid thermal conductivity of all compositions to zero binder fraction, true thermal conductivity ( $\lambda_{true}$ ) of zeolite Y was found to be 0.104 W/(m·K) and zeolite SAPO-34 of 0.047 W/(m·K) at room temperature.

Furthermore, experimental results were compared to Loeb, Morser, Eucken and Russell's theoretical models, and fitting parameter was inserted to adjust the effective porosity. Modelling results showed that apparent thermal conductivity of zeolite Y could fit in Loeb, Morser and Eucken's models well with porosity parameters of approximately 1.35, 1.43 and 1.25, respectively, while SAPO-34 was observed with lower values of approximately 1.25, 1.34 and 1.14 for each model. Differences in thermalphysical properties between the two types of zeolite could be explained by microstructural characteristics which influence the heat transfer by phonons.

## Phase Equilibria (PE)

### Oral Session 2: Phase Equilibria I

15:30 - 17:30 Monday HS PHEG016

### PE – O1 15:30 -15:50 Monday

#### Room HS PHEG016

Chair: M. Monte

## REFERENCE MATERIALS FOR PHASE EQUILIBRIUM STUDIES (PRELIMINARY RESULTS OF IUPAC PROJECT 2011-037-2-100)

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The objective of IUPAC project 2011-037-2-100 is to provide a list of recommended reference materials with reliable, critically evaluated property values for phase equilibrium studies (such as VLE, LLE, and SLE). Such recommendations, which are currently lacking, are needed for instrument/method validation, including inter-laboratory comparisons and assessment of uncertainties.

During the first stage of the project implementation, we summarized classifications of phase equilibria as well as methods of measurements and decided to cover simple binary equilibria as the appropriate first choice for experimentalists. Previous recommendations for testing distillation columns were considered in the project; some mixtures proposed for distillation columns can also be reference materials for realization of VLE, but they cover only part of the project needs (mixtures with similar volatility of the components at moderate and high pressures), while the scope of the project also includes mixtures of components with different volatility and nature. Criteria of selection have been developed as follows: availability of reliable data from several consistent literature sources, convenience of handling, safety, availability of materials, established methods of purification and analysis. Candidate mixtures with the largest numbers of available phase equilibrium data have been selected from the NIST data collection (SOURCE database). The initial screening excluded hazardous and unstable components, components needing extreme conditions (extremely low or high temperatures), and mixtures with highly inconsistent literature data. The second project stage constitutes validation and modeling that involves assessment of experimental errors and scattering, consistency with other properties, and trends in series of similar mixtures. This data analysis and modeling is being primarily conducted with the use of the ThermoData Engine (TDE) expert system. Models providing smoothing and interpolation will also be a part of the recommendation.

The presentation will bring to discussion preliminary results of the project (tentative reference systems), the initial list of mixtures, and the proposed final selection with the reasons of each decision.

#### PE – O2 15:50 - 16:10 Monday

#### **Room HS PHEG016**

## SOLID-LIQUID PHASE DIAGRAM PREDICTION OF SALT HYDRATE MIXTURES USING THE MODIFIED BET MODEL

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Latent heat storage using phase change materials (PCM) provides thermal energy storages with high storage capacities in small temperature ranges. In order to select PCM for an application, the entire phase change has to take place within the application temperature range. Most of the PCM used in applications are solid-liquid PCM storing heat in repeated melting and crystallisation processes. Among the common PCM material classes, salt hydrates are comparably cheap and offer high volumetric enthalpy changes.

However, in certain application-relevant temperature ranges, there is a lack of PCM based on salt hydrates that are cost-effective and thermally cycling stable. Since most salt hydrates are known, mixtures of two salt hydrates or mixtures of one salt hydrate and a salt (i.e. ternary mixtures of two salts and water) are being investigated. In order to identify interesting compositions (e.g. ternary eutectics) and to reduce the experimental effort, prediction models are applied to determine solid-liquid phase diagrams.

The modified BET model requires only two model parameters and has proven to be able to predict phase diagrams of salt hydrate mixtures over a wide concentration and temperature range. The model parameters can be determined from the water activity of the two binary subsystems which in turn can be calculated from water vapour pressure data. Independently of the prediction model, the solid phases have to be known that occur in the investigated temperature and concentration range. In the case of salt hydrate mixtures, the solid phases to be known are binary salt hydrates and possible ternary double salts.

In this work, ternary solid-liquid phase diagrams of systems containing water and salts with  $NO_3-$ , Cl-, Br-, and  $ClO_4-$  as anions have been predicted via the modified BET model. Thereby, PCM-relevant ternary and pseudo-binary eutectics have been identified. For example, the projection of the ternary solid-liquid phase diagram of the system  $LiBr + LiNO_3 + H_2O$  on the composition triangle is shown in Figure 1. The intersection of the boundary curves at the point E corresponds to a ternary eutectic between  $LiBr \cdot 3H_2O$ ,  $LiNO_3$ , and  $LiNO_3 \cdot 3H_2O$  with a calculated melting temperature of 261.6 K. In order to verify the predicted phase diagrams, calorimetric measurements of such eutectic compositions and/or measurements of the solubility of ternary mixtures have to be carried out.



**Figure 1**. Phase diagram of the system  $LiBr + LiNO_3 + H_2O$ ; solid phases: LiBr (1),  $LiBr \cdot H_2O$  (2),  $LiBr \cdot 2H_2O$  (3),  $LiBr \cdot 3H_2O$  (4),  $LiNO_3$  (5), and  $LiNO_3 \cdot 3H_2O$  (6); ternary eutectic E

#### PE – O4 16:10 - 16:30 Monday

#### **Room HS PHEG016**

# APPLICATION OF DENSIMETRY FOR PHASE-EQUILIBRIUM MEASUREMENTS ON CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub> AND THEIR MIXTURES

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Phase equilibria of fluid mixtures are important in numerous industrial applications and improved data, particularly along the dew line, are needed to improve model predictions. Near the dew line, sorption effects can distort the composition and introduce systematic errors in the measurement. In this work, we measure (carbon dioxide + propane) mixtures. This system is important for natural gas processing and is of interest as a natural refrigerant. Furthermore it is well suited for studies of sorption phenomena because both components are well known and their similar molecular mass eliminates certain confounding effects.

The  $(p, \rho, T, x)$  behaviour of two (carbon dioxide + propane) mixtures as well as pure carbon dioxide and pure propane was investigated with a two-sinker magnetic suspension densimeter. The measurements were carried out along isotherms over a temperature range of 253.15 K to 293.15 K and extended from low pressures into the two-phase region. The mixtures were gravimetrically prepared with compositions of (0.75 and 0.90) mole fraction CO<sub>2</sub>.

An alternative solution of the working equations for the two-sinker experiment allowed us to determine the adsorbed mass on the sinker surfaces. We used the sharp increase in adsorbed mass with increasing pressure and density to deduce the dew point density. The single-phase data were fitted to a virial model, and it was found that, because of increased uncertainties

in the measured pressure near the dew point, calculating the dew-point pressure from the dew-point density using the virial model gave a more reliable dew-point pressure compared to a direct interpretation of the pressure data. We compare our results with literature data, but find that the large uncertainty and scatter in the literature data preclude any definitive confirmation of the present method.

We have previously demonstrated this measurement technique on other binary mixtures [1], but report here, for the first time, its application to pure fluids. Since the dew-point pressure and density of carbon dioxide and propane are accurately known we can use the literature data to conclude that the analysis of adsorbed mass through the use of densimetry provides an accurate determination of the dew point.

#### References

[1] McLinden, M.O.; Richter, M., J. Chem. Thermodyn. 2016, 99, 105-115.

### PE – O5 16:30 - 16:50 Monday

#### **Room HS PHEG016**

### CALORIMETRIC INVESTIGATION OF HYDRATES OF PURE ISOBUTANE AND ISO-AND NORMAL BUTANE MIXTURES

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The results of calorimetric investigations of phase behavior of pure isobutane, normal butane and their mixtures in water-saturated quartz powder and in bulk under the hydrate formation conditions are presented. Kinetics of phase transitions, including hydrate formation and dissociation is studied. Investigations were performed in the temperature range from 235 to 280 K and at pressure up to 10 MPa. The main thermodynamic parameters of water normal butane - isobutane ternary system are obtained. Based on the experimental data of specific heat and temperature derivative of pressure at constant volume, the phase diagrams of isobutane and normal butane and their mixtures including the gas hydrate field have been constructed. The range of compositions for isobutane and normal butane mixtures has been defined when hydrates are still formed. The lower and upper quadruple points of pure isobutane hydrate and the quintuple point of isobutane hydrate formed by the mixture of isobutane and normal butane are detected. Isobutane in mixture of butanes is a main hydrate former component. Normal butane effects on thermodynamic parameters of hydrate formed by isobutane. An upper quadruple point of the pure isobutane hydrate is transformed into a line of upper quadruple points of isobutane hydrate, which is in equilibrium with binary mixture of isobutane and normal butane. A line of upper quadruple points starts at the upper quadruple point of pure isobutane hydrate (T = 275,14 K, P = 0,169 MPa) and stretches to the quintuple point of isobutane hydrate formed by the mixture of isobutane and normal butane (a three-component system of water, isobutane and normal butane in quartz powder) at T = 273,16 K, P = 0,146 MPa. On the other hand, a low quadruple point of the pure isobutane hydrate at T = 273,16 K, P = 0,122 MPa is transformed into a quintuple point of water normal butane - isobutane ternary system. The content of normal butane at quintuple point is 29,9  $\pm$ 0,5% mol. Accordingly, the content of isobutane is 70,1  $\pm$ 0,5% mol. Concentration of isobutane is not dependent on concentration of this one in initial mixture (before hydrate formation). Stability of isobutane concentration in mixture of butanes is provided due to partial dissociation (or formation) of hydrate formed by isobutane. A three-component system of five phases (water - ice - hydrate - liquid butanes - gaseous butanes) has zero degree of freedom in quintuple point. There is only one value of the pressure, temperature and content of butanes for which the five phases can exist together in equilibrium.

#### Acknowledgment

This work was supported by the Russian Foundation for Fundamental Research under Grants No. 16-08-00032\16.

### PE - O6 16:50 - 17:10 Monday

#### **Room HS PHEG016**

### SOLUBILITIES OF DERIVATIZED ANTHRAQUINONES IN SUPERCRITICAL CO2

K. Tamura

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In the process design and development of the supercritical dyeing process, the solubility and phase equilibria of dyestuffs in supercritical carbon dioxide ( $scCO_2$ ) are fundamental physical properties. Disperse dye molecule used in the dyeing process is based on anthraquinone molecule with substitutional groups, hydroxyl, amino, nitro, chloro, and their complexes. The solubility of anthraquinone derivatives changes variously with the additional groups on the anthraquinone. To understand the solubility of anthraquinone dyestuffs in  $scCO_2$ , we have to find out the effect of substituted groups on the solubilities in  $scCO_2$ .

In the present work, we have measured the solubilities of anthraquinone, 1-hyroxyanthraquione, 1-aminoanthraquinone, 1-nitroanthraquinone, 1-chloroanthraquinone, and 2-methyl anthraquinone, 1-(methylamino)anthraquinone, and 1,4-dihydroxyanthraquinone in scCO<sub>2</sub> at the temperature ranges of (323.15, 353.15 and 383.15) K and over pressure ranges of (12.5 to 25.0) MPa by a flow type apparatus and examined how the solubility of anthraquinone compounds in scCO<sub>2</sub> changes with the substitutional groups on the anthraquinone. We found that the additional groups of anthraquinone derivatives make the solubility of anthraquinone in scCO<sub>2</sub> increase in order of methyl, hydroxyl, chloro groups, and decrease by amino and nitro groups.

The experimental results were correlated by semiempirical models expressed in terms of CO2 density. Moreover, the solubilities of anthraquinone derivatives were analyzed thermodynamically by the regular solution model with the Flory-Huggins theory and by a modified PSRK equation of state. The binary interaction parameters between the additional groups of the PSRK model were determined from the correlation. Good agreement between the experimental and calculated solubilities of the anthraquinone derivatives was obtained.

#### PE - 07 17:10 - 17:30 Monday

#### VAPOR-LIQUID PHASE EQUILIBRIA OF R1234ZE(E)/IONIC LIQUIDS AS THE WORKING PAIRS FOR ABSORPTION REFRIGERATION

Lihang Bai, Siqi Liu, Xiangyang Liu, Maogang He

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Ionic liquids are composed of a cation and an anion, which are liquid at room temperature. They have the advantages of negligible vapor pressure, high thermal and chemical stability, etc. Trans-1,3,3,3-tetrafluoropropene (R1234ze(E)) has zero ozone depletion potential, very low global warming potential, good chemical stability and very low boiling point. Ionic liquids + R1234ze are considered to be promising working pairs for the absorption refrigeration cycle, which can overcome the drawbacks of the commonly used working pairs  $NH_3/H_2O$  and  $H_2O/LiBr$  including crystallization, corrosion, negative pressure operation and being toxic. The solubility of refrigerant in absorbent has an important influence on the efficient of the absorption refrigeration cycle. A large amount of solubility data of different gases in ionic liquids have been reported in recent years for the various applications of ionic liquids. Only our group reported the experimental solubility data of R1234ze(E) in 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ([HMIM][Tf\_2N]).

In this work, the solubilities of R1234ze(E) in 1-hexyl-3-methylimidazolium tetrafluoroborate ( $[HMIM][BF_4]$ ), 1-hexyl-3-methylimidazolium hexafluorophosphate ( $[HMIM][PF_6]$ ) and 1-hexyl-3-methylimidazolium trifluoromethanesulfonate ([HMIM][TfO]) at temperature from 293 K to 343 K and at pressures up to 0.6 MPa were measured with an isochoric saturation method. The experimental data was correlated with Non-random Two Liquid equations with a good accuracy. The performances of the absorption refrigeration cycle with the studied systems as the working pairs were analyzed.

#### Acknowledgment

This work was supported by the National Natural Science Foundation of China (No. 51506172).

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Room HS PHEG016

### Oral Session 3: Phase Equilibria II

10:20 - 12:40 Tuesday HS PHEG016

Chairs: A. Bazyleva, M. O. McLinden

#### PE - 08 10:20 - 10:40 Tuesday

#### Room HS PHEG016

#### VAPOR-LIQUID EQUILIBRIUM OF WATER+1-BUTANOL MIXTURES ABOVE UCST

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Government policies in several countries are encouraging the use of renewable energy, by implementing directives such as "Directive 2009/28/EC of the European Parliament and of the Council on the promotion of the use of energy from renewable sources". However, the large portion of the world's energy is still based on fossil fuels. In the case of transportation, biofuels have achieved major breakthroughs, but much remains to be studied in this area. The main objective in the use of biofuels is to mitigate carbon dioxide emissions, through its recycling from atmosphere by storage in plant's cellulose, hemicellulose, starches, sugars and oils, that are process by man into biofuels used in transportation [1]. This processing by man is what delay's further progresses in the area, since there's still much concern about the cost/benefit of the processes that generate biofuels. One example is biobutanol. With more carbons than ethanol, biobutanol proved to have superior fuel properties than bioethanol, depending on the isomer used. Another advantage on its use is the non-restriction in its blend with gasoline, allowing this biofuel to fully substitute gasoline, in comparison with bioethanol. However, its processing is still more expensive than bioethanol.

These facts have come to our attention that much has to be studied for the implementation of new biofuels in Portugal, starting with its thermodynamic properties and behaviours for process design, namely alcoholic mixtures. Several binary mixtures of alcohol and water have been studied using Vapor Liquid Equilibria (VLE) and densimetry, to better understand the dynamic of these mixtures [2-4]. In this paper, we present our complete study on VLE of water+1-butanol above upper critical solution temperature (UCST), using a flow VLE apparatus. Despite all advantages that the equipment proven to have in the past, modifications were made to permit this type of studies with immiscible systems.

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[4] A.F. Cristino, S. Rosa, P. Morgado, A. Galindo, E.J.M. Filipe, A.M.F. Palavra and C.A. Nieto de Castro, *Fluid Phase Equilib*, 398, 5-9 (2015).

#### PE - O9 10:40 - 11:00 Tuesday

#### **Room HS PHEG016**

#### A NEW EXPERIMENTAL METHODOLOGY FOR THE STUDY OF HYDROCARBON PHASE-BAHAVIOUR UNDER CONFINEMENT

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Improved geophysical evaluation, extended-reach drilling and hydraulic fracturing have enabled greatly increased production of hydrocarbons from shale reservoirs; this has, in turn, led to growing interest and research into shales. Those unconventional reservoir formations are characterised by low permeability and small pores, typically in the nanometer range. At these scales, confinement effects upon the phase behaviour and physical properties of the hydrocarbon fluids are thought to be significant as evidenced by molecular simulations [1] and experiments [2]. The main goal of the present work is to study such confinement effects experimentally for hydrocarbon mixtures under conditions of elevated pressure and temperature. Understanding such effects is of course important in the evaluation of hydrocarbon-bearing shale formations [3].

A bespoke constant-volume synthetic phase-behaviour apparatus has been constructed with which it is possible to determine bubble points at pressure up to 70 MPa and temperatures up to 473 K with or without the presence of a porous medium. As a model for the complex fluids and minerals found within a shale oil formation, we study idealized systems comprising a mesoporous medium (SBA-15) and a binary hydrocarbon mixture. The SBA-15, with pore-throat diameters below 10 nm, was prepared in-house and characterized by standard techniques. Carbon coated SBA-15, to replicate the organic content of shales, has also been studied. To date, the fluid mixtures considered are (methane + pentane) and (methane + decane) and experiments have been performed at pressures up to about 24 MPa and temperatures up to 400 K. The methodology employed, including a Monte Carlo uncertainty analysis, will be presented together with experimental results for the systems mentioned.

### References

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#### PE – O10 11:00 - 11:40 Tuesday

## PHASE BEHAVIOR OF TERNARY MIXTURE WATER + ALKANE + NON-IONIC SURFACTANT

Hiroyuki Matsuda, Risa Emata, Yoshihiro Inoue, Yuki Nakazato, Kiyofumi Kurihara, and Katsumi Tochigi

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*n*-Alkyl polyglycol ethers  $CH_3(CH_2)_{i-1}(OCH_2CH_2)_jOH(C_iE_j)$  are the most important class of non-ionic surfactants. They are widely used in many different industrial processes such as the surfactant flooding in tertiary oil recovery, production of herbicides, drugs, cosmetics and nano particles. Understanding the phase behaviours of the ternary mixture water + alkane +  $C_iE_j$  is very crucial in order to choose a suitable surfactant and surfactant concentration for the flooding process [1]. It is also important in the fundamental research of critical phenomena and wetting transitions.

The object of this study is an accurate determination of the liquid-liquid equilibrium (LLE) data of ternary mixtures water + *n*-alkane +  $C_iE_j$  using a cloud point method with laser scattering technique. Phase diagram of water + *n*-alkane +  $C_iE_j$  has been reported to exhibit complex behavior called "Fish-Shaped" [1]. *n*-Octane was selected as alkane. 2-butoxyethanol ( $C_4E_1$ ) and 2-(2-hexyloxyethoxy)ethanol ( $C_6E_2$ ) were selected as non-ionic surfactant. In the measurement of ternary mixtures, the  $C_iE_j$  free basis mass fraction of *n*-octane " $\alpha$ " was changed from 0.1 to 0.9. As an example of experimental results, experimental LLE of two ternary mixtures water + *n*-octane +  $C_4E_1$  and water + *n*-octane +  $C_6E_2$  in  $\alpha = 0.5$  and 0.7 are illustrated in Figs. 1 (a) and (b). The number "1", "2", "2", and "3" in these figures indicate the number of liquid phase. In the fish-type phase diagram, body is three-liquid phase, tail is one-liquid phase, and other region is two-liquid phase. An intersection of the body and tail is called "X-point". Two-liquid phase, and the region " $\overline{2}$ " and " $\overline{2}$ " is W/O (Water in Oil) microemulsion phase. X-point was determined from the experimental LLE data. LLE moved to lower temper-atures and lower mass fraction of  $C_iE_j$  way with an increase of carbon number of  $C_iE_j$  in fixed  $\alpha$ .





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PE – 011 11:20 - 11:40 Tuesday

**Room HS PHEG016** 

# EXPERIMENTAL AND MODELLING STUDIES ON THE VAPOR-LIQUID EQUILIBRIA OF LNG MIXTURES AT CONDITIONS RELEVANT TO THE SCRUB COLUMN

S. Z. Al Ghafri, T. J. Hughes, F. Perez, C. J. Baker, B. F. Graham and E. F. May

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LNG distillation (scrub) columns are used to remove heavy components that may freeze out and foul or even block the main cryogenic heat exchanger (MCHE) used in liquefied natural gas (LNG) processes. The hydrocarbons in natural gas that pose the greatest risk of forming solids are the so called BTEX (benzene, toluene, ethylbenzene and xylenes) compounds. To prevent the possible occurrence of such blockages, one possible way is to improve the predictive reliability of existing models, in particular cubic equations of state (EOS). However, the model?s accuracy depends on the availability of relevant experimental VLE data.

To better represent those industrial conditions, the VLE of a ternary methane + propane + toluene mixture was studied over a wide range of conditions with toluene as the minor component in both the liquid and vapor phases. Measurements of the VLE of this ternary mixture were conducted along different isochoric paths at temperatures between (213 and 298 K) and pressures up to 8.3 MPa. Two apparatus were used for the VLE measurements. The first apparatus was used for measurements from (263 to 298) K while the second one was

mainly used for measurements down to 213 K. Both apparatus incorporated sampling of the liquid and gas phases by means of using sampling valves and a GC that was fitted either with a FID or BID detector.

The measured VLE data were compared to results calculated with the HYSYS Peng Robinson (PR) equation of state (EOS) that is used widely in LNG industry [1]. The amount of toluene in the vapour phase was found to be under-predicted by the HYSYS PR EOS by an average of around 50%, with the error increasing as temperature and toluene concentration decreased. These VLE measurements unambiguously demonstrate that the HYSYS PR EOS as well as other cubic EOS substantially under-predict the possible toluene content of saturated vapours that could be present in the overhead of the LNG scrub column. The current work also underscores the importance of improving predictions of the allowable threshold concentration of BTEX in fluids entering the MCHE so as to avoid potential freeze-out.

The predictions of the HYSYS PR EOS were improved by tuning the model interaction parameters using our VLE data. The present work also demonstrates the prediction capability of different cubic EOS. Furthermore, the effect of the increased amount of toluene content in the vapor phase on process designing and process operating conditions was investigated by using ASPEN PLUS [1].

#### References

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### PE - O12 11:40 - 12:00 Tuesday

#### **Room HS PHEG016**

### STUDY OF SOLID-LIQUID PHASE DIAGRAMS OF METHYL ESTERS AND ALKANES BY DIFFERENTIAL SCANNING CALORIMETRY

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The availability of energy is essential for the humanity and nowadays a key factor of progress and sustainability. The use and availability of energy at relatively low cost and abundance, are dependent of alternative sources and types of energy. Biodiesel is an important alternative to mineral sources of energy, but some challenges should be overcome in order to optimize their production, usability, sustainability and to decrease their environmental impact.

The study of low temperature behavior of biodiesel and Blends, namely the study of the effect of the composition in the crystallization on Blends of diesel with Biodiesel. In this work was explored different mixtures with molar fractions between 0 and 1 to create solid-liquid phase diagrams of methyl esters like methyl stearate and methyl palmitate, with alkanes like hexadecane and octadecane, to understand the crystallization behavior of the main compounds in Biodiesel with an alkane present in the Diesel fuel.



**Figure 1**. DSC of a mixture of 30% (mol/mol) of methyl stearate and 70% (mol/mol) of hexadecane and a typical phase diagram.

### Acknowledgments

This work was financially supported by Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, European Social Fund (ESF) for the projecto CIQUP, University of Porto (Projects: PEst-UID/QUI/00081/2013, FCUP-CIQ-UP-NORTE-07-0124-FEDER-000065), the project CICECO-Aveiro Institute of Materials (Ref. FCT UID /CTM /50011/2013 and FEDER under the PT2020 Partnership Agreement.) and Galp Energia. N.F.M.B. thanks FCT and Galp Energia for the PhD Research Grant: PD/BDE/113540/2015. A.I.M.C.L.F thanks FCT for the Post-Doc: SFRH/BPD/84891/2012.

### PE - 013 12:00 - 12:20 Tuesday

**Room HS PHEG016** 

## UNUSUAL PHASE BEHAVIOR OF HYDROCARBON MIXTURES WITH LOW CONTENT OF HIGH MOLECULAR COMPONENTS

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A method of precision adiabatic calorimetry for investigation of phase behavior of binary (methane, propane), ternary (methane, propane, heptane) and seven-component (methane, ethane, propane, butane, pentane, heptane, decane) hydrocarbon mixtures was applied. The thermodynamic properties, phase behavior and kinetics of phase transitions of liquid and gaseous hydrocarbons have been studied in the temperature range from 100 to 370 K and in pressure range from 0.1 to 40 MPa. A method of precision adiabatic calorimetry makes

possible to construct the phase diagrams of hydrocarbon mixtures, as well to determine with higher accuracy PVT data of condensate dew points. Phase transitions are determined by the discontinuity of directly measured specific heat and temperature derivative of pressure at constant volume. Our particular attention was paid to the hydrocarbon mixtures with low content of high molecular components (content of  $C_{5+}$  components is less then 2.0 mol%) due to the fact that standard methods with the use of conventional PVT experiments not guarantee the efficiency and accuracy of phase diagram. Our investigations showed that phase behavior of hydrocarbon mixtures with low content of high molecular components is qualitatively differed from traditional phase behavior. The region of phase state of hydrocarbon mixtures with low content of high molecular components includes the extensive domain of uncertainty and cannot be studied by conventional PVT experiments and cannot be prognosticate theoretically.

Data of our measurements showed that phase diagram of seven-component hydrocarbon mixture with low content of high molecular components is drastically transformed compared to traditional concepts. Hydrocarbon mixture is split on a macroscopic phase concentrated by methane, ethane, propane and two microscopic phases concentrated by isobutane, pentane, and heptane, decane. It was found out that these phases are equilibrium phases. To prove that all phases are equilibrium phases the cooling regime of measurements was used. At the cooling regime of measurements the same phase transitions as at the heating regime occur. These phase transitions correspond to formation of two microscopic phases concentrated by heptane, decane and isobutane, pentane and formation of a macroscopic liquid - vapour phases concentrated by methane, ethane and propane. To reveal the impact of individual hydrocarbon components on seven-component phase diagram the binary and ternary mixtures have been studied.

#### Acknowledgment

This work was supported by the Russian Foundation for Fundamental Research under Grants No. 16-08-00032\16.

### PE - O14 12:20 - 12:40 Tuesday

Room HS PHEG016

#### VAPOR-LIQUID EQUILIBRIUM FOR DIFLUOROMETHANE (R32) + 1,1-DIFLUOROETHANE (R152a) + 2,3,3,3-TETRAFLUOROPROP-1-ENE (R1234yf) TERNARY SYSTEMS

#### Tao Yang, Xianyang Meng, Jiangtao Wu

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The Paris agreement, adopted by the United Nations Framework Convention on Climate Change (UNFCCC) in 2015, is a crucial point in the global challenge of climate change, aiming at creating a more suitable way of living for human beings collectively. China has issued many specific policies on climate change, especially limiting the greenhouse gas emissions and developing the low GWP refrigerants. According to China's Policies and Actions for Addressing Climate Change (2016), the large majority of artificial refrigerants (R134a, R404A, R410A) with high GWP should be phased out gradually. 1,1-difluoroethane (R152a) and 2,3,3,3-Tetrafluoroprop-1-ene (R1234yf) were paid close attention as replacements

for 1,1,1,2-tetrafluoroethane (R134a) [1]. Difluoromethane (R32) is a refrigerant with superior thermodynamics properties, which is commonly used as one component in mixtures. The thermophysical properties of the refrigerant blends, especially vapor-liquid equilibria, are essential to develop the equation of state and identify the phase behaviour. Following our previous work [2], the vapor-liquid equilibrium for the ternary system of difluoromethane (R32) + 1,1-difluoroethan (R152a) + 2,3,3,3-tetrafluoroprop-1-ene (R1234yf) were measured with a quasi-static analytical apparatus in the temperature range from 283.15 to 323.15 K. The Peng-Robinson-Stryjek-Vera (PRSV) equation of state combined with the Wong-Sandler (WS) mixing rule and the non-random two-liquid (NRTL) activity coefficient model was employed to describe the ternary VLE properties. With the parameters of PRSV+WS+NRTL model for binary mixtures (R32 + R152a, R32 + R1234yf and R152a+ R1234yf), the calculated values for the ternary VLE show excellent agreement with the experimental results.

### Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51476130) and the Specialized Research Fund for the Doctoral Program of Higher Education of China (No.20130201110046).

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#### Oral Session 4: Phase Equilibria III

15:30 - 17:30 Tuesday HS PHEG016

Chairs: Ch. Rathgeber, J. Oliveira

#### PE - 015 15:30 - 15:50 Tuesday

#### **Room HS PHEG016**

# THE INTERACTION BETWEEN DEPLETION FLOCCULATION AND MOLECULAR LIQUID-LIQUID PHASE SEPARATION MECHANISMS

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There is growing interest in the formulation and application of nano-colloids in fields as diverse as medicine, hydrocarbon production, and environmental science. Successful applications rely on a detailed understanding of the related fluid physics and chemistry. Depletion flocculation, the interaction of a non sorbing polymer with nano-colloids in a good solvent leading to phase separation with polymer-rich and colloid-rich phases, is a well-established phase separation mechanism with diverse applications [1]. In the present work, we explore the interaction between depletion flocculation and molecular liquid-liquid (LL) phase separation mechanisms in a near critical binary mixture experimentally [2] based on mixtures of polystyrene (mean molar mass ~200 kg/mol, atactic form) + cyclohexane. This binary possesses cloud points and an upper critical end point (UCEP) close to 25 °C [3]. 7 nm diameter fumed silica nanoparticles, which do not sorb polystyrene on their surfaces, are added at temperatures above the UCEP. Impacts of nanoparticle addition on phase compositions at temperatures below cloud points and on cloud point temperature values at fixed polystyrene to cyclohexane ratios are reported along with impacts of nanoparticle addition on UCEP temperature and composition. Large deviations in phase behaviour are observed. For example, in mixtures comprising a 1:9 polystyrene to cyclohexane ratio, addition of 1 wt.% silica pushes the cloud point temperature above 50  $^{\circ}$ C (the upper limit of the experiments) and phase compositions observed at 23  $^{\circ}$ C persist at high temperatures. This change in behaviour, while significant, is readily anticipated and attributable. By contrast, at 2.5 wt.% silica nanoparticles, only one liquid phase is observed above 25 °C for the same mixture. For this case, the attribution is less apparent. These and other experimental outcomes are discussed and compared with experimental outcomes related to the impacts of toluene and heptane (1 and 5 wt.%) on the polystyrene + cyclohexane LL phase envelope.

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#### PE – O16 15:50 - 16:10 Tuesday

**Room HS PHEG016** 

### QUANTIFICATION OF SORPTION PHENOMENA ON NONPOROUS MEDIA NEAR MIXTURE DEW POINTS BY DENSIMETRY

M. Richter<sup>1</sup>, M. O. McLinden<sup>2</sup>, R. Kleinrahm<sup>1</sup>, K. Moritz<sup>1</sup>, C. Tietz<sup>1</sup>

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Phase equilibria of fluid mixtures are important in numerous industrial applications and are, thus, a major focus of thermophysical property research. Improved data, particularly along the dew line, are needed to improve model predictions. Here we present experimental results utilizing highly accurate densimetry to quantify the effects of sorption and capillary condensation, which exert a distorting influence on measured properties near the dew line. With a two-sinker densimeter, modified for sorption studies, we investigated the (p,  $\rho$ , T, x) behavior of binary (CH<sub>4</sub> + C<sub>3</sub>H<sub>8</sub>) and (Ar + CO<sub>2</sub>) mixtures over the temperature range from (248.15 to 273.15) K starting at low pressures and increasing in pressure towards the dew point along isotherms [1]. Three distinct regions were observed: (1) minor sorption effects in micropores at low pressures; (2) capillary condensation followed by wetting in macro-scale surface scratches within approximately 98% of the dew-point pressure; (3) bulk condensation. We postulate that the true dew point lies within the second region.

Based on these results we conclude that to achieve the goal of significantly improving the data situation for dew-point pressures and densities of fluid mixtures, sorption phenomena near the dew point need to be accurately quantified. The present experiments were the first step in a comprehensive investigation of sorption phenomena and their distorting effects on thermophysical property measurements near the dew line, and here we go on to outline our future plans. This will require a combination of experiment and modeling. To that end, a special four-sinker densimeter has been designed that is optimized for both gas-density measurement and for gravimetric sorption analysis; the fabrication of this instrument is in progress. Moreover, we are applying molecular simulation to give us a qualitative understanding of the sorption processes on an atomistic level, which will help us to identify the location of the true dew point within the capillary condensation/wetting region. The modeling studies are being compared to experimental results obtained with a modified commercial gravimetric sorption analyzer as presented in a companion talk [X. Yang, et al.]. Modeling insights will be combined with experimental results to develop an empirical model that will account for, and correct, sorption effects.

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#### PE - 017 16:10 - 16:30 Tuesday

## BUBBLE PRESSURE MEASUREMENT AND PREDICTION FOR n-ALKANE + NAPHTHENIC HYDROCARBON BINARY MIXTURES

#### S. Ahitan, J. M. Shaw

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Cubic equations of state are widely used for phase equilibrium calculations due to their simplicity and reliability, especially for hydrocarbon mixtures. Unfortunately, common choices such as the Peng-Robinson and Soave-Redlich-Kwong equations of state systematically predict both qualitatively and quantitatively incorrect phase behaviors for long chain n-alkane + aromatic and naphthenic mixtures unless negative binary interaction parameter (kij) values are used [1, 2]. Binary interaction parameters are typically obtained by fitting vapour-liquid equilibrium (VLE) data for binary mixtures. Experimental VLE data for these mixtures are scarce. In this study, VLE data for representative binary mixtures of naphthenes with long chain n-alkanes are presented. The selected n-alkanes range from  $n-C_{20}$  to  $n-C_{28}$ . These compounds are paired with naphthenes including cyclohexane, alkyl-cyclohexanes and decahydronaphthalene. These experimental data are compared with computed bubble pressures using the Peng-Robinson, Soave-Redlich-Kwong and PC-SAFT equations of state in order to evaluate the accuracy of predictions and to obtain custom k<sub>ij</sub> values. In a parallel companion works, bubble pressure data and the corresponding fitted  $k_{ii}$  values for 15 representative long chain n-alkanes + aromatic binary mixtures are reported [3] and strategies for estimating k<sub>ii</sub> in the absence of experimental data are discussed [4]. Expected applications of these contributions include improved phase behavior model accuracy for hydrocarbon production, transport and refining environments, and improved corresponding state based transport property predictions, particularly for viscosity, that require accurate phase behaviors and phase compositions as inputs.

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### MUTUAL SOLUBILITY OF TRANS-1,3,3,3-TETRAFLUOROPROPENE (R1233ZD(E)) AND A POE OIL FOR LOW TEMPERATURE ORC

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The application of a refrigerant as working fluid implies the identification and optimal choice of the compressor lubricant, which must ensure a proper lubrication of the moving parts and at the same time sufficient gas sealing in all the operative conditions. In particular, a proper level of mutual solubility between oil and refrigerant is essential: too high solubility can cause dangerous decrease of viscosity and oil foaming, while partial immiscibility could inhibit oil return to the compressor. Solubility, that is the thermodynamic phase-equilibrium (VLE or VLLE), depends strongly on temperature and concentration, and its knowledge is of great importance for designing the system and selecting lubricants.

Within the group of hydrofluorocarbons (HFO) identified as possible low-GWP substitutes for the present high-GWP refrigerants, trans-1-chloro-3,3,3-trifluoroprop-1-ene (R1233zd(E)) is one of the most interesting working fluids for chiller applications, high temperature heat pumps, and organic Rankine cycles (ORC) due to its relatively high NBP (291.14 K).

In this paper, the mutual solubility of R1233zd(E) and a commercial POE oil with ISO viscosity of 173 mm<sup>2</sup>/s, suitable for ORC applications, has been experimentally studied in a wide range of temperatures and concentrations. The measurements, based on a static synthetic method, have been performed at isothermal conditions in a stainless steel cell, endowed with observation windows, immersed in a thermostatic bath.

Mutual solubility data have been obtained along four isotherms in the range between 293 K and 353 K, exploring all the range of mass fraction between the two pure components and paying special attention to the region at very high refrigerant concentration (mass fraction >98%), closer to the actual circulating composition of the oil/refrigerant mixture inside a circuit. The estimated uncertainties were  $\pm 0.03$  K for temperature,  $\pm 2$  kPa for pressure, and a maximum of  $\pm 0.015$  for the liquid phase mass fraction.

### PE - 019 16:50 - 17:10 Tuesday

### Room HS PHEG016

# VISUAL MEASUREMENTS OF SOLUBILITY AND INDUCTION TIMES FOR HYDROCARBON MIXTURES

A. Siahvashi, S. Z. Al Ghafri, J. H. Oakley, T. J. Hughes, B. F. Graham and E. F. May

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Production of LNG is technically demanding, as it requires the exploitation and detailed understanding of phase equilibrium in multi-component mixtures at high pressure and low temperatures. Avoiding the conditions of solid-liquid equilibrium is particularly important for the multi-component hydrocarbon mixtures found in the main cryogenic heat exchanger of an LNG plant. Compounds heavier than pentane ( $C_{6+}$ ), which are normally present only at trace concentrations in the methane-dominant liquid mixture, can potentially freeze-out and block the narrow tubing networks within the heat exchanger if process upsets occur and/or the composition of the feed natural gas changes more than expected.

A specialized apparatus designed for visual measurements of solid-liquid equilibrium (SLE) and solid-liquid-vapor equilibrium (SLVE) was constructed and used to measure liquidus (melting) temperatures in binary mixtures of cyclohexane ( $C_6H_{12}$ ) and octadecane ( $C_{18}H_{38}$ ) across the entire range of composition and at pressures from about (0.004 to 10) MPa. A Peltier-cooled copper tip immersed in the liquid mixture was used to determine both freezing and melting temperatures by varying the temperature of the copper tip relative to the stirred, bulk liquid. With the bulk liquid held at the mixture's SLVE temperature, the induction time required to nucleate solid octadecane decreased exponentially as the subcooling of the copper tip increased, halving approximately every 0.25 K. At higher pressures, while the melting temperature of pure cyclohexane (cyC<sub>6</sub>) increased by about 0.3 K.MPa<sup>-1</sup>, at xcyC<sub>6</sub> = 0.5675 it increased by only 0.09 K.MPa<sup>-1</sup>. The new data were compared with measurements reported in the literature, empirical correlations describing those literature data, and the predictions of models based on cubic equations of state (EOS), including the Peng-Robinson Advanced (PRA) EOS implemented in the software Multiflash. The best description of the data was achieved by adjusting the binary interaction parameter in the PRA model from 0 to 0.0324, which reduced the deviation of the SLVE data at the eutectic point (xcyC<sub>6</sub>  $\approx 0.95$ ) from (12.8 to -0.2) K. Although the accuracy of predictions made with the SLVE-tuned PRA EOS deteriorated at pressures around 10 MPa, they were still as good as, or better, than the empirical correlations available for this system. Furthermore, the SLVE-tuned PRA EOS was more accurate at describing literature VLE data for this binary than the default PRA EOS, reducing the r.m.s. deviation in bubble temperature predictions by an order of magnitude from (6.7 to 0.67) K.

In future work, the visual SLE cell will be integrated into a cryostat to allow operation at temperatures around 100 K, and combined with a sampling system to allow the liquid composition to be monitored. This will enable the acquisition of new data and improvement of models able to describe SLE and related phenomena in mixtures relevant to LNG production such as those containing high-risk BTEX compounds.

### PE - O20 17:10 - 17:30 Tuesday

#### **Room HS PHEG016**

### ESTIMATION OF VAPOR PRESSURE OF HALOGENATED FLUORENES

J. A. S. A. Oliveira, M. J. S. Monte

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Fluorene and polyfluorene derivatives have been increasingly used as optically active components for electronic devices, such as organic light emitting diodes (OLEDs) and organic solar cells (OSCs), drawing the attention of the scientific and technological communities. The use of halogenated fluorenes has been described in the literature as intermediates in the synthesis of high performance light-emitting oligomers and polymers based in fluorene core. The vapor pressure and other thermodynamic properties of fluorene and of its derivatives have been studied over decades. Their low volatility has hindered the accurate experimental determination of their vapor pressures and related thermodynamic properties. So, these important data are scarce and often inaccurate.

Following our studies on the thermodynamic characterization of fluorene derivatives, the present work focuses on the vapor pressure study of halogenated fluorenes. Vapor pressures of fluorene [1] and of eight fluorene derivatives with halogen substituents in positions 2-, 2,7-[2,3], and 9- [4] have been reported. Their sublimation properties (standard molar enthalpy, entropy and Gibbs energy) were derived from the dependence of the vapor pressure with temperature. In this study, we present a user-friendly equation that enables the accurate estimation of the vapor pressure, at T = 298.15 K, of fluorene and of halogenated fluorenes where the halogen atoms occupy the positions (2-, 2,7-, or 9-). Using the derived equation (1) the standard Gibbs energy of sublimation (and then the vapor pressure) can be calculated just taking into account the temperature of fusion of those compounds and the molecular *van der Waals* volume.

$$\begin{split} \Delta^g_{\rm cr} G^o_m / {\rm kJ \cdot mol^{-1}} &= -65.1 + 0.0994 \, (T_{\rm f} / {\rm K}) + 0.389 \, \left( V_{\rm vdW} / {\rm \AA}^3 \right) \\ R^2 &= 0.997; \ \sigma / {\rm kJ \cdot mol^{-1}} = 0.6 \end{split}$$

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### Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, for the financial support to Project UID/QUI/0081/2013 and to FEDER (COMPETE 2020) for the financial support to Project POCI-01-0145-FEDER-006980 and to Project NORTE-01-0145-FEDER-000028 that also supports a research grant to J.A.S.A.O.

## **Engineering Applications (EA)**

**Oral Session 5: Engineering Applications** 

10:05 - 12:25 Wednesday HS PHEG016

Chairs: L. Mitterhuber, R. Černy

### EA - O1 10:05 - 10:25 Wednesday

**Room HS PHEG016** 

### PROPERTY NEEDS FOR THE LOW-GWP REFRIGERANTS

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Hydrofluorocarbons (HFCs), currently used as refrigerants in air-conditioning and refrigeration systems, are potent greenhouse gases, and their contribution to climate change is projected to increase. A phase-down of HFCs is mandated in the European Union, and a 2016 amendment to the Montreal Protocol mandates a global phase-down. Thus, replacement fluids must be found, but the thermophysical properties of many of the proposed replacement refrigerants are not known well enough to optimize equipment using the new fluids.

In this talk, we will outline the property data needed for the design of refrigeration systems. The thermodynamic properties largely determine the efficiency and refrigeration capacity of the vapor compression cycle and are thus the key data needed for the comparison of one refrigerant with another. Most useful is a formulation of the thermodynamic properties in terms of an equation of state (EOS), and thus we will discuss the experimental data needed for EOS development. The transport properties are a secondary priority although they also have a major impact on the design of equipment.

The fluids under consideration for future systems include natural refrigerants, such as ammonia, carbon dioxide, and simple hydrocarbons as well as new olefin-based fluorinated fluids (*i.e.*, molecules containing a carbon-carbon double bond that are termed HFOs). For many applications, refrigerant blends will be used, and the lack of mixture data is the major impediment to the development of more-accurate equations of state. Current projects to fill in these data gaps will be summarized.

Standard values for the thermodynamic properties of several "traditional" refrigerants are specified in the 2005 edition of ISO Standard 17584—Refrigerant Properties. A revision to this standard to include the new, low-GWP fluids is in progress, but has been stymied by a lack of experimental data and suitable property models. We thus invite the larger thermophysical properties community to become involved in this effort both through research and in participation in the ISO Working Group revising the Standard (which will meet in Graz following the ECTP).

#### EA – O2 10:25 - 10:45 Wednesday

#### TEMPERATURE-DEPENDENT HEAT PATH ANALYSIS OF A LED MODULE

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In the solid state lighting sector the thermal management is a key aspect, due to reliability and efficiency issues. Thermal investigations of light emitting diode (LED) modules during operation gain more and more importance. A powerful tool for this investigation provides the thermal transient analysis. The thermal transient contains thermal information of the LED module, which can be exposed by the conversion to a structure function. The structure function presents a map of thermal capacitances ( $C_{\rm th}$ ) with respect to thermal resistances ( $R_{\rm th}$ ) along the heat flow path of the device, starting from heat source to the heat sink. Structural changes in the heat flow path of LED module are reflected by the structure function.

The aim of this study was to analyse the heat flow of a four flip-chip LED module. This heat path analysis was performed by the combined approach of experiments and simulations. The structure functions were obtained by both, thermal transient experiments via T3ster setup and finite volume simulations. The simulations were adjusted via validation process to the measurements. The validated simulation allowed assigning regions of the function with physical sections in the module and regions could be visualized via isothermals. A further investigation of the LED module was made to study its thermal behavior at different operating conditions (heat-sink temperature, operating current and usage of different attachments to the heat sink). The operating conditions were systematically varied by a Design of Experiment (DOE) approach.

Although the operating condition should cause no differences in the structure functions under idealistic assumptions, the result of the DOE revealed that the temperature of the heat sink caused the main influence of the device's thermal behavior. The temperature dependency of the corresponding experimental structure function was observed by the shifts of the  $R_{\rm th}$  values. Assuming, this originated from temperature-dependent thermal conductivities of the device's materials. The validated simulation model was used to implement the temperature dependent thermal conductivities, and so the temperature dependence under the described conditions could be confirmed.

#### EA – O3 10:45 - 11:05 Wednesday

## MILESTONE THERMODYNAMICS OF THE RENEWABLE FUELS AND HYDROGEN STORAGE

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Biofuels derived from biomass are a promising alternative energy source due to the potential for such fuels to be carbon neutral. Efficient process design requires accurate thermodynamic property information. We set an establishing benchmark thermodynamic properties and prediction of feasibility for the renewable fuel processing and alternative to conventional hydrogen storage technologies as a main goal of this project. The complex of modern thermochemical and theoretical methods was designed, developed and established in the Thermochemical lab at the Samara State Technical University. The procedure included extended experiments, critical evaluation of available data and prediction of the missing thermodynamic properties in order to provide the best possible property values as the milestones for the assessment of the feasibility of processes intended for valorisation of the natural products and the optimal hydrogen storage using favourable chemical reactions. Focus of our project has been on thermodynamic analysis of the following processes: production of dimethylfuran for liquid fuels from biomass, utilization of building block chemicals produced from sugars and lignocellulosic biomass via biological or chemical conversions, and utilization of glycerol. A challenging part of the project has been thermodynamic analysis and selection of liquid organic heteroaromatics for hydrogen storage as an auspicious alternative to conventional technologies.

#### Acknowledgments

This research (work, investigation) was supported by the Government of Russian Federation (decree No. 220 of 9 April 2009), agreement No. 14.Z50.31.0038.

#### EA – O4 11:05 - 11:25 Wednesday

**Room HS PHEG016** 

### HEAT AND MOISTURE TRANSPORT AND STORAGE PARAMETERS OF BRICKS AFFECTED BY THE ENVIRONMENT

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Most computational models of heat and moisture transport applied currently for the calculation of moisture and temperature fields are generally suitable for the assessment of hygrothermal performance of building envelopes. However, any model can provide reliable information only in the case that the quality of input data is very good. This is not always true because the standard lists of thermal and hygric parameters given by the producers as well as the material databases included in the simulation tools are usually far from complete. In particular, the data often do not include the dependencies of heat and moisture transport and storage parameters on moisture content. The time dependence of the values of thermal and hygric parameters caused by damage cumulation is taken into account only exceptionally.

In this paper, we present the time-dependent measurements of thermal conductivity, specific heat capacity, moisture diffusivity, water vapor diffusion coefficient and sorption isotherms of several types of bricks currently used on the territory of Central Europe over a wide range of moisture content. Basic physical properties are determined as well, in order to assess the possible damage and correlate it with the heat and moisture transport and storage parameters. The samples are exposed to the external environment in a test facility located in the city of Prague. The upper horizontal surfaces of the specimens are covered so that the wind, rain, snow and sun radiation affect only the vertical surfaces, similarly as in their practical application on building site. The time duration of the experiment is three years while testing of the particular specimen groups is performed every year. Reference samples are tested as well, for the sake of comparison. The measured heat and moisture transport and storage parameters are then used as input data in a set of computer simulations of hygrothermal performance of building envelopes based on the analyzed types of bricks, and the effects of cumulated damage on moisture and temperature fields are discussed.

#### EA – O5 11:25 - 11:45 Wednesday

**Room HS PHEG016** 

# EXPERIMENTAL MODEL DESIGN AND NUMERICAL VERIFICATION OF AERO-THERMAL-STRUCTURAL INTERACTION

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Thermal protection system, which is related to the safety of hypersonic vehicle, is one of the most key techniques in design and manufacture of hypersonic vehicles. The new thermal protection mode based on multi-channel coupling is becoming the main mode for new generation hypersonic vehicle. The computation strategy and method of aero-dynamic-thermal-structural coupling problem must be considered under this new mode. It is quite important to verify the effectiveness of multi-field coupling calculation method. Thus a wind tunnel test for verification is unavoidable. In this paper, to meet the requirements for the coupling verification experiment, the wind tunnel selection, the model size estimation, the model aerodynamic design, the model material and its structure design are carried out based on materials available and equipment capacities. Finally, various fields around and within the test model are calculated using the coupled analysis platform for thermal environment and structure response (FL-CAPTER) developed by China aerodynamic research and development center (CARDC). The results show that the test model is feasible for verification test. This work establishes the foundation for improving the test model design.



**Figure 1**. Temperature Profile of Windward Exterior.



**Figure 2**. Structural Deformation Schematic of 60s

**Room HS PHEG016** 

### EA - O6 11:45 - 12:05 Wednesday

# IMPACT OF COUPLING INDUCED STRUCTURAL DEFORMATION ON HYPERSONIC TRAJECTORY

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The new generation near space aircraft is expected to achieve the aim of rapid global reach. The research and investigation on it opens a new and full swing era. Some lightweight material and thin walled structures are chosen to lightweight the aircraft, in order to fulfill the requirement of long distance glide. There are strong coupling and interaction phenomena existed between the thermal environment, temperature, structure stress and strain. Hence, the coupling induced structural deformation comes out and impacts the flight trajectory obviously.

Based on the background of studying the impact of the coupling induced structural deformation on flight trajectory, a new trajectory simulation method taking the impact of structural deformation into account was developed based on the established fluid-thermalstructural coupled method and the six degrees of freedom trajectory simulation model. The characteristics of flight trajectory with different coupled time scales were studied, and the correlation rules of the time-scale of aerodynamic/ trajectory coupled problems were obtained.

For the configuration shown in Figure 1, the results are obtained and shown in Figure 2. The results indicate that the head turned up because of the aerodynamic heating. And it leads to the increase of the lift, the drag, the pitch moment and the trim angle of attack. Conversely, the lift to drag ratio and the trajectory range decreace obviously. These influences are significant, and they lead to the adjustment of control strategy directly. Therefor, the coupling and interaction between the multiple physics fields are important, and it must be considered in the

design process.



**Figure 1**. The aerodynamic configuration.



**Figure 2**. Coupling induced head displacement and trajectory departure.

### EA – O7 12:05 - 12:25 Wednesday

#### **Room HS PHEG016**

# LIGHTWEIGHT DESIGN OF INTEGRATED THERMAL PROTECTION SYSTEM WITH NON-UNIFORM HEAT FLOW LOAD

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A comprehensive consideration of effects of non-uniform aerodynamic heating and lightweight design is of prime importance in the optimization of integrated thermal protection system (ITPS), which would be useful for the security and low cost of a hypersonic aircraft. In order to achieve the different thicknesses of diverse locations of ITPS, non-uniform thickness design would be a new and feasible approach. This paper focuses on: a new approach using the arbitrary shape deformation (ASD) technique is developed to solve the optimization problem of ITPS that include non-uniform thickness design and effect of non-uniform aerodynamic heating.

Figure 1 and Figure 2 respectively present the optimization shapes of ITPS. Numerical examples show that the developed method based on the ASD technique and thermo-mechanical coupled model can be used to availably solve the problems of lightweight design of ITPS with non-uniform aerodynamic heating. Moreover, this method can automatically and rapidly update the meshes without any change of the mesh topology in optimization process, so it can helpful for improving the efficiency of optimization. It also indicates that optimization based on the proposed method can help ITPS to fulfill their potential more sufficiently while to achieve a lower weight.



Figure 1. Optimization of the nose cone.



**Figure 2**. Optimization of the thermal protection tile.
## **Optical and Thermal Radiative Properties (OTRP)**

**Oral Session 6: Optical and Thermal Radiative Properties** 

10:30 - 12:10 Thursday PHEG016

Chairs: B. Wilthan, K. Boboridis

## OTRP - O1 10:30 - 10:50 Thursday

Room HS PHEG016

## NON-CONTACT TEMPERATURE MEASUREMNT OF COMBUSTION GASES AT HIGH TEMPERATURES AND HIGH PRESSURES

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Stationary gas turbines are an important part of today's power supply. For process optimization, the exact knowledge of the gas temperatures during operation is essential, as with increasing temperature of the hot combustion gas the efficiency factor and thus the energy efficiency of a turbine increases. For this reason, engineers seek to operate the turbine at the highest possible temperature. Therefore, in the combustion chamber and especially at the position of the first stage guide vanes the gas temperature needs to be measured reliably.

To determine the gas temperature, thermocouples are placed directly in the gas flow as state-of-the-art. Due to the present severe conditions, the sensor materials rapidly degrade and the sensor properties drift drastically. Hence, the life-time of the used sensors is significantly reduced. An alternative temperature measurement method is needed to solve this problem. The setup of a non-contact method using a radiation thermometer is one promising approach. A radiation thermometer can measure the gas temperature although it is placed outside of the harsh environment.

At ZAE Bayern, a high temperature and high pressure gas cell has been developed for this purpose in order to investigate gases and gas mixtures under defined conditions at high pressures and high temperatures. This gas cell can be placed in a FTIR-spectrometer in order to characterize the infrared-optical properties of the gases.

In this work the measurement setup is introduced and gas mixtures, which are relevant for gas turbine applications are analyzed. The derived results are presented and discussed in detail. To identify suitable wavelength regions for non-contact gas temperature measurements, first tests have been performed on different optical path lengths and several gas mixtures. Based on these tests, an appropriate wavelength region could be chosen, where future gas temperature

measurements can be carried out.

## OTRP – O2 10:50 - 11:10 Thursday

**Room HS PHEG016** 

## EMISSIVITY, REFLECTIVITY AND TRANSMISSIVITY OF SEMITRANSPARENT FIBRE REINFORCED PLASTIC COMPOSITES

A. Adibekyan, E. Kononogova, C. Monte, B. Gutschwager and J. Hollandt *Physikalisch-Technische Bundesanstalt (PTB), Berlin, Germany* albert.adibekyan@ptb.de

Fibre reinforced plastic (FRP) composites have excellent mechanical properties, low weight, fatigue and corrosion resistance yielding to notable advantages for renewable energy, oil and gas and transport applications. However, certain defects and damage mechanisms reduce the full possibilities of exploitation as well as the life of FRP based structures. Non-destructive testing (NDT) and in particular active thermography are important methods to ensure the quality of FRPs.

The accurate knowledge of the radiative properties of the investigated material, i.e. its spectral emissivity, reflectivity and transmissivity, is a prerequisite for quantitative active thermography. To improve the state-of-the-art of this technique, the uncertainty of emissivity measurements of FRP materials in the visible and in the infrared wavelength range has to be lower than 0.01. This was the objective of PTB as one partner within the ERMP Project "Validated Inspection Techniques for Composites in Energy Applications" (VITCEA) [1]. The measurement of the emissivity of partially transmitting materials with this uncertainty is very challenging, especially at temperatures close to the room temperature. We employed two setups for these measurements: the setup for spectral emissivity measurement [2,3] and the setup for diffuse reflectivity and transmissivity measurement at PTB.

The directional spectral emissivity was determined at a nominal temperature of 40 °C in the wavelength range from 5  $\mu$ m to 25  $\mu$ m and at angles of observation from 10° to 70° with respect to the surface normal. From these measurements, the total directional emissivities and the hemispherical emissivities were calculated.

The directional-hemispherical spectral transmissivity and directional-hemispherical spectral reflectivity were determined using a gold coated integrating sphere and a vacuum FTIR-Spectrometer. The directional-hemispherical spectral transmissivity was observed under an angle of incidence of 0°, the directional-hemispherical spectral reflectivity under an angle of incidence of 10°. These measurements were done in the spectral range from 1  $\mu$ m to 16.7  $\mu$ m and compared in the overlapping wavelength range with the emissivity measurements performed with the setup for spectral emissivity.

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## A NOVEL INDEX FOR THE OVERALL PERFORMANCE OF OPAQUE BUILDING ELEMENTS COMBINING THERMAL INSULATION, INERTIA AND RADIATIVE PROPERTIES

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A "solar transmittance index" (STI) has been proposed to rate the overall dynamic behavior of an external opaque building element subjected to the cycle of solar radiation. It includes in a single performance parameters the effects of both thermal radiative properties of the external surface such as solar reflectance and thermal emittance, and thermo-physical properties of the materials under the surface such as thermal conductivity, specific heat, mass density. Such single performance parameter can allow to overcome the difficulties of individuating a tradeoff between thermal insulation and thermal inertia, respectively represented through separate parameters such as thermal trasmittance or resistance and decrement factor or time shift, also exploiting the radiative thermal properties to return solar energy to the atmosphere. The utilization of STI may be greatly helpful in defining requirements and policies to prevent building overheating, reduce cooling energy demand and mitigate the fallouts of the urban heat island effect.

In this work, key elements for the complete definition of the index are investigated, considering the typical building techniques in several locations all over the world and the correlation between the index and the energy needs for building cooling.

#### OTRP – O4 11:30 - 11:50 Thursday

#### **Room HS PHEG016**

## MID-INFRARED OPTICAL PROPERTIES OF PYROLYTIC BORON NITRIDE AT HIGH TEMPERATURE

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We present an exhaustive experimental and theoretical study on the temperature dependence of the mid-infrared optical properties of pyrolytic boron nitride (pBN) by using spectral emissivity measurements. The measured spectra were fitted to a dielectric function model and an effective medium approximation in order to account for the presence of carbon impurities, as revealed by X-ray diffraction and electron microscopy. This approach showed a better agreement between the theoretical and experimental spectra than previous attempts.

The phonon frequencies and dielectric constants calculated by this method agreed well with room temperature experimental values from the literature, as well as to *ab initio* calculations. Their temperature dependence was reported here for the first time. The phonon frequencies of the perpendicular mode and the dielectric constants of the parallel mode showed a parabolic temperature dependence, while no significant evolution could be observed for the other parameters. The dielectric function obtained by the fitting procedure compared favourably to that obtained by the standard Kramers-Kronig transform.

These results prove that thermal emission spectroscopy is a powerful technique for the characterization of ceramics at high temperatures. Knowledge of the emissivity spectra of this material is necessary for many interesting applications, such as protective and selective coatings for the aerospace industry. Moreover, accurate values of the dielectric function are also crucial for numerical simulations of complex materials based on BN, such as tunable infrared absorbers.

## OTRP – O5 11:50 - 12:10 Thursday

#### **Room HS PHEG016**

# RETRIEVAL OF COUPLED THERMAL PROPERTIES AND THERMAL CONTACT RESISTANCE OF $\rm Al_2O_3$ FOAMS

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High-porosity open-cell ceramic foams are widely used in various industrial areas for their outstanding thermal, mechanical and exchange properties. A precise characterization of heat transfer process for is crucial to successful design and optimization of foam materials working at these high temperature hostile environments. However, in many practical engineering applications, reliable determination of coupled thermal properties in describing absorbing, emitting, and anisotropic scattering radiation and conduction effects within these foam materials is still full of challenges. Aiming at this problem, the present paper interests in the inverse determination of thermal properties of Al<sub>2</sub>O<sub>3</sub> ceramic foams on basis of coupled heat transfer analysis and transient thermal tests. The thermal resistance effects in the experimental testing process are being taken into account in the thermal analysis, and the conductive and radiative properties as well as the thermal contact resistance are simultaneously retrieved from the simple experiments. Finally, the reliability of the results is discussed and evaluated by comparison with experimental measurements. It is found that the established inverse model considering thermal resistance effect demonstrates superior behavior to that without considering it. The proposed analysis provides a simple and rapid approach for experimental characterization of coupled thermal properties, which significantly contributes to accurate analysis and optimization of foam thermal performances, especially when the foam morphology, solid composition, and fundamental properties of constituents are unknown.

## Standard Data and Standard Materials (SDSM)

#### **Oral Session 1: Standard Data and Standard Materials**

11:05 - 13:05 Monday HS BMT

Chairs: B. Wilthan, K. Kroenlein

## SDSM – O1 11:05 - 11:25 Monday

**Room HS BMT** 

## EUROPEAN INTERLABORATORY COMPARISON IN CALORIMETRY WITHIN EURAMET TCT

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Calorimetry is one of the oldest quantitative measuring techniques in physical chemistry. It has been invented by Joseph Black (born 1728 in France) around 1760 in Glasgow and brought to a first peak by Antoine Laurent de Lavoisier and Pierre-Simon Laplace in Paris around 1780. The accuracy of their ice calorimeter on relative measurements of specific heat was claimed to be approximately 1:60.

Measurement technology has made large advances and currently most instruments used in industry and academia are commercial differential scanning calorimeters (DSCs) with uncertainties associated to heat measurements around 1-2 %. Modern DSCs require in particular a calibration of the heat flow scale over their operating temperature range, whose magnitude depends on the calorimeter and is usually included in the temperature domain from -100 °C to 1500 °C. Many different materials have been proposed for this purpose [1] but most of them lack a reliable and traceable determination of their properties, in particular validated uncertainties.

As a remedy, the French and the German national metrology institutes (NMIs), LNE and PTB, agreed upon performing a bilateral comparison on the enthalpy of fusion of some pure metals (foremost Indium and Tin, but also Gallium, Bismuth, Aluminium or others, depending on their mutual measurement capabilities) in the framework of the EURAMET project 771 [2].

The facilities employed were commercial Calvet calorimeters [3] equipped with custom-made probes or instrumented crucibles [4] for electrical calibration and compensation.

The obtained results demonstrate a perfect agreement in the overlapping temperature range (from 100  $^{\circ}$ C to 300  $^{\circ}$ C) of the two instruments [5], with a relative difference in the enthalpy of fusion values lower than 0.05 % (for Indium and Tin) and within the measurement

uncertainties assessed by the two NMIs. It can now be stated that the measurement and calibration capabilities of France and Germany are fully compatible and that determinations of heats of fusion are possible with uncertainties of 0.2 % for moderate temperatures and 0.8 % for elevated ones. Some calibration materials have been certified and are available in the temperature range from 30 °C to 300 °C.

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## SDSM – O2 11:25 - 11:45 Monday

#### Room HS BMT

## QUEST FOR A REFERENCE STANDARD FOR VISCOSITY AT HIGH TEMPERATURES AND HIGH PRESSURES

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This communication is dedicated to give notice of the present situation concerning the proposal of tris(2-ethylhexyl) trimellitate (TOTM) to be a reference standard fluid for viscosity at high temperatures and high pressures. This proposal stems from an internal project of the International Association for Transport Properties (IATP).

A general overview of the efforts carried out so far by the scientific community towards that objective will be made. This will be complemented by a description of its main characteristics that support its proposal. In particular, the present work is concerned with the determination of the shear dependence of the viscosity of TOTM.

Moreover, new results for the density of TOTM at moderately high temperatures and pressures up to 70 MPa are presented.

## THERMOML—AN XML STORAGE AND EXCHANGE STANDARD FOR THERMOPHYSICAL AND THERMOCHEMICAL DATA

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ThermoML is an XML-based storage and exchange protocol for experimental and critically evaluated thermophysical and thermochemical property data. Its development began in 2001 to facilitate the communication of experimental data and its necessary metadata in a human and machine readable format (1). In 2003, it was proposed as a data transfer standard for thermophysical and thermochemical property information for well described chemical systems under the auspices of the International Union of Pure and Applied Chemistry (IUPAC) standard. Modifications to the standard were done in to account for uncertainties (2); critically evaluated data, predicted data and equation representation (3); biomaterials (4); speciation (5). As of 2017, ThermoML is under a structural revision to update to more modern XML usage and to add elements necessary for the representation of metal-based systems as well as maintain the traditional representation for organic based systems.

While ThermoML expands its domain of applicability, it will maintain its ability to store data in a structured way, including provenance of the data, sample characterization, and measurement uncertainty. While there are many consistent concepts in the revision, support for the wide array of sample preparation methods, and complex phase characterization required substantial refactoring of the document structure. The standard still relies extensively on well-developed enumerated lists for selection of many elements, to limit errors due to data input and to avoid ambiguities. All data will be stored in SI units, to simplify interoperability and avoid confusion. New elements for the metallic system include: (1) microstructural characterization of specimens, (2) crystallographic identification of phases, and (3) reporting of detailed processing histories associated with each datum.

## SDSM – O4 12:05 - 12:25 Monday

## **Room HS BMT**

# THEREDA - THERMODYNAMIC REFERENCE DATABASE FOR THE NUCLEAR WASTE DISPOSAL IN GERMANY

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The disposal of nuclear waste including the assessment of long-term safety is still an open question in Germany. In addition to the still pending decision about the repository host rock (salt, granite, or clay) the basic necessity of a consistent and obligatory thermodynamic

reference database persists. Such a database is essential to assess potential failure scenarios accurately and to make well-founded predictions about the long-term safety. Specific challenges are comprehensive datasets covering also high temperatures and salinities. Against this background, available databases do not suffice and are limited in their use, partly because of high restrictions and resulting incompleteness of reactions. Other databases rely on heterogeneous and therefore inconsistent data leading to incorrect model calculations. Due to these deficiencies THEREDA, a joint project of institutions leading in the field of safety research for nuclear waste disposal in Germany and Switzerland, was started in 2006.

THEREDA contains a relational databank whose structure has been designed in a way that promotes the internal consistency of thermodynamic data. Data considered cover the needs of Gibbs Energy Minimizers (ChemApp) and Law-of-Mass-Action programs (Geochemist's Workbench, EQ3/6, PHREEQC) alike. Parameters for a variety of models describing interactions in mixed phases are included. Namely, the Pitzer parameters to describe activity coefficients of hydrated ions and molecules are considered. Both thermodynamic and interaction parameters can be described by temperature functions.

THEREDA offers evaluated thermodynamic data for many compounds (solid phases, aqueous species, or constituents of the gaseous phase) of elements relevant according to the present state of research. In particular, all oxidation states expected for disposal site conditions are covered.

Ready-to-use parameter files are created from the databank in a variety of formats (generic ASCII type, and formats required by the geochemical speciation codes) and offered to the users. They are also used for internal test calculations - one essential element of the quality assurance scheme. The results are documented and provided to the users.

THEREDA is accessible via internet through www.thereda.de. This is not only a portal to the database, but shall also serve as an information and discussion platform on issues concerning the database. Thus, we are confident to generate helpful feedback from the anticipated user community.

## SDSM – O5 12:25 - 12:45 Monday

#### **Room HS BMT**

## REFERENCE VALUES AND REFERENCE CORRELATIONS FOR THE THERMAL CONDUCTIVITY AND VISCOSITY OF FLUIDS

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As the accurate measurement of the thermal conductivity of liquids was not easy, it was not until 1951 that any proposal was made for standard reference data for this fluid property. At that time Riedel<sup>1</sup> suggested that liquid toluene be adopted as a standard reference material and proposed a set of standard reference values. In 1977, a reference correlation for thermal conductivity of water, amended in 1982,<sup>2</sup> was proposed by the International Association for

the Properties of Steam (IAPS). Following this, in 1986, Nieto de Castro *et al.*<sup>3</sup> published a paper under the auspices of the Sub-Committee on Transport Properties of Commission 1.2 of the International Union of Pure and Applied Chemistry, proposing thermal conductivity reference values for water, toluene and heptane.

In the case of viscosity reference data, in 1952, Swindells *et al.*<sup>4</sup> proposed the value of water at 20 °C as a reference viscosity value. This value, with slight modifications, is still the internationally agreed reference value for viscosity (ISO/TR 3666:1998).

Ab-initio calculations<sup>5</sup> in 2000 of the viscosity and thermal conductivity of helium have also been proposed as reference standards for gases.

In the current paper we discuss the criteria employed for a fluid to be considered as a reference for thermal conductivity and viscosity. Since reference correlations are based on the most reliable (primary) measurements, the criteria employed for the selection of primary measurements from all existing measurements, are discussed. Following this approach, existing reference correlations for a variety of fluids are discussed.

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## SDSM – O6 12:45 - 13:05 Monday

#### **Room HS BMT**

# CHARACTERISATION OF THERMAL CONDUCTIVITY REFERENCE MATERIAL USING THE NPL AHF APPARATUS

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The National Physical Laboratory (NPL) has developed a new thermal conductivity reference material based on Stainless Steel 304. This batch of material has been characterised over the temperature range 100 °C to 500 °C using NPL's absolute Axial Heat Flow (AHF) apparatus and checked using two indirect measurement approaches.

The primary thermal conductivity measurements used to generate the certified values were made using the NPL Axial Heat Flow apparatus based on an absolute technique that is suitable for specimens with thermal conductivities in the range  $10 \text{ W m}^{-1} \text{ K}^{-1}$  to  $240 \text{ W m}^{-1} \text{ K}^{-1}$  and at temperatures between 50 °C and 500 °C. Comparisons were then made between the measurement data from the Axial Heat Flow apparatus and thermal conductivity values obtained indirectly from: (i) measurements of thermal diffusivity, specific heat capacity, density and thermal expansion; (ii) measurements of electrical resistivity via the Wiedemann-Franz

relationship. The average of the direct measured thermal conductivity values from the Axial Heat Flow apparatus and those calculated from measurement of electrical resistivity agreed to within 2 %. Those values calculated from measurements of thermal diffusivity, specific heat capacity, density and thermal expansion were in agreement to better than 4 % with the direct thermal conductivity measurements using the NPL AHF apparatus.

This new thermal conductivity reference material, NPL 2S09 is being made available from NPL and can be used to calibrate or check thermal conductivity measurement apparatus that include the temperature range 100 °C to 500 °C and the corresponding thermal conductivity range 16 W m<sup>-1</sup> K<sup>-1</sup> to 22 W m<sup>-1</sup> K<sup>-1</sup>. The overall uncertainty on the certified values is estimated to be within  $\pm 4.8$  %, based on a standard uncertainty multiplied by a coverage factor k = 2, providing a level of confidence of approximately 95 %.

## Ionic Liquid and Properties Ionic Liquids (ILPIL)

**Oral Session 2: Ionic Liquid and Properties Ionic Liquids I** 

15:30 - 17:50 Monday HS BMT

Chairs: L. Santos, M. Shifflet

#### ILPIL – O1 15:30 - 15:50 Monday

Room HS BMT

# CRITICAL AND NON-CRITICAL FLUCTUATIONS IN MIXTURES OF IONIC LIQUIDS WITH ALCOHOLS

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Mesoscopic heterogeneities in binary mixtures of the ionic liquid ethyl-ammonium nitrate (EAN) with alcohols (pentanol and heptanol) are investigated by Small Angle X-ray Scattering as function of concentration and temperature ranging from 193 to 313 K. Such systems in general show a liquid-liquid phase transition which is driven by Coulomb interactions but modified by hydrogen bonding. Though macroscopically homogeneous, the mixtures are heterogeneous at the mesoscopic spatial scales. Two different heterogeneities are present: Critical concentration fluctuations centred at scattering vector Q = 0, well known as precursors of the liquid-liquid phase transition e.g. for EAN/Octanol mixtures [1], and heterogeneities caused by segregation into ionic and non-ionic regions. The latter ones were predicted by simulation [2] and verified experimentally [3] in ionic liquids containing cations with long hydrocarbon chains. In pure EAN such structuring is observed as well giving rise to a band centred near  $Q = 6 \text{ nm}^{-1}$  [4]. A similar band at  $Q = 5 \text{ nm}^{-1}$  is also observed in alcohols, again suggesting a segregation into polar and no-polar regions as a special case of charge ordering. Those heterogeneity bands of EAN and alcohols merge in mixtures. When approaching the critical composition and lowering the temperature towards the critical temperature, critical concentration fluctuations dominate and overshadow the ionic-non-ionic heterogeneity band. A careful analysis shows that this band reveals but is shifted towards small figures of the scattering vector. The Q = 0 band varies with concentration, temperature and Q as expected for critical fluctuations. For the system EAN / heptanol the phase diagram was measured with an upper critical solution point at 259 K and a critical composition at x = 0,64. In the case of the pentanol system [5] the critical solution point is virtual as it lays inside the solid phase region and thus cannot be reached in the experiment. For this system the critical temperature is estimated by extrapolation to  $T_c \approx 190$  K. A pseudo spinodal is constructed applying the scaling laws of critical fluctuations .

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## ILPIL – O2 15:50 - 16:10 Monday

#### **Room HS BMT**

## THERMOPHYSICAL PROPERTIES OF BINARY MIXTURES OF 1-ETHYL-3-METHYIMIDAZOLIUM AND WATER

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Lignocellulosic biomass represents one of the most important renewable energy sources for Europe, being mainly used for energy production through combustion. The growing awareness of the need for energy efficiency gains requires new approaches for problems that, during the time of cheap energy and unlimited raw materials resources, were not the object of special care for industry and consequently, for research. Lignocellulosic biomass is composed of cellulose (35 to 50 %), lignin (18 to 30 %), hemicelluloses (15 to 30 %), and small amounts of extractive compounds.<sup>1,2</sup> Due to the complex composition and structure of this type of biomass, their fractionation, in an effective and rentable way, is still a challenge target.

Industrially, biomass fractionation into cellulosic pulp and lignin is mainly accomplished by the kraft process, which is not comprehensive in the utilization of noncellulosic components and causes complaints from the standpoint of environmental concerns. Most of the cellulose dissolution processes also cause serious environmental problems due to the solvents used.<sup>3,4</sup> In recent years, a need for more "green" solvents and processes as gain the attention of the researchers. Ionic liquids (ILs) have been recently explored as novel "green" solvents for lignocellulosic materials.<sup>5</sup> 1-methyl-3-ethylimidazolium acetate ([emim][OAc]) has been studied as one of the most promissory ILs to dissolve cellulose<sup>1-3,6,7</sup> although its properties are not well known. The amount of water in the ionic liquid influence their capacity to dissolve cellulose<sup>8-10</sup> despite this fact there also a lack about the influence of water in the physical properties of the ILs, even in the case of the [emim][OAc].

In this work the thermal and electrical conductivity, density, speed of sound and viscosity of binary mixtures of 1-ethyl-3-methyl imidazolium acetate ([emim][OAc]) and water, and infinite dilution diffusion coefficients were measured at atmospheric pressure. Total miscibility of the two liquids was found in the temperature range studied (293.15 to 333.15 K).

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#### ILPIL – O3 16:10 - 16:30 Monday

#### **Room HS BMT**

#### THERMOPHYSICAL PROPERTIES OF IONIC LIQUIDS AT PRESSURES UP TO 140 MPa AND OVER A WIDE RANGE OF TEMPERATURES

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Any application of ionic liquids (ILs) relies on known thermophysical behaviour within the operational region. Does the targeted IL keep its characteristics, and do we have consolidated data over an extended range for confirmation? Models that correlate or even predict thermophysical properties can thus only be built on consolidated data.

In this work, we will present the  $(p, \rho, T)$  properties of nine imidazolium and pyridinium ILs up to p = 140 MPa and over a temperature range T = (273.15 to 413.15) K:

- 1-ethyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [EMPy][NTf<sub>2</sub>], and methanesulfonate, [EMIM][MeSO<sub>3</sub>];
- 1-propyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [PMPy][NTf<sub>2</sub>];
- 1-butyl-3-methylpyridinium bis(trifluoromethylsulfonyl)imide, [BMPy][NTf<sub>2</sub>];
- 1-butyl-3-methylimidazolium tetrachloroferrate, [BMIM][FeCl<sub>4</sub>], tris(pentafluoroethyl) trifluorophosphate, [BMIM][FAP], tetrafluoroborate, [BMIM][BF4], and trifluoromethanesulfonate, [BMIM][TFO];
- 1-methyl-3-octylimidazolium tetrafluoroborate, [OMIM][BF<sub>4</sub>].

Investigations covering such an extended p, T-range were performed the first time for these ILs. The experiments were carried out using a specially adapted high pressure - high

temperature Anton Paar DMA HPM vibration-tube densimeter with an estimated relative combined standard uncertainty of  $\Delta \rho / \rho = \pm (0.01 \text{ to } 0.08) \%$  in density. The temperature *T* in the measuring cell is administrated with an error of  $\pm 10$  mK and is measured using the (ITS-90) Pt100 thermometer with an experimental error of  $\pm 15$  mK. Pressure *p* is measured with a relative uncertainty of 0.1 % (for *p* up to 100 MPa) and 0.5 % (for *p* up to 140 MPa), respectively, of the measured value. The extended range of pressure and temperature required a viscosity correction.

The literature values available were subject to a consistency check with our data. Additionally, the heat capacity at ambient pressure  $c_p(p_0, T)$  was determined by using differential scanning calorimetry. An equation of state was established using parameters based on the new results to calculate the isothermal compressibility  $\kappa_T$ , isobaric thermal expansibility  $\alpha_p$ , thermal pressure coefficient  $\gamma$ , internal pressure  $p_{int}$ , specific heat capacities at constant pressure  $c_p$  and at constant volume  $c_v$ , speed of sound u, and isentropic exponent  $\kappa_s$  for each IL.

#### ILPIL – O4 16:30 - 16:50 Monday

#### Room HS BMT

## FORCE FIELD TRANSFERABILITY FOR 1-ALKYL-3-METHYLIMIDAZOLIUM TETRACYANOBORATE IONIC LIQUIDS

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The present study shows how to utilize the mutual benefits of molecular simulations and experiments for the determination of equilibrium and transport properties of tetracyanoborate  $([B(CN)_4]^-)$ -based ionic liquids (ILs) carrying homologous 1-alkyl-3-methylimidazolium  $([AMIM]^+)$  cations  $[EMIM]^+$  (ethyl),  $[BMIM]^+$  (butyl),  $[HMIM]^+$  (hexyl),  $[OMIM]^+$  (octyl), and  $[DMIM]^+$  (decyl). For these potential working fluids in gas separation, heat storage, and electrolyte applications, reliable thermophysical property data are needed but generally lacking in literature. Besides providing an accurate experimental database, the evaluation of the transferability of the molecular models within the homologous IL series reducing the computational effort in molecular simulations was the main focus of the investigation.

Equilibrium Molecular Dynamics (MD) simulations were performed based on molecular models which account for the complex interplay of electrostatic and non-electrostatic interactions in ILs differently. The non-electrostatic part optimized for  $[EMIM][B(CN)_4]$  by employing our experimental density and viscosity data was transferred to all other  $[B(CN)_4]^-$ -based ILs. For the latter, only one single dispersive parameter in the anion was tuned to match with our experimental density at a single temperature. The electrostatic partial charges obtained from quantum calculations were both calculated for the ILs containing  $[EMIM]^+$ ,  $[BMIM]^+$ , as well as  $[HMIM]^+$  cations and directly transferred from  $[BMIM][B(CN)_4]$  to the longer-chained ILs. The simulated data are compared with experimental results for density and ion self-diffusivities from conventional techniques as well as for viscosity and surface tension from surface light scattering (SLS).

For comparable simulated and experimental densities, the calculated and measured data for viscosity and self-diffusivities of the homologous  $[B(CN)_4]^-$ -based ILs at atmospheric pressure mostly agreed within combined uncertainties for the probed temperatures from (283 to 393) K. Only for a very coarse transfer from  $[BMIM][B(CN)_4]$  to  $[OMIM][B(CN)_4]$ , more distinct deviations between the simulated and experimental dynamic properties could be found at low temperatures. The matching results for  $[HMIM][B(CN)_4]$  calculated on the basis of its precise electrostatic charges and the charges approximated from  $[BMIM][B(CN)_4]$  denote a negligible influence of the varying electrostatic potential in the cation alkyl chain on the IL properties. This suggests that the charges associated with relatively short-chained ILs are transferable to longer-chained homologues without a significant loss in accuracy. In comparison to ILs carrying other anions, the thermophysical property data for the  $[B(CN)_4]^-$ -based ILs show relatively high self-diffusivities and low viscosities. This behavior can be attributed to the distinct charge delocalization in the relatively small-sized  $[B(CN)_4]^-$  anion.

#### ILPIL – O5 16:50 - 17:10 Monday

#### **Room HS BMT**

## THE FLUORINATION EFFECT ON THE SOLVATION OF ALCOHOLS IN IONIC LIQUIDS

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In a recent work addressing the study of the solvation properties of ILs using alcohols as molecular probes<sup>1</sup>, we showed that studying the solvation of propan-1-ol, butan-1-ol and pentan-1-ol could probe the nanostructuration of  $[CNC1im][NTf_2]$  IL family and that the alcohols are preferentially located at the IL polar domain. In the present work, heats of solution at infinite dilution of various alcohols with different degrees of fluorination in Ionic Liquids (ILs) were measured by Isothermal Titration Calorimetry (ITC). From the enthalpy of solution at infinite dilution, the enthalpy of solvation was derived using enthalpy of vaporization data. The study of the solvation of alcohols with different levels of fluorination (tert-butanol, trifluoro-tert-butanol, hexafluoro-tert-butanol and nonafluoro-tert-butanol) was made in order to explore the effect of the alcohol acidity into the -OH interaction with  $[C_4C_1im][NTf_2]$ , 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide.

The analysis of the experimental enthalpies of solvation was complemented with a quantum chemical calculation study of the interaction of alcohols and IL anion in the gas phase.



**Figure 1**. Schematic representation of the solvation of tert-butanol with different levels of fluorination in the IL  $[C_4C_1im][NTf_2]$ .

The differentiation of the heats of solvation with the level of fluorination of tert-butanol together with the quantum chemical calculation results were used for the qualitative and quantitative evaluation of the H-bond interactions between alcohols and ionic liquids.

#### Acknowledgments

Thanks are due to Fundação para a Ciência e Tecnologia (FCT), Lisbon, Portugal, for the financial support to Project UID/QUI/0081/2013 and Inês C. M. Vaz acknowledges the financial support from Fundação para a Ciência e Tecnologia (FCT) for her PhD Research Grant PD/BD/114575/2016.

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## ILPIL - O6 17:10 - 17:30 Monday

#### Room HS BMT

## ACTIVITY COEFFICIENTS OF HYDROCARBONS IN PROTIC IONIC LIQUIDS: COMBINED EFFECT OF H-BONDS AND ION-PAIRS

I. A. Sedov, T. I. Magsumov, T. M. Salikov and B. N. Solomonov

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The properties of protic ionic liquids (PILs) are characterized to a lesser extent in comparison with aprotic ionic liquids (AILs). Only a small number of studies was dedicated to the solvation properties of PILs despite their prospective use as industrial solvents. Measurement of the infinite dilution activity coefficients in PILs is complicated by their significant volatility, viscosity and low rate of dissolution.

In the present work, gas-chromatographic headspace analysis technique was successfully used to measure the limiting activity coefficients  $\gamma^{\infty}$  of n-alkanes and arenes in two PILs, n-propylammonium nitrate and n-butylammonium nitrate at 298 K. The obtained values are

significantly lower than those for the same solutes in many aprotic ionic liquids. We have previously shown [1] that in aprotic ionic liquids, the excess chemical potential  $\mu_{ex} = RT \ln \gamma^{\infty}$  of alkanes is correlated with concentration of ion pairs per unit volume of the neat solvent, which is equal to inverse of its molar volume. Our new data for PILs fall out of this correlation, indicating that the excess chemical potential of a hydrocarbon in a PIL is lower than in an AIL with the same molar volume. This is especially surprising because of the presence of intermolecular hydrogen bonds in PILs, which were expected to further decrease of solubility of apolar species in comparison with AILs by an analogy with molecular solvents.

To understand the reasons of the observed phenomena, we calculated the excess chemical potential of hard spheres in PILs and AILs using Widom test particle insertion method. Molecular dynamics simulations of neat ionic liquids were conducted using OPLS force field in orthogonal cells containing 500 molecules. After proper equilibration, 50 ns-long production runs in the NPT ensemble at 298 K and 1 bar pressure were recorded. To calculate  $\mu_{ex}$ , 1000000 insertions at random positions were done in 50000 configurations written each 1 ps of simulation. The calculated excess chemical potential of hard spheres of various sizes is found to be much lower in butylammonium nitrate than in its aprotic isomer, tetramethylammonium nitrate, and even lower than in trimethylbutylammonium nitrate with much higher molar volume, which is in perfect agreement with our experimental observations. This finding means that the increased solubility of low polar molecules in PILs is caused by lower Gibbs free energy cost of cavity formation in comparison with AILs, which is complemented with the evidence that PILs have lower enthalpies of vaporization than AILs [2]. The uncooperative effect of intermolecular hydrogen bonds and ion-pairs seems to be responsible for the peculiar solvation properties of PILs.

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## ILPIL - 07 17:30 - 17:50 Monday

**Room HS BMT** 

# SEPARATION OF 1,4-DIOXANE FROM ITS AZEOTROPIC AQUEOUS SOLUTION WITH THE AID OF BIOCOMPATIBLE IONIC LIQUID

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In the present study, we have found that the biocompatible and self-buffering Good's buffer ionic liquid (GBIL), [TMA][EPPS], could induce liquid-liquid phase splitting in an aqueous solution of 1,4-dioxane at ambient conditions. The investigated GBIL is composed of tetramethylammonium (TMA) as a cation and a biological buffer, 4-(2-hydroxyethyl)-1-piperazinepropanesulfonic acid (EPPS), as an anion. The separation efficiency of this bufferbased GBIL for the 1,4-dioxane from its aqueous solution has been analyzed by measuring solid-liquid equilibrium (SLLE) and liquid-liquid equilibrium (LLE) data for the ternary system of 1,4-dioane + water + [TMA][EPPS] at 298.2 K and under atmospheric pressure. The

experimental LLE phase boundary data were correlated with an empirical equation and the effective excluded volume (EEV) model, respectively. The consistency of the LLE tie-line data was confirmed by using the Othmer-Tobias model. The binary interaction parameters were obtained by correlating experimental tie-line data with the non-random two liquid (NRTL) activity coefficient model. By using [TMA][EPPS] as an auxiliary agent, the maximum concentrations of 1,4-dioxane (97.8 wt %) in the organic-rich phase found is greater than the azeotropic compositions (87.82 wt %) of the corresponding aqueous system. These results clearly indicate that the investigated GBIL can be served as a high efficiency, non-corrosive, and biocompatible green agent for recovering high purity of 1,4-dioxane from its aqueous solution. Based on the phase diagram obtained from the present study, a conceptual flowsheet (Fig. 1) is proposed, for separating 1,4-dioxane from its aqueous solution with the aid of GBIL, [TMA][EPPS].



**Figure 1**. Conceptual flowsheet for the separation of 1,4-dioxane from its aqueous solution with the aid of GBIL, [TMA][EPPS].

#### **Oral Session 3: Ionic Liquid and Properties Ionic Liquids II**

10:20 - 12:40 Tuesday HS BMT

#### ILPIL - 08 10:20 - 10:40 Tuesday

## Room HS BMT

## IONANOFLUIDS AS WORKING FLUIDS FOR THE NEW GENERATION SOLAR COLLECTORS

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The new generation solar collectors require working fluid with high heat storage capacity and high temperature thermal stability. Ionanofluids, composed of ionic liquids and nanoparticles, are a new and innovative class of heat transfer fluids which exhibit significantly improved thermophysical properties compared to their base ionic liquids. This work deals with the findings of specific heat capacity, viscosity, and density of Ionanofluids composed of 13 nm  $Al_2O_3$  with 1-ethyl-3-methylimidazolium ethyl sulfate ( $[C_2C_1im][EtSO_4]$ ) or 1,3-diethylimidazolium ethyl sulfate ( $[C_2C_2im][EtSO_4]$ ) as a function of temperature and concentration of nanoparticles.

The microstructure of the  $Al_2O_3$  nanoparticles were observed by transmission electron microscope. The stability and the structural changes in time were examined using UV-Vis and the dynamic light scattering method. Specific heat capacity, density and viscosity of these Ionanofluids were measured for different weight fractions and at varying temperatures, demonstrating that the Ionanofluids exhibit higher specific heat capacity, density and viscosity than that of their base fluids. An enhancement in specific heat capacity by about 15.6 % and 2.6 % has been achieved at 298.15 K for  $[C_2C_1im][EtSO_4]$  and  $[C_2C_2im][EtSO_4]$ , respectively at mass fraction of  $Al_2O_3$  as low as 0.25 %. The growth of the viscosity is less than 1 % in comparison with pure ionic liquid. When the temperature rises, the specific heat capacity of the Ionanofluid increase clearly, while the viscosity decreases sharply. At higher temperatures (i.e. 323.15 K) even 20.2 % growth in specific heat capacity for  $[C_2C_1im][EtSO_4] + 0.25$  %  $Al_2O_3$  was observed. Moreover, the density of prepared Ionanofluids is higher only about 1 % than that of the base fluid. All these advantages make them good candidate fluids for heat transfer and thermal storage.

#### COMPLEXATION OF DIOXOVANADIUM (V) WITH D-(-)-QUINIC ACID IN [BMIM]BF<sub>4</sub> AQUEOUS SOLUTIONS AT DIFFERENT TEMPERATURES

#### K Majlesi, S Rezaienejad

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Quinic acid is a natural metabolite and involved in the synthesis of the antiviral drug oseltamivir used in the treatment of both influenza A and influenza B. It has been reported as an antioxidative, anti-inflammatory and antimutagenic agent as well as the ability to chelate transition metals in vitro and can reduce the effective dose and nonspecific toxicity of chemotherapy [1]. Quinic acid is the key intermediate in the biosynthesis of aromatic compounds in living systems [1]. One of the metals emerging as a potential anticancer agent is vanadium. Nowadays vanadium compounds are widely studied for their antidiabetic, anticancer properties, as well as against parasitic diseases.

Although many applications about ionic liquids are available in the literature, the number of reports on protonation constants and complex formation thermodynamics is small. The corresponding data in the International Union of Pure and Applied Chemistry (IUPAC) database for Room temperature ionic liquids (RTILs) and related thermodynamic functions are even less common [2]. Knowledge of the complex formation thermodynamics is essential in separation and purification technologies. We have published two papers about protonation and stability constants in [bmim]BF<sub>4</sub> aqueous solutions in recent years [3, 4]. Ionic strength dependence and solvatochromic parameters for the complex formation of dioxovanadium(V) with D-(-)-quinic acid at  $T = 298 \,\mathrm{K}$ ,  $I = 0.1 \,\mathrm{mol} \cdot \mathrm{dm}^{-3}$  of sodium chloride in various [bmim]BF<sub>4</sub> aqueous solutions (by using potentiometric and UV spectrophotometric techniques) were published previously [4] and part of the results were presented at the 19<sup>th</sup> ECTP [5]. Therefore in the current research more experimental works have been performed at the same conditions but at different temperatures (283 < T/K < 310) with the aim of obtaining knowledge about the complex formation thermodynamics. The complex formation reaction is spontaneous according to the negative values of  $\Delta G^0$ . The obtained values of  $\Delta H^0$  0 and  $\Delta S^0$  are also in agreement with the solvation effect of the [bmim]BF<sub>4</sub> aqueous solution. It seems that solvation concept is important for the interpretation of the thermodynamic parameters.

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Room HS BMT

#### FROM THE PREDICTION OF THE PHYSICAL PROPERTIES OF IONIC LIQUID MEDIA TO THEIR APPLICATIONS

## J. Jacquemin,<sup>1,2</sup>

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During this talk, the original research approach shown in Figure 1 will be presented to define a structure-properties relationship for media containing ionic liquids and their uses in various applications such as the energy storage, separation and carbon capture and utilisation processes, for example. The physical properties of the several mixtures containing an ionic liquid (IL) have been predicted by using the COSMOthermX program (Version C30\_1601) which is based on the COSMO-RS method (COnductor-like Screening MOdel for Real Solvents), Equations of State, Activity Coefficient Models (UNIQUAC, UNIFAC, etc.) and/or Group Contribution Methods which allow the determination of their critical, thermal, transport, volumetric and related thermodynamic properties as the function of temperature, composition, IL and/or solvent structure and pressure. These properties have been then compared with data available into the National Institute of Standards and Technology ILs property database. Based on this data analysis a structure properties relationship has been dressed by combining collected physical properties along with molecular descriptors obtained by using ab-initio calculations. Molecular and physical-properties' descriptors were then implemented within Aspen Plus (version 8.4) to further evaluate the ILs' performance for given applications to further validate the proposed methodology.



Figure 1. Strategy develop to screen ILs for a given application.

#### ILPIL – O11 11:20 - 11:40 Tuesday

#### MELTING BEHAVIOUR OF EUTECTIC SOLVENTS CONTAINING QUATERNARY AMMONIUM SALTS

M. A. R. Martins<sup>1</sup>, E. A. Crespo<sup>1</sup>, L. P. Silva<sup>1</sup>, S. P. Pinho<sup>2</sup> and J. A. P. Coutinho<sup>1</sup> <sup>1</sup>CICECO-Instituto de Materiais de Aveiro, Departamento de Química, Universidade de Aveiro, Aveiro, Portugal <sup>2</sup>Associate Laboratory LSRE-LCM, Departamento de Tecnologia Química e Biológica, Instituto Politécnico de Bragança, Bragança, Portugal

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Deep eutectic solvents are a neoteric ecological class of solvents intensively investigated in the recent past. Prepared by mixing Lewis and Brønsted acids and bases, their combination give rise to low melting points mixtures by hydrogen bond complexation. The formulation does not involve any chemical reaction or additional purification steps, and also due to their promising applications in areas such metal processing, extractions, among others, efforts have been devoted to their characterization.

However, for many mixtures the eutectic point is not well established, phase diagrams are very incomplete, and even the melting properties of the pure compounds composing the binary eutectic solvents are not known, limiting severely any theoretical description of the solid-liquid phase diagrams.

Contributing to overcome some of these limitations, in this work, an automatic glass capillary device model M-565 from Buchi was used to measure the melting temperatures of more than 40 binary mixtures constituted by one tetra-alkyl ammonium chloride and some other ionic compound.

The new gathered data was used to qualitatively interpret structural and functional effects in the eutectic coordinates, and were also combined with the reference solvent approach to estimate binary interaction parameters of conventional thermodynamic models. This was particularly useful for the indirect assessment of the fusion properties of the pure tetra-alkyl ammonium chlorides, which in some cases cannot be found using conventional thermal analysis. The reliability of the obtained fusion properties has been checked analysing the consistency of the data and the quality of the calculated phase diagrams.

Room HS BMT

## ILPIL – 12 11:40 - 12:00 Tuesday

#### IONANOFLUIDS FROM GRAPHENE. THE RIGHT APPROACH?

S. I. C. Vieira<sup>1</sup>, F. E. B. Bioucas<sup>1</sup>, K. Kreek<sup>2</sup>, Angela Lamas<sup>3</sup>, M. J. V. Lourenço<sup>1</sup>, F. J. V. Santos<sup>1</sup>, X. Paredes<sup>1</sup>, C. A. Nieto de Castro<sup>1</sup>, M. Koel<sup>2</sup>

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The research on nanofluids raised several problems about the characterization of nanomaterials used, preparation and short/long term stability of the prepared dispersions, and the adequacy of the experimental techniques used to measure the thermophysical properties, namely thermal conductivity, due to the scatter of published data. These problems are aggravated with IoNanofluids, because the structure of the base liquids, the ionic liquids (IL's), is by far more complex than the common molecular solvents like water, glycols, and also because their interactions with nanomaterials are more complex, due to specific interactions between the ions and the nanoparticles [1].

It is the purpose of this paper to report on a systematic study of IoNanofluids of one very well characterized nano-graphene (NG), in several ionic liquids ( $[C_2mim][N(CN)_2]$ ,  $[C_2mim][SCN]$ ,  $[C_2mim][CH_3SO_3]$ ,  $[C_2mim][C(CN)_3]$ ) and ( $[C_{12}mim][N(CN)_2]$ ), by using the same method of preparation, and stability assessment. Graphene was obtained from Sky Spring Nanomaterials Inc. USA (Product #041DX), with thickness (6-8 nm) and average particle diameter of 15  $\mu$ m. The nanomaterial particle dimensions were characterized by TEM imagining.

Measurements of thermal conductivity were performed with a thermal conductivity meter, Hukseflux model (TPSYS02), with probe TP08. A special thermostated cell was constructed, and temperature was controlled within 0.1 °C. The instrument quality was tested with water (Millipore<sup>®</sup>) between room temperature and 70 °C. Deviations from the IUPAC standard reference correlation of Ramires et al [2] (accuracy 0.5 %) where found smaller than 1.5 %. The estimated uncertainty of the data herein presented is assumed to be 2 %.

The results show that good and coherent experimental results can be obtained when well planned experiments are used, demonstrating that IoNanofluids can be used in many applications with success.

## References

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## FORMATION KINETICS OF METHANE HYDRATES IN THE PRESENCE OF TETRABUTYL AMMONIUM BROMIDE

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Tetrabutyl ammonium bromide (TBAB), could form semiclathrate hydrate under milder conditions as compared to gas hydrate and thus effectively improve the thermodynamic stability of gas hydrate. Within the past decade, particular attention has been paid to TBAB as a prospective hydrate promoter. While compared with the hydrate's thermodynamic properties which are time-independent, the time-dependent formation kinetics is still not completely understood.

The focus of this study is to investigate the formation kinetics of methane hydrates in the presence of TBAB. Prior to the kinetic study, the three-phase equilibrium conditions of TBAB + CH4 hydrates at various concentrations were measured by employing the isochoric pressure search method to determine the thermodynamic stability. Then, the formation kinetics of TBAB + CH4 was investigated with an isobaric method at 7.0 MPa with salt mass fraction (*w*) and subcooling degree ( $\Delta T$ ) varying from (0.05 to 0.60) and from (4 K to 10 K), respectively, to evaluate the effect of TBAB. The investigated kinetics included the parameter of induction process (the induction time) and those of growth process (normalized gas consumption, and gas consumption rate).

The results showed that the induction time generally decreased with the increase of  $\Delta T$ , showing that a higher  $\Delta T$  resulted in a shorter induction time. Considering the effect of mass fraction, with the increase of w, the length of induction time generally increased in the system of w < 0.20 and decreased in the systems of w > 0.20. The study of the normalized gas consumption showed that it was almost same in different systems except that in systems with Tbelow 282 K, which was the condition under which pure CH4 hydrate could be formed. In addition, the results of experiments on gas consumption rate revealed that with the same w, in systems with higher  $\Delta T$ , the value of gas consumption rate was higher and the growth time was shorter, which meant that the hydrate was formed faster. Under the same  $\Delta T$ , systems with higher w showed higher gas consumption rate and shorter growth time. These results could provide important information for hydrate based industrial applications, such as gas separation and storage.

#### ILPIL – 014 12:20 - 12:40 Tuesday

#### Room HS BMT

## SPECIATION OF PROTIC IONIC LIQUIDS

Filipe Ribeiro<sup>1</sup>, Carlos Lima<sup>1,2</sup>, André Melo<sup>3</sup>, Artur Silva<sup>2</sup> and Luís Santos<sup>1</sup>

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Protic Ionic Liquids (PILs) have unique properties as solvents. These properties can be used in several applications (biomass processing, cellulose extraction,  $CO_2$  absorption, reaction media, catalysts etc.).<sup>1</sup> This work shows how the cohesive energy and gas phase speciation affects the thermal behaviour and vaporization enthalpies of ten [DBNH]/[DBUH] [RCOO<sup>-</sup>] PILs.

Calvet micro-calorimetry and Knudsen effusion methods were used to evaluate the complex vapour-liquid equilibrium of ten PILs, synthesized using two different superbases 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and five different carboxylic acids, namely acetic, propionic, butyric, hexanoic and octanoic acids. The obtained results were compared, analysed and discussed concerning the effect of different bases/acids on their cohesive energy, volatility and speciation of the PILs with the base/acid ratio. It was found that the effect of changing the superbase in each PIL is stronger than the effect of changing the acid. It was also found that the base/acid composition shifts with the distillation process resulting in property changes.



Figure 1. Thermodynamic cycle of the vaporization process of a PIL, e.g. [DBNH][MeCOOH].

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Materials (M)

**Oral Session 4: Materials** 

15:30 - 18:10 Tuesday HS BMT

Chairs: M. Rohde, H. Mehling

## M - O1 15:30 - 15:50 Tuesday

## Room HS BMT

# THERMOPHYSICAL PROPERTIES OF CERAMIC SOLID ELECTROLYTES FOR LI-ION CELLS

Y. Cui<sup>1</sup>, M. Mahmoud<sup>2</sup>, M. Rohde<sup>1</sup>, H. J. Seifert<sup>1</sup>, C. Ziebert<sup>1</sup>

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Within the current development state Li-ion batteries for energy storage with high capacity and power density liquid electrolytes are applied. These organic liquids are not thermally stable and tend to degrade at higher temperatures. Most of these liquids are flammable which can be an important security issue in high power battery systems. In contrast to the organic liquids solid electrolytes made of a glass-ceramic do not have these disadvantages. Even at higher temperatures they are very stable and do not degrade and therefore reduce the efforts of a sophisticated thermal management. However, one of the main obstacles for the application of solid electrolytes in Li-ion cells is the relatively low ionic conductivity, which can be about one order of magnitude lower than in liquid electrolytes at room temperature.

Within this work we have studied two  $\text{LiO}_2$ -based glass-ceramic systems, which are candidate materials for solid state electrolytes. LAGP  $(\text{Li}_{1+x}\text{Al}_x\text{Ge}_{2-x}(\text{PO}_4)_3, x \approx 0.5)$  and LATP  $(\text{Li}_{1+x}\text{Al}_x\text{Ti}_{2-x}(\text{PO}_4)_3, x \approx 0.5)$  substrates were prepared using a melt quenching route and by applying different compaction methods. In order to develop a better understanding of the relationship between the specific microstructure and the ionic as well as the thermal conductivity, respectively, the samples were characterized by scanning electron microscopy and x-ray diffraction. The ionic conductivity was measured using impedance spectroscopy while the thermal diffusivity and the specific heat were determined by Laser Flash technique and differential scanning calorimetry, respectively. Additionally, thermal analysis was performed in order to evaluate the thermal stability a higher temperatures and also to identify the optimum temperature range of the thermal post-processing.

The glass chemical composition and the developed microstructure in LAGP glass-ceramics via each specific route were very critical to the thermal and ionic conductivity. The measured values of the ionic conductivities were in the range of  $10^{-4}$  to  $10^{-3} \Omega^{-1}$ cm<sup>-1</sup> at room temperature, but exhibited an increasing behaviour as a function of temperature reaching a level of the order  $10^{-2} \Omega^{-1}$ cm<sup>-1</sup> above 200 °C. The thermal conductivity varies only slowly as a function of temperature but its level is very sensitive to the details of the heat treatment. It was shown that the

glass-ceramics samples with higher ionic conductivity have also higher thermal conductivity. Furthermore, the temperature dependence of the thermal conductivity cannot be explained by a single mechanism or by Wiedemann-Franz law. Therefore, there might be also a contribution of the mobile ions to the thermal transport.

## M - O2 15:50 - 16:10 Tuesday

**Room HS BMT** 

# CHANGE OF INTER-PARTICLE BOND TYPE WITH PHASE AND ASSOCIATED CHANGES IN MATERIAL PROPERIES

H. Mehling

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The inter-particle forces between atoms and molecules in materials, and the associated bonds, are usually classified as atomic / covalent (e.g. ceramics), metallic (metals), ionic (e.g. salts), and Van-der-Waals bond (molecules and noble gases). They affect the chemical and physical structure of a material. As a result, material classes having characteristic material properties and bond type are strongly connected. For example, the presence of the electron gas in a metal is the reason for their typical electrical conductivity, optical reflectance, and thermal conductivity; thus, these properties are connected as they are based on the bond type. And the strength of the bonds determines the hardness, the speed of sound, the coefficient of thermal expansion, or melting and boiling temperature.

It is common to classify materials as metals, salts etc. and to assume that their bond type stays the same no matter if the material is solid, liquid, or gaseous. However, this assumption, which is typically used in textbooks, can not be generally correct: covalent bonds are based on sharing specific electrons between partners, a situation that is impossible in a liquid or a gas where particles slide past each other. Thus, when the particles in a material are bound by covalent bonds in the solid the bond type must change when they become liquid, and associated material properties must change in an uncommon way and possibly much stronger. The study of such exceptional cases is important to understand the limits of current models, and to see the full range of possible material properties.

In this paper, such exceptional cases are described in more detail, specifically a number of cases in a wide range of situations is shown, as well as for some specific cases the degree of the deviation from common material behaviour. For this, the study was done in two ways.

The first way was looking at available information on the bond type in materials. The focus was on the elements. Here, C, Si, and Ge have covalent bonds in the solid phase, while investigations of the thermal and electrical conductivity of the liquid phase show properties characteristic for metals and thus metallic bonds. This is the case mentioned above. As, Sb, and Bi have a layer structure in the solid phase (like C as graphite), while the liquid phase consists of 4-atomic molecules; the vapour consists of 4- and 2-atomic molecules and single atoms depending on the temperature. This means the particle structure changes with increasing temperature from an infinite layer to molecular and atomic. Even more complex is the behaviour of sulphur. For the case of ionic bonds, not possible in elements, the case of KCl shows ionic structure in the solid, ionic in the liquid, and molecular in the gas phase.

The second way of study was looking at a specific property class, and identifying and studying specifically materials with an uncommon behavior. Here, the cases of melting enthalpy and melting temperature, where the common behavior is described by the rule of Richards, and the case of the enthalpy of evaporation and boiling temperature, where common behavior is described by the rule of Trouton, were investigated. Again, examples showing the connection between highly uncommon behavior regarding material properties and change of bond type were identified.

This shows that such an exceptional behavior is worth studying more deeply.

## M - O3 16:10 - 16:30 Tuesday

## **Room HS BMT**

## ELECTRICAL CONDUCTIVITY OF AAS WITH CONDUCTING PARTICLES: COMPARISON OF METHODS AND APPLICATIONS

L. Fiala, R. Černý

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Design of progressive building materials with increased utility value is the key issue in development of more reliable building structures. One possible way of such enhancement is based on increase of the electrical conductivity of conventional materials by addition of a sufficient amount of chosen conductive phase. Such enhanced materials called intrinsic self-sensing materials can detect defects by itself without the need of incorporation of an external monitoring system. Another possible application is in the field of self-heating systems. Concrete, due to its wide production, is a typical representative of commonly enhanced materials. However, other materials such as alkali-activated aluminosilicates can be enhanced in the same way. In order to assess effect of added amount of electrically conductive admixture, electric properties need to be determined. In this paper, methodology of electric properties measurements with description of strengths and weaknesses of each method is introduced. Besides, demonstration examples of experimentally determined electric properties of enhanced alkali-activated aluminosilicates by using different measurement methods are presented and discussed.

## M - O4 16:30 - 16:50 Tuesday

#### Room HS BMT

# COMPUTATIONAL MODELING OF TEMPERATURE FIELDS IN ELECTRICALLY CONDUCTIVE ALUMINOSILICATES

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In general, aluminosilicates are electrically non-conductive building materials. However, ad-

dition of specific electrically conductive admixtures such as steel fibers, carbon fibers, carbon black, graphite powder, nickel powder etc. in appropriate amount leads to increase of the electrical conductivity which allows such materials to generate the Joule heat under the influence of electric voltage. Aluminosilicates with enhanced electrical properties can be then used in self-heating or de-icing systems. In order to assess effect of added amount of electrically conductive admixture and behaviour of heating system in different ambient temperatures, theoretical description of the Joule heat model and its application by means of FEM modelling are good prerequisities for selection of promising mixtures. In this paper, several examples of application of the model considering the Joule heat evolution in terms of FEM for aluminosilicates with various electrical conductivity and for different initial ambient temperatures are presented and compared.

#### M - O5 16:50 - 17:10 Tuesday

#### Room HS BMT

## UTILIZATION OF SHAPE-STABILIZED PCM IN INTERIOR PLASTER FOR LATENT HEAT STORAGE

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The worldwide development in building industry accompanied with population boom enhances demands on the housing quality and further increases energy consumption for the buildings operation. Nowadays, a share of the total energy consumed by building sector is responsible for about 26 % of the total energy consumption in USA and EU region. The focus on reduction of the greenhouse gases emissions and sustainable development principles lead to development of the new materials and technical solutions oriented to the energy efficiency. Application of the Phase Change Materials (PCMs) represents a promising way for increasing the thermal mass of buildings. The ability of PCMs to store and consequently release thermal energy predetermines their use in several building elements. However, despite of the evident positive effects of microencapsulated PCMs on the thermal energy storage of building components, their wider use is unfortunately limited due to the inert polymer shell, which decreases all mechanical parameters of cement-based composites. This phenomenon restricts addition of the adequate portion of PCM for the sufficient thermal energy storage, therefore influence of PCMs on interior temperature fluctuation and delays of the temperature peaks is reduced. In order to avoid possible problems with inert polymer shell, development of Shape Stabilized Phase Change Material (SS-PCMs) was developed.

Firstly, the filter diatomite was chosen for SS-PCM composite preparation. Dodecanol also known as lauryl acid was chosen as PCM medium due to its suitable temperature interval of the phase transition and the high latent heat. On this account, SS-PCM based on dodecanol with the phase change temperature in desired range and diatomite with suitable pores structure was prepared. For the origination of SS-PCM, the vacuum impregnation method was employed and Dodecanol/Diatomite composite was formed in this sense. In order to preserve the pozzolanic properties of diatomite, test of pozzolanic activity was carried out to find optimal proportion between dodecanol and diatomite. Successful impregnation of the dodecanol into the porous structure of diatomite was proved by the measurement of the particle size distribution and Fourier transform infrared spectroscopy.

Developed SS-PCM composite was consequently utilized as admixture in the cement-lime plaster to improve its thermal storage properties. Influence of the incorporated Dode-canol/Diatomite composite in cement-lime plaster was determined by meaning of the heat storage capacity. Here, DSC analysis was employed for identification of the phase change temperature. The revealed phase change temperatures vary from the 21.08 °C during cooling to the 18.32 °C during heating. The specific enthalpy of phase change was proportionally decreased according to the volume of the applied PCM compared to the original material. However, the phase change enthalpies of about 9.9 J/g during cooling and 10.2 J/g during heating are satisfying from the perspective of the future utilization in building practice.

## M - O6 17:10 - 17:30 Tuesday

#### **Room HS BMT**

## INFLUENCE OF TEXTURE ON DC CONDUCTIVITY OF ILLITE AND KAOLIN

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The influence of technological texture on DC conductivity of illite (from Füzérradvány, Hungary) and kaolin (from Podbořany, Czech Republic) was studied. The textured samples was created by layering a wet plastic mass. Anisotropy of samples was studied through DC con-

created by layering a wet plastic mass. Anisotropy of samples was studied through DC conductivity ( $\sigma$ ) and relative length changes ( $\epsilon$ ) as a function of firing temperature in two directions (parallel and perpendicular to the basal planes of illite/kaolinite crystals). It was found, that the samples shrinkage after firing is more significant in perpendicular direction. Any firing at high temperatures (1200 °C) does not remove the texture. Compared to illite, the influence of technological texture in kaolin is more significant.

## M - O7 17:30 - 17:50 Tuesday

## Room HS BMT

# DOPED SINGLE WALL CARBON NANOTUBES IN PEDOT: PSS LAYER IN ORGANIC SOLAR CELL

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Zinc oxide doped single wall carbon nanotubes (ZnO:CNT) are incorporated in PEDOT:PSS aqueous solution to serve as a hole transport buffer layer in the preparation of thin film organic solar cells (TFOSC). The solar cells were fabricated according to bulkheterojunction design whose photoactive layer is composed of poly (3 hexythiophene) (P3HT) and [6,6]-phenyl-C61-butyric acid methyl ester (PCBM) blend. Significant improvement in harvesting photogenerated currents and low series resistances were observed which lead to higher power conversion efficiencies compared to the devices without ZnO:CNT. The optical properties and sur-

face morphologies of ZnO:CNT/PEDOT:PSS hole transport layers are investigated and compared with the changes in the measured parameters of the solar cells. The power conversion efficiency of the devices increased by nearly 116 %, 63 % and 42 % for ZnO:CNT loading at 2.5 %, 5 % and 10 % by weight, respectively, from the devices that uses only PEDOT:PSS as a hole transport layer. Furthermore, a complete recovery of device performance was found by storing the device in warm nitrogen atmosphere.

## M – O8 17:50 - 18:10 Tuesday

#### **Room HS BMT**

## THERMOELECTRIC PROPERTY OF BISMUTH TELLURIDE THIN FILMS CONTROLLED BY COMBINATORIAL SPUTTER COATING METHOD

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p, n-types bismuth telluride thin films have been synthesized by a combinatorial sputter coating system (COSCOS). The crystal structure and crystal preferred orientation of the thin films were changed by controlling the coating condition of the radio frequency (RF) power during the sputter coating. As a result, the p- and n-type films and their dimensionless figure of merit (ZT) were optimized by the technique. The properties of the thin films such as the crystal structure, crystal preferred orientation, material composition and surface morphology were analyzed by X-ray diffraction, energy- dispersive X-ray spectroscopy and atomic force microscopy. Also, the thermoelectric properties of the Seebeck coefficient, electrical conductivity and thermal conductivity were measured. ZT for n- and p-type bismuth telluride thin films was found to be 0.27 and 0.40 at RF powers of 90 and 120 W, respectively. The proposed technology can be used to fabricate thermoelectric p-n modules of bismuth telluride without any doping process.

## Nanomaterials (N)

#### **Oral Session 5: Nanomaterials**

10:05 - 12:05 Wednesday HS BMT

Chair: W. Sprengel

#### N - O1 10:05 - 10:25 Wednesday

Room HS BMT

# HEAT CAPACITIES AND EXCESS ENTROPIES OF BULK AND NANO Fe\_3O\_4-Co\_3O\_4 AND Fe\_3O\_4-Mn\_3O\_4 SPINEL SOLID SOLUTIONS

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We have measured the heat capacities of several well-characterized bulk and nanophase  $Fe_3O_4 - Co_3O_4$  and  $Fe_3O_4 - Mn_3O_4$  spinel solid solution samples from which magnetic properties of transitions and third-law entropies have been determined. The magnetic transitions show several features common to effects of particle and magnetic domain sizes. From the standard molar entropies, excess entropies of mixing have been generated for these solid solutions and compared with configurational entropies determined previously by assuming appropriate cation and valence distributions. The vibrational and magnetic *excess* entropies for bulk materials are comparable in magnitude to the respective configurational entropies indicating that excess entropies of mixing must be included when analyzing entropies of mixing. The excess entropies for nanophase materials are even larger than the configurational entropies. Changes in valence, cation distribution, bonding and microstructure between the mixing ions are the likely sources of the positive excess entropies of mixing.

#### N - O2 10:25 - 10:45 Wednesday

#### Room HS BMT

## ELECTRICAL, THERMAL AND SURFACE PROPERTIES OF HDPE/AG NANOCOMPOSITES

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Over last few decades, polymer nanocomposites have attracted much attention due to the possibility of producing new materials with enhanced physical properties. As it is known, the addition of metallic filler particles into a polymer may result in significant improvements in thermal and electrical properties of polymer. Size of metallic fillers, their shape, dispersion, concentration and method of the preparation influence properties of prepared polymeric composite materials, including electrical conductivity. Among metal particles, silver (Ag) demonstrates the highest thermal and electrical conductivity and is known as the antimicrobial agents. In addition, high density polyethylene (HDPE) is one of the most popular thermoplastic materials as a matrix for preparing nanocomposite materials.

The aim of this work was to investigate the effects of Ag concentration on the electrical, thermal and surface properties of HDPE/Ag (40-50 nm) nanocomposites. The HDPE nanocomposites with various concentration of Ag (up to 5 vol %) were prepared by melt mixing method using a Brabender Plasticorder at 180 °C with a rotor speed of 35 rpm and a mixing time of 15 min, followed by compression molding. Broadband dielectric measurements were performed, in the frequency range of  $10^{-1} - 10^{6}$  Hz, by means of an Alpha-N Frequency Response Analyser by Novocontrol Technologies GmbH (Hundsangen, Germany). The thermal properties (heat capacity, heat fusion and melting temperature) measurement of the samples was carried out at a heating rate of 10 °C/min between -10 °C and 200 °C temperature range by using Perkin Elmer Diamond DSC (Differential Scanning Calorimeter). The contact angles of composite samples measured by sessile drop method and carried out using a professional SEE (Surface Energy Evaluation) device.

The electrical measurements showed that the electrical conductivity ( $\sigma'$ ) increased by increasing the concentration of Ag. A maximum value of  $\sigma'$  was found  $1.85 \times 10^{-1}$  S/cm for the highest Ag concentration (5 vol %), corresponding to an increase of 16 orders of magnitude in the electrical conductivity relative to the pure HDPE ( $4.68 \times 10^{-17}$  S/cm). In addition, the percolation threshold of HDPE/Ag nanocomposites was found approximately 2 vol %. The results of DSC demonstrated that the specific heat of polymer nanocomposites decreases from 1.820 to 1.276 kJ/kgK with increase in Ag concentrations from 0 to 5 vol %. The incorporation of Ag didn't lead to respectable change on the melting temperature of HDPE matrix, but the heat of fusion decreased by increasing the concentration of Ag. For all nanocomposites, the melting temperature was similar (~132 °C). It was found that the water contact angles of nanocomposites decreased with increasing the concentration of Ag due to the hydrophilic nature of Ag particles.

## N - O3 10:45 - 11:05 Wednesday

#### **Room HS BMT**

## THERMOPHYSICAL PROPERTIES OF POLYMER NANOCOMPOSITES REINFORCED WITH CONDUCTIVE FILLERS

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In this study, mechanical and thermal properties (thermal conductivity, specific heat capacity, and melting temperature) for high density polyethylene (HDPE) filled with aluminum (Al) nanoparticles (80 nm) were investigated up to 30 vol % of Al particles content. Thermal conductivity of samples was measured experimentally, and compared with numerical analyses and theoretical models. Numerical study was carried out by ANSYS Workbench 14.0 based on finite element analysis software as function of concentrations of filler materials. Series, Parallel, Geometric Mean, Maxwell, Cheng & Vachon's, Springer & Tsai's Model, Russell, Rayleigh's, Woodsite & Messmer's Theoretical Model, Lewis & Nielsen's Semi-Theoretical Model, Hamilton & Crosser's, Bashirrow & Selenew, Zehner & Schlünder's, Meredith & Tobias and Agari & Uno Model were used in this study.

As is known, the thermal conductivity of nanocomposites increased with increasing the Al content. The thermal conductivity of nanocomposites with 30 vol % of Al content increased by 2.3 times with respect to pure HDPE. At low filler concentrations, there is good agreement between the numerical and theoretical estimations, the reason for this being that the fillers are evenly distributed in the matrix without any interactions between them. In addition, the closest model to numerical analysis is "Baschirow & Selenew Theoretic Model" and Maxwell's, Hamilton & Crosser's, Meredith & Tobias's, Lord Rayleigh's, Agari & Uno's, Lewis & Nielsen's (A=1.5, Øm=0.637) theoretical models were closer to experimental values. As expected, the dependence of specific heat on the weight filler fraction is linear and the experimental results are in a good agreement with the calculated values from mixture law. While the specific heat of nanocomposites decreased by addition of Al particles, the melting temperature didn't show any significant change.

## N – O4 11:05 - 11:25 Wednesday

#### Room HS BMT

# INFLUENCE OF NANOPARTICLES ON THE THERMOPHYSICAL PROPERTIES OF INORGANIC NITRATE SALTS FOR THERMAL ENERGY STORAGE APPLICATIONS.

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The development of economic and effective thermal energy storage (TES) systems is a key technological issue for concentrated solar power (CSP) plants and industrial waste heat recovery. The inorganic nitrate salts are not only the most used materials for sensible heat storage (Solar Slat, 60 wt. % NaNO<sub>3</sub> + 40 wt. % KNO<sub>3</sub>) in commercial CSP plants but also the most promising studied materials for latent heat storage applications. Enhancing their specific heat capacity ( $C_p$ ) and thermal conductivity by means of adding small amount of nanoparticles is being increasingly topical area, which aims to greatly improve the thermodynamic cycle efficiency of the TES system and consequently to bring CSP technology on the next level of competitiveness and to improve the efficiency in the industrial processes.

In this study, we investigated how thermophysical properties of some nitrate salts are modified by means of adding nanoparticles in a small concentration of around 1 %wt. Particularly, specific heat capacity and thermal conductivity of the nanosalts (nanoparticles + salt) were measured using differential scanning calorimetry (DSC) and laser flash apparatus (LFA), respectively. Additionally, the effect of adding nanoparticles on the viscosity of nanosalts was investigated. In order to understand the pronounced effect of nanoparticles on the mentioned above thermophysical properties the nanosalts were also characterized by using different techniques such as scanning electron microscopy (SEM), Fourier transform infrared spectroscopy (FTIR), X-ray powder diffraction (XRD) and X-ray photoelectron spectroscopy (XPS).

## N - O5 11:25 - 11:45 Wednesday

**Room HS BMT** 

# ENHANCEMENT OF THE RADIATIVE AND THE CONVECTIVE HEAT DISSIPATION PROPERTIES BY THE CARBON NANOTUBES

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The integration levels of electronic devices continue to increase and the redundant generating heat power result in the on-going increase of working temperatures of related devices. So heat dissipation properties of heat dissipation devices could seriously influence the working efficiency and lifetime of electronic devices. So far, thermal properties of heat dissipation devices have posed important obstacles for rapid developments of electronic devices. Carbon nanotubes (CNTs) and their macroscopic materials are presently attracting immense research interests on the global level because of their perfect properties. Our results reported here offer insights and avenues to achieve effective passive heat dissipation devices based on CNTs.



**Figure 1** a) SEM images of the CNT films; b) Schematic diagram of the heat dissipation property testing setup; c) The surface emissivity of different layers of CNT films.

Firstly, the radiative heat dissipative and the natural convective heat dissipation properties of different layers of CNT films (Fig. 1a) are investigated by an assembled thermal analyzer (Fig. 1b). It is found that the CNT films could have very high surface emissivity (>0.95, Fig. 1c), which indicate that the CNT films could have outstanding radiative heat dissipation properties.

Then a novel kind of CNT-based cooling devices are fabricated by the method shown in the Fig. 2a-e. The novel cooling devices consist of monolayer SACNT films and underlying microchannels. As shown in the Figure 2k, our results prove that the novel CNT-based devices could show an 86.6 % larger total natural heat dissipation properties than bare copper plate due to the synergistic effects of microchannels and SACNT films. We believe that the CNT-based heat dissipation devices would replace the traditional metal-finned heat dissipation devices and have promising applications in electronic devices, such as photovoltaic devices.



**Figure 2** a-e). The fabricating methods of the CNT/microchannel cooling devices; h-j) SEM images of the CNT/microchannel devices; k) The natural convection heat transfer coefficients (*h*) of the novel cooling devices and the pure copper plate, respectively.

## N - O6 11:45 - 12:05 Wednesday

## Room HS BMT

## SURFACTANT-ASSISTED DISPERSION OF CARBON NANOTUBES IN EPOXY RESIN TO ENHANCE CARBON FIBRE REINFORCED POLYMER COMPOSITES PERFORMANCE

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Carbon Fibre Reinforced Polymers (CFRPs) offer excellent and superior mechanical performances at low weight, such as very high strength- stiffness to-weight ratios making them widely used in several structural applications, where the weight is a critical aspect, such as in aerospace and in sports, but are emerging very significantly in other sectors, such as in the automotive and energy. Conventional CFRPs have inherently non-isotropic properties, with in-plane properties dominated by mechanical, electrical and thermal properties of the fibres. However, in several structural applications, the demand for better properties in the through thickness direction, such as improved electrical and thermal conductivity as well as mechanical performance, makes metals still a preferable choice.

Many studies have been done to enhance CFRPs properties by incorporation of Carbon Nanotubes (CNTs). CNTs are known to possess exceptional mechanical, electrical, thermal and optical properties and therefore are excellent candidates to provide multifunctionality to CFRPs. Nevertheless, due to the strong van der Waals cohesive forces established between them, CNTs tend to agglomerate, leading to poor dispersibility and distribution and weak interfacial interactions with the polymer matrix, leading to inferior properties than those that would be theoretically expected. Several strategies have, thus, been followed to improve their dispersion and control their distribution. One of them is the use of non-covalent dispersion methods, which do not require the chemical functionalization of the CNT. These involve the adsorption of amphiphilic molecules (such as conventional surfactants, biomacromolecules
or polymer-based surfactants) on the surface of CNTs driven by hydrophobic interactions and further stabilization by steric and/or electrostatic repulsions provided by the surfactant headgroups.

In this work, it is evaluated the ability of different conventional and polymer-based surfactants, to promote the dispersion of CNTs in epoxy resins. Its effect on processing epoxy relevant characteristics was assessed through differential scanning calorimetry and rheology. Optimised formulations were further used to prepare carbon fibre pre-impregnated materials and their mechanical properties correlated with the resin composition.

The obtained results provide indication for the best surfactants molecular structure to disperse CNTs in epoxy resins and the best balance between processing characteristics and final CFRPs properties.

## Photothermal and Photoacoustic Thermophysics Properties (PPTP)

**Oral Session 6: Photothermal and Photoacoustic Thermophysics Properties** 

10:30 - 11:30 Thursday HS BMT

Chair: A. Mandelis

## PPTP - O1 10:30 - 10:50 Thursday

## Room HS BMT

## A PHOTOPYROELECTRIC APPROACH FOR ELECTROCALORIC EFFECT CHARACTERIZATION OF POLAR MATERIALS

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Electrocaloric refrigeration is an alternative emerging technology to the conventional gascompression refrigeration in food preservation and air conditioning applications. It shows real potential to enter conventional markets. The electrocaloric effect (ECE) is characterized by an entropy change, associated with a temperature change when varying the electric field.

ECE is evaluated using both traditional indirect methods where entropy change ( $\Delta S$ ) and temperature change ( $\Delta T$ ) are deduced using Maxwell's relations and newly developed direct techniques, where  $\Delta S$  and/or  $\Delta T$  are measured from specially designed calorimeters.

In the present work, the ECE in polar materials is investigated using the photopyroelectric (PPE) technique. This technique exploits the complex pyroelectric signal generated by a periodically heated pyroelectric sample using a modulated light source. The PPE method has shown to be an efficient approach for measuring thermal parameters of a pyroelectric sample [1]. Furthermore, the pyroelectric signal is also useful for studying the behavior of the polarization in ferroelectrics associated with an electric field [2].

Here, we show that the PPE can be employed to determine the electrocaloric adiabatic temperature change. The advantage of this indirect approach lies in the fact that the slightly variation of heat capacity as function of temperature is taken into account, unlike the previous studies [3]. Measurements have been carried out on the well-known ferroelectric material, a Triglycine Sulfate single crystal. Obtained results are consistent with those determined by repolarization current technique and values available in the literature [4].

With the increasing need for higher accuracy measurement, the PPE technique may represent a promising approach for evaluating polar materials performance in real electrocaloric applications.

## References

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## PPTP – O2 10:50 - 11:10 Thursday

### Room HS BMT

## MODEL OF LOCK-IN SIGNALS FOR PULSED LIGHT HEATING THERMOREFLECTANCE TECHNIQUE TO MEASURE THERMOPHYSICAL PROPRTIES OF THIN FILM

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Pulsed light heating thermoreflectance techniques (*i.e.* TDTR) using ultra-fast pulsed lasers are widely used for measuring thermophysical properties of thin films. Because of weak thermoreflectance (TR) coefficients, almost instruments utilize a lock-in detection technique, where pump laser pulse train is modulated at a certain frequency, and then the TR signal synchronized with the modulation frequency is selectively detected by a lock-in amplifier. Therefore, to analysis the thermophysical properties of thin films, it is of importance to understand relation between temperature response of the film induced by the modulated pump pulse train and lock-in signals, such as lock-in amplitude and phase. Here, we construct a temperature response model: accumulating responses by a single pulse heating for the whole modulation period. Then, output of the lock-in signal is described based on the temperature response model through the conversion of a probe laser signal into an electrical signal by a photodetector. Finally, lock-in phase and amplitude signals are estimated using our model for the whole delay time range.

Figure 1 shows experimental lock-in phase data for a 450 nm-thick Mo film deposited on a quartz glass substrate measured using our pulsed light heating thermoreflectance apparatus. Two kinds of modulation frequency, 200 kHz and 1 MHz, were used. Furthermore, two kinds of heating arrangement were applied; heating at the surface (FF) and rear face (RF) of the film. The TR measurement was carried out at the surface of the film. Other parameters and thermophysical properties of the sample are listed in Table 1. Our model using the parameters in Table 1 can reproduce the experimental data in not only shape of the signal but also the magnitude of the phase change in whole range of the delay time.



**Figure 1**. Experimental and calculated lock-in signal of phase for the Mo film (450 nm)/quartz glass substrate, where the pulse frequency is 20 MHz and the modulation frequencies are 200 kHz (upper figure) and 1 MHz (lower figure).

Table 1. Parameters used for phase signal calculation of Mo 450 nm/quartz glass.

Material	Thickn ess [nm]	Thermal diffusivity [m <sup>2</sup> s <sup>-1</sup> ]	Thermal effusivity [Jm <sup>-2</sup> s <sup>-0.5</sup> K <sup>-1</sup> ]	Thermal boundary resistance [m <sup>2</sup> K W <sup>-1</sup> ]
Мо	450	2.98×10 <sup>-5</sup> (RF) 3.25×10 <sup>-5</sup> (FF)	14200 (RF) 14800 (FF)	_1.5×10 <sup>-9</sup>
Quartz glass	1	9.06×10*	1450	
Absorption coefficient (Mo) [m <sup>-1</sup> ]		Pulse frequency [Hz]	Modulation frequency [Hz]	Pump spot diameter [µm]
4.15×10 <sup>7</sup>		2×107	2×10 <sup>5</sup> 1×10 <sup>6</sup>	41

## PHOTOPYROELECTRIC CHARACTERIZATION OF A FERROELECTRIC LIQUID CRYSTAL UNDER ELECTRIC FIELD

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Many devices exploit the wide range of useful properties of ferroelectric materials. Among them, Ferroelectric Liquid Crystals (FLCs) hold their importance in display technology due to their interesting properties as fast switching response under electric field, bi-stability, gray scale level, wide viewing angle, etc. Nevertheless the studies on their physical properties are still relevant to analyze more precisely the switching behaviors, anchoring effects, depolarization effects and so on [1].

The switching behavior of a surface stabilized FLC (Felix 017/100) in its SmC\* phase under an external electric field (EF) is studied by analyzing sample generated pyroelectric signal obtained by heating it with an intensity modulated laser source [2]. The sample is sandwiched between two glass plates with electrode coatings inside and separated by a 15  $\mu$ m spacer. Primarily, sample's thermal conductivity,  $\kappa$ , as a function of EF is found, which showed the presence of hysteresis behavior. In order to understand the switching behavior of the molecules, the free energy model [3] is used to establish relations between  $\kappa$  and the azimuthal angle,  $\Phi$ , characterizing the molecular tilt within the SmC\* layers, for each EF. The anchoring energy of the FLC molecules at the cell surfaces is also evaluated by doing a curve fitting of the established theoretical model to the experimental data.

Depth dependent studies are conducted by varying the laser intensity modulation frequency, up to 40 kHz (corresponding to a thermal diffusion length of about half a micron), in order to understand the molecular reorientation near to the cell boundaries. Experimental phase data obtained are used to analyze and understand the observed behaviors. Our investigations reveal that the switching of FLC layers in the vicinity of the cell plates happen for EFs higher than required for the molecular layers away from the boundaries. The effects of the anchoring energy due to alignment layers and preferred molecular orientations are considered to interpret the switching behavior as a function of thickness.

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## Theory and Modelling (TM)

Oral Session 1: Theory and Modelling I

11:05 - 13:05 Monday HS BE01

Chairs: D. Lager, P. Burgholzer

## TM – O1 11:05 - 11:25 Monday

Room HS BE01

## VIRIAL EQUATION OF STATE FOR THE (CH<sub>4</sub> + CO<sub>2</sub>) SYSTEM FROM ACCURATE INTERMOLECULAR POTENTIAL ENERGY SURFACES

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The second to sixth virial coefficients of gaseous ( $CH_4 + CO_2$ ) mixtures have been calculated for temperatures up to 1200 K using the Mayer-sampling Monte Carlo method of Singh and Kofke [1]. Highly accurate intermolecular potential energy surfaces for the  $CH_4 - CH_4$  [2],  $CO_2 - CO_2$  [3], and  $CH_4 - CO_2$  [4] interactions have been employed. They are based on quantum-chemical *ab initio* calculations and were fine tuned to the most accurate experimental data for the second virial coefficients of the pure gases and the  $CH_4 - CO_2$  cross second virial coefficient. To account for nonadditive three-body interactions, empirically adjusted Axilrod-Teller-Muto potentials and a more complex model for three  $CO_2$  molecules based on *ab initio* calculations [5] have been used. Quantum effects have been accounted for by applying the quadratic Feynman-Hibbs modification of the pair potentials [6]. For densities at which the sixth-order virial equation of state is converged, the calculated pressures agree within  $\pm 0.1$  % with those of the best experimental ( $p, \rho, T$ ) data [7].

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## A NEW APPROACH TO MODEL MIXED HYDRATES CONSISTENT WITH MULTIPARAMETER EQUATIONS OF STATE

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Major progress has recently been made regarding the combination of hydrate models with highly accurate property models for the fluid phases in equilibrium. A model for the determination of phase equilibria and thermodynamic properties of pure gas hydrates (water + one hydrate forming substance), which is consistent to the best available models for other phases than hydrate, was developed by our group [1-4].

In this study, the model for pure hydrates has been extended to systems with more than one hydrate forming substance (mixed hydrates). It is intended for modelling of mixed hydrates in carbon capture and storage (CCS)-relevant mixtures. The model is based on the model developed by Ballard and Sloan [5], which itself is based on the statistical model by van der Waals and Platteeuw [6]. The model of Ballard and Sloan, which was developed for natural gas systems, contains a considerable number of adjustable parameters for mixed hydrates and comparatively complex mixing rules, especially for the molar volume of mixed hydrates. For the newly developed mixed hydrate model, a simple mixing rule for the volume is used, which does not contain any adjustable parameters. The new model is consistent with accurate multiparameter equations of state for fluid phases of the corresponding mixtures.

New phase equilibrium algorithms were developed for the evaluation of the model. A comprehensive study on phase equilibria considering up to four phases of ternary mixtures forming gas hydrates and other pure solid phases, i.e. water ice and dry ice, was carried out. It is shown that the new model is consistent with the Gibbs' phase rule, i.e. in a p-T diagram the four-phase line is independent of the overall composition at given pressure. Furthermore, the transitions from four to three phases are consistent and physically reasonable. Comparisons of the new model with experimental data for mixed hydrates in the ternary systems carbon dioxide + methane + water, carbon dioxide + carbon monoxide + water, nitrogen + oxygen + water and in the quaternary system nitrogen + oxygen + argon + water are presented.

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## TM – O3 11:45 - 12:05 Monday

### **RESOLUTION LIMITS FOR THREE-DIMENSIONAL THERMOGRAPHIC IMAGING**

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Thermographic imaging using an infrared camera for signal detection has a big advantage compared to ultrasonic imaging using acoustic transducers: it does not need any coupling media and parallel detection of many camera pixels is possible. The main disadvantage of pulsed thermography is the degrading spatial resolution with increasing depth. This is the reason why often only one-dimensional thermographic reconstruction is performed, which can be applied for layered structures, where the lateral extension is big compared to their depth. For other structures, using a one-dimensional reconstruction gives additional artifacts, as the heat propagates not only perpendicular to the surface but also in the lateral direction. Solving directly the inverse three-dimensional heat diffusion equation is rather ambitious, even for simple geometries of embedded structure, e.g. rectangular vertical cracks [1].

In this work, it is shown that image reconstruction methods from ultrasonic imaging can be employed for thermographic signals. Before using these imaging methods, a virtual signal is calculated by applying a local transformation to the temperature evolution measured on a sample surface. The introduced transformation describes all the irreversibility of the heat diffusion process and can be used for every sample shape in two and three dimensions. The feasibility of this approach is demonstrated through simulations and experiments. For the latter, e.g. small steel beads embedded in an epoxy resin are imaged.

In acoustical or optical imaging, this blurring of structures is usually modeled by convolution with a point - spread - function. We can introduce such a point - spread - function for thermographic imaging, which shows that the lateral resolution is approximately twice the axial resolution. The resolution for pulsed thermography is proportional to the depth of the point source divided by the natural logarithm of the signal-to-noise ratio.

## References

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## TM – O4 12:05 - 12:25 Monday

Room HS BE01

# COSMO-RS, THE BRIDGE FROM QUANTUM CHEMISTRY TO FLUID PHASE THERMODYNAMICS AND PROPERTY PREDICTION

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COSMO-RS is a method for the *a priori* prediction of chemical potentials in pure liquid solvents and solvent mixtures. Typical properties derived from these chemical potentials include

solubility, activity coefficients,  $pk_a$ , free energy of solvation for chemical reaction modeling, vapor-liquid, liquid-liquid and solid-liquid phase equilibria, two-phase partitioning (e.g.  $logk_{OW}$ ) and vapor pressures.

In contrast to many popular methods, such as group based approaches, COSMO-RS generates the information about the intermolecular interactions from uni-molecular quantum chemical calculations on the compounds. It thus fills the gap between quantum chemistry and more empirical methods such as ClogP, UNIFAC, or force field based MD or MC. If applied to general organic chemistry COSMO-RS can largely predicted the same properties with similar or better accuracy than the more empirical models and still uses orders of magnitude less parameters.

Hence COSMO-RS is able to build a bridge between quantum chemistry, physics and theoretical and empirical chemistry. Due to its sound physical basis, its strengths are a broad applicability, extrapolation power and the systematic physical insight into the mixture behavior of these systems.

While the predictions are not accurate enough to replace experimental data, they are invaluable where experimental data are missing or cannot be obtained. Typical usages of COSMO-RS include focused experimental setups, virtual screening, high energy chemicals, transition states or intermediates, fast response trouble shooting and physical interpretation of predicted or experimental behavior.

In this paper we provide a brief general overview of the method, its strengths and limitations, as well as selected property examples and results of a recent blind test.

### TM – O5 12:25 - 12:45 Monday

### Room HS BE01

## THE ROLE OF POLYMER TOPOLOGY IN SURFACE MODIFICATION OF PLASTIC MATERIALS

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Techniques for surface modification of plastics are very important in modern technologies, and they can be chemical, in which reactions are used to transform the surface layer, or physical, in which surface-active agents are placed at the surface and allowed to self-assemble. If we focus our attention on the second approach, we easily realize that many important thermoplastics are polymer blends, and there is considerable interest to understand the extent the composition of the surface layer differs from that in the bulk for molten polymer mixtures. Dynamical and structural properties of polymers in the melt state are strongly influenced by molecular architecture [1-4] and blending polymers with different molecular topologies could be potentially exploited to control interfacial segregation of the polymer film, and to achieve optimal mechanical properties of the thermoplastic material [5,6]. However, a deep understanding of the role of chain architecture and molecular mass in determining

which species preferentially adsorb at a given interface is lacking. Experiments to resolve the matter are typically conducted by mixing polymers possessing the same repeat chemistry, but different molecular architecture [10-14]. Here we show the results obtained in large-scale molecular dynamics simulations of linear-cyclic polymer films, and we find clear evidence of enhancement of linear polymers at the interface [7], in agreement with recent experimental results [8]. The behavior predicted by the self-consistent field theory (SCF), i.e., enhancement of cyclic polymers at the interface [9], emerges for relatively long chains. In our presentation, we provide a picture of the microscopic mechanisms through which the chain length arbitrates the competition between the different packing constraints imposed by the loop and linear geometry of the two polymers. We also discuss the role of enthalpic and entropic factors of the interfacial free energy of the system in determining which species in the blend preferentially adsorbs at the interface.

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## TM – O6 12:45 - 13:05 Monday

## Room HS BE01

## ACCURATE MODELLING OF INTERFACIAL AND PHASE EQUILIBRIUM PROPERTIES OF RESERVOIR FLUIDS

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The development of a consistent thermodynamic model capable of accurately describing the properties of both bulk and interfacial phases in reservoir fluids systems is of paramount importance for the deployment of more efficient reservoir engineering strategies. This include a proper evaluation of storage capacities, enhanced recovery plans and assessment of the quality and quantity of extracted fluids, to name but a few. Reservoir fluids systems are typically comprised of three broad fluid phases: oil, gas and water. In turn, depending on pressure and temperature conditions, a number of these phases can coexist simultaneously in the pore space of reservoir rocks, with the volume occupied by each depending on the nature

of the reservoir – petroleum or aquifer – and may vary as a result of injection/production operations.

In this communication, a theoretical sound approach has been used to describe simultaneously the bulk and interfacial properties of model reservoir fluids at relevant reservoir conditions. The examined approach combines the performance of a molecular-based equation of state, soft SAFT EoS [1], with the extended Density Gradient Theory of van der Waals for interfaces [2], both fully established on statistical mechanics concepts. The required input parameters were obtained from vapour-liquid saturation properties and surface tension data of pure substances, and subsequently transferred for the description of mixtures.

The adopted modelling approach has been successfully applied for the description of volumetric, phase composition and interfacial property data of various hydrocarbon and aqueous systems, and as function of pressure, temperature and composition. The systems examined here are relevant for a variety of applications, from water-alternating-gas injection schemes in the Oil & Gas industry to geological sequestration of CO<sub>2</sub>. In addition to interfacial tension, other interfacial properties such as density profiles, interface thickness and activity were also analysed. The good agreement observed between calculations and experimental data confirmed the capability of our modelling approach for describing both bulk and interfacial behaviour of reservoir fluids at relevant process conditions.

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## Oral Session 2: Theory and Modelling II

15:30 - 18:10 Monday HS BE01

Chairs: N. Milošhević, R. Kovács

## TM – O7 15:30 - 15:50 Monday

## Room HS BE01

## 2D MODEL AND INTEGRATIVE DATA REDUCTION PROCEDURE FOR LASER FLASH THERMAL DIFFUSIVITY MEASUREMENTS

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This paper presents a two-dimensional model of the laser flash experiment and an integrative computational procedure for the analysis and reduction of laser flash experimental data. The model implies the analytical solution of a 2D heat conduction problem with boundary and initial conditions that usually exist in reality, such as radiation heat transfer between disk shaped specimen surfaces and environment, non-uniform pulse heating and finite pulse duration. The solution obtained by the separation of variable technique is presented in a complete form together with relating transcendent equations for roots finding. The transient temperature of the rear specimen surface is special case of the solution and may be expressed as the response at a single point or at the entire specimen surface, which corresponds for temperature measurement by thermocouple or infrared detector, respectively.

The values of the model, computed by using the chosen a priori values of unknown quantities, such as thermal diffusivity and Biot number, enter the data reduction procedure together with related experimental data. The procedure is iterative and based on the nonlinear Gauss parameter estimation technique and the maximum a priori criterion. First derivatives of the model in respect to parameters for estimation are time dependent and create the matrix of sensitivity coefficients, while standard deviations of experimental data and uncertainties of a priori parameters generate the corresponding variance-covariance matrices. In this work, introduction of additional variance components representing the uncertainties and sensitivities of known or fixed parameters is proposed. Beside their contribution to the total uncertainty of final results, these additional components set the limits of reliable estimation which support, in return, a better design of each particular experiment.

Overall, presenting the solution of a 2D model having usual boundary and initial conditions and the advanced data reduction procedure which integrates the influence of uncertainties of both experimental values and known parameters, a new consistent tool for thermal diffusivity estimation from laser flash experiments is proposed.

## ANALYSIS OF LASER FLASH EXPERIMENTS: FINDING NON-FOURIER HEAT CONDUCTION AT ROOM TEMPERATURE

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The first experimental evidences of non-Fourier heat conduction are found in the middle of last century. The measured deviation was wave-like and occurred at low temperatures around 10 K. However, this is not the only observation indicating heat conduction beyond Fourier equation.

The theory of non-equilibrium thermodynamics predicts deviation from classical law at room temperature and on macroscale as well. According to the famous experiment of Mitra et al. [1], the appropriate extension of Fourier equation is in the form of Maxwell-Cattaneo-Vernotte (MCV) equation. However, no one was able to reproduce their results and the feasibility of MCV equation at room temperature become questionable.

Recently, we have started an experimental project where we assumed that additional dissipation mechanisms may suppress the wave-like characteristics of the propagation at room temperature; therefore, the quantitative analysis of the experiments is unavoidable [2]. The next correction term leads to the Guyer-Krumhansl equation. The derived corrections are universal because the derivation is based on the general principles of non-equilibrium thermodynamics [3]. This extension is used to evaluate the experiments accomplished at the Department of Energy Engineering, BME.

Now we can identify several natural and artificial heterogeneous materials where non-Fourier effects are observed [4]. Our experimental method is similar to the heat pulse experiments at low temperatures and to the laser flash experiments of engineering practice. A short heat pulse is applied at one end of the sample and the time dependency of temperature is measured at the other end. In the presentation, we summarize the technical details of the experiments as well as the theoretical aspects leading to the observation.

## References

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## TM – O9 16:10 - 16:30 Monday

## INTERMOLECULAR POTENTIAL ENERGY SURFACE AND THERMOPHYSICAL PROPERTIES OF THE $(CO_2 + N_2)$ SYSTEM

J. C. Castro-Palacio<sup>1</sup>, J.-P. Crusius<sup>1</sup>, R. Hellmann<sup>2</sup>, V. Vesovic<sup>1</sup>

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A new  $CO_2 - N_2$  intermolecular potential energy surface has been developed based on highly accurate quantum-chemical *ab initio* computations of pair interaction energies. An analytical representation of the pair potential has been used to determine the  $CO_2 - N_2$  cross second virial coefficient and values for the traditional transport properties in the dilute gas limit for the ( $CO_2 + N_2$ ) system at temperatures up to 2000 K.

The cross second virial coefficient was calculated using the Mayer-sampling Monte Carlo method of Singh and Kofke [1]. Quantum effects were accounted for by using an effective pair potential following the approach of Feynman and Hibbs [2].

Values for the thermal conductivity, shear viscosity and the product of density and selfdiffusion coefficient in the zero-density limit have been calculated with the TRAJECT program [3] utilising the new pair potential in conjunction with previously published pair potentials for the two pure substances [4, 5].

We present the potential energy surface and a comparison of our results for the calculated values of the thermophysical properties with the best available data from the literature.

### References

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## TM – O10 16:30 - 16:50 Monday

### Room HS BE01

## SHEAR VISCOSITY OF n-ALKANES IN THE ZERO-DENSITY REGION

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The shear viscosity of *n*-alkanes in the zero-density limit has been calculated by the classicaltrajectory method that has been successfully used to predict the viscosity of real dilute gases [1]. The *n*-alkane molecules were modelled as rigid linear chains consisting of  $n_c$ -1 spherical

segments ( $n_c$  being the number of carbon atoms) that interact through a combination of site-site Mie n-6 potentials (n = 9-14). The moment of inertia of each n-alkane was used to determine the site-site separation. The work builds on the specific case of the 12-6 (Lennard-Jones, LJ) site-site potential [2], where it was demonstrated [3] that it is not possible to find a unique pair of LJ parameters,  $\epsilon$  and  $\sigma$ , to reproduce the measured viscosity values of all *n*-alkanes. However, based on the best fit values of  $\epsilon$  and  $\sigma$ , for C<sub>3</sub>H<sub>8</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>6</sub>H<sub>14</sub> and *n*-C<sub>7</sub>H<sub>16</sub>, it has been shown that the ratio  $\sqrt{\epsilon}/\sigma^2$  is a linear function of  $n_c$ . Hence, a model was developed that predicts the viscosity values to within  $\pm 5$  %, of experimental ones, for *n*-alkanes from  $C_3H_8$  to  $n-C_9H_{20}$  and within  $\pm 5-10$  % for longer *n*-alkanes. Here we present new results that allow for a greater flexibility in the steepness of the repulsive wall by employing the Mie site-site potential. Based on the best scaling parameters (n,  $\sigma$  and  $\epsilon$ ) obtained by fitting to the experimental viscosity of C<sub>3</sub>H<sub>8</sub>, *n*-C<sub>4</sub>H<sub>10</sub>, *n*-C<sub>6</sub>H<sub>14</sub> and *n*-C<sub>7</sub>H<sub>16</sub>, a new model was developed that predicts shear viscosities of long *n*-alkanes to within  $\pm 5$  %. We also discuss a limiting case of the site-site potential, namely the representation by an effective spherical LJ 12-6 potential [4]. This correlative approach, which makes use of a semi-empirical relationship for the LJ parameter  $\sigma$ , yields viscosities to within  $\pm 2-3$  % of experimental ones.

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## TM – O11 16:50 - 17:10 Monday

## Room HS BE01

## A NEW MODEL FOR THE ESTIMATION OF MULTICOMPONENT INTERFACIAL TENSION AND DENSITY PROFILES

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Interfacial properties, such as surface or interfacial tension, have recently acquired a renewed interest, particularly for multicomponent mixtures, as they are relevant for a wide variety of applications: from oil and gas production to emulsions and detergents. The density profiles of the species across coexisting phases may show preferential accumulation (adsorption), and this is directly related to the interfacial profiles and tension. Among other approaches, the gradient theory is perhaps one of the most widely accepted approaches, provided the interface density profiles, as well as the influence parameters, are known or can be estimated in a robust manner. From a calculation perspective, it is in the estimation of the density profiles where the application of the method may run into several obstacles that are not always easy to overcome,

such as numerical convergence problems.

In a recent related work, we have already proposed an alternative theory for the calculation of multicomponent interfacial profiles. This has resulted in a procedure that independently solves the interfacial density profiles of the species in a robust and efficient way. We are now turning our attention to the development of robust models for the actual calculation of the interfacial tension in any general multicomponent fluid system.

Having the problem of the interfacial density profile already solved for multicomponent systems, in this work we extend our previous work on the correlation of surface tensions of pure fluids (J. Phys. Chem. B 2009, **113**, 3504-3511) to multicomponent systems. The ideas that are explore in this work are further illustrated and verified from Molecular Simulation results.

## TM – O12 17:10 - 17:30 Monday

Room HS BE01

## THERMAL MANAGEMENT OF MULTILAYERED SYSTEMS THROUGH MATERIALS INFORMATICS: FROM BULK TO NANO-SCALE

Yen-Ju Wu, Yibin Xu, Tianzhuo Zhan, Lei Fang

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The interface thermal resistance, which is hard to directly measure, needs extra thermal properties of the materials during the measurement, such as time-domain thermos-reflectance (TDTR) and frequency-domain thermos-reflectance (FDTR). Those parameters and function modulation usually have restrictions for some samples, therefore, enhance the inaccuracy and analysis time. The development of mathematical algorithms associating with experimental and simulation results allows efficient materials systems design. The data collection for data base, the descriptors, and data platform design have close impact on the machine learning for interface thermal resistance prediction.

In this work, there are two main parts (a) layered systems from bulk to nano-scale, and (b) descriptors selection. The bulk and thin film materials have large different thermal properties, especially for thermal conductivity. Some parameters depend on the thickness and temperature. Therefore, the data collection of both thin film and bulk information was input to the data platform systematically. For the descriptors selection, we found that more descriptors don't lead to better prediction by various models, such as support vector machine (SVM), generalized linear regression (GLR) and Lasso. No matter selecting the descriptors manually or automatically, the physics hidden behind the models and each descriptor reveal the correlation among the original data set and prediction can be extracted.

By means of excluding the crystal structure-related parameters, the amorphous materials can also be predicted. Besides, we also find some interesting results of heat flux direction dependence of bi-layer systems, which can bring the data to new knowledge. The combination of machine learning prediction and thermal resistance measurement embark a new way for thermal management. Once the prediction model is constructed, it can accelerate further design and development. And, the more detail will be discussed in the talk.

### TM – O13 17:30 - 17:50 Monday

## THERMAL CONDUCTIVITY OF CROSS-LINKED POLYETHYLENE FROM MOLECULAR DYNAMICS SIMULATION

Ming Yang<sup>1</sup>, Xue Xiong<sup>1</sup>, Changlin Liu<sup>2</sup>, Xiaobo Li<sup>2</sup> and Dawei Tang<sup>3</sup>

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Thermal conductivity of polymers has been studied for several decades. It is well known that polymers usually have low thermal conductivity in the range of  $0.1 \sim 0.4 \text{ W m}^{-1} \text{ K}^{-1}$ . It has shown that the thermal conductivity of polymers can be significantly enhanced through the alignment of the polymer chains. Most previous studies are on non-crosslinked polymers, however, a large portion of polymers are cross-linked ones, for example rubbers and thermosetting resins. The thermal application of cross-linked polymer is rather wide, from hot water pipes to underfills for electronic packaging, and to silicone lenses of the light emitting diodes (LEDs). In this talk, we report the study on the thermal conductivity of cross-linked bulk polyethylene using molecular dynamics (MD) simulation. The atomic structure of the cross-linked polyethylene (PEX) is generated through simulated bond formation using LAMMPS. The thermal conductivity of PEX is studied with different degree of crosslinking, chain length and tensile strain. Generally, the thermal conductivity increases with increasing degree of crosslinking. When the length of primitive chain increases, the thermal conductivity increases linearly. When the polymer is stretched along one direction, the thermal conductivity increases in the stretched direction and decreases in the direction perpendicular to it. However, the thermal conductivity varies slightly when the polymer is stretched in three directions simultaneously.

### TM – O14 17:50 - 18:10 Monday

### Room HS BE01

## A DATA APPROACH TO PREDIC INTERFACIAL THERMAL RESISITANCE OF MATERIALS

Yibin Xu, Tianzhuo Zhan, Lei Fang, Yen-Ju Wu

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Interfacial thermal resistance (ITR) is a key property for the thermal management of high power micro- and opto-electronic devices and for the development of high efficiency thermal barrier coatings and thermoelectric materials. Prediction of ITR is important for guiding the discovery of interfaces with very low or very high ITR. Several physical methods have been used for predicting ITR. The most common methods are the acoustic mismatch method (AMM) and diffusion mismatch method (DMM). The input parameters of AMM and DMM to calculate ITR are temperature, density, speed of sound (longitudinal and transverse) and unit cell volume.

In this presentation, we report the prediction of ITR by machine learning method. We established an experimental database of ITR, which including 876 ITR values measured on 368 interfaces as a function of temperature and other conditions. The 368 interfaces are composed by combination of 45 different materials. The experimental data of ITR are collected from 64 published papers. The collection of descriptors used to determine ITR includes measuring temperature, film thickness, specific heat, thermal conductivity, Debye temperature, melting point, density, speed of sound (longitudinal and transverse), elastic modulus, bulk modulus, thermal expansion coefficient and unit cell volume. The machine learning algorithms used in this work are generalized linear regression (GLR), LASSO of GLR, Gaussian process regression (GPR), and support vector regression (SVR).

We found that the machine learning models have much better predictive accuracy than AMM and DMM. Among the used machine learning algorithms, the Gaussian process regression model has the best predictive accuracy. Also, by comparing the prediction results using different descriptor set, we found that besides the physical properties of the component materials, the film thickness is an important descriptor in the prediction of ITR. These results show that machine learning methods have great potential in prediction of ITR, mechanism study of ITR by descriptor selection, and control of ITR by interface design.

## Acknowledgement

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## Instrumentation and Measuring Techniques (IMT)

**Oral Session 3: Instrumentation and Measuring Techniques I** 

10:20 - 13:00 Tuesday HS BE01

Chairs: H.-P. Ebert, G. Lohöfer

## IMT – O1 10:20 - 10:40 Tuesday

Room HS BE01

## A NEW DISPLACEMENT TRANSDUCER FOR PUSHROD DILATOMETERS

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Exact analysis of thermal induced dimensional changes is important in modern material research, e.g., analysis in the field of zero-expansion materials, ceramics, foams, sandwich materials and polymers. Pushrod dilatometry is a well-established and standardized method for the measurement of properties such as the thermal expansion, shrinkage during sintering and determination of coefficient of thermal expansion (CTE) of a wide range of solid and liquid materials. For decades, pushrod dilatometers have used LVDT systems (linear variable displacement transducers) for the detection of the length change of a sample and converting this into an electronic signal. Those systems are reliable and robust, feature a nm-resolution and a measurement range of several mm. The disadvantage was that they could not be used for the determination of the initial sample length under all possible conditions and that they are not fully linear. Presented in this work is a new detector system for dilatometers. A schematic design of the new system is shown in figure 1.



Figure 1. Schematic design of the new transducer system.

The newly developed system works with a modified interferometer for measurement of the length change. In combination with a force sensor and an active movement of the pushrod, the new system allows for constant pushrod forces, similar resolutions as LVDTs, a broader measurement range of up to 52 mm and improved linearity. The system cannot only measure initial sample length with a high resolution but also overcomes major issues related to pushrod dilatometry over the last decades. The active force control enables measurement on soft materials as well as detection of force impacts on, for example, sintering of a ceramic raw material.

## IMT - O2 10:40 - 11:00 Tuesday

## Room HS BE01

## DE-SMEARING OF DSC SIGNALS USING A DATA-DRIVEN EXTRAPOLATION APPROACH

Andreas Sommer<sup>1</sup>, Tilman Barz<sup>2</sup>, Wolfgang Hohenauer<sup>2</sup>

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In a heat-flux DSC, the most common operating mode is to increase the furnace temperature with a constant rate, heating both a usually empty reference crucible and a crucible with the sample to be measured. The (empty) reference crucible heats faster, resulting in a temperature difference that is detected by thermocouples. According to standard calibration and standard test procedures (DIN EN ISO 11357), the measured voltage is transformed into a heat flux into the sample. Further processing of this signal gives the (apparent) specific heat of the sample as a function of temperature.

Repeated measurements with increasing heating rates and/or sample masses give considerably different results. Sample-internal temperature gradients and the absorbed heat increase. As a consequence, the recorded melting peaks are shifted to higher temperatures; this effect is known as smearing. Whereas smearing is rarely observed in pure materials, it is a serious problem for phase change materials (PCM), as the target information is the shape of the measured signals (shape of the apparent specific heat) [1]. Low heating rates close to zero would deliver the most informative output, but result in a poor signal-to-noise ratio; further, they are also very time consuming. On the other hand, elevated heating rates deliver strong but smeared signals due to the thermal conductive properties of the sample.

This contribution analyses a potential PCM, namely the commercial grade polyethylene RIGIDEX HD 6070. As expected, heat-flux DSC signals (rates of 0.3 to 20 K/min, masses of 4.08, 6.46, 10.47 mg) are strongly affected by smearing, with moving and broadening peak signals for higher heating rates. The visual similarity with the evolution of a probability density under drift and diffusion catches the eye. Such a density evolution can be described using the Fokker-Planck equations (FPE).

We present a data-driven extrapolation to a (hypothetical) zero-temperature-rate signal as desmearing technique: The zero-temperature-rate signal is described by (1) a low-dimensional transformation (scaling and deformation) of measurement data and/or (2) by a suitable low-dimensional superposition of linear, trigonometric, or other basic functions. Its parameters, together with the drift and diffusion parameters (assumed constant) of the FPE, are fitted against the DSC measurement data. For the studied PCM, the proposed de-smearing algorithm yields narrow peak signals and since the FPE maintains the integral, the heat of fusion is also maintained.

## References

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## IMT – O3 11:00 - 11:20 Tuesday

Room HS BE01

## CALORIMETRIC MEASUREMENTS ON PCM - EXISTING STANDARDS AND ACHIEVED IMPROVEMENTS

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Phase Change Materials (PCM) have received considerable attention in the past two decades because of their potential for thermal energy storage. Their phase change, in most cases between solid and liquid phase, shows a comparatively high storage density in a narrow temperature range, which is advantageous in many applications. For example, the phase change of water, the most widely used PCM, between solid and liquid at 0 °C requires about 330 kJ per kilogram, which is about the same as is necessary to heat water by 80 °C. While water changes phase at a well-defined temperature, many other materials used as PCM

change phase in a temperature range, for example alcane mixtures and many salt-hydrates. Application of PCM for temperature stabilization in transport boxes as well as for special clothes is today widely commercialized. For applications in buildings, e.g. in plasterboards and cooling ceilings, commercial products are available, but not yet widely applied.

When PCM are applied in a small temperature range, knowledge of their ability to store heat as a function of temperature is of prime importance, especially because the temperature also enters the heat flow. Therefore, calorimetric measurements have to be performed in a way to give high accuracy in the temperature. Compared to other materials, PCM however pose specific problems. A sample in a measurement has to be isothermal to assign the measured heat flow to the measured temperature. In a sample with phase change it takes however much longer until an isothermal state is reached, and measurements are often done too fast. Another problem special to PCM is that upon cooling from the liquid to the solid state the phase change can be delayed until a temperature significantly below the phase change temperature is reached; this effect, called subcooling or supercooling, can depend on the sample size used in the calorimetric measurement. Calorimetric measurements on PCM to achieve the needed accuracy are therefore significantly different compared to other materials.

In the past decade, considerable work has been done to improve calorimetric measurements on PCM, and the developed procedures have been standardized. Currently, two standards exist. The first standard is a standard developed by the ZAE Bayern and the FhG-ISE for the "RAL-Gütegemeinschaft PCM e.V.", for quality control by experienced institutes using a wide range of calorimetric methods. The second standard, which is based on the first one, is a standard developed by a group of institutes within the IEA, specifically for R&D users of DSC in dynamic mode.

The paper discusses the needed accuracy, the procedures defined in the standards, and achieved improvements. At the core of the procedures are ways to assure that the sample within a measurement is close enough to an isothermal state. While results in a prior ring test deviated by up to several °C, results in recent ring tests following the standards show deviations well below 1 °C, using completely different methods like DSC, T-history, 3-layer calorimetry, with sample sizes differing by many orders of magnitude.

The existing standards therefore lead to significant improvements in calorimetric measurements.

## IMT – O4 11:20 - 11:40 Tuesday

### Room HS BE01

## CALORIFIC VALUES OF BIOMETHANE MEASURED BY GAS CALORIMETRY

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Within the European Metrology Research Programme (EMRP) a three-year project was started to support the use of green gas. This EMRP Metrology for Biogas project aims to specify chemical and physical properties of biogas and biomethane, especially the development and validation of traceable methods for determining key impurities, moisture, particulates, calorific value, and density. PTB, as part of the European Consortium working on this EMRP project, would like to introduce its results of calorific-value measurements with reference-gas calorimetry.

A Rossini-type calorimeter [1-3] is operated at PTB in order to perform high-accuracy measurements of the superior calorific value (SCV) of natural gas components and gas mixtures. The Rossini-type calorimeter is an isoperibol gas calorimeter with a stirred water bath where approximately 1 g of gas is burnt in an open flame and a temperature rise of approximately 3 K is recorded. The calorimeter is calibrated with an electrical heater and the adiabatic temperature rise represents the total amount of energy produced by combustion or during calibration. The SCV is the ratio of the energy released by the combustion and the gravimetrically determined mass of the burnt gas.

SCV measurements of biomethane are a step further of SCV investigations of combustible pure gases. The main components of the biomethane samples are methane, oxygen, nitrogen and carbon dioxide. These gas samples are already refined raw biogas where the moisture content is removed and the methane mole fraction is more than 90 %. The challenge of SCV measurements is the establishment of proper conditions for an almost complete combustion and the determination of the amount of unburned gas. The first time traceable measurements of SCV on gas compositions with reference gas calorimetry are reported and compared with the results of state-of-the-art gas chromatography analysis.

## Acknowledgments

This work is part of the EMPRP ENG54 Biogas "Metrology for biogas". The EMRP is jointly funded by the EMRP participating countries within EURAMET and the European Union.

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## IMT – O5 11:40 - 12:00 Tuesday

## Room HS BE01

## EFFECTIVE THERMAL CONDUCTIVITY MEASUREMENTS OF PACKED BEDS FOR THERMOCHEMICAL ENERGY STORAGE

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The effective thermal conductivity  $\lambda_{\rm eff}$  of mainly powdery packed beds of thermochemical materials has an important implication on the performance of a thermochemical energy system (TCES). Several commercial available transient and steady-state measurement methods enable to measure the effective thermal diffusivity  $\alpha_{\rm eff}$  and  $\lambda_{\rm eff}$  of packed beds. The intention of this work is to compare the applicability of different transient methods and to analyse their assets and drawbacks.

Yttria-stabilized zirconia (YTZ) as spherical shaped powder ( $\emptyset = 50$ , 100 and 200  $\mu$ m) as well as solid cylinder ( $\emptyset = 12.7 \text{ mm}$ ,  $\rho = 5.92 \text{ g} \cdot \text{cm}^{-3}$ ) was chosen as reference material for the following experiments. To calculate  $\lambda$  of the solid YTZ, specific heat capacity  $c_p(T)$  was evaluated by differential scanning calorimetry (DSC) and a(T) by laser flash analysis (LFA). To analyse  $\alpha_{\text{eff}(T)}$  and  $\lambda_{\text{eff}}(T)$  of the different powder sizes, package densities and gas conditions, several LFA and transient hot bridge (THB) experiments were conducted.

Specific heat capacity  $c_p(T)$  of YTZ was compared to literature data for  $\operatorname{ZrO}_2$  from the NIST-JANAF thermochemical tables [1] and shows slightly lower values with  $c_p = 442 \,\mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$  and a combined uncertainty of  $u_c = 15 \,\mathrm{J} \cdot \mathrm{kg}^{-1} \cdot \mathrm{K}^{-1}$  at  $T = 25 \,^{\circ}\mathrm{C}$  and  $p = 101.3 \,\mathrm{kPa}$  (SATP). Indirect thermal conductivity evaluation of the YTZ solid based on  $\lambda = a \cdot \rho \cdot c_p$  resulted in  $\lambda = 2.91 \,\mathrm{W} \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1}$  with  $u_c = 0.16 \,\mathrm{W} \cdot \mathrm{m}^{-1} \cdot \mathrm{K}^{-1}$  at SATP. For the 50  $\mu\mathrm{m}$  powder with a bulk density of  $\rho_{\mathrm{B}} = 4.367 \,\mathrm{g} \cdot \mathrm{cm}^{-3}$ , the LFA measurement indicated  $\alpha_{\mathrm{eff}} = 0.147 \,\mathrm{mm}^2 \cdot \mathrm{s}^{-1}$  under vacuum conditions and  $\alpha_{\mathrm{eff}} = 0.493 \,\mathrm{mm}^2 \cdot \mathrm{s}^{-1}$  under helium atmosphere. LFA sample preparation in a special 3-layer sample holder system setup led to higher bulk densities and higher  $\lambda_{\mathrm{eff}}$  compared to the THB measurements.

At this point of the work the cause for the differences of  $\lambda_{\text{eff}}$  between LFA and THB experiments are not fully understood and further investigations are planned. Steady-state heat flow meter (HFM) experiments should give further indications as complementary method. Additional a finite element model of the 3-layer LFA sample holder should identify the influences of the sample holder on the measured LFA detector signal.

## References

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## IMT – O6 12:00 - 12:20 Tuesday

Room HS BE01

## DETERMINATION OF THE THERMAL CONDUCTIVITY OF NANOFLUIDS WITH A RING GAP APPARATUS

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The physically correct determination of the thermal conductivity is a key of qualifying thermal properties of materials. We have developed a static ring gap apparatus (RGA) for measuring thermal conductivities of fluids, such as oils and their mixtures [1], gases [2] and nanofluids [3, 4]. In this work, we study and develop our RGA further. RGA measurements belong to the steady-state methods for determining. thermal conductivity of liquids and gases. The physical principle is equal to coaxial-cylinder cell apparatuses, as described in textbooks. Nevertheless, we have had good measurement results with our RGA, steady-state methods have some basic problems, which we wanted to reduce by developing a new RGA device. Silver was chosen as the sample holder material in order to increase the temperature conductivity as well as to minimize the corrosion problems. Furthermore, the measurement error of the device was

decreased by changing some of the measurement instruments. As next step the amount of distance pieces, which centre the inner cylinder, were reduced to a minimum. Therefore, the area of thermal transfer of such pieces is reduced.

The measured conductivity values were corrected with new literature values and a round robin test was used with intent to improve the correctness of the method. With the new RGA, we can determine over 0.5 % enhancements in nanofluids in a reliable manner.

In this work, measurement principle as well as the design of the measuring cell will be shown briefly, and all the development steps of the new RGA apparatus will be discussed [1-4]. According to an appropriate error analysis based on the Gaussian law of propagation of uncertainties, the measured thermal conductivity values had a relative error < 0.2 % in the case of water based nanofluids. For comparison of two of those fluids, the uncertainty is 0.4 %, because of the relative measurement method. For absolute values the uncertainty of the literature values is to be added, resulting in an overall uncertainty of 1 %. The calibration of the measuring device will be described to measure nanofluids and the best calibration extrapolation will be discussed. First measurements of thermal conductivity of water based nanofluids with diamond, silver or gold nanoparticles will be presented and compared with the literature data and theory.

## Acknowledgements

We thank Josephine Rank and Alexander von Wedelstedt, students of University of Applied Sciences Dresden, for supporting us with the experiments. Research was carried out under grants MF 120019 and NanoUptake COST Action CA15119.

### References

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## IMT – O7 12:20 - 12:40 Tuesday

## Room HS BE01

## THERMAL CONDUCTIVITY MEASUREMENT OF A DROP OF LIQUID SAMPLE USING A MICRO-BEAM SENSOR

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A device was developed for measuring thermal conductivity of small liquid sample using a micro-beam sensor. The sensor is a free-standing platinum strip suspended across a trench on a substrate. Heating the sensor in a sample liquid by DC, the temperature of the sensor was measured from the electrical resistance. The principle of the measurement is based on the fact that the temperature rise of the sensor depends on the thermal conductivity of surrounding liquid. The advantage of the method includes: 1) the system has a steady state because the substrate at both ends of the sensor remains at a constant temperature irrespective of heating, 2) the steady state is reached within several hundred microseconds because the sensor is only  $\sim 10 \,\mu\text{m}$  long, 3) the temperature of the sensor does not change after an initial rise by heating because the effect of free convection is negligible, 4) the sensor is useful for measuring small samples. Comparing the measured temperature rise with the result obtained by numerical analysis of steady-state heat conduction, we can determine the thermal conductivity of the sample liquid.

To demonstrate the advantage of the method, we developed a device that consists of a microbeam MEMS sensor placed in a micro chamber, and measured four kinds of liquid, *i.e.* FC-72, toluene, ethanol and methanol. The fabricated sensor was  $9.5 \,\mu m \log_7 73 \,\mu m$  wide and 40 nm in thickness. The electrical and thermal properties were first determined as a function of temperature by a calibration experiment in a vacuum chamber and also two-dimensional electrical/thermal analyses. Then measurement was done at atmospheric pressure and temperature. A sample of ~  $30 \,\mu L$  was injected into the chamber with a micropipette. The measured thermal conductivity agreed with literature values within 5 % error. The measurement was also demonstrated for an expensive medical agent lipiodol. Lipiodol, also known as ethiodized oil, is a radio-opaque contrast agent that is used for radiological investigation, and considered as a candidate for an injectable adjuvant for lung cryosurgery. The measured thermal conductivity was  $0.127 \,W/(m \cdot K)$ .

## IMT – O8 12:40 - 13:00 Tuesday

### Room HS BE01

## SIMULTANEOUS MEASUREMENT METHOD FOR THERMOELECTRIC PROPERTIES WITH FILM-TYPE SENSOR

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Thermoelectric power generation is attracting attention as an unutilized thermal energy. New thermoelectric materials with high figure-of-merit are being researched actively. As a performance evaluation method for thermoelectric materials, it is necessary to measure thermoelectric properties such as the Seebeck coefficient, electrical resistivity, and thermal conductivity. Generally, the Seebeck coefficient is measured by using the steady-state condition. Electrical resistivity is measured by the four-terminal sensing. Thermal conductivity is measured by the laser flash method. However, since the current does not coincide with the heat flow direction by using these methods, they lead to erroneous performance evaluation. Therefore, a highly accurate evaluation method of the performance of thermoelectric materials has become necessary.

In this study, a simultaneous measurement method for the measurement of the three thermoelectric properties with a film-type sensor has been proposed. The Seebeck coefficient is measured by using the steady-state condition. Electrical resistivity is measured using the fourprobe method. Thermal diffusivity is measured using the periodic heating method. In this presentation, a new thin film sensor which can measure three thermoelectric properties is fabricated. The measurement system is assembled. The efficacy of this method was verified with a constant as a reference material. Then, the measurement of three thermoelectric properties of  $Bi_{0.3}Sb_{1.7}Te_3$  was performed. The temperature dependence of thermoelectric properties of this material was also discussed.

## **Oral Session 4: Instrumentation and Measuring Techniques II**

15:30 - 18:10 Tuesday HS BE01

Chairs: C. Gaiser, C. Glorieux

## IMT – O9 15:30 - 15:50 Tuesday

### Room HS BE01

## THE T-HISTORY METHOD FOR THE DETERMINATION OF THE ENTHALPY OF PHASE CHANGE MATERIALS - AN ANALYSIS

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The T-history method has established itself as one of the methods of choice for the determination of the enthalpy of phase change materials (PCMs) due mainly to its simple setup, an accessible analytical model and especially the ability to measure larger specimens. A measurement is done by calibrating a fixed thermal resistance using a material with known thermal properties and then using an identical thermal resistance to measure the heat flux into or out of a sample. The used evaluation model is based on two assumptions. The lumped capacitance model, which says that the sample and reference are always isothermal, and, in case an insulation is used around the reference and the sample, the assumption of it having no thermal mass. As neither a commercial instrument nor a standard is available for this method, different implementations have found their way into the labs with and without an extra insulation around sample and reference, using various geometries and slightly differing evaluation methods.

The T-History method is examined to better understand the influence of different setups and boundary conditions on its results. Sources of uncertainties are identified and their impact on the final overall uncertainty for the determined enthalpy and temperature is assessed.

All parameters affecting the calibration process and the measurement of the enthalpy as well as their influence on the final uncertainty are examined, these being, the thermal conductivity of reference and sample, the thermal mass of the insulation (if used) and the identity of the thermal resistances around reference and sample. Furthermore, the results show how the temperature gradient in the sample during measurement results in a hysteresis in the measured enthalpy over temperature curves.

#### IMT – O10 15:50 - 16:10 Tuesday

### DEVELOPMENT OF A NEW THERMOGRAVIMETRIC APPARATUS TO MEASURE LOW VAPOUR PRESSURES

**Room HS BE01** 

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The vapour pressure of a pure substance only depends on the temperature. Depending on the substance and the temperature the vapour pressure varies between some mPa for substances like benzoic acid and anthracene and some hPa for substances like different alcohols. The best measurement method to be chosen depends on the vapour pressure range. The OECD guidelines for the testing of chemicals describe eight different methods to measure the vapour pressure. The aim of this research is to develop a modular measuring system to measure vapour pressure over a wide range of pressure. Each module uses another method. The main component of the system is a Magnetic Suspension Balance (MSB) constructed by Rubotherm GmbH. In the present work the first module to measure low vapour pressures < 1 Pa based on the knudsen effusion technique in a temperature range from 0 °C to 150 °C is presented.

A schematic drawing of the developed measuring system is shown in figure 1. The sample is located in the knudsen-cell at the bottom of the MSB. Here, the vapour phase in the cell is close to thermodynamic equilibrium with its condensed phase. The vapour of the substance effuses through a small orifice in the lid of the knudsen-cell into a high vacuum. The calculation of the vapour pressure is based on the effused mass, the area of the orifice and the velocity of the molecules. All effused molecules condense on a cooled condensation plate which is attached to the microbalance. The mass increase of this plate is recorded. One of the particular features of the new system is the cooling of the condensation plate with liquid nitrogen, which prevents the re-evaporation of the condensed molecules. Together with the MSB precise vapour pressure measurements, especially long-term measurements, can be performed.



Figure 1. Schematic drawing of the apparatus.

## IMT – O11 16:10 - 16:30 Tuesday

### NOVEL TORSIONAL CRYSTAL VISCOMETER FOR LIQUIDS AT HIGH PRESSURES

Room HS BE01

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A torsional quartz crystal viscometer has been developed for absolute measurements of liquids. The instrument covers the temperature range from 200 K to 420 K with pressures up to 100 MPa. The viscosity sensor consists of a piezoelectric quartz cylinder with a diameter of 3 mm and a length of 50 mm, which is surrounded by four electrodes in a quadrupole arrangement. The crystal is excited to vibrate torsionally by an alternating electric field generated by the electrodes. When surrounded by a measuring fluid the vibration of the crystal is more strongly damped than in vacuum, resulting in a reduction of the resonance frequency and increase of the bandwidth of the vibration. This effect is used to determine the viscosity x density product of the measuring fluid. When the density of the fluid is known, the viscosity can easily be obtained.

One aim of this project is to reduce the measurement uncertainty of the torsional crystal technique from currently approximately 2 % to well below 1 %. This will be achieved by a well-founded analysis of the electrical field in the viscosity sensor and the mechanical vibration of the anisotropic quartz crystal. In a first step, the electric field in the sensor was analysed in much greater detail than in previous studies. This analysis yielded previously unknown results, which lead to a novel sensor design. With the novel sensor, the bandwidth of the vibration in vacuum could be reduced by about 20 % compared to previous torsional crystal sensors described in the literature. Furthermore, the mechanical vibration of the quartz crystal was analysed within the St. Venant theory of torsion. Due to the anisotropic and symmetric properties of quartz, the torsional motion is accompanied by warping of the end surfaces of the cylinder. These results are used to quantify the parasitic energy dissipation due to sound waves emitted by the end surfaces.

The viscosity sensor is mounted in a pressure vessel, which is thermostatted in a circulating liquid bath thermostat. The temperature in the pressure vessel is kept constant within 1 mK and measured with a 25 Ohm SPRT calibrated on ITS-90 and a high-precision bridge system with an uncertainty of 3 mK. The pressure is measured with an uncertainty of 0.01 MPa. The resonance frequency and bandwidth of the vibration of the crystal are determined in the frequency domain from the conductance and susceptance curves of the sensor in the vicinity of the resonance measured by an impedance analyser. First results of validation measurements with several fluids, for which the viscosity is well known, and a detailed uncertainty analysis will be presented.

## IMT – O12 16:30 - 16:50 Tuesday

## MEASUREMENT OF THERMAL CONDUCTIVITY OF LIQUIDS BY HOT WIRE METHOD: COMPARISON BETWEEN TRANSIENT AND STATIONARY APPROACHES

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The most commonly used method for measuring the thermal conductivity of liquids is the hot wire method. This relies on the heating of a very fine metallic wire, immersed in the liquid that has to be characterized, by means of an electric current. The variation of the temperature of the wire depends on the exchanges with the liquid, and therefore on the thermal conductivity of the liquid and the contact resistance. The electrical power supplied to the heating wire must be constant and low enough in order to maintain a rise in temperature of no more than a few degrees, which minimizes convective exchanges in the liquid. The temperature of the wire can be measured either by means of a thermocouple welded to the wire or by measuring the electrical resistance of the wire during its heating. The conductivity of the liquid can be determined in two ways: transient or steady state.

For a characterization in a transient mode, a modeling of the heat exchange considering a cylindrical geometry and a transfer in semi-infinite medium makes it possible to have an equation of variation of the temperature of the wire over time from which it is possible to estimate the thermal conductivity of the liquid by identification. This approach allows a characterization with a short measurement time.

On the other hand, ASTM D2717 proposes a steady-state characterization. The measurement must be continued until a stable temperature is reached. The increase in temperature obtained then allows the calculation of the thermal conductivity. The measurement time is more important here than by transient method. The calculation of the thermal conductivity is simplified, but it is nevertheless necessary in this second approach to characterize the measurement cell with the aid of reference liquids whose thermal conductivity is supposed to be known.

A glass measuring cell with a 50  $\mu$ m diameter platinum wire was developed as part of this work. The measurement of the temperature of the wire is made by measuring its electrical resistance over time by a 4-wire method which makes it possible to overcome the electrical resistance of the contacts. The device permits characterization in transient or steady state. In this article, we propose a comparison between these two approaches on the basis of the study of different liquids. A comparative study of measurement uncertainties is also submitted.

## IMT – O13 16:50 - 17:10 Tuesday

## INVESTIGATION OF MICROEMULSIONS BASED ON SUPERCRITICAL CO $_2$ BY DYNAMIC LIGHT SCATTERING

Room HS BE01

M. S. G. Knoll<sup>1</sup>, S. P. Cadogan<sup>1</sup>, C. J. Hahn<sup>2</sup>, M. H. Rausch<sup>1</sup>, and A. P. Fröba<sup>1</sup>

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In the Principle of Supercritical Microemulsion Expansion (POSME) process, the formation of a microemulsion where micelles swollen with supercritical carbon dioxide ( $scCO_2$ ) reside in a hydrophilic solvent is the basis for the production of solid foams with excellent thermal insulation properties. The size of the  $scCO_2$ -swollen micelles in the microemulsion stage is one of the key governing parameters of the final size distribution of the pores and, thus, of the insulation properties of the produced foam. For the optimization of the foam production process, an inexpensive yet reliable technique for the determination of the size and size distribution of the droplets of  $scCO_2$  in the microemulsion is required.

In this contribution, it is shown that dynamic light scattering (DLS) is a suitable method for this task. DLS is commonly used for the characterization of the size of dispersed bodies in microemulsions and colloidal systems by applying a homodyne detection scheme. However, an accurate implementation of the technique is necessary when its application range is expanded to new systems or conditions. If, for example, it cannot be proven that the impact of spurious light superimposing the analyzed scattered light is negligible - which has to be ensured to realize a purely homodyne detection scheme - the obtained size information can be incorrect by up to a factor of 2. Another concern is whether or not the obtained DLS signals attributed to the diffusion of, e.g., swollen micelles truly represent a hydrodynamic mode. Such issues have been thoroughly and successfully addressed in our study for scCO<sub>2</sub>-swollen micelles formed in a multicomponent polyether polyol-based microemulsion with nonionic surfactant for temperatures up to 338 K and pressures up to 10 MPa. The results in terms of the relaxation times of microscopic fluctuations associated with translational diffusion of swollen micelles in the continuous liquid phase were found to decrease with increasing temperature. This may be primarily attributed to the effect of decreasing viscosity of the continuous phase, but can also be associated with changing size of the micelles.

For the evaluation of the hydrodynamic diameters and respective size distributions of swollen micelles in the microemulsions from DLS results via the Stokes-Einstein equation, refractive index and dynamic viscosity data of the investigated systems are required. For this, an experimental setup allowing for the simultaneous application of DLS, a beam displacement method for the measurement of the refractive index, and rotational viscometry to access the dynamic viscosity of the microemulsions for temperatures up to 373 K and pressures up to 20 MPa has been realized. Currently produced first results from this setup in the form of absolute droplet size data for the investigated POSME-related microemulsions will also be part of our conference contribution.

#### IMT – O14 17:10 - 17:30 Tuesday

## BINARY DIFFUSION COEFFICIENTS IN REFRIGERATION OIL-REFRIGERANT MIX-TURES BY DYNAMIC LIGHT SCATTERING

Room HS BE01

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Mixtures of refrigeration oils with refrigerants are subjected to composition changes during, e.g., switching operations in refrigeration plants. For the characterization of the corresponding mass transport processes, binary diffusion coefficients are required for both the refrigerant-rich and the oil-rich phases. Reliable data for these transport coefficients are, however, lacking in the open literature. In this contribution, it is demonstrated that dynamic light scattering (DLS) allows for an accurate measurement of binary diffusion coefficients in both liquid phases of refrigeration oil/refrigerant mixtures over a wide range of well-defined temperatures and pressures. Besides the effects of these thermal properties of state on the transport coefficients, the influence of the selected substances is pointed out by comparison of results for varying refrigerants and refrigeration oils. The influence of molecular mass and dynamic viscosity of the refrigerants on the binary diffusion coefficient are discussed.



**Figure 1**. Binary diffusion coefficient as function of temperature for selected refrigeration oil-refrigerant mixtures.

#### IMT – O15 17:30 - 17:50 Tuesday

## MEASUREMENT OF THERMAL DIFFUSIVITY AND EFFUSIVITY OF SOLIDS BY FRONT PHOTOPYROELECTRIC TECHNIQUE

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The photopyroelectric (PPE) technique in the front configuration consists on illuminating one surface of a pyroelectric slab while the other surface is in contact with the test sample. A frequency scan of the PPE signal allows measuring the thermal effusivity of liquids. Recently, it has been applied to measure the thermal effusivity of solids, by taking into account the effect of the thin grease layer used to guarantee the thermal contact between sample and sensor [1]. The thickness of the sample is high enough so that it can be considered thermally very thick. In this work, we extend this method to measure simultaneously the thermal diffusivity (D) and effusivity (e) of solid plates. We have developed a complete model of the PPE signal generation, including not only the grease layer, but also heat losses by convection, radiation and conduction to the surrounding gas. The scheme of the PPE cell is shown in Fig. 1. It is demonstrated that the PPE signal depends on four unknown parameters: The thermal diffusivity and effusivity of the solid plate, the thermal thickness of the grease and the coefficient of heat losses. The frequency scan of the amplitude and the phase of the PPE signal are fitted simultaneously. PPE measurements performed on a set of solid plates confirm the ability of this method to obtain D and e accurately. As an example, Fig. 2 shows the results on a 0.265 mm thick polyether-ether-ketone (PEEK) sample. Dots are experimental data and the continuous lines are the fittings to the model. The retrieved thermal parameters  $(D = 0.18 \text{ mm}^2/\text{s} \text{ and } e = 625 \text{ Ws}^{0.5} \text{m}^{-2} \text{K}^{-1})$  agree with the reported values for this material.



**Figure 1**. Geometry of the PPE cell in the front configuration.



Room HS BE01

**Figure 2**. Experimental frequency scans of the amplitude phase of the normalized PPE signal for a 0.265 mm thick PEEK sample. Dots are the experimental data and the continuous lines are the fittings to the model.

## Acknowledgments

This work has been supported by UPV/EHU (GIU16/63).

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## IMT - O16 17:50 - 18:10 Tuesday

## Room HS BE01

## TIME-RESOLVED COMPRESSIBILITY MEASUREMENT REVEALS DRIVING FORCE OF PROTEIN REACTIONS

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The thermodynamics have been very important for revealing the nature of molecules. Recently our group has been working on time-resolved studies of thermodynamic properties in a time range of milliseconds by using the pulsed laser induced transient grating (TG) and transient lens methods for quantitative measurements in time domain. We applied these techniques to photochemical reactions of various protein systems. Here we will show our recent studies on the time-resolved compressibility measurements for revealing the driving force of a protein reaction, in particular, of a blue light sensor protein, SyPixD.

SyPixD is a relatively short photosensor protein, which consists of the BLUF domain and additional short helices. The photochemical reaction of SyPixD studied by absorption spectroscopy revealed that this protein exhibits a red-shifted intermediate generated within 100 ps after photoexcitation. The spectrum does not change after this initial reaction, and returns back to the dark state. We used the time-resolved thermodynamics to reveal the spectrally silent dynamics, which should be essentially important for the biological function.

It was shown that the main reaction of SyPixD after photoexcitation is the dissociation reaction from the decamer to the dimer by using the time-resolved diffusion measurement. The effect of pressure on the volume change associated with the dissociation reaction of SyPixD was investigated by high-pressure TG technique. The TG signal intensity representing the dissociation reaction of the SyPixD significantly decreased by applying a relatively small pressure. Upon blue-light illumination with a sufficiently strong intensity, the TG signal, which represents the dissociation of the SyPixD, was observed at 0.1 MPa, and the signal intensity significantly decreased with increasing pressure. This behaviour shows that the dissociation of the decamer is suppressed by the pressure. However, while the decamer undergoes no dissociation upon excitation of one monomer unit at 0.1 MPa, dissociation is gradually enhanced with increasing the pressure. For solving this strange behaviour, the compressibility changes of the intermediates were measured as a function of pressure at weak light intensity. We found that the compressibility change was negative at low pressure, but became positive with increasing pressure. Because the compressibility is related to the volume fluctuation, this observation suggests that the driving force for this reaction is fluctuation of the protein. The relationship between the cavities at the interfaces of the monomer units and the reactivity will be also discussed.
## **Oral Session 5: Instrumentation and Measuring Techniques III**

10:05 - 13:05 Wednesday HS BE01

Chairs: S. Vidi, D. Urban

# IMT – O17 10:05 - 10:25 Wednesday

Room HS BE01

# INFLUENCE OF DIFFERENT LEVITATION TECHNIQUES ON THE "OSCILLATING DROP" MEASUREMENT METHOD

## G. Lohöfer

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For the determination of thermophysical properties of liquids it is very often favorable to perform the handling of the liquid specimen containerlessly and the measurement process contactlessly [1]. Dealing in general with hot metallic melts, this treatment avoids chemical reactions between the droplet and crucible walls or solid measurement probes. Furthermore, containerless processing in a vacuum or inert gas environment, which avoids any contact of the specimen with impurities, offers the additional benefit that the melts can in many cases be undercooled below their freezing temperatures, which enlarges the temperature range of the measured sample property in the liquid state.

For the containerless handling (levitation) of the specimen against gravity or external residual accelerations the electromagnetic levitation on ground and under low gravity, and the electrostatic levitation techniques are often used. For the contactless determination of viscosity and surface tension of levitated liquids the oscillating drop method is generally applied [2]. This technique bases on the fact that the surface tension acts as a restoring force for surface oscillations of liquid drops. Apparently the frequency of the free oscillation is closely associated with the surface tension of the liquid drop and the damping with its viscosity. This supposes, however, that additional surface forces and turbulent flow damping mechanisms, originating from an interaction of the external levitation force field with the fluid flow inside the oscillating droplet, can be neglected.

In the present talk we compare the influence of both levitation techniques on the measurement of surface tension and viscosity by the oscillating drop method.

# References

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# APPLICATION OF DUAL-WAVELENGTH REFLECTANCE-RATIO METHOD TO HIGH-TEMPERATURE METALS

Yuma Kurokawa<sup>1</sup>, Hidekazu Kobatake<sup>2</sup>, Hiroyuki Fukuyama<sup>1</sup>, Yoshiro Yamada<sup>3</sup>, Naohiko Sasajima<sup>3</sup> and Yu Yamagichi<sup>3</sup>

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A combined technique of electromagnetic levitation (EML) with a static magnetic field has been developed for accurate thermophysical property measurements of liquid metals and alloys by Fukuyama's group and their collaborators [1-3]. However, non-contact temperature measurement using a pyrometer still remains a technical issue for unknown emissivity materials. In the meantime, Yamada et al has developed the dual-wavelength reflectance-ratio (DWR) method in the National Institute of Advanced Industrial Science and Technology (AIST) [4], which does not require the emissivity data of a sample. Thus, this study aims to apply the DWR method to a levitating liquid metal droplet. As a feasibility study, we first demonstrated the temperature measurement of spherical solid metals by the DWR method.

Principle of the DWR method is briefly explained as follows. In this method, a sample is irradiated by an auxiliary light source, and the radiances from sample surface are measured with and without auxiliary light irradiation at two different wavelengths. From the measured radiances and the radiation intensity ratio of the irradiation light source, the reflectance ratio  $(R_{\rho} = \rho_{\lambda 1}/\rho_{\lambda 2})$  can be derived. Here,  $\rho_{\lambda i}$  is the reflectance at each wavelength. Combining the  $R_{\rho}$  with the Kirchhoff's law ( $\epsilon_{\lambda} + \rho_{\lambda} = 1$ , where  $\epsilon_{\lambda}$  is the emissivity), emissivity terms can be cancelled from the procedure of temperature determination based on the Planck's law. Thus, this technique does not require the emissivity of the sample.

In this study, Cu, Ni and Pt spheres were used as a sample, and they were inductively heated. The sample temperature was monitored with a thermocouple. The radiance from the sample was detected by a pyrometer at two wavelengths with and without auxiliary light source irradiation. The obtained temperatures by the DWR method agreed with the temperatures measured by a thermocouple within 50 K in the temperature range from 850 to 1800 K. In the conference, more details of the DWR method will be presented.

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## IMT – O19 10:45 - 11:05 Wednesday

# RECENT DEVELOPMENTS IN THE DYNAMIC EMISSIVITY MEASUREMENT ABOVE 1000 K

## D. Urban, K. Anhalt, D. R. Taubert

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The precise knowledge of the spectral emissivity is key in precision radiation thermometry, the design of high temperature applications and modeling of radiative heat transfer. It becomes increasingly important at elevated temperatures above 1000 K where the heat transfer is dominated by radiation.

In the past years the PTB has developed a new method for the measurement of spectral emissivity in the temperature range above 1000 K, a dynamic emissivity measurement (Ad $\epsilon$ M). The measurement is based on a commercially available laser flash apparatus - a well-established method used for determining the thermal diffusivity. The setup has been modified to measure in situ the absolute energy of a laserpulse used to heat the sample, and the resulting temperature rise of the rear side of the sample.

Recently, the conventional tube furnace was replaced by an inductive heating system, which allows for the sample to be heated in a cold environment. Any interreflections between hot furnace walls and the sample are therefore minimized.

Furthermore, a characterised array spectrometer has been added to extend the spectral emissivity measurement to a spectral range of 550 nm - 1100 nm. The spectrally resolved emissivity is determined in a stationary fashion by measuring the spectral radiance of the sample. The recent developments and the improved measurement setup will be explained and first, preliminary results will be shown.

### IMT – O20 11:05 - 11:25 Wednesday

### Room HS BE01

# CALVET CALORIMETER CALIBRATION AND HEAT CAPACITY MEASUREMENT FROM -180 $^\circ\text{C}$ to 190 $^\circ\text{C}$

Daeho Kim, Suyong Kwon, and Joohyun Lee

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Calvet calorimeter is an improved measurement technique of caloric properties. It has three-dimensional fluxmeter sensor, and samples can be put in the vessel in solid and liquid phase. For measuring calorific values with a wide range of temperature, careful instrument calibration should be carried out. There are two well-known calibration methods which can be applied in differential scanning calorimeter. The first is using an electrical calibration heater installed in the sample holder and the second is using standard reference material, continuous  $C_p$  method. We selected the second method, which has the advantage of no heat leakage and it is easy reproducible process. A calvet calorimeter (SETRAM, BT2.15) was calibrated using  $\alpha - Al_2O_3$  NIST SRM720 and heat capacity was measured from -180 °C to 190 °C. Firstly, temperature calibration of the instrument was performed by measuring the transition

temperature of high purity n-heptane, DI water, gallium and indium for covering the whole temperature range. The heating rate was 0.1, 0.25, 0.4 K/min. The onset temperatures of the materials' reaction peak were used to correct the true temperature based on the ITS-90 and reference data. Secondly heat flow rate calibration was carried out with a known reference sample and measurement results were obtained by analysis. The accuracy for the heat capacity measurement has been improved with this calibration of temperature and heat flow rate. In this presentation, we will represent detail calibration process of the calvet calorimeter and results of heat capacity measurement.

## References

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## IMT – O21 11:25 - 11:45 Wednesday

Room HS BE01

# ACCURATE AND HIGH-RESOLUTION MEASUREMENTS OF THE SPECIFIC HEAT CAPACITY AND ENTHALPY BY PELTIER-ELEMENT-BASED ADIABATIC SCANNING CALORIMETRY (PASC)

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Knowledge of the temperature dependence of equilibrium thermal properties, in particular the specific heat capacity and enthalpy, of condensed matter systems are very important in any fields of research and application. Conceptually the measurement of the temperature evolution of the specific heat capacity and enthalpy of materials is very straightforward, only involving measurement of the time dependence of the temperature of the sample (with known mass) and of the heating power going to or coming from the sample.

In practice, attaining high absolute accuracy is often hampered in many experimental implementations by the need of comparison with a reference sample, and data processing involving baseline subtraction and slope correction. Lack of thermal equilibrium in the sample as a result of a too high scanning rate with many commercial DSC (differential scanning calorimetry) instruments is often a serious problem in particular near phase transitions.

In this contribution we present how, by virtue of a dedicated way of controlling the energy flow to the sample in a Peltier element based adiabatic scanning calorimeter (pASC), an absolute accuracy of better than 2 % can be obtained on the equilibrium specific heat capacity and enthalpy of samples with masses of a few tens of mg. The pASC device allows scans at a temperature heating or cooling rate determined by the enthalpy evolution of the sample upon steady state power input, thus allowing to go through second-order and first-order phase transitions in perfect thermal equilibrium, contrary to constant rate calorimeters as DSCs. Also other modes of operation like step-scans and DSC-type constant rate scans are possible with a pASC.

The performance of the pASC will be demonstrated with new data of detailed investigations of the phase transitions in several phase change materials (PCMs) of practical importance for energy storage and in mixtures of aqueous NaCl solutions exhibiting ice and eutectic melting.

# VALIDATION AND PERFORMANCE CHECKS OF THE NPL SMALL GURADED HOT PLATE APPARATUS

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The National Physical Laboratory (NPL) has designed and built a new small guarded hot plate (SGHP) apparatus specifically for absolute measurements on thin specimens of medium thermal conductivity materials, such as the polymer composites that are becoming more widely used in aerospace and other advanced manufacturing sectors. The apparatus can be used either in single-specimen mode or double-specimen mode. The details of the design of the apparatus were published in 2014. This paper presents the validation and the performance checks of the newly developed NPL small guarded hot plate apparatus in the mean specimen temperature range -5 °C to 165 °C.

Before the start of the validation, the traceability of temperature measurements needs to be established for the NPL SGHP. This paper includes the details of the technique used for in-situ calibration of the temperature sensors in the heater plate and the heated-cold plates.

A series of rigorous performance checks were carried out to evaluate the limitations and the factors that can influence the resulting measurement uncertainty of the newly developed Small Guarded Hot Plate. The clause 2.4 of international standard ISO 8302:1991 was used as a guidance for the performance check process. The results of imbalance error, edge heat loss and linearity test are presented in the paper. It is then followed by a series of validation measurements performed on an existing NPL thermal conductivity reference material of polymethylmethacrylate (NPL batch 05/01) and European certified thermal conductivity reference materials of Pyrex glass (BCR - 039) and Pyroceram 9606 (BCR - 724). The comparison of the measurements between single-specimen mode and double-mode of the apparatus is also included in the paper.

There are currently only a few manufacturers in the world that produce commercial instruments for steady-state thermal conductivity measurements on medium thermal conductivity materials, and these instruments use comparative techniques that require calibration against reference materials. Following validation the new NPL facility will be used to characterise a wider range of reference materials, including a reference for the thermal resistance of a layered composite.

#### IMT – O23 12:05 - 12:25 Wednesday

# INVESTIGATION OF THE THERMAL DIFFUSIVITY OF WATER AT FREEZING AND MELTING BY TEMPERATURE OSCILLATION

Room HS BE01

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The modified temperature oscillation i.e. Ångström's technique at scanning mode operation has been applied to perform continuous measurements of the thermal diffusivity (TD) of water. The investigations have been done at both heating and cooling within the range from -35 °C to 45 °C but a special attention has been put on TD measurements close to the melting/freezing transition. In this case low heating/cooling rates and low amplitudes of the temperature oscillation have been utilized to preserve high temperature resolution of measurements. The TD diffusivity has been calculated independently from two transcendental relations based on the measured amplitude attenuation and the measured phase shift of the temperature oscillation respectively. By comparing so called amplitude and phase TD results one can confirm their correctness or can identify any possible measurement uncertainty source. In addition to measurements performed on pure ice/water also investigations of porous cellulose and wool structures filled with water have been carried out. The purpose of the study has been to confirm phenomena revealed at the course of main measurements while supressing fluid convection above melting. The experimental investigation has been accompanied by numerical modeling of the measurement procedure.

The experiments have proved performance of the applied method for systematic studies of thermophysical properties of substances at phase transitions. They revealed gradual decrease of the ice TD while approaching the melting (Fig. 1). Unique results of the TD of water supercooled to even about -7 °C have been obtained also.



**Figure 1**. Typical TD measurement results for ice from below melting (points) and theirs B-spline approximation (line) showing a gradual TD decrease with increasing temperature.

# APPLICATION OF A COMMERCIAL DENSIMETER TO COMPARE SORPTION PHE-NOMENA ON POROUS AND NONPOROUS MEDIA

Room HS BE01

X. Yang<sup>1</sup>, M. A. Ben Souissi<sup>1</sup>, R. Kleinrahm<sup>1</sup>, M. O. McLinden<sup>2</sup>, M. Richter<sup>1</sup>

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A modified commercial gravimetric sorption analyser (incorporating a magnetic-suspension coupling) of Rubotherm (now TA Instruments), which we consider a tandem-sinkers densimeter, was utilized to study sorption phenomena on porous and nonporous media. Measurements were carried out near dew points of ethane, carbon dioxide, and their mixtures, which were prepared gravimetrically. We made improvements to the measuring system to obtain an accuracy much higher than usual for this type of commercial device. The achieved expanded measurement uncertainties (k = 2) were 20 mK for temperature, 1.4 kPa for pressure and 0.05 % for density.

When the highest accuracy for gravimetric experiments involving a magnetic-suspension coupling is the goal, the force transmission error (FTE) [1] of the coupling must be carefully investigated. For the present type of instrument, this was done for the first time. To that end, two different sinkers were systematically weighed in the two weighing positions of the instrument. An approximately linear relationship between the FTE at vacuum conditions (induced by the magnetic properties of the apparatus' components) and the mass loaded to the coupling was observed. Values between approximately 20 ppm and 50 ppm were determined. Furthermore, the FTE induced by the magnetic properties of the sample fluid was roughly linear to the loaded mass as well. The results were less than 300 ppm in most cases.

All measurements employed a highly polished density sinker ( $m \approx 20 \text{ g}$ ) made of titanium with an accurately determined volume to measure the fluid density. To study sorption phenomena, a well-investigated porous material (zeolite 13X granule, m < 10 g) was contrasted with the results from the nonporous materials. For those, we made use of three stainless steel sorption sinkers ( $m \approx 10 \text{ g}$ ) with a large surface-to-volume ratio and with different surface finishes (smooth and roughness of 125  $\mu$ m or 250  $\mu$ m). The volumes of all the sinkers were determined by a hydrostatic comparator. Measurements were carried out along isotherms with pressure-increasing steps slowly approaching the dew line. Once the dew line was crossed, possible hysteresis effects were investigated with pressure-decreasing steps. In line with our previous work [2], three distinct regions were observed: (1) minor sorption effects in micropores at low pressures; (2) capillary condensation followed by wetting in macro-scale surface scratches within approximately 98 % of the dew-point pressure; (3) bulk condensation.

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## IMT – O25 12:45 - 13:05 Wednesday

# IMPROVEMENT OF MEASUREMENT SENSITIVITY OF OPTICAL HAND-HELD VIS-COSITY SENSOR

Room HS BE01

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A quick and single *in situ* viscosity sensor is required in the various field. For example, in medical field, the simple and fast measurement of blood viscosity realizes diagnosis of cardiovascular disorders with new perspective. However, the conventional viscometers such as the capillary method and the rotational viscometer are unable to meet such requirements because these devises need a long measurement time and contact with samples. Therefore, we have developed a new viscosity sensor that is named OHVS (Optical Hand-held Viscosity Sensor) based on an optical measurement method called laser-induced capillary wave method (LiCW method).

The OHVS consists of tiny optical components integrated on a hand-held compact device, as shown in Fig. 1. This sensor can perform non-contact and fast optical measurement by observing attenuation of the capillary wave on the sample surface. In addition, the irradiation angle of the heating laser and the probing laser are stabilized by two-axis steering mirror, therefore this sensor is able to measure under disturbance. In this study, measurement conditions (such as interference fringe spacing, pulse energy of the heating laser, scattered light) are investigated to enhance the measurement sensitivity of OHVS, and the applicability of proposed hand-held sensor is experimentally confirmed by using the organic solvent sample.



Figure 1. Schematic image of Optical Hand-held Viscosity Sensor.

# Acknowledgment

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**Oral Session 6: Equation of State** 

10:30 - 12:10 Thursday HS BE01

# ES – O1 10:30 - 10:50 Thursday

Room HS BE01

Chair: W. Schröer

# ON CUBIC EOS INTERACTION PARAMETER ESTIMATION FOR LONG CHAIN N-ALKANE + AROMATIC BINARY MIXTURES

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Cubic equations of state are widely used for phase equilibrium calculations. They are simple and reliable, especially for hydrocarbon mixtures. Unfortunately, common choices such as the Peng-Robinson and Soave-Redlich-Kwong equations of state, systematically predict both qualitatively and quantitatively incorrect phase behaviors for long chain n-alkane + aromatic and naphthenic mixtures unless negative binary interaction parameter  $(k_{ij})$  values are used [1, 2]. Binary interaction parameters are typically obtained by fitting vapour-liquid equilibrium (VLE) data for binary mixtures. In the absence of data, interaction parameter values are obtained from generalized correlations typically leading to positive values [3,4] or are set to zero. Experimental VLE data for these mixtures are scarce and therefore reliable methods for estimating  $k_{ij}$  values in the absence of experimental data are needed to support industrial process design and optimization calculations. In this study, methods for estimating  $k_{ij}$  values for cubic EOS for binary mixtures of aromatics with long chain n-alkanes are evaluated. Options explored include obtaining  $k_{ij}$  values by regressing liquid phase activity coefficients from an *a* priori predictive model, the COnductor like Screening MOdel for Real Solvents (COSMOS-RS) [5] and the PC-SAFT EOS [6] (based on statistical associating fluid theory), and a predictive group-contribution  $k_{ij}$  estimation approach - PPR78 (predictive 1978, Peng-Robinson EOS) [7]. Calculated temperature-dependent interaction parameter values for 15 representative long chain n-alkane + aromatic binary mixtures are benchmarked against Peng-Robinson EOS  $k_{ii}$ values fitted to high precision VLE data [8]. The resulting skew and dispersion of predicted vs experimental  $k_{ij}$  values is discussed and best practices for estimating cubic EOS  $k_{ij}$  values for such mixtures are described.

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# ES – O2 10:50 - 11:10 Thursday

### Room HS BE01

### TRANSFERABILITY OF ASSOCIATIVE PARAMETERS USING A MODIFIED CPA EOS

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Contrary to cubic equations of state (EoS), advanced EoS generally use a set of parameters which need to be fitted to pure compound and/or mixture data. Predicting these parameters with simple methodologies would lead to an easier and more widespread use of these equations.

To describe associating compounds with CPA, besides the physical term, it is needed to fit two association parameters. Enabling the transfer of these parameters for a specific group between different molecules would bring an important boost in predictive capacities for this EoS. Previous studies have shown, that for the hydroxyl group, this is possible using a modified CPA<sup>1</sup>, which honours the description of the pure component critical temperature and pressure. Beside the transferability of the association parameters for this group, this approach eliminates the need to fit the energy and co-volume parameters from the cubic term of CPA.

Expanding this type of analysis to different association groups and enabling its application to multifunctional compounds is of great interest to the industry, especially if these methods are able to simultaneously and accurately predict a large set of properties. In this work this analysis is expanded to other association groups, including amines and sulphydril groups, while analysing both pure component properties (vapour pressure, liquid density, heat of vaporization and isobaric liquid heat capacity), as well as some selected mixture equilibria from the literature.

# Acknowledgments

This work was funded by KBC Advanced Technologies Limited (A Yokogawa Company) under project "Extension of the CPA model for Polyfunctional Associating Mixtures". André M. Palma acknowledges KBC for his PhD grant. Tony Moorwood is acknowledged for mentoring this project and providing helpful insights.

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# ES – O3 11:10 - 11:30 Thursday

Room HS BE01

# A HELMHOLTZ ENERGY EQUATION OF STATE FOR CIS-1-CHLORO-2,3,3,3-TETRAFLUOROPROPENE (R-1224YD(Z))

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A first fundamental equation of state is presented for cis-1-chloro-2,3,3,3-tetrafluoropropene (R-1224yd(Z)). Due to its high normal boiling-point and critical temperature, this novel refrigerant appears to be a possible alternative for 1,1,1,3,3-pentafluoropropane (R-245fa) in the use of high-temperature heat pumps and organic Rankine cycles. Recent research revealed that this refrigerant is non-flammable and non-toxic. R&D activity for the refrigerant has just started, and this requires an equation of state suitable for engineering applications.

The equation of state presented here is explicit in the Helmholtz energy of the refrigerant with independent variables of temperature and density. It is composed of two parts; one for the ideal-gas representing properties at ideal states, and the other for the residual contribution from the influence of intermolecular forces. The ideal-gas part is analytically formulated from a correlation for the ideal-gas isobaric heat capacity. The residual part, on the other hand, is determined empirically from experimental data. Following recent trends in the development of accurate equations of state, this work employs a functional form that includes Gaussian bell-shaped terms for the residual part and optimizes them through nonlinear least-squares fitting of critical parameters, vapor pressures, liquid and vapor densities (including those at saturation), isobaric heat capacities in the liquid phase, and sound speeds in the vapor phase. In addition, various thermodynamic constraints are applied to ensure that the equation of state is well behaved in the vicinity of the critical point, and reliably extrapolates beyond the range of the experimental data.

This new equation is valid for temperatures from 280 K to 480 K and for pressures up to 10 MPa. Typical deviations in calculated properties from experimental data in this range are 0.05 % for vapor pressures, 0.5 % for saturated liquid densities, 1.5 % for saturated vapor densities, 0.2 %

for liquid densities, 1 % for vapor densities, 1 % for liquid-phase isobaric heat capacities, and 0.03 % for vapor-phase sound speeds. These uncertainties are sufficient enough for practical use of this refrigerant. Several plots of such derived properties as heat capacity, sound speed, Gruneisen coefficient, and the phase identification parameter illustrate that the equation shows physically correct behavior even when extrapolated to regions far from the experimental data.

## ES – O4 11:30 - 11:50 Thursday

#### Room HS BE01

# CONSISTENT VOLUME-TRANSLATED SRK EQUATION OF STATE FOR ASSOCIATING FLUIDS AND MIXTURES

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Associating fluids, such as water, ammonia and alcohols, are widely utilized as working fluids and chemical agents. Accurate description of their thermodynamic properties is the cornerstone of their industrial utilization. Cubic equation of state (EoS) is able to accurately reproduce gaseous pvT(x) and vapour-liquid equilibria (VLE). However, its scope of application is restricted by its low accuracy in the liquid region, and the non-physical behaviour as temperature increases. Furthermore, the generalized formulations of alpha function, such as in SRK EoS and PR EoS, are not fit for associating fluids. Accuracy of volumetric properties can be improved with the volume translation technique, leaving the VLE results unchanged. The non-physical behaviour can be resolved by introducing an appropriate alpha function, while improving VLE representation accuracy of associating fluids. In this work, a consistent cubic equation with a constant volume translation term and a piecewise alpha function is presented for associating fluids. The equation was applied on mixtures containing associating fluids with modified van der Waals mixing rules.

Literature high-precision Helmholtz-type EoSs and experiment data sets were selected as reference data. Deviation was calculated and compared with the original SRK EoS, PR EoS, and volume-translated modifications of SRK EoS. The modified EoS is able to reproduce pvT(x), VLE, and derivative properties in a wide range of temperature and pressure in the mean-field region. Specifically, density is calculated with acceptable accuracy up to  $5p_c$  (over 100 MPa for water). Furthermore, an alternative EoS is proposed for applications where saturation densities close to the critical point are concerned. By introducing a new volume translation term expression, saturated liquid density representation accuracy is significantly improved. Further issues, such as consistency violation temperature, isotherm crossover, and mixture critical point prediction are also discussed.

## ES – O5 11:50 - 12:10 Thursday

# ISOBARIC HEAT CAPACITIES OF LIQUID R1233zd (E) AT TEMPERATURES FROM 303 K TO 423 K AND PRESSURES UP TO 12 MPA

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Currently, trans-1-chloro-3,3,3-trifluoropropene (R1233zd(E)) has been paid much attention. It was considered an alternative refrigerant in chillers due to its plenty of desirable features, such as its short atmospheric lifetime, very low global warming potential, nonflammability, low toxicity. Although it is not chlorine-free, its ozone depletion potential can be neglected.

Physical properties of R1233zd(E) are of necessity not only in chemical process but also in product design. Some researchers have investigated its physical properties. Hulse et al. reported its boiling point, critical parameter, vapor pressure, liquid density, surface tension and the ideal gas heat capacity. Kondou et al measured the surface tension of R1233zd(E) in the temperature range from 270 K to 360 K using the differential capillary rise method. Mondejar et al measured its densities at temperatures from 215 K to 444 K and pressures from 0.3 MPa to 24.1 MPa as well as sound speed data in the temperature range from 290 K to 420 K and pressures from 0.07 MPa to 2.1 MPa. They also obtained the vapor pressure from 280 K to 438 K and developed an equation of state for R1233zd (E). However, no work has been done on the isobaric heat capacity of R1233zd(E).

In this paper, isobaric heat capacities were measured in the temperature range from (303 to 423) K with pressures from (1.0 to 12.0) MPa. An empirical equation was applied to represent the isobaric heat capacity. The expanded uncertainty of the heat capacity was estimated to be within 1.0%. Additionally, heat capacities in saturated liquid phase were also obtained on the basis of the experimental values.

# Solids and Properties Solids (SPS)

**Oral Session 1: Solids and Properties Solids** 

11:05 - 13:05 Monday HS P2

Chairs: M. Fulem, G. Pottlacher

# SPS – O1 11:05 - 11:25 Monday

Room HS P2

# THERMAL AND ELECTRICAL CONDUCTIVITY OF CONVENTIONAL AND SELECTIVE LASER MELTED TI 6AL 4V AT ELEVATED TEMPERATURE

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Thermal diffusivity, specific heat capacity, density at room temperature, and thermal expansion of conventional and selective laser melted Ti-6Al-4V was measured in the range room temperature to 1200°C. From these results, thermal conductivity as a function of temperature was calculated.

Additionally, electrical resistivity was measured by millisecond pulse-heating in the temperature range room temperature to melting at 1670 °C. The measurement results of electrical resistivity as a function of specific enthalpy were combined with results of specific heat capacity measurements to obtain the relation between resistivity and temperature.

Thermal conductivity in the high temperature beta-phase up to melting is estimated from the results of electrical resistivity. The relation between electrical and thermal conductivity can be well described by a modified Wiedemann-Franz law using an equation of the Smith-Palmer type.

A comparison between conventional and selective laser melted Ti-6Al-4V shows only small differences in electrical and thermal conductivity.

# Acknowledgment

This work was supported by the European Space Agency (ESA), Paris, France, under contract no. 40000110952/14/NL/PA.

### SPS – O2 11:25 - 11:45 Monday

# HOW TRANSMITTANCE INFLUENCES THERMAL DIFFUSIVITY MEASUREMENTS WITH FLASH METHOD OF GNP

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Flash method for measuring thermal diffusivity of samples in the shape of thin plates assumes the following hypotheses: pulse heat source on the irradiated surface of the samples (generally approximated by a Dirac delta function in time), and opaque samples, i.e. the heat pulse is totally stopped on the front surface where the light pulse impinges (a Dirac delta function also in space). Nevertheless when these hypotheses are not completely satisfied, a meaningful uncertainty can arise. When thermal diffusivity of graphene nano-platelets (GNP) is measured with the flash method, a laser should be avoided in order to prevent an excessive temperature rise of the irradiated surface, and a normal photographic flash is preferable. But the standard method must be modified in order to take into account the time length of the pulse, which results comparable with the total time length of the thermal transient. Another problem arises when the material results not completely opaque to the impinging radiation, as was verified during the tests. In fact different results are obtained with the samples as produced, and when they are covered with a thin layer  $(1 \, \mu m)$  of colloidal graphite to make them completely opaque and not reflecting. This difference is even more evident for low density samples, while compacted samples result practically completely opaque. A reverse method was developed to evaluate the transmittance of the samples which takes into account such difference. In order to confirm the results obtained with the reverse method, some very thin samples (in the range between 0.1 mm and 0.5 mm) with low density were produced and their transparency measured.

### SPS – O3 11:45 - 12:05 Monday

#### Room HS P2

## THERMOPYSICAL PROPERTIES OF INTERMETALLIC Fe-Al COATING DEPOSITED BY GAS DETONATION SPRAYING

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Methodology and results of thernophysical property (TP) investigation of the Fe-Al intermetallic coating created by gas detonation spraying (GDS) are discussed. Intermetallics are known for their unique mechanical and thermal properties and thus they are used as materials to be applied in constructional protective layers. Several techniques are usually utilized to apply such layers but a special protective barrier features can be achieved at GDS process. It is because the cyclic interactions of a two-phase, supersonic metalizing flux result in multiphase coating final structure. The structure contains both intermetallic phases and the oxide ceramics. However, the GDS process is sensitive to changes of the metalizing process parameters and for that reason properties of the protective layer parameters can vary also. This creates needs for punctilious studies of TPs of the produced coatings both for their characterization and for the GDS process optimization also.

At this particular instance TPs have been investigated for a coating produced of a Fe40Al metal powder (40 stands for a declared atomic fraction) at certain GDS process conditions. The measured parameters are: specific heat, thermal diffusivity and thermal linear expansion. The specific heat has been measured in the course of differential calorimetric studies by applying a Perkin-Elmer Pyris 1 apparatus. The thermal diffusivity has been investigated using a Netzsch LFA 457 instrument while the linear expansivity has been studied applying a Netzsch Dil 402 C dilatometer. All the measurements have been done at repeating heating/cooling cycles covering at least the temperature range from the room temperature to 600 °C. On the basis of the measured parameters the forth complementary parameter, i.e. the thermal conductivity has been calculated.

Analysis of the obtained results have proved effectiveness of the applied investigation procedures. In the course of the performed measurements all basic TPs have been obtained for the analyzed heterogeneous intermetallic coating. The developed methodology will be utilized in forgoing systematic studies of GD sprayed layers.

## Acknowledgments

This study was supported by National Science Centre, Poland, Research Project No. 2015/19/B/ST8/02000.

# SPS – O4 12:05 - 12:25 Monday

### Room HS P2

# EXPERIMENTAL DETERMINATION OF FROST RESISTANCE AT DIFFERENT LEVEL OF MOISTURE SATURATION

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A frost resistance of building materials has to be determined according to relevant standards. Principles of testing methods usually consist in exposing a saturated sample to alternating environment in order induce cyclic freezing and thawing of the water contained in the sample. Each standard defines the duration of freezing and thawing, temperatures during freezing and thawing periods and requested number of freeze-thaw cycles. Then, usually a comparative strength analysis is performed. The frost resistance can be also expressed as percentage weight loss of the sample. However, building materials exposed to real weather conditions become fully saturated only seldom. And even if the saturation occurs, it covers only minor part of the construction for a short period of time. Additionally, the temperatures drop below -20 °C, which is usually requested by the standards, only occasionally so the freezing conditions defined by the standards are practically impossible to be fulfilled in the real applications. Based on above mentioned it can be concluded that experimental results are not able to offer a

comprehensive view of the hygrothermal behaviour and frost durability of the material under real weather conditions.

Main objective of this paper is to bring deeper knowledge about hygrothermal behaviour of building materials exposed to low temperatures which can be later exploited in computational models for description of ice formation inside porous bodies. Such an approach is supposed to provide more precise information about frost durability of building materials than the standard tests.

Following the standard procedure, samples made of autoclaved aerated concrete, but at different level of moisture saturation, are exposed to controlled alternating environment in order to induce possible freezing and thawing. As it was expected, the preliminary results indicated that the resistance of studied materials to the water/ice phase changes vary depending on the saturation level. The results also confirmed that freeze/thaw cycles may occur when the sample is not fully saturated, although the number is smaller. Anyway, it is inconsistent with the standards. The topicality of the presented research is additionally supported by a computational investigation of hygrothermal performance of external wall exposed to dynamic climatic conditions which reveals the probable moisture distribution over the reference year. It was found out that full saturation occur only rarely. It is therefore believed that further connection of obtained results with computational modelling can be beneficial from the point of view of prediction of freeze/thaw damage.

### SPS – O5 12:25 - 12:45 Monday

#### Room HS P2

# ANISOTROPIC THERMAL DIFFUSIVITY AND MICROSTRUCTURE OF THERMAL BARRIER COATINGS

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Thermophysical properties of Thermal Barrier Coating (TBC) are interesting. The typical TBC which consist of ceramics-based top-coat (TC) and bond-coat (BC) on the metal substrates are used as heat and wear shields of gas turbine blades. It is expected that the gas turbines are operated at higher temperature over 1700 °C from the view of energy efficiency. The strict thermal design of gas turbines and developments of new TBCs is necessary for realization of it. TBC which used for the gas turbines are produced by the thermal spray process in many cases. TC has high porosity and it shows low thermal conduction. It is known that the thermal conduction strongly depends on microstructure. However, details have been not clear yet.

We have been research on thermal diffusivity of TBC. One is a development of practical procedure in order to obtain thermal diffusivity of TBC attached on the substrate. We established a method using the multi-layer model for the flash method. It was published as ISO 18555 in 2016.<sup>1</sup> The other is a research on thermal diffusivity of TC which has various microstructures in order to be clear a relationship between structure and thermal diffusivity.

In this study, we measured thermal diffusivity of the yttria stabilized zirconia (YSZ) top-coat

samples were prepared by plasma spray processing changing conditions. The self-standing samples were removed from substrates. The cross-sectional SEM images were observed from cross-plane and in-plane directions to check microstructures. The porosity ratio of pores which is distinguished by pore shape, for example, gobbler and liner, was estimated from the images. The cross-plane and in-plane thermal diffusivities were measured by the flash method. The bulk density was estimated by size and mass of the samples. It was found that thermal diffusivity of TC shows anisotropy between cross-plane and in-plane related to pore-shape and its porosity. We confirmed a trend of thermal diffusivity on pore shape similar to the recent report which said that porosity dependence of thermal conductivity changes according to aspect ratio of the pore.<sup>2</sup> Thermal diffusivities measured in vacuum and in air shows difference between them. It is indicated that the pores are almost open pores.

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### SPS – O6 12:45 - 13:05 Monday

# STUDIES OF THERMOMECHANICAL PROPERTIES OF PAC AND H2 SOLID ROCKET PROPELLANTS

Room HS P2

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Double-base (DB) homogeneous PAC and composite H2 solid rocket propellants have been selected for experimental studies with respect to their thermophysical and mechanical properties. PAC of density  $1.51 \text{ g/c}^3$  at room temperature, containing 47.7 wt % of nitrocellulose (NC), 28.4 wt % nitroglycerin (NG), 7.3 wt % dinitrotoluene (DNT), 16.6 wt % (additives) and heterogeneous H2 of density  $1.77 \text{ g/cm}^3$  containing 70.0 wt % of ammonium perchlorate (AP), 15 wt % aluminum powder, 15.0 wt % (additives) were tested using DMA, STA(TG-DTA, TG-DSC), STA-QMS methods by applying NETZSCH thermal analyzers. Dynamic Mechanical Analysis conducted in dual cantilever bending mode using the NETZSCH DMA 242C over temperature range from -110 °C to +120 °C revealed glass transition temperature for PAC at -38.9 °C and at -56.6 °C for H2 as they were taken from peak of loss modulus E'' at a frequency of f = 1 Hz. The activation energy of glass transition derived from peak temperatures of  $\tan \delta$ curves for several test frequencies  $f = 0.1, 1.0, 10 \,\text{Hz}$  in DMA experiment was found to be  $181.389 \pm 35.363 \,\text{kJ/mol}$  for PAC. Thermal effects and heat capacity were tested using the NET-ZSCH DSC 404F1 Pegasus at heating rate HR =10 K/min. Liquid nitrogen (for cooling) and helium as a sample inert gas atmosphere (50 ml/min) were applied. Measurements of the specific heat  $c_p$  were performed within temperature interval from -100 °C to +120 °C and  $c_p$  values corresponding to temperature from -50 °C to +100 °C was ranging from 0.977 to 1.310  $J/(g \cdot K)$ for H2 and from 0.858 to 1.686  $J/(g \cdot K)$  for PAC. In case of PAC it was observed a peak at

104.6 °C ( $c_p = 1.889 \text{ J/(g \cdot K)}$ , onset 100.7 °C, end 107.1 °C) which is probably connected with NG evaporation during heating (enthalpy  $\Delta H = +1.691 \text{ J/g}$ ). Thermal decomposition of PAC and H2 were carried out using the NETZSCH STA 2500 Regulus (TG-DTA) and separately using the NETZSCH STA 449 F5 (TG-DSC). The mass spectroscope QMS 403D working in the range 1-300 emu was used together with STA 449 F5 to determine the thermal decomposition products of tested materials. The results of Simultaneous Thermal Analysis (STA) performed over temperature range from 30 °C to 1000 °C have shown that the main exothermic peak of PAC and H2 occurred at 102.7 °C and 344.5 °C, respectively. For H2 it has been found two endothermic peaks occurring at 244.3 °C and 656.3 °C and for PAC the main exothermic peak was preceded by a small exothermic peak occurring at 180.1 °C. The activation energies and pre-exponential factors calculated from TG measurements at HR = 2.5; 5; 7.5; 15 K/min for PAC and H2 according to ASTM E1641 were determined as equal to be  $73.75 \pm 3.61 \, \text{kJ/mol}$ ,  $\log(A, s^{-1}) = 6.36$  and 48.94 kJ/mol,  $\log(A, s^{-1}) = 4.01$ , respectively. The results of thermomechanical properties obtained experimentally for PAC and H2 presented in this paper can be further used for numerical simulations of heat and mass transfer problems occurring in such energetic materials.

# Properties of Material Science at High Temperatures (PMSHT)

# **Oral Session 2: Properties of Material Science at High Temperatures I**

15:30 - 17:50 Monday HS P2

Chairs: D. Matson, G. Pottlacher

# PMSHT – O1 15:30 - 15:50 Monday

Room HS P2

# INDUCTIVE MEASUREMENT OF ELECTRICAL RESISTIVITY AND THERMAL EXPANSION OF MOLTEN $\rm Zr_{64}Ni_{36}$ ALLOY

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For investigations on highly reacting metallic melts, metallic melts at high temperatures, or undercooled metallic melts, containerless handling methods of the liquid as well as contactless measurement methods are beneficial or even mandatory. For the containerless processing of our metallic melts we use the well-established electromagnetic levitation technique, which utilizes high frequency alternating magnetic fields for the contactless, inductive positioning and heating of electrically conducting samples. The existence of high frequency magnetic fields suggests to use also inductive methods for noncontact measurements of liquid metal properties. Within a joint ESA project of DLR and TU Graz a measurement device was designed and constructed by DLR which utilizes the high frequency magnetic fields of the "International Space Station microgravity electromagnetic levitation facility (EML)" simultaneously also for an inductive determination of thermophysical properties of levitated metallic melts like the electrical resistivity and the thermal expansion.

In the present talk we report on first measurements of these quantities for the liquid  $Zr_{64}Ni_{36}$  alloy in the electromagnetic levitation facility (EML) operated under microgravity in the "International Space Station (ISS)".

# INVESTIGATION OF THE IRON-NICKEL SYSTEMS SURFACE TENSION BY MEANS OF ELECTROMAGNETIC LEVITATION

Room HS P2

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The temperature dependent surface tension and density of the iron-nickel alloy system in the liquid phase is investigated using the oscillating drop (OD) method in combination with an electromagnetic levitation (EML) device.

EML is an elegant experimental approach to determine surface tension and density of melts of pure metals and alloys by facilitating a non-contact, container-less measurement procedure. High-speed cameras and edge detection software are used to generate a frequency spectrum of the samples' surface oscillations as well as to determine the volume of the sample. By analysing the frequency spectrum, surface tension can be calculated, whereas the volume is needed to determine density. All parameters are measured as a function of temperature, which is obtained with a commercial single-wavelength pyrometer emissivity - calibrated at a reference temperature, e.g. at the melting/solidification plateau. A dual-wavelength pyrometer is also available to cross-check the temperature measurement.

The experimental setup was installed within a recently finished research project by the thermophysics and metalphysics group at Graz University of Technology (TU Graz). First, pure metals like nickel, copper and aluminum were investigated and the results were successfully published in literature. On the road to the investigation of complex alloy systems within a new research project, the scope was put on the binary iron-nickel alloy system. With data of pure nickel already available, the measurements start with pure iron, followed by Fe80Ni20, Fe60Ni40, Fe40Ni60 and Fe20Ni80.

Recent results of the measurements will be presented and a comparison of the data obtained with reference values from literature (if available), will be given. Results already obtained for pure iron show a good agreement with reference values from literature, however, the influence of the process gases? composition on the surface tension has still to be investigated. The uncertainty of the measured data is evaluated according to GUM.

# Acknowledgment

Work is partially funded by the Austrian Research Promotion Agency (FFG) within the 23rd "Bridge" program, Project "Surfacetension-Steel" (Project-Nr. 855678).

## PMSHT – O3 16:10 - 16:30 Monday

# THE PREDICTION OF LIQUID DENSITY FOR SELECTED ALLOYS AND COMPARISON WITH EXPERIMENT

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The simulation modelling of metal processes requires realistic; accurate and self-consistent thermophysical properties as input data. In particular, solidification models have been shown to be sensitive to small changes in the density of the liquid alloy.

This paper compiles selected experimental data for the density of liquid aluminium; magnesium and nickel alloys taken from our own measurements, mainly performed by piston dilatometry, and measurements in the literature. Each alloy type presents different experimental challenges.

The density at the liquidus temperature is compared to an ideal mixtures model based upon volumetric data for the elements extracted from a compilation by Mills and Li.<sup>1</sup> This ideal model is extended to allow for non-ideality of mixing of the binary components (and some cases tertiary interactions where data is available) using the method described by Brillo.<sup>2</sup>

For the aluminium and magnesium alloys, for the compositions considered, there is reasonable agreement (1-2 %) between the ideal mixing calculations and experiment within the measurement uncertainties. The corrections for binary and in two cases tertiary interactions make little difference to the calculated densities.

For nickel alloys with significant aluminium content (up to 14 at. %), it is known that there is a significant difference between the density predicted by an ideal model and measured values. In this work, these differences are interpreted in terms of the measured non-ideality of mixing of the Ni-Al binary system taken from the literature, as well as considering the smaller Co-Al; Cr-Al and Ni-Cr binary interactions. Both this model and the Mills et al. model,<sup>3</sup> based on a parameter derived from the density data of a selection of nickel-base alloys and ideal mixture calculations, give similar agreement (about 2 %) with the measured values.

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Room HS P2

## THERMOPHYSICAL PROPERTIES OF METALLIC ALLOYS IN THE LIQUID PHASE: CONTAINERLESS PROCESSING ON BOARD THE INTERNATIONAL SPACE STATION

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Thermophysical properties of liquid metallic alloys are of interest from an applications point of view as well as from a more basic metal physics point. The latter regards the connection between the microscopic structure of the melt as inferred from scattering experiments and the macroscopic properties such as viscosity and specific heat capacity. Other issues include the investigation of the undercooled liquid phase such e.g. phase separation and nucleation kinetics. From an applications point of view thermophysical properties in the liquid phase are required for the modeling of industrial melt processing in particular casting but also gas atomization for the production of metallic powders. However, for many industrial alloys due their high reactivity in the liquid phase and high temperature these data are not available. This pertains in particular to the further development of high temperature alloys for energy production and transportation. Containerless processing in an electromagnetic levitation device (eml) was conceived to alleviate these problems.

Here we report about non-contact thermophysical property measurements in an eml device installed on the International Space Station for thermophysical property measurements on liquid metallic alloys. Thermophysical properties investigated include the specific heat capacity and thermal transport coefficients, the viscosity and surface tension and the density. We describe the set up, processing with the facility, measurement methods and first results on e.g. Ni-based superalloys and a Ti6Al4V alloy.

# PMSHT - O5 16.50 - 17:10 Monday

### Room HS P2

Room HS P2

# PHYSICAL PROPERTIES OF CARBIDES AND CARBON AROUND THE MELTING REGION AND IN A LIQUID STATE

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A fast (microseconds) heating method by electrical current is very useful for investigation of carbon and refractory compounds at high temperatures. Of particular interest was the publication of the melting of zirconium carbide with a high content of carbon.<sup>1</sup> It is used in rocket technology for heavy-duty work (resistant to thermal shock); and excess of carbon under sublimation takes energy away, lowering the temperature of the nozzle. This carbide is the least explored in the calculated phase diagram. Our study in this final period was generally aimed at the investigation of thermophysical properties of coatings (carbides,<sup>1</sup> nitrides,<sup>2</sup> and carbon<sup>3–5</sup>) that are used in aviation and aerospace, as well as in the matrix of the new nuclear fuels. We may measure properties starting from 2000 K (at this stage), and starting from

1000 K, when change the model of fast optical detector.

Volume heating by current allows you to measure not only temperature, but also to investigate the bulk properties of substances (resistance, heat capacity, input energy). Two laboratories (G. Pottlacher and R. Hixon) were the first who obtained the whole temperature plateau under graphite melting.<sup>6</sup> Our first step was a study of thermophysical properties of carbon<sup>3</sup> close to the melting point and the establishment of the melting temperature of graphite (4800-4900 K). Graphite specimens were placed into the cells of quartz glass or sapphire to create a certain pressure (graphite melted only at a pressure higher 120 bar). In all of these experiments it was observed a rapid increase of the specific heat before the melting that gives a slight excess of energy required for steady state melting. It can be attributed to the formation of pairs of non-equilibrium Frenkel defects at fast heating. Apparently, the equilibrium diffusion processes cannot ensure the saturation of lattice by the defects in a short time of heating. It leads to the appearance of non-equilibrium defects to provide structural "freedom" for lattice melting. The same effect of specific heat increasing (just before melting) was observed earlier for metals<sup>7</sup> also at fast heating. Thus, a slight excess of energy (prior to melting) goes to the formation of non-equilibrium defects in the lattice, but not to the increase in melting temperature.<sup>7</sup>



### Figure 1.

(1) Temperature measurement of carbon melting versus time of heating. Arrow 1 indicates the start of melting; Arrow 2 indicates finish of carbon melting.

(2) Specific heat of Carbon in solid state, up to melting. Points - steady state data (up to 3820 K - experiment, further - calculation). Solid curve: pulse (microseconds) experiment.

(3) Specific heat of ZrC+C in solid and liquid state. Left-hand arrow: start of melting (eutectic line); right-hand arrow: finish of melting.

### Acknowledgments

The study is executed under support of the Russian Science Foundation in the framework of the grant No. 17-19-01099.

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## PMSHT – O6 17:10 - 17:30 Monday

Room HS P2

## A NEW TRIAL TO DETERMINE THERMAL CONDUCTIVITY OF OXIDE FILMS RELEVANT TO STEELMAKING PROCESSES

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Oxide films play an important role in steelmaking processes. In continuous casting of steel, for example, silicate film called mould flux exists between the molten steel and the mould to control heat extraction from the steel to avoid the occurrence of surface defects such as longitudinal cracking. On the other hand, in the water-spray cooling process after hot rolling the steel is cooled via iron oxide scale formed on the steel surface by the reaction with air in the hot-rolling process. These oxide films act as resistance to heat transfer, and the thermal conductivities are required to optimise the steelmaking processes.

Thermal conductivities ( $\lambda$ ) of oxide films is usually determined from thermal diffusivities ( $\alpha$ ) measured by the laser flash method using densities ( $\rho$ ) and specific heat capacities ( $C_p$ ) of the samples according to  $\lambda = \alpha \rho C_p$ . However, this determination can be applied to single phase samples; on the contrary, mould flux film and oxide scale consist of multi-phases; also, the former contains glassy phases and the latter even voids and cracks. These complex situations make it difficult to evaluate the density and the specific heat capacity.

Hence it is noted that the determination of thermal conductivity requires the product of  $\rho C_p$  but not independent values of  $\rho$  and  $C_p$ . The product can also be expressed as  $\rho C_p = e/\alpha^{1/2}$ , where *e* is the thermal effusivity. The value of e can be measured by the non-stationary hot strip method, and its combination with the laser flash method can offer the thermal conductivity without values of  $\rho$  and  $C_p$ . Consequently, the present work aims to experimentally confirm the above methodology to determine the thermal conductivity of complex samples.

In the present work, oxide scale was used as a model sample. The oxide scale was formed on ultra-low carbon steel plates (1-mm thick) by oxidation in air at 1173 K. The laser flash method was applied to measure apparent thermal diffusivity of the oxide scale + substrate system, which was converted to thermal diffusivity of oxide scale itself.<sup>1</sup> The thermal effusivity of oxide scale was measured by the hot-strip method at room temperature. The thickness of oxide scale was measured by a cross-sectional image of scanning electron microscope.

The thermal effusivity of oxide scale determined is  $2.52 \text{ kJ s}^{-1/2} \text{ m}^{-2} \text{ K}^{-1}$ . The apparent thermal diffusivity of the steel with 200  $\mu$ m-thick oxide scale has been measured as  $2.14 \times 10^{-6} \text{ m}^2 \text{ s}^{-1}$ . These values provide a thermal diffusivity value of  $3.66 \times 10^{-7} \text{ m}^2 \text{s}^{-1}$  for the oxide scale; in addition, a thermal conductivity value of  $1.55 \text{ W m}^{-1} \text{K}^{-1}$ . This method would apply to samples consisting of multi-phases such as mould flux films as well.

# Acknowledgments

This work was supported by the Iron and Steel Institute of Japan and the JFE 21st Century Foundation.

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PMSHT – 07	17:30 - 17:50	Mondav

## Room HS P2

# MULTI-RECALESCENCE AND SOLIDIFICATION MICROSTRUCTURES OF LEVITATED MoSiBTIC ALLOY MELTS

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MoSiBTiC alloys have excellent high-temperature strength, high liquidus temperature (> 1900  $^{\circ}$ C), and comparable density to Ni-based superalloys. They are expected to be used as ultra-high temperature materials of next generation high-pressure turbine blades without cooling system.

Multi-recalescence is observed in levitated MoSiBTiC alloy melts during cooling using electromagnetic levitation (EML) technique in a static magnetic field. The origin of the multi-recalescence has not been identified in these alloys.

These alloys were prepared by arc melting and cut into several pieces in weight of 1.2-1.3 g. A sample was levitated by Lorentz force and melted by inductive heating with laser heating. Sample temperature was measured by a monochromatic pyrometer (wavelength:  $\lambda = 160 \,\mu$ m) and controlled by adjusting power of a heating laser. Ar-5 vol%H<sub>2</sub> gas was flowed at a rate of 3 L / min during melting. A static magnetic field of 10 T was applied to the sample droplet to suppress both translational motion of the sample and convections in the sample. Sample temperature was kept for about 10 min immediately after recalescence was occurred, and subsequently the sample was quenched by He gas blowing. In-situ observation from top surface of the sample during EML was conducted with a high-speed camera, and solidification microstructures in a cross section of the quenched sample were observed and analyzed by SEM and XRD.

A sample of Mo-5.0Si-10.0B-7.5Ti-7.5C (at%) presented a three-step recalescence during the EML experiment. Coarse grains of  $Mo_{ss}$  (Mo solid-solution) phase in solidification microstructures were observed after first recalescence.  $Mo_{ss}$ -TiC eutectic structure,  $Mo_2B$  phase, and  $T_2$  ( $Mo_5SiB_2$ ) phase were observed in the solidification microstructures of the sample after third recalescence. These phase changes are related to each recalescence.

## **Oral Session 3: Properties of Material Science at High Temperatures II**

10:20 - 13:00 Tuesday HS P2

Chairs: H. Shibata, G. Pottlacher

# PMSHT - O8 10:20 - 10:40 Tuesday

Room HS P2

# ESTIMATION OF CRITICAL DATA AND PHASE DIAGRAMS OF PURE MOLTEN METALS AND SALTS

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Measurements of thermophysical properties of liquid metals are demanding and thus rare. A recently published data collection provides high temperature data for a set of 22 metals.<sup>1</sup> Although the measurements concern data in the range up to 5000 K, the critical region however, is mostly far beyond the region accessible experimentally at present, with exceptions of Alkali metals. Knowledge of the phase diagrams and of the critical data is important for high-temperature technologies and also of fundamental interest. Therefore an attempt is made to extrapolate the available data into the critical region. A novel approach for extrapolating the density data<sup>2</sup> is applied taking into account recent theoretical developments in the field of critical phenomena, which are the crossover from the universal criticality of the 3d-Ising model towards mean-field behavior, and the theory of complete scaling that describes the nonlinearity of the diameter of the phase diagrams. The method is tested on phase diagrams of Caesium, Rubidium for which accurate phase diagrams up to the critical region are available and compared with simulation results and other estimation methods e.g. such that are based on inter-atomic potentials or surface tension measurements. In the same way salts, Ionic Liquids and ionic solutions are considered. Comparison is made with measurements of the critical temperature by the 'exploding-wire technique' e.g. of Gold, Lead, Zinc and Aluminium. Corresponding state behavior of the metals is established.

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## DENSITY OF LIQUID TANTALUM AND ESTIMATION OF CRITICAL POINT DATA

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Critical point data of high-melting metals are scarce but of fundamental interest. Due to the extremely high temperature and pressure at this point, it cannot easily be reached experimentally for high-melting metals. However, extrapolation of the liquid phase density according to theoretical models provides a possibility to estimate the critical point. Even though density data for high-melting metals exist in literature, they often suffer from large uncertainties and are not consistent with each other. The situation is aggravated by the fact that the data often do not reach far beyond the melting point.

In order to obtain best starting conditions for the extrapolation procedure, two things are crucial. First, the density data should extend as far as possible into the liquid phase and second, the data should exhibit small uncertainties.

In order to meet both requirements, the density of liquid tantalum was re-measured in this work by means of ohmic pulse-heating. The thermal expansion of the sample wires was imaged with an adapted CCD-system. A newly integrated high-power photoflash and improved triggering of the experiment allowed the acquisition of high-contrast shadow-images of the expanding wires every 2.5  $\mu$ s. To reduce the uncertainty arising from simultaneous pyrometric temperature measurement, the change in emissivity was additionally taken into account.

In this work, density versus temperature of tantalum is reported over the entire liquid phase. Critical point data were estimated via extrapolation of the newly obtained liquid phase density.

# PMSHT - O10 11:00 - 11:20 Tuesday

Room HS P2

Room HS P2

# THERMODYNAMICAL EXAMINATION OF METALS AND CERAMIC COATINGS USING PULSE HEATING TECHNIQUE

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The pulse heating technique is a well-known method for examining thermophysical properties of electrically conducting materials, such as metals and metal alloys. The method uses a current pulse to heat up the sample via Joule-heating from room temperature up into the range of the melting point, while the temperature is measured as a function of time on the sample surface. The data provided by a measurement enables the calculation of the specific resistivity, the specific heat capacity and the hemispherical total emittance as functions of temperature.

The heating phase of a measurement is in the sub second regime and data can be achieved from 1000 K up to melting point of the sample. Temperature profiles are gained by scanning the specimen during heating and cooling. It is furthermore possible to compute the thermal conductivity of the sample by fitting the data using the long thin rod approximation,<sup>1</sup> where the thermal conductivity can be described as a low order polynomial of temperature.

A system provided by the Istituto di Metrologia "Gustavo Colonnetti" (IMGC) is modified and renewed with up to date data acquisition technology. High-speed measurements have been done on thermal barrier coatings. These coatings are fundamental to raise the temperature in gas turbines in order to maximize their efficiency. For deriving the properties of the ceramic-based thermal barrier coating, calibration measurements of the metal-based pure substrate are necessary. In this work, the measurement setup is presented together with the obtained results for the investigated specimen.

## Acknowledgments

This work was done in cooperation with the Istituto di Metrologia "Gustavo Colonnetti" (IMGC). Special thanks go to Dr. F. Righini for supporting.

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# PMSHT – O11 11:20 - 11:40 Tuesday

Room HS P2

# SURFACE TENSION AND VISCOSITY OF $\gamma$ -TiAl ALLOYS MEASURED IN AN ELECTROMAGNETIC PROCESSING DEVICE ON BOARD PARABOLIC FLIGHTS

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In recent years  $\gamma$ -TiAl based alloys with additions of further alloying elements such as Cr, Nb, Ta, B and C in the 1 - 8 at % range have progressed into application ready structural materials for high temperature applications. The main production route is casting which is however difficult because of the high temperatures, high chemical reactivity, low thermal mass and resulting high cooling rates. In that context thermophysical properties in the liquid phase are required as input parameters to casting and solidification modelling which is widely used to improve and further develop casting techniques for this class of alloys. Due to the same reasons, however, such values are difficult to obtain by conventional methods where the liquid to be tested is in contact with a container. Here we report on the results of measurements of the surface tension and viscosity of the alloys Ti<sub>46</sub>Al<sub>46</sub>Nb<sub>8</sub>, Ti<sub>46</sub>Al<sub>46</sub>Ta<sub>8</sub> and Ti<sub>48</sub>Al<sub>48</sub>Cr<sub>2</sub>Nb<sub>2</sub>. The measurements were performed by the oscillating drop method in an electromagnetic levitation device (eml) under reduced gravity ( $\mu$ -g) conditions on board a parabolic flight airplane. The method, processing and results will be described. The results of the surface tension measurements obtained in the experiments compare very well with values from ground based eml. Values of the viscosity have been obtained for all three alloys in the  $\gamma$ -g experiments. In addition, some results

from conventional high temperature calorimetry will be described.

## PMSHT – O12 11:40 - 12:00 Tuesday

Room HS P2

# DENSITY MEASUREMENT OF LIQUID STATE BINARY PLATINUM ALLOYS USING EML METHOD WITH STATIC MAGNETIC FIELD

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The correlations between excess volume and thermodynamic functions of liquid state binary alloys have been reported since 1937.<sup>1</sup> In 1988, Iida and Guthrie summarized the relationship between excess volume and enthalpy of mixing.<sup>2</sup> In the report, they concluded that enthalpy of mixing was expected to have negative value for the binary alloys having negative excess volume. However, in our recent research,<sup>3</sup> it was clarified that Fe-Ni, Cu-Au, Fe-Co and Bi-Tl systems had positive value of excess volume with negative enthalpy of mixing, thus, these systems do not follow the correlation proposed by Iida and Guthrie. These four alloy systems have a common characteristic feature in their phase diagrams, i.e., they have a wide solid solution and intermetallic compounds at lower temperatures.

In this study, we have picked up the following binary alloy systems: Fe-Pt, Cu-Pt, Ni-Pt, Co-Pt, which have a common characteristics in their phase diagrams. The densities of those alloys in a liquid state were measured using electromagnetic levitation (EML) method with a static magnetic field. Based on the results, we discussed relationship between excess volume and enthalpy of mixing and also relationship between excess volume and excess Gibbs energy of alloys. Details of experimental procedure, results, and discussions will be presented in the conference.

# References

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### PMSHT – O13 12:00 - 12:20 Tuesday

# REFERENCE CORRELATIONS FOR THE THERMAL CONDUCTIVITY OF 13 LIQUID METALS

K. D. Antoniadis<sup>1,2</sup>, M. J. Assael<sup>1</sup>, M. L. Huber<sup>3</sup>, W. A. Wakeham<sup>4</sup>

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In recent years there has been an increasing use of mathematical models to simulate a variety of processes involving liquid metals such as shape-casting; primary and secondary metal production; powder production by spray-forming; and welding. In order to model any of these processes, there is a need for density, viscosity, and thermal conductivity data for the relevant alloys. For these reasons, a project was initiated in 2009 by the International Association for Transport Properties, IATP (former Subcommittee on Transport Properties of the International Union of Pure and Applied Chemistry, IUPAC), initially, to evaluate critically the density and the viscosity of selected liquid metals at 0.1 MPa. Subsequently, in 2006, reference correlations for the density and the viscosity of liquid aluminum and iron<sup>1</sup> were published, in 2010 of liquid copper and tin<sup>2</sup>, in 2012 of liquid antimony, bismuth, lead, nickel, and silver<sup>3</sup>, of liquid cadmium, cobalt, gallium, mercury, indium, silicon, thallium, and zinc<sup>4</sup>, and finally in 2012 of liquid eutectic alloys (Al+Si), (Pb+Bi), and (Pb+Sn).<sup>5</sup>

In the present work, also carried out under the auspices of IATP, the aforementioned task is continued by proposing reference correlations for the thermal conductivity of 13 liquid metals: antimony, bismuth, cerium, cobalt, copper, gallium, indium, iron, lead, nickel, silicon, tin and zinc. These are based on critically-assessed measurements of the thermal conductivity; all measurements are separated into a primary set founded on strict criteria, upon which the correlations are based, and a secondary set which are employed only for comparison purposes.

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## PMSHT – O14 12:20 - 12:40 Tuesday

## EXPERIMENTAL SET-UP FOR DYNAMIC MATERIAL INVESTIGATION

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Room HS P2

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Advanced material processing and application require more and more detailed investigation methods to characterise the involved materials. In particular high-temperature applications in energy conversion and process technologies as well as additive manufacturing processes for novel industry 4.0 manufacturing are essentially requiring such information. Several applications in these fields additionally require layered structures, e.g. thermal barrier coatings for protecting turbine blades for high temperatures and harsh environments. Also novel applications in additive manufacturing are based on a layer-to-layer process, e.g. laser beam melting for 3D printing. In these cases also the mechanical contact between the layers and the overall characteristics of such a layered structure are of vital importance for their further application and life time.

To address the required need in advanced material characterisation, University of Applied Science Wurzburg - Schweinfurt and the Bavarian Center for Applied Energy Research (ZAE Bayern) supported by the companies KE Technology and Techno Team Bildverarbeitung GmbH started an attempt to develop an unique measurement set-up for advanced material characterisation based on the well know laser flash principle. By adding additional heating sources with different time varying possibilities to actively heat the investigated samples, e.g. by modulated and/or step-like heating, the spread of heat will be investigated with point like measuring devices, i.e. radiation thermometers, or with imaging systems, i.e. thermal cameras. By varying the wavelength of the optical heating, different information of opto-thermal parameters with increased lateral and depth resolution will be assessed. Additionally, information of other material properties, e.g. mechanical contact, electrical conductivity or optical data, which also depend or affect the flow of heat, can be addressed by this set-up.

The present paper presents the fundamental idea, the underlying physical and mathematical concepts as well as the experimental realisation. First promising results are also presented.

### Acknowledgement

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## PMSHT – O15 12:40 - 13:00 Tuesday

## THERMOPHYSICAL PROPERTIES OF NITRIDE ZrN FROM 2000 K UP TO 5000 K

Room HS P2

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Two series of the experiments were fulfilled: with sputtered ZrN and with sintered ZrN.

#### 1) Coated layer of ZrN as a thin film

The zirconium nitride specimens were obtained as a thin (2.5  $\mu$ m) specular reflecting layer deposited on the insulating K-8 glass substrates by the magnetron sputtering technique. The coating density estimated according to the specimen mass growth was taken equal to 6.7 g/cm<sup>3</sup>. The composition of the deposited specimens (in at %): Zr - 36.8 %; N - 49 %; O - 10.8 %.

The pulse current heating permitted reaching the nitride melting region in 5  $\mu$ s. The current, the voltage, and the radiation at the wavelength of 856 nm were registered. The Joule energy input - *E*, the heat capacity - *C*<sub>p</sub>, the resistivity -  $\rho$  (referred to the initial specimen dimensions), and the temperature - *T*, were calculated.

The electrical pulse heating method makes it possible to measure the volume properties of a material (the resistivity, the enthalpy, and the specific heat). For the investigation, the pulse current heating facility described in [1] was applied. The specimen temperature was measured by the fast response pyrometer described in [2] and calibrated against the SI-10-300 temperature lamp. Temperature measurements were fulfilled with a blackbody design, that allow to measure the temperature more accurately.

The melting of the zirconium nitride investigated in the present work takes place at 2700 K, whereas, according to the published data available, the ZrN melting temperature would equal  $3250 \pm 50$  K. However, it is known that the oxygen content of 0.5-1 wt % reduces the melting temperature of the zirconium nitride by 200-300 K. In our case, the oxygen content was sufficiently high (4.05 wt %); it might serve as an explanation of that sufficient decrease in the melting temperature (by 550 K) for the investigated zirconium nitride. Furthermore, there was sufficient nitrogen excess (N/Zr) = 1.33, that is, the zirconium nitride had a super-stoichiometric composition, which would also cause a decrease in the melting temperature of the specimens as compared to the same for the stoichiometric composition ZrN.

The result obtained for the specimen pressed between two glass plates confirms that the melting begins at 2700 K.

2) The research of sintered carbo-nitride zirconium (ZrCxNy), (the thickness of the specimen is near 100  $\mu$ m) is in progress and the results will be presented at the report.

### Acknowledgments

The study is executed under support of the Russian Science Foundation in the framework of the grant No. 17-19-01099.

## References

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## **Oral Session 4: Properties of Material Science at High Temperatures III**

15:30 - 18:10 Tuesday HS P2

Chairs: H. Fukuyama, G. Pottlacher

# PMSHT - O16 15:30 - 15:50 Tuesday

Room HS P2

# THERMOPHYSICAL PROPERTY MEASUREMENTS USING THE ELECTROSTATIC LEVITATION FURNACE ON THE ISS

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The use of a containerless technique for materials processing has many technological and scientific advantages. The absence of a crucible allows the handling of chemically reactive materials such as molten refractory metals, alloys, semiconductors, or oxides and eliminates the risk of sample contamination in overheated as well as in undercooled states. The lack of a crucible also suppresses nucleation induced by the walls of a container (heterogeneous nucleation) thus increasing the possibility of producing new materials such as glasses. Several levitation methods, including acoustic, electromagnetic, aerodynamic and electrostatic have been applied for containerless processing in space as well as on the ground.

Japan Aerospace Exploration Agency (JAXA) has been designed and developed the electrostatic levitation furnace since 1993. Through a sounding rocket experiment conducted in 1997 and following ground-based research, several key technologies necessary for stable sample positioning and scientific diagnostics have been developed. Finally, an electrostatic levitation furnace for the International Space Station (ISS-ELF) has been launched in Aug. 2015, and the check-out of the facility has been conducted since Feb. 2016.

Molten oxide materials, which are very difficult to be levitated and melted on the ground electrostatic levitators, will be mainly processed in the ISS-ELF. This presentation briefly describes the ISS-ELF, status and results of check-out, and thermophysical property data obtained using this facility.

# PMSHT - 017 15:50 - 16:10 Tuesday

Room HS P2

# MEASUREMENT OF THERMAL AND RADIATIVE PROPERTIES OF LIQUIDS AT HIGH TEMPERATURE

J. Meulemans<sup>1</sup>, 2, V. Schick<sup>2</sup> and B. Rémy<sup>2</sup>

<sup>1</sup>Saint-Gobain Recherche, Aubervilliers, France <sup>2</sup>Laboratoire d'Energétique et de Mécanique Théorique et Appliquée, Vandoeuvre, France johann.meulemans@saint-gobain.com This paper describes a pulse method implemented to measure the thermal and radiative properties of semi-transparent liquids at high temperature (i.e., for temperatures between 1000 °C and 1500 °C). The liquid sample is placed in a parallelepipedic hollow cell (40 x 40 x 6 mm<sup>3</sup>) made of Platinum/Rhodium. A heat flux stimulation controlled in energy and time is generated on the front face of an experimental cell through a shuttered continuous  $CO_2$  laser beam. The temperature rise is measured on the rear face of the experimental cell with a cooled infrared camera.

The main difficulties of the non-linear parameters estimation problem arise from the geometry of the experimental cell and the coupling between the heat transfer modes (conduction, convection and radiation). The direct model implemented is three-dimensional and neglects the natural convection within the liquid due to very low Rayleigh numbers. The radiative transfer equation is solved numerically with the spherical harmonics method (PN approximation).

The identifiability of the thermal and radiative properties of semi-transparent liquids is investigated through a sensitivity analysis to the following parameters: the phonic thermal diffusivity, the heat loss coefficient, the optical thickness, the Planck number, the internal wall emissivity of the experimental cell and the maximum of the rear face thermogram.

The nominal values chosen for the parameters correspond to the configuration of the experimental set-up (dimensions, material of the experimental cell) and the thermo-physical and radiative properties of molten silicates. The influence of the optical thickness and the Planck number for a given value of the phonic thermal diffusivity (0.5  $\text{mm}^2/\text{s}$ ) is discussed.

A stochastic study of the parameters estimation is then carried out from noisy thermograms generated with the direct conducto-radiative model. The results show that the estimation of both the phonic thermal diffusivity and the grey mean absorption coefficient is possible for semi-transparent liquids at high temperature with the proposed pulse method.

Finally, we present some experimental results on molten silicates.

# PMSHT – O18 16:10 - 16:30 Tuesday

### Room HS P2

# THERMAL RADIATIVE PROPERTIES OF V-BASED ALLOYS FOR FUSION REACTORS AT WORKING TEMPERATURE

R. Fuente<sup>1</sup>, I. González de Arrieta<sup>2</sup>, T. Echániz<sup>3</sup>, I. Urcelay<sup>4</sup>, W. Ran<sup>5</sup>, H. Fu<sup>5</sup>, J. Chen<sup>5</sup>, P. F. Zheng<sup>5</sup>, M. J. Tello<sup>3</sup>, G. A. López<sup>2</sup>

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Vanadium based alloys, mainly V-Cr-Ti ones, are attractive structural materials for fusion reactors due to their low activation properties, promising radiation resistance, high temperature strength, etc. [1,2]. Among other roles and requirements for materials used in the first
wall/blanket environment the conversion of the kinetic energy of neutrons into heat and the extraction of this heat to generate power can be mentioned [3]. Therefore, the study of the thermal radiative properties at working temperatures becomes highly interesting, even more if the increase of the operational design window reaches temperatures higher than the current accepted limit of 700  $^{\circ}$ C.

In the present work the directional spectral emissivity of two V-based alloys was investigated using a self-designed high-accuracy infrared radiometer equipped with a Fourier transform infrared spectrometer [4]. The data were acquired at 700 and 750 °C. Room temperature reflectivity measurements were also performed on these alloys. One of the alloys is the typical V-4Cr-4Ti produced by melting and hot-rolling, and the other one, a V-4Cr-4Ti-1.8Y-0.4Ti3SiC2 alloy obtained by mechanical alloying and hot isostatic pressing, belongs to recently developed improved V-based materials for extreme conditions [5]. The measurements were performed under high vacuum to prevent oxidation, which significantly affects the emissivity data.

Similar directional spectra were found for both alloys, although the V-4Cr-4Ti sample showed a slight emissivity increase during the measurements due to oxidation even under turbo-molecular vacuum. Two regions were observed in the spectra according to their angular dependence. Below 4  $\mu$ m, the emissivity decreased with the angle of observation in a dielectric-like manner, whereas it followed the typical metallic behaviour above that threshold. This type of behaviour had been previously observed in Ni-based superalloys, but not in pure metals. Integration of these data allowed calculation of the total hemispherical emissivity, the most important heat transfer parameter in high temperature and high vacuum systems, such as nuclear reactors.

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## PMSHT - O19 16:30 - 16:50 Tuesday

Room HS P2

# IMPEDANCE MEASUREMENT OF ALKALI SILICATE MELTS UNDER ALTERNATING CURRENT FIELD

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## 1. Introduction

The silicate based melts are utilized in many fields such as steel smelting and glass manufacturing processes, which are microscopically consisted of silicate network structure associated with modifier cations. The fluid properties, as viscosity, of silicate melts are strongly affected by these structures, hence numerous structural analyses of the melts have been performed by using Nuclear Magnetic Resonance, Raman spectroscopy, etc., although structure analyses of the melts is time consuming. In the present work, in order to accumulate basic data for in-situ estimating the network structures of the melts, we systematically investigated the relationships between the network structures of the silicate melts and measured alternating current parameters.

#### 2. Experimental

The crucible and rod of Pt-20 mass %Rh alloy were utilized for contact materials (electrodes for a cylindrical configuration). Impedance and phase angle of the sample in the crucible were measured by an electric circuit formed by connecting Pt wires to each electrodes. The nyquist plot was illustrated from the obtained impedance and phase angle, and equivalent circuit was analyzed by fitting. The measurement samples were  $(100-n)SiO_2 - nK_2O$  (n = 20, 33.3 and 50) (mol %), and the structure of this composition has been identified. The samples were measured after 3 hours keeping at 1540 K under air.

#### 3. Results and Discussion

Fig.1 shows a typical example of the nyquist plot and the results of equivalent circuit analysis of  $66.7 \text{SiO}_2$ - $33.3 \text{K}_2\text{O}$  (mol %) melt. It was found that the estimated equivalent circuit were consisted of the resistors  $R_1$  and  $R_2$ , the electrical capacitance C and the Warburg impedance  $Z_{\text{w}}$ . Generally, it is known that the equivalent circuit can be obtained when the nyquist plot consists of a semicircular and a line part. The solution resistance, R1, decreased with increasing the amount of K<sub>2</sub>O. By contrast, the charge transfer resistance and the capacitance,  $R_2$  and C, increased with increasing the amount of K<sub>2</sub>O.



**Figure 1**. Nyquist plot for 66.7SiO<sub>2</sub>-33.3K<sub>2</sub>O (mol %) melt. and equivalent circuit calculated by fitting method.

#### 4. Conclusions

• From the obtained impedance and phase angle, we were possible to prepare a nyquist plot and to set an equivalent circuit of the melt including the electrodes.

• The equivalent circuit was represented by solution resistance, electron-charge transfer resistance and electrical capacity, etc. It was suggested that any of them may be affected the amount of alkali oxide or change of polarization by the structural change of the melts.

## ELECTRICAL CAPACITANCE MEASUREMENT FOR DUALPHASE FLUID AT HIGH TEMPERATURE

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Silicate melts found in the high temperature processes, as iron and steelmaking, other metal productions, glass smelting, solid waste melting, etc., are basically utilized and/or generated not in uniform liquid but in solid-liquid and gas-liquid dispersion system. The presence of these secondary phases in the silicate melts will affect many of heat and mass transfer properties, which will be controlled by the fraction and size of the dispersed phases.

A novel- and in situ- quantifying method for the crystallinity (solid phase fraction) of supercooled silicate melts was proposed by the measurement of their electrical capacitance at high temperature. It is well known that the electrical capacitance of ionic liquids is generally much higher than that of solids owing to the differences in their respective polarization mechanisms. These differences were exploited as a sensitive indicator of the crystallization of silicate melts in an experimental furnace equipped with an electrical capacitance measuring system.

The system comprised a Pt-based alloy crucible and a rod connected to a LCR meter. For the calibration of electrode composition employed, a theoretical capacitance model based on the dimensions of electrodes was proposed. It was found that the calculated capacitance values in accordance with the theoretical model and dielectric constants of samples successfully reproduced the experimental values of various liquid phases and aqueous suspensions at r.t.

Then, for the estimation of crystallinity in super-cooled silicate melts, Nielsen's equation was employed, which can allow us to calculate the dielectric constant of silicate-based suspension. Consequently, the calculated capacitance values successfully reproduced the experimental values at h.t., which suggests capacitance can provide crystallinity of silicate melt even at high temperature. Then after, an experimental setup for simultaneous measurements of viscosity and capacitance was developed for silicate melts at high temperature, which can provide widerange of rheological information of silicate melts with decreasing temperature in super-cooled region, namely, the fluid transition from Newtonian to non-Newtonian associated with in-situ crystallinity measurement by the strategy proposed in the present work.

## PMSHT - O21 17:10 - 17:30 Tuesday

Room HS P2

# TEMPERATURE DEPENDENCE OF THERMAL CONDUCTIVITY FOR IRON OXIDE SCALE

M. Li<sup>1</sup>, R. Endo<sup>1</sup>, M. Akoshima<sup>2</sup>, M. Susa<sup>1</sup> <sup>1</sup>Tokyo Institute of Technology, Tokyo, Japan <sup>2</sup>National Institute of Advanced Industry Science and Technology, Tsukuba, Japan li.m.ae@m.titech.ac.jp Thermal conductivity of oxide scale formed on the surface of steel slabs during the hot-rolling process is a decisive factor to improve the quality of steels. There are some reports about thermal conductivity determinations of iron oxides, most of which have used sintered FeO,  $Fe_3O_4$  and  $Fe_2O_3$  as samples.<sup>1</sup> However, actual oxide scale consists of these oxide layers and contains voids as well. It is also very difficult to estimate apparent thermal conductivity of actual oxide scale from the thermal conductivity and volume fraction of each oxide phase. Against this background, it is practically useful to measure the apparent thermal conductivity of entire oxide scale on steel as a function of temperature. Consequently, as a first step, the present work aims to measure the thermal conductivity of thermally grown FeO scale on steel using the newly-developed quasi-steady state hot plate method<sup>2</sup> and the laser flash method.

Samples used were iron plates (99.99 % purity) having thermally grown FeO scale about 50 and 100  $\mu$ m thick. The quasi-steady state hot plate method was based upon the principle of the Bunsen Ice Calorimeter, and is outlined below: A container (calorimeter) that is filled with an ice/water mixture inside is hermetically sealed by a copper plate with fins, upon which a sample is placed. A heater is placed upon the sample, and then heat is transferred *via* the sample to the ice/water mixture to melt part of ice. The amount of ice melted provides the heat flux across the sample. In this work, the amount was measured as the volume change of the ice/water mixture. Thermal conductivity of the sample was derived from the difference between heat fluxes obtained in two measurements using samples with different thicknesses. At the same time, the thermal diffusivity of FeO scale was also measured by the laser flash instrument with the curve fitting method and multi-layered model. This experiment was carried out in a vacuum lower than  $1.2 \times 10^{0}$  Pa to avoid further oxidation of samples. The thermal diffusivity was converted to the thermal conductivity using the density and heat capacity of FeO.

Values of thermal conductivity for FeO scale at room temperature have been derived as  $6.44 \,\mathrm{W}\,\mathrm{m}^{-1}\,\mathrm{K}^{-1}$  from the quasi-steady state hot plate method and  $2.28 \,\mathrm{W}\,\mathrm{m}^{-1}\,\mathrm{K}^{-1}$  from the laser flash method. This difference is still under consideration. The thermal conductivity of FeO scale increases up to 673 K, beyond which it decreases and keeps constant above 1023 K.

## Acknowledgment

This work was conducted as one of the projects in Research Group II, the Iron and Steel Institute of Japan (ISIJ) and was partly supported by the 25th ISIJ Research Promotion Grant.

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### APPLICATION OF ELECTRICAL-OPTICAL HYBRID PULSE-HEATING METHOD TO THERMAL DIFFUSIVITY MEASUREMENT ON IRON OXIDE SCALE

Y. Yang<sup>1</sup>, H. Watanabe<sup>2</sup>, M. Ueda<sup>1</sup>, M. Hayashi<sup>1</sup>, M. Susa<sup>1</sup>, R. Endo<sup>1</sup>

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Values of thermal diffusivity ( $\alpha$ ) of FeO scale are required for stricter temperature control of steel in the water-spray cooling process after hot rolling. There have been several reports about values of  $\alpha$  for sintered FeO and thermally grown FeO samples at different temperatures; however, these data are supposed to be affected by decomposition of FeO.<sup>1</sup> To avoid such a situation, the electrical-optical hybrid pulse-heating method has been applied to the measurements on FeO scale,<sup>2</sup> in which values of  $\alpha$  for FeO scale were measured at around 800 K within a time as short as 1 s to minimize the decomposition. However, the values derived had considerable uncertainty, which might be because FeO scale was as thin as 20.5  $\mu$ m. The objective of this study is to obtain more accurate values of  $\alpha$  for FeO scale at high temperature using thicker FeO scale samples in the same method.

Iron plates (99.99 % purity, ca. 10 mm x 40 mm x 0.5 mm) were oxidized so as to form FeO scale thicker than 50  $\mu$ m on both surfaces. The sample was rapidly heated to a steady experimental temperature by Joule heating in a vacuum chamber, and then one surface of the sample was irradiated by a laser pulse, followed by temperature recording of the rear surface. The value of  $\alpha$  for the sample was derived according to the principle of the flash method.<sup>3</sup> The value of  $\alpha$  for FeO scale was derived from the difference between values of  $\alpha$  for samples with and without FeO scale, based on the method introduced in ISO 18555.<sup>4</sup>

Values of  $\alpha$  for the samples with FeO scale have been derived as  $4.09 \times 10^{-6} \text{ m}^2/\text{s}$  for 692 K and  $4.15 \times 10^{-6} \text{ m}^2/\text{s}$  for 745 K in the present work, while the previous work reported a value of  $8.29 \times 10^{-6} \text{ m}^2/\text{s}$  for 804 K.<sup>3</sup> On the other hand, values of  $\alpha$  for iron have been reported as  $1.02 \times 10^{-5} \text{ m}^2/\text{s}$  for 692 K,  $9.51 \times 10^{-5} \text{ m}^2/\text{s}$  for 745 K and  $8.63 \times 10^{-6} \text{ m}^2/\text{s}$  for 804 K.<sup>5</sup> Comparison between the present and previous data indicates that the difference between values of  $\alpha$  for samples and iron is larger in this work, which is beneficial to obtain more accurate values of  $\alpha$  for FeO. These values of  $\alpha$  for the samples with FeO obtained in this work have produced values of  $\alpha$  for FeO as  $8.58 \times 10^{-7} \text{ m}^2/\text{s}$  for 692 K and  $9.01 \times 10^{-7} \text{ m}^2/\text{s}$  for 745 K.

#### Acknowledgment

This work has been conducted as one of the projects in Research GroupII, the Iron and Steel Institute of Japan (ISIJ) and was partly supported by the 25th ISIJ Research Promotion Grant.

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### HIGH-TEMPERATURE MASS SPECTROMETRY OF LASER EVAPORATED $\mathsf{ZRC}_{\mathbf{x}}$

A. M. Frolov<sup>1,2</sup>, M. A. Sheindlin<sup>1</sup>, T. M. Falyakhov<sup>1</sup>

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The present study is aimed at the analysis of molecular composition of zirconium carbide vapors up to 4200 K. The earlier studies of vapor composition of zirconium carbide are dated back to the beginning of 70's where the sublimation of solid zirconium carbide was investigated using conventional Knudsen cell mass spectrometry limited to temperature of *ca* 3000 K.<sup>1</sup> Nowadays this temperature limit can be easily overcome using laser induced evaporation. The current method is based on millisecond-pulse laser heating combined with time-of-flight mass spectrometry developed recently for investigation of refractory materials<sup>2</sup> namely graphite up to 4100 K and UO<sub>2</sub> up to 3500 K.

The similar approach was developed and applied in the present work to examine the vapor composition of zirconium carbide at temperatures much above 3400 K and higher towards high temperature evaporation of liquid ZrC. Samples of various starting composition ranging from  $ZrC_{0.65}$  to  $ZrC_{1.0}$  within the homogeneity domain were investigated. Brightness temperature was measured by ad hoc fast pyrometer operated at the wavelength of 908 nm. In order to determine the true temperature of the sample some special extra measurements of spectral emissivity of ZrC in the domain of the melting point were performed using laser melting and multiwavelength pyrometry.<sup>3</sup> Temperature dependences of relative partial pressures of  $C_1 - C_3$  molecules, zirconium isotopes, ZrC, ZrC<sub>2</sub> and Zr<sub>2</sub>C species were obtained. The measured sublimation enthalpy of an atomic Zr during evaporation of ZrC<sub>0.85</sub> sample revealed to be in a good agreement with the value obtained using Knudsen cell evaporation.<sup>1</sup> The atomic ratio C/Zr in the gas phase in a wide temperature range comprising evaporation of the solid and liquid ZrC was evaluated. It was found that molecular composition of zirconium carbide vapor does depend only on temperature of evaporating surface.

## Acknowledgment

This work was supported by the Russian Science Foundation, project no. 14-50-00124.

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## **Emittance, Emissivity (EE)**

## Oral Session 5: Emittance, Emissivity

10:05 - 13:05 Wednesday HS P2

Chairs: J. Hartmann, K. Boboridis

## EE - O1 10:05 - 10:25 Wednesday

### Room HS P2

## RADIATION RATIO THERMOMETRY ON MIXED BLACK-NONBLACK TARGETS

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Radiation ratio thermometry, commonly referred to as two-color or ratio pyrometry, involves measuring thermal radiance at two different wavelengths and inferring the temperature from the ratio of these spectral radiances [1]. The technique's strength lies in the fact that it is insensitive to disturbances that affect both spectral radiances to the same degree, leaving their ratio unchanged. For instance, it finds application in the case of small, moving targets that only partially fill the field-of-view, targets that are partially and perhaps intermittently obscured, or targets occluded by gray absorbers. In all cases, however, the ratio of the target's directional spectral emittance at the thermometer's two operating wavelengths must be known a priori or determined by some sort of in-situ calibration and remain constant over the temperature range of interest.

Here, we model the case of a radiation ratio thermometer aimed at a blackbody cavity with an aperture that is smaller than the thermometer's measurement spot, whose residual area is then filled by nonblack material. We examine the effect of this area's nonblack spectral emittance on the apparent temperature measured by the ratio thermometer and compare to the case of using a narrow (single) band thermometer instead. We then validate the model with measurements performed with both types of radiation thermometers, i.e. ratio and single band, on metallic Knudsen cells up to  $2000^{\circ}$ .

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#### EE – O2 10:25 - 10:45 Wednesday

## HIGH TEMPERATURE TEST-RIG FOR EMISSIVITY AND NON-CONTACT TEMPERATURE MEASUREMENTS

J. Manara<sup>1</sup>, T. Stark<sup>1</sup>, M. Zipf<sup>1</sup>, M. Arduini<sup>1</sup>, H.-P. Ebert<sup>1</sup>, J. Hartmann<sup>2</sup>

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An important approach to improve energy efficiency is the thermophysical improvement of materials, components and systems for usage in high temperature applications, particularly in terms of reducing the heat transfer between the surfaces. As the contribution of thermal radiation to the total heat transfer significantly increases with increasing temperature, the emissivity of the surfaces need to be precisely characterised at high temperatures. Furthermore, reliable in-situ determination of temperatures in high temperature applications are important for advanced process control and accordingly enhanced efficiency.

Therefore, in this work an improved laboratory test-rig has been developed which enables the measurement of the emissivity of surfaces at high temperatures for materials characterisation as well as the determination of surface temperatures for process optimisation.

Firstly, the emissivity of specimen surfaces can be measured by a direct radiometric method under vacuum using a spectrometer in a black body environment at ambient temperature. The emissivity can be derived in dependence on temperature up to 2400 K, on wavelength between 0.5  $\mu$ m and 20  $\mu$ m and on emission angle up to 90°. Secondly, the temperature of specimen surfaces with known emissivity can be determined contactless up to 2400 K using several radiation thermometers. For this purpose, the surrounding conditions can be customized by adjusting different hot gas atmospheres and hot enclosures, which are usually present in high temperature applications or processes. This enables the reproduction of industrial and process conditions in the laboratory with the aim of transferring the derived results for non-contact temperature measurements to on-site and in-situ measurements in industrial applications.

Thus, the main advantages of the test-rig are the facilities for varying the surrounding conditions between vacuum and gas atmosphere on the one hand and the temperature of the black enclosure between ambient and high temperature on the other hand. Moreover, with this test-rig the applied spectrometer and the radiation thermometers are detecting the emitted radiation simultaneously in each configuration for gaining additional exploitable information.

The set-up of the developed test-rig will be described together with the two configurations for measuring firstly the emissivity under well-defined conditions as explained above and secondly the temperature under application conditions, which occur in gas turbine engines (such as hot infrared active gases and hot environment). The resulting spectral-directional emissivities are presented for metal-based and ceramic-based materials, which are used in gas turbines. Furthermore, non-contact temperature measurements on the same specimen using two radiation thermometers, which are sensitive around 1  $\mu$ m and around 10  $\mu$ m, respectively, are presented. The derived results show a significant influence of the surrounding conditions and the spectral range on the detected signal, which has to be considered for proper data analysis and accurate temperature measurement. Finally, the measurement uncertainties for both configurations and surrounding conditions are introduced and discussed.

## SPECTRAL AND HEMISPHERICAL EMISSIVITY IN NEW AIR-RESISTANT SELECTIVE ABSORBERS

T. Echániz<sup>1</sup>, I. González de Arrieta<sup>2</sup>, R. Fuente<sup>3</sup>, H. C. Barshilia<sup>4</sup>, G. A. López<sup>2</sup>, M. J. Tello<sup>1</sup>

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In order to analyze heat losses in solar absorber surfaces (SAS) used in solar thermal collectors (STC), a complete knowledge of the radiative properties of the coating structure is essential for their use in high-temperature in the solar thermal energy industry. However, a systematic study of direct spectral emissivity as a function of the temperature was not performed until recently.<sup>1,2</sup> Usually, the values of emissivity at working temperatures (between 400 and 600 °C) are obtained by extrapolating reflectivity values obtained at room temperature, which can introduce significant errors in the final emissivity value estimation. These errors are mainly due to the assumption that the spectral emissivity measurements between 10 and 80° that allow us obtaining the hemispherical emissivity. These measurements were made between 200 and 500 °C and 1.43 and 25  $\mu$ m showing promising results. They were performed in both vacuum and in air for a new set of tandem absorbers consisting of W/WAIN/WAION/AI2O3 nanometric layers and in their substrate (SS316L).<sup>3,4</sup> The coatings were prepared by DC/RF magnetron sputtering. Their thermal properties stability under an air atmosphere was studied and no significant changes were observed.

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### EE – O4 11:05 - 11:25 Wednesday

## DEVELOPMENT OF A SAMPLE HOLDER FOR THE EMISSIVITY MEASUREMENT OF SEMITRANSPARENT MATERIALS

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Materials which partially transmit as well as partially absorb incident electromagnetic radiation are known as semitransparent materials. Active thermography and nondestructive testing are increasingly applied when observing and analysing semitransparent components.<sup>1</sup> Furthermore, the knowledge of the emissivity of components, which are used as refractive or transmitting optical elements in the mid infrared wavelength range, is often a requirement when designing and operating critical optical systems. Hence, in order to obtain quantitative data with small uncertainties in the preceding applications, knowledge of the emissivity is required. For this purpose, the facilities for the measurement of emissivity<sup>2,3</sup> of the PTB were expanded to enable emissivity measurements of semitransparent samples.

For the measurement the sample is heated between two annular heating plates to a temperature distributed as homogenous as possible within the sample. This can be done in a temperature range from 10 °C to 90 °C. From the backside the sample is, additionally, irradiated by a black flat plate radiator operated in the temperature range from -50 °C to 90 °C. Its radiation enters the sample and the resulting spectral radiance, which is a combination of the transmitted radiation of the flat plate radiator and the emitted radiation from within the sample is measured by a Fourier transform-infrared spectrometer (FTIR).

A corresponding sample holder was designed, optimized by simulations and realized. The sample holder's heated components have a complex internal structure to achieve a good thermal uniformity. These parts were manufactured by selective laser melting (SLM) of copper at the Fraunhofer Institute for Production Systems and Design Technology (IPK).<sup>4</sup>

To evaluate the data measured with the newly designed sample holder, a simple, mathematical model of radiative transfer with emission was derived.

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#### EE – O5 11:25 - 11:45 Wednesday

## DIRECTIONAL ROADWAY EMISSIVITY MEASUREMENT FOR ROAD SURFACE TEMPERATURE MEASUREMENT

Room HS P2

N. Lalanne<sup>1</sup>, M. Marchetti<sup>2</sup>, L. Ibos<sup>3</sup>, J. P. Monchau<sup>1</sup>, B. Saintot<sup>2</sup>

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Winter risk is a recurring problem that affects economy. The massive salting of roads modifies the ecology of soils, surface waters and groundwater. To mitigate this, thermal mapping of roads is a solution that enables to predict the risk of ice storms and limit the salting to what is strictly necessary. To achieve an unbiased result it is necessary to know the thermal behaviour of the road.

In order to measure the surface temperature of the road with a radiative method, its emissivity and the radiation from the half space seen from the surface have to be determined. Since the thermal and environmental characteristics of the road may change along the section considered, the temperature measurement must be carried out on the entire road. This method is conventionally called "thermal mapping". It consists in measuring the radiation emitted from the road using an apparatus set on a vehicle. The first objective is to determine the directional emissivity of the road in the spectral band and in the look direction of the detector. The second objective is to determine the illumination of the target surface while the vehicle is in motion. A method grounded on an infrared camera combining the measurement of environmental radiation and a calibration in the process of acquisition is shown here.

This study presents directional emissivity measurements carried out in the laboratory on road samples, both in broadband and in the spectral band of the thermal camera that was used. Spectral measurements have also been made. To complete these measurements, directional emissivity was measured in the 8 to 14  $\mu$ m band according to the function of the incidence on representative samples.

These directional emissivity values have been used to correct the surface temperature measurements made on the roadway in the city of Paris. Measurements and an aerial thermography campaign have been carried out simultaneously. These data are compared with those acquired by a radiometer.

### EE – O6 11:45 - 12:05 Wednesday

#### EMISSIVITY ESTIMATION IN BUILDING APPLICATIONS

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Building measurements are more and more interested in materials thermophysical properties after the global awareness of the energy saving obligations. The actual Built2Spec EU Project is concerned by reducing the performance gap and quality check enhancement. In this framework thermophysical properties should be well determined and shared on a work platform.

In thermophysical properties estimation, one of the most interesting parts is to assess the heat transfer on a wall surface to be characterized. This is highly influenced by the emissivity value. In this work we present a dual method based on measurements and analytical calculations to estimate the emissivity of a surface.

A laboratory test is performed to observe a thermal scene heated by an infra-red lamp. Different sensors were used: thermocouples and Heat flow meters. These lasts were covered each by a black paint and an aluminium tape to make them emissive and reflective successively. Heat transfer analysis on a boundary surface considers radiative and convective balance. Thus, a direct analytical solution is proposed for the performed test. Then, measurements were compared to the analytical solution to estimate the mean emissivities of heat flow meters surfaces.

The method validation can be a first step to a larger application. In fact, it can be considered as a complete investigation tool if the sensor surface is the same as the studied wall one. Otherwise it can provide a well approximated emissivity to enhance existing methods limited by low emissive surfaces.

## EE – O7 12:05 - 12:25 Wednesday

Room HS P2

## A FACILITY FOR HIGH TEMPERATURE EMITTANCE WITH EMPHASIS ON SELECTIVE LASER MELTING

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The National Institute of Standards and Technology (NIST) is currently developing a facility for the study of the process of selective laser melting (SLM) used in powder-bed fusion for additive manufacturing. This project is a collaborative effort exploiting both the Engineering Laboratory's (EL) and Physical Measurement Laboratory's (PML) expertise in instrument design and measurement science. The primary function of the Additive Manufacturing Metrology Testbed (AMMT) is to provide a platform for developing and testing process monitoring and control techniques that can be used to improve SLM build quality and reliability. PML is further expanding the purpose of the AMMT by increasing the radiometric capabilities to include means for emissivity, radiance and temperature measurement with the Temperature, Emissivity of Melts, Powders and Solids (TEMPS) system being integrated into the AMMT. With the commissioning of the TEMPS system, PML will expand its established emittance and radiance measurement capabilities to include higher sample temperatures and the additional sample forms of powders and liquids, as well as providing traceability for the primary functions of the AMMT.

The TEMPS system under development must accommodate not only the challenges of high sample temperatures, but also those associated with the SLM process like debris, contamination, high speed source motion and nonuniformity. Beyond SLM however, the TEMPS system provides a platform for high temperature emittance measurements of materials of a variety of forms in vacuum and/or inert atmospheres, giving PML the capabilities necessary to cater to customer requirements that are currently out of reach. In this paper, we shall present an overview of the AMMT facility and TEMPS system with an emphasis on the measurement techniques required for the SLM environment. In addition, we shall provide results from the table top commissioning of the TEMPS optical system.

## EE - 08 12:25 - 12:45 Wednesday

Room HS P2

# NEW FACILITY FOR THE MEASUREMENT OF THE HIGH TEMPERATURE SPECTRAL EMISSIVITY AT NIM

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Accurate emissivity measurement at high temperature, especially above 1000 °C plays a vital role in the high temperature processing, thermal modelling and radiation thermometry. However, it's extremely difficult to achieve a satisfying result, and few results were published before.

The key issue of accurately measuring the high temperature emissivity is to maintain a hot surface without reflection of hot environment, precisely determine the surface temperature and avoid material evolution due to passive or active oxidation. In this paper, a new facility is established at NIM, using the integral blackbody technique in combine with vacuum chambers to solve such problems.

The spectral emissivity of graphite in the temperature range  $(1000 \sim 1500)$  °C and spectral range  $(500 \sim 1600)$  nm is measured. The results and the associated uncertainty of the measurement is rigorously estimated and will be reported in this paper.

#### EE – O9 12:45 - 13:05 Wednesday

## A NEW EMISSIVITY MEASUREMENT PREDICTION ROUTE FOR COAL DEPOSIT SYSTEM

Room HS P2

YZ Chai<sup>1</sup>, HT Yu<sup>1</sup>, W Dong<sup>2</sup>, JH Wang<sup>2</sup>, YY Duan<sup>1</sup>, Z Yang<sup>1</sup>

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Radiation heat transfer is important in particle aggregate systems in many fields such as coal deposit, soot, aerosol etc. The emissivity of the particle aggregate system plays a vital role in the heat transfer process analysis of these systems. However, the emissivity measurement of the particle aggregate systems is quite complicated, especially at high temperatures. In this paper, we develop a theory model to predict the optical properties of the particle aggregate systems which helps to understand the radiation heat transfer mechanism of such systems. The Multiple Sphere T-Matrix (MSTM) method is used to calculate the electromagnetic scattering and absorption properties of coal deposit system as a typical aggregate sphere system, the different structures, particle size, and component aggregate systems are considered in the method. With the MSTM results, the Discrete-Ordinates Method (DOM) is used to calculate the emissivity of the system. With the ideal model, we can predict the optical properties of the particle aggregate systems with higher accuracy than the traditional method such as Mie theory. To verify the reliability of this model, the emissivity measurements of different size and component particles covered nickel planes in 500-900 K are carried out. A Fourier transform infrared spectrometer is used to compare the spectral radiation of the sample and a blackbody at the same temperatures. The experimental results agree well with the theoretical model in the spectral range 3-14  $\mu$ m.

## New Measuring Techniques (NMT)

**Oral Session 6: New Measuring Techniques** 

10:30 - 12:50 Thursday HS P2

## NMT – O1 10:30 - 10:50 Thursday

Room HS P2

Chair: J. Blumm

## MEASUREMENT OF PHYSICAL PROPERTIES ON THIN FILM MATERIALS

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Due to new research efforts in various fields with a focus on size effects, there is a growing need for measurement setups dedicated to samples with small geometrical dimensions like thin films and nanowires with considerably different physical properties than bulk material. The characterization of these samples is important to learn more about their structure and conduction mechanism but also important for technical applications e.g. in the semiconductor industry.

We report about new developments to characterize thin films in the range from 10 nm to 200  $\mu$ m. The first one is a Transient Thermoreflectance Method which enables the measurement of the thermal conductivity on thin films with high accuracy. On various application examples it can be proved that the thermal conductivity is strongly dependent on the thickness of the material. The thermal conductivity of some thin film thermoelectric materials decreases with decreasing sample thickness by one or two orders of magnitude.

The second approach is a chip based system which measures simultaneously the electrical and thermal conductivity, the Seebeck Coefficient and the Hall Constant of a thin film sample in the temperature range from liquid nitrogen up to 350 °C. Due to the simultaneous measurement at only one sample, errors caused by different sample compositions, different sample geometries (thickness) and different heat profiles can be avoided. The system consists of two main parts, a structured Si-wafer and a suitable measurement setup. The sample deposition and handling is kept easy and optimized to meet a very broad range of use.

### NMT – O2 10:50 - 11:10 Thursday

#### MEASUREEMENT OF SOFT CLAY LOAM MATERIALS BY TRANSIENT METHOD

Room HS P2

Vlastimil Boháč<sup>1</sup>, Peter Dieška<sup>2</sup>, Viliam Vretenár<sup>1</sup>, Ján Hudec<sup>1</sup>, V. Lukáč<sup>3</sup>

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The measurement of soft materials having plastic properties is more or less difficult as they can change the shape during the long time monitoring measurements. The example for this kind of measurements is the drying of clay loam from plastic to up to dry state. The problem is when the specimen is not keeping the shape. Usually, the specimen geometry e.g. the thickness is expected to be the constant during all the time of recording data. In a case of plastic clay loam, it can change the form during the measurement because the material is squeezing even under the free gravity condition. Thus the specimen surface wall should be reinforced by special dimensionally well-defined thin wall container to neglect the mass of it. For this kind of experiment, the special container consisting of two thin tube rings has been constructed. The soft plastic clay loam material fill-up the inner space of tube rings in such a way to fulfill the geometry conditions given by theoretical model for this method. The heat source was inserted in between the tube rings and the thermocouple was inserted through the drilled openings at defined distance from the heat source. This distance represents the thickness of tested specimen.

The need of thermophysical properties measurement of the soft clay loam is due to the interest to use it as the seasonal heat storage material below the buildings. The measured clay loam in the free nature contains some moisture have quite high values of specific heat. The ide to use it as the seasonal heat storage material is promising. The heat exchangers made in the form of soil screws drilled down to soil in length of several meters are the cheap solution in comparing large and expensive water containers besides the buildings. The transient methods were used to get the thermophysical parameters of these materials. We use the pulse transtient technique<sup>1</sup> and planar hot disk technique developed recently.<sup>2</sup> Specimens were drilled out from the depths 50, 150 and 250 cm from the surface.

#### Acknowledgement

This work was supported by the Slovak Academy of Sciences under the contract No. 2/0192/17 "Development of sensors and measurement methods for transient techniques for the measurement of thermophysical properties of materials and their application for seasonal storage of heat energy" in cooperation with ETOP Alternative Energy, s.r.o. (ltd.) with the VA research agency support.

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### NMT – O3 11:10 - 11:30 Thursday

Room HS P2

## MORPHOMETRIC PROPERTIES IN DOUBLE-BEAM OPTICAL DILATOMETRY MEASUREMENT OF THERMAL EXPANSION

Daniele Paganelli<sup>1</sup>, Piero Scotto<sup>1</sup>, Mariano Paganelli<sup>2</sup>

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This study demonstrates how valuable morphometric information about sample surface can be collected during an expansion test with dual beam optical dilatometer, and how these can be used to significantly improve thermal expansion measurements.

Optical dilatometry measures the dimensional changes of a solid sample framing two opposite sides of a sample, placed vertically or horizontally, and calculates its displacement relative to the start of the measurement without direct contact with the measurement system. The visible portion of each side of the sample is around 250 micron of length and 150 micron of width (sample "profile"). At this scale, even finely machined samples show surfacial defects of several tens of microns. This can induce a measurement error up to two orders of magnitude bigger than the resolution of the instrument, regardless if optical or pushord.

Defects are not static: as the sample expands isotropically, it also expands vertically and possibly brings into the framed area unexpected surface features. Also, when at high temperatures the sample starts deforming, the framed profile can change its angle with respect to the initial profile. All these dynamics can produce an apparent expansion or contraction.

Statistical image analysis techniques are applied to the visible sample portion, in order to filter out both noise and morphologic defects.

An iterative noise-reduction algorithm allows to determine a stable sample's mean position. Each iteration consists of a linear regression to calculate the best line approximating the sample's profile, combined with the exclusive filtering of most distant points from the fitted line. Effective angular correction is then provided by calculating displacement as mean line-to-line distance between the current profile fit and the initial fitting line - recorded at the start of the measurement.

The method has been applied both on standard samples and industrial ceramic materials. The positive impact on reducing the influence of samples preparation process, and of improved stability and accuracy of the final thermal expansion measurement were evaluated and are herein presented.

## NMT – O4 11:30 - 11:50 Thursday

### STUDY ON OPTICAL MANIPURATION FOR MICRO OPTICAL DIFFUSION SENSOR

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The diffusion coefficient is important parameter for the analysis of the conformation changes of bio-sample such as protein. An irregular structural conformation of protein causes diseases such as Alzheimer and Parkinson's disease. Therefore, the measurement of the diffusion coefficient benefits a clinical diagnosis and drug discovery. In these aspects, we have developed a micro optical diffusion sensor (MODS) using laser induced dielectrophoresis, enabling high speed measurement of bio-sample such as a protein with a small sample volume. Figure 1 shows a schematic image of the diffusion coefficient measurement principle of MODS. The lattice-shaped electrical conductivity distribution is generated by irradiating the optical fringe pattern on the photoconductive layer, therefore the bio-sample is manipulated along the optical pattern based on the laser-induced dielectrophoresis. When the probing laser beam passes through the concentration distribution, the diffracted light is generated. By stopping the AC voltage between transparent electrodes and the irradiation of the excitation laser, the mass diffusion phenomenon occurs. By observing the diffracted light, the diffusion coefficient can be obtained. In this paper, we proposed an optical manipulation technique for measurement of the diffusion coefficient of low concentration sample. Figure 2 shows an image of concentration distribution of sample observed using the differential interference optical system. The condition of manipulation process for high sensitive measurement is easily observed in real time.



Figure 1. Principle of MODS.



Room HS P2

**Figure 2**. Image of concentration distribution.

## Acknowledgment

This work has been supported in part by Grants-in-Aid for Scientific Research (S)(No. 24226006) and Grant-in-Aid for Challenging Exploratory Research (No. 15K13890) from the Japan Society for the Promotion of Science (JSPS). Fabricating the device has been supported in part by Kawasaki city subsidy for promoting R&D of nano?micro technology by SMEs based on academia-industry cooperation, the academic consortium for nano and micro fabrication of four universities and Kyodo International, Inc.

# TEMPERATURE DEPENDENCE OF PHOTOCONDUCTIVE THIN FILM FOR MICRO OPTICAL DIFFUSION SENSOR

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The diffusion properties of the bio-sample (*e.g.* the protein) are crucial to understand the protein dynamics. Several diffusion sensing techniques have been developed for the bio-sample analysis, such as the dynamic light scattering, however, the diffusion sensing techniques, which are sensitive to the change of the structure in a short time (ms  $\sim$  s) or applicable to the purpose of the point-of-care testing (POCT), have not been established. In order to realize a high-speed, additives-free sensing of the nano-size bio-sample, *e.g.* the protein aqueous solution, a micro optical diffusion sensor (MODS) has been developed. The proposed method realizes a high-speed sensing by forming the microscale lattice-shaped concentration distribution using the optoelectronic manipulation, and observing the diffusion phenomena by the diffractive detection.

As a photoconductive layer, which is required for a microfluidic device utilizing the optoelectronic manipulation, the hydrogenated amorphous silicon deposited by a plasma-enhanced chemical vapor deposition is generally used. For the optoelectronic manipulation of nanoscale bio-sample, the photoconductive layer with a proper photoconductivity is required. The photoconductive layer deposited by the reactive RF magnetron sputtering method is proposed for the easy tuning of the properties.

In this study, the photoconductive layer is deposited under several sputtering conditions. In order to investigate the applicability to the nanoscale bio-sample manipulation and the diffusion sensing, the measurement devices are fabricated by changing the property (the photoconductivity and the thickness of the photoconductive layer, the height of the microchannel). The temperature dependence of the photoconductivity is measured to validate the fabricated hydrogenated amorphous silicon, and the feasibility of the proposed method for the diffusion sensor is experimentally confirmed.

## Acknowledgment

This work was partially supported by JSPS KAKENHI Grant Number JP24226006, JP15K13890, and Kawasaki city subsidy for promoting R&D of nano-micro technology by SMEs based on academia-industry cooperation. The microfabrication of this work was conducted at the clean room in "Global nano micro technology business incubation center (NANOBIC), Kawasaki city, Japan" supported by the academic consortium for nano and micro fabrication of four universities (Keio University, Waseda University, Tokyo Institute of Technology, and the University of Tokyo).

### 3-D THERMAL DIFFUSIVITY MEASUREMENT AND EVALUATION OF CFRTP'S FIBER ORIENTATION WITH THERMOGRAPHY

Room HS P2

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In recent years, the requirement to reduce the weight of automobiles has accelerated the usage of carbon fiber materials. Particularly, CFRTP (Carbon fiber reinforced thermoplastic), which is reinforced by discontinuous fiber, has attracted attention as it can be molded into complicated shapes in a short amount of time. Present day, LFT-D method (Long fiber thermoplastic-direct method), a method for producing CFRTP is being extensively researched.<sup>1</sup> There is a drawback in this method. When a material consisting of fibers and resins is extruded, towards the flow direction, there is a possibility that the local strength of the molded sample might decrease. In order to guarantee the quality of the molded sample, rapid evaluation of the fiber orientation becomes necessary. Currently, the visualization method using X-ray computed tomography is very effective. This method can evaluate the three-dimensional fiber orientation distribution of carbon fiber reinforced plastics (CFRP).<sup>2</sup> However, it takes a long period of time to measure a specimen of considerable area, such as automobile parts. Therefore, in this report, a new non-destructive inspection method using thermal anisotropy measurement method was proposed.

In this method, a three-dimensional thermal diffusivity measurement method using lock-in thermography is applied as a non-destructive inspection method for evaluating fiber orientation in a carbo-based composite material. For measurement of thermal diffusivity, a laser spot heating method is used. This method measures the thermal diffusivity by forming a periodic point heat source with a laser and measuring the phase lag of unsteady heat conduction occurring in the sample. The experimental apparatus comprises a diode laser, function generator, microscope, pc, and thermographic camera. The surface of a sample is heated periodically by a laser spot, and the thermal response on the rear side of the sample is measured by a lock-in thermographic camera to obtain thermal diffusivity distribution. This thermal diffusivity angular distribution is directly related to the fiber orientation distribution (FOD). In this study, FOD density function can be obtained to fit the thermal diffusivity angular distribution. At first, the validity of the proposed method was confirmed by using a unidirectional (UD) CFRP sheet whose fiber orientation was known. The FOD of the UD sample can be estimated within 2.1 degree at the maximum. Furthermore, the feasibility of wide-area measurement was shown from measurements of CFRTP sheet whose orientation is unknown. However, there was a problem that the dispersion of the fiber orientation cannot be evaluated directly from the thermal diffusion behavior. Finally, the correction method was reported using the anisotropic ratio of carbon fiber's thermal diffusivity.

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### NMT – O7 12:30 - 12:50 Thursday

## A NOVEL TECHNIQUE OF IN-PLANE THERMAL DIFFUSIVITY MEASUREMENT OF THIN FILMS USING THE FLASH METHOD

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The flash method<sup>1</sup> has been extended to measure thermal diffusivity in the radial direction of thin films with substantial surface heat losses. A small doughnut shape portion of the front surface of the sample is exposed to the laser light and resulting temperature rise is recorded on a small radius area on the opposite side of the sample. The thermal diffusivity is calculated using a novel mathematical model based on so called "fin approximation", when the axial temperature gradient in the sample is negligible small in comparison with the radial gradient. The technique was experimentally verified on OFHC Copper with foils of available thicknesses ranging from 25  $\mu$ m to 0.5  $\mu$ m. Results show that in-plane thermal diffusivity of thin film samples can be measured without accounting for actual sample thickness. This technique has been applied to determine in-plane thermal diffusivity of graphite/graphene-based foils.

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Room HS P2

## **POSTER CONTRIBUTIONS**

Chair: G. Pottlacher

## Fluids and Properties Fluids (FPF)

### FPF – P1

#### First Floor

## CALORIMETRIC MEASUREMENT OF MELTING TEMPERATURES AND ISOBARIC HEAT CAPACITIES IN HYDROCARBON MIXTURES

J.H. Oakley, T.J. Hughes, S.Z. Al Ghafri, B.F. Graham and E.F. May

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There is a lack of physical property data at pressures above the critical point for multicomponent hydrocarbon mixtures despite their importance in the design of gas gathering, treating and processing equipment. Consequently, this poor understanding of physical properties can lead to over-design and higher capital and operating costs in gas plant facilities. Additionally, poor understanding of the solid-liquid equilibria (SLE) in hydrocarbon mixtures can cause freeze-out of heavy hydrocarbons within liquefied natural gas production facilities resulting in shutdown of the plant.

A differential scanning calorimeter (DSC) was utilised to measure the melting temperatures,  $T_{melt}$ , and isobaric heat capacities,  $c_p$ , of cryogenic, high pressure hydrocarbon mixtures. Heat capacity measurements are reported at (200 and 255) K at pressures between (10 and 32) MPa for two supercritical mixtures of methane (1) + propane (3) + heptane (7) at  $x_7 \approx 0.05$  and 0.10. At 200 K and  $x_7 \approx 0.05$ , our data are consistent with the GERG-2008 EOS across the pressure range measured. However, for  $x_7 \approx 0.10$  deviations as high as 6.5% occur. At 255 K and  $x_7 \approx 0.05$ , GERG-2008 EOS deviates from the measured  $c_p$  by 4.1% at 31.6 MPa, which increases to 7.7% at 20.7 MPa. For  $x_7 \approx 0.10$  larger deviations are seen, which increase from 4.8% at 32.0 MPa to 9.5% at 20.6 MPa. These results highlight the general poor ability of EOS models to predict heat capacities for hydrocarbons mixtures containing heavy components, especially at conditions near the mixture's critical point.

Melting temperature measurements are also reported for both mixtures over a temperature range from (138 to 198) K at (11 and 32) MPa. Comparisons of the measurements against the PR-Advanced EOS (implemented in the software package Infochem Multiflash) show deviations of less than 3 K for  $x_7 \approx 0.10$  and as high as 5 K for  $x_7 \approx 0.05$ ; this is in part due to the increasing sensitivity of melting temperature on composition as solute fraction decreases. The EOS predictions fell outside of the experimental uncertainty for all measurements, identifying

a need to improve EOS performance for predicting SLE in hydrocarbon mixtures.

### FPF – P2

#### **First Floor**

# INTERFACIAL TENSION AND PHASE BEHAVIOUR OF METHANE + PROPANE + HEPTANE MIXTURES

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Natural gas, during extraction and purification, often exists as a mixture of vapour and liquid phases. Simulations are required for the successful design and operation of Liquefied Natural Gas (LNG) production facilities. The cryogenic scrub column, that separates heavier hydrocarbons from natural gas prior to liquefaction, is particularly difficult to simulate due to the number of components present and the requirement for accurate predictions of properties including vapour liquid equilibrium (VLE), interfacial tension and the critical point. Predictive models for the interfacial tension and Equations of State (EOS) for calculating phase equilibrium in natural gas mixtures need to be validated by accurate experimental data. There are, however, limited data for interfacial tension and vapour liquid equilibrium of complex mixtures of hydrocarbons. Additionally the location of the mixture critical point is itself a stringent test for thermodynamic models of multi-component hydrocarbon mixtures: for a mixture of 0.85CH4 + 0.10C3H8 + 0.05C7H14, the difference between the critical temperatures predicted with the Peng Robinson and GERG-2008 equation of state (EOS) is almost 100 K. In this work, we report measurements of the interfacial tension, vapour liquid equilibrium and critical point of ternary mixtures containing methane, propane and n-heptane.

A differential capillary rise apparatus consisting of a high-pressure visual sapphire equilibrium cell was constructed and used to measure mixture VLE and interfacial tension along isotherms ranging from 203.15 K to 363.15 K at pressures up to 24 MPa. The cell was charged with fixed amounts of (normal) heptane and propane, and then pressurized by injecting metered amounts of methane to raise the system's pressure at constant temperature. Measurements were made along the mixture's bubble-point curve towards the critical point, where the interfacial tension vanishes. The mixture's phase compositions were measured using a Gas Chromatograph and interfacial tension was determined from measurements of liquid height in the capillaries, together with estimates of the meniscus radii and the densities of the liquid and vapour phases. Critical points were also measured from observations of critical opalescence and the application of critical scaling based on the phase equilibrium data collected from sampling.

The measured interfacial tensions were compared with predictions of various models, including the Parachor method and Linear Gradient Theory (LGT). The Parachor method was able to describe the data within their uncertainty whereas LGT struggled to predict the interaction with heptane. The default interfacial tension model for hydrocarbon mixtures implemented in the widely-used software package REFPROP 9.1 was revealed to have poor predictions for hydrocarbon mixtures implemented based on the results; this was rectified through the implementation of the Parachor method in a beta-version of REFPROP 9.2. The measured VLE data and critical points were compared with different EOS, with GERG2008 having the best performance with an average relative deviation of 5% in in the predicted bubble point pressure.

### FPF – P3

#### **First Floor**

# MEASUREMENTS AND MOLECULAR SIMULATIONS OF DENSITY AND VISCOSITY OF n-HEXANE + n-DODECANE BINARY MIXTURES

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In order to increase and improve the production of oil, several enhanced oil recovery techniques are available. One of these techniques consists of injecting light molecules ( $CO_2$ , light alkanes) in petroleum reservoirs. By doing so, these small molecules are put into contact with in-situ heavy molecules of crude oil, which constitute the so-called asymmetric mixtures. The thermophysical properties characterization of these asymmetric mixtures is therefore of primary importance to optimize these recovery processes. Thus, we have initiated a set of experimental measurements and simulation of thermophysical properties, such as density and viscosity, on model asymmetric mixtures to test existing models on well controlled systems. In a first step we have investigated the binary mixture made up of n-hexane and n-dodecane. Density measurements were carried out using an Anton-Paar oscillating U-tube density meter whereas viscosity was measured with an Ubbelohde viscosimeter at atmospheric pressure and with a falling body viscosimeter for higher pressure. Measurements were performed on six sample mixtures ranging from 0 to 100% of n-Dodecane, at temperatures from 293.15 to 333.15 K and pressure up to 100 MPa. Computations of the above properties were also carried out by molecular simulation using Molecular dynamics and Monte Carlo methods. Two different force fields were evaluated. An in-house coarse grained model based on the Mie chain fluid and a usual fine grained model, the Transferable Potential for Phase Equilibria (TraPPE) united atom force field.

#### FPF – P4

#### **First Floor**

### LIQUID DENSITY OF CO2 AND N-DECANE BINARY MIXTURES AT TEMPERATURES FROM 283.15 K TO 363.15 K AND PRESSURES UP TO 100 MPA

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Density data for a binary system of carbon dioxide (CAS NO. 124-38-9)+decane, CAS NO. 124-18-5) were measured at temperatures from 283 K to 363 K and pressures up to 100 MPa with  $CO_2$  mole fractions of 0.2032, 0.3838 and 0.7589, respectively. The purpose of this study is to provide reliable thermophysical data on the carbon sequestration and evaluate the density data consistency of  $CO_2$ +decane mixtures. The experiment was conducted using a high pressure

vibrating-tube densimeter. The performance of the apparatus was tested by measuring the thermal conductivity of R134a from (283 to 363) K, which agreed with recommended values with a maximum deviation of 0.2%. The densities of binary mixtures obtained in this work were correlated using modified Tait equation. The maximum relative deviation of experimental density data and calculated data was 0.04%. In addition, the experimental density data of different literature were compared with those of the GERG-2008 equation of state.

## FPF – P5

### **First Floor**

#### SURFACE TENSION OF FIVE FUEL ADDITIVES: EXPERIMENT AND CORRELATION

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Biodiesel has numbers of advantages in comparison to the fossil diesel and the addition of a variety of oxygenated compounds to diesel have been a hot topic in recent years. Surface tension is one of the important physical properties of liquid fuels contributing to atomization and efficiency in a diesel engine and reducing pollutant emissions. Experimental surface tension data for biodiesel over a wide range of composition and temperature are scarce and their measurements tend to be expensive and time-consuming, so the reliable data on surface tension can provide support for developing universal and accurate prediction model of oxygenated compounds to diesel system. A pendant drop apparatus was developed including pressure vessel, temperature control and measurement, pressure measurement, vacuum setup, image capture, and data processing. Toluene were used to test the accuracy and reliability of the apparatus, and the uncertainty is estimated to be  $\pm 1.1\%$ . The surface tension of five fuel additives which are considered promising candidates, including 2-Methoxyethanol, 2-Methoxyethyl ether, 2-Methoxyethyl acetate, 2-Ethylhexyl acetate and Diethyl succinate, were conducted in the temperature range from (303.15 to 393.15)K. Brock Bird model, Pitzer model, Sastri model, Rao model and Di Nicola model were used to correlate the experimental data. Moreover, a new surface tension correlations were developed as a function of temperature with the experimental data and gives the possibility to identify the best predictive model.

## FPF – P6

## **First Floor**

# VISCOSITY OF FATTY ACID METHYL ESTERS UNDER PRESSURE: METHYL OLEATE AND METHYL LINOLEATE.

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Biodiesels are promising fuels for use in compression ignition engines. While retaining comparable capacities of petroleum-derived fuel as regards the heat of combustion and ignition delay time, these substances exhibit additional environmental benefits. The use of biodiesel instead of fossil fuels results in a reduction of unburned hydrocarbons, carbon monoxide and particulate matter. Consequently, replacing either totally or partially petrodiesel with biodiesel has the potential to reduce the overall emissions of gases to the atmosphere and therefore improves air quality if engines are specially designed and optimized for working with biodiesels.

The performances of compression ignition engines are mainly influenced by the way how fuel is injected and atomized in the combustion chamber. Fuel properties play a critical role in the spray characteristics and atomization process and it is consequently essential to know the thermophysical properties of biofuels to adapt engines for working efficiently with biodiesels. Among all the liquid properties, viscosity is the most important property that affects atomization. It acts on the spray pattern as well as on droplet size distribution in the spray. Viscosity also influences the flow within nozzle as well as the output flow rate. In addition, viscosity affects lubrication and leakage within the moving parts of the pump and injectors. Therefore, optimization of the formulation of biodiesels requires an accurate knowledge of biodiesel viscosity over a wide range of pressure. This property can be measured for each biodiesel or evaluated from ester composition by using correlations and mixing rules when properties of pure esters are known. However, these predictive methods are so far limited to atmospheric pressure conditions as only few works have been dedicated to the measurement of Fatty acid methyl ester viscosities under high pressure.

To address this limitation, we have initiated a measurement program of viscosity of pure fatty acid methyl (and ethyl) ester viscosity coming from the transesterification of fatty acids of chain length ranging from 10 to 20 carbon numbers.

The present work aims at reporting experimental data of viscosity of liquid methyl oleate (C18:1) and methyl linoleate (C18:2) measured at pressures from atmospheric to 200 MPa and temperatures ranging from 293 K to 353 K using two different techniques. The former method relies on the falling body principle in which viscosity is directly related to the time taken for a sinker to fall freely inside a vertical cylinder containing the liquid sample. The latter is based on thickness shear mode (TSM) quartz resonator technique which relates the electrical response of a quartz crystal resonator fully immersed in a liquid to the viscous friction at the interface between the liquid and the quartz.

## FPF – P7

## **First Floor**

# AN EXPERIMENTAL STUDY ON THE THERMOPHYSICAL PROPERTIES OF TETRAHYDROFURAN WITH PROPAN-2-OL, BUTAN-2-OL AND HEPTANE

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When two liquids are mixed together, the resulting changes in physical and thermodynamic properties can be considered as a sum of several contributions due to free volume change, change in energy, change in molecular orientations and steric hindrances. The interaction between cyclic ethers and linear hydrocarbons or alcohols has been subject of many investigations and, particularly, much attention has been paid to the analysis of the thermodynamic

properties of these kinds of liquid mixtures [1-4].

The liquids used in the present study are important due to their various in industrial applications. Tetrahydrofuran THF is used as a solvent in many chemical industries due to its proton accepting nature. Alcohols are self-association organic liquids and are widely used as the basic organic compound for synthesis of other organic compounds. With the considerations, excess volumetric properties of ternary systems of THF + 2-propanol, or, + 2-butanol with n heptane and their corresponding binary mixtures at different temperatures.

Excess molar volumes  $V^E$  have been investigated from density  $\rho$  measurements, using vibrating-tube densimeter an Anton Paar 5000, at 293.15 K, 298.15 K, 303.15 K, 308.15 K and 313.15 K. Experimental results were correlated using Redlich-Kister type equation. For the ternary systems, a ternary term type Cibulka was added to the Redlich-Kister equation. Other empirical equations were tested to predict experimental data of ternary systems. Thermal expansion coefficients  $\alpha$  and their excess values  $\alpha^E$  were also evaluated.

## FPF – P8

First Floor

## DENSITY MEASUREMENTS OF IAPSO SEAWATER BY SINGLE-SINKER HYDROSTATIC BALANCE

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Despite seawater has not the necessary characteristics to be considered a metrological fluid, it has so much influence on humanity that its study cannot be neglected. Among its thermodynamic properties, density is considered one of the most requested since it is used in many different kinds of oceanographic models, for example to interpret ocean dynamics leading to medium and long term climate changes or even ENSO phenomena which have tangible impact on economy.

The scope of this work is to adapt an already available single-sinker hydrostatic densimeter for carrying out density measurements of seawater samples at atmospheric pressure. For this reason materials adopted in the realization of the instrument have been carefully chosen and tested. Sinkers of different materials (i.e. silicon, titanium and JGS1) have been compared for selecting the one capable of limiting the interaction with the seawater. Water evaporation has evaluated using different kind of closures and main surface tension effects, playing a role in the measurement, have been investigated.

A sample of IAPSO seawater, with a nominal practical salinity of 30, has been used during these preliminary tests carried out at atmospheric pressure in the temperature range of (15 and 40) °C. These results are used to highlight and rule out any weakness of the hydrostatic balance densimeter in order to make it able to operate with this particular fluid.

### FPF – P9

## ON THE VISCOSITY AND OTHER PROPERTIES OF POLY(ETHYLENE GLYCOL) 600

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The present work is part of a program to study the viscosity of a series of pure poly(ethylene glycols) (PEG) and their mixtures saturated with supercritical  $CO_2$ . PEGs have been used as model compounds for several applications, as green solvents and heat transfer fluids (HTF). In particular, PEG600 is suggested as a promising phase change material (PCM).

In this work, preliminary results for the measurement of the viscosity of PEG600 using the vibrating wire technique are presented together with measurements made with suspended level capillaries for comparison. Both measurements were carried out under atmospheric pressure, covering the temperature range from (303 to 353) K.

As a complement of those measurements, preliminary results for the density of PEG600 were obtained by means of an Anton Paar DMA 5000 U-tube densimeter.

The surface tension was determined using the pendant drop method, under atmospheric pressure and at temperatures from (303 to 353) K.

The sample used was characterized, aiming in particular to obtain its average molar mass and to characterise the shear dependence of its viscosity, at low shear stresses.

The viscosity results were correlated with the temperature using a Vogel type equation. The root mean square deviation is of the order of 0.5%. The density and the surface tension data were correlated with the temperature by means of polynomial equations. The root mean square deviations for the density and surface tension are of the order of 0.0015% and 0.18%, respectively.

#### **FPF – P10**

#### **First Floor**

# ANALYSIS OF THE HIGH PRESSURE VISCOSITY OF TRIOCTYL TRIMELLITATE AND TRIMETHYLOLPROPANE TRIOLEATE

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To exploit wells of greater depth involves some difficulties due to the lack of viscosity standards. The petroleum industry needs reference fluids with well-known dynamic viscosity

at high pressures and temperatures. A number of reference fluids, such as trioctyl trimellitate (TOTM), have been proposed in the recent years [1,2] to solve this problem. TOTM is a trimellitate ester with low vapour pressure. In this work we analyse the pressure and temperature dependence of the dynamic viscosity of this fluid. Moreover we study an unsaturated polyol ester, trimethylolpropane trioleate (TMPTO), which is used as base fluid for industrial applications such as hydraulic fluids, two-stroke engine oils and metal working oils [3]. The knowledge of the dynamic viscosities of both fluids over wide pressure intervals is a key factor for their success implementation.

In this work we present experimental dynamic viscosity data of both fluids (TOTM and TMPTO) from 303.15 to 353.15 K at pressures from 0.1 to 150 MPa, and from 278.15 K to 353.15 K at atmospheric pressure as well as the viscosity index. The experiments were performed with falling body and rotational viscometers. Technical details of both apparatus were reported previously [4]. Temperature-viscosity coefficient, pressure-viscosity coefficient and film thickness have been estimated from the measurements of the viscosity as a function of temperature and pressure. The obtained dynamic viscosity values range from 9 to 2570 mPa  $\cdot$  s for TOTM and from 8.5 to 525 mPa  $\cdot$  s for TMPTO. Accordingly to the measured viscosity index (83 for TOTM and 190 for TMPTO) viscosity of TOTM increases more strongly with temperature than that of TMPTO. The universal pressure-viscosity coefficient values obtained for trioctyl trimellitate present relative deviations of 5.6% at 313.15 K and 2.5% at 343.15 K with those reported by Bair [2]. The deviations are 4.2% and 1.3% for the reciprocal asymptotic isoviscous pressure.

## Acknowledgment

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## FPF – P11

## First Floor

# PREDICTION OF FLASH POINTS OF COMBUSTIBLE MIXTURES USING VLE MODELS

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Flash point measurements of various types are used as a measure of the flammability of liquid

combustible materials. The flash point is also related to the lower flammability limit, which is the minimum content of the combustible in a combustible-air mixture that will propagate flame. Many manufacturing processes involve flammable chemicals; therefore, flash points and flammability limits are essential to maximize safety in process design and operational procedures. Flammability is an important factor in the development of safe practices for handling and storage of liquid mixtures.

Flash point temperature is the key property for classifying liquids according to their degree of flammability. Based on these classifications, regulators then specify or provide guidance on the appropriate methods for transporting, handling, packaging, storing, dispensing, and protecting these materials. The flash point can be used to determine the level of risk in different stages of a process because it is the temperature at which sufficient vapor is generated to bring the concentration of flammable vapor above the lower flammability limit. Knowledge of flammable limits at elevated temperatures and pressures is needed for safe and economical operation of some chemical processes. Flash points are available for most pure liquids, but the information for mixtures is very limited and is usually at ambient pressures.

Predictive theoretical methods are needed to estimate the flash point of liquid mixtures when experimental data are unavailable. Some of the available methods are based on group contribution methods that depend on knowledge of chemical structure. In this paper, general correlations and prediction methods for calculating flash point and lower flammability of pure liquids and mixtures are presented. The flashpoints of a few binary mixtures have been predicted using the popular VLE models including UNIFAC and the results are compared with the experimental values.

## FPF – P12

First Floor

# THERMAL CONDUCTIVITY MEASUREMENT OF HFO REFRIGERANTS WITH HIGH TEMPERATURE REGION

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Hydrofluoroolefins (HFOs) have gotten great attention as promising candidates of next generation refrigerants because of their low GWP. For example, R1234yf, R1234ze(E) and R1234ze(Z) of which GWP are below 1 will be used as alternative refrigerants of car air-conditioners, turbo refrigerators and high tempareature heat pump systems, respectively. Because of initial evaluations, many experimental data of thermodynamic properties of these refrigerants have been reported and accurate equation of state (EOS) of them have also been developed. On the other hand, there are very limited experimental data of transport properties of these refrigerants. In order to design heat pump system using alternative refrigerants, transport properties such as thermal conductivity and viscosity data are indispensable.

In this study, new experimental data on the thermal conductivity of low-GWP refrigerants such as R1234ze(Z) and R1336mzz(Z) are reported in order to contribute for development of alternative heat pump systems supplying high temperature up to 200 °C. The measurement is carried out by transient hot-wire method in which two platinum fine wires with different

length to eliminate the end effect of the connection. This study also deals with correlation which can be available in wide temperature and pressure range. The correlation is developed based on Extended Corresponding States (ECS) model and there are good agreement between measurements and predictions by the model.

## FPF – P13

### **First Floor**

# MASS DIFFUSIVITIES OF BINARY MIXTURES OF NORMAL ALKANES WITH DISSOLVED GASES

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Knowledge on the mutual diffusivities of gases dissolved in liquids is of increasing interest for the optimization of processes such as the Fischer-Tropsch synthesis of high valued petroleum products from synthesis gas or the separation of flue gas components. Here, mass transfer is often the rate limiting step compared to, e.g., chemical reactions and/or heat transfer. In a related research project, the benefits of experimental and modelling methods are combined to get a better understanding on how molecular diffusion is affected by the characteristics of the mixture components, which contributes to the development of reliable predictions.

In the present contribution, dynamic light scattering (DLS) experiments and molecular dynamics (MD) simulations were performed at macroscopic thermodynamic equilibrium for a first set of model systems based on liquid normal alkanes and dissolved gases. The solvents *n*-hexane and *n*-decane in their binary mixtures with the solutes hydrogen, helium, nitrogen, and carbon monoxide were studied over a broad temperature range from (298 to 423) K at gas mole fractions below 5%. With DLS, the relaxation behavior of microscopic fluctuations in the properties of state is analyzed. In the case of concentration fluctuations in binary mixtures, their mean decay time is related to the mutual diffusivity which can be accessed by DLS in an absolute way without calibration. The present measurements document that even for small gas concentrations implying weak light scattering signals, reliable mutual diffusivities with typical uncertainties below 5% (k = 2) can be obtained. These results serve as a database for MD simulations. Here, thermophysical properties are computed by investigating the dynamics of molecules interacting with each other. Based on suitable models for the mixture components, the self-diffusion coefficient of the gas was determined with uncertainties of about 10% (k = 2).

In agreement with theory, similar values for the mutual diffusivity and the self-diffusivity were found. Furthermore, no detectable influence of the solute concentration on the mass diffusivities could be found by DLS and MD simulations within the narrow investigated mole fraction range between about (1 and 5)%. The broad range of mass diffusivities of the studied gas-liquid systems covering about two orders of magnitude from about  $(10^{-9} \text{ to } 10^{-7}) \text{ m}^2 \cdot \text{s}^{-1}$  allow for developing structure-property relationships. Here, effects of the molecular weight and polarity of the various gases as well as the varying alkyl chain length of the solvents on the mass diffusivities are discussed. To further develop the intended prediction scheme, two additional

classes of alkane-based solvents featuring the hydroxyl group - namely normal alcohols - as well as bulky charged structures in the form of ionic liquids will be studied in their binary mixtures with the aforementioned gases in a next step. In the same context, the DLS data will be used to test how reliably mutual diffusivities can be computed in MD simulations for the various fluid systems by different approaches.

### FPF – P14

#### **First Floor**

# EXCESS PARTIAL MOLAR ENTHALPIES OF 3-ETHOXYPROPAN-1-AMINE IN WATER AT 298.15 K

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Alkoxyamines are interesting amphiphilic molecules characterized by having ether and amine functional groups. They have proved to be important in industry, namely in the controlled production of polymers. Recently, they have been considered a new family of pro-drugs against cancer.

Continuing our work of property determination and in order to gather information regarding effects on hydration and changes in aggregation patterns across the whole composition range, partial molar enthalpies in the system water (1) + 3-ethoxypropan-1-amine (EPA) were obtained by experimentally exploring the enthalpic response of the entire system when infinitesimal amounts of EPA or water are added to aqueous mixtures of different compositions.

We used a thermometric precision solution calorimeter [1] with resolution close to 1 K, corresponding to a heat resolution of 1-4 mJ in a 100 ml reaction vessel. Each value of enthalpy was obtained with the average of four values, using both a dynamic and a break method with a calibration before and after ampoule breaking. Mixtures, used as solvent, were prepared by weight in volumetric flasks provided with tight Teflon stoppers to prevent evaporation. The enthalpic contribution of the empty ampoules was considered negligible.

Enthalpic contributions of pair-wise interactions are derived and interpreted in terms of important aggregative processes occurring in this system. This study provides new information concerning molecular interactions in these mixtures in relation to previous volumetric studies obtained by our group [2,3].

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### FPF – P15

#### **First Floor**

# THERMAL CONDUCTIVITY MEASUREMENTS OF DIFLUOROMETHANE IN THE NEIGHBORHOOD OF CRITICAL REGION

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The thermal conductivity measurements in the critical region of the difluoromethane - hydrofluorocarbon HFC-32 were carried out with a steady state method for which a coaxial cylinder apparatus was employed. The sample fluid has been located in a narrow gap between two coaxial vertical cylinders. The design allows measurements of the thermal conductivity at temperatures from 294 to 356 K and at pressures up to 7 MPa. All section of the cell were made of electrolytic cooper. All heaters, platinum thermometers and copper-constantan thermocouples located in the holes inside the cylinders and electrically insulated from the copper sections. The width  $\delta = 0.220$  mm of the gap between two cylinders has been fixed by three glass spacers. The geometrical configuration of the cell is one where convection is least likely to occur. To avoid laminar convection the Rayleigh number has been restricted by the thickness of the gap and by the applied temperature difference  $\Delta T$  as small as possible.

The difluormethane (refrigerant HFC-32) used for thermal-conductivity measurements was supplied by the Russian Scientifique Center «Applied chemistry» with a stated purity of 99.84%. As a check on the stability of the cell the thermal conductivity of nitrogen, helium, toluene and HCFC-22 was first measured at temperatures from 300 to 360 K. The set of new experimental results obtained for the thermal conductivity of difluoromethane (HFC-32) in the critical region has been obtained. The singular behavior of the thermal conductivity in the neighborhood of critical region has been experimentally observed.

#### **FPF – P16**

#### **First Floor**

# ISOBARIC HEAT CAPACITY MEASUREMENTS OF R1234ZE (E) IN LIQUID PHASE AT TEMPERATURES FROM 304 K TO 378 K AND PRESSURES UP TO 12 MPA

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European Union's F-gas regulation has established a schedule to restrict the use of high GWP fluorinated gases. Moreover, hydrocarbon's flammability raised some doubts about its safety. Therefore, searching new promising substitute is necessary. Recently, Great attention has been paid to trans-1,3,3,3-tetrafluoropropene (R1234ze (E)). It has zero Ozone depletion potential and a very low global warming potential. In addition, it offers a mild flammability and high

similar thermodynamic performance to that of R134a. All of these makes it a promising alternative refrigerant.

Thermophysical properties of R1234ze (E) are required in chemical-process and product design. Although many studies have been published concerning its thermophysical properties, little research has been done on the heat capacities. To the author's knowledge, only two sets of data have been published on the isobaric heat capacity of R1234ze (E) in liquid phase. Tanaka et al measured the isobaric heat capacity of liquid R1234ze (E) covering a temperature range from (310 to 370) K and pressures up to 5 MPa. Gao et al reported heat capacity data in liquid phase at temperatures from 310.15 to 365.15 K and pressures up to 5.5 MPa. However, its isobaric heat capacities at pressures above 5.5 MPa have not been published yet.

For this reason, isobaric heat capacities of R1234ze (E) were studied in compressed liquid phase by using a modified flow calorimeter. A total of 185 heat capacity data were acquired covering a temperature range of (304 to 378) K and pressures up to 12 MPa. The uncertainty in measurement of the heat capacity was estimated to be less than 1%. An empirical equation was developed to reproduce the experimental data. The saturated liquid heat capacities of R1234ze (E) were also obtained. In addition, a comparison was made between the present data and literature values.

#### **FPF – P17**

First Floor

## THERMOPHYSICAL PROPERTIES OF AMINE SOLUTIONS AT HIGH PRESSURES

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There is growing concern that anthropogenic carbon dioxide emissions are contributing to global climate change. Therefore, it is critical to develop technologies to mitigate this problem. Absorption is the most established technique to separate  $CO_2$  where amines are commonly used as solvent. Accurate determination of physical properties of solvents, in wide ranges of pressures and temperatures, is essential for rational design and optimization of  $CO_2$  capture units.

In the present work, thermophysical properties such as density ( $\rho$ ), dynamic viscosity ( $\eta$ ) and isobaric heat capacity ( $c_p$ ), were accurately measured for aqueous solutions of piperazine at mass fractions w = 0.10 at wide temperature and pressure ranges.

Densities were measured using an Anton Paar DMA HPM densimeter [1] with an standard uncertainty of  $\pm 0.7 \text{ kg} \cdot \text{m}^{-3}$  and viscosities by means of a falling body viscometer (stainless steel falling cylinder) [2] with a relative standard uncertainty better than 2.9%. Both properties were measured from 293.15 K to 393.15 K and up to 100 MPa.

An automated flow calorimeter was used for isobaric heat capacity measurements whose relative standard uncertainties are 1% [3]. Heat capacities were measured at (313.15, 333.15 and 353.15) K and pressures up to 25 MPa.

In addition, experimental data were correlated with different models and the results will be presented and discussed.

### Acknowledgment

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## FPF – P18

## **First Floor**

# PROPOSING SURROGATE FUELS FOR BRAZILIAN GASOLINES BASED ON VISCOSITY MODELLING

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Automotive gasoline consists of a large number of compounds and, due to its complexity, it is convenient to work with surrogates, mixtures of selected compounds that are able to represent the original fuel combustion, thermodynamic, and transport properties. The aim of this work is to formulate a surrogate for gasoline that emulates the fuel viscosity, which is predicted by means of the model developed by Martins and co-workers [1], based on Eyring's absolute rate theory and UNIQUAC equation. To calculate the viscosity of multicomponent systems, UNIQUAC pure component parameters and binary interaction parameters, two for each binary subsystem, are necessary.

The representative compounds were chosen according to the work of Pitz and co-workers [2], and 28 possible binary subsystems were identified. Nevertheless, the viscosity data were available in the literature only for 20 binary systems containing cyclohexane, ethanol, heptane, toluene, isooctane, methylcyclohexane and p-xylene. The data have been correlated and the corresponding binary interaction parameters were determined. The overall mean relative standard deviation for each binary system investigated was lower than 1,5%.

The compositions of the surrogate mixtures were determined according to our investigation on viscosity and density of Brazilian gasoline samples. The measurements were performed with a previously calibrated automatic viscometer (Stabinger SVM 3000/G2, Anton Paar), at the temperatures of 283.15 K, 288.15 K, 293.15 K, and 298.15 K. At least 8 repetitions were performed for each sample at each temperature investigated.

Since heptane, isooctane and toluene are the constituents of the toluene reference fuel (TRF), the viscosity mixtures of these components have been calculated by the model previously mentioned and the COSTALP equation [3] was used to compute their densities. Using deviations of 1% between experimental and calculated viscosities values and 1%, in the case of densities, a TRF mixture containing 60% (mol) of n-heptane, 5% (mol) of isooctane and 35% (mol) of toluene was proposed for non-oxygenate, type A gasoline. For the commercial type C gasoline, which contains 25% (v/v) of ethanol, a surrogate mixture composed of 20% (mol) of n-heptane, 30% (mol) of isooctane, 5% (mol) of toluene, and 45% (mol) of ethanol was proposed, considering deviations of 1% between experimental and calculated viscosities values and 1.5% for densities.

### Acknowledgment

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## FPF – P19

# SPEED OF SOUND OF HYDROFLUOROETHER FLUID HFE-7500 + DIPE UNDER HIGH PRESSURE

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Hydrofluoroether fluids (HFEs) are a type of fluorinated ethers investigated since the decade of the '90s as substitutes of CFCs, HCFCs and PFCs among other fluorocarbons, due to their desirable environmental properties, that is, zero ozone depletion potential, low global warming potential and short atmospheric lifetimes, and due to their thermophysical properties. 2-trifluoromethyl-3-ethoxydodecafluorohexane, known as HFE-7500, is proposed to be a good alternative to PFCs and PFPEs replacement because it is a dielectric fluid with low viscosity, high liquid density and low surface tension.

Diisopropyl ether (DIPE) is used in a wide variety of applications, for example it is used as solvent or as cleaning agent. The addition of the fluorinated compound HFE-7500 implies a reduction on the flammability of Diisopropyl ether, making this binary mixture a good option to be used in high precision cleaning, or as solvent as oil-based solutions dissolve in it.

In this work the speed of sound and density of the binary mixture x HFE-7500 + (1-x) Disopropyl ether have been determined experimentally at pressures up to 100 MPa and at temperatures from (293.15 to 353.15) K for five mole fractions, x = (0.250, 0.375, 0.500, 0.625)

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and 0.750). Derivative properties such as isentropic compressibility, isothermal compressibility and isobaric expansion were also determined from these measurements.

### Acknowledgment

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#### **FPF – P20**

### **First Floor**

## DENSITY OF DIPE + 2-PROPANOL AT TEMPERATURES UP TO 353.15 K AND AT PRESSURES UP TO 100 MPa

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Tertiary alkyl ethers like di-isopropylether DIPE, having similar properties (e.g., vapour pressures) to hydrocarbons and the potential to increase the octane number and to decrease the emission of carbon monoxide, have become important additives for gasoline. The ethers increase the amount of oxygen in gasoline in order to reduce the CO content in the exhaust gas of automobiles. DIPE, pure or mixed with alkanols or alkanes, has been recommended as a high octane blending agent for motor gasoline.

Ether + alcohol mixtures are of interest as model mixtures for gasoline in which the ether and the alcohol act as non-polluting, high octane number blending agents. Despite of this interest, density data of binary mixtures containing ether + alcohol at pressures other than the atmospheric pressure are very scarce in the literature. Density of the binary mixture DIPE + 2-propanol have been measured under pressure and reported in this work using a vibrating tube densitometer. No literature date on the density at high temperature and pressure for the same binary mixture has been found.

Experimental densities for the binary system DIPE + 2-propanol have been measured at, 298.15, 313.15, 333.15 and 353.15 K and at nineteen isobars up to 100 MPa. For each composition, the experimental values were correlated using a Tait-type equation. Furthermore, the excess molar volume and the isothermal compressibility were calculated from the density data.

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### FPF – P21

## VOLUMETRIC PROPERTIES FOR THE 2,5-DIMETHYLFURAN + N-DODECANE SYSTEM AT PRESSURES UP TO 70 MPA

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Thermodynamic properties obtained through experimentation are fundamental basis for the development of models used to represent and predict the behaviour of fluids. Volumetric properties are important in chemical engineering for the design, simulation and optimisation of various separation processes. Knowledge of the density at different temperatures and pressures is also essential for the calculation of properties such as solubility or viscosity, both crucial in different fields of technology.

In this work, volumetric properties (PvT) in the compressed liquid region are reported for the organic compounds system: 2,5-dimethylfuran (1) + n-dodecane (2) and were measured from 293 K to 373 K and pressures up to 70 MPa. PvT properties of this binary system were obtained at five different compositions to cover all the range, x(1) = 0.1, 0.2, 0.5, 0.6, and 0.9 mole fraction. Measurements were performed using a vibrating tube densitometer based on the FPMC calibration method, which uses vacuum and water as reference. The experimental variable that is measured is the vibration period and through an equation, densities are calculated at a specific temperature and pressure.

In order to check for the performance of the vibrating tube densitometer, densities of ndodecane were obtained from 293 K to 373 K in temperature intervals of 20 K. Values of density for n-dodecane were found to be in agreement and within the deviation whit data from the literature over the range studied from which it is considered that the apparatus is able to measure densities with good precision.

Ideal behaviour can be assumed for the binary (2,5-dimethylfuran + n-dodecane) system. The excess molar volumes were calculated in order to know the deviation of the behaviour with respect to the ideal. The results show that the deviations are positive for all cases, showing parabolic behaviour; the positive values of excess molar volumes are attributed to the dispersion forces presented by the alkanes and the generation of empty spaces due to the accommodation of the molecules of alkanes with 2,5-dimethylfuran molecules.

### **FPF – P22**

**First Floor** 

## THERMOPHYSICAL PROPERTIES OF HIGHLY CONCENTRATED BORIC ACID SOLUTIONS AT 298-363 K

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In order to calculate the processes of accumulation and crystallization of boric acid in the core

of the WWER reactor in the event of an accident, it is necessary to know the thermophysical properties of highly concentrated aqueous solutions of boric acid. This is due to the fact that in new NPP projects with a WWER reactor, a cooling of the reactor core is expected to take place (up to 72 hours) by supplying a aqueous solution of boric acid with a concentration of 16 g/kg  $H_2O$  from the passive systems of hydroaccumulators of the first (HA-1), the second (HA-2) and the third (HA-3) steps. Considering the duration of the emergency process, the boiling of the coolant and the low content of boric acid in the steam leaving the reactor, it is possible to increase the concentration of boric acid in the core and its crystallization on the surface of the fuel rods and elements of the reactor internals.

At present, the data on the density and viscosity of boric acid solutions are very general and do not cover the whole range of parameters (temperature, pressure, acid concentration) typical of the emergency situation at WWER NPPs.

Experimental studies were carried out at IPPE to determine the thermophysical properties of aqueous solutions of boric acid in the range of elevated concentrations characteristic for emergency regimes of NPPs with WWER. Measurement of the density of solutions of boric acid occurred by the pycnometr method. For the experiments, glass pycnometers of 10 ml volume were used. To study the effect of temperature on the density of a solution of boric acid, the experiments were repeated at several temperatures. The viscosity of solutions of boric acid was determined by means of a Ubbelohde viscometer with a capillary diameter of 0.34 mm.

As a result of the studies, the values of the density and viscosity of boric acid in the concentration range of 2.5-200 g  $\rm H_3BO_3/kg~H_2O$  were measured at several temperatures in the range 298-363 K.

### Acknowledgment

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### **FPF – P23**

### **First Floor**

### TRACEABILITY OF CURRENT THERMOPHYSICAL DATA USED FOR ENTHALPY AND CALORIFIC VALUE CALCULALTIONS OF LIQUEFIED NATURAL GAS (LNG)

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LNG is a strategic and in case of long distances a more economical alternative for pipeline gas. A three-year project 'Metrological support for LNG custody transfer and transport fuel applications (LNG II)' is part of the European Metrology Research Programme (EMRP) and aims to further develop the metrological framework for LNG by reducing measurement uncertainties in density, volume and energy content. PTB's task, as part of the European Consortium working on this EMRP project, is to examine the literature data used in the enthalpy and calorific value calculations with respect to uncertainties and traceability. The results of these investigations will be presented.

For example, the enthalpy of formation of methane, which is the main component of natural

gas and LNG, shall be determined by experimental data. To do this, the knowledge of the enthalpy of formation of water (and also of carbon dioxide) is necessary which is a fundamental quantity for all combustion processes where hydrocarbons are involved. The CODATA book [1] mentions the investigations of Rossini [2, 3] and King and Armstrong [4]. The relative uncertainty (coverage interval k = 2) of Rossini's experimental value of the enthalpy of formation of water is approximately ten times smaller (±0.014%) than the uncertainty (±0.12%) given by King and Armstrong. Rossini determined the uncertainty by calculating the standard deviation of the mean values measured. This calculation procedure does not comply with currently accepted methods to estimate uncertainties of measurements like GUM [5], e.g. reporting an uncertainty budget. Therefore, a comparison with Rossini's experimental findings and usage as key thermodynamic data is doubtful. Nevertheless, the experimental value and its uncertainty determined by Rossini still serve as reference value.

### Acknowledgments

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### **FPF – P24**

### **First Floor**

## VAPOR-PHASE (P,V,T,X) BEHAVIOR AND VIRIAL COEFFICIENTS FOR THE $({\rm C_2H_6+CO_2})$ SYSTEM

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Accurate density measurements of the  $(C_2H_6 + CO_2)$  system were carried out at temperatures T = (273.15, 283.15, 293.15, and 323.15) K with pressures up to about 8 MPa or the dew-point pressure, whichever was lower. A well-proven two-sinker magnetic suspension densimeter was utilized for the measurements, and a preheating device for the gas sample was specially designed and integrated in order to avoid condensation when filling and flushing the densimeter. Considering all measurement uncertainties in temperature, pressure, density, and composition, the relative combined expanded uncertainty (k = 2) in density was estimated to be less than 0.05%. The mixtures were prepared gravimetrically according to state-of-the-art metrological protocols with compositions of about 0.05, 0.20 and 0.50 mole fraction  $C_2H_6$ ; the

expanded uncertainty (k = 2) in composition was estimated to be 0.0004.

In the context of present measurements, we note that a key challenge in accurate gas density measurements of mixtures is to avoid a compositional distortion caused by surface phenomena such as adsorption and desorption [1] or capillary condensation [2]. Such phenomena become particularly distinct when approaching dew point conditions. Once the composition of the gas mixture is altered, the property under study changes leading to a wrong measurement result. Thus, appropriate measures have to be considered to obtain a reasonable reproducibility.

The measured densities were compared to the GERG-2008 equation of state [3], and relative deviations were mostly within the reported uncertainty of the GERG-2008 equation of 1.0% for the  $(C_2H_6 + CO_2)$  system (where no binary specific departure function is available). Furthermore, values and uncertainties of the second and third virial coefficients were determined by fitting a third-order virial equation to the experimental results. The second interaction virial coefficient was calculated as well. With our careful uncertainty analysis, the new experimental data together with the virial coefficients can be considered accurate and could be used to further improve the performance of multi-parameter equations of state for fluid mixtures.

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### FPF – P25

# DENSITIES OF $(CO + CO_2)$ MIXTURES DETERMINED FROM DIELECTRIC PERMITTIVITY MEASUREMENTS

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The key objective of the present work was to determine densities of binary  $(CO + CO_2)$  mixtures from dielectric permittivity measurements. Until today, such mixtures are not well investigated because of their high toxicity and limited materials compatibility. For the determination of molar densities of fluid mixtures, accurate experimental data for the dielectric permittivities of the mixture's pure components are also required. Microwave re-entrant cavity resonators offer a rapid way of measuring fluids that are difficult to handle whilst consuming just small amounts of sample. A detailed description of our apparatus, which has proven to be also capable of accurate dew-point measurements in  $CO_2$ -rich mixtures, has been recently published [1]. Vapour-phase molar mixture densities can be derived from dielectric permittivity measurements by using mixture polarizabilities calculated with the state-of-the-art mixing rule of Harvey and Prausnitz [2]. Inverting this mixing rule to obtain molar densities from experimental dielectric permittivities of fluid mixtures is a novelty [3] and an important basis for the current work.

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As the data situation for pure CO was very limited (dielectric data only up to 0.6 MPa were found in literature), we measured dielectric permittivities of pure CO over a temperature range from (255.10 to 313.28) K and for the first time at pressures up to 8 MPa. This enabled us to test ab initio calculations of CO's molecular polarizability and dipole moment. We estimated a relative expanded combined uncertainty (k = 2) in the dielectric permittivities of two commercial binary (CO + CO<sub>2</sub>) mixtures with CO mole fractions of approximately 0.50 and 0.75 were measured. The measurements were carried out in the temperature range from (273.15 to 313.15) K and at pressures to about 8 MPa. We observed relative deviations in the derived molar densities from the reference equation of state (EOS-CG) of Gernert and Span [4] of up to approximately -1.4%.

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### **FPF – P26**

### **First Floor**

### THERMOPHYSICAL PROPERTIES OF GEOTHERMAL AND SEAWATERS

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Geothermal energy is a renewable energy that encourages conservation of natural resources. Various geothermal water resources has temperatures up to  $\sim 140$  °C. Mainly, these resources potentially use for bottled water production, medicinal purposes, for spas and health clinics that utilize the waters to treat arthritis, dysfunction of the nervous system and skin diseases. But they can be also used for: thermal heat, for warming soil, hotbeds and hothouses with the aim of early and rapid growth of vegetables and fruits (40 - 50 °C).

The majority of water on earth is seawater, a solution of salts of nearly constant composition dissolved in water. For scientific investigations and design of many natural and technical processes which have to do with seawater, it is of great importance to have a reliable base of various physical and chemical properties of water samples. The most recent standard formulation for seawater is restricted in its range of applicability due to a lack of density measurements at higher temperatures and elevated pressures.

To use the water resources the investigation of the chemical and thermophysical properties of water samples in a wide range of parameters are necessary. In this work, we present the chemical and thermophysical properties of geothermal and seawater resources using the various

installations (Spectrometer, Chromatography, Densimeter, Viscometer, DSC calorimeter etc.)

The samples were filtered and degassed slowly using the vacuum system. To stop vaporisation of pure water, the vacuum procedure was very slow (the groove of the flask valve, which held the sample, was very slightly opened). These investigations have been examined for the first time.

An empiric equation of state for fitting of the  $(p, \rho, T)$  data of these water samples has been developed as a function of pressure and temperature. The molecular weight of water samples was analysed. The fitting of properties of water resources are discussing. The equation of state is used for the calculation of the thermophysical properties of samples, such as isothermal compressibility, isobaric thermal expansibility, thermal pressure coefficient, internal pressure, isobaric and isochoric heat capacities, speed of sound and isentropic expansibility.

### FPF – P27

### First Floor

### SPEED OF SOUND MEASUREMENTS OF BIOGAS

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Biogas is a potential new energy source and the knowledge of their thermodynamic properties, such as the equation of state and heat capacity, is important to assure the gas quality. In addition, the accurate knowledge of both data allows the calculation of other thermodynamic properties which are required in the simulation and design of production, storage or transport processes.

A spherical resonator is used for the measurements of the speed of sound [1,2]. It is a spherical cavity, with an internal radius of 40 mm and thickness of 10 mm, which consists in two different hemispheres fixed by electron beam welding, fabricated from grade 321 austenitic stainless steel and manufactured at Imperial College. It is equipped with two capsule-type platinum resistance thermometers which provide a standard uncertainty in temperature measurements of  $\pm 1$  mK at 273.16 K. The pressure is measured by means of two resonant quartz-crystal manometers for the pressure ranges (0 to 2) MPa and (1 to 20) MPa with a relative standard uncertainty of  $\pm 10^{-4}$ . The total uncertainty of the speed of sound is not worse than 0.02%.

The measurement of the speed of sound is used to calculate isothermal and isochoric heat capacities and it is also possible to develop an equation of state as the speed of sound can be expressed as a function of the density through the acoustic virial coefficients. The results obtained for a mixture of biogas from municipal waste (Valdemingómez, Madrid) are presented.

### Acknowledgment

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and Junta de Castilla y León for the economic support through VA035U16 project.

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**FPF – P29** 

### **First Floor**

## PHASE INVERSION AND RHEOLOGICAL BEHAVIOR OF EMULSIONS STABILISED BY SOLID PARTICLES

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A typical problem during the production of heavy crude oil is the formation of water-in-oil (W/O) emulsions in reservoir rocks. The viscosity of these W/O emulsions is higher than the viscosity of the pure oil itself [1]. Reservoir rocks normally contain both hydrocarbons and water. Chemical components of the oil such as naphthenic acids form viscoelastic films at the interface between water and oil and thereby stabilise the water-in-oil emulsions. An innovative technological solution for this problem is inducing a phase inversion into a oil-in-water (O/W) emulsion, which has a significantly lower viscosity. The use of solid particles is an advanced technology that has a potential to cause a phase inversion and to thereby facilitate oil recovery [2].

It is crucial to have a detailed knowledge about parameters that may influence the oil production process. The aim of this study is to study the phase inversion from W/O to O/W emulsions with the help of hydrophilic solid particles. The phase inversion of particlestabilized emulsions can be achieved by adding different concentrations of particles. As model system emulsions were formed with solid particles dispersed in low salinity brines, paraffin oil and naphthenic acid as surfactant. The phase inversion and the emulsion type (W/O vs. O/W) were detected by measuring the electric conductivity. Close to inversion, the stability of different emulsions was analysed with the conductivity meter under pressure. The conditions necessary for a phase inversion in emulsions stabilized by solid particles are discussed. The phase behaviour and the viscosity of such emulsions were investigated in the range from 40 °C and 80 °C and under pressure up to 150 bar. As expected it was found that the viscosity is increasing with the particle content and decreasing with increasing temperature. Compared to the temperature influence, the viscosity increased slightly with the pressure. Rheological measurement show that the phase inversion leads to low viscous O/W emulsions in comparison to the higher viscous pure oil. The results clearly demonstrate that phase inversion can be achieved and that low viscous oil-in-water emulsions can be formed. Thereby the high potential for Enhanced Oil Recovery (EOR) is illustrated.

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### FPF – P30

### **First Floor**

## VAPOR PRESSURES AND THERMOPHYSICAL PROPERTIES OF SELECTED OXYGENATED COMPOUNDS

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In this work, a thermodynamic study of dimethyl carbonate (CAS RN: 616-38-6), diethyl carbonate (CAS RN: 105-58-8), dipropyl carbonate (CAS RN: 623-96-1), ethylene carbonate (CAS RN: 96-49-1), propylene carbonate (CAS RN: 108-32-7),  $\gamma$ -valerolactone (CAS RN: 108-29-2),  $\gamma$ -butyrolactone (CAS RN: 96-48-0), dimethoxymethane (CAS RN: 109-87-5), and 1,2-dimethoxyethane (CAS RN: 110-71-4) is presented. These compounds belong to the class of large-scale production solvents; besides, they have been recently used as electrolytes in lithium-ion batteries, thanks to their good electrical properties.

Experimental work includes vapor pressure measurements using two static apparatuses (described previously [1, 2]) covering pressure range 1 Pa to 1300 Pa and calorimetric measurements of the phase behavior (using heat-flux differential scanning calorimeter) and condensed phase heat capacities (using calorimeter of Tian-Calvet type).

The thermodynamic properties in the ideal gaseous state were calculated using the methods of statistical thermodynamics based on calculated fundamental vibrational frequencies and molecular structure data (the R1SM model presented recently [3]). Calculated ideal-gas heat capacities and experimental data on vapor pressures, condensed phase heat capacities, and vaporization enthalpies (including literature data) were treated simultaneously (using the SimCor method [4]) to obtain a consistent thermodynamic description. Recommended data cover technologically important temperature range from 260 K to 315 K.

### Acknowledgment

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### FPF – P31

### **First Floor**

## HIGH-PRESSURE LIQUID DENSITIES OF N-DECANE AND O-XYLENE MIXTURES: EXPERIMENTAL AND MODELING

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Density of pure liquids and multi-component mixtures is indispensable for chemical engineering processes and influences their operations such as separation of chemicals, fluid flow and exceedingly valuable in controlling the process parameters and manufacturing facilities with accurate design [1]. Alkanes and aromatics are the main components of crude oil and the thermophysical properties of their mixtures are crucial. However, high-pressure densities for these mixtures are scarce in the literature [3].

In this work, the liquid densities for *n*-decane and *o*-xylene binary mixtures were measured over the entire composition range from 293.15 to 363.15 K and pressures up to 60MPa using vibrating-tube densimeter (DMA HPM, supplied by Anton Paar). The combined relative uncertainty was estimated within 0.001 with a confidence level of 0.95. The experimental results were correlated to a Tait-like equation. In addition, derived volumetric properties, such as excess molar volumes, isobaric thermal expansion coefficients and isothermal compress-ibilities, were calculated from the experimental density data. Three different equation of state including PC-SAFT, CPA, and cubic equation of state were used to evaluate the accuracy of density prediction of *n*-decane and *o*-xylene binary mixtures in liquid phase.

### Acknowledgments

The authors are grateful to the National Natural Science Foundation of China (Grant No. 51476129).

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### MEASUREMENTS OF THERMAL CONDUCTIVITY OF N-DODECANE IN LIQUID PHASE AT TEMPERATURES FROM 322 K TO 673 K AND PRESSURES UP TO 20 MPA

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Hydrocarbon fuels are widely used in the fields of energy and chemical industry. They are mainly used as engine fuels in the energy sector. The thermal conductivity is one of the most important thermophysical properities in the process of transportation, storage, combustion and cooling of hydrocarbon fuels. These petroleum distillate fuels, including commercial jet fuels Jet A, Jet A-1 and kerosene rocket propellants RP-1 and RG-1, are composed of hundreds-to-thousands of hydrocarbons. However, it is difficult to investigate the thermal conductivity of these fuels directly in the high temperature region. We can start with the research of pure components in hydrocarbon fuels. N-dodecane as pure hydrocarbon was first studied.

It can be found from literature [1] that the composition of RP-1 and RG-1 were measured by GC-FIMS(Gas Chromatograph-Field Ionization Mass Spectrometry) and the weight percentage of n-dodecane are 0.687% and 0.075%, which are very high in n-paraffins. So n-dodecane has a certain contribution and value in hydrocarbon fuels and the research of n-dodecane is very important.

According to the transient short-hot-wire method, one new experimental apparatus was developed. The measurements of thermal conductivity of n-dodecane in liquid phase were conducted at temperatures from 322 K to 673 K and pressures up to 20 MPa. The experimental results were correlated as a function of temperature and pressure. In addition, the results were compared with literature values.

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### **FPF – P33**

### **First Floor**

## THERMAL CONDUCTIVITY OF *TRANS-*1-CHLORO-3, 3, 3-TRIFLUOROPROPENE (R1233ZD(E)) IN LIQUID PHASE

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The compound trans-1-Chloro-3, 3, 3-trifluoropropene (also known as R1233zd(E)) is considered to be a promising alternative refrigerant and new foam blowing agent due to its

environmental protection characteristics. Its ozone depletion potential (ODP) is suggested to be 0.0005, its global warming potential (GWP) is upper limit to be 14, and it has a short atmospheric lifetime of (30 to 40) days. Also, R1233zd(E) is regarded as a potential aerosol and solvent.

For serious application, accurate thermophysical properties are necessary. Several groups have reported their research on the properties of R1233zd(E), including critical constants, vapor pressure,  $(p, \rho, T)$  behavior, liquid density, viscosity, speed of sound, and surface tension. However, little information has been published on the experimental data of the thermal conductivity of R1233zd(E) in liquid phase.

In this work, the thermal conductivity of R1233zd(E) over the temperature range from 303 K to 473 K and pressures up to 20 MPa was measured by the transient short hot-wire method. The experiment system mainly consists of measuring apparatus, thermostatic bath, temperature and pressure measuring system, and data acquisition system. The thermal conductivity of toluene was measured as a standard reference to verify the reliability of the experiment system. Additionally, an empirical equation was correlated to reproduce the experimental results of R1233zd(E).

### Phase Equilibria (PE)

### PE – P1

### Basement

## MEASUREMENTS OF SOLUBILITIES FOR THE BINARY SYSTEM TOCOPHEROL + CAPSAICIN IN CARBON DIOXIDE

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The purpose of this work was measuring solid solubility of a mixture of tocopherol + capsaicin in supercritical carbon dioxide (CO<sub>2</sub>) based on the dynamic - analytical apparatus. The solubility of ternary system was measured at 308.15 and 328.15 K and pressures ranging from 10 to 35 MPa. The experiments were replicated at least three times and the data reported are the average of these values. The studied mixture was prepared in order to obtain a mass composition of 50% of tocopherol. The cell was charged in excess with a quantity of .3 gr of each solid component, the supercritical  $CO_2$  is made to flow into the cell of balance to obtain the desired pressure conditions. The solubility results were obtained by flow conditions of  $CO_2$  at intervals of 4 to 10 ml/min with a time of experimental of 120 minutes. Fraction mol of tocopherol and capsaicin for the ternary system are located at intervals of  $10^{-4} - 10^{-3}$  and  $10^{-5} - 10^{-4}$ , respectively. The uncertainty of measurements is as follows: temperature is 0.2 K, for pressure .01 MPa, for the solubility is in the order x  $10^{-6}$ .

The solubility of tocopherol and capsaicin increased as the temperature was increased. The same effect was observed with pressure. The solubilities of both compounds were increased in the ternary system, compare with those of binary systems. This can be the result of cosolvent effect of one of the solutes whit the other one.

### **PE – P2**

### Basement

## MEASUREMENTS OF SOLUBILITY DATA OF RESVERATROL IN SUPERCRITICAL CARBON DIOXIDE IN THE PRESENCE OF COSOLVENTS AT 308.15 K

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The study of ternary solubilities of solids is essential for the efficient design of extraction processes. The ternary solubilities of solids for cosolvent systems are complex functions of temperature, pressure and cosolvent composition. The intermolecular interactions between the molecules have a significant role in the solubilities of mixed solids in supercritical carbon dioxide cosolvent ternary systems.

Resveratrol is a compound present in the skin of the grape and their seeds. This compound has some therapeutic properties. Extraction of resveratrol using supercritical  $CO_2$  is complicated because of its polar nature. Unfortunately, their applications are reduced by the low bioavailability because of its poor solubility in water and its instability as compound.

The main goal of this work was performing solubilities of resveratrol in supercritical  $CO_2$  dioxide using ethanol and ethyl lactate as cosolvent. Measurements were made in an analytical-static apparatus using UV-Vis as analytical method.

Solubilities were made at 308.15 K and pressures from 14 to 26 MPa. The solubility of pure resveratrol is in the order  $x10^{-7}$  in mole fraction, to improve significantly when using ethanol and ethyl lactate from 4 to 11% molar compositions; in the case of resveratrol + methanol solubility is improved up to  $x10^{-5}$ , in the same way for resveratrol + ethyl lactate. The solubility for ternary systems increases with increasing pressure.

### **PE – P3**

## INFLUENCE OF PRESSURE IN THE GAS LIQUID SOLID PHASE DIAGRAM FOR THE MIXTURE DOTRIACONTANE + $\mathrm{CO}_2$

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The aim of this work was to determine the effect of a compressible gas (carbon dioxide) on the different melting point conditions for a long chain linear alkane (n-dotriacontane). The phase equilibrium of this binary system is presented in a pressure - temperature diagram. For this study, the static-visual method was used with assistance of a computer data acquisition system.

The experimental method is based on the technique of the "first freezing point". This technique consists on temperature rising of the mixture contained inside an equilibrium cell up to reach a fluid(s) phase(s). Once the temperature and pressure are stabilized, temperature is slowly decreased and consequently pressure also decreases at constant volume. This step is carried out to observe the first solid formation. The binary system was measured from 1.8 bar to 275.6 bar and in a temperature range from 59.91 °C to 69.85 °C.

Because the studied mixture is highly asymmetric, it presented a behavior that falls within the classification type IIb proposed by Lu-Zang. This consists in obtaining data melting temperatures lower than the melting temperature of the pure solid compound as the pressure increases, until reaching a minimum in the temperature. In this condition, a point of inflection is showed due to the solubility of the gas in the solid phase, characteristic of this classification. Once this point has been reached, the melting temperature increases as the pressure also increases.

### **PE – P4**

### Basement

## ISOBARIC VAPOR-LIQUID EQUILIBRIUM OF ALCOHOL + ALCOHOL OR ESTER AT 1.73 KPA BY THE DSC TECHNIQUE

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Detecting the incessant need to improve the production and purification steps of biodiesel, which is a promising alternative to non-renewable fuels, comprehension of vapor-liquid equilibria of binary and multicomponent systems containing ester and alcohol is of a great interest to the biodiesel production [1]. In addition to that, searching in the recent literature from 2014 to 2016 for experimental vapor-liquid equilibrium data of fatty systems, with at least one fatty compound (e.g.: fatty acid + n-paraffin), it was found 1,522 experimental data points. These data represent almost one-third of all experimental data published from 1900 to 2013 for VLE of fatty systems [2]. That represent a significant increase of interest of the scientific community in biofuel and oil/fat industry related resources. Thus, this work aims at determining isobaric vapor-liquid equilibrium data for two systems: 1-hexadecanol

+ 1-octadecanol and 1-hexadecanol + methyl myristate at 1.73  $\pm$ 0.04 kPa. The methodology applied was the Differential Scanning Calorimetry (DSC) technique. This procedure uses small amounts of mass (4 - 5 mg) and less time of work, when compared to other methodologies [3,4]. The activity coefficient model NRTL was applied to regress experimental data using the gamma?phi approach. Also, the group contribution method, original UNIFAC, was used to predict vapor-liquid equilibria. The NRTL model showed low average relative deviation (ARD) equal to 0.06% (alcohol + alcohol) and 0.20% (alcohol + fatty ester). The UNIFAC method successfully predicted for both systems with ARD = 0.21% to 1-hexadecanol + 1-octadecanol, and ARD = 0.33 to 1-hexadecanol + methyl myristate. Both systems presented ideal behaviour with  $\gamma$  close to unity.

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### PE – P5

Basement

# MEASUREMENT OF L-V AND L-S PHASE TRANSITIONS IN LIVE CRUDE OILS UNDER HIGH PRESSURE BY USING QCM

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Direct observation of phase transitions are hard to achieve in live oils under pressure due to the high level of opacity of crude oils. Because of this difficulty, various methods have been proposed to detect indirectly phase changes by monitoring physical properties such as volumetric, calorimetric, and dielectric properties and by noting the point of discontinuity in these properties during scanning experiments. However, in some crude oils, the discontinuity is not so pronounced and phase changes only result in small variations in physical properties. For such fluids, an interesting alternative consists in using acoustic measurements which can be carried out with a high degree of accuracy including at high pressure, and which presents the advantage of giving access to various derived properties.

Acoustic sensors are conveniently small, very sensitive and capable of measuring a variety of input quantities depending on the wave mode and the configuration chosen. It is because of these far-reaching characteristics that acoustic sensors have been more and more used in chemical and biochemical sensing as well as in measuring physical properties. All these potentialities have been exploited here for the development of an acoustic technique for probing both liquid-vapour and liquid?solid phase separations. The experimental setup used to determine phase changes by such acoustic technique involves an automatic PVT cell containing a quartz crystal resonator connected to a network analyzer and an additional syringe pump. It allows carrying out constant mass expansion measurements and isobaric

cooling (or heating) experiments. It is also able to perform high pressure titration experiments by injecting at fixed rate liquid or gas solvents within the PVT cell.

The proposed technique was used here to determine the full P,T phase diagram of a north sea crude oil in the pressure range 0.1 to 100 MPa for temperature between 293 to 393 K. The bubble points were measured by constant mass expansion experiments whereas waxy solid appearance temperatures were determined during isobaric cooling measurements. Finally, the asphaltene instability domain was estimated by doing pressure scanning experiments at fixed temperature. The upper asphaltene onsets were determined during compression measurement whereas the lower asphaltene thresholds were measured during compression experiments starting from the liquid vapour domain.

### **PE – P6**

#### Basement

#### EVALUATION OF THERMODYNAMIC MODELS FOR CCS PROCESSES

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prediction equilibria the  $CO_2$ The of phase for mixtures containing SO<sub>2</sub>, N<sub>2</sub>, NO, H<sub>2</sub>, O<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, Ar, and H<sub>2</sub>O is important to design the CO<sub>2</sub> capture and sequestration (CCS) process. These impurities cause serious problems of multi-phase flow, pipe corrosion, and gas hydrate formation. To predict the phase behaviour of the mixtures, many researchers have developed various types of equation of states (EOS) and evaluated the reliability of the models for  $CO_2$ -impurity binary systems. However, it is difficult to find studies on comparisons of modelling for  $CO_2$ -water and multi-component ( $CO_2 - H_2O$  - gas) systems.

In this work, the evaluation of thermodynamic models was performed for vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE) of CO<sub>2</sub>-mixtures. PSRK, CPA, PC-SAFT, NLFHB and GERG-2008 models are selected, considering the association effect of water in mixtures. PSRK combines cubic EOS with  $g^{E}$ -EOS mixing rule, CPA is cubic EOS with association term, PC-SAFT is hard-sphere chain based association model, NLFHB is lattice-fluid based association model, and GERG-2008 is empirically fitted Helmholtz free energy model. It was found that PSRK has problems in predicting phase equilibria at low temperature ( $_{i}$  260 K) region and CO<sub>2</sub>-rich LLE phase in CO<sub>2</sub> – H2<sub>O</sub> system. GERG-2008 showed good agreement with VLE for CO<sub>2</sub> mixtures containing Ar, N<sub>2</sub>, CH<sub>4</sub>, H<sub>2</sub>S, and H<sub>2</sub>O. However, there are large deviations on CO<sub>2</sub> – O<sub>2</sub>, CO<sub>2</sub> – H<sub>2</sub>, and H2<sub>O</sub>-rich LLE phase in CO<sub>2</sub> – H<sub>2</sub>O system shows reasonable predictions, compared with the other EOS. PC-SAFT showed reasonable results for VLE in most cases except for CO<sub>2</sub> – H<sub>2</sub>O system. For CO<sub>2</sub> + H<sub>2</sub>O mixture, NLFHB is the most appropriate model to predict the phase equilibria in both CO<sub>2</sub> and H<sub>2</sub>O-rich phase. From the results, it was possible to suggest guide-lines for using EOS for CCS processes.

### **PE – P7**

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Acetonitrile is widely used in chemical and pharmaceutical industries. Unfortunately, this solvent forms azeotrope with water and thus it is unable to recover high purity of acetonitrile from its aqueous solution by conventional distillation technique. However, the interactions between acetonitrile and water may significantly change in the presence of proper salts or organic entrainers and may lead to dramatically shift the composition of the azeotrope or induce liquid-liquid phase splitting. As a consequence, these effects may be helpful to improve the efficiency of the separation processes. As we know, high concentration of salts may cause corrosion in the equipment and light organic entrainers may cause VOC problem. Finding a new green auxiliary agent to overcome the drawback of using inorganic salts or organic entrainers may be economically attractive.

Typically buffer is used for keeping pH at a nearly constant value in a wide variety of chemical applications. 3-(N-Morpholino)propane sulfonic acid (MOPS), one of Good's buffers with  $pK_a = 7.2$  at 298.15 K, is a zwitterionic amino acid. In the preliminary study, we found that MOPS can induce liquid phase splitting for the aqueous solution of acetonitrile. By taking this advantage, MOPS could be a potential green auxiliary agent to assist the recovery of high purity acetonitrile from its aqueous solution.

In the present study, the phase equilibrium properties of the mixtures containing acetonitrile, water, and MOPS were measured. While the phase boundaries of solid-liquid equilibrium (SLE) were determined by densimetry, those of liquid-liquid equilibrium (LLE) and solid-liquid-liquid equilibrium (SLLE) were determined by cloud-point method. The phase compositions of coexistence phases for acetonitrile + water + MOPS, including at LLE and at SLLE, were also measured at 298.2 K under 101.3 kPa with an analytical method. The reliability of the experimental tie-lines data was confirmed by testing with the Othmer-Tobias equation. While the LLE, SLLE, and SLE phase boundary data can be fitted satisfactorily to the effective excluded volume (EEV) model, the experimental tie-line data were also accurately correlated with the NRTL model. A conceptual process flowsheet was suggested for recovering high purity of acetonitrile from its aqueous solution using MOPS as an auxiliary agent. The model parameters of the NRTL model obtained from this study can be used further for developing this new green separation process.

Basement

### **PE – P8**

## PHASE EQUILIBRIA AND EXCESS ENTHALPY OF BINARY MIXTURES FOR THE DEVELOPMENT OF BIOFUELS

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Continuing with the target of the Directive  $\ll 20-20-20 \gg$  on decreasing CO<sub>2</sub> emissions, 195 nations plus the EU have adopted a new global climate agreement in Paris which will take effect in 2020. About 25% of the EU CO<sub>2</sub> emissions come from the transport sector. Within this sector, road transport is the biggest emitter accounting for more than 70% of all greenhouse gas emissions. One of the main strategies is the deployment of low-emission alternative fuels for transport, such as biofuels.

Thermodynamic properties of biofuels are different and, as a consequence, experimental characterization of these properties is required in order to introduce their use and the development of new predictive models. The methodology consists of measuring properties of binary systems, as the simplest mixture, of an oxygenated additive of renewable origin and a hydrocarbon representative of fossil fuels.

In this paper, accurate experimental data of excess enthalpies and vapour-liquid equilibria (VLE) were carried out for two binary systems: (1-pentanol + 1,2,4-trimethylbenzene) and (2-pentanol + 1,2,4-trimethylbenzene). Excess enthalpies were measured at two different temperatures T = (298.15 and 313.15) K using an isothermal flow calorimeter [1], with a standard uncertainty less than 0.5%, and were correlated by Redlich-Kister equation. In addition, an isothermal total pressure cell [2] was used for measuring VLE at T = 313.15 K. Data were correlated applying Margules, Wilson, NRTL and UNIQUAC models.

Both mixtures present strong endothermic behaviour when 1-pentanol or 2-pentanol is mixed with 1,2,4-trimethylbenzene, which is enhanced with increasing temperature. Moreover, the two mixtures exhibit a high positive deviation from the ideality forming an azeotrope with maximum vapor pressure.VLE data are used to obtain excess Gibbs energy and excess entropy are calculated at T = 313.15 K.

### Acknowledgments

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### HYDRATE-CLATHRATE PHASE EQUILIBRIUM AND CONSUMPTION GAS DETERMINATION FOR WATER + SURFACTANT + METHANE SYSTEMS

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In this work, dissociation conditions  $(L_w?H?G)$  and consumption gas were measured for methane hydrates in presence of a surfactant (Synperonic PE/F127 and SDS), measurements were based on the isochoric method. Synperonic PE/F127 and SDS were previously synthetized in aqueous solutions around its corresponding CMC for each one. Hydrate formation kinetics were determined in order to know the induction time and the gas consumption. These variables were compared with those obtained from water + methane system.

The experimental equipment for measuring equilibrium ( $L_w$ ?H?G) and consumption gas hydrate (clathrates) points is based on the isochoric method. The main component is a visual cell made of stainless steel, which is designed to work from 248.15 to 393.15 K and pressures up to 36 MPa.

The isochoric method, as its name implies, has no variation in the volume of the cell, so the variables to measure are pressure and temperature. The relative composition between the liquid and gas phases can be known and varies for each experiment.

Hydrate formation consists of three different steps: nucleation, crystallization and growth (where the gas consumption happens). On the last one, nets between water molecules are formed. These nets form cages where the gas is trapped, this process is repeated several times until the maximum gas consumption.

With this, equilibrium conditions were calculated for methane hydrates systems; these conditions were determined at a concentration around CMC. Gas consumption was compared in the process of clathrate formation between systems with and without surfactant thus the influence of the surfactant in these hydrate clathrate systems was determined. Experimental data of this work were compared with those available in literature and there is concordance between them.

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### PE – P10

### PHASE TRANSITION PROPERTIES OF THYMOL, CARVACROL AND BIOSOL

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A straightforward method for predicting vapor pressures and enthalpies of sublimation of substituted benzenes taking into account their temperatures of fusion and the contribution of several different substituents of benzene derivatives was published [1]. To enlarge the database that supports this method, the group isopropyl,  $-CH(CH_3)_2$ , that was absent in the database, is one of the substituents of the benzene derivatives isomers selected for this study.

Thymol, carvacrol and biosol are monoterpenic phenols that have been used as fragrance ingredients, and cosmetics preservatives or biocides [2]. The first two isomers have also an extensive applicability in pharmaceutical, chemical and food industries and several studies report their biological and pharmacological activity, such as antioxidant, anti-inflammatory, antimicrobial, and fungicide properties [3].

Using a diaphragm manometer static method [4], the vapor pressures of both (crystalline and liquid) condensed phases of thymol and biosol were measured in the temperature ranges from T = (283.1 to 362.4) K and T = (312.9 to 395.8) K, respectively. This experimental technique was also used to measure the vaporization vapor pressures of carvacrol through the temperature interval T = (300.9 to 366.2) K. The Knudsen mass-loss effusion technique [5] was also used for complementing the range of the vapor pressure measurements of biosol between T = (293.3 to 315.2) K.

From the experimental results, the standard molar Gibbs energies and the enthalpies of sublimation and of vaporization, at T = 298.15 K, were derived. The temperature and molar enthalpy of fusion were determined by differential scanning calorimetry. The contributions of the isopropyl group to the sublimation properties of the compounds studied were calculated.

### Acknowledgments

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### PE – P11

## WATER ACTIVITY MEASUREMENT AND THERMODYNAMIC MODELLING OF AQUEOUS SOLUTIONS OF MANGANESE NITRATE

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Despite its importance for ore extraction or soil pollution control, experimental measurements and thermodynamic modeling of aqueous solutions of transition metal nitrates has still a lot of room for improvement. The available experimental data is rather old displaying a lot of scatter and inconsistencies, while only a few studies on modeling thoses systems are known from the open literature.

Contributing to overcome some of these limitations, in this work an humidity sensor instrument was used to measure water activity of aqueous solutions of manganese nitrate up to almost the saturation molality, at 298.15 K. The accuracy of the data was checked by comparing with well established values for sodium bromide, or lithium chloride, aqueous solutions at the same temperature.

The new experimental data as well as the available freezing point data for this system were used to elaborate a comprehensive model to describe the behaviour of the solution in a wide range of a temperature and concentration. The use of Pitzer model enables us to propose the first set of parameters for this system able to describe the salt molal activity activity coefficients, water activity and the osmotic coefficients.

### PE – P12

### Basement

## MODELLING AND EXPERIMENTAL DETERMINATION OF THE SLG EQUILIBRIUM FOR BINARY SYSTEMS

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In this work, the modelling of solid-liquid-gas (SLG) equilibrium for the binary systems  $CO_2$  + n-Docosane and  $CO_2$  + n-Dotriacontane is presented in a pressure-temperature diagram.

The Cubic Equations of State Peng-Robinson and Soave-Redlich-Kwong, and the non-cubic equation of state PC-SAFT (Perturbed-Chain Statistical Associating Fluid Theory) was used for the modelling. The binary interaction parameters were obtained by minimizing the sum of relative errors between the experimental and calculated solidification temperatures. The SLG equilibrium line was determinate by means of the first freezing point technique in a constant-volume cell over the pressure range from 0 to 35 MPa.

A reliable constant volume static-visual apparatus was developed to perform SLG measurements for binary systems. Experimental visual procedure based on the first freezing point was suitable to observe the first solids formation from fluid phase(s). The main advantage of our methodology was the use of a data acquisition system to simultaneously confirm the observation of first solid formation through a pressure increasing at this point while temperature was still decreasing.

The curve P-T for the SLG equilibrium of the both systems were a Type II according to Lu and Zhang. We observed that the temperature and pressure of SLG data increased as the number of carbon chain grew at similar conditions.

In general, the results obtained with the equation of state PC-SAFT, not major improvement over those obtained with equations PR and SRK state mixing rules using two binary interaction parameters. The results of the performance showed that at least two binary interaction parameters to better represent the data of SLG equilibrium of  $CO_2$  + n-alkanes binary systems are required.

### PE – P13

Basement

## EXTRACTION OF FATTY ACID FROM PEACH KERNEL (PRUNUS PERSICA) BY SUPERCRITICAL CARBON DIOXIDE

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Peach seed was attractively forcused for useful bio resources. Especially, the kernel of peach seed contained various fatty acid, which is used in herbal medicine in East Asia. Peach kernel oil performs important therapeutic properties and is nutritionally attractive due to the unsaturated fatty acid (oleic acid 63.8%, linoleic acid 15.4%, palmitic acid 13.4%) [1].

Peach kernel contains amygdalin as a cyanogentic glycoside. This is converted by the body into cyanide, which is poisonous. Selectively extraction of fatty acid without amygdalin is important for safety medical products. Supercritical carbon dioxide (SCCO<sub>2</sub>) has been used as the hydrophobic solvent which extracted oil. It has high selectivity of separation and no toxicity.

In this study, the fatty acids were extracted using  $SCCO_2$  at 313 K and 10-30MPa for 30 min. Oleic acid, linoleic acid and palmitic acid were extracted from peach kernel by  $SCCO_2$ . Extracted amount of oleic acid and palmitic acid were lineally increased with increasing

pressure. It was corresponded to  $SCCO_2$  density. In contrast, linoleic acid was almost constant with changing pressure of  $SCCO_2$ . Fatty acid was successfully extracted in high yields from peach kernel using  $SCCO_2$ .



Fig.: Extracted amount of fatty acids from peach kernel using SCCO<sub>2</sub> [313 K, 30 min].

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### PE – P14

### **Basement**

## A CYLINDRICAL MICROWAVE RESONATOR FOR HIGH PRESSURE PHASE EQUILIBRIUM DETERMINATION

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In addition to the need for accurate and reliable high-pressure phase equilibrium in numerous applications, the search of new renewable energy sources, as biogas, leads to develop new experimental techniques capable of accurately characterizing the phase equilibrium properties of new blends. Moreover, obtaining experimental data is necessary for the development of equations of state and models as the GERG-2008 [1], which is applied to natural gas and other similar mixtures. Experimental determination of phase equilibrium at high pressure is often the only suitable method for obtaining reliable data, because the behaviour at these conditions is complex and difficult to predict.

A novel technique based in a cylindrical microwave resonator was developed and checked measuring  $CO_2$  behaviour. The physical principle of detection is based on the discontinuity which occurs in the dielectric constant with phase transition and also carries a discontinuity in the resonance frequency of the cavity. This experimental technique is classified as synthetic method with no visual phase transition and operates on isothermal mode. Synthetic methods

consist of preparing a mixture of known composition. The experimental procedure involves programing pressure ramps, starting with the sample in homogeneous phase until the appearance of a new phase (bubble and dew points).

The objective of this work is to measure phase behaviour of mixtures involved in biogas process. Phase enveloped is determined for two mixtures of methane and carbon dioxide at methane mole fractions of 0.4 and 0.6.

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### PE – P15

### Basement

# EXCESS MOLAR GIBBS ENERGIES OF HEPTAN-2-ONE + 1.4-DICHLOROBUTANE OR 1,6-DICHLOROHEXANE

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The purpose of this work is the determination of the vapour-liquid equilibria, of heptan-2-one + 1,4-dichlorobutane or 1,6-dichlorohexane with view to study the effect of specific interaction (carbonyl-chlorogroup) on the excess Gibbs energies of heptan-2-one + halogenated hydrocarbons.

Halogenated hydrocarbons are manufactured in large quantities and have many application (as refrigerant, organics solvents, medicines).

The vapor pressure of the the pure compounds and the binary mixtures were measured by means of a static apparatus at temperatures between (263.15 and 343.15)K. The apparatus allows measurements in the P range from 27 to  $200 \cdot 10^3$  Pa and from 258 to 468 K. Vapor pressure are measured by means of pressure gauges (Rosemount, model 1151 DPE 22S2, Minneapolis, Minn, USA), protected by a differential pressure indicator (MKS, Model615D, MKS Instruments, USA).

The experimental data of excess molar Gibbs energies,  $G^E$ , have been compared with values using the DISQUAC group contribution Model.

### **PE – P16**

## BUBBLE POINT PRESSURE MEASUREMENT FOR DIMETHYL ETHER + CHLOROFORM +ETHANOL AT 313.15 K

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Ethanol and chloroform are well known as standard solvents for pharmacological active compounds. For example the solubility of pharmacological active compounds were available in the handbook, where the solubility is defined as minimum volume of solvent to solve unit mass of the compounds around the room temperature. Otherwise propane and dimethyl ether (DME) are widely used as a splay propellant. However, there is few solubility for the mixture of solvent. In our project, solid-liquid equilibria and bubble point pressure have been measured for some systems composed of antipyrine, chloroform, ethanol, propene and dimethyl ether [1,2]. Therefore this study is a successive report for the project. The bubble point pressure was measured for the two binaries, DME + chloroform and DME + ethanol, by use of a static apparatus in the temperature range from 283.15 to 313.15 K. The bubble point pressure was also measured for a ternary, DME + chloroform + ethanol at the temperature of 313.15 K. For the ternary system, the mole ratio of chloroform : ethanol was set to be 1:1.

The detail procedure and equipment have been already described elsewhere [2]. The apparatus was based on a static method. The cell was made from Pyrex glass with the inner volume about  $40 \text{ cm}^3$ . It was specially designed, and the maximum safe working pressure was 7.5 MPa. A magnetic stirrer was in the cell to agitate the liquid phase. Temperature was measured by a thermistor thermometer (Technoseven, D461, Yokohama, Japan) and the precision was assume to be 0.03 K. The pressure was measured by a diaphragm type pressure gauge PH-100 KB (Kyowa Electronic Instruments Co., Tokyo) with a maximum capacity 10 MPa and the resolution was 0.1 kPa.

In the whole temperature range, the bubble point pressure of DME + chloroform showed a negative deviation from Raoult's law. Otherwise that of DME + ethanol showed a positive deviation. That of DME + chloroform + ethanol behaved as a quasi-ideal solution following Raoult's law. The bubble point pressure for the two binaries was correlated with NRTL eq. According to the reports of Scatchard and Raymond [3], chloroform + ethanol shows azeotropes at 308, 318 and 328 K. The parameters for chloroform + ethanol were determined from the data at 308 and 318 K. The calculated results showed good reproducibility for the three binaries. By using the parameters for three constituent binaries, the bubble point pressure was well predicted even for the ternary.

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### PE – P17

## MODELLING THE SOLID-LIQUID-GAS PHASE EQUILIBRIUM OF CARBON DIOXIDE + (FATTY ACID) SYSTEMS

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Process design requires precise phase equilibrium data as well as thermodynamic and transport properties. Solubility and solid-liquid-gas phase equilibrium are important for applications in particle formation processes using supercritical fluids since these are referred to the minimum temperature and pressure conditions where solids are formed. For this instance, carbon dioxide is the most used solvent due to their well-known properties and benefits.

Experimental solid-liquid-gas phase equilibrium for the binary carbon dioxide + fatty acid systems obtained by our group were represented using the Peng-Robinson and Sanchez-Lacombe equations of state, coupled to the two-parameter van der Waals one-fluid mixing rules. Peng-Robinson equation of state with van der Waals mixing rules has been used to represent this kind of phase equilibrium for these systems. For the best of our knowledge, Sanchez-Lacombe equation of state was used for representing the phase equilibrium for first time.

Fugacity coefficients of the liquid and gas phases can be evaluated using the equations of state. Fugacity of the solute (fatty acid) in the solid phase was evaluated using the approximation proposed by Kikic *et al.* Binary interaction parameters were computed by minimizing an objective function (root mean square error of temperatures of the solid-liquid-gas phase equilibrium, RMST) and the performance of the modelling was evaluated by calculating the average absolute deviation in temperature (AAD).

The optimized interaction parameters did not exhibit a trend with respect to the number of carbon atoms in the fatty acid chain. The maximum AAD% in temperature did not exceed 0.24%. The used equations of state were capable to describe the equilibrium curve throughout the minimum melting temperature region.

### **PE – P18**

### Basement

### SOLID-LIQUID-GAS PHASE DIAGRAMS OF CARBON DIOXIDE + (LAURIC OR MYRISTIC ACID) OBTAINED NON-VISUALLY

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The research on supercritical fluids and their uses in industrial sectors such as extraction and

chromatography operations are well documented in the literature. New processes have been suggested. However, these cannot be implemented fully by the lack of experimental data on phase equilibria. Particle formation processes with supercritical fluids have applications in the pharmaceutical industry. Knowledge of phase behaviour and the solubility of compounds of interest in the supercritical fluid as a function of pressure, temperature and composition are important for the design, simulation and optimisation.

In the solid-liquid-gas phase transition for a binary mixture constituted by a solid and a supercritical fluid, the P-T diagrams are drawn by identifying a phase change. This kind of diagrams might coexist if the melting point of the solid is greater than the critical temperature of the supercritical fluid and the solid is thermostable up to its melting point.

In this work, the solid-liquid-gas phase diagrams are reported for the lauric acid or myristic acid (solute) + carbon dioxide (solvent) systems in a wide range of temperature and pressure and using the static non-visual method and the first freezing point technique.

The proposed measuring procedure depends on solid formation detection from fluid phases by a pressure change. The experimental apparatus uses a stainless steel cell where windows are not required. The mixture is slowly cooled while temperature and pressure are decreasing at isochoric conditions. Therefore, the solid-liquid-gas phase equilibrium data are considered when pressure exhibits an abrupt increase while temperature is still decreasing.

The systems are classified as type B-II behaviour according to the tendency of solid-liquid-gas line. The solid-liquid-gas lines have a minimum temperature below triple point temperature of the solid and the temperature of a upper critical ending point, this happens for relevant effects to increased solubility and the increase in hydrostatic pressure, which exert influence on the behaviour of the lines. The minimum melting point temperature increased as the carbon chain length increased for the fatty acid.

### PE – P19

### Basement

### THE AZEOTROPIC REFRIGERANTS BASED ON AMMONIA

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Ammonia is a natural refrigerant with excellent thermodynamic properties, zero ozone depleting potential (ODP) and very low global warming potential (GWP). However, the poisonousness and flammability of ammonia limited its civil application. Besides, ammonia is immiscible with mineral lubricants, which may lead to a weakened heat transfer coefficient due to the film of oil presented in the evaporator. In recent years, with the search for substitutes with less influence on global warming, the use of ammonia has come into focus again.

One of the most promising ways to extend ammonia's application in refrigeration systems is searching for new refrigerant mixtures based on ammonia. The improved properties of working agent were offered in the way to mix pure ammonia with other refrigerants having low values of GWP and zero ODP. In our previous work, the vapor liquid phase equilibrium of ammonia + n-butane/1-butene/1, 1-difluoroethane/1,1,1,2-tetrafluoroethane/2, 3, 3, 3 - tetrafluoroprop-1-ene systems were investigated, and all of them showed azeotropic behaviours. In this paper, an evaluation of mixed refrigerants based on ammonia in the vapour compression refrigeration system was performed, synthetically considering the coefficient of performance (COP), volumetric refrigeration capacity (VRC) and discharge temperature. Both binary and ternary azeotropic mixtures were investigated, along with some commercial zeotropic refrigerants as references. The azeotropic mixtures were predicted with a simple method based on the extreme value of pressure at the azeotropic point. The mixed thermodynamic properties were calculated by Peng-Robinson equation of state with the regressed interaction parameters. The tests on more than 100 systems show that all the positive azeotropic refrigerants achieved better VRC than its compositions. Theoretically, a higher saturation pressure implies a working fluid with a higher volumetric capacity. The COP of the mixtures was generally lower than that of the individual refrigerants, except for some azeotropic systems comprising of ammonia and hydrofluorocarbons. The discharge temperatures of all the azeotropic refrigerants were attractile, especially for ammonia?s mixtures. The present results suggest the superiorities of the azeotropic refrigerants, especially for binary and ternary systems including ammonia.

### Theory and Modelling (TM)

### TM – P1

#### **Basement**

### NUMERICAL SIMULATION FOR THE EFFECT OF AMPHIPATHIC MOLECULES ON THERMAL CONDUCTIVITY OF THEIR AQUEOUS SOLUTION

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An amphiphilic molecule is fascinating molecule since it behaves its self-organization in aqueous solution. The atomic bonds in the amphiphilic molecule are much stronger compared to the interaction between water molecules. Therefore, higher thermal conductivity of single amphiphilic molecule is expectable than that of water. It means that the aqueous solution shows higher thermal conductivity than pure water. However, the effect of self-organization of amphiphilic molecules on the thermal conductivity is not clear. In order to clarify the effects of self-organization, the thermal non-equilibrium dissipative particle dynamics (NEDPD) simulations were conducted. In the simulation, a virtual particle (DPD particle), group of molecules, is generally treated.

The amphiphilic molecule was modelled by coarse graining the actual amphiphilic molecule (cetrimonium bromide; CTAB), which consists of a hydrophilic head group and two hydrophobic tail groups. On the other hand, 5 water molecules were coarse-grained as a DPD particle. The temperature of each DPD particle was entertained by taking account of the internal energy. The thermal conductivity was obtained from the temperature gradient and heat flux passing through the system. The simulations were carried out for the 2000 particles system in the concentration range of CTAB molecule from 0 to 50 mass%.

As for the simulation results, it is found that CTAB molecules congregate with the increase of concentration and form various structures. Especially, the spherical micelles and the thread-like micelles were observed at the concentration of CTAB molecules less than 25 mass%, and the layered micelles were observed at the CTAB concentration more than 25 mass%. Moreover, the migrations of micelles, which is assumed to be a thermophoresis, along the temperature gradient were observed. As for the thermal conductivity, the thermal conductivity increased in proportion to the concentration of CTAB molecule. However, the thermal conductivity showed a low value when the micelles were located at the low temperature controlled area.

### TM – P2

### Basement

### **RESEARCH ADVANCES FOR THE THERMAL CONDUCTIVITY OF THIN FILMS**

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With the development of the Micro-Electro-Mechanical System (MEMS) in recent years, the thermal management on micro devices has become a focal point, making the characterization of thermal conductivity of the micro-nanoscale film materials particularly important. However, thermal conductivity of thin films are quite different from that of their bulk materials due to size effects. Therefore, a new set of measurement, theory and simulation methods for microscopic materials are needed.

This review introduces four methods for measurement of thermal conductivity, which are the 3-Omega method, the transient thermoreflectance (TTR) methods including the frequencydomain thermoreflectance (FDTR) method and the time-domain thermoreflectance (TDTR) method, the micro-Raman technique using Raman scattering and the scanning thermal microscopy (SThM) method. Applicable conditions, advantages and disadvantages of these methods are discussed, which provides a reference for the selection of measurement methods. Theoretical approaches such as Callaway model and Holland model are proved to have great potential in giving accurate descriptions for the thermal conductivity. Molecular dynamics simulation technology is an effective method for investigating the thermal conductivity of thin films, which does not need to consider the various phonon scattering mechanisms and relaxation times.

Thermal conductivity data of typical thin films determined by different methods are collected and analyzed. All of temperature, film thickness, film composition and film preparation technique have important influence on thermal conductivity. The choice of measurement method also leads to different thermal conductivities even for the same sample.

### Acknowledgment

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TM – P3

### Basement

## MASS DIFFUSION COEFFICIENTS OF BINARY GAS MIXTURES BY EXPERIMENTAL AND THEORETICAL METHODS

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Reliable data for diffusion coefficients of gas mixtures are required for the optimum design of apparatus and processes in, for example, natural gas purification, catalytic reactions, or fuel cell applications. As it is virtually impossible to measure diffusion coefficients for all relevant systems at each thermodynamic state, the experimental determination needs to be accompanied by theoretical methods. In turn, theoretical calculations can only be as accurate as the experimental data used for their validation. In the present research project, experimental and theoretical methods are combined to get a comprehensive understanding about the mass diffusion of gaseous systems at various densities ranging between the dilute and dense gas regime. Besides providing a reliable experimental database from optical-based measurement techniques, the main objective of this study is to develop the Molecular Dynamics (MD) simulation method with respect to the prediction of diffusivities of gas systems by applying new molecular models derived from *ab initio* calculations.

As model systems, binary gas systems containing methane, propane, and carbon dioxide were investigated at temperatures from (293 to 373) K. Holographic interferometry combined with a Loschmidt cell (HILC) employs a defined initial macroscopic concentration gradient between two half-cells to establish an instationary mass transport. The latter is approximated as an ideal diffusion process in the binary mixture at constant pressure and temperature. From the concentration analysis in both half-cells applying two interferometers, the binary diffusion coefficient could be accessed in the diluted low-density regime at pressures up to 1 MPa over a mole fraction range between 1/6 and 5/6. The experimental data with uncertainties of less than 5% (k = 2) serve as reference for equilibrium Molecular Dynamics (MD) simulations. Using reliable atomistic models of the studied gases, thermophysical properties are accessible at any desired state by analyzing the molecular dynamics. Despite the relatively low densities

implying poor statistics, the self-diffusion coefficients for the pure gases and in the binary systems could be calculated over a broad density range for pressures between (0.1 and 10) MPa with typical uncertainties of 5% (k = 2). In this context, the results from commonly employed empirical molecular models are compared with those from new pair-specific models obtained by *ab initio* calculations at the proximity of zero-density. For the binary mixtures, the self-diffusivities calculated by MD simulations are in reasonable agreement with the HILC-based binary diffusion coefficients at the boundaries of the mole fraction range and with the theoretical *ab initio* calculations at low pressures.

In a next step, the experimental database of binary diffusion coefficients will be expanded to the dense gas regime at pressures up to 10 MPa by performing dynamic light scattering (DLS) measurements. These data will also be used to test the capabilities of MD simulations regarding the computation of gas binary diffusion coefficients via independent calculations of the Maxwell-Stefan diffusion coefficient and the thermodynamic factor.

TM – P4

#### Basement

### TWO DIMENSIONAL NUMERICAL SIMULATIONS OF NANOSCALE ALGAN/GAN HIGH -ELECTRON MOBILITY TRANSISTORS WITH A METAL FIELD-PLATE STRUCTURE

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Wide band-gap and high breakdown electric field allows high terminal voltage operation of the transistor based on Gallium nitride technology. The excellent microwave power performance demonstrated in AlGaN/GaN HEMTs (high-electron mobility transistors) results from the combination of high current density with high voltage operation [1], which benefits from the high sheet charge density in these hetero-structures ( $10^{13} \text{ cm}^{-2}$ ), the high carrier mobility ( $1500 \text{ cm}^2/\text{Vs}$ ) and saturation velocity ( $1.5 \times 10^7 \text{ cm}^2/\text{s}$ ) in the channel and the high breakdown voltage inherent in the GaN material. However, their reliability still limits their applications in today's electronic systems.

The newly developed field-plated AlGaN/GaN high electron mobility transistors show improved performance due to the electric field reduction in the device channel and surface modification [2]. We report on two dimensional numerical simulations of gate-recessed and field-plated AlGaN/GaN HEMTs where all the important device parameters have been defined, the insulator thickness under the field plate is also an important design parameter to attain higher breakdown voltage, thus an improvement of the performances of HEMT devices.

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### TM – P5

#### **Basement**

# MOLECULAR MODELLING AND DYNAMIC DISSOLUTION STUDIES OF CARBAMAZEPINE CO-CRYSTAL

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Co-crystal exhibits characteristic properties which differ from the individual pure crystals and several researches have been conducted to understand such behaviour. Especially, dissolution rates are important for drug-delivery applications. Experimental results and dissolution mechanism of carbamazepine (CBZ) co-crystal are investigated using a molecular modelling method. CBZ co-crystal was synthesized with polyphenols such as 7-hydroxyflavanone (F), pinocembrin (P) and naringenin (N) as coformers. 7-hydroxyflavone (FV), chrysin (C) and apigenin (A) did not form co-crystal despite they have very similar structures with F, P and N. These polyphenols have a double bond in a ring which is the only difference with F, P, and N. Polyphenols were observed at the molecular level in order to confirm factors which have major effect on forming co-crystal. Interaction energies between CBZ and coformers show little difference because they have similar functional groups. Molecular dynamic simulation was used to promote understanding of CBZ-N co-crystal dissolution on the molecular scale. The simulation was performed in water solution at 298 K and the interaction energies between molecules were calculated as simulation time progresses. It can be assumed that molecules which have the lower initial energies with crystal molecules are dissolved faster into the solution. A qualitative analysis was performed to verify experimental observations.

### TM – P6

### Basement

# A NEW CORRESPONDING STATES MODEL FOR THERMAL CONDUCTIVITY OF LIQUID HYDROCARBONS

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The thermal conductivity is an important transport property for fluids. It is required in many engineering applications including transportation, storage and combustion. Since experimental thermal conductivity data have not been reported yet for some substance, prediction of the thermal conductivity values is of great necessity.

The corresponding states principle is a powerful method, which can be used to estimate the thermophysical behavior beyond the range of existing data. An extended corresponding states model was reported by Hanley and Mo&Gubbins to predict the viscosity and thermal conductivity of complicated structured fluids by introducing the shape factors. The shape factor can be regarded as the function of the reduced temperature and the acentric factor and the critical compressibility factor. In addition, it is usually considered density-independent to simplify calculation. However, the effect of density on shape factors cannot be neglected in liquid phase.

In this study, a new shape factors equation was proposed for liquid hydrocarbon on the basis of the extended corresponding states. The empirical equation can be used to calculate the shape factor, and then obtain the thermal conductivity of liquid n-paraffin. Applying the new model, values of the thermal conductivity for selected pure substances were calculated. The result showed that average absolute deviation between the calculated values and the literature data is less than 5%.

### TM – P7

### Basement

## A NEW CORRESPONDING STATES MODEL OF THE VAPORIZATION HEAT FOR LIQUIDS

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The heat of vaporization is one of the basic thermodynamic properties of a pure fluid. It is required in plenty of engineering applications involving the liquid-vapor phase change such as the condenser in the steam turbine, the water wall in boilers, the condenser and evaporator in air-conditioning systems, the reboiler in devices for chemical processing. The vaporization heat can be obtained from experimental measurements as well as theoretical method. Since experimental values are not available for some substances, it is necessary to propose predictive models for the estimation of the vaporization heat. Note that equations of state can be applied for calculating thermodynamic properties including the heat of vaporization. However, this method requires some knowledge of equations of state and other thermodynamic properties, some of which are usually hard to acquire. For this reason, to propose a new calculated model with less parameter is increasingly important.

Many empirical equations or theoretical models for calculating the vaporization heat of liquids were proposed. Group contribution models were used to predict the enthalpy of vaporization, which requires the information of the chemical groups and molecule's chemical structure. In other correlations, it is necessary to obtain the heat vaporization at its normal boiling temperature. The corresponding states principle (CSP) is also a common method, in which it is required to know the critical parameters and the acentric factor. Plenty of models were reported on the basis of CSP. However, all the models reported cannot obtain the high accuracy in the low temperature range.

In this paper, a new vaporization heat equation was presented based on the CSP, Applied the new equation, the values of the vaporization heat for 52 pure substances were calculated. A

comparison between the calculated results and the literature data showed the average absolute deviation 1.71%. Moreover, the behavior in the low temperature range was improved. This paper provided a new method to calculate the vaporization heat.

### TM – P8

### Basement

## ESTIMATING THE VISCOSITY OF BINARY LIQUID MIXTURES THROUGH VAPOUR-LIQUID EQUILIBRIUM CORRELATION

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A comparison between the thermodynamic and the viscous behavior of 20 binary liquid mixtures containing pentane, hexane, heptane, cyclohexane, benzene, toluene, chloroform, acetone, methanol, ethanol, water, and n,n-dimethylacetamide has been carried out.

Isothermal vapour-liquid equilibrium data, available in the literature, have been correlated through the UNIQUAC equation [1] and the corresponding binary interaction parameters were obtained. The corresponding viscosity data, also available in the literature, have been correlated through the model of Martins and co-workers [2]. The basic hypothesis of this model is that the activation energy for viscous flow is a thermodynamic potential, whose excess is given by the UNIQUAC equation. Therefore, for each binary system investigated, the corresponding pair of viscous binary interaction parameters have been obtained through the minimization of experimental viscosity data.

According to the UNIQUAC model, the molar excess Gibbs energy is the sum of a combinatorial and a residual term. However, the combinatorial contribution is independent of the adjustable parameters. Using the parameters previously determined, the viscous and thermodynamic residual excess Gibbs energies have been calculated, for each binary system investigated. Since the two sets of experimental data were obtained under different compositions, the values have been calculated in the maximum common interval of molar fraction.

The values of the two types of residual contributions are strongly related. For the systems investigated in this work, the residual term calculated through viscosity modeling can be described by a linear, as well as quadratic, dependence on the thermodynamic residual Gibbs energy. For the binary systems investigated in this work, good results have been obtained with the linear adjustment. Average deviations lower than 4% were obtained, except for the system ethanol - water, for which the average deviation was 8%. Nevertheless, a deviation of 1.5% was obtained using the quadratic correlation.

Therefore, using the UNIQUAC equation and the model of Martins and co-workers, VLE data can be used to estimate the viscosity of binary mixtures. Also, viscosity data correlation can be used to estimate vapor pressures and activity coefficients of binary systems

### Acknowledgments

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### TM – P9

### **Basement**

## BEHAVIOR OF PHASE-CHANGE MATERIALS AT DECREASING HEATING RATES: EXPERIMENTAL AND THEORETICAL STUDY

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Materials with a phase change, or phase-change materials (PCMs), may be used to store/release thermal energy within a small temperature range. This is of interest in various industrial applications, for example, in civil engineering (heating/cooling of buildings) or cold storage applications. A phase change (such as melting or freezing) is associated with a jump and peak in the temperature dependence of enthalpy and heat capacity, respectively. The fact that these jumps and peaks are of finite widths and heights is not of purely non-equilibrium origin: they may remain finite even at very slow scanning rates (for example, when adiabatic scanning calorimetry is used). Here we study the behavior of heat capacity peaks for three selected PCMs as the heating rate is decreased in the sequence  $1 \text{ Ks}^{-1}$ ,  $0.8 \text{ Ks}^{-1}$ ,  $0.4 \text{ Ks}^{-1}$ ,  $0.2 \text{ Ks}^{-1}$ , and  $0.1 \text{ Ks}^{-1}$ . Experimental results are analyzed by an equilibrium theory that we had previously developed to fit the peaks and determine the corresponding latent heats and phase-change temperatures. We focus on the dependence of the latter two quantities on the heating rate and point out the resulting differences that could be a source of their imprecise determination.

### TM – P10

### Basement

### **QSPR MODEL FOR THERMAL EXPANSION COEFFICIENT OF LIQUID EDIBLE OILS**

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The thermal expansion coefficient ( $\beta$ ) is a thermophysical property that relates a response of any material to the application of heat. Its thermodynamical definition is:

$$\beta = -\frac{1}{\rho} \cdot \left(\frac{\partial \rho}{\partial T}\right)_p$$

Applying this definition to the Lund correlation was obtained the following QSPR (Quantita-

tive Structure-Property Relationships) equation to predict the thermal expansion coefficient:

$$\beta = \frac{6.4 \times 10^{-4}}{8.71 \times 10^{-1} + (3.0 \times \text{IS} + 1.4 \times \text{II} - 6.4 \text{ T}) \times 10^{-4}}$$

IS, II and T represent the molecular characteristics (saponification and iodine values respectively) and the temperature of the liquid oil. The  $\beta_{\text{Calc}}$  figures were calculated and compared to the experimental measurements for some edible oils as exemplified in the table.

Óleo vegetal	IS	II	Т	$\beta_{\mathrm{Exp}}$	$\beta_{ ext{Calc}}$	Error
	(mg/g)	(cg/g)	(°C)	$(^{\circ}\mathrm{C}^{-1})$	$(^{\circ}\mathrm{C}^{-1})$	(%)
Corn	190.0	115.5	23.9	$7.075\times 10^{-4}$	$6.995\times 10^{-4}$	1.13
Crambe	167.5	93.0	23.9	$7.387\times10^{-4}$	$7.071\times10^{-4}$	4.28
Milkweed	195.5	125.4	23.9	$7.397\times10^{-4}$	$6.972\times10^{-4}$	5.75
Peanut	191.5	92.0	27.0	$6.587\times10^{-4}$	$7.032\times10^{-4}$	6.76
Rape	175.0	102.5	23.9	$7.275\times10^{-4}$	$7.043\times10^{-4}$	3.19
Rice bran	185.3	99.9	20.0	$6.526\times10^{-4}$	$7.003\times10^{-4}$	7.31
Seal	290.7	142.7	5.0	$6.903\times10^{-4}$	$6.865\times10^{-4}$	0.55
Soy	192.0	130.5	23.9	$7.295\times10^{-4}$	$6.974\times10^{-4}$	4.40
Sperm Whale	193.5	72.5	5.0	$7.376\times10^{-4}$	$7.077\times10^{-4}$	4.06
Sunflower	191.0	130.5	20.0	$6.619\times10^{-4}$	$6.958\times10^{-4}$	5.12

The  $\beta_{\text{Exp}}$  values were determined using experimental densimetric measurements, in the liquid state, from the literature over wide temperature ranges (5-100 °C). Obviously this equation requires accurate measurements of T, IS and II parameters. The proposed QSPR model predicts acceptable values for  $\beta$  with average error less than 5%.

### TM – P11

#### **Basement**

## CORRELATION AND PREDICTION OF THE VISCOSITY FOR FATTY ACID ESTERS BASED ON HARD-SPHERE SCHEME

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Biodiesel is a promising renewable and environmentally alternative fuels, it can be used in diesel engine with little or no modifications. The main components of biodiesel include fatty acid methyl esters (FAMEs) and fatty acid ethyl esters (FAEEs) which are derived from vegetable oils or animal fats. During the last few years, researchers have carried out the investigation of thermophysical properties of biodiesels and its pure constituents (FAMEs or FAEEs) from experimental or theoretical aspects. Among different properties, viscosity and density are the most important parameters that affect the engine performance. Therefore, reliable viscosity models for FAMEs and FAEEs are necessary for the simulation and optimization of engine.

For engineering purposes, a viscosity model is more reliable if it has some physical basis. There have different theoretical or semi-theoretical viscosity models in the literature, such as
corresponding state principle, free volume theory, friction theory, and hard-sphere theory, etc. Among the above models, hard-sphere scheme, which developed by Dymond and Assael, has achieved considerable success in modeling the viscosity of different liquids[1-6].

In the present work, the hard-sphere scheme is extended to correlate and predict the viscosity of fatty acid esters, including 22 FAMEs and 16 FAEEs. 555 viscosity data for FAMEs and FAEEs are considered. Generalized forms of the parameters in the hard-sphere model for FAMEs or FAEEs are presented. In addition, the viscosity of biodiesel can be determined via the mixture rules if the viscosity of pure fatty acid eters and the constituents of biodiesel are known.

## Acknowledgment

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## TM – P12

#### **Basement**

# INVESTIGATION OF LIQUID AND VAPOR DENSITYES: SCALING MODELS AND NUMERICAL DATA ON DENSITIES OF ${\rm SF_6}$ AND ${\rm H_2O}$

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Some thermodynamic functions are discussed in the work. They have a form,  $F(\tau, D, C)$  and are associated with one of thermodynamic properties at the saturation line (the fluid density  $(\rho_l)$ , the gas density  $(\rho_g)$ , the order parameter  $(f_s)$ , the middle diameter  $(f_d)$ , etc.) in a specified neighborhood of the critical temperature,  $T_c$ . The model,  $F(\tau, D, C)$ , follows to the scale theory of critical phenomena and includes critical characteristics,  $D = (\alpha, \beta, T_c \dots)$ , a relative temperature,  $\tau = (T_c - T)/T_c$ , indexes,  $\alpha, \beta$ , and adjustable coefficients, C. We have investigated several models,  $f_d(\tau, D, C) = (\rho_l - \rho_g)(2\rho_c)^{-1} - 1$ , those contain scaling and linear components. Among them there is a model proposed by Anisimov et al [1]. The model includes a component with index,  $2\beta$ , a component with the index  $(1-\alpha)$  and a linear component.

Another type of  $f_d(\tau, D, C)$  is developed in the work. The model is referred to as a combined scaling model. Its structure contains a component with index,  $2\beta$ , a component with the index  $(1 - \alpha)$  and regular components [2]. Similar combined models are developed for  $\rho_l$ ,  $\rho_g$  and  $f_s$ . There is considered a nonlinear technique, which let us calculate the characteristics

 $D = (\alpha, \beta, T_c...)$  and adjustable coefficients, C, those are related to the combined models. The technique has been used to estimate the model parameters on a based on experimental  $(\rho_l, \rho_g, T)$  data of the sulfur hexafluoride. A comparison has showed that our calculated  $(\rho_l, \rho_g, T)$  data values are in a satisfactory agreement with accurate experimental values those are related to investigation of Wagner et al (1997) and placed in a wide temperature range including the critical region. Numerical data on  $(f_d, f_s, \rho_l, \rho_g)$  properties are compared with calculated data those are based on known literature modes.

The second part of the work is devoted to an interesting task: an investigation of  $f_d(\tau, D, C)$  function of H<sub>2</sub>O. There are got numerical estimates those are connected with the combined model and based on accurate IAPWS - IF 97 ( $\rho_l, \rho_g, T$ ) data of H<sub>2</sub>O. Numerical data on  $f_s, \rho_l, \rho_g$ , properties are elaborated too in the interval  $\tau = 3 \ 10^{-5} - 0.35$ . A comparison of these values is done with tabulated data as well as with calculated data those are based on known literature modes in the critical region.

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#### TM – P13

#### Basement

## DEVELOPMENT OF INTERNET ALGORITHMS AND SOME CALCULATIONS OF POWER PLANT COP

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The authors have analyzed Internet resources containing information on the thermodynamic properties of technically important substances (the water, the air etc.). There are considered databases those are hosted in organizations (Joint Institute for High Temperatures (Russian Academy of Sciences), Standartinform (Russia), National Institute of Standards and Technology (USA), Institute for Thermal Physics (Siberian Branch of the Russian Academy of Sciences), etc.) and possess such resources. Currently, a typical form is an Internet resource that includes a text files, for example, it is a file containing tabulated properties, ( $R = \rho, S, h, ...$ ), here  $\rho$  – the density, s – the entropy, h – the enthalpy of a substance.

It is known a small number of Internet resources those have the following characteristic. The resource allows a customer to realize a number of options, for example:

- i) to enter the input data, Y = (p, T), here p the pressure, T the temperature,
- ii) to calculate *R* property using "an exe-file" program,
- iii) to copy the result  $X = (p, T, \rho, h, s, ...)$

In this variant, the program is closed for a client and there is no such options as: a) "to copy a mathematical formula" used to calculate R(p,T), b) "copy a code as a whole". Recently, some researchers (including the authors of this report) have requested a software (SW) that

is designed for R properties calculations and has a form of an open interactive (OI) Internet resource ("a client function") [1]. A computing part OI resource linked:

- 1) with a formula, which is applied to calculate *R* property,
- 2) with a Mathcad program, Code\_1(R,Y).

The interactive part of OI resource is based on Informatics and Internet technologies. We have proposed some methods and the tools those are related to this part and let us:

- a) to post OI resource on a remote server,
- b) to link a client PC with a remote server,
- c) to implement for clients a number of options.

The latter include, for example:

- i) to calculate *R* property at given *Y* arguments,
- ii) to copy mathematical formulas,
- iii) to copy Code\_1(R,Y) as a whole.

In frame of the work, some OI - resources are developed [2]. They are focused on sharing:

- 1) SW that is used to design power plants, for an example, Code\_2(Z,R,Y),
- 2) client functions those are aimed to determine R properties of the working fluid at fixed points of the thermodynamic cycle.

Code\_2(Z,R,Y) let us calculate the energy criteria, Z, including the thermal coefficient of performance (COP); for example, it is COP of a complex power plant included: 1) several gas turbines and compressors, 2) several steam turbines, 3) a heat recovery boiler etc. The work is executed at support of RFBR.

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## Instrumentation and Measuring Techniques (IMT)

### IMT – P1

## NEW APPROACHES ON INCREASING THE SENSIBILITY AND ACCURACY OF INFRARED RADIOMETERS

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The present work indicates that the sensitivity and accuracy of a radiometer depends not only on its design and the measurement method associated to it, but also on the spurious radiometer radiation. Spectral emissivity measurements performed on pure magnesium under vacuum at 300°C showed that the radiation emitted by the detector can return and be detected after it is reflected on the sample surface we intend to measure. Besides, a small portion of the sample radiation is reflected first in the IR-window and then in the sample surface, and therefore is also detected.

This spurious radiation sources must be taken into account in the calibration processes since they can be of the same order of magnitude as that of the sample at low temperatures (up to 300°C) in highly reflective surfaces such as polished metals. The presence of this spurious radiation may also be the cause of the inability to detect small surface emissivity changes induced by any surface or bulk properties (anomalous skin effect, structural and magnetic phase transitions, etc.). In this work the analysis of the spurious radiation is performed for a T-form radiometer and the *blacksur* measurement method. In any case, the results and conclusions that are obtained can be extended without difficulty to any type of radiometer and to all measurement methods.

### IMT – P2

#### Basement

## SORET FORECED RAYLEIGH SCATTERING METHOD TO MEASURE $\mathrm{D}_{12}$ OF AQUEOUS TREHALOSE SOLUTIONS

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Basement

Our aim is to measure the mutual diffusion coefficient of aqueous trehalose solutions using Soret forced Rayleigh scattering (SFRS) method at high concentration to the glass transition point. In this technique, a heating laser ( $\lambda = 532 \text{ nm}$ ) interferes in the sample to form an intensity grating. By absorbing the heating laser, this intensity grating creates a sinusoidal temperature distribution. From this temperature distribution, a sinusoidal concentration distribution is induced by the Soret effect; which is a mass diffusion flux driven by the temperature gradient. This sinusoidal concentration distribution is then transformed into a diffraction grating. After heating, the formed concentration distribution will be relaxed by mass diffusion. We are able to observe mass transport phenomena as an intensity decaying of diffracted light from a probing laser ( $\lambda = 639 \text{ nm}$ ). Thus it is possible to obtain the mutual diffusion coefficient by measuring this decaying time constant and fringe spacing of the grating.

To measure the mutual diffusion coefficient by using SFRS, it is necessary for the sample to absorb the power at the wavelength of the heating laser. For this reason, we added a small amount of a dye called neutral red, which absorbs power at a wavelength of 532 nm, to the sample. Using this dye, we confirmed that the instrument operates in accordance with the mathematical description of it. Decaying time constant should be directly proportional to the square value of the fringe spacing and also have an intercept of zero.

We have checked the validity of our measurement by comparing our results of aqueous ethanol solutions with the reference values measured by other conventional methods. Using SFRS technique, we have measured aqueous ethanol solutions at temperature of  $25.0^{\circ}$ C and concentration of 5 to 60 wt%. And then we apply this technique to aqueous trehalose solutions concentrations above 40 wt% at temperature of  $25.0^{\circ}$ C.

#### Acknowledgment

This work has been supported by JSPS KAKENHI Grant Number JP24226006.

IMT – P3

#### Basement

# USING THERMOMETRY TO ESTIMATE THE VAPOUR PRESSURE OF PURE COMPOUNDS

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The vapour pressure of a pure substance only depends on the temperature. Depending on the substance and the temperature the vapour pressure varies between some mPa for substances like benzoic acid and some hPa for substances like different alcohols. To choose the best measurement method, the OECD guidelines for the testing of chemicals recommend eight different methods for different vapour pressure ranges. The development of a modular measuring system, which measures the vapour pressure over a wide range of pressure, is the aim of this research. Each module uses another method. The main component of the system is a Magnetic Suspension Balance (MSB) constructed by Rubotherm GmbH. In the present work the second module to estimate vapour pressures ranging from 1 to 100 hPa in a temperature range from  $0^{\circ}$ C to  $100^{\circ}$ C is presented. In this work a simplified approach to estimate the vapour pressures based on a thermogravimetric method is presented. About 3 ml of a sample to be investigated are located in a partially filled, open stainless steel cylinder, which is continuously weighed by a MSB. An inert gas, in his case nitrogen, flows from up to down vertically through the measuring cell of the MSB alongside the sample cylinder. The pressure inside the measuring cell is 1 bar. The flow of the inert gas is high enough to remove all evaporated vapour of the substance. Based on the work of Heym et al. [1] the mass transport is divided into two parts: internal and external transport. The internal part only consists of diffusion while outside the cylinder diffusion and convection are overlapped. Based on selected experiments a uniform equation, which is only valid for the geometry used, is formulated to estimate the vapour pressure of the sample. As input values some geometry data, the volume flow of the inert gas, the diffusion coefficient and the detected mass loss of the cylinder are required. The results are validated with simulations with the software Comsol Multiphysics.



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#### IMT – P4

#### **Basement**

# DYNAMIC VISCOSITY MEASUREMENTS OF A GLASS USING THERMO MECHANICAL ANALYSIS

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Thermo Mechanical Analysis (TMA) is the measurement of the dimensional changes of a sample when it is exposed to a specific thermal profile under a controlled load applied with a probe.

The TMA technique can be employed to determine viscosity using the indentation method [1]. It involves the use of a probe with a small contact area allowing its penetration in the sample and the determination of the impression velocity, i.e. the rate of penetration of the probe in the sample. The dynamic viscosity can then be determined from its relationship with the steady-state impression velocity and the pressure of the applied load.

The method was validated by tests on a certified DGG standard glass I [2]. A SETSYS Evolution TMA was used isothermally in the 570°C-600°C range with loads ranging between 10 and 90 g. The certified dynamic viscosity value for the DGG standard glass I at 600°C is  $5,66 \cdot 10^{10} \text{ Pa} \cdot \text{s}$  (or Poise) which fits well with the average value ( $5.79 \cdot 10^9 \text{ Pa} \cdot \text{s}$ ) obtained with the TMA method at that temperature.

The method showing reliable results on the characterization of the tested reference glass can be applied to other materials with adapted temperature / load ranges.

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## IMT – P5

## Basement

# ASSESSMENT OF THERMODYNAMIC PROPERTIES AT HIGH TEMPERATURE WITH THE DROP CALORIMETRY TECHNIQUE

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A call for the production of more experimental thermodynamic data has recently been published [1]. Although calorimetry is not the most well-known calorimetric technique, a lot of the high-temperature heat capacity and enthalpy of formation data found in the literature come from its use. Moreover, since the 1960's, the number of published papers mentioning the use of the drop calorimetry technique has been increasing [2-4]. Different types of drop calorimeters have been designed, especially because it has historically been a home built technique. But in most of the systems, tens or hundreds of milligrams scale samples, initially held at a set temperature (most of the time room temperature) above the calorimeter are pushed into the calorimetric well at the bottom of which a calorimetric vessel sits. The sample falls into this vessel because of its own weight. The vessel, which is held isothermally at the test temperature, is surrounded by a calorimetric detector.

Two kinds of commercially available drop calorimeters have been employed for the presented examples. MultiHTC is an isothermal or temperature scanning calorimeter with operating temperatures up to 1600°C. It can be equipped with a standard heat flow DSC detector, but also with a quasi-Calvet drop sensor. Alexys is a true, high-sensitivity Calvet calorimeter optimized for high temperature drop calorimetry isothermal operations at temperatures up to 1000°C.

The presentation will cover drop calorimetry methods for signal calibration, heat capacity, enthalpy of formation and surface energy measurements using this technique.

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## THERMOPHYSICAL PROPERTIES OF GAS HYDRATES WITH STIRRED, HIGH PRESSURE CALORIMETRIC CELLS

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High pressure differential scanning calorimetry (HP-DSC) is of importance in several fields involving gas hydrates, such as oil and gas production, flow assurance, carbon dioxide capture and storage,  $CO_2$  hydrates reversible formation/dissociation for refrigeration loops. However, the technique suffered for some limitations linked to the fact that the gas hydrate formation in the calorimetric cell occurs at the gas-liquids interface, leading to problems such as inefficient gas dissolution, formation of a hydrate crust covering the gas/liquid interface, low hydrate to water conversion, and difficulties to crystallize these compounds even at low temperature. It is for example rather difficult to determine accurately the heat capacities and the enthalpies of formation/dissociation of several systems involving gas hydrates.

To overcome such limitations, we present two prototypes of calorimetric cells equipped with an in-situ mechanical agitation system, which allow performing experiments under pressure (150 bar max). The first one is called MIXCEL<sup>®</sup>, and was developed for macro-calorimetry analysis (experiments carried out with a BT 2.15 Calvet Calorimeter from SETARAM Instrumentation). The second one, called MICROMIXCEL<sup>®</sup>, was developed for micro-calorimetry analysis (experiments carried out using a microDSC7 evo from Setaram Instrumentation). In this study, technical details of the two cells and results obtained both at macro and micro scales will be presented, and compared to the case with no agitation. Thermophysical properties of the cyclopentane hydrate (phase change enthalpy, and specific heat) will be given and commented. The use of such novel calorimetric cells opens a wide range of possibilities for complex systems, such as gas hydrates, which must be analysed in both pressurized and agitated conditions.

#### IMT – P7

#### **Basement**

# A THERMAL CONDUCTIVITY MEASUREMENT DEVICE BASED ON MICROHEATER ON A THIN PDMS FILM

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Conventionally, plastics are electrically and thermally insulators. Additives such as carbon

nanotube (CNT), graphene and etc. can be added to plastics to enhance heat transfer and electrical performances. These functional composites can be applied to various industrial products where light, cheap and chemically inert material is needed.

However, polymer composites with high loading of additives suffer from non-homogeneous dispersion of additives. This can lead to non-homogeneous physical property within a product and may affect the consistency of the product quality. But, quantification of the addictive distribution in a polymer matrix is an extremely difficult matter. Many factors such as thermal history during the preparation and fabrication process, mold configuration and so on, affect the additive dispersion. In order to accurately analyze the *in situ* detection technique of the additive dispersion is needed.

In this study, a 3-omega ( $3\omega$ ) method is utilized to thermally characterize the additive distribution within a polymer composite sample. A microheater fabricated on a thin PDMS(Polydimethylsiloxane) film is fabricated as the measurement device. This attachable "stamp" is placed on different locations within the sample and the temperature response is measured while various frequencies of sinusoidal current are applied to the microheater. The special resolution of the thermal conductivity measurement can be manipulated by changing the input current frequency and is as small as  $10 \,\mu\text{m}$ . The experiment results suggest that measurement at low frequency (<  $10 \,\text{Hz}$ ) is desired to enhance the measurement sensitivity. Furthermore, to expand the measurement range to materials with higher thermal conductivities (>  $2 \,\text{W/m/K}$ ), both amplitude and phase lag of the temperature oscillation measured at the heater should be utilized.

#### IMT – P8

#### **Basement**

# A PRELIMINARY STUDY TO MEASURE CONCENTRATION OF DILUTE GLUCOSE AQUEOUS SOLUTIONS

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We focus on the measurement of the concentration of glucose aqueous solution at low concentration range (about 0-200 mg/dL). This concentration range is less than 0.4% of its saturated solubility. In measuring the low concentration sample, the high measurement resolution is needed. In this study, the aim is to measure the dilute glucose concentration in aqueous solution by sensing the small change of thermophysical properties at room temperature. And we aim for less than 10 mg/dL as a measurement resolution.

As a first step, we investigate the sensitivity of several properties of glucose aqueous solution (absorbance, refractive index, viscosity, optical rotation and diffusion coefficient) when the glucose concentration changes by 10 mg/dL. Then, we have selected the optical rotation as a candidate sensing property, because it is the most sensitive to the change of the glucose concentration compared to the other properties. When the glucose concentration changes from 130 mg/dL to 140 mg/dL, optical rotation degree increases 7% at the wavelength of 632 nm.

We constructed the preliminary apparatus to measure the optical rotation. We measured the intensity of the transmitted light through the sample for each polarization angle by using a rotation analyser. The optical rotation angle depends on the laser wavelength. We are attempting to utilize the wavelength dependence with three different wavelengths of 637, 785 and 1550 nm to gain more accurate glucose concentration resolution.

## Acknowledgment

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IMT – P9

#### **Basement**

The

## STAT8 APPARATUS FOR VAPOR PRESSURE MEASUREMENTS: THERMODYNAMIC STUDY OF SELECTED MONOTERPENES

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A newly developed static apparatus STAT8, capable of measuring the vapor pressure in the temperature range 273-368 K and in the pressure range 0.1-1333 Pa, is presented. The sample temperature is controlled using conduction air thermostat with stability better than 0.01 K. The apparatus was calibrated by measuring the vapor pressure of recommended reference materials, naphthalene, n-decane, and ferrocene, and thoroughly tested. combined expanded uncertainty (k = 2) of vapor pressure measurements can be described as  $U_c(p/Pa) = 0.01p/Pa + 0.05$ . After an extensive calibration and testing, the apparatus proved

to be a powerful tool for thermodynamic studies of low-volatile compounds interesting from environmental point of view such as monoterpenes, widely occurring compounds produced by variety of plants profoundly influencing chemical processes of the lower atmosphere with the tendency to contribute to secondary organic aerosol formation [1].

Experimental work on monoterpenes presented in this contribution includes vapor pressure measurements using two static apparatuses and calorimetrical measurements of the phase behavior and condensed phase heat capacities. Ideal-gas heat capacities and entropies were obtained by the combination of quantum chemical calculations and statistical thermodynamics applying the R1SM model presented recently [2]. A thermodynamically consistent description of vapor pressures, phase transition enthalpies, and differences in heat capacities was obtained using the simultaneous correlation method. This work follows our long-term efforts on the development of thermodynamically consistent data for monoterpenes. Special attention was dedicated to the study of polymorphs of L- and DL-menthol, for which a complex phase behavior was recently discussed [3]. Several thermodynamic techniques and x-ray powder diffraction were applied to describe relative stability of the polymorphic phases. For the same compound, a detailed conformational study was performed to complement similar recent studies searching for the most stable conformer [4, 5].

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## IMT – P10

## Basement

## THERMAL CONDUCTIVITY DETERMINATION BY TDTR METHOD UNDER ULTRAHIGH PRESSURE

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Physical properties and behaviors of materials may change remarkable under Giga-Pascallevel high pressure, and these changes are due to many reasons such as atomic recombination, lattice and electronic structure changes etc. One of the most important physical properties is the thermal conductivity, and the study of thermal conductivity under ultrahigh pressure can help us to understand the microstructure changes and energy transport mechanism under ultrahigh pressure, which is of great importance in the field of earth science and high temperature superconductivity.

Due to the great difficulty in the measurement of high pressure thermophysical properties, the experimental study on the thermal properties of high pressure is relatively few. Time-domain thermoreflectance (TDTR) method combine with diamond anvil cell (DAC) is one of the most suitable system for thermal conductivity determination under ultrahigh pressure. TDTR method requires all the other parameters are known except the one or two to be determined. However, thermal properties may change under ultra-high pressure and the data are quite lacking, so the data under ambient pressure or extrapolated from known pressure range are usually used.

In this paper, we investigate the influence of all the other parameters to thermal conductivity determination of silicon under 2 GPa pressure, including the thickness, thermal conductivity and volumetric heat capacity of the aluminum transducer layer, the thermal conductivity and volumetric heat capacity of the pressure transmitting medium, and the volumetric heat capacity of the silicon itself. Here we find the volumetric heat capacity of the silicon has the largest sensitivity compared with other parameters, and it is the only key parameter to extract the right thermal conductivity. This result simplify the data processing and gain the measuring accuracy. Finally, the thermal conductivity of silicon is found to be  $146.3 \text{ W/m} \cdot \text{K} \pm 4.9\%$  under

#### 2 GPa from our TDTR measurement.

## IMT – P11

#### Basement

# ADIABATIC CALORIMETER FOR ISOCHORIC HEAT CAPACITY MEASUREMENTS OF FLUIDS

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Isochoric specific heat capacities is closely related with other important thermodynamic properties, such as enthalpy and entropy. Isochoric heat capacity data are also used to develop reliable equation of state for fluids and gain a better understanding of molecular theory. In this work, an adiabatic calorimeter has been developed to measure the isochoric specific heat capacities of both compressed liquid and liquid in equilibrium with its vapor, especially the fluids of promising alternative refrigerant which are efficient and environmentally friendly. A spherical bomb fabricated from titanium alloy was used to hold the measured liquid. The spherical bomb was surrounded by a high vacuum. Two adiabatic shields were arranged to reduce the heat loss of thermal radiation by keeping the temperatures between the spherical bomb and the two adiabatic shields in a small difference. The decrease in temperature was realized by a mixed-refrigerant refrigerator together with helium gas. The temperature of the bomb was controlled by an automatic control system. Operating conditions for the calorimeter cover a range of temperatures from 150 to 350 K and at pressures up to 15 MPa. In order to verify the new apparatus, measurements on pure R134a (from 180 to 320 K) were carried out. The maximum relative standard uncertainty is 1.0 %. The maximum standard uncertainty in temperature is 30 mK, and that in pressure is 5.0 kPa. The experimental data were compared with selected literature data and good agreements were found.

## EA – P1

### Basement

## SIMULATION AND DESIGN IMPROVEMENT OF AN INSTRUMENT

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Thermal design and analysis of a satellite borne instrument is introduced in this paper. A finite element model was built. Through thermal simulation it was found that the temperatures of some components in origin structure are higher than the derated maximum junction temperatures, which didn't match the requirements of the thermal analysis. Through the analysis it could be found that the temperature of aluminum structure of PCB one is from 71.9 °C to 81.5 °C and PCB three is from 69.4 °C to 72.3 °C, which are more than 24 °C higher than the environment. So although the heat of component could be transfer to aluminum structure, it is difficult to be transfer to environment because these two board are on the top two layers of the whole box and the radiation area is not enough. So the horizontal layers structure was changed to vertical layers structure to help conduct heat of every boards. The new structure was simplified, meshed, and a new finite element model was built and computed. In the end, temperatures of all components are lower than the derated maximum junction temperatures themselves, which match the requirements of thermal analysis. A thermal balance test was completed after the designed box was yielded. The experiment results also showed that the thermal design of the instrument match the design requirements.

## EA – P2

## Basement

## EFFICIENT ADSORPTION CHARACTERISTICS OF CESIUM ON NOVEL CHITOSAN MEMBRANE WITH EMBEDDED PRUSSIAN BLUE PARTICLES UNDER DIFFERENT TEMPERATURE

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Novel chitosan membrane with embedded Prussian Blue particles was successfully prepared by using low-molecular-weight polyethylene glycol. This study demonstrates efficient adsorption characteristics using batch adsorption of cesium ion under two different temperatures, 298 K and 308 K.

Chitosan is a well-known biopolymer produced from deacetylation of chitin, which is available in shells of crabs and shrimps. It is known to use as a carrier material due to a biological compatibility and an environmental adaptability, such as membrane and beads. Prussian Blue is a pigment of dark blue color, which has a simple face-centered crystal structure. It has been used as an adsorbent in separation of cesium because of its high selectivity. Crystal of Prussian Blue has a cage size similar to the hydration radius of  $Cs^+(3.25 \text{ Å})$ , which are smaller than those for  $Na^+(3.6 \text{ Å})$ ,  $Ca^{2+}(4.1 \text{ Å})$  and  $Mg^{2+}(4.25 \text{ Å})$  [1].

Stable chitosan membrane with embedded Prussian Blue was prepared as followed. Chitosan, Prussian Blue, and polyethylene glycol (molecular weight:  $1000 \text{ g mol}^{-1}$ ) were dissolved into  $1.7 \text{ mol } \text{L}^{-1}$  acetic acid aqueous solution. The 2 g of mixture was casted onto polypropylene mold and dried (60°C, 24 h). The dried membrane was immersed in pure water. And then, polyethylene glycol was washed out in 100mL pure water with shaking bath at 60°C. The mass fraction of Prussian Blue in the membrane (MFPB) was defined as the following Eq. (1),

$$MF_{\rm PB} = \frac{W_{\rm PB}}{W_{\rm chitosan} + W_{\rm PB}},\qquad(1)$$

where  $W_{\text{chitosan}}$  is weight of chitosan [g].  $W_{\text{PB}}$  is weight of Prussian Blue [g]. In this study, four  $MF_{\text{PB}}$  membranes were examined,  $MF_{\text{PB}} = 0, 0.3, 0.5, 0.7$ .

Prussian Blue particles were successfully embedded in chitosan membrane from  $MF_{PB} = 0$  to  $MF_{PB} = 0.7$  by using low-molecular-weight polyethylene glycol. Stable embedding of Prussian Blue particles was confirmed by Scanning Electron Microscope.

Adsorption ability of cesium ion was evaluated by isothermal adsorption test at 298 K and 308 K. Maximum adsorption capacity and adsorption equilibrium constant at 298 K obtained from Langmuir model were increased with increasing the mass fraction of Prussian Blue. Maximum adsorption capacity of  $MF_{\rm PB} = 0.7$  membrane at 298 K and 308 K were  $112.36 \,\mu {\rm mol} \,{\rm g}_{-{\rm memb}}^{-1}$  and  $109.89 \,\mu {\rm mol} \,{\rm g}_{-{\rm memb}}^{-1}$ , respectively. On the other hand, adsorption equilibrium constant of 308 K ( $1.625 \,\mu {\rm mol}^{-1}$ ) was higher than that of 298 K ( $0.3771 \,\mu {\rm Lmol}^{-1}$ ). Adsorption data sufficiently fitted with Langmuir model. It indicated that adsorption of cesium ions was like a monolayer adsorption ability of cesium ion but also mechanical stability. New adsorption process combined with filtration was expected for sufficient cesium removal application through the use of this novel adsorption membrane.

# PREPARATION OF PICKERING EMULSIONS STABILIZED BY STEARATE MICROPARTICLES AND THEIR THERMAL STABILITY

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Pickering emulsions are emulsions stabilized by solid adsorbed at liquid-liquid interface. They are expected as food, pharmaceutical, and cosmetic media because this emulsion system can reduce the use of artificial surfactant. In this study, preparation of Pickering emulsions by food additive magnesium stearate microparticles and their thermal stability were investigated. Magnesium stearate has insolubility in water and no toxicity, and used as a thicker and an antiadherent agent in the manufacture of medical tablets. Stearate magnesium powder was added to a mixture of aqueous solution containing  $0.01 \text{ M CaCl}_2$  and n-heptane (aq. soln./n-heptane = 1:1 vol.), and mixed by using magnetic stirrer for 30 min. After mixing the emulsion phase was formed. In the emulsion phase, emulsions with diameters less than 1 mm were successfully prepared without any surfactant. After preparing the emulsions in the presence of aqueous fluorescence dye calcein under the same condition, fluorescence microscopy revealed the formation of water-in-oil (W/O) emulsion. The size distribution of emulsions slightly changed after a month while the average diameter increased. The prepared emulsions were stable for a long time, more than 2 months. The Sauter mean diameter  $(d_{32})$  was changed with particle concentration and there was a concentration to show a minimum  $d_{32}$  of 0.262 mm. At lower particle concentrations particles cannot cover the interface enough. On the other hand, at higher concentrations many particles in the bulk emulsion reduce the turbulent energy dissipation rate and stabilization efficiency. The average diameter of emulsions decreased with increasing rotation speed of magnetic stirrer in the range of 1,600-2,800 rpm. The  $d_{32}$  was proportional to the rotation speed  $(N^{-1.22})$ . The effect of temperature on the emulsion stability was investigated using emulsions prepared with olive oil as a continuous phase. The emulsions settled at 3 °C were stable for more than 1 day while the emulsions settled at 40 °C were destroyed after 6 hours. Since olive oil exhibits a higher temperature dependency of viscosity, higher viscosity of the continuous phase at low temperatures would provide a stronger interfacial film of the emulsions, which make the emulsions stable to coalescence.

#### **EA – P4**

Basement

## EVALUATION OF FLEXIBLE INSULATION OF LAUNCH VEHICLE

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KARI (Korea Aerospace Research Institute) is developing the three-stage LV (Launch Vehicle) called KSLV-II (Korea Satellite Launch Vehicle II). The first stage of KSLV-II is propelled by

clustered four liquid engines. To protect the LV from the exhaust plume gas which has high temperature over 1400 °C, the base of the LV should be properly insulated.

Most of the base is covered by a rigid insulation material but the area around engine nozzles should be protected in a different way because each engine has rotational gimbal motion for the thruster vectoring. For this reason, the flexible insulation is adopted to block the heat and to ensure the engine motion at the same time.

The insulation has multiple layer structure. Fire proof felt and wool are stacked repeatedly, the external surface facing the high temperature plume is covered by the metal meshed felt and the innermost surface is covered by the rubber coated felt.

Several tests are conducted to evaluate the flexible insulation. Insulation performance is qualified by the heating test. The specimen is heated in the test chamber by the electric heater and temperature of innermost surface is measured. Heat transferred to the specimen during the test is 150% higher than that of during the flight. The maximum temperature of specimen fulfils the requirement condition. In the environmental test, the soundness of the flexible insulation is assured by simulating two important conditions; high heating rate and repeated folding. The flexible insulation composed of several pieces and the joint between them receives tension during the flight due to pressure difference between the bay and the atmosphere. The strength of the joint is qualified by pressurizing test using a blower. Finally, the motion of the engine with the flexible insulation is verified using the simulator of the gimbal motion.

The overall function of the flexible insulation as a part of the whole system will be further verified by ground firing tests and a test flight. The main launch of KSLV-II is scheduled on 2020.

## EA – P5

#### **Basement**

# REDUCTION OF SILVER CONTENT IN THERMAL INTERFACE MATERIAL WITH ULTRAHIGH THERMAL CONDUCTIVITY

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Manipulation of contact thermal resistance is very important for efficient thermal management in many applications. Thermal interface materials (TIMs) typically consist of conductive fillers and polymer matrix are widely used for dramatic reduction of the contact thermal resistance at the interface between electronic components and heat sinks. Recently, we reported a new TIM with significantly enhanced  $\kappa$  using multi-walled carbon nanotubes functionalized with silver nanoparticles, and silver epoxy [1]. Excellent characteristics of the TIM in terms of printing, thermal expansion matching, and CPU cooling were demonstrated. However, extremely high content (83.3 wt%) of the noble metal could hinder industrial use of the TIM. Here, we significantly reduce the silver content of the TIM based on understanding of the mechanism underlying the thermal conductivity enhancement and show that its high thermal conductivity is maintained from a series of thermal property measurements including a pycnometry and a laser flash method.

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EA – P6

**Basement** 

# ACCELERATION OF REACTION ACTIVITY IN ENZYMATIC REACTION OF CELLULOSE WITH PRETREATMENT USING ULTRASONIC IRRADIATION

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Enzymatic hydrolysis of cellulosic with pretreatment using ultrasonic irradiation was successfully appeared. The cellulase (from Trichoderma ressei) was employed. Three kinds of cellulose (carboxymethyl cellulose (CMC) and crystalline cellulose, Kenaf) were employed. An assay of the enzymatic hydrolysis of cellulose was evaluated based on production of glucose. The kinetic parameters (Maximum reaction rate;  $V_{max}$  and Michaelis-Menten constant;  $K_m$ ) and the initial reaction rate were discussed to the evaluate reactivity of the reaction. The initial reaction rate was commonly increased by ultrasonic irradiation in all cellulose species. The effect of ultrasound power on the initial reaction rate increased with increasing ultrasound power. In the case of the kinetic parameters,  $V_{\text{max}}$  was enhanced and  $K_{\text{m}}$  was decreased by ultrasonic irradiation in all substrate. The viscosity of CMC was decreased by ultrasonic irradiation. It was speculated that the distance of the CMC polymer chain in the solution was loosed by ultrasonication. The particles seize of crystalline cellulose was smaller by ultrasonic irradiation. Fresh surface of Kenaf were exposed by cavitation produced from ultrasonication. The effective surface area of cellulose seemed to increase because the ultrasonic pretreatment removed some of the covering material, thus inducing a higher association of cellulase and cellulose. Ultrasonication is an effective pretreatment for accelerating the enzymatic hydrolysis of cellulose and designed lower energy industrial processes for cellulose degradation.

#### EA – P7

#### Basement

#### PREPARATION OF THERMORESPONSIVE EMULSIONS BY BIOPOLYMER ADDITION

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Gelatin is a mixture of peptides and proteins obtained by collagen hydrolysis. Gelatin is soluble in hot water and the solution loses its fluidity to form a gel at a lower temperature (288-293 K)

reversibly, which is due to the change in the molecular structure of gelatin, thereby used in a wide variety of fields including food products, pharmaceutical products and photo films. Emulsion system is a mixture of two or more liquids where one liquid is dispersed in the others, and there are many applications in a wide range of fields such as foods, cosmetics, pharmaceuticals, and paints. In this study, thermoresponsive emulsions were prepared by adding biopolymer gelatin to the system. Gelatin powder was dissolved into hot water at 333 K, and a mixture of the gelatin aqueous solution and n-heptane solution (aq. soln./ n-heptane = 1:1 vol.) was mixed by vortex mixer for 2 min. After mixing, the emulsions less than 1 mm formed. The prepared emulsions were stable for a long time, for more than 3 months. On the other hand, without gelatin no emulsions formed. Fluorescence microscopy of the emulsions with hydrophobic fluorescence dye Nile Red revealed the formation of oil-in-water (O/W) emulsions. The emulsion size was measured by optical microscopy. The average size of emulsion was  $109\,\mu\mathrm{m}$  with a size distribution of 28.1%. The prepared emulsions were moved to petri dishes and settled at 293 K and 313 K, respectively. The emulsions settled at 293 K showed almost no change in size after 2 hours while the emulsions settled at 313 K were destroyed after 2 hours. In contrast, in the case of polysaccharide biopolymer agarose, whose gelation and melting temperatures at 303 K and 333 K, respectively, the emulsions with agarose settled at 293 K showed almost no change in size after 2 hours and even at 313 K the emulsions were preserved after 2 hours. These findings indicate that the addition of biopolymer brings thermoresponsibility to the emulsion system and its property can control the emulsion stability.

## EA – P8

## Basement

# VOLUMETRIC PROPERTIES OF BINARY LIQUID MIXTURES OF ALKANE-2-ONE WITH CHLOROALKANE

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The present work is focused on the study of binary mixtures of ketones with chloroalkane at different temperature and atmospheric pressure, and is part of a systematic program of research for the measurement of physical properties of binary mixtures containing halogenated hydrocarbons such 1,2-dichloroethane.

Halogenated hydrocarbons are manufactured in large quantities and have many application (as refrigerant, organics solvents, medicines ).

Excess molar volumes of liquid mixtures of 1,2-dichloroethane with (2-propanone, 2-pentanone, 2-octnone) have been calculated using the experimentally measured densities of the pure liquids and those of their mixtures over the hole composition range and at 288.15, 293.15, 298.15, 303.15, 308.15, 313.15 K. Thermal expansion coefficient, partial molar volumes and excess partial molar volumes, at in infinite dilution, have also been calculated. All properties have been correlated with standard polynomials against temperature and composition, and the excess function have been correlated using Redlich-Kister polynomial.

The effects of the 2-alkanone chain length as well as the temperature on the excess function

have been studied. The results have been qualitatively used to explain the molecular interaction between the components of these mixtures. Thermal expansion coefficient, partial molar volumes and excess partial molar volumes, at in infinite dilution, depend not only on solutesolute, solvent-solvent, solute-solvent interactions, but also on the structural effects arising from interstitial accommodation due to the difference in molar volume and free volume between components present in the solution.

## EA – P9

## Basement

# FLAMMABILITY LIMITS OF BENZENE, TOLUENE, XYLENES AND THEIR BINARY MIXTURES WITH NITROGEN AND CARBON DIOXIDE

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Benzene, toluene and xylenes, as important chemical raw materials and chemical solvents, have important applications in dyes, pesticides, perfumes, paints, pharmaceuticals, footwear, furniture manufacturing and other industries. However, because of their flammability, they also threaten human life and property at all times. In this paper, flammability limits for benzene, toluene, *p*-xylene, and *o*-xylene were measured from 373 K to 473 K, and flammability limits for binary mixtures of benzene, toluene, *p*-xylene, and *o*-xylene were measured at 423 K. The measurements were made in a 12 L spherical glass flask using ASHRAE method. The experimental results were correlated with the extended Le Cartelier's formula. In addition, flammability limits for the binary mixtures of benzene, toluene, *p*-xylene, *m*-xylene, and *o*-xylene with nitrogen and carbon dioxide were compared with the estimated values based on the adiabatic flame temperature method. This research provides the needed data for secure application and fire estinguishing system of benzene substances.

Key words: flammability limits; dilution effect; benzene; toluene; xylenes

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## Equation of State (ES)

## ES – P1

#### **Ground Floor**

## EXPERIMENTAL DETERMINATION OF (p, $\rho$ , T) DATA FOR THREE BINARY MIXTURES OF NITROGEN AND HYDROGEN

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Interest in hydrogen as an energy-storage medium is increasing. A practical alternative to transport and distribute hydrogen is using the existing infrastructure for natural gas. The use of mixtures of natural gas with hydrogen addresses safety issues, facilitates the deployment of hydrogen as an energy carrier and can be managed with less capital investments than a pure-hydrogen infrastructure.

Experimental characterization of the thermodynamic behaviour of binary gas mixtures of hydrogen with the main components of natural gas is of great importance. These data are essential for validation and improvement of the established reference equation of state for natural gases and related mixtures, GERG-2008. The framework of GERG-2008 equation of state is based on a multi-fluid mixture model that is explicit in the reduced Helmholtz free energy and has been developed for 21 constituting pure components and for the binary mixtures of these components. Due to the lack of consolidated experimental data that still exists for a considerable number of binary mixtures and to the complexity of the calculation processes within the equation-of-state framework, most of the binary systems were taken into account by using adjusted reducing functions for density and temperature. Only for those binary mixtures for which sufficient accurate experimental data were available, binary specific departure functions or at least a generalized departure function were developed. For the binary mixture nitrogen-hydrogen no departure function could be developed so far due to insufficient data.

In this work, accurate density measurements for three binary mixtures of nitrogen with hydrogen (amount-of-substance fraction  $x(H_2) = 0.05, 0.10, 0.50$ ) are presented. Measurements were performed at temperatures between (240 and 350) K and pressures up to 20 MPa using a single-sinker densimeter with magnetic suspension coupling, which is one of the state-of-the-art methods for density determination over wide ranges of temperature and pressure. The binary mixtures for this investigation were prepared by the gravimetric method according to the ISO 6142, and then validated, at the BAM Federal Institute for Materials Research and Testing in Berlin, Germany. In addition, the second virial coefficients for the (N<sub>2</sub> + H<sub>2</sub>) binary mixture at temperatures from (240 to 350) K were estimated from these new experimental values.

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ish Ministry of Economy and Competitiveness for the support to the project ENE2013-47812-R and Junta de Castilla y León for the economic support through project VA035U16.

## ES – P2

### **Ground Floor**

#### FUNDAMENTAL EQUATION OF STATE FOR N-TETRADECANE

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Normal tetradecane is one of the technically important substances and accurate information on its thermodynamic properties is desired for many applications. The accurate knowledge of thermodynamic properties of n-tetradecane is a precursor to modeling the surrogate fuels and reservoir fluids. The use of n-tetradecane in industry has made it one of the most important substances for which the development of accurate equation of state is needed.

Equations of state for pure fluid properties are often expressed as fundamental equations explicit in the Helmholtz energy, with the density and temperature as independent variables. From these equations, most single-phase thermodynamic properties can be calculated using density or temperature derivatives of the Helmholtz energy. An equation of state that can be used to calculate the thermodynamic properties of n-tetradecane at liquid, vapor, and supercritical states is given here.

The present equation of state is explicit in terms of the Helmholtz energy  $\alpha$ , which can be separated into an ideal gas part  $\alpha^0$  and a residual part  $\alpha^r$ ,

$$\frac{\alpha(\rho,T)}{RT} = \frac{\alpha^0(\rho,T) + \alpha^r(\rho,T)}{RT} = \alpha^0(\delta,\tau) + \alpha^r(\delta,\tau).$$
(1)

To describe the residual part of the reduced Helmholtz energy, an optimized functional form has been used,

$$\alpha^{r}(\delta,\tau) = \sum_{k=1}^{6} N_{k} \delta^{d_{k}} \tau^{t_{k}} + \sum_{k=7}^{14} N_{k} \delta^{d_{k}} \tau^{t_{k}} \exp\left(-\delta^{l_{k}}\right).$$
(2)

Optimization of the coefficients and temperature exponents of Eq. 2 took place simultaneously in a nonlinear form. The underlying dataset consists of experimental and molecular simulation data. The experimental data are available for temperatures from the triple point up to 473,15 K. Molecular simulation data are used to extend the validity to the liquid state and up to a maximum temperature of 650 K and a maximum pressure of 150 MPa. A corresponding dataset was generated containing the density and isobaric heat capacity at 30 state points using the NPT molecular dynamics simulations. The simulations were performed by simulating 216 randomly placed molecules using the optimized force field. The physical behavior of the equation of state in regions where no experimental data are available was controlled by various constraints, which were imposed in the form of inequalities on the thermodynamic surface. In the report the results of comparisons of calculated data on the Eq. 1 with the most representative experimental data are presented.

## ES – P3

## **Ground Floor**

## MIXTURE CRITICAL POINTS USING A MODIFIED CPA EOS

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Mixture critical points define indistinguishable coexisting phases. They are the most important point in a vapour-liquid phase envelope setting the conditions where the bubble curve becomes the dew curve and vice versa. They also help in defining the nature of a single phase outside the phase envelope as being "gas like", "liquid like" or supercritical.

The condensation of gases and hydrate formation are some of the risks that need to be understood and prevented in the oil and gas industry. Applications in the near/supercritical region have also been increasing in importance such as is the case of producing  $CO_2$  rich reservoirs or using gas injection processes. In all of these cases the previous knowledge of the mixture critical point is relevant to avoid production problems and to optimize processes in the near and supercritical regions.

Associative equations of state such as CPA have well known advantages for mixtures with associating components, but are also well known to fail to provide the right pure component critical points, what has been considered as a consequence of getting improved vapour pressure and liquid density estimates away from the critical point. We have recently proposed a modified CPA<sup>1</sup> model where the pure component critical point is reproduced without affecting the description of pure component vapour pressure and liquid density. This new version of CPA, which has shown interesting predictive capacities, while being able to describe both pure component properties and phase equilibria is applied in this study.

This work concerns mostly binary and ternary systems containing alcohols, hydrocarbons and/or water, using previously obtained pure component parameters in association with binary interaction parameters obtained at subcritical conditions. These results are compared with those obtained using cubic equations of state, namely SRK

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#### ES – P4

#### **Ground Floor**

## HIGH YIELD EXTRACTION OF BIOACTIVE COMPONENTS FROM HERBAL PLANT RESOURCES BY SUPERCRITICAL CARBON DIOXIDE

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Bioactive components have been extracted from various herbal plant resources. They were applied for medicine, cosmetic and sapplement for human health. Parsley (*Petroselinum crispum L.*) contained apigenin and apiin. They perform anti-inflammatory and anti-cancer properties [1]. Apiin is a glycoside of apigenin. Licorice (*Glycyrrhiza uralensis*) extensively applied in herbal medicine. Glycyrrhetinic acid (La) and glycyrrhizin (Rg) have been attained for their strong anti-inflammatory action [2]. Glycyrrhizin (Rg) is a glycoside of glycyrrhetinic acid (La). High yield and non-residue toxicity extraction of bioactive components was successfully realized by supercritical carbon dioxide combination with effective pretreatment of natural bio-resources. Suitable thermodynamic property of  $SCCO_2$  was attained by desirable pressure and temperature. It donated for minimization of required energy for extraction and achieved high yield of bio-active components extracted.

Extracted amount of aglycone (apigenin and glycyrrhetinic acid) were higher than of glycoside (apiin and glycyrrhizin), because  $SCCO_2$  performed hydrophobic character. Extracted amount was increased with increasing of pressure of  $SCCO_2$  and decreasing with elevation of temperature. Pressure and temperature are dominant factors to determine the density of the  $SCCO_2$ . Density closely related to solubility parameter of  $SCCO_2$ . Required energy for extraction was estimated by difference in the solubility parameters between solute and solvent, indicated by Eq.1,

$$\Delta E = V_A \,\varphi_{\rm solv.}^2 \, (\delta_{\rm solv.} - \delta_A)^2, \qquad (1)$$

where  $\Delta E$  is required energy for extraction  $[J \cdot mol^{-1}]$ ,  $V_A$  is molar volume of target component  $[cm^3 \cdot mol^{-1}]$ ,  $\varphi_{solv}$  is volume fraction of solvent [-],  $\delta_{solvent}$  and  $\delta_A$  are solubility parameters of target component and solvent that is  $(\Delta E/V)^{0.5}$   $[J \cdot cm^{-3}]$ .

When the parsley leaves were soaked in hot water (353 K) for 10 min and then vacuum freeze-dried, the extracted amount of apigenin was  $1.03 \times 10^{-7}$  [mol-apigenin/g-sample/mol-SCCO<sub>2</sub>], which is 45 times higher than that of extracted from flesh raw parsley. Extracted amount of glycyrrhetinic acid was increased with ultrasonic irradiation to licorice at 40 W, 24 kHz for 10 min. It was  $1.2 \times 10^{-7}$  [mol-glycyrrhetinic acid/g-dried sample/mol-SCCO<sub>2</sub>], which is 5 times higher than that of extracted amount from non irradiation sample. The complete degradation of the cellular structure of the plant material proved to be a very important factor for SCCO<sub>2</sub> extraction.

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## Ionic Liquid and Properties Ionic Liquids (ILPIL)

## ILPIL – P1

## **Ground Floor**

## MAKING THERMOPHYSICAL PROPERTIES DATA OF [C<sub>2</sub>MIM][CH<sub>3</sub>SO<sub>3</sub>] USEFUL

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The thermophysical properties of the binary system water and 1-ethyl-3-methylimidazolium methanesulfonate ( $[C_2MIM][CH_3SO_3]$ ), with an assay  $\geq 95\%$  were studied in order to decide the use of this binary system as a possible heat transfer fluid in an industrial processes. For a successful transfer of technology between research and industry, reliable supporting thermophysical property data has to be presented in their most simple format (% wt vs x) to build strong analysis, since its conclusions can greatly affect the choice of the cheaper and more efficient solution.

The importance of an accurate measurement can have large consequences in projected costs [1]. A careful consideration was made to its interaction with water since this component of the binary system greatly affects the  $[C_2MIM][CH_3SO_3]$  properties. After that, using the adequate techniques, density, speed of sound, viscosity, heat capacity, thermal conductivity and electrical conductivity were obtained from temperatures between 293 - 353 K. From the density, speed of sound and viscosity the excess properties were calculated. Furthermore to assess the toxicity of the ionic liquid two simple tests were made.

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# IONIC LIQUIDS AND IONANOFLUIDS - AN UPDATE ON THERMAL CONDUCTIVITY

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Most of the applications of ionic liquids (ILs) are related with chemistry and chemical engineering. Material properties (heat capacity, thermal conductivity, viscosity and other thermophysical properties) play an important role in the applications. These properties can be obtained by molecular simulation, prediction/estimation methods and by measurements. However, the number of combinations of cations and anions is immense. Being "target oriented" or "duty oriented" materials, the flexibility of their properties needs not only experimental measurements (very limited and time consuming), but theoretical developments and computer simulation, in order to develop sustainable and useful tools for project design, as it has been done by us in the past for molecular liquids [1-3].

Due to our current understanding at a nano dimension, the existing intermolecular forces and the supporting theories, it was not possible up to today to have a molecular based theory for the thermal conductivity of ionic liquids. Even the application of estimation techniques has proved to have a limited applicability.

An IoNanofluid is defined as a stable dispersion of the nanomaterial in an ionic liquid. Ionanofluids are one of the most promising applications of ionic liquids in the area of heat transfer. All the models developed to model the thermal conductivity of nanofluids, assume on one and that the thermal conductivity of the ionic liquid is known (?), and no effort to take into account the molecular structure of the ionic liquid has been developed with success, although molecular dynamics based simulations that involve this structure and the special type of interaction with the nanomaterial, permiting us to start to understand this complex problem [4-6].

It is the purpose of this paper to give an update of the situation in the calculation of the thermal conductivity of ionic liquids and IoNanofluids.

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## THE CHARGE COMPENSATION EFFECT OF CATION SPECIES ON THE SULFUR SOLUBILITY OF HIGH TEMPERATURE IONIC LIQUIDS

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The charge compensation effect of  $Ca2^+$  and  $Fe2^+$  on the sulfur solubility of  $CaO - FeO - Al_2O_3 - SiO_2$  melts has been studied. The content of cation species (MO, M = Ca, Fe) and anion groups ( $AlO_4^{5-}$ ,  $SiO_4^{4-}$ ) were varied to determine the effect of charge compensation [1,2] on the sulfur solubility in high temperature ionic liquids. The coordination number of aluminum ion in the super-cooled liquids was identified by deconvolution with PeakFit<sup>TM</sup> 4.0 of 27 Al 500MHz Solid NMR Spectra [3,4]. The proportion of Fe – O – Si was analyzed by Raman spectroscopy [5,6].

As a result, the sulfur solubility represents a linear relationship according to the MO activity, as an index of the basicity. In the case of the cationic excess region ( $M^{2+}/Al^{3+} > 1.0$ ), the sulfur solubility is directly proportional to the basicity due to high  $S^{2-}$  - stabilization by excess cation. However, in the case of the cation deficient region ( $M^{2+}/Al^{3+} < 1.0$ ), the sulfur solubility was shown to be constant depending on the basicity.

Charge Balancing Join:

$$\left(X_{\mathrm{Ca}^{2+}} + X_{\mathrm{Fe}^{2+}}\right) / \left(X_{\mathrm{Fe}^{3+}} + 2 \cdot X_{\mathrm{Al}_{\mathrm{s}}\mathrm{O}_{3}}\right) = 1$$

The reason is that  $S^{2-}$  activity coefficient of the melts increase due to the absence of  $M^{2+}$  required for charge balancing with  $AlO_4^{5-}$  and  $FeO_4^{5-}$ . Also, the sulfur stabilization region was determined by the kind of the cation species ( $M^{2+}$ ). The charge balancing region is changed by the stabilization of  $Al^{3+}$  with  $Fe^{3+}$  [7] and influences on the cation substitution effect on the sulfur solubility.

Keywords: Sulfur solubility Charge Compensation, Iron Redox Equilibria, Cation Substitution, Aluminosilicate melts

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## VOLATILITY OF 1-ALKYLPYRIDIUM $\rm NTf_2$ SERIES

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The vapor pressure at several temperatures for the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series,  $[C_n Py][NTf_2]$  (n = 5-9), were measured by a Knudsen effusion method combined with a quartz crystal microbalance. The experimental vapor pressure data was fitted to the integrated form of the Clausius-Clayperon equation and the enthalpies and entropies of vaporization were derived.



The derived thermodynamic properties of vaporization of the 1-alkylpyridinium bis(trifluoromethylsulfonyl)imide series,  $[C_nPy][NTf_2]$  (n = 5-9), are analyzed together with the results obtained previously for the shorter alkyl chain length  $[C_nPy][NTf_2]$  [1] and the volatility of the Imidazolium series  $[C_{N-1}C_1im][NTf_2]$  in order to evaluate the effect of the alkyl side chains of the cation and to get additional insights concerning the nanostructuration of ionic liquids. It was found that the lower volatility of alkylpyridinium derivatives (is five times lower than the imidazolium series) is driven by their higher enthalpy of vaporization.

## Acknowledgments

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## **Ground Floor**

## THERMOPHYSICAL PROPERTIES OF PROTIC IONIC LIQUIDS

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The thermal behavior, glass transition temperatures, crystallization, melting temperatures, enthalpies and entropies of isotropization, of ten protic ionic liquids (PILs), using two different superbases, 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) and five different carboxylic acids, namely acetic, propionic, butyric, hexanoic and octanoic acid, are presented and discussed concerning the effect of different bases/acids.



Heat capacities of the condensed phases were measured by continuous and step method in the temperature interval from 278 K to 358 K by Tian-Calvet microcalorimeter and, at T =298.15 K, by the drop calorimeter method [1].

It was found that the effect of changing the superbase in each PIL is stronger than the effect of changing the acid. It was also found that the base/acid composition shifts with the distillation process resulting in property changes.

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## DENSITY, SPEED OF SOUND, VISCOSITY OF 1-ETHYL-3-METHYLIMIDAZOLIUM METHANESULFONATE AND METHANOL BINARY MIXTURES

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Ionic liquids (ILs) are mostly stable liquids in the range of over 300 K. They have wide application possibilities, which are increase during the last years in catalysis, separation process, electrochemistry etc. branches, because of good physical and chemical properties, such as small vapor pressure, a wide range liquid characteristics. ILs are good substances for using as heat transfer fluids in absorption refrigeration and heat pump systems, because they have very low vapor pressure and good solubility with different natural solvents (refrigerants) such as aliphatic alcohols. The using of binary mixtures of ILs with organic solvents in such systems needs the thermophysical properties of pure components and mixtures.

This work is the part of our investigations in the field of application of IL + Alcohol system in absorption refrigeration and heat pump systems. In this presentation, we will inform the density, speed of sound, viscosity of 1-ethyl-3-methylimidazolium methanesulfo?nate and methanol binary mixtures {xCH<sub>3</sub>OH + (1 - x)[EMIM][MeSO<sub>3</sub>]} at ambient pressure and at various mole fraction of methanol x = (0 to 1). The density values  $\rho(p_0, T)/\text{kg} \cdot \text{m}^{-3}$ at temperatures T = (263.15 to 413.15) K were investigated using the Anton Paar DMA 5000M, DSA 5000M and DMA HPM vibration tube densimeters with an uncertainty of  $\Delta \rho = \pm (5 \cdot 10^{-3})$  to  $3 \cdot 10^{-1} \text{ kg} \cdot \text{m}^{-3}$ . The speed of sound values  $u(p_o T)/\text{m} \cdot \text{s}^{-1}$  at temperatures T = (278.15 to 343.15) K were studied using the Anton Paar DSA 5000M vibration tube densimeter and sound velocity meter with intervals of  $\Delta T = (5 \text{ to } 10)$  K and an uncertainty of  $\Delta u = \pm 0.1 \text{ m} \cdot \text{s}^{-1}$ . The dynamic viscosity  $\eta(p_0, T)/\text{Pa} \cdot \text{s}$  at temperatures T = (278.15 to 373.15)K were measured using an Anton Paar SVM 3000 Stabinger Viscometer and Rheometer MCR 302. The accuracy of measured dynamic viscosity  $\eta(p_0, T)$  values at p = 0.101 MPa according the manufacture instructions is  $\Delta \eta = \pm 0.35\%$ .

Obtained experimental values were analysed and various empiric equations were used for the fitting of these results dependence temperature and concentration of methanol. These investigations were carried out at the first time.

### CARBON DIOXIDE SOLUBILITY IN 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE AT HIGH PRESSURES AND TEMPERATURES

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Greenhouse gases absorb infrared energy radiated from the earth and this process increase the temperature of the troposphere. There are various greenhouse gases and one most important from them is carbon dioxide ( $CO_2$ ). Using the traditional fossil fuels has and will continue to increase  $CO_2$  in the atmosphere. In this case,  $CO_2$  capture is very important and actively studying during the last decades. There are various technical processes for this purpose. One of these is the solvation of  $CO_2$  into liquids (ILs). ILs are regarded as environmentally green solvents due to their very low vapor pressure and can be applied for defusing the  $CO_2$  problem within the atmosphere. The prediction of  $CO_2$  solubility in ILs is a fundamental step toward the development of simulation tools to aid in the process calculations prior to industrial applications.

We want to report our new wide range experiments together large literature comparison to determine the high pressure solubility of  $CO_2$  in 1-Butyl-3-methylimidazolium hexafluorophosphate [BMIM][PF<sub>6</sub>] IL at various temperatures at T = (273.15 to 413.15) K, which are performed in a stainless steel measuring cell in equilibrium by using the isochoric method. Experiments were carried out in four different pressure steps: in the first step, the maximum possible pressure (about 5 MPa) is created in the gas reservoir. The other steps with maximum pressure are: second step - about 3 MPa, third step - about 1.5 MPa, and the final step - about 0.5 MPa. The temperature dependency of Henry's law constant was calculated. Thermodynamic properties of solution such as the free energy of solvation  $\Delta_{sol}G$ , enthalpy of solvation  $\Delta_{sol}H$ , entropy of solvation  $\Delta_{sol}S$  and heat capacity of solvation  $\Delta_{sol}c_p$  were calculated at various temperatures T to evaluate the solute- solvent molecular interactions. The measured  $CO_2$  solubility in [BMIM][PF<sub>6</sub>] as a function of temperature and pressure were fitted to a virial equation using mole fraction dependence.

### ILPIL – P8

#### **Ground Floor**

## AQUEOUS SOLUTIONS OF [EMIM] 1,1,2,2-TETRAFLUOROETHANESULFONATE AND [EMIM] TRIFLUOROMETHANESULFONATE: A THERMODYNAMIC STUDY

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Ionic liquids (ILs) based on a trifluoromethanesulfonate ([OTF]) anion and their mix-

tures with other compounds have been widely studied both for theoretical interest and technological applications. On the other hand, information about structurally similar 1,1,2,2tetrafluoroethanesulfonate-based ([TFES]) ILs is scarce and that on their mixtures with water is not even available. For this reason and as a follow-up to our previous studies on [EMIM]-based ILs [1,2], the aim of this study is to provide a reliable global thermodynamic characterization of the aqueous solutions of [EMIM][TFES] and [EMIM][OTF], where the study of the aqueous solutions of the latter IL acts as a benchmark for our approach. First, sample identity and purity of [EMIM][TFES] were verified by NMR spectroscopy and DSC measurements were carried out to characterize phase transitions of this barely studied IL. Then, after checking the mutual consistency of the respective literature data, we systematically measured vapor-liquid equilibria (water activity), mixing enthalpy and density in the entire composition range or specifically in the highly dilute IL region between the temperatures 288.15 K and 318.15 K. Effective IL sample saving experimental techniques were used. The obtained VLE and excess enthalpy data were simultaneously correlated by an NRTL-type model, leading to thermodynamically consistent and adequate representation of the data. Comparison with literature data on the aqueous solutions of [EMIM][OTF] proved that the model provides reasonable extrapolations. Both systems display small S-shaped excess Gibbs energy and large positive excess enthalpy and entropy. While the influence of structural variation in the anion on the excess enthalpy and entropy is significant, it is hardly discernible in case of excess Gibbs energy.

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## ILPIL – P9

## **Ground Floor**

# EXPLORING THE NATURE OF THE ANION AND CATION IN THE SOLVATION OF ALCOHOLS IN ILS

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In this work we used a molecular probe to study the effect of the nature of anion and cation of the ionic liquids (ILs) on their solvation properties, by using calorimetry and quantum chemical calculations. Propan-1-ol was used as the molecular probe, taking advantage of its polar and apolar structure components. Its hydroxyl group allows us to explore the interactions by hydrogen bond or dispersive forces with the polar domain of the IL and its alkyl chain its interactions with IL non-polar domains [1].

## ITC... Alcohol interaction in ILs



Figure 1. Scheme representative of methodology and main results obtained in this work.

The study of the influence of ILs' anion and cation nature was made by comparative analysis of the results of the enthalpies of solution at infinite dilution of propan-1-ol in several ILs, measured by Isothermal Titration Calorimetry (ITC) and of the heats of solvation derived thereof using literature enthalpies of vaporization data. In parallel, quantum chemical calculations of the interaction of the hydroxyl group of propan1-ol with the anions of the ILs in the gas phase were performed. The combination of the experimental and theoretical approaches to the study of the solvation of propan-1-ol in ILs with different combinations of anion and cation led to important insights into the preferential location of the alcohol and the intermolecular interactions established with the ionic liquids. Overall, this study allowed us to unravel the role of the anion and the cation acidity on the interactions with the alcohol and to show how the acidity will tune the preferential interactions established between the IL and the alcohol in the solvation process.

## Acknowledgments

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# EFFECTS OF CO-SOLVENTS ON THE THERMOPHYSICAL PROPERTIES OF IMIDAZOLIUM-BASED IONIC LIQUIDS

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Ionic liquids (ILs) are composed of the inorganic or organic anions and organic cations. The ions can be re-organized and that makes ionic liquids designable. A large number of ionic liquids can be synthesized by combining various cations and anions to satisfy the properties for the special purpose and applications [1]. Therefore, ILs are considered as the green solvents and have been widely explored in making biofuels from biomass.

Rogers et al. firstly reported the work that ILs of 1-alkyl-3-methylimidazolium chloride  $([C_n mim][Cl])$ , where *n* is the number of carbon in alkyl chain) can dissolve cellulose, and then more and more studies begin to focus on the use of ILs for the sustainable energy [2]. It has reported that the acetate- and chloride-based imidazolium ionic liquids, e.g. 1-butyl-3-methylimidazolium chloride and 1-butyl-3-methylimidazolium acetate, are recognized as the promising solvents for the biofuels manufacturing. However, the viscosity of IL is high that will impede the dissolution of biomass materials. Co-solvent can minimize the major problem of high viscosity of IL; much research has shown that the organic co-solvent could lower the viscosity of IL without affecting the pretreatment result [3]. Although the literature is rich in the thermophysical properties of IL, little attention has been given to effects of solvents on the thermophysical properties of ILs, especially of the viscosity.

In this work, it is the purpose to study the effects of organic solvents, N,N-dimethylformamide and pyridine, on thermophysical properties of imidazolium-based ionic liquids of 1butyl-3-methylimidazolium chloride. In addition, the mixture is characterized by infrared spectroscopy for further understanding of the microstructure of the solution.

## Acknowledgment

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# THERMODYNAMIC AND STRUCTURAL APPROACH ON THE MgO SOLUBILITY IN HIGH ALUMINA-BEARING OXIDE MIXTURE AT HIGH TEMPERATURE

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Research on the formation of spinel layer at the interface between molten melts and solid oxide such as MgO,  $Al_2O_3$  in high temperature have been studied in various fields not only for obtaining epitaxy spinel layers but also steelmaking process. These has been only studied based on the diffusion of cations at the spinel, oxide solid interface. However, there is a lack of the thermodynamic and structural consideration of melts for dissolution at the spinel, liquid interface with respect to the spinel growth and the dissolution behaviour of MgO oxides.

In present study, the MgO crucible and the molten oxide systems which of the saturated equilibrium phase is MgAl<sub>2</sub>O<sub>4</sub> spinel are equilibrated in high temperature. The equilibrium chemical composition and the coordination state of Al ions in molten oxide are confirmed by XRF analyzer and <sup>27</sup>Al MAS NMR, respectively.

The effect of basicity which is typical thermodynamic properties of free oxygen ion in  $MgAl_2O_4$  spinel equilibrium is changed by not only the spinel formation between MgO crucible and molten oxide, but also the coordination state of Al ion in molten melts. Also, stability function which is thermodynamic parameter and the degree of Al avoidance classifying species of BO linkage in molten melts are used for certifying the activity coefficient of alumina having influence on spinel dissolution. In conclusion, dissolution mechanism of spinel could be represented by the equation as below.

 $MgAl_2O_4 + 4\mathbf{n}O^{2-} = Mg^{2+} + 2\mathbf{n}(AlO_4)^{5-} + 2(1-\mathbf{n})Al^{3+} + 4(1-\mathbf{n})O^{2-}.$ 

Key Words: Magnesium aluminate Spinel, Spinel Dissolution, MgO Solubility, <sup>27</sup>Al MAS NMR, Liquid, Solid Interface

## ILPIL – P12

## **Ground Floor**

## THERMAL AND CRYSTALLOGRAPHIC PROPERTIES OF HYDRATES FORMED FROM CARBON DIOXIDE AND TETRA-BUTYL AMMONIUM BROMIDE

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Ionic clathrate hydrates are crystalline compounds comprised of differently shaped hydrogenbonded cages formed from water molecules. These cages are mostly stabilized by ionic guest substances with large alkyl-substituted cations. Ionic clathrate hydrates are stable around room temperature and can also incorporate guest gases such as  $CH_4$ ,  $CO_2$ , or  $H_2$ . They are thus expected to be a potential material for greenhouse gas storage. With suitable shape of the cation for host water cages, the ionic hydrates having tetra-butyl ammonium cation show well thermodynamic stability. However, the gas storage capacity is found to be reduced because of fewer empty cages left guest gas molecules per unit cell. To determine whether ionic clathrate hydrates can coexist with simple gas hydrate and further help to elevate the gas storage capacity, the thermal and crystallographic properties of hydrates formed from carbon dioxide  $(CO_2)$  and tetra-butyl ammonium bromide (TBAB) should be investigated.

In current work, ionic clathrate hydrates were allowed to form from mixed aqueous solutions with TBAB concentrations ranging from 0.1 wt% to 40 wt%. Phase equilibrium measurements, Raman spectroscopy and powder X-ray diffraction were employed. The equilibrium conditions were measured in a 160 mL stirring vessel by pressure search method. The hydrate samples were prepared at 283 K with the initial pressure around 1.5 MPa above the equilibrium pressure. The spectra were obtained to illustrate the effect of TBAB concentrations on structural types and  $CO_2$  concentrations in solid hydrate phase. Meanwhile, the micro-morphology could also be observed by microscope equipped in Raman spectroscopy.

Results showed that the equilibrium temperature was greatly reduced by 6.3 K on average as TBAB concentration increased from 0.1 wt% to 40 wt%. When TBAB concentration was below 5 wt%, hydrates generally presented as structure I. When TBAB concentration was between 5 wt% and 32 wt%, structure I and B were found to coexist in hydrate phase, and the volume of structural B increased with the increasing TBAB concentration. When TBAB concentration was above 32 wt%, structure I disappeared in hydrate phase and TBAB hydrate could form independently without participation of  $CO_2$ . The morphology of type I hydrate presented as smooth particles on hydrate surface, while the mixed  $CO_2$ -TBAB hydrates formed around structure I hydrate and showed flat surface with irregular margins, suggesting that the type I hydrate served as the core for the growth of the mixed  $CO_2$ -TBAB hydrates.

## Properties of Material Science at High Temperatures (PMSHT)

#### PMSHT - P1

#### Basement

# EXPERIMENTAL INVESTIGATION OF THERMAL EXPANSION OF PYROLITIC GRAPHITE AT HIGH TEMPERATURES

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Using the experimental setup for investigation of the thermophysical properties of conductive refractory materials under high pressure and temperature a few experiments with pyrolytic graphite were carried out. The melting temperature of graphite does not allow using stationary methods of investigation at the temperature range close to the melting region, thus some thermophysical properties of this material are still studied insufficiently. In particular thermal

expansion coefficient of pyrolytic graphite at the temperatures close to the melting point is of special interest.

Our approach allows adjusting the heating rate in a wide range from  $10^6$  to  $10^7$  K/s at a high static pressure of the surrounding gas argon up to 1 kbar. Temperature T(t) is measured by special two-channel optical pyrometer. Beside that current I(t) and voltage drop e(t) across the potential probes in the central part of the specimen during the experiment are determined, so change of specific enthalpy can be measured during the experiment. For the measurement of thermal expansion of material a technique based on the thermal radiation images of the hot specimen was used.

The density of the material was equal to  $2.18 \text{ g/cm}^3$ . Experimental data on the linear thermal expansion in the perpendicular and parallel to the basal plane directions were obtained. Thermal expansion in the perpendicular to the basal plane direction during the heating from room temperature up to the melting point was  $16.4 \pm 1.6\%$ .

The results obtained allow calculating the density of pyrolytic graphite in the wide range of high temperatures up to the melting point and in the two-phase region.

## PMSHT – P2

## Basement

#### RECENT RESEARCH OF THERMAL EXPANSION STUDIES AT HIGH TEMPERATURES

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In recent decades in many technical industries it has become necessary to use various high temperature materials such as carbides, composite carbon-carbon materials, ceramics, pure and alloyed metals. There is a need to study their thermophysical properties. In particular reliable data on the thermal expansion of materials are required for many engineering tasks. Quantitatively thermal expansion characterized by the thermal expansion coefficient (TEC).

During last years the VNIIM has been constantly working to study the dimensional stability over time of new materials at repeated temperature changes. Until now TEC measurements were carried out using reference interference dilatometers in the temperature range from 90 to 1800 K. To expand the temperature range a new high-temperature dilatometer was developed, that based on the absolute optical method of measuring the elongation of the samples under study. It allows to study the thermal expansion of materials in the temperature range up to 3000 K.

The materials selected for the studies have homogeneous structure and the minimum of phase transitions in the temperature range from 1000 to 3000 K. This selection criterion was introduced to investigate materials that could be used to transfer the unit of TEC measurements as standard reference materials later.

The results of studies of some high-temperature materials including tantalum carbide, zirconium oxide, graphite of GIP-4 grade and others are presented in this talk as well as the descrip-
tion of a high-temperature dilatometer that used to TEC measure the listed materials.

#### PMSHT – P3

#### **Basement**

## INFLUENCE OF CALCITE AND DOLOMITE CONTENT ON THERMAL BEHAVIOR OF SELECTED ROCKS

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Calcite is a highly abundant mineral; it is the dominant component of sedimentary limestones and metamorphic marbles. Other group of calcite containing rocks are calcareous sandstones where calcite acts as a cementing component of clastic particles. In these rocks calcite is often combined with a varying amount of dolomite. The thermal decomposition of calcium carbonate is a widely studied process with a high technological importance. The paper deals with the calcite and dolomite decomposition in rocks where these carbonates are accompanied with other minerals. The aim of this study is to characterize the influence of the rock's composition on the process of the carbonates decomposition and thermal expansion. Seven rocks (three types of sandstone, three marbles, and one marlstone) from different Czech localities with the calcite and dolomite content ranging from 7 to 100% are studied, using a simultaneous thermal analysis (TG/DSC) and thermodilatometry in the temperature range from 25 to 1000 °C. The supporting characterization of rocks is acquired by XRD and chemical analysis. The calcite decomposition is found to be slower in the presence of accompanying components than in the case of pure calcite. Thermal expansion is highly influenced by the composition of the studied stones as well. Even a small amount of a "foreign" component changes the dilation behavior of the studied rocks.

#### PMSHT - P4

#### Basement

## CONTACT ANGLE MEASUREMENTS OF STEEL ON WATERGLASS-BONDED $Al_2O_3-SiO_2\ COMPOSITE\ MATERIALS$

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In the beginning of the aluminothermic welding process, the thermite reaction takes place in crucibles made of waterglass-bonded  $Al_2O_3 - SiO_2$  composite materials which withstand melt temperatures above 2200 °C for the process time. A topic of interest is the numerical simulation of various subprocesses in the field of aluminothermic welding. One of these include multiphase flow simulations of the crucible discharge and mould filling after the highly exothermic redox reaction of thermite producing liquid steel and slag. In this context, thermite steel is one of the products of the aluminothermic reaction.

In order to obtain accurate numerical results, realistic thermophysical data of the multiphase system is needed. An experimental setup has been developed and optimized for the sessile drop technique of thermite steel on waterglass-bonded  $Al_2O_3 - SiO_2$  composite materials at temperatures ranging from melting point Tm of thermite steel to a maximum atmosphere temperature  $T_E$  of 1750 °C.

The measurements have been conducted in an induction heated  $Al_2O_3$  tube with an internal diameter of 34 mm, purged with Argon during the experiment at volume flow rates which can be varied. The tube includes a glass window at one end through which the thermite steel sample can be observed. A thermite steel cube with a feed size of 5 mm rests on the substrate while the tube is heated up to Tm and subsequently to TE. Two thermocouples are fixed behind the sample and underneath the substrate respectively. Furthermore, the oxygen content in the Argon gas has been measured during the measurement to guarantee a non-oxidizing atmosphere.

Static contact angles have been measured using the sessile drop technique for three different material combinations: thermite steel (a) on waterglass-bonded  $Al_2O_3 - SiO_2$  composite, (b) on waterglass-bonded  $SiO_2$  and (c) on pure  $Al_2O_3$  substrate. The measured angle is highly depending on oxidation of the sample and reactions between sample and substrate and first results yield  $152^\circ$ ,  $137^\circ$  and  $133^\circ$  for (a), (b) and (c) respectively. The temperature below the substrate is 20-25 K higher, compared to the value behind the thermite steel sample. This is due to the fact that the substrate serves as a heat reservoir while the thermocouple behind the sample is cooled by the Argon gas stream. Moreover, the measured oxygen content at the tube inlet and outlet after 12 h of purging amounts to 10 ppm and 25 ppm respectively. During the experiment at temperatures above  $400^\circ$ C, the oxygen content at the outlet of the tube decreased to 0 ppm due to the reducing effect of glowing steel. The static contact angle has been found to be influenced by the oxygen content of the substrate. Moreover, a temperature dependence of the static contact angle in the given temperature range for thermite steel could not be confirmed.

#### PMSHT – P5

#### Basement

#### THERMOPHYSICAL PROPERTIES OF LIQUID Mg-BASED ALLOYS

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Magnesium alloys, as the lightest structure alloys, have received increasing research interests due to their high specific strength, excellent damping property, good electromagnetic shield-

ing, environmental friendly, etc. Besides, the potential use of magnesium alloys in the field of electronic packaging, such as heat dissipation for light entropy dioxides (LEDs), has drawn new research interest, resulting from their excellent electrical and thermal transport properties. Particularly, the most popularly used Mg alloys now in the automotive industry are based on the Mg-Al system, which possess both good mechanical properties and outstanding castability at ambient temperature. However, these alloys exhibit poor creep resistance even when exposed to a low level of load at the performance temperature (> 100 °C) due to the low melting point of the Al12Mg17 phase. The wide application of low cost alloys would thus be remarkably inhibited.

In light of this, several researches have been taken to improve the high temperature properties of Mg-Al based alloys by modifying the phase types either through formation of new stable phases or via reducing the discontinuous precipitations of the Al12Mg17 phase. Ternary Mg-Zn-Al alloys (ZA alloys) were therefore successfully developed, which yielded an improved creep resistance. Consequently, cast ZA alloys have great potential to be used in the field of power train and motorcar, such as the engine cover.

Design and manufacture of Mg-based alloys with high enough thermal conductivity helps to solve numerous problems connected with their practical applications at elevated temperature. In this study, some thermophysical properties of liquid Mg-based alloys were studied and the results of electrical conductivity and thermal conductivity, measured in the wide temperature range above the liquidus, are analysed.

## Materials (M)

## M – P1

#### **Basement**

## ENERGETIC VS STRUCTURAL EFFECTS OF BULKY SUBSTITUENTS IN THE MORPHOLINE CORE

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A significant number of morpholine derivatives have relevant applications in the industry, namely as corrosion inhibitors and optical brighteners, as well as in the pharmaceutical area (analgesics, local anesthetic, and antibiotic agents).

In this work, experimental and computational studies were performed in order to evaluate and understand the energetic effect inherent to the substitution of the hydrogen of the amino group of the morpholine by bulky functional groups (R = methyl, ethyl, 2-aminoethyl, 3-aminopropyl), according the molecular structure depicted in figure 1. The standard enthalpies of vaporization and the standard internal energies of combustion of the morpholine derivatives obtained, respectively, from Calvet microcalorimetry and combustion calorimetry measurements, are reported. These data were used to derive the standard enthalpies of formation of the morpholine derivatives, in the liquid and gaseous phases, at T = 298.15 K. Computational calculations of the enthalpies of hypothetical gaseous reactions involving these molecules were performed, using the G3(MP2)//B3LYP composite method. This procedure enabled to calculate the gaseous enthalpies of formation of the four compounds.

The structural changes and the inherent energetic effects, associated with the substitution of the hydrogen's amino group by the bulky substituents will be analyzed. The comparison of the present results with other ones reported for related molecules will be presented [1].



**Figure 1**. Structural molecular scheme for morpholine derivatives (atom color code: red, oxygen; blue, nitrogen; grey, carbon; white, hydrogen; light blue, bulky substituents).

## Acknowledgments

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## M – P2

## Basement

## MASS TRANSFER CHARACTERIZATION OF CALCIUM ALGINATE BASED MULTIPLE BIO-POLYMER MEMBRANE

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A stable membrane made of calcium alginate with multiple domains of bio-polymers was successfully prepared. Mass transfer characterization was evaluated from effective diffusion coefficient of water soluble components, urea, glucose and methyl orange. Polyethylene glycol or agarose were employed as co-polymers of preparing membrane.

Mechanical strength of the membrane was examined by stress-strain tensile test. Maximum stress at membrane rupture for PEG 4000 membrane was increased with increasing mass fraction of PEG. In contrast for agarose contained membrane, it was decreased with mass fraction of agarose. Maximum strain was increased with increasing with mass fraction of bio-polymers. Especially for PEG contained membrane, it was remarkably increased with increasing mass fraction of PEG. Flexible character was enhanced by additive PEG. Morphology of membrane surface was investigated by scanning probe microscope (SPM) image. The membrane asperity of alginate-PEG membrane indicated smoother surface rather than that of alginate-agarose membrane.

Water permeation flux of calcium alginate solo membrane was almost same with alginate-PEG 4000 membrane. In the case of alginate-agarose membrane, it was inferior to that of calcium alginate solo membrane. It suggested that the number of water permeation channel in alginate-agarose membrane was lesser than that of calcium alginate solo membrane and/or alginate-PEG 4000 membrane. Water permeation flux was almost increased with 2nd. power of pressure. Dependency was twice larger than that theoretically supposed in laminar flow of channel.

Mass transfer characterization was evaluated based on effective diffusion coefficient of water soluble components (urea 60Da, glucose 180Da and methylene blue 373Da). In this range of molecular weight, diffusion coefficient in pure water phase changes 2.6 folds according to Wilke-Chang?s empirical formula. Effective diffusion coefficient in bio-polymer membrane was remarkably decreased with increasing molecular weight of water soluble components. It performed 36 folds change in alginate-PEG membrane (PEG mass fraction = 0.1), and it changed 180 folds in alginate-agarose membrane (agarose mass fraction = 0.1). Calcium alginate based multiple domain membrane was anticipated as a tailor-made selective separation device for water soluble components for bio-industry.

#### M - P3

#### **Basement**

## ABLATIVE PROPERTIES OF POLYMER COMPOSITES IN CONJUNCTION WITH A **SUPERALLOY**

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Fibre-metal laminates combine the properties of both a metal and a composite material reinforced with fibres. Their rapid development was forced by the demands of industry, mainly aviation and later aerospace ones, for modern materials with high mechanical properties and low weight, and also low operating costs. With the advent of spacecraft repeatedly crossing the layers of the Earth's atmosphere, where the outer shell of the vehicle heats up to temperatures exceeding 1,000 °C, there arose a demand for new materials of increased heat resistance. In addition, high heat resistance is also required for the construction of protective shields in flight data recorders. In order to protect the space vehicle against large amounts of heat produced as a result of friction in the atmosphere, ablative materials have been commonly used. In addition, the shields made with ablative polymer composites are characterized by improved thermal insulation properties.

The authors have attempted to determine the ablative properties of polymer composites in conjunction with a superalloy and their effect upon the temperature rise on the rear surface of the superalloy itself. The composites were made on plates of superalloys Inconel/Alloy 600 and Inconel/Alloy 625. They were aramid and carbon-reinforced, whereas the matrix base was made with resin Epidian 52 and TFF hardener.

Tests were carried out with regard to the temperature rise by means of thermocouples K and J type, in several places of the sample (mainly on both surfaces of the metal and the inside the laminate) caused by forced convection on the surface of the front of equalling approximately 1,100 °C over a period of around 150 seconds. In addition, the authors conducted a simultaneous measurement of the temperature rise on the rear surface using thermal imaging methods. In order to determine the destruction of individual layers of the sample (laminate) after conducting thermal investigations, photos of the surface were taken with a scanning microscope, which confirmed the effect of a heat flux on the structure of the composite.

## M – P4

### Basement

## A MOLECULAR BEAM SOURCE FOR EROSION STUDIES OF POLYIMIDE-BASED THERMAL CONTROL MATERALS IN LEO

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Upper atmosphere of Earth is composed mainly of atomic oxygen (AO) and  $N_2$  depending on the altitude. Orbiters encounter simultaneous hyperthermal (8 km/s) collisions of these molecules. Recently, it has been reported that the simultaneous collisions of inert molecules, such as Ar or  $N_2$ , greatly affect the erosion phenomena of polyimide. Therefore, effects of simultaneous collisions of AO and  $N_2$  over the collision velocity of > 8 km/s, which occurs in low Earth orbit (LEO), need to be studied.

A pulsed supersonic valve (PSV) system was developed for the upper atmospheric simulation experiments. We developed a fast piezoelectric-driven PSV system. Figure 1 shows the photograph of the PSV system. It consists of conventional low-voltage piezoelectric actuator (Max 150 V) with a displacement enlargement mechanism. Viton O-ring and Au reflector were specially designed for laser-detonation method that enables acceleration of electrically neutral molecules up to 8 km/s. Most characteristic feature of this system is that two PSVs could be attached to a single nozzle (Fig.2). Two PSVs are controlled individually so that freedom of formation of hyperthermal beam is much larger than the previous systems. The composition and velocity of the ejected gases were analyzed by time-of-flight (TOF) spectra measured by a quadrupole mass spectrometer (QMS).



**Figure 1**. Piezoelectric-driven supersonic pulsed valve with displacement enlargment mechanism.





In this presentation, the performance and experimental results on the formation of hyperthermal beams formed by this system will be presented. This system will provide a new approach to study very complicated erosion phenomena of polyimide-based thermal control systems in LEO.

## Acknowledgment

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## M – P5

## **Basement**

# INVESTIGATION OF FE71NI29 AND FE65NI35 ALLOYS THERMAL DIFFUSIVITY BY MEANS OF MODIFIED FLASH METHOD

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Research into thermal diffusivity of materials has long been and still remains a huge challenge for metrology, especially when changes of this value in the temperature function are large. It mainly refers to changes of this value in the immediate vicinity of points of phase transitions as well as to identifying the distribution of these points in ferromagnetic materials.

The aim of this study is to present the research findings with regard to the characteristics of thermal diffusivity  $\alpha(T)$  of the Fe71Ni29 and Fe65Ni35 alloys. The modified pulse method has been applied for the  $\alpha(T)$  investigations. It allows to narrow down the interval of averaging the  $\alpha(T_i = \pm 0.5 \Delta T)$  in the range lower than  $\Delta T = 1$  K, whereas the estimated error of measurement of this quantity is below 4%. The  $\alpha(T)$  value was studied in the temperature range 20 - 800 °C, during both heating and cooling of the samples. The authors confirmed the occurrence of the temperature hysteresis loop of the thermal diffusivity  $\alpha(T)$  characteristics in the case of the Fe71Ni29 alloy.

This paper is a further attempt to apply the modified pulse method of determining the temperature characteristics of thermal diffusivity  $\alpha(T)$  to identify phase transitions in ferromagnetic [1,2,3]. This approach is justified by a much higher accuracy of determining discrete values of thermal diffusivity  $\bar{\alpha}(T_i) = \alpha(T)|_{T_i-0.5 \Delta T}^{T_i+0.5 \Delta T}$  as opposed to the traditional pulse method [4,5] and a much lower temperature interval of averaging  $\Delta T$ , which may be narrowed down to values considerably lower than 1 K.

The authors believe that the study on the binary iron-nickel alloys is still quite relevant, demanding further attention.

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## M – P6

## Basement

## A CONSIDERATION ON DEGRADATION OF FEP-BASED RADIATORS EQUIPPED TO SUPERLOW-ALTITUDE SATELLITES

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Thermal control materials used in the exterior surfaces of spacecraft orbiting in the low earth orbit (LEO) experienced severe erosion by the hyperthermal collision with atomic oxygen (AO) that is the major atmospheric species in LEO [1, 2]. Due to its high-orbital velocity of spacecraft (8 km/s), the impact energy of AO to the spacecraft surface reaches as high as 5 eV, which is higher than the interatomic bonding energy of many materials. Thus, the chemical reactions occurred at the spacecraft surfaces are under the effect of high-impact energy of AO. Many

flight projects have been conducted to clarify the erosion properties of materials in LEO, for example, Materials International Space Station Experiment (MISSE) series (see Figure 1) [3]. It has been evaluated that fluorinated ethylene propylene (FEP) is durable in AO attack in LEO. On the other hand, FEP is eroded much faster in a ground-based facility. The inconsistency is problematic on the reliability of FEP-based radiator systems of the spacecraft [4].





In this presentation, a series of experiments relating FEP degradations in simulated space environments will be reported. Based on a series of experimental data, it is considered that the origin of FEP erosion in space environment is the collision-induced etching of FEP that may be activated by the high-energy (> 9 eV) collisions of AO as well as the other inert molecules. This experimental result discovers high-risk on the N<sub>2</sub>-induced erosion of FEP-based radiators that will be equipped to future very low-altitude LEO satellites.

## Acknowledgments

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## **Thermal Insulation (TI)**

### TI – P1

#### Basement

## THERMAL CONDUCTIVITY EFFECTS OF THE EMISSIVITY COATING AT HIGH TEMPERATURE THERMAL INSULATION

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For the measurement of thermal conductivity of thermal insulation for high temperature, a high-temperature GHP (guarded hot plate apparatus) was developed at KRISS, which is following the guidelines of ISO 8302 and ASTM C177. It is the suitable operating temperature between 100 °C and 700 °C. The applications of high temperature thermal insulation are engineering factory, gas turbine, buildings and a large vessel. The high temperature thermal insulations were fabricated, which had the composition of amorphous silica, titanium oxide, aluminium oxide and glass filament. The insulation was an open pore structure and voidage was approximately 90%. We made the thermal insulation same dimension with 300 mm x 300 mm x 25 mm but it had two types of different density which was 270 kg/m<sup>3</sup> and 400 kg/m<sup>3</sup>. We measured thermal conductivity of this insulation temperature at (100, 300, 500, 700) °C and we analyzed density effects. In the case of 270 kg/m<sup>3</sup> insulation, the emmisivity coatings of insulation surfaces were carried out. And then, we measured thermal conductivity and compared with no coating thermal conductivity data. In this study, thermal conductivity effects of thermal insulation density and surface emissivity coating was discussed.

## TI – P2

#### **Basement**

## EFFECT OF NANOPARTICLES ON THE THERMAL CONDUCTIVITY OF NANOTUBE/POLYMER COMPOSITES

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Thermal interface materials (TIM) have become popular and essential for efficient heat removal from integrated circuits, display panels, and ultrafast high-power density communication devices etc. Carbon nanotube (CNT)/polymer composites have shown good performance as a TIM due to the high aspect ratio of the CNTs with respect to the metallic nanofiller. The high aspect ratio of CNTs can cause great thermal transport properties through networks of CNTs even at a small loading of CNTs in the polymer matrix. For these reasons, many theoretical and experimental studies have been conducted on thermal conductivity increase of CNT/polymer composites.

We have studied the thermal conductivity of Ag nanoparticles-carbon nanotube/polymer composites as a function of the CNT and Ag nanoparticle volume fraction using a steady-state measurement technique, guarded hot plate method. The results show an increase in the thermal conductivity at a small loading of Ag nanoparticles volume fraction. However, the thermal conductivity drops suddenly at a certain volume fraction. After that the thermal conductivity increases again. This kind behavior can be understood as breaking thermal transport through networks of carbon nanotubes in the polymer matrix by Ag nanoparticles. In this study, we would to describe this kind of percolating network breaking of the carbon nanotube and their effects on the thermal conductivity of the composites.

## **Emittance, Emissivity (EE)**

EE – P1

### **Basement**

## HIGH-ACCURACY EMISSIVITY DATA ON SURREY VANTABLACK, SURREY VANTABLACK S-VIS IR AND ACKTAR ULTRA BLACK

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Black coatings featuring a high emissivity from the visible to the far infrared spectral range are widely used in optical instruments to reduce stray light, in control panels or automotive instrumentation to enhance contrast and readability, in thermal applications to control and maximize radiative cooling, in spectroscopy as reference surface and radiance standards. For these applications reliable data of their optical properties is mandatory. However, emissivity data of black coatings published in literature or in standardization documents often do not provide angular resolved information and/or lack reliable uncertainties. This is of particular importance for newly emerging Carbon Nano Tube (CNT) based coatings, directly grown on substrates because of their potential use for optical surfaces of flat plate reference blackbodies.

This is the second publication in a series relating to the measurement of the directional spectral emissivity of technically relevant black coatings at the Physikalisch-Technische Bundesanstalt (PTB). Here, emissivity data on SURREY Vantablack, SURREY Vantablack S-VIS IR and Acktar Ultra Black is given with an associated measurement uncertainty. The measurements were performed angularly resolved over a range from  $\pm$  70 °C. The emissivity data provided covers the typical temperature range for the application of the respective coating and is given over a wide wavelength range from 4  $\mu$ m to 100  $\mu$ m. The respective total directional emissivities and total hemispherical emissivities are given as well. The measurements were performed under vacuum at the Reduced Background Calibration Facility (RBCF) [1,2] of PTB to achieve the lowest possible uncertainties and complement the results published in [3].

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## EE – P2

### Basement

## EFFECT OF DIFFUSIVE MICROSTRUCTURAL CHANGES IN THE EMISSIVITY OF NICKEL AND $\mu\text{-}\mathsf{METAL}$

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Several anomalies in the emissivity of Ni and  $\mu$ -metal (Ni-17Fe-5Cu-4Mo) in the 2-20  $\mu$ m range are reported in this paper. Several interesting features concerning the spectra of these metals were observed. In both cases, a change of slope was found in the temperature dependence of the spectral emissivity at  $T_{\rm C}$ , which could be traced back to the spin-dependent scattering of s-d electrons in the expression for the electrical resistivity of ferromagnetic metals.

Each metal showed distinct optical features that could be related to in situ microstructural changes ocurring during the measurements. Nickel showed a dynamic change of emissivity at sufficiently long wavelengths in the ferromagnetic phase which could be linked to the magnetoexpulsion process of S impurities to the surface. This led to changes of up to 30% in the optical spectra at 20  $\mu$ m that had never been reported before. In the case of  $\mu$ -metal, a continuous increase in the emissivity values was observed when annealing, which was related to an order-of-magnitude grain growth as seen by electron microscopy. To our knowledge, this is the first time that grain size is found to be responsible for any significant changes in the emissivity.

These results prove that thermal emission spectroscopy can be a useful tool for the study of free-carrier dynamics, phase transitions and microstructure changes in metals. We show that the optical behaviour of ferromagnetic metals is much richer than that accounted for in the Drude and extended Drude models.

#### Photothermal and Photoacoustic Thermophysics Properties (PPTP)

#### PPTP – P1

## Basement

## CRITICAL BEHAVIOR IN RVO3 (R = RARE EARTH) STUDIED BY THERMAL DIFFUSIVITY MEASUREMENTS

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The thermal diffusivity (*D*) of *RVO*<sub>3</sub> single crystals (*R* = Ce, Pr, Nd, Sm, Gd, and Er) has been measured with an ac photopyroelectric calorimetry in the temperature region in which orbital ordering as well as spin ordering take place. Detailed measurements in the close neighbourhood of the spin ordering temperature *TN* have allowed to extract the critical parameter  $\alpha$  and the critical ratio A<sup>+</sup>/A<sup>-</sup> for this transition using the well known equation which is fulfilled in the critical region:

$$\frac{1}{D} = B + Ct + A^{\pm} |t|^{-\alpha} \left( 1 + E^{\pm} |t|^{0.5} \right), \qquad (1)$$

where  $t = (T - T_N)/T_N$  is the reduced temperature. The antiferromagnetic transition in the samples containing Ce, Nd, Sm and Er belongs to the 3D-XY universality class (showing that the spins have an easy plane anisotropy), while in the case of Gd it belongs to the 3D-Ising class, in agreement with the reported presence of a magnetic easy axis. Finally, PrVO<sub>3</sub> shows an effective isotropic behavior, as the critical parameters found agree with the 3D-Heisenberg class. Figures 1 and 2 show an example of the experimental curves obtained and the fittings performed for the case of SmVO<sub>3</sub>.





**Figure 1**. Thermal diffusivity of SmVO<sub>3</sub>.  $T_N$ : Néel temperature;  $T_{OO}$ : orbital ordering temperature.

**Figure 2**. Inverse of thermal diffusivity of  $SmVO_3$ . Experimental points and fitted curves to Eq. (1).

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### PPTP – P2

**Basement** 

## MEASUREMENT OF THERMAL DIFFUSIVITY AND SPEED OF SOUND OF [P(14)666][TMPP] BY LASER LIGHT SCATTERING METHOD

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The research areas on ionic liquids (ILs) are growing rapidly during the last twenty years because of their unique properties such as negligible volatility, wide liquidus range, non-flammability, high thermal conductivity, chemical and physical stability, high potential for recycling and high solubility. ILs can be chosen to have different anions and cations so that one can form an IL with the desired properties. In previous work of our group, the trihexyl tetradecylphosphonium bis (2, 4, 4-trimethylpentyl) phosphinate ([P(14)666][TMPP]) was found to has higher solubility for several gases such as carbon dioxide, oxygen, krypton and so on. It has been considered as a potential substitute for conventional solvents in the absorption-based separation process. So it is important to understand its fundamental thermodynamic and transport properties. As an important thermodynamic property, speed of sound is mainly used to calculate other thermodynamics properties, such as compressibility, bulk modulus, heat capacity, virial coefficient and so on. Thermal diffusivity is important for investigating the mechanism of conductive heat transfer in various chemical processes and can be used to estimate thermal conductivity combined with heat capacity and density.

Laser light scattering (LLS) method has been greatly developed to measure the transport properties and thermodynamic properties in recent years. Our group have been devoted to the study of laser light scattering (LLS) method for many years and a series of measurements have been reported on speed of sound and thermal diffusivity of DIPE, MEBE, ETBE and TAME etc. In present work, the speed of sound and thermal diffusivity of [P(14)666][TMPP] were measured over a wide p - T range, from room temperature to 650 K and from normal pressure to 15 MPa. The relative experimental uncertainties were estimated to be within 2.5% for thermal diffusivity and 1.3% for sound speed.

#### Acknowledgment

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## Nanomaterials (N)

## N – P1

### Basement

### NANOFLUIDS TO IMPROVE THE EFFICIENCY IN WIND TURBINES: THERMOPHYSICAL PROFILE

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Heat transfer fluids are used in many industrial sectors as those of the wind turbines. Temperature is a limiting factor of the generated power in order to avoid overheating of electrical and mechanical components. The replacement of heat transfer fluids employed in the wind turbine cooling systems by nanofluids can increase this power.

In this work, a commercial heat transfer fluid based on an ethylene glycol-water mixture, Havoline XLC 50/50 was chosen as base fluid because it is currently used in heat exchangers of wind turbines. As conductive material a powder, graphenit-HYDRO, based on polycar-boxylate chemically modified graphite nanoplatelets was selected. This material was provided by NanoInnova Technologies S.L. (Madrid, Spain) and was specially designed to obtain useful good performances and high stability in aqueous mediums. The analysed nanofluids have mass concentrations (0.25, 0.50, 0.75 and 1.0) wt.% of the nanoplatelets and sodium dodecyl benzene sulphonate, SDBS, at a mass concentration of 0.125% in relation to the base fluid. Following a similar procedure as in a previous work [1], stability was assessed through zeta potential and dynamic light scattering measurements. Tests for determining thermal conductivity were conducted with a transient hot wire technique in a wide temperature range. In addition, densities, dynamic viscosities and specific heat capacities of the samples were experimentally determined at different temperatures in order to carry out further studies such as experimental convective heat transfer coefficients and pressure drops.

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## N – P2

## Basement

## THERMOPHYSICAL PROPERTIES OF NANOLUBRICANTS BASED ON A BIODEGRADABLE OIL AND GRAPHENE OR BORON NITRIDE

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The main role of lubricants is to reduce friction and wear of moving surfaces as well as to dissipate heat and remove contamination from the system [1]. Additives are needed in order to improve properties of base lubricants such as oxidation stability, or both anti-friction and anti-wear capabilities [1]. Among the different additives, nanoadditives have the feature of their size enabling them to fill valleys between asperities in the contact area, resulting in a positive lubrication effect and an increase of heat dissipation [2,3]. The aim of this work is to study nanolubricants composed of an ester base oil, trimethylolpropane trioleate (TMPTO) and nanoparticles of boron nitride (BN) and graphene nanoplatelets (GnP) as potential additives. Dispersions based on TMPTO with 0.5, 0.75 and 1 wt% of BN or 0.05, 0.1, 0.25 and 0.5 wt% of GnP were prepared. The dispersions are stable for much longer time than necessary to carry out the experiments. The dependence with temperature (from 278.15 to 373.15 K) and concentration of the viscosity, density and speed of sound was studied by means of a rotational viscometer-densimeter and a mechanical oscillation densimeter. Both density and viscosity increase as the concentration of nanoparticles in the nanolubricant increases, whereas the speed of sound slightly decreases. The most significant increase for dynamic viscosity (10%) was observed when the base oil is additivated with GnP nanoplatelets.

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#### N – P3

## THERMAL CONDUCTIVITY OF EPITAXIAL $\mathrm{VO}_2$ FILM AT THE METAL-INSULATOR PHASE TRANSITION

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Vanadium dioxide (VO<sub>2</sub>) undergoes a transition from the low-temperature insulating phase to the high-temperature metal phase at near 341 K. The phase transition accompanies electrical conductivity change by factor of  $10^3 - 10^4$ , and magnitude of the change strongly depends on the crystal orientation. Kizuka *et a*1.<sup>1)</sup> have reported that the thermal conductivity of the polycrystalline VO<sub>2</sub> film changed at the metal-insulator phase transition corresponding to Wiedemann Franz law. However, the effect of crystal orientation on the thermal conductivity change along with the metal-insulator phase transition has not been reported yet. In this study, we prepared the epitaxial VO<sub>2</sub> thin film with the crystal orientation of b-axis and investigated the change in their thermal conductivity around the metal-insulator transition temperature.

 $VO_2$  films were deposited on sapphire(0001) substrates heated at 673 K by reactive rf magnetron sputtering using a  $V_2O_3$  target and a mixture of  $Ar - O_2$  gas. The thermal conductivity was measured using a front heating/front detection type picosecond pulsed light heating thermoreflectance apparatus.



**Figure 1**. Temperature dependence of the out-of-plane conductivity of the epitaxial  $VO_2$  film on sapphire(0001) and polycristalline  $VO_2$  film.<sup>1</sup>)

Epitaxial relation between the VO2 film and the substrate was (010)||(0001) sapphire. Figure 1 shows the temperature dependence of the thermal conductivity of the epitaxial and a reported<sup>1)</sup> polycrystalline film. At all the temperature range, the thermal conductivity of

the epitaxial film is almost twice larger than that of the polycrystalline film1), leading to smaller phonon scattering in the epitaxial film. The thermal conductivity of the epitaxial film monotonically increases with the temperature. For the polycrystalline film, the thermal conductivity, in contrast, shows a steep change.

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## Solids and Properties Solids (SPS)

SPS – P1

**First Floor** 

## THERMAL CONDUCTIVITY OF WASPALOY SERIES

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The nickel-based superalloys are gamma prime strengthened alloy with excellent mechanical and thermal properties at elevated temperatures as well as at cryogenic temperatures. The nickel-based alloys were improved to be resistant to creep and become stronger by changing the heat-treatment conditions. The applications of superalloys are in the aerospace, gas turbine, turbine blades for the jet engines, and automotive applications. The Waspaloy is a nickelbase, age hardenable superalloy with excellent high-temperature strength and good corrosion resistance. The Waspaloy series were modified with tungsten, manganese and silicon etc. The thermal diffusivity was measured using a laser flash method, and the specific heat capacity was measured using a differential scanning calorimeter. The thermal conductivity was calculated by the results of the thermal diffusivity and specific heat capacity in the temperature range of room temperature to 1,000 °C. The thermal conductivity of the Waspaloy series improved with varying amounts of chemical composition.

## SPS – P2

## HEAT CAPACITY OF SELECTED POLYCYCLIC AROMATIC HYDROCARBONS

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Heat capacity belongs among important physicochemical quantities which characterize a compound. In this work, we present results of heat capacity measurements of selected polycyclic aromatic hydrocarbons (benz[a]anthracene, benzo[a]pyrene and chrysene) in temperature range 2 K - 300 K. For measurements, we used commercially available thermal relaxation calorimeter PPMS (Physical Property Measurement System) by Quantum Design (USA, San Diego). This work is a part of our continuous effort to establish reliable thermodynamic data for PAHs, which are subject of regulation and monitoring because of their negative influence on the environment and human health [1, 2].

Despite the fact that PAHs studied in this work are sparsely volatile organic compounds, we could not use the usuall method for heat capacity measurement applicable for crystaline inorganic compounds. First reason is that PAH are available in form of powder which cannot be placed directly on measuring platform. Second reason is that measurement is carried out at low pressure and samples of even very sparsely volatile PAHs sublime at these conditions. In the literature, there are suggested methods for heat capacity measurements of powdered samples using PPMS (see for example review by Shi et al. [3]). We employed the method using DSC pan for sample closure, samples of PAHs were pressed into pellets. First, we tested the suitability of two different aluminum DSC pans (PerkinElmer, Kit No. 0219-0062, mass of ca 25 mg, and TA Instruments, T Zero #901683.901, #901684.901, mass of ca 50 mg). For testing, as sample was used anthracene, for which are available high quality data on heat capacity measured by adiabatic calorimetry [4]. Better results were obtained when the hevier DSC pan by TA Instruments was used. Finaly, heat capacities of benz[a]anthracene, benzo[a]pyrene and chrysene were measured. In case of benzo[a]pyrene, the results are in very good agreement with previously published data by Růžička et al. [1]. For benz[a]anthracene and chrysene, there are no available data on heat capacity in the literature.

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## NEW APPROACH IN THERMAL CONDUCTIVITY DETERMINATION FOR RIGID THERMAL PROTECTION MATERIALS

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The determination of thermal conductivity and thermal resistance by the GHP method involves the measurement of the temperature difference between the opposite faces of a parallel faced specimen at steady state when a constant, unidirectional heat flux density of known magnitude passes normally through it. The technical specification CEN/TS 15548-1 defines mandatory limits for equipment performance and test conditions. Respective values of individual clauses are mostly adopted from ISO 8302:1991 but are not fully adapted to measurements at elevated temperatures up to 850 °C. With respect to the declaration of the temperature dependent thermal conductivity values till the maximum service temperature of insulation materials and also for evaluating the conformity of thermal insulation products, improvement of measurement capabilities at elevated temperatures is required.

Usually the specimen surface temperatures are measured by temperature sensors embedded in the heater plate and cold plate, resulting in a potentially great influence of non-vanishing thermal contact resistances (TCR) between the sample and the elements of the measuring instrument on the measurement results, causing significant discrepancies.

This paper presents an alternative technique based on temperature sensors embedded in the surfaces of the specimens. The technique is suitable for quantifying and minimising the effect of thermal contact resistance (TCR) arising between a rigid specimen and the heated plate, as well as accurate determination of the specimen temperature and of the heat loss at the lateral edge of the specimen.

Using the conventional equation for determining the thermal conductivity, presented in technical specifications, the temperature difference across the specimen is limited by an unknown relationship existing between temperature and heat transfer properties. By providing a novel equation, this problem can be ignored. Using this novel method, the thermal conductivity will not depend on specimen thickness, on the mean temperature of the specimen and on the temperature of the specimen cold face, but will depend only on the derivative of temperature at the specimen's hot faces, determined by extrapolating the values measured inside the specimen.

This paper would like to contribute to the standards development work related to thermal conductivity measurements at elevated temperatures from 100 °C to 850 °C via guarded hot plate method by investigating different effects using both experimental and theoretical approaches.

## THERMAL DIFFUSIVITY MEASUREMENT OF ZEOLITE COATINGS WITH MULTI-LAYERED ANALYSIS OF LASER FLASH METHOD

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Structured reactor with functional zeolite-based coating has drawn increasing attentions due to its improved catalytic performance. And lot of interests have been focused on the zeolite film grown on metallic substrate resulted in better mechanical stability. Since the heat transfer properties of catalyst coating are of great importance concerning the energy efficiency in a reactor, apparent thermal diffusivity of zeolite coatings was determined by Laser Flash method and multilayer data analysis. In this study, as model systems, zeolite Y and SAPO-34 coatings on planer aluminum-plate prepared from spray (ex-situ) and reactive (in-situ) coating methods were examined for the comparison purposes.

During spray coating zeolite powders were mixed with 20 wt.% of attapulgite as binder, and ethanol as solvent was added to form slurry solution. Spray gun was used to distribute the mixture onto plate homogeneously. Followed with high temperature treatment, spray-coated samples were prepared. On the other hand, Partial Support Transformation (PST) method was applied for reactive coating, where zeolite growth directly from clean or seeded plate in a reactive solution with Al-plate as Al-source. The zeolite synthesis was carried out in autoclaves at high temperature for various of days.

Coated sample's morphology was characterized using various techniques, including X-ray diffraction (XRD), scanning electron microscopy (SEM), laser scanning microscopy (LSM), and also nitrogen-sorption. Results indicated that homogenous zeolite coatings with controllable thickness in the range of  $20 - 200 \,\mu\text{m}$  were successfully prepared.

The zeolite-coated sample can be seen as a two-layer composite, whose thermal diffusivity was measured by Laser Flash (LF) method at 20-200 °C and under vacuum condition. With 'two-layer analysis', in which the thermalphysical properties (density, heat capacity, etc.) of the plate and coating materials were pre-determined, the coating layer's apparent thermal diffusivity was then calculated separately. This method allows to measure non-free-standing samples with LF.

In addition, the influence of graphite coating on FL-samples was also examined. The additional thermal resistance could be neglected, but the additional thickness decreased the measured thermal conductivity linearly. Therefore, the final results were calibrated. This approach improved the accuracy of measurement with very thin samples.

Results showed spray coatings of zeolite Y and SAPO-34 have various thermal diffusivity at level of lower than 0.100  $\text{mm}^2/\text{s}$ , while reactive coatings have much better performance at around 0.181 and 0.153  $\text{mm}^2/\text{s}$ . Thickness of the coating didn't play a role in the apparent thermal diffusivity, but various surface roughness dependent on the fabrication conditions influenced the result within a certain range.

## **Biomaterials (BM)**

#### BM – P1

#### **First Floor**

#### PREPARATION OF MICROGELCAPSULES USING SPRAY ATOMIZATION

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Microcapsulation makes it possible to control the release of the included substances, and the wall materials act as physical regulator and extend the shelf-life of the encapsulated products. Especially, the microcapsules made of biocompatible materials applied for food, cosmetics, medical technology. Previously, vibrational dropping process has been known as one of major technique to prepare microcapsules. That produced seamless microcapsules with diameter of 300 2000  $\mu$ m. In contrast, air-assist spray atomization has attractively attained to prepare the fine microgel capsules made of biocompatible materials less than 300  $\mu$ m in diameter.



Figure 1. The schematic set-up to prepare microcapsules..

The schematic set-up was shown in Fig.1. Equal volume of gelatine 10 wt% aq. and sodium alginate 0.7 wt% aq. were mixed as a wall material aqueous solution. Alginate was expected to donate high mechanical strength to capsule wall. And gelatine was anticipated as thermore-sponsive polymer networks to control releasing flux of inner substance throughout capsule wall. Castor oil was used as the inner substance of capsule. Firstly, the O/W emulsion was prepared by the wall materials aqueous solution and the inner substance organic solution (volume ratio 5:1) by homogenizing by high speed agitation at 13500 min<sup>-1</sup> for 20 minutes. The microgel capsules were quickly prepared by spraying the O/W emulsion into the dispersion

medium that was a calcium chloride 1.1 wt% aqueous solution. The prepared microgel capsules were investigated by the optical microscope. Fig.2 (a) showed the microgel capsules prepared by the spray atomization. The mean outer diameter of microcapsules was 54.3  $\mu$ m, and dispersed oil pools were observed in the microcapsule. Fig.2 (b) showed the size distribution of the microcapsules. Size distribution in variance of outer diameter has still large. It was necessary to find the optimal condition to prepare the fine and monodispersed microgel capsules.



**Figure 2**. (a) The microscopic picture of the prepared microcapsule. (b) The size distribution of the microcapsules.

## **New Measuring Techniques (NMT)**

#### NMT – P1

## **First Floor**

## MEASUREMENT OF THERMAL CONDUCTIVITY OF ANISOTROPIC INSULATING MATERIALS WITH THE CONSIDERATION OF THERMAL CONTACT RESISTANCE

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Thermal conductivity is one of the important thermal physical parameters used to describe the heat transfer properties of materials. The accurate measurement of the thermal conductivity plays a crucial role in successful application of various materials. In practical experiments, the accuracy of its measurement is inevitably affected by the thermal contact resistance, which is generally neglected in most measurement methods. Therefore, it is desired to develop methods with the consideration of the effect of thermal contact resistance and subsequently to

the measurement error.

The objective of this study is to propose a new method based on the small-plane heat source method for simultaneously measuring the in-plane and across-plane thermal conductivities of anisotropic insulating materials when the effect of the thermal contact resistance is taken into account. A two-dimensional model involving the thermal contact resistance was established, and the corresponding analytical solution was derived using the Laplace transform method, variable separation approach, and inverse Laplace transform method. Based on the sensitivity analysis, the improved Gauss-Newton method was applied to calculate the in-plane and across-plane thermal conductivities, thermal diffusivity, and thermal contact resistance by combining the experimental data and calculated value of the temperature at the measuring point of the sample.

According to the proposed method, the corresponding experimental system was established. The experimental measurements for anisotropic insulating materials were carried out by using proposed model involving the thermal contact resistance and the method without consideration of the thermal contact resistance, respectively. Comparing with the results obtained by the latter method, it is found that the in-plane and across-plane thermal conductivities measured by the proposed model decreased. It is reasonable because the temperature rise increased at the measuring point due to the existence of the thermal contact resistance. The results of the thermal conductivity measurement for a standard reference material proved the feasibility and reliability of the proposed method.

## NMT – P2

**First Floor** 

## AN IMPROVEMED T-HISTORY METHOD TO MEASURE THERMOPHYSICAL PROPERTIES AT HIGH TEMPERATURES

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High temperature phase change materials (PCMs) are being investigated as thermal energy storage media to store energy for solar concentrating power plants over a small temperature range. PCMs are able to store latent heat and also sensible heat. They have been used for applications in solid-solid and solid-liquid heat storage during melting and freezing cycles. The thermophysical properties of PCMs, such as the enthalpy, heat capacity, thermal conductivity, density and viscosity need to be defined to facilitate system design and cost analysis. Several methods have been used to measure the enthalpy and heat capacity of materials such as differential scanning calorimetry (DSC) which uses small samples and is suitable for homogenous elements. Eutectic salt PCMs are heterogeneous substances and their behavior depends on volume, and may be subjected to separation and supercooling during solidification. The temperature history method (T-history) has been developed for low-temperature bulk quantities of PCM about 1000 times the sample size normally used with DSC. This paper demonstrates how to measure thermophysical properties of high temperature PCMs in the range of 200 °C and 400 °C by using improved T-history apparatus, which was designed and built at the University of South Australia. Sodium nitrate (NaNO<sub>3</sub>) with available thermophysical properties in the

literature is used to validate the accuracy of the measurement and data collected.

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