

Oral Session 3: Phase Equilibria II

10:20 - 12:40 Tuesday HS PHEG016

Chairs: A. Bazyleva, M. O. McLinden

PE – O8 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.

References

[1] K.R. Szulczyk, *Int. J. Energy and Environment* 1, 501-512 (2010).

[2] 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.*, 341, 48-53 (2013).

[3] A.F. Cristino, S. Rosa, P. Morgado, A. Galindo, E.J.M. Filipe, A.M.F. Palavra and C.A. Nieto de Castro, *J. Chem. Thermodyn.*, 60, 15-18 (2013).

[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-BEHAVIOUR 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

[1] Pitakbunkate et al, 2014, Society of Petroleum Engineers. doi: 10.2118/170685-MS

[2] Luo et al, 2016, *AIChE J.*, 62:1772-1780. doi: 10.1002/aic.15154

[3] Ambrose et al, 2010, Society of Petroleum Engineers. doi: 10.2118/131772-MS