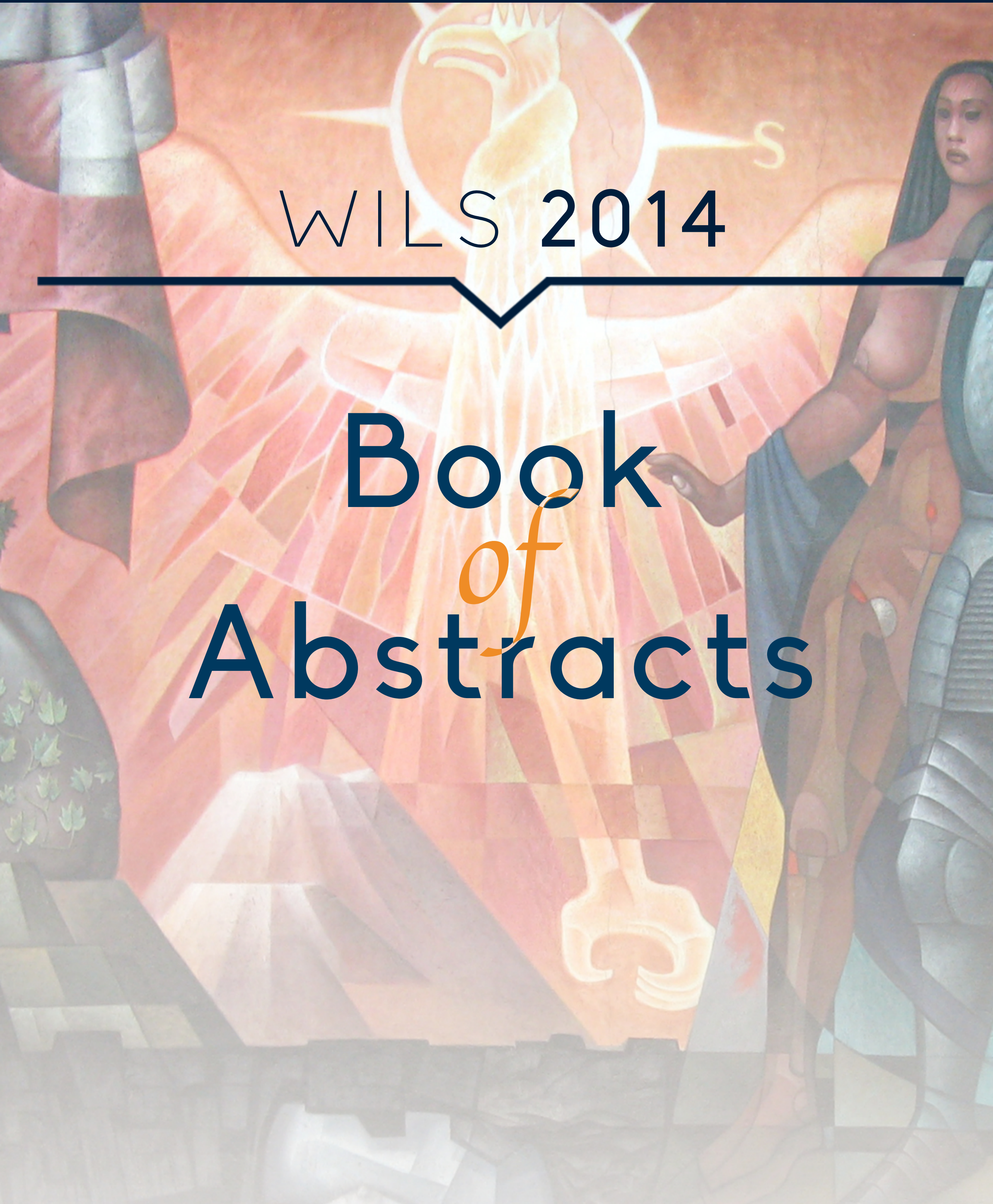
24 - 25 March 2014

Department of Chemical Engineering - Universidad de Concepción - Concepción - Chile



WILS 2014

Book *of* Abstracts

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BOOK OF ABSTRACTS

WILS 2014
International Workshop on Ionic Liquids

Tuning properties of Ionic Liquid based mixtures for novel applications

24-25 March 2014, Concepción, Chile

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WILS 2014
International Workshop on Ionic Liquids

Tuning properties of Ionic Liquid based mixtures for novel applications

24-25 March 2014, Concepción, Chile

Organized by:
Department of Chemical Engineering, Engineering Faculty,
Universidad de Concepción, Concepción, Chile

Group of Applied Thermal Engineering – CREVER, Universitat Rovira i Virgili, Spain

&

Centro de Ciências Moleculares e Materiais (CCMM), Faculdade de Ciências da Universidade de Lisboa, Portugal

Editors:
Hugo Segura
Andrés Mejía
Héctor Quinteros-Lama

Preface

Dear Colleagues, Friends and Students

Thank you for attending this third international workshop on Ionic Liquids WILS 2014, an initiative that was started in 2012 in Lisbon (Portugal) with Professor Carlos Nieto de Castro and then was held in 2013 in Pune (India), under the hosting of Professors Anil Kumar and Kashinath R. Patil. It is a real great pleasure for us to warmly welcome all you to Concepción, this southern city of Chile where our almost centenary university with a large research tradition in the field of chemistry is located.

Let us start by briefly introducing the original purpose of this meeting: the WILS workshop series is a relevant outcome of the NARILAR`s project whose primary objective is to promote the development of new working fluids based on mixtures of ionic liquids. However, the continuous development of new ionic liquids with interesting properties and the potential fields of application of these materials are increasing so fast that naturally we have come to a condition that calls people from both industry and academia to share interdisciplinary research experiences, to envisage new trends and applications, to discuss new findings and, mainly, to stimulate multidisciplinary collaboration and academic exchange between research groups.

The present version of the workshop has been organized in single working session where plenary lectures and thematic talks will be presented on Tuesday 25. We will close then this cycle of talks with a round discussion table about the potential impact of Ionic Liquids for Chemical processes and products in a global changing environment. As in previous versions of the workshop, all these activities have been focused in contributing to stimulating and strengthening the ILs' research in Chile, and also in promoting applications that may impact in the economic growth and social welfare.

UdeC, Chile, March 24-25 2014

Hugo Segura & Andrés Mejía (Chairs)
Alberto Coronas & Carlos Nieto de Castro (Co-chairs)
Héctor Quinteros-Lama, José Matías Garrido (Secretary)

Scope

WILS 2014 is an event of the NARILAR European Project: New Working Fluids based on Natural Refrigerants and Ionic Liquids for Absorption Refrigeration. In this opportunity, The Department of Chemical Engineering, Concepción University (Chile), in a joint effort with the Universitat Rovira i Virgili (URV), Tarragona (Spain) and the University of Lisbon (Portugal) are promoting its 3th version on potential applications of Ionic Liquids solutions to novel processes. Main purposes of the Workshop are to promote further scientific and technologic exchange between people from both industry and academia, to share research experiences, to envisage new trends and new findings and, as a central outcome of the activity, to stimulate research collaboration between multidisciplinary groups working on ILs.

Workshop Topics

- Collaboration schemes among theory, accurate models and experimental results for simultaneously predicting phase equilbria, thermophysical properties and transport properties.
- Quality and coherency of phase equilibrium data and transport properties.
- Screening of new working fluid pairs based on ILs for refrigeration, co-generation and heat transfer applications,
- Designing properties of new IL based solutions as materials for optimizing renewable energy technologies and greenhouse gas capture applications,

- Improving the performance IL based solutions by adding strategically selected co-solvents.
- Other topics concerning the application of ILs.

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Workshop location and secretariat

Location. The workshop will be held on the Central Campus of the Universidad de Concepción (UdeC), 4070386 Concepción, Chile. The Campus is located in Concepción, very near from Concepción's Civic Center and close to Concepcion Airport (about 7 km). Downtown Concepcion and the Main Campus of the University of Concepcion are within walking distance. Public transportation is readily available connecting downtown Concepcion and the local communities. A detailed map of the City may be found in Google maps

The University of Concepción, UdeC, was founded in 1919 and is one of the most prestigious universities in Chile. It is the third oldest university in the country, and it is part of the Chilean Council of Rectors.

The Main Campus, venue of Wils 2014, is located in Concepcion's University City. Two additional campuses are located in the cities of Chillan and Los Angeles. Founded in 1919, the University of Concepcion enrolls over 20,000 students in its undergraduate programs. To date, there are more than 1,600 postgraduate students taking any of the 23 doctorate programs, 49 master programs and 34 health specialties given at University of Concepción. CNA (National Accreditation Commission) has accredited 18 doctoral programs and 18 master's program

Information about Concepción City. Concepcion is located along the Bio - Bio River, next to the Pacific Ocean, approximately 500 km at the south of the Chilean capital, Santiago. The city, which was founded by Spanish conquerors in 1550, is the capital of the Bio - Bio Region, and has been traditionally regarded as a University and Industrial city. It is the frequent venue of national and international scientific congresses, workshops, seminars and symposiums. Major Concepcion's urban areas include: Talcahuano, San Pedro de la Paz, Hualpén, Chiguayante, Penco, Tomé, Lota, Coronel, Hualqui and Concepción downtown. In addition, Concepción City offers a number of touristic and cultural attractions which are worthy to knowing. Among others, you may consider to visit the following places during your stay:

- Convent of San Francisco
- Convent of La Merced
- Museum Cathedral of the Santísima Concepcion
- Museum of Natural History
- Museum and Park Hualpen
- Museum of History
- The Pinacoteca or Art Museum of Concepción
- Parque Ecuador where t is possible to visit the Gallery of History, which displays from each era the city's history
- Caracol hill
- The Naval base at Talcahuano for a tour of Huáscar ship, a historic relic from the Pacific War
- Lota City and Chiflón del Diablo (see details in www.lotasorprendente.cl)
- Salto del Laja, a spectacular waterfall in the Parque Salto del Laja
- National Park Laguna del Laja

Local weather during March (which is when autumn season begins) is mostly windy though sunny and cold during the mornings, with an average temperature of 15 ºC. We hope you will enjoy your stay in Concepción.

Secretariat

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41. Cabinas 7, 8, 9, 10 y 11

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64. Sociedad de Académicas y Profesionales UdeC

Monday 24

Venue: Engineering Faculty, Central building hall. Edmundo Larenas 219, Concepción.

15:00 – 18:00	Inscription and general information
20:30	Reception cocktail and dinner

Tuesday 25

Venue: Direction of Postgraduate students. Conference Room. Edmundo Larenas 234, Concepcion.

9:30	**Alberto Coronas:** A general overview of Narilar's initiative: status and progress
	Ionic Liquids, properties and Modelling. Chairs: Alberto Coronas (URiV) and Andrés Mejía (UdeC)
10:00	**Carlos Nieto de Castro:** Ionic Liquids. Can We Predict Their Thermophysical Properties?
10:30	**Guillermo Reyes:** Coarse grained molecular dynamic simulations and experimental determination of selected thermo-physical properties of ionic liquids

11:00 Coffee break

11:30	**Josefa García:** Modelling of New Ionic Liquids Derived from Ammonium with Ammonia Refrigerant Using PC-SAFT Equation for Absorption Chillers
12:00	**Héctor Quinteros-Lama:** Progressive Modelling of ionic liquid mixtures: from minimal to detailed experimental data
12:30	**Fernando J. V. Santos:** Thermophysical properties of ionic liquid based systems
13:00	**Pablo Sánchez:** Thermal analysis of pyridinium and choline based ionic liquids

13.30 Lunch break

	Ionic Liquids, applications. Chair: Fernando J. V. Santos (FCUL)
15:00	**Esteban Quijada:** Pilot plant study on the Extractive Distillation of Toluene-Methylcyclohexane mixture using NMP and the ionic liquid [hmim][TCB] as solvents.
15:30	**Allison Leyton/Cristina Ravanal:** Forest and agricultural residues pretreated by ionic liquids (ILs) for bioethanol production.
16:00	**Carlos Nieto de Castro:** Thermodynamic and transport properties for selected ionic liquids and mixtures with natural refrigerants and co-solvents for absorption refrigeration

16:30	***Coffee break***
	Ionic Liquids, new and improved experimental results. Chair: Hugo Segura (UdeC)
17:00	**Daniel Salavera:** Measurement and Estimation of some Thermophysical Properties of Ionic Liquids
17:30	**Andry Cera:** Measurement and Modelling of the Solubility of Ammonia in 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate, choline
18:00	***Coffee break***
18:20	**Round Table:** Ionic Liquids. Actual and future importance for Chemical processes and products, in a global changing environment. (**Carlos Nieto Castro** and **Alberto Coronas**)
19:20	Closure
20:30	Closing dinner

Ionic liquids. Can we predict their thermophysical properties?

Carlos A. Nieto de Castro*, Manuel Matos Lopes

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Abstract

Ionic liquids (ILs), molecules entirely composed of organic cations and inorganic anions that are liquid at ambient temperature, are known for about a hundred years, but there was little interest in them due to their stability in presence or air and water. In last ten years, ILs have attracted a lot of scientific attention[1-3] because the production of stable ILs that were over a wide range of temperature was successful. The nature of the low melting salts is governed by a complex combination of Coulombic, hydrogen bonding and Van der Waals interactions of their ions.[4] These ILs have desirable properties that make them suitable for a variety of applications and efforts for research (property and new liquids driven), applications and industrial production have been launched in many countries, with special emphasis in Europe.

Most of the applications of ILs are related with chemistry and chemical engineering. Wide applications of these ILs are in chemical process[5-7], synthesis of inorganic materials[8], catalysis[9], CO_2 capture[10], and optoelectronic applications[11].

Negligible vapour pressure is one of the most remarkable properties of the ionic liquids. They also show interesting solvating properties and many of them are excellent solvents for gases such as ammonia and CO_2 and some of them are completely miscible with water. Most of the ionic liquids have high heat capacity,

high thermal and chemical stability and non-toxicity and non-flammable which reduces fire and explosion hazard. With these properties ionic liquid shows good perspectives for applications as heat transfer fluids and as absorbent in absorption refrigerators for several refrigeration fluids, utilization of waste heat and reduction of CO_2-emissions.

Although the vital question of environmentally friendliness, that includes toxicity to biota and biodegradability are still at its infancy, there is no doubt among researchers and chemical companies that members of this class of liquids will be used, in an increased fashion, in the chemical and allied industries.

Material properties (heat capacity, thermal conductivity, viscosity and other thermophysical properties) play an important role in the applications. The combination of cation and anion of ILs allows optimization of their properties, being possible to choose a suitable cation and anion to design ionic liquids to give desirable properties for specific applications. Moreover, additives can be used to boost the heat and mass transfer performance in industrial or domestic applications. These properties can be obtained by molecular simulation, prediction/estimation[1] 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[12-14].

Predictive/Estimation methods are then a fundamental tool to be developed, to be incorporated in Process design simulators. However, due to our current understanding at a nano dimension, the existing intermolecular forces and the supporting theories, it is extremely difficult to develop theoretical based predictive schemes.

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[1] The term prediction has been widely used in the past to nominate methodologies that have totally different theoretical or empirical basis. The readers are referred to references 16 (chapter 3) and 17 for clarification of the methodology classification in prediction, semi-theoretical estimation, semi-empirical estimation and estimation.

In the current talk an overview of the current situation will be given, trying to stress the needs for theoretical information for the development of powerful and liquid independent powerful algorithms for ionic liquids and their mixtures with water, carbon dioxide, ammonia and nanomaterials.

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Coarse grained molecular dynamic simulations and experimental determination of selected thermo-physical properties of ionic liquids and its mixture with Ar, CO_2

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Abstract

Ionic Liquids (IL's) in contact to supercritical fluids are part of the so-called neoteric solvents due to their tunable properties, lower environmental impact and its applications in biology, electrochemistry, organic chemistry, separation, extraction and catalysis fields [1-3]. Nowadays, mixture of IL's with gases have gained interest due to IL`s can be used as a capturing agent of greenhouse gases (i.e. carbon dioxide - CO_2, methane - CH_4 and vapour water - H_2O) [4, 5] and ILs can be stored in an inert gas atmosphere (Ar or He) as well. Notwithstanding the current background, it is still necessary to increase our knowledge in the interaction of ILs with gases. In this contribution thermodynamic properties of two ionic liquids (IL): 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-ethyl-3-methylimidazolium ethyl sulfate ([emim][C_2SO_4]) in pressurized atmospheres of argon and carbon dioxide have been studied.

Coarse Grained (CG) Molecular Dynamics (MD) simulations have been performed to compute bulk properties (e.g. liquid density, shear viscosity, radial

distribution functions and self-component of van Hoove correlation function) of pure ([bmim][PF_6]) [6] and interfacial properties (e.g. interfacial density profile, surface tension, molecular orientation) for pure [bmim][PF_6] and its mixture with Ar and CO_2.

Surface tensions of two IL's, [bmim][PF_6] and [emim][C_2SO_4] in pressurized atmospheres of Ar and CO_2 have been measured in the temperature range (303 to 366) K and over the pressure range (0.1 to 15) MPa for the case of argon atmosphere and (0.1 to 5) MPa for the case of carbon dioxide atmosphere by using a pendant drop tensiometer[7].

RESULTS

Experimental results revealed that the surface tension of the mixtures in the first minutes is a process controlled by diffusion within the drop, the time required to attain diffusion equilibria (according to one-dimensional fickian diffusion model) agrees well with the time required to reach stationary values of surface tension at the experimental runs.

In general terms, the surface tensions decrease as the temperature and pressure increases. Figure 1. shows the isothermic surface tensions for the mixture [bmim][PF_6] + Ar.

At isothermal conditions, the lowering of the surface tension as the pressure increases evidences that the gas is adsorbed at the IL surface, which is confirmed by the positive values of the relative Gibbs adsorption isotherms calculated from the surface tension data and the Guggenheim model. At the same pressure and temperature, the adsorption of CO_2 was greater than Ar, and this adsorption process was greater for [bmim][PF_6] than [emim][C_2SO_4].

Finally through molecular simulations the radial distribution functions and species densities profiles can be observed that solubility behaviour is due fundamentally to the association between the gas molecules and the IL anion.

Figure 2 shows the density profile for mixture [bmim][PF_6] + CO_2 at T=313K and 0.43MPa .

At the interface the gas is accumulated besides the anions and apolar chains of cations.

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Keywords: (Molecular Dynamics, Ionic Liquids, Surface Tension, [bmim][PF_6], [emim][C_2SO_4]).

Figure Captions

[1] Isothermic surface tensions (g) for [bmim][PF_6] + Ar as a function of the pressure (p) at (●) T/K = 303.15, (○) T/K = 313.15, (▼) T/K = 323.15, (Δ) T/K = 343.15, (■) T/K = 363.15

[2] Density profile for mixture [bmim][PF_6] + CO_2 at T=313K and 0.43MPa. Red line (CO_2), green line ([bmim][PF_6]).

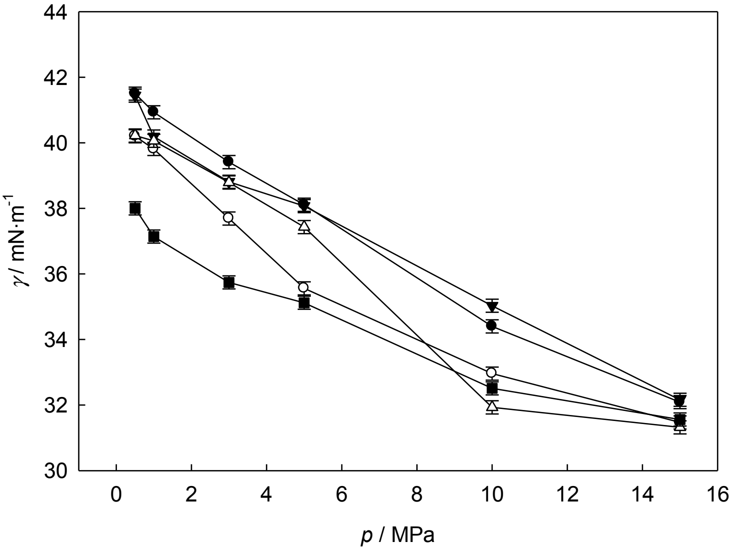

Figure 1

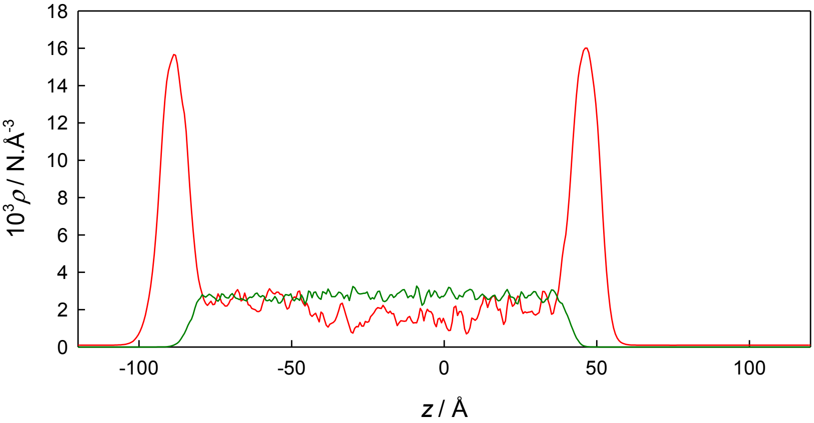

Figure 2

Progressive modeling of Ionic Liquids: from minima to detailed experimental data

Héctor Quinteros-Lama[1], Hifni Mukhtar Ariyadi[2], Jorge Albornoz[1], Alberto Coronas[2] & Hugo Segura[1]

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Abstract

The determination of an appropriate set of parameters for a given equation of state (EOS) plays a central role in the physical coherence of the model and in its predictive ability, especially when the parameterization has to be undertaken from limited experimental data as usually happens with pure Ionic Liquids. The parameterization problem becomes extremely important in the applications of molecular EOS that, usually, depend on three to six parameters, namely: three parameters for the reference term representing dispersion contributions of a molecular chain, two parameters for the association model and one additional parameter for capturing the macroscopic effect of polarity. The quoted parameters are customary within the molecular contribution framework traditionally used in well established models as the case of PC-SAFT[1], soft-SAFT[2] or the original SAFT[3,4] model.

This work focuses on the development of a reliable methodology for the determination of a physically consistent set of parameters applicable to molecular EOSs. The method combines a principle of corresponding states[5] with a zero pressure reference[6] and exploits the predictive/corrective effect of derivative properties, thus suggesting additional experimental measurements that may be critical for the purpose of improving the prediction ability of complex EOS models. It is clearly shown that the zero pressure reference gives an accurate

prediction of the properties of the liquid phase and it does not accumulate considerable errors over the low temperature range where, usually, experimental measurements of thermo-physical properties of ionic liquids are available and reliable. The zero pressure approximation, in fact, is especially suitable and recommendable for data reduction purposes of this kind of compounds.

The additional experimental data suggested by the approach proposed here allows further refinement of the parameterization and, additionally, points to the possibility of predicting more accurate derivative thermo-physical properties of pure Ionic Liquids over a wider temperature range. This latter capability is especially recommended for applications involving binary and ternary mixtures; whose prediction is relevant for screening technological applications of ionic liquids. A set of representative ionic liquids has been parameterized using a PC-SAFT reference function, from which we exemplify the capabilities and weakness of the present approach in comparison with other parameterization methodologies.

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Thermophysical properties of ionic liquid based systems

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Abstract

Ionic liquids (ILs) either on their own or as one of the components of a liquid based system are one the promising materials to solve present days economic and ecological concerns. Over the last ten years the focus shifted from the simple development and characterization of new ILs, the measurement of their chemical and thermophysical properties, to the preparation and study of binary systems of ILs, binary mixtures of IL and other solvents (non ILs) such as water, the development of ILs made from renewable resources like sugars, aminoacids or other natural compounds, and more recently to IoNanofluids, where the valuable characteristics of ILs are enhanced by the presence of nanomaterials.

The desirable characteristics of ILs that make them so appealing to a variety of applications in chemistry and chemical engineering already operating in several countries, mostly in Europe, are the negligible vapor pressure, the extended operational temperature range allowed by their very good thermal stability, their extended solvating properties including water and gases as CO_2 and ammonia, good chemical stability, very low to non-flammability, extended electrochemical window, etc. Those applications of ILs range from chemical process [1-3], synthesis of inorganic materials [4], catalysis [5], CO_2 capture [6] to optoelectronic applications [7] in spite of growing concerns about the greenness of the ILs based systems, mostly because the studies of biodegradability, toxicity and environment dispersion are still in a very incipient level of maturity.

Thermophysical properties like heat capacity, thermal conductivity and viscosity supported by other material properties like density, sound velocity and diffusion are essential to the design of any real life industrial applications. The use of ILs is not different from any other chemical except for the generally higher viscosity and density of most ILs based systems when compared with non-ILs systems, situation that must be properly addressed in the design of the process. This presentation will make an overview of the current situation, pointing out some common problems and shortcomings of the available experimental techniques. Two especial types of systems studied in our laboratories will be dealt, namely IoNanofluids and mixtures with water.

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Thermal analysis of pyridinium and choline based ionic liquids

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Introduction

The objective of this work is the characterization of new Ionic Liquids (ILs) for absorption heat pumps and refrigeration systems to enlarge their operation range and improve the performance. Selection of suitable ionic liquids for each refrigerant considered will be made taking into account thermophysical properties such as melting point, thermal stability, solubility and viscosity, among others.

A first step to select an IL for any application is to know its liquid range, especially if we are looking for absorbents for sorption heat pumps. Depending on its liquid range any given IL would fit in a particular refrigeration system.

In this work, thermal analysis techniques are employed to determine liquid range for three ILs selected as potential absorbent candidates in refrigeration cycles.

Materials and methods

Ionic liquids (ILs) selected for this work, purchased from IoliTec, are 1-Ethylpyridinium bis(trifluoromethylsulfonyl)imide ($[C_2py][NTf_2]$), 1-Ethylpyridinium triflate ($[C_2py][OTF]$), Choline bis(trifluoromethylsulfonyl)imide ($[Chol][NTf_2]$). Their mass fraction purity is higher than 0,99 and they were used without further purifications.

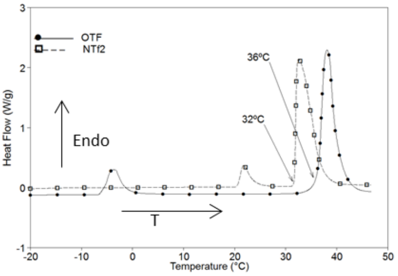
Melting point of these ILs was found using a differential scanning calorimeter DSC Q100 TA-Instruments with aluminium pans hermetically sealed using a sample encapsulating press. Nitrogen liquid was used as cooling fluid. The sample was firstly heated from room temperature to 100ºC, maintained during 5 minutes at this temperature to remove impurities and to erase thermal history of the sample. Then, it was cooled from 100ºC to -80 ºC, maintained at this temperature 2 minutes and finally heated from -80ºC to 50ºC. The heating and cooling rate was 10ºC.min^{-1}.

Maximum operation temperature of the ILs was determined using a thermogravimetric analyser (TGA 7- Perkin Elmer) operating in dynamic and isothermal modes under dry air atmosphere. Samples of 4-7 mg were placed in an open platinum pan. Dynamic experiments were performed at temperatures from 100ºC to 800 ºC, using 10 ºC.min^{-1} as heating rate and a purge gas flow of 20 cm^3.min^{-1}. Experimental procedures were widely described in previous papers [1, 2]. On the other hand, isothermal TG analysis at temperatures lower than T_{onset}, was used to determine the long-term thermal stability of these ILs.

Main Results and Discussion

Melting point of selected ILs was found from DSC curves as the onset temperature of the peak, obtaining values in the interval 25ºC – 36ºC. Figure 1 shows, as an example, the second heating step of DSC curves of ILs with cation [C_2Py] and anions [NTf_2] and [OTF].

TG curves of the three ILs are characterized by a fast degradation step at temperatures higher than 300ºC (see Figure 2). Onset temperature shows the following trend, [C_2py][NTf_2] ≈[Chol][NTf_2]>[C_2py][OTF] agreeing with literature results, which suggested that the influence of anion is higher than that of the cation [1, 2].



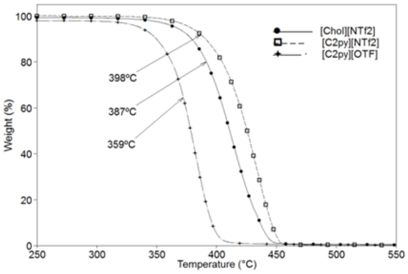


Figure 1: DSC curves of two ILs with [C_2py] common cation

Figure 2: TG curves of the three ILs. Onset temperatures are presented

As it is well known, dynamic TG results often overrate thermal stability of ILs. Thus, isothermal scans at temperatures lower than T_{onset} were performed. As an example, thermal response of these ILs at 300ºC is presented in Figure 3a, showing approximately a weight loss of 20% in 100 minutes.

Dynamic and isothermal scans show the same trend for thermal stability of these ILs. No significant differences have been observed between ILs with NTf_2 anion; nevertheless IL with OTF anion presents a slightly lower thermal stability for dynamic and isothermal studies. Furthermore, on isothermal analysis, loss mass slope is significantly affected when temperature goes from 300 ºC to 260ºC as can be seen in figure 3.

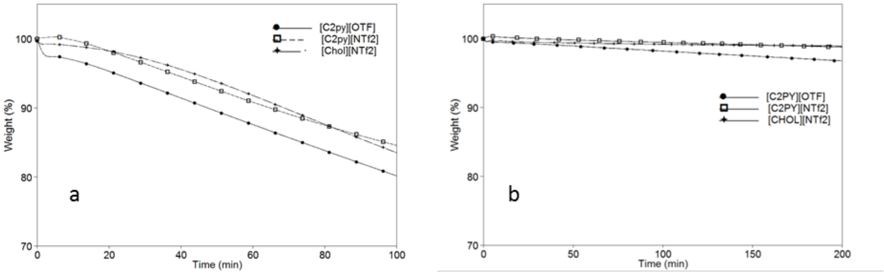


Figure 3: Isothermal scans of three ILs at 300ºC (a) and 260ºC (b)

Acknowledgements

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Pilot plant study on the Extractive Distillation of Toluene-Methylcyclohexane mixture using NMP and the ionic liquid [hmim][TCB] as solvents.

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Abstract

The separation of toluene-methylcyclohexane mixtures (aromatic/aliphatic) is challenging by normal fractional distillation due to the proximity of the boiling points (b.p.: 110.8°C and 101°C respectively). However, this mixture can be efficiently separated by means of extractive distillation when the concentration of aromatic in the mixture is between 65 and 90 wt% [1]. The commonly used organic solvent for this mixture is *N-methyl-2-pyrrolidone* (NMP).

Recently, the ionic liquid *1-hexyl-3-methylimidazolium tetracyanoborate* [hmim][TCB] has been proposed as potential replacement of the organic solvent since it produces much higher relative volatilities than NMP. Despite of this, the ionic liquid shows a high viscosity (47.83 mPa s at 25°C) that could possibly reduce the mas transfer efficiency [2]. Besides that, high solvent-to-feed ratios are required to avoid producing two-liquid phase in the column. This increases even more the liquid phase viscosities.

Therefore, the objective of this work is first exploring different operating conditions and second to compare the mass transfer efficiencies produced by [hmim][TCB] and the reference solvent NMP. To do this, an extractive distillation pilot plant equipped with Mellapak® 750Y structured packing was built [3].

Experiments in the extractive distillation pilot plant were carried out in a continuous mode and the results indicate that from two distillate rates and two reboiler duties all the selected operating conditions allowed the operation of the

pilot plant in the one-liquid phase region. However, when using [hmim][TCB] as solvent, high liquid phase viscosities are produced. As a consequence of this, the use of this ionic liquid produces lower mass transfer efficiency than the mass transfer efficiency produced by the use of NMP as solvent.

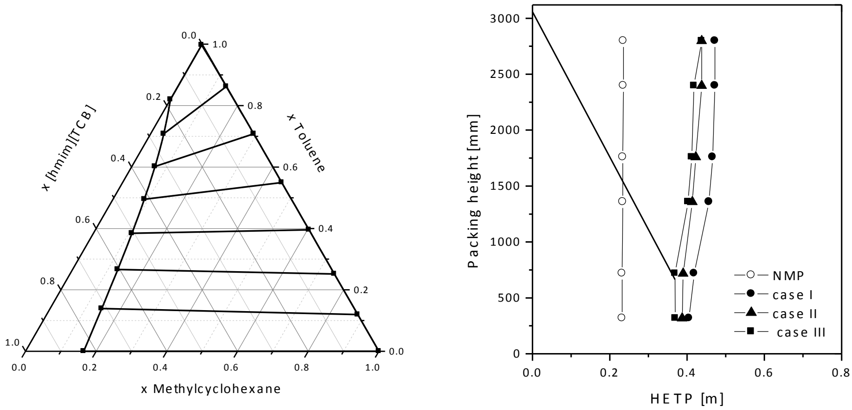

Figure 1. (a) Ternary diagram of the mixture toluene-methylcyclohexane-[hmim][TCB] mixture indicating the one and two liquid phase regions. (b) Mass transfer efficiency profiles (HETP) for all the operating conditions. White symbols correspond to experiments with NMP and black symbols correspond to experiments with [hmim][TCB].

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Forest and agricultural residues pretreated by ionic liquids (ILs) for bioethanol production

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Pretreatment of lignocellulosic materials is an important step to achieve higher amounts of simple sugars, mono- and disaccharides, to obtain ethanol as a biofuel. Different pretreatment methods have been employed such as biological, chemical, physical and physico-chemical methods but these have some disadvantages. A novel pretreatment method was discovered a few years ago which uses non-volatile solvents called ionic liquids (ILs), which are able to dissolve significant amounts of cellulose. The present study shows the effect of different process configurations for the saccharification and fermentation steps, a Separate Fermentation step after the hydrolysis (SHF) and Simultaneous Saccharification and Fermentation (SSF), of lignocelluloses residues pretreated with different ionic liquids, pure and recycled, to obtain bioethanol.

The lignocellulosic materials used were forest residues (Eucalyptus *(Eucalyptus globulus* Labill) and Lenga (*Nothofagus pumilio*)) and agricultural residues (wheat and corn). The ILs used as solvents in the pretreatment were: Aprotic (AILs) 1etil-3 methyl imidazole chlorine [EMIM+][Cl-], 2ethyl-3 methyl imidazole acetate [EMIN+][OAc-] and Protic (PILs) 2-hidroxyethylamonie acetate [2-HEAA], 2-hidroxyethylamonie lactate [2-HEAL], 2-hidroxydiethylamonie acetate [2-HDEAA]. The procedure was evaluated at different temperatures and incubation times, for [EMIM+][Cl-] 80, 121, 150 and 170 °C for 30 and 60 min. In the case of [EMIM$^+$][OAc$^-$] the conditions were 121 and 110°C for 60 min, and for PILs 60 and 70°C for 30 and 60 min, respectively. The process SHF was carried out for the saccharification and fermentation steps at 50°C, for 72 h with commercial cellulases and at 40°C for 72h with stirring using *S.cerevisiae* Red Star. The process SSF was carried out at 40°C for 72 h with commercial cellulases and *S.cerevisiae* Red Star. In all cases, reducing sugars, glucose and ethanol concentrations were analyzed.

The results demonstrate that the best experimental conditions for pretreatment of wheat and corn residues were the following: [EMIM+][Cl-] at 150 °C, for 60 min, yielding a total of 46 and 48% sugars, respectively. In the case of Lenga residues the optimum conditions were: [EMIM+][Cl-] at 150 °C for 30 min, yielding a total of 40% sugars; and in the case of Eucalyptus residues the optimum conditions were: [EMIM$^+$][OAc$^-$] at 110°C for 60 min, yielding a total of 63% sugars after saccharification. Temperatures exceeding 170 °C are not recommended for this type of pretreatment with [EMIM+][Cl-], because significant portions of cellulose could be dissolved in the ionic liquid. The best process configuration for the saccharification and fermentation steps to obtain bioethanol are SSF in combination with a pretreatment using ionic liquid. Additionally, the reutilization of the ionic liquid after a distillation step is possible with good saccharification and fermentation levels.

Measurement and Estimation of some Thermophysical Properties of Ionic Liquids

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Abstract

The potential of Ionic Liquids (ILs) as a new absorbent in refrigeration by absorption is an area in continuous growth [1-3]. In order to get desired thermophysical properties, ILs can be tailor made by altering their cation and anion combination. There are many, about 10^{18} million, possible ILs combinations [4]. Therefore, the available information on their thermophysical properties is limited. Also, the determination of these properties using experimental procedures would be expensive and arduous task. Although, there are methods based on groups contribution for the estimation of thermophysical properties of ILs, though their number is reduced [5]. Nonetheless, it has been found that this methodology can be used with good accuracy to evaluate thermophysical properties easily and quickly in engineering applications [6]. In addition, among the drawbacks in the experimental determination of thermophysical properties of the ILs are the presence of impurities and their handling care [7].

This work is focused on the measurement and estimation of some thermophysical properties of commercially available and novel ILs as potential absorbents of

ammonia for absorption refrigeration systems. For this purpose, three ILs were characterized through several techniques. Water content was determined using a Karl Fischer titration (Mettler Toledo, mod. C20). ^{1}H NMR spectra were measured on a Varian 400 MHz spectrometer, using DMSO as a solvent with TMS as the internal standard to confirm identity of ILs. IR spectra were measured with a FTIR 680 Plus Jasco. The thermal stability measurement of all ILs has been carried out by thermo gravimetric analysis (Perkin Elmer TGA-7 instrument).

The thermal conductivities were measured by Thermal Properties Meter (Decagon, mod. KD2-PRO). The isobaric heat capacities were determined using differential scanning calorimeter (Setaram micro-DSC III). The densities and viscosities of pure ILs were determined by an Anton-Paar vibrating tube densimeter (DMA60/512P) and a piston-type viscometer (Cambridge, mod. SPL372) respectively.

Finally, in order to know the capability of some methods based on group contribution for estimating thermophysical properties, calculated values were compared with the experimental data obtained.

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Thermodynamic and transport properties for selected ionic liquids and mixtures with the natural refrigerants and co-solvents for absorption refrigeration

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Ionic liquids (ILs) have become an important class of novel solvents. Composed mostly by a combination of organic cations with organic or inorganic anions with alkyl chain, the possibility of changing this combination provides an excellent opportunity to adapt to a specific application becoming the most versatile solvents.

Excellent reviews of ionic liquids on separation techniques [1] thermodynamic of non-aqueous mixtures [2], analytical applications [3] and in the field of catalysis [4] are available in the literature. However, much work remains to fully uncover the large potential of this novel class of liquids. For example, the technology of absorption heat pumps and refrigeration using absorption cooling cycles with ionic liquids has received growing attention in the past years.

Classical working fluids such as $LiBr/H_2O$ (which is corrosive and presents solidification problems) and H_2O+NH_3 (which is toxic and an odour nuisance) systems have safety and environmental impacts that can be avoided simply by replacing them with IL-natural refrigerants (e.g; IL-H_2O, IL-CO_2 and IL-NH_3), although mostly used in closed circuits. So, this fact alone contributes to the exponential growth of the need for information on thermodynamic and transport properties of the combinations of ILs with H_2O, CO_2 or NH_3, for a better choice for new environmentally friendly absorption refrigerants.

From the properties needed we can select for example vapor pressure, activity coefficients, molar fractions, solubility, viscosity. An extensive review on all these systems is currently under preparation, and will be presented soon. This work pretends to present some information already obtained, calling the attention to the further experimental data necessary for a future optimal designing of absorption refrigeration systems.

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Measurement and Modelling of the Solubility of Ammonia in 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate, choline bis(trifluoromethyl sulfonyl) imide and N,N-methyl-N-ethyl-N-(2-hydroxyl) ammonium trifluoromethane sulfonate

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Abstract

Ionic Liquids (ILs) or low temperature molten salts are considered today to constitute the class of liquids with the highest potential as "green" solvents [1]. In absorption refrigeration systems, ILs are presented as very interesting solvents to replace the conventional absorbers and avoid the problems that these present. In the conventional working fluid ammonia + water, the main drawback is the low relative volatility of the compounds, because vapor pressure of water is considerable. Substitution of water for adequate ILs could solve this problem, which greatly increase the efficiency of the system.

Regarding thermophysical properties of the mixtures ammonia + ILs, the knowdlege of the solubility is essential, because indicates the capacity of absorption of the refrigerant in the absorbent. In this work, solubility of ammonia in three ILs, 1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate [hemim][BF_4], choline bis(trifluoromethyl sulfonyl) imide [choline][NTf_2] and N,N-methyl-N-ethyl-N-(2-hydroxyl) ammonium trifluoromethane sulfonate [N_{112}(2-OH)][CF_3SO_3] has been determined. For this purpose, vapor pressure of the mixtures of ammonia with each Ionic Liquid at several compositions was measured by the static method [2]. Composition of ammonia in liquid phase, i.e. solubility, was determined in each case using Barker's method [3] with a Redlich-Kister equation for calculating the liquid activity coefficients and Redlich-Kwong equation of state to characterize the vapor phase. Also, an Antoine-type Equation and Non Random Two Liquids (NRTL) model [4] were used to fit the data. Finally, solubilities of the three mixtures were compared with conventional absorption refrigeration fluids to determine which IL is the best absorbent for ammonia.

Acknowledgment: The authors gratefully acknowledge the support of Indo-Spanish Joint Programme of Cooperation in Science and Technology (PRI-PIBIN-2011-1177 and DST/INT/Spain/P-40/11), Ministry of Economy and Competiveness (DPI2012-38841-C02-01) and the FP7-People- 2010-IRSES Program (NARILAR -New Working Fluids based on Natural Refrigerants and Ionic Liquids for Absorption Refrigeration, Grant Number 269321).

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Modelling of New Ionic Liquids Derived from Ammonium with Ammonia Refrigerant Using PC-SAFT Equation for Absorption Chillers

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Introduction

In the last years, Ionic Liquids (ILs) are being investigated as possible absorbents for absorption chillers in order to present an alternative to the conventional working pairs. Many of these investigations are focused on developing new absorbents for natural refrigerants as H_2O, NH_3 or CO_2. The objective of this work is to extend theoretical approaches to characterize new ILs for a specific application. The volumetric behaviour and phase equilibria of NH_3 + IL systems were modelled by using the so-called perturbed-chain statistical associating fluid theory (PC-SAFT) [1,2].

The design and synthesis of the new ILs was made in base on their expected low toxicity, high stability and thermophysical properties such as, solubility, density, viscosity, among others. Thus, in this work, three ILs derived from ammonium incorporating three different anions were designed and synthesized as potential absorbent candidates in refrigeration cycles for ammonia refrigerant.

Materials and methods

The selected ILs incorporate the common cation N-ethyl-N-(2-hydroxyethyl)-N,N-dimethyl, $[EM_2N(CH_2)_2OH]$, and three different anions: bis(trifluoromethylsulfonyl)imide, $[NTf_2]$, trifluoromethanesulfonate [TfO] and dicianoamidure [DCN].

Thermal stability was determined using a thermogravimetric analyser TGA7-Perkin Elmer. For the density and viscosity measurements, an Anton Paar DMA-4500 U-shape vibrating-tube densimeter and a rotational viscometer Anton Paar Stabinger SVM3000 were used, respectively. In the case of solubility, an apparatus consisting in an equilibrium cell with pressure and temperature control operating in static method was applied.

Modelling

In this work, a challenging test for PC-SAFT equation was to check its capability to provide the thermodynamic properties of mixtures composed of the natural refrigerant NH_3 together with the synthesized ILs. NH_3 was modelled as a no-associating substance, with three characteristic parameters, the number of segments (m), the diameter of each segment (σ) and the dispersive segment energy (ε/k_B). These parameters were optimized using vapor pressures and saturated densities. For the ILs, densities at atmospheric pressured were used to optimize the above cited parameters together with two more parameters (energy and volume association). In addition, following the studies performed by Chen et al. [3], $[EM_2N(CH_2)_2OH][NTf_2]$ and $[EM_2N(CH_2)_2OH][TfO]$ were modelled as modified square-well chains considering three associating sites whereas for $[EM_2N(CH_2)_2OH][DCN]$ self-associating with one associating site was used.

Main Results and Discussion

For the same cation ($[EM_2N(CH_2)_2OH]$), the thermal stability and density of the synthesized ILs follows the anion trend $[NTf_2]>[TfO]>[DCN]$, whereas the tendency for the viscosity is the opposite, $[NTf_2]<[TfO]<[DCN]$. In relation to solubility, none of the ILs was found to be immiscibility in NH_3. Figure 1 shows the experimental and predicted solubility data of NH_3 in $[EM_2N(CH_2)_2OH][TfO]$.

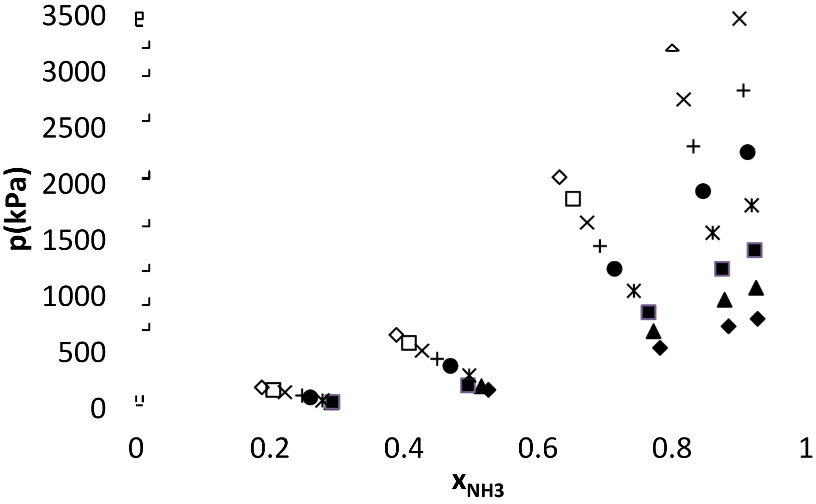

Figure 1. Solubility of NH_3 in $[EM_2N(CH_2)_2OH][TfO]$. Symbols: experimental data. Lines: PC-SAFT predictions.

PC-SAFT modelling shows an average relative deviations (ARD%) of the volume in liquid phase for the three ILs considered in this work lower than 0.7%. Thus, it can be concluded that the density is fairly well correlated as it can be seen in Figure 2. In addition, the predictions of solubility for NH_3 in $[EM_2N(CH_2)_2OH][TfO]$ are in very good agreement with the experimental data for mole fractions of ammonia higher than 0.6 (Figure 1). For mole fractions of ammonia lower than 0.4 a binary interaction parameter, k_{ij}, is necessary in order to obtain better quantitative results. This could be due to the use of IL parameters only optimized with experimental density data since no vapor pressures and saturated densities values were available.

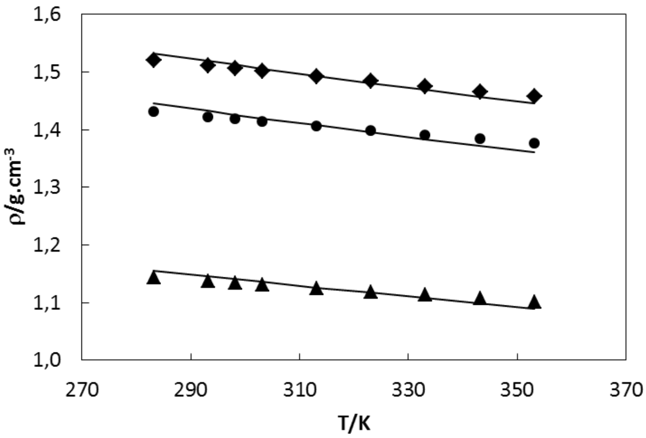

Figure 2. Density against temperature. Experimental density data: (▲)$[EM_2N(CH_2)_2OH][DCN]$, (◆)$[EM_2N(CH_2)_2OH][NTf_2]$, (●) $[EM_2N(CH_2)_2OH][TfO]$. PC-SAFT correlations (–).

Acknowledgements

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Barotropic behavior in binary and ternary mixtures composed of ionic liquids

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Introduction

Barotropy constitutes a singular case of sub-critical phase equilibrium where the densities of, at least, two of the co-existing phases of a heterogeneous mixture become equivalent[1]. At barotropic points mixtures may exhibit either mass or molar density inversion (MaDI or ModI, respectively) thus affecting the relative distribution of the phases in a gravitational field in the former case, or the group of thermo-physical and interfacial properties directly related to molar density gradients of multiphase systems[2,3] in the latter case.

Shiflett and Yokozeki have reported clear experimental evidence about molar barotropic inversions in supercritical mixtures composed of ionic liquids and CO_2, as the case of CO_2 + [bmim][PF6] and CO_2 + [bmim][PF4][4]. Molar barotropy has also been detected by Yokozeki and Shiflett in the analysis of vapor-liquid equilibrium data of mixtures composed of ionic liquids and refrigerants over the high pressure range, as the case of R-23 + [bmim][PF6][5]. According to the results presented in these references, molar barotropic inversion begins at the three-phase line (where the liquid phase exhibit immiscibility gaps) and it evolves with increasing temperature and pressure up to the critical state. It is interesting to establish here that well-known experimental examples of barotropic inversions have been mainly reported for mixtures exhibiting Type III behavior (according to the classification suggested by van Konnyneburg and Scott[6]). The reported cases affecting ionic liquid based mixtures, however, constitute clear experimental examples of barotropy affecting Type V behavior as we show in this work. Despite of the increasing interest that ionic liquid based mixtures have gained for designing new potentially useful working pairs, the characterization of their barotropic behavior has received minor attention. For instance, although MoDIs and MaDIs are related by characteristic molar or mass density inversions, they belong to completely different classes of phase equilibrium phenomena and, therefore, their existence and persistence is governed by physical mechanisms which have not clearly identified so far for the quoted mixtures. In addition, the evidence presented in this work points to the fact that the barotropic effects accompanying mixtures composed of ionic liquids may constitute potentially useful constraints for assessing and/or parameterizing phase equilibrium models. Accordingly, this work is undertaken to give a introductory characterization of mass and molar barotropy in binary and ternary mixtures composed of ionic liquids, with special emphasis in the analysis of CO_2 based supercritical mixtures.

Theory and methods

In previous references[2,3] we have demonstrated that the critical density invasion points (CDIPs) of binary mixtures play a key role in defining the basic necessary and sufficient conditions for detecting barotropy. It has been demonstrated that the binary molar CDIP (aka CMoDIP) is exactly given by the following constraints to the Helmholtz energy of a mixture

$$A_{xv} = A_{2x} = A_{3x} = 0 \tag{1}$$

Equation 1, simultaneously solved with the necessary phase equilibrium conditions for an additional phase gives place to a critical end point (CEP) characterized by molar barotropy. In this work we demonstrate that for the case of a binary mass CDIP (aka CMaDIP) is exactly given by the following relationship

$$\frac{A_{xv}}{A_{2v}} + v\frac{1-q}{q+x_1\left(1-q\right)} = G_{2x} = G_{3x} = 0 \tag{2}$$

Where q represents the ratio of molecular weights M_w of the constituents (q = M_{w2}/M_{w1}) Equations 1 and 2 become equivalent if q = 1, however for the case of mixtures composed of CO_2 + ionic liquids q ~ 6, thus significantly displacing the geometrical locus of the MaDI line to an extent to be determined in this work. Equation 2 clearly shows that mass and molar density inversions are not directly correlated for the case of ILs based mixtures. Some preliminary results concerning the simultaneous prediction of solubility and molar density inversions, as calculated from the model proposed by Yokozeki[4], are shown in Figures 1 to 3. From these Figures we may conclude that molar barotropy may be predicted by simple equation of state (EOS) models, thus constituting an additional constraint for modeling solubility data.

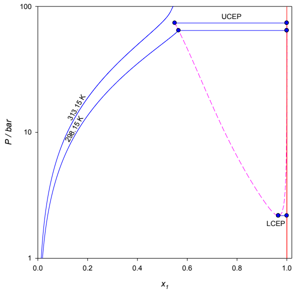

Figure 1. Solubility phase diagram predicted from Yokezekí's model for CO_2 (1) + [bmim] [BF_4] (2). (▬ ▬) : immiscible liquid phases. (▬) : liquid phase, (▬) : vapor phase

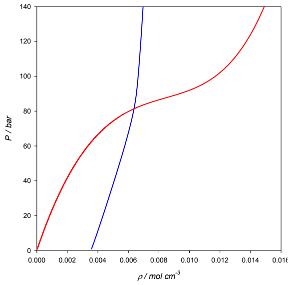

Figure 2. P-ρ diagram predicted from Yokezeki's model at 313.15 K for CO_2 (1) + [bmim] [BF_4] (2). (▬) : liquid phase, (▬) : vapor phase

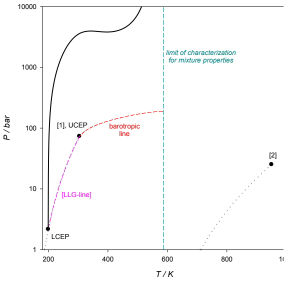

Figure 3. P-T global projection predicted by Yokezeki's model for CO_2 (1) + [bmim] [BF_4] (2). (▬ ▬) : three phase line, (▬ ▬) : barotropic inversion locus. (▬) : critical line. (●●●): vapor pressure line

Results shown in Figures 1 to 3, where it has been assumed that the IL is not decomposed by thermal effects, also reveal that molar barotropy persist to the high temperature and pressure range, with a MoDI line clearly characterized by a lower slope than the slope of the three phase line. This latter result suggests a new finding directly related to the chemical nature of the mixture: molar barotropy starts at a three phase line involving an immiscible liquid phase rich in IL and a significantly compressible gas phase rich in CO_2. Usually, experimental results in reportedly barotropic mixtures have shown that density inversions may be observed between liquid phases. Finally, although the low temperature range of Figure 3 clearly resembles a Type V behavior for the predicted mixture, it is interesting to note that the trend of the barotropic and critical lines evidence a physical incoherence of Yokozeki's model.

Main conclusions and future work

In this work we have demonstrated that simple EOS models are able to predict interesting features for the phase behavior of mixtures composed of ionic liquids. Particularly, molar density inversions occur in Type V mixtures involving liquid and vapor phases. The validity of these preliminary results is being analyzed now for other mixtures and for the case of mass density inversions. We are analyzing also the possibility of promoting or inhibiting mass and molar barotropy by the addition of co-solvents.

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