CURSOS E CONGRESOS

BOOK OF ABSTRACTS
Santiago de Compostela-A Coruña
July, 20-22 2011

2ndIMIL
2nd Iberian Meeting on Ionic Liquids

EDITED BY
Luis M. Varela
Oscar Cabeza
Jesús Carrete
Trinidad Méndez-Morales

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Foreword

Dear colleagues:

It is our great pleasure to welcome you to the 2nd Iberian Meeting on Ionic Liquids (2nd IMIL) taking place in Santiago de Compostela and A Coruña (Spain) from July 20 to July 22, 2011. Our two cities are among the most beautiful towns in Northern Spain, with solid cultural backgrounds and landscapes in their surroundings of exceptional beauty. Santiago de Compostela is the capital of Galicia, a World Heritage City and a traditional pilgrimage destination since the Middle Ages, which attracts thousands of visitors due to its singularity. A Coruña is a thrilling modern city with a great past as a former capital of Galicia, as well as a business capital which combines tradition and modernity, and brings together sea and land in a unique manner.

2nd IMIL continues and consolidates the successful tradition started in Aveiro in June 2009 of holding meetings of the Iberian community of researchers on ionic liquids every two years. The main aim of these meetings is to bring together Iberian specialists (as well as contributors from other parts of the world) working in this field in order to share our respective knowledge and expertise in the many fields of research connected to ionic liquids. We aim to create the perfect environment to bring about fruitful synergies among the Iberian Community in this promising, exciting and rapidly evolving field.

The program for 2nd IMIL includes 28 oral and 58 poster presentations. Included among the oral presentations are an opening lecture and four invited plenary lectures regarding the different topics to which the several sessions are devoted: synthesis and extraction, experimental measurements and theoretical and simulation models.

We thank you for your participation in the 2nd Iberian Meeting on Ionic Liquids, and we wish you have a stimulating and rewarding time at the conference and a pleasant visit to our two friendly cities.

On behalf of the Organizing Committee of 2nd IMIL

Óscar Cabeza Gras

Luis Miguel Varela Cabo

2nd IMIL Chairmen

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- **P4.9:** "ACTIVITY OF THERMOMYCES LANUGINOSUS LIPASE IN THE PRESENCE OF DIFFERENT FAMILIES OF IONIC LIQUIDS", D. Ruivo, A. Rodríguez, F. J. Deive, J. M. S. S. Esperança, I. M. Marrucho, L. P. N. Rebelo
- **PL1:** "SIMULATION, SOLVATION AND SCREENING IN IONIC LIQUIDS", R. M. Lynden-Bell
- **PL2:** "THERMOPHYSICAL PROPERTY MEASUREMENTS OF IMPORTANCE TO THE OIL AND GAS INDUSTRY", J. A. Boxall, T. J. Hughes, M. E. Kandil, K. N. Marsh, E. F. May
- **PL3:** "IONIC LIQUIDS: SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES. STUDIES OF THEIR MIXTURES WITH WATER", M. Turmine
- **PL4:** "THERMODYNAMIC PHASE-BEHAVIOUR OF IONIC LIQUIDS", U. Domanska

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OPENING LECTURE

OL: ACCURATE VAPOUR PRESSURE DATA OF IONIC LIQUIDS: WHICH INSIGHTS CAN WE GET FROM THERMODYNAMICS?

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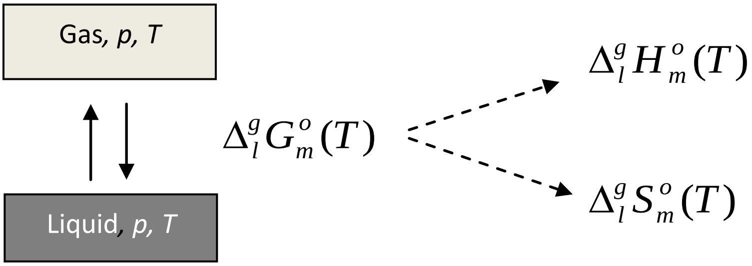
A high accuracy and a high resolution of the experimental results concerning vapour pressure data of ionic liquids are essential to derive fundamental thermodynamic properties such as standard molar enthalpies and entropies of vaporization. In turn, these quantities can be directly used for absolute and comparative interpretations of the structure and dynamics of ILs as well as to support the development, parameterization and test of computational models in the field.

Especially due to their high thermal stability and high purity, imidazolium-bis(trifluoromethylsulfonyl)imide ionic liquids belong to one amongst few families for which reliable vapour pressure data can be obtained. In this work, very accurate vapour pressure experimental data for an extended number of imidazolium bis(trifluoromethylsulfonyl)imide ionic liquids have been attained using a Knudsen effusion apparatus combined with a quartz crystal microbalance. Based on the measured vapour pressures, the standard molar enthalpies, entropies and Gibbs energies of vaporization were derived.



The resolution and accuracy of the obtained results were sufficiently good to dissect reliable enthalpic and entropic contributions to the vaporization equilibrium. Thus, the relationship between the cohesive energies, volatility and structure will be evaluated and rationalized based on the enthalpic and entropic contributions. They will be used to establish the bridge between the thermodynamic trend and structural effects, yielding some insights to the percolation phenomenon in ILs.

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PLENARY LECTURES

PL1: SIMULATION, SOLVATION AND SCREENING IN IONIC LIQUIDS

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Simulations complement experiments by giving insight into the behaviour of ionic liquids at the molecular level and complement theory by allowing one to test theoretical predictions.

Considered as solvents, ionic liquids are, in many ways, very different from organic solvents, or even hydrogen-bonding solvents. The interaction between the solvent molecules (or ions) is very strong, and in the case of neutral solutes dominates the behaviour.

Solvation of polar and non-polar solutes has been studied since the earliest simulations, while simulations of charged solutes in ionic liquids are now common. The interest in charged solutes arises from the use of ionic liquids in electrochemical applications (including solar cells) and as solvents for chemical reactions between charged species.

An important question is the extent of screening provided by the ionic liquids and how it varies with distance. I will discuss three examples: firstly the screening of single ions[1], secondly screening between pairs of dissolved ions[2] and finally work in progress concerning the screening of an ion by the ionic liquid as a function of distance from a charged electrode.

For single ions screening of the electrostatic potential occurs over distances comparable to the radius of the first solvation shell, after which the Poisson potential oscillates about the asymptotic value. However the screening is even greater for pairs of dissolved ions either with the same charge or with opposite charges. Ion pairs are barely stabilised (~kT) and are predicted to dissociate. This is relevant to the study of reaction mechanisms in ionic liquids [3].

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PL2: THERMOPHYSICAL PROPERTY MEASUREMENTS OF IMPORTANCE TO THE OIL AND GAS INDUSTRY

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Downhole properties that are of major importance are the dew points of natural gas + oil mixtures and the density and viscosity of heavy oils. The techniques presently used in industry for dew point measurements require massive equipment and measurements cannot be made at downhole conditions. A microwave resonance cavity method for the measurement of dew points, with possible applications downhole, has been developed based on changes in the resonance frequency in the vicinity of the dew point of a gas mixture. The apparatus will be described and some results reported. The viscosity of downhole fluids is a property important in reservoir simulation. A technique based on the measurement of the resonance frequency of a vibrating wire will be described.

Natural gas hydrate plugs can form during the transport of moist natural gas. A knowledge of the dissociation of gas hydrates formed from methane rich gases with varying compositions of ethane, butane, propane, and carbon dioxide is necessary to accurately predict plug dissociation times using various techniques including electrical heating. Pure methane exists as hydrate structure I (sI) while natural gas lean in components heavier than methane exists as hydrate structure II (sII) at three-phase equilibrium conditions. However at higher pressures a phase transition from sII to sI occurs. Our measurements of two-sided depressurization of an sI and an sII hydrate indicates that the sII hydrate takes about 25 % longer to dissociate.

Liquefied natural gas (LNG) is the leading technology for bringing remote natural gas resources to market. Process simulators are used to design the LNG process, however the differences in compositions observed in the actual plant and those predicted by the simulator at the same operating conditions are often substantial. The current practice is to over-engineer the plant to compensate for these discrepancies but this leads to increases in the costs of constructing and running the plant. One reason for the inaccurate process simulations is that the equations of state used by the simulator are not tuned to thermodynamic data representative of plant conditions and furthermore there is a lack of data at the operating conditions.

New experimental $pTxy$ data are reported for methane-dominant binary systems where the minor component is one of ethane, propane, 2-methylpropane, hexane or other higher hydrocarbons. The data were measured at pressures to 6 MPa over the temperature range 130 K to 300 K using a custom-built vapour-liquid equilibria apparatus. Rapid On-Line Sampling Injectors and a gas chromatograph were used to measure the composition of representative samples from the liquid and gas phases in the cell. Another apparatus has also been developed to measure density data for similar mixtures over the same range of conditions. This second apparatus uses the same sampling technique but incorporates circulation pumps to mix the phases and allow the densities of the saturated phases to be measured with vibrating tube densimeters. The experimental data are compared with modern reference equations of state of natural gas, and the experimental techniques are discussed in detail.

PL3: IONIC LIQUIDS: SYNTHESIS AND PHYSICOCHEMICAL PROPERTIES. STUDIES OF THEIR MIXTURES WITH WATER

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For many years, chemists have become increasingly interested in ionic liquids as reaction media. Ionic liquids can be used pure (molten salt at room temperature), or mixed with water or other solvents. The increasing number of publication and feature revues on these liquids attests to this interest. Ionic liquids have low vapour pressures and for this reason they are considered as “green solvents”. Therefore, they are excellent candidates for replacing organic solvents in many industrial processes. However, their main advantage is the possibility of modulating and adjusting their physicochemical properties by changing the nature of the anion or the cation or by adding a molecular solvent. This currently occupies the main body of work on these media. However, only a few studies have investigated the physicochemical extents likely to affect the reactivity, such as, for example, their acid–base properties, particularly for imidazolium salts such as 1-butyl-3-dimethylimidazolium tetrafluoroborate (bmimBF_4).

We have particularly studied some physicochemical properties of water – ionic liquids mixtures. One of our objectives was to describe the behaviour of such mixtures. For that, we needed a model. The pseudo-lattice theory introduced by Bahe [1, 2] and supplemented by Varela et al. [3] seemed to us to be a powerful tool to describe these particular media. We showed that this approach can suitably describe the partial molar volume of ionic liquids throughout the composition scale from the infinitely dilute state to the pure room temperature molten salt [4, 5]. Moreover, this same approach can be used to explain the variation of the acid-base properties of these particular media [6, 7].

Ionic liquids are often described in the literature as “structured” or even organised media. Then, it would be interesting to study the behaviour of surfactant in such systems.

These particular liquids are very interesting in electrochemistry. Organic or inorganic compounds can dissolve in ionic liquids. Moreover, these solvents are sufficiently conductor to avoid the addition of a support electrolyte. We studied the electrochemical behaviour of ferrocene in four ionic liquids by different methods in order to determine the diffusion coefficient of ferrocene.

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PL4: THERMODYNAMIC PHASE-BEHAVIOUR OF IONIC LIQUIDS

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The activity coefficients at infinite dilution, γ_{13}^{∞} for many solutes: alkanes, alkenes, alkynes, cycloalkanes, aromatic hydrocarbons, alcohols and water in various ionic liquids (ILs), determined by gas-liquid chromatography at different temperatures, and the partial molar excess enthalpies at infinite dilution values $\Delta H_1^{\mathrm{E},\infty}$ will be discussed [1,2]. The selectivities for the hexane/benzene, cyclohexane/benzene, or any two chosen solvent's separation problems, calculated from the γ_{13}^{∞} will be presented.

(Solid + liquid) and (liquid + liquid) phase equilibria in binary and ternary systems that contain the IL and an alcohol, or water, or aliphatic hydrocarbons, or aromatic hydrocarbons have been measured at normal pressure by a dynamic method in the whole mole fraction range, *x* from 0 to 1. Many factors that control the phase behavior of ILs with other liquids, especially with alcohols, water and hydrocarbons, have been discussed in recently published papers focusing on imidazolium, pyridinium, pyrrolidinium, ammonium, phosphonium, and quinolinium-based ILs [3-5]. These ILs mainly exhibit simple eutectic systems with immiscibility in the liquid phase with upper critical solution temperature (UCST), or in the case of strong interaction with solvent (water, alcohols) complete miscibility in the liquid phase. The ILs chosen as the most interesting in the separation process – namely, 1-alkyl-3-methylimidazolium, or pyridinium-, or pyrrolidinium-, or piperidinium-thiocyanate ([AlMIM][SCN], [AlMPy][SCN], [AlMPyr][SCN], [AlMPip][SCN],) [3,4], or imidazolium, or pyridinium-, or pyrrolidinium-tosylate based ILs, ([BMIM][TOS], [BMPy][TOS], [BMPyr][TOS]), or ethyl(2-hydroxyethyl)dimethylammonium bis{(trifluomethyl)sulfonyl}imide (C_2NTf_2), or tetra-*n*-butylphosphonium *p*-toluenesulfonate ($[Bu_4P][TOS]$) [5], or tetra-*n*-butylphosphonium methanesulfonate ($[Bu_4P][CH_3SO_3]$) [], or [3] showed UCST behavior with an aromatic, or aliphatic hydrocarbons. High solubility of aromatic hydrocarbons in the IL was observed. An increase in the alkyl chain length of an alkane at the benzene ring resulted in an increase in the UCST. By increasing the alkyl chain length of an alkane, the lower solubility was observed. The UCST increases from hexane to decane in these systems. Complete miscibility was observed for the systems of thiocyanate-based ILs + an alcohol C_1-C_{12} at the temperature 298.15 K. The selectivities of the different separation problems in LLE ternary systems will be presented [6].

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ORAL PRESENTATIONS, SESSION 1:

Synthesis and extraction

O1.1: EXTRACTION OF CAFFEINE FROM GUARANA SEEDS USING AQUEOUS IONIC LIQUIDS SOLUTIONS

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Caffeine, a well known alkaloid presenting antibacterial and antifungal properties, is found in diverse natural products, such as in beans, leaves, and fruits, where it acts as a natural biocide protecting the plants.[1] In agriculture, products used in the pest control possess disadvantages to human health, such as high toxicity, high volatility and related environmental hazards. Caffeine could be used as an alternative and environmentally safe repellent/toxicant for the control of pest on food crops. Guarana is a climbing plant especially common in Brazil. Guarana seeds contains about twice the caffeine found in coffee beans.[2] Therefore, the caffeine recovery and purification from natural sources by cost-effective and environmentally-safe processes is of significant interest.

In this work, aqueous solutions of ionic liquids (ILs) were investigated for the extraction of caffeine from guarana seeds. ILs were selected as main solvents due to their unique properties, namely their negligible vapor pressures and flammability, high chemical stability and large solvating capacity for the most diverse compounds. Four operational parameters were optimized: IL concentration, extraction contact time, solid–liquid ratio and temperature of extraction. Since the properties of ILs can be tuned by the proper combination of the cation and/or anion, ILs can be optimized with particular features. After the optimization of the operational conditions, the influence of the IL cation and anion nature was further evaluated. The data obtained reveal a high potential of IL-based systems for the extraction of caffeine from natural matrices.

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O1.2: RECOVERY OF VANILLIN USING IONIC-LIQUID-BASED AQUEOUS BIPHASIC SYSTEMS

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The use of conventional volatile organic compounds (VOC’s) in extraction procedures brings up some associated problems such as high volatility, toxicity and flammability and the possibility of denaturating biomolecules, which in turn may influence the quality and purity of these to be recovered and implies additional environmental hazards. The development of new techniques and replacement of VOC’s for the most diverse biomolecules separation and purification aiming at improving the extraction operationally and environmentally conditions is actually crucial. Nowadays, ionic-liquid-based aqueous biphasic systems (ABS) are object of great interest due to their potential in the design of novel separation routes.

Ionic liquids (ILs) present several physical and chemical advantages over VOC’s, such as, negligible vapour pressures, non-flammability, high chemical and thermal stability, and do not inactivate enzymes if a proper selection of the ionic medium is carried out. In addition, once the ILs physicochemical properties are strongly dependent on the IL nature, the possibility of changing their physicochemical properties through the tailoring of their anions and cations represents an important and additional advantage. On the other hand, ABS are extraction processes that possess major advantages through typical liquid-liquid extractions between two immiscible solvents, as the concentration and purification procedures can be integrated in one single step, the high selectivity that can be achieved, the harmless environment derived from the use of aqueous phases, the scaling-up facility and the capability of maintaining the integrity of the biomolecules to be recovered.

In this work the extraction of vanillin, one of the most appreciated fragrant substances to create artificial flavors and aromas in a wide range of products, using ABS composed by imidazolium-based ILs, K_3PO_4 and water was studied. For that purpose, three main parameters were evaluated though the vanillin partitioning process: the IL cation and anion nature, the temperature of equilibrium and the available concentration of vanillin in the global system. In all systems and conditions tested, vanillin preferentially migrates for the IL-rich phase. Moreover, viscosities and densities of both aqueous phases were experimentally measured at the mass fraction compositions for which the partition coefficients were determined. The results indicate that IL-based ABS can be further employed in the extraction and purification of vanillin from different matrices as confirmed by the large partition coefficients obtained and improved low viscosity systems [1].

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O1.3: LIPASE PURIFICATION USING AQUEOUS TWO-PHASE SYSTEMS WITH IONIC LIQUIDS – THE QUEST FOR NEW ALTERNATIVE SEPARATION TECHNIQUES

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A considerable number of lipases (EC 3.1.1.3) are produced by microorganisms such as yeast, molds and bacteria [1]. Microbial lipase is usually obtained by fermentation processes the broth being a complex mixture of substrates and bioproducts. For the success of the commercial production of enzymes and proteins, efficient downstream processing techniques are required. In this context, aqueous two-phase systems (ATPS) appears as a promising technique aiming at the enzymatic purification steps, since they can be considered as non aggressive for biomolecules due to the high water content and the possibility of maintaining the neutral pH value [2-3]. A recent alternative for ATPS is the use of ionic liquids (ILs) and water-structuring salts.

The aim of this work was to study the lipase *Candida antarctica* lipase B (CaLB) partition using different ATPS systems, varying the type of salt, ionic liquid and also, several system conditions, such as the temperature, salt and IL composition and finally, the pH. As a result, the purification factors and recoveries of each system for both phases were determined. The salt solution used was a K_2HPO_4/KH_2PO_4buffer. The ILs studied belong to different families: pyrrolidinium, piperidinium, pyridinium and imidazolium. The results show that the hydrophobic ILs with longer alkyl chains were responsible for the higher purification factors [4].

Based on $[C_8mim]Cl$ a systematic study of the effect of parameters such as the salt (20-30 wt %) and IL concentration (25-35 wt %), the temperature (278.15-313.15 K), and the pH (7.0 and 7.8) was carried and is discussed. The results reported prove the ability of ILs-based ATPS as an alternative in the purification of proteins from a fermentation broth.

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O1.4: LIPASE-CATALYZED BIODIESEL PRODUCTION FROM SUNFLOWER OIL IN IONIC LIQUIDS

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Alternative fuels have existed for many years, nevertheless their use has been so far somewhat restricted. However, this is about to change. The present situation of petroleum market instability, limited availability of crude oil, refineries reaching their peak production and the impact of the use of petroleum-based fuels on the environment, have all positively impacted the spread of alternative fuels, such us biodiesel. Biodiesel is part of the family of biofuels and is a term used to define a fuel used instead of diesel fuel and that is produced from a biological source. Although biodiesel has different chemical composition than diesel fuel, it exhibits some similar properties. Biodiesel, also known fatty acid methyl esters (FAMEs), has become more attractive as an alternative fuel resource because of its environmental benefits such as biodegradable, nontoxic and low emission profiles [1, 2]. In this work, we analyse the use of different ionic liquids as reaction media for enzymatic biodiesel production. A commercial lipase was used as catalyst (*Candida antarctica* lipase B immobilized on a macroporous acrylic resin, Novozym 435) in biodiesel synthesis by direct transesterification of sunflower seed oil and of waste frying oil with methanol. The relationships between the reaction variables (conversion, product distribution, the effect of substrate molar ratio and water content) have been examined.

Among tested 11 ionic liquids, the highest fatty acid methyl esters (FAMEs) production after 70 h at 40 ºC was achieved in $[\text{omim}^+][\text{PF}_6^-]$. For the ILs based on the same anion, the hydrophobicity increased with increasing length of the alkyl group on the cation. and the synthetic activity was higher when the most hydrophobic ionic liquid was used as medium, which could be explained by the fact that the increase in hydrophobicity of the medium could allow the preservation of the essential water layer around the protein molecule, thus reducing the direct interaction with the enzyme.

The optimum substrate molar ratio of methanol to sunflower oil for FAMEs production in $[\text{omim}^+][\text{PF}_6^-]$ was found to be 12:1 and the synthetic activity exhibited by CALB showed a maximum at about at 1% of water added.

Our results of high production yield in ionic liquids show that ionic liquids are potential reaction media for biodiesel production.

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O1.5: ILS MEDIATED SYNTHESIS OF HAJOS DIONE

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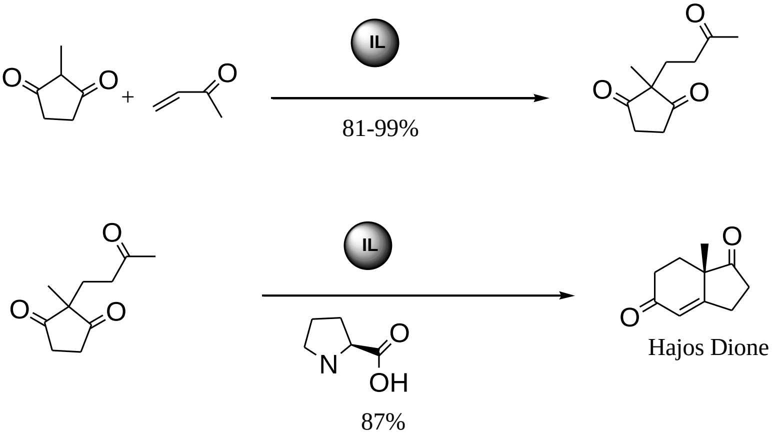
In the last years, ionic liquids (ILs) have attracted considerable interest as environmentally benign reaction media because of their unique properties such as high thermal and chemical stability, negligible vapour pressure, tuneable polarity, nonflammability, friction reduction, antiwear performance, high loading capacity and easy recyclability[1].

In this presentation, we report an efficient and environmentally friendly procedure for the synthesis of Hajos dione, a useful starting material for the synthesis of vitamin D metabolites and analogues[2].



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ORAL PRESENTATIONS, SESSION 2:

Experimental measurements

O2.1: INTERFACIAL PROPERTIES OF CHOLINE-BASED IONIC LIQUIDS

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Room-temperature ionic liquids (RTILs) are presently widely studied due to their unusual physico-chemical properties that make them promising replacements for the traditional organic solvents. However, their practical application is still limited by toxicological, ecological and economic issues. An alternative approach to overcome the toxicity problem is to use ILs composed wholly of biomaterials. In particular, the cation choline has been found to be an adequate green substitute for synthetic cations [1,2]. Since the bio-ILs constitute a new field of research, a systematic study of the relation between their physico-chemical properties and component ion structure is still missing. In the present work, the interfacial properties of three choline-based ILs, choline propionate, [Ch][Prop], choline tiglate, [Ch][Tig], and choline H-maleate, [Ch][Ma_l], were studied. The surface tensions were measured using the pendant drop method in a wide temperature range (293.15 – 393.15 K) and the contact angles were measured on both hydrophilic (BK7 glass) and hydrophobic (PTFE) substrates using the sessile drop method. Although these ILs present high hydrogen bonding, low surface tension values were obtained (between 40 – 35 $mJ \cdot m^{-2}$) in comparison with other IL with strong hydrogen bonding (e.g. [C_2OHMIM][BF_4]) [3], thus moderately high contact angle values were observed on PTFE. The influence of water on these properties was also evaluated. An interpretation of the results based on the ionic liquid structure is attempted.

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O2.2: THERMOPHYSICAL PROPERTIES OF 1-BUTYL-1-METHYLPYRROLIDINIUM TRIS(PENTAFLUOROETHYL)TRIFLUOROPHOSPHATE (BMPLFAP)

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Thermophysical properties of 1-Butyl-1-methylpyrrolidinium tris(pentafluoroethyl) trifluorophosphate (BMPLFAP) are reported for the first time, in temperature range 283 K to 373 K, at atmospheric pressure. Tris(pentafluoroethyl) trifluorophosphate (FAP) - ionic liquids have shown an excellent hydrolytic stability, low viscosity and high electrochemical and thermal stability, which makes them appealing for use in electrochemical devices and as a new media or working fluids for application in chemical synthesis and heat transfer technologies [1,2].

The success for high accuracy data has to be based on a characterization of the working samples (purity, water content, halide content), and on careful measurements and data analysis [3-5]. BMPLFAP was prepared in-house, analyzed by 1H and 13C NMR and elemental analysis. In addition, the water content was measured using Karl−Fischer titration before and after each measurement. The chloride content was determined using ion chromatography.

Density, viscosity, heat capacity, and speed of sound have been determined. Other thermodynamic properties such as isothermal compressibility and isobaric expansivity have been obtained from density data. The density and speed of sound data were obtained with a vibrating tube densimeter (DSA 5000 M) and processed with the new calibration method recently presented [6]. Viscosity was measured using a rheometer (TA AR1500ex), the heat capacity using DSC [3].

Comparison with the values of other similar ionic liquids will be done, trying to understand the effect of the anion and cation in thermophysical properties.

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O2.3: ACTIVITY AND STABILITY OF CANDIDA ANTARCTICA LIPASE B (CALB) – EFFECT OF DIFFERENT IONIC LIQUIDS

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In this work, a systematic study of the effects of different ionic liquids on the enzymatic activity and stability of *Candida antarctica* lipase B was carried. Various parameters were considered and studied such as the ionic liquid concentration, the effect of different anions, cations and the cation alkyl chain length. The cation structure of these ILs was based on imidazolium, pyrrolidinium, pyridinium and piperidinium. The imidazolium cation was used in the study of the effect of the alkyl chain lenght, which varies from 2 to 8 carbons. The anions investigated were bis(trifluoromethylsulfonyl)imide [NTf_2], hexafluorophosphate [PF_6], trifluoromethanesulfonate [CF_3SO_3], methanesulfonate [CH_3SO_3], chloride Cl, bromide [Br], trifluoroacetate [CF_3COO], hydrogenosulfate [HSO_4], acetate [CH_3COO] and dicyanamide [$N(CN)_2$]. The enzyme activity and stability were assayed spectrophotometrically. The results indicate that the enzymatic activity and stability are affected by all the parameters studied, as was suggested by recent reports in literature [2-5]. The hydrophobic anions seem to induce smaller losses on the enzyme activity and stability than the hydrophilic ones. The imidazolium cation has the smallest influence on the enzymatic activity, while the piperidinium cation induced the largest losses. In order to explain the ionic liquids effects on the enzymatic activity the protein conformational modifications were investigated by quantification of SH groups. It was observed that the decrease in the enzymatic activity and stability is related with an increase on the SH groups observed.

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O2.4: ON THE MEASUREMENT OF THE VISCOSITY OF IONIC LIQUIDS USING THE VIBRATING WIRE TECHNIQUE

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The vibrating wire technique for the measurement of the viscosity has several advantages over most of the current experimental methods. The vibrating-wire sensor we employ is essentially made of a metallic wire, immersed in a fluid and subjected to a magnetic field and can be operated either in forced or transient mode. In the forced mode of operation, an alternating current of variable frequency is passed through the wire, sweeping a range of frequencies around its resonance frequency. As a consequence, the wire undergoes transverse oscillations inducing an electromotive force across the wire. The analysis of the signal in the frequency domain (resonance curve) enables the determination of the viscosity of the fluid[1].

The main advantages of this method are: (i) the existence of a complete set of working equations which have a rigorous theoretical basis[1]; (ii) the ability to perform measurements in large ranges of temperature and pressure, without the need to perform extensive calibration procedures; and (iii) the adequacy to be used for in-line and on-line measurements.

Recently, this group developed a new vibrating-wire equipment which has shown to be able to measure viscosities in the range of 0.5 to 270 mPa.s, with an overall uncertainty lower than +/-1%, after calibrating with the primary viscosity standard (water at 293.15 K) and the results obtained contributed to an international proposal of an industrial reference fluid for moderately high viscosity at atmospheric pressure.[2]

The measurement of the viscosity of room temperature ionic liquids poses some particular problems on the utilization of the vibrating wire method, mainly due to their often high viscosity and to the fact that they are electrical conductors.

Some tests are described suggesting that the method can conveniently be applied within the ranges of viscosity and electrical conductivity of the ionic liquids used. Recently, the group published results of high viscosity measurements.[3] Nevertheless, in the present work, the tests have been performed on samples with viscosities up to approximately, 500 mPa.s, which is the highest we have measured so far, using the vibrating wire technique.

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O2.5: THERMODYNAMIC BEHAVIOR OF IONIC LIQUIDS SOLUTIONS WITH ORGANIC SOLVENTS. EXPERIMENTAL RESULTS AND ERAS-MODEL CALCULATIONS

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The experimental study of the thermodynamic properties of room temperature ionic liquids (RTILs) in solution with organic solvents allows understanding the basic mechanisms which lead mixing and, eventually, through the use of some modelization scheme, determining the microscopic processes which configure the macroscopic observed behavior. Once they have been obtained, they can be used to extrapolate the results and thus, to predict the properties of other ionic liquid solutions. In this context, analyzing the behavior of RTILs in solution with compounds which are representative of the main categorization of organic solvents – polar, apolar and associating- presents high interest. In this work, the thermodynamic properties of binary mixtures of seven RTILs with ethanol and nitromethane, which constitutes paradigmatic examples of associating and polar fluids, respectively, are analyzed. Density, heat of mixing and heat capacity per unit volume have been experimentally determined over the whole composition range at atmospheric pressure and within the temperature interval (293.15 – 318.15) K. From these data, excess volume, excess enthalpy and excess isobaric molar heat capacity were determined. Excess properties as well as pure-product properties were used to fit the parameters of the ERAS (Extended Real Associated Solution) model [1]. Following previous contributions, [2-3] and as a first approximation, it has been supposed that ethanol presents homo and heteroassociation with RTILs, but nitromethane and RTILs only heteroassocation. It was found that ERAS correctly describes the behavior of excess enthalpy and volume, but fails to predict excess heat capacity of ethanol systems, mainly due to the existence of liquid-liquid inmisciblity relatively close to experimental conditions. The parameters obtained for ERAS model present high consistence and show clear tendencies against the nature of the RTIL.

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O2.6: HOW LINEAR IS THE TREND IN HEAT CAPACITY OF THE $[C_NMIM][NTF_2]$ SERIES?

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Room temperature ionic liquids, RTILs, have been intensively studied due to their unusual and interesting properties. The application of these systems in industry requires accurate values for their physicochemical properties, such as heat capacities, vapour pressures, viscosities, etc.

Heat capacities of a large number of ionic liquids have already been published in the literature.[1] However, most of the published data are obtained with a large uncertainty that in some cases hides subtle irregularities in the heat capacity trend. In the present work we were able to obtain accurate heat capacity data, at T = 298.15 K, for the complete alkyl series (odd and even) of the imidazolium based ionic liquids ($[C_nmim][NTf_2]$, n = 1 – 8, 10, 12). The heat capacities of the nine ILs were measured by means of a precise Drop heat capacity calorimeter developed by Wadsö [2-3] which was now adapted at our Lab, both as regarding temperature sensors, electronics and to enable the use of computer data acquisition in a user-friendly environment. The obtained heat capacities are comparable with the best accurate data derived from adiabatic calorimeters.

The results will be used to detect and understand subtle changes in heat capacity as a function of alkyl side chain length. The present data allowed us to address the question: How linear is the trend in heat capacity of the $[C_nmim][NTf_2]$ series?

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ORAL PRESENTATIONS, SESSION 3:

Theoretical models and numerical simulation

O3.1: MODELING: THE CRITICAL, INTERFACIAL AND SURFACE PROPERTIES OF IONIC LIQUIDS

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Precise measurements of ionic liquids (IL) physical properties near the critical point are an unexplored field. Experimental data at these extreme conditions is very difficult to achieve due to the low vapor pressures and the thermal degradation of ionic liquids far before the critical region is reached. However, in order to design thermally stable ILs information about the critical region is a requirement for industrial purposes. Hence, the need of a reliable prediction of the critical properties of ionic liquids has pushed the development of theoretical methods based on molecular-based approaches with physical meaning. In this contribution within the framework of the soft-SAFT EoS [1] coupled with the Density Gradient Theory (DGT) [2], the surface tension as well as the critical temperature, pressure and density have been estimated, for three different ionic liquid families, and compared with those reported in the literature from experimental [3-5] or simulation data [6].

In addition, for the [C_n-mim][Tf_2N] IL family a correlation for the influence parameter as a function of the molecular weight was obtained, empowering the predictive capabilities of the equation for interfacial tensions of compounds of the family for which experimental data is scarce or unavailable [3]. Finally, surface thermodynamic properties were also derived from the dependence of the surface tension values, and compared with those obtained within the same framework [3-5]. The results presented here show the robustness of using an accurate and versatile equation of state for the evaluation of bulk, interfacial [7] and surface properties [8] with a very modest computational effort.

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O3.2: SOLVENT POTENTIAL IMPROVEMENTS OF THE REACTIVE IONIC LIQUIDS FOR THE OLEFIN/PARAFFIN GAS MIXTURE SEPARATION

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The separation of olefins from paraffins is essential in the chemical and petrochemical industry. Olefins are crucial petrochemical feedstocks, commonly used in the production of polymers and other important chemicals. Olefins are produced by cracking of lights olefins (C_2-C_4) from natural gas or from refinery gas streams. The separation of the olefins from the cracker streams is a necessary and costly process. The energy requirements of the process could potentially be reduced by separating the olefin from the paraffin via reactive absorption. Olefins can form reversible complexes with transition-metal cations (Ag^+, Cu^+) via π-bond complex formation mechanism. In the complexation reaction, the olefin and the metal cation work as the electron donor and the acceptor, respectively. The complex formed can be easily reverted by temperature or pressure swings. However, there are a number of disadvantages associated to the absorption solvent related to the selective olefin absorption, stability of the transition metal, solvent losses and maximum temperature conditions that can be used. So that solvents with high olefin-capacity, selectivity and resistance to contaminants and process conditions are still desired. In this way, the use of Room-Temperature Ionic liquids (RTILs) as reaction media can provide an encouraging alternative and may be attractive in this respect.

RTILs are salts composed exclusively of ions that remain in the liquid phase at or below 373 K. RTILs are compounds that have negligible vapour pressure, high chemical and thermal stability, and relatively large electrochemical windows. They can be water soluble depending on the hydrophilicity of the ionic moieties. Polarity and hydrophilicity/hydrophobicity can be tuned by a suitable combination of cation and anion; therefore they have been termed ‘‘designer solvents’’. Their lack of volatility gives ionic liquids the feature that they can perform clean gas separations without any loss of solvent or contamination of the gas stream. Silver ions or complexing agents can be added or “doped” into ionic liquids. RTILs can be used to control the interaction between the silver cation (Ag+) and its counteranion (X-) in a RTILs/silver salt system, with the result that the silver cation becomes chemically more active and stable in forming silver-olefin complexes.

Improvements of the solvent potential of the ionic liquid for the olefin/paraffin separation have been presented in previous works [1-2]. The main objective of this work is to investigate the absorption of propylene-propane, and ethylene-ethane mixtures in Ag^+-RTILs media in order to find the most suitable combination. The effects of the length of the radical chain and type of cations and anions in Ag-based RTILs structure on the absorption of the gases have been studied. We include both experiments and a theoretical study devoted to the analysis of different concentrations of silver salt between 288 K and 308 K and up to 6 bar.

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O3.3: SOLUBILITIES OF SOUR GASES IN IONIC LIQUIDS - THE NON-IDEALITY AND PREDICTION USING FLORY-HUGGINS MODEL

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Ionic liquids (ILs) are a class of *neoteric* solvents composed of large organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature. The outstanding characteristics of these fluids, and the easy manipulation of their properties due to the possibility of interchange among thousands of cations and anions, make of the ILs “designer” solvents with a wide range of foreseeable applications.

Nonetheless, and despite of the promising properties of ILs, further research is still required in order to make them solvents feasible candidates for real applications. Being a key parameter in the design of equilibrium stage– and rate–based separations, reliable gas solubility data is of most interest and a fundamental step towards the development of industrial applications, either by the data itself or by developing predictive and simulation tools to aid in the development of such applications.

Using a high pressure cell, previously used for extensive studies of CO_2 solubilities, VLE isotherms up to 363 K and pressures up to 100 MPa were measured for mixtures of CO_2 or CH_4 with several aprotic and protic ionic liquids. Furthermore, the nonideality of sour gases (CO_2 , NH_3, SO_2, and H_2S) solutions in ionic liquids is here investigated and shown that these systems present negative deviations to the ideality in the liquid phase, that these deviations are dominated by entropic effects and that the gas solubility can be predicted using the Flory-Huggins model.

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O3.4: COULOMBIC VERSUS SOLVOPHOBIC CRITICALITY

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Singh and Pitzer stated [1,2] that liquid-liquid phase equilibrium data for solutions of the organic salt triethly-*n*-hexylammonium triethyl-*n*-hexylboride in diphenyl ether were consistent with mean-field critical behavior: specifically, in analyzing the composition X of the coexisting phases (’ and ’’) via the asymptotic law $X' - X'' \sim (T_c - T)^{\beta}$ (where T_c is the upper consolute temperature and β the so-called critical exponent of the order parameter), they encountered $\beta \approx 0.47$, close to the mean-field value $\beta = 1/2$. Such a suggestive result greatly stimulated further experimental and theoretical work (see the review article of Weingärtner and Schröer [3]).

From a theoretical standpoint, the long-range nature of Coulombic forces could in principle lead to mean-field behavior; however, Debye screening makes interactions effectively short-ranged so that Ising criticality is expected. In fact, experiments (see Ref. 4 for a recent account) demonstrated that fluids and fluid mixtures belong to the universality class of the three-dimensional Ising model (i.e., $\beta \approx 0.326$). Such conclusion was supported by careful simulations for the restrictive primitive model electrolyte RPM [5].

Mainly because of good chemical stability, employing organic salts which exist in the liquid state at, say, room temperature [that is, ionic liquids (ILs)] have provided insights into a number of specific features of liquid-liquid critical behavior in ionic solutions [4]. One such issue of major interest is the characterization of Coulombic criticality (in which phase separation is driven by Coulombic forces) as opposed to solvophobic criticality (in which nonionic interactions are responsible for phase separation).

The experimental analysis of Coulombic versus solvophobic criticality has been focused on coexistence curves. Here we complement the available information, first, by showing that isobaric heat capacities of IL-nonelectrolyte mixtures are consistent with expectations. At a more subtle level, we will see that singular coexistence-curve diameters [6] distinguish Coulombic from solvophobic criticality, and agree with simulations for the RPM [7]. As noted previously, it is found that solvents characterized by a low dielectric constant lead to Coulombic behavior while those with a high dielectric constant give rise to solvophobic behavior.

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O3.5: THERMODYNAMIC STUDY OF IMIDAZOLIUM IONIC LIQUIDS WITH DIFFERENT ANIONS USING THE SOFT-SAFT EOS

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Room Temperature Ionic Liquids (RTILs) are receiving great attention in recent years due to the fact that their properties can be tuned with a well-judged selection of the cation-anion pair. Their versatility and unique properties make them a good alternative to conventional volatile organic compounds (VOCs) used in reaction and separation processes, solvents for cleaning and purification operations, as electrolytes in fuel cells, lubricants, heat transfer fluids and storage media. However, these ionic liquids should be fully characterized before put into use for a specific application, and a good understanding of the dependence of their physico-chemical properties on their microscopic structure is necessary in order to enhance the design of new ionic liquids for promising chemical and industrial processes in a systematic and efficient manner. This is not an easy task, due to the relative complexity of the molecule, and several efforts have been done in the recent years in order to find appropriate models for their accurate description [1].

In this contribution, we present a complete thermodynamic characterization of the three main families of current imidazolium ionic liquids, those with [BF_4], [PF_6] and [Tf_2N] as anions, by means of the statistical mechanics based soft-SAFT equation of state [2]. This characterization proposes a relatively simple molecular model [3]-[4], where the cation and the anion are considered as a chain, keeping the basic physics of the compound. Temperature-density and pressure-density diagrams, enthalpy of vaporization, interfacial tension and derivative properties are provided in a wide range of conditions in good agreement with experimental data. Then, the solubility of several gases and low hydrocarbons in these families is predicted. Finally, a study of the behavior of IL mixtures with associating compounds such as alkanols and water is included and different phase equilibria are reproduced and compared to experimental data. This tool helps in getting additional insights into the underlying mechanisms governing the behavior of these systems, which are the basic knowledge needed for a rational design previous to their use.

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O3.6: WATER CLUSTERIZATION INSIDE IONIC LIQUIDS: A MOLECULAR DYNAMICS STUDY

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Room temperature ionic liquids (RTILs) are solvents with many interesting properties that make them a good alternative to conventional organic solvents. The hydrophilic/hydrophobic behavior is important for the solvation properties of the liquids and very significant in many of their applications, such as dissolution of reactants or solvent extraction. However, an intensive theoretical or computational study of IL-water mixtures has been less frequently reported [1, 2].

For this work we have performed a series of molecular dynamics simulations of LI-water mixtures using GROMACS [3] with a united-atom force field GROMOS96 and an all-atom force field OPLS. The simulations of imidazolium-based ILs were done with several lengths of the alkyl chain and anions with different level of hydrophobicity, and the parameters of the force field were taken from results of computational simulations of LIs reported in the literature [4, 5].

Our research shows the formation of water clusters inside the mixture at high water concentrations and the fact that the hydrophobicity increases with the alkyl chain length and the size of the anion. Moreover, we studied the water network and cluster formation in the mixtures analyzing the size of clusters of connected water molecules.

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O3.7: A PSEUDOLATTICE THEORY OF THE THERMAL CONDUCTIVITY OF IONIC LIQUIDS

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We present a theoretical study of the thermal conductivity of ionic liquids in the general framework of the Bahe-Varela pseudolattice theory [1,2]. Based on the now well-established fact that, at concentrations above a modest threshold, ionic liquids display a "loose" lattice structure, our model incorporates ideas from the study of thermal conductivity in another class of systems with short-range order and global disorder: amorphous solid-state materials or glasses. More specifically, inspired by the general features of the experimental conductivity curves reported in the literature [3,4], such as the presence of a plateau, we base our work on the "phonon hopping" model [5,6] which posits the idea that the vibrational spectrum of the pseudolattice can be conceptually split in two parts, one consisting of localized short-wavelength phonons and the other of extended low-energy modes. In this framework, energy propagation is due to anharmonic interactions between the two kinds of modes.

In addition to assessing the suitability of our model by comparing its results to our own experimental measurements on a range of different ionic liquids, we discuss the influence of some important parameters specific to liquid state theory, such as the presence of a solvent or other impurities, as well as possible improvements to the model which could result from taking into account dynamic changes in the pseudolattice structure not present in the glass analogy.

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294 PR and 10-PXIB-206-294 PR). T. Méndez-Morales and J. Carrete thank the Spanish Ministry of Education for their FPU grants.

ORAL PRESENTATIONS, SESSION 4:

Industrial applications

O4.1: SOLUBILITY OF CARBON DIOXIDE IN MAGNETIC IONIC LIQUIDS (MILS)

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Carbon dioxide (CO_2) is one of the major contributors to the greenhouse effect. The power and industrial sectors combined account for about 60% of the global CO_2 emissions [1] thus; its recovery is a key issue to guarantee the sustainability of industrial processes. The well-know process for CO_2 capture is amine scrubbing because of high alkanolamine absorption rates [2]. Although high product yields and purities can be obtained, the main disadvantage of this method is the high solvent losses due to their evaporation in the stripper [3] and the energy penalty.

Ionic liquids are compounds that have reached an enormous interest in the recent research as absorption liquids for gas recovery [3-5] due to their attractive properties, such as their negligible vapour pressure [6], avoiding solvent losses caused by volatilization of solvent into gas streams [7]. One of their key advantages is their tuning properties by modifying the kind of cation, anion or the hydrocarbon chains linked to the cation that makes them be considered as 'designer solvents' [8]. This property has made possible the substitution of common anions for others with a metal ion that confers them a magnetic response, such as $FeCl_4^-$. These magnetic ionic liquids (MILs) have opened a broad field of research to recover target compounds from gas streams, since the compound may have higher or lower solubilities in the MIL depending on the applied magnetic field [9].

In the present study, solubilities of CO_2 in MILs are measured using a DTGA-60H Shimadzu thermobalance at atmospheric pressure and room temperature, to supplement ionic liquid literature data. Because of the numerous ways of combining counter ions to form ionic liquids, the final aim is to develop a predictive method based on a group contribution for solubility of CO_2 in magnetic ionic liquids.

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O4.2: IONIC LIQUIDS AS LUBRICANTS OR LUBRICANT ADDITIVES

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The study of the influence of the molecular structure on the thermophysical properties of ionic liquids (ILs) is essential for their use in lubrication applications. In this work, we analyze the trends, with the cation and the anion, of viscosity and its dependence with temperature and pressure, thermal and oxidation stability as well as the tribological properties [1,2]. Some of these trends can be explained taking into account the size of the polar and non polar domains obtained by molecular simulation [3]. In terms of additives, miscibility with base oils is the first concern; however, due to the high polarity of ILs and the low polarity of conventional oils, ILs actually display very poor miscibility with them [1,4]. We also analyze the literature results on miscibility of ILs in base oils together with those obtained in our laboratory.

Under hydrodynamic and elastohydrodynamic EHL regimes, when the fluid viscosity and sliding speed are high enough or the load is low, the viscosity and viscosity–pressure coefficient α, of the lubricating oil dictate the friction coefficient whereas at high loads (or low speeds and low viscosities) there is an increase of metal-on-metal contact, causing increased friction and resulting in the formation of boundary layers. At a given temperature, the pressure-viscosity coefficient, quantifies the film-generating capability of a lubricant in tribological contacts at EHL regime, at isothermal conditions. In a previous work [2] we determined α values for seven ILs. Subsequently, these values were used in studies of different authors on the film thickness of three nanoconfined ILs under electric fields, to study the transition in wear performance for two ILs for the calculation of the ratio between the film thickness and the surface roughness of some ILs in order to analyze their potential for diesel engine lubrication. So, it is clear that not only practical lubrication technology necessitates consideration of the pressure and temperature to make a reasonable evaluation of the viscosity, but also to develop new lubricant formulations and lubricant bases. In this work we will also present how this coefficient should be determined and an analysis of its dependence on the structure for ILs.

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O4.3: NEW PYRIDINIUM IONIC LIQUIDS AS SOLVENTS FOR DESULFURIZATION OF FUELS

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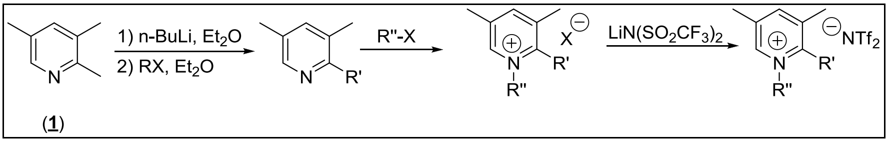
Production of low sulfur fuel has become a main objective of petroleum refining industry. One of the most promising techniques for this proposal is the extractive desulfurization, and researching efforts over the last years are being focused on finding the most suitable solvent for desulfurization purposes.

Because of their good qualities as solvents, such as a negligible vapor pressure, thermal stability, wide liquid range and nonflammability, ionic liquids (ILs) have been proposed as suitable solvents for the extraction of sulfur compounds from transportation fuels [1]. From these salts, highly substituted pyridinium based ILs with high cation size are showing the most promising results [2].

In this work we describe the synthesis of a series of highly substituted pyridinium based ILs from commercial 2,3,5-trimethylpyridine (**1**). The treatment of **1** with *n*-BuLi, followed by addition of an alkylating agent afforded the corresponding 2-alkyl-3,5-dimethylpyridine. Different reaction conditions (temperature, time, reagent concentrations and solvent) were needed to be tested in order to avoid undesirable polyalkylated compounds. Target ILs were then prepared using standard methodology, which involved alkylation of the substituted pyridine with an alkyl halide and subsequent metathesis reaction (Scheme 1).



Scheme 1: Synthesis of 1,2,3,5-tetralkylpyridinium ILs.

Physical properties such as densities, heat capacities and viscosities of this series of ILs have been measured. Phase transitions were determined by DSC.

The suitability of [EMMPPy][NTf$_2$] as solvent in extraction of sulfur compounds from fuels was analysed by testing the IL capacity to extract thiophene from heptane. Liquid-liquid equilibrium data for ternary systems were obtained. Composition of the equilibrium phases was analyzed by NMR.

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O4.4: SELECTIVE EXTRACTION OF WOOD LIGNIN WITH NOVEL IONIC LIQUIDS

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Overall depletion of fossil energy resources and the simultaneous increase in demand for energy and composite materials by a growing population are urgent concerns that need to be addressed. A partial solution to these problems is represented by our planet's most abundant biopolymer, wood. It is quickly renewable and it does not compete as a human food source. Its cellulosic materials can be extracted and used in various ways, such as for the production of biofuels or as feedstock for bio-composites. It is a common aim to gradually replace petroleum based products with biocompatible materials. A key step for unlocking the full potential of wood biomass is the efficient retrieval of its lignins, as this biopolymer represents a major barrier to the successful processing of wood cellulose. To date, the over 120 year old Kraft pulping process still dominates the industrial delignification of wood, producing 26 million tones of lignin annually. The main disadvantages associated with this process are pollution, odor problems, large water usage and energy intensive plants. There is a need to establish a more ecofriendly separation processes for the future. It has been shown that some ionic liquids have the potential to extract wood cellulose in a more energy efficient and biocompatible way than traditional approaches. However, many of these ionic liquids also dissolve lignin to various degrees, and its subsequent separation from the cellulosic material still lacks efficiency. This presentation aims to describe our latest results on a new class of ionic liquids that have the potential to selectively extract wood lignin with minimal dissolution of cellulosic materials, thus offering a promising alternative way for the extraction of wood lignin.

O4.5: UNDERSTANDING CO_2 SOLUBILITY IN IONIC LIQUIDS USING COSMO-RS METHODOLOGY

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Quantum chemical COSMO-RS method [1] was evaluated as theoretical framework to computationally investigate the application of room temperature ionic liquids (ILs) in absorptive technologies for capturing CO_2 from power plant emissions [2,3], in order to reduce efficiently both experimental efforts and time consuming. Firstly, different molecular models to simulate ILs and computational methods in geometry calculations were investigated to optimize the COSMO-RS capability to predict Henry's Law coefficients, using a demanding solubility sample test with 35 gaseous solute-IL systems and 20 CO_2-IL systems. Simulation results were in good agreement with experimental data, indicating that using an ion-pair molecular model optimized in gas phase environment allows finer COSMO-RS description of the IL structure influence on the CO_2 and other solute solubilities. Moreover, COSMO-RS methodology was used for the first time to achieve a deeper insight into the behavior of the solubility of CO_2 in ILs from a molecular point of view. For this purpose, further analyses of the energetic intermolecular interactions between CO_2 and ILs were performed by COSMO-RS, with results revealing that the Van der Waals forces associated to the solute in the liquid phase determine the absorption capacity of CO_2 in ILs, measured in terms of Henry's Law coefficients. These findings were finally driven by a rational screening with COSMO-RS, over an amount of 170 ILs, to design new ILs with favorable characteristics for increasing the CO_2 solubility. Indeed, the potential use of highly brominated ILs was suggested to enhance the CO_2 capture by physical absorption.

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POSTER PRESENTATIONS, SESSION 1:

Synthesis and extraction

P1.1: ILS MEDIATED SYNTHESIS OF THIACYCLIC SYSTEMS

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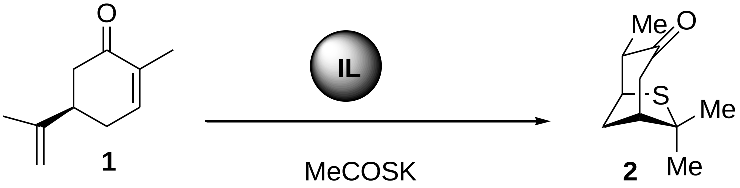
Ionic liquids (ILs) have attracted considerable attention in the last decade as a new media due to their unique physical and chemical properties. They are often referred to as green alternative to volatile organic solvents[1]. The range of known and available ILs has been rapidly growing and nowadays many ionic liquids are commercially available. In consonance with a current trend in academic and industrial research, in recent years we have also begun to work towards the replacement of toxic volatile organic solvents with ionic liquids (ILs).

In this communication we will describe the serendipitious synthesis of enantiopure thiabicyclic compound **2**, while carrying out Michael additions with MeCOSK, using carvone **1** as acceptor and ILs as solvent. Compound **2** is an interesting platform for sulfonium ylide promoters for the asymmetric epoxidation of aldehydes [2].



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P1.2: SEPARATION OF BENZENE FROM HEXANE USING IONIC LIQUIDS

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The ionic liquids (ILs) are an attractive alternative to replace the organic solvents in the separation of aromatics from aliphatic compounds.

The extraction of benzene from hexane was analyzed by liquid extraction with 1-butyl-3-methylimidazolium methylsulfate, [BMim][MSO_4], and 1-butyl-3-methylimidazolium bis{(trifluoromethyl)sulfonyl}imide, [BMim][NTf_2], ionic liquids as solvent. The experimental liquid- liquid equilibrium (LLE) data were determined at T = 298.15 K and atmospheric pressure. Solubility curves were obtained by the cloud point method and tie-lines compositions were determined by density measurement. An analysis of the influence of different ionic liquids on the extraction was performed.

The effectiveness of the extraction of benzene from hexane was evaluated by means of the solute distribution ratio (β) and selectivity (S) values. The degree of consistency of the experimental LLE data was ascertained using the Othmer-Tobias and Hand equations. The experimental data of liquid-liquid equilibria of the ternary systems were correlated with the Non-Random Two-Liquid (NRTL) and UNIversal QUAsi-Chemical (UNIQUAC) thermodynamic models. In Figure 1, it can be observed that the miscibility region in the system containing [BMim][NTf_2] is wider. Comparing the behavior of both systems, the S values are higher for the system with the IL [BMim][MSO_4], however, the β values are higher than the unity for the system hexane + benzene + [BMim][NTf_2].

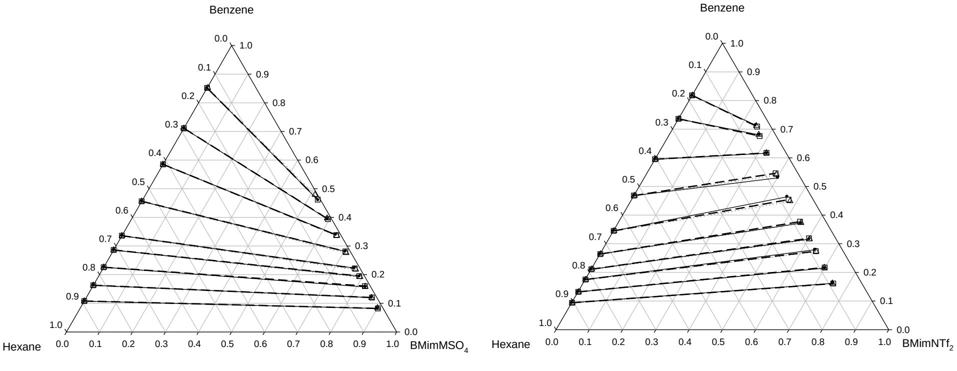

Figure 1: Tie-lines for the ternary mixtures hexane + benzene + ILs at T = 298.15 K, a) [BMim][MSO_4] and b) [BMim][NTf_2]. Solid lines and full points indicate

experimental tie-lines, and dashed lines and empty squares indicate calculated data from NTRL model.

P1.3: ILS SUPPORTED SYNTHESIS OF OXACYCLIC COMPOUNDS

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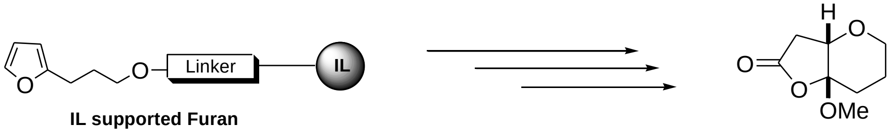
In the last years, ionic liquids (ILs) have attracted considerable interest as environmentally benign reaction media because of their unique properties such as high thermal and chemical stability, negligible vapour pressure, tuneable polarity, nonflammability, friction reduction, antiwear performance, high loading capacity and easy recyclability [1].

An attractive feature of ionic liquids is that their solubility can be tuned readily. Therefore, phase separation from organic solvent or aqueous phase is allowed depending on the choice of cations and anions. This suggests the possibility of using ILs as soluble support for organic synthesis. Substrates anchored on ionic liquids are expected to retain their reactivity, as in solution reactions. One advantage of ILs supported synthesis over solid phase synthesis is that conventional spectroscopic analysis can be carried out during the synthetic process. The feasibility of ionic liquid supported organic synthesis has been demonstrated by many research groups [2].



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P1.4: SYNTHESIS OF NEW TASK SPECIFIC ILS

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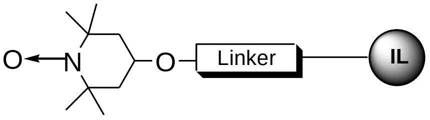
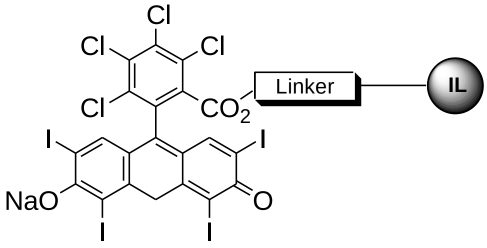
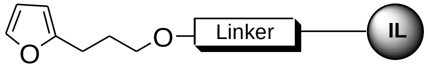
In the last years, ionic liquids (ILs) have attracted considerable interest as environmentally benign reaction media because of their unique properties such as high thermal and chemical stability, negligible vapour pressure, tuneable polarity, nonflammability, friction reduction, antiwear performance, high loading capacity and easy recyclability[1]. An attractive feature of ionic liquids is that their solubility can be tuned readily. Therefore, phase separation from organic solvent or aqueous phase is allowed depending on the choice of cations and anions. This suggests the possibility of using ILs as soluble support for organic synthesis. Substrates anchored on ionic liquids are expected to retain their reactivity, as in solution reactions. One advantage of ILs supported synthesis over solid phase synthesis is that conventional spectroscopic analysis can be carried out during the synthetic process. The feasibility of ionic liquid supported organic synthesis has been demonstrated by many research groups [2]. In this communication we will describe the synthesis of IL supported Furan, TEMPO and Rose Bengal and their application in organic synthesis.



IL supported TEMPO



IL supported Rose Bengal



IL supported Furan

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P1.5: SUPPORTED IONIC LIQUID NANOPARTICLES: SYNTHESIS, CHARACTERIZATION AND CATALYTIC APPLICATION

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Preparation of 5-hydroymethylfurfural (HMF) through the dehydration reaction of sugars is one of the most important approaches to transform biomass to useful chemicals [1]. HMF is known as a potential biofuel and one of its oxidative derivatives, 2,5-furandicarboxylic acid, may replace terephthalic acid as a monomer in the production of plastics [2]. Therefore, though studies on the dehydration of hexose to HMF have taken place over many years, new efforts towards an efficient and easy-to-use process for the preparation of HMF are ongoing, particularly in the context of the increasing demands for alternative energy sources [3]. Homogeneous acid catalyzed processes are effective and can achieve 70.0 to 90.0 % fructose conversion with moderate (40.0 to 60.0 %) HMF yield, however it has severe drawbacks in terms of equipment corrosion, separation and recycling; while heterogeneous acid catalysts can be recycled and have high (60.0 to 90.0 %) HMF selectivity, but very low fructose conversion (30.0 to 60.0 %) even after a very long (2 h) reaction time [2,4].

In the present study, supported ionic liquid nanoparticles (SILnPs) of various sizes have been prepared by immobilization of ionic liquid, 1-(tri-ethoxy silyl-propyl)-3-methyl-imidazolium hydrogen sulfate (IL-HSO_4) on the surface of silica nanoparticles and investigated as solid acid catalysts for the dehydration of fructose to HMF in the presence of dimethylsulphoxide (DMSO) as a solvent. The reaction temperature and amount of catalyst have been optimized for dehydration of fructose over SILnPs using experimental design leading to 99.9 % fructose conversion and 63.0 % HMF yield using silica SILnPs (d= 610 ± 11) nm at 130.0 ^{o}C in 30 minutes reaction time. The SILnPs catalysts developed in this study showed improved performances over other catalysts, and they have been efficiently and very easily recycled over seven times without any significant loss in activity and selectivity in dehydration of fructose to HMF.

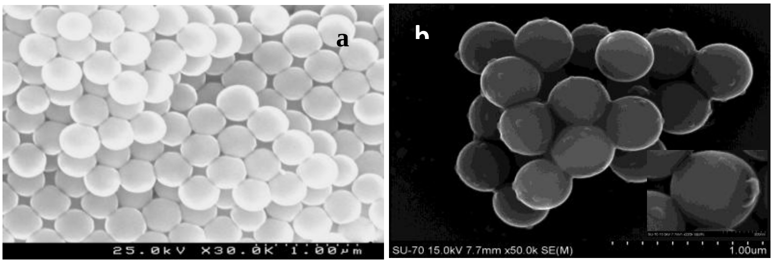

Figure: SEM images of (a) silica NPs and (b) IL immobilized silica NPs.

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P1.6: IMPROVED SEPARATION OF ETHANOL-WATER MIXTURES BY LIQUID-LIQUID EXTRACTION USING PHOSPHONIUM-BASED IONIC LIQUIDS

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Bioethanol is an important biorefinery product that can be used as a liquid transportation fuel. One of the main problems associated with ethanol production is its separation from fermentation broths. Distillation is commonly used; yet, due to the presence of the ethanol-water azeotrope, the production of anhydrous ethanol is economically and energetically expensive. In this work, the use of phosphonium-based ionic liquids (ILs) for the extraction of ethanol from fermentation broths is investigated. A study on ternary phase diagrams comprising water, ethanol, and IL, was made using tetradecyltrihexylphosphonium-based ionic liquids combined with several anions, namely bis(trifluoromethylsulfonyl)imide, dicyanamide, bromide, chloride, bis(2,4,4-trimethylpentyl)phosphinate, decanoate, and methanesulfonate. The experimental ternary phase diagrams were correlated with the NRTL model and further predicted with the COSMO-RS model. Due to the satisfactory results obtained with COSMO-RS, a scan of different ILs not experimentally available was carried out. The predictions suggested that tricyanomethane- and tetracyanoborate-based ILs could also be used for improved extractions. The gathered data indicate that phosphonium-based ionic liquids are the best ionic solvents yet reported to perform ethanol-water separations. The economic and environmental advantages of the approach here proposed will be presented and discussed.

P1.7: ILS SUPPORTED CATALYST FOR THE “ONE POT” SYNTHESIS OF HAJOS DIONE

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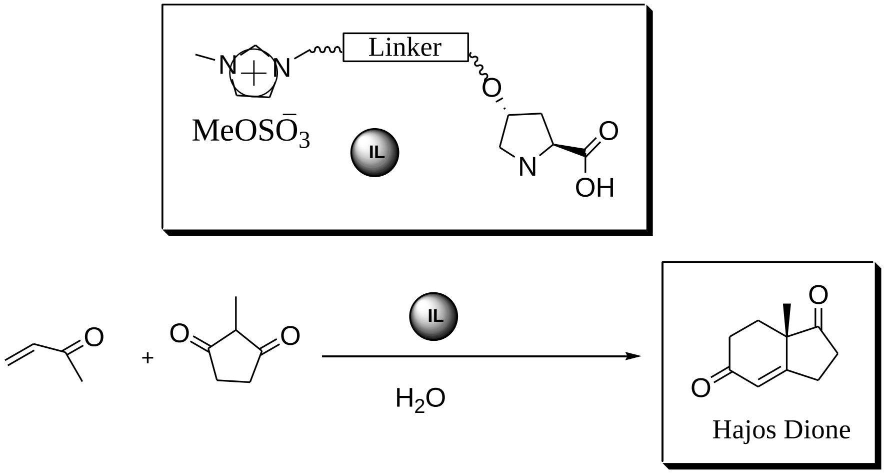
In consonance with a current trend in academic and industrial research, in recent years we have begun to work towards the replacement of toxic volatile organic solvents with ionic liquids (ILs) in organic reactions; the intense interest of organic chemists in ILs as solvents is due not only to the probable nontoxicity of many members of this family (though by no means all!) [1], nor solely to such general characteristics as thermal and chemical stability, negligible vapour pressure, and non-flammability (many of which properties contribute to environmental friendliness), but also to the wide spectrum of choices for anion and cation, which allows their optimization as regards such parameters as loading capacity or solubility in other solvents.

In this presentation, we report the synthesis of an IL-supported catalyst and its use for the efficient and environmentally friendly procedure for the « one pot » synthesis of Hajos dione, a useful starting material for vitamin D analogues [2].



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P1.8: APPLICATION OF PHOSPHONIUM-BASED IONIC LIQUIDS FOR “GREENER” EXTRACTION PROCESS OF L-LACTIC, L-MALIC AND SUCCINIC ACIDS

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Organic acids constitute a key group among the building-block chemicals since they are extremely useful as starting materials for the chemical industry [1]. However, the extraction processes of these acids from dilute waste water and fermentation broths normally use organic solvents which imply additional environmental hazards [2]. At present, when pollution is a topic of general concern, the development of new “greener” sustainable technologies has been receiving increased attention from academia and industry. Among these alternative solvents ionic liquids play a central role as potential substitutes of volatile organic compounds [3]. Therefore, the main objective of this work is to test the efficiency of ionic liquids to extract three short chain organic acids (L-lactic, L-malic and succinic) from dilute aqueous solutions, as a raw model for the use of ionic liquids to extract bioproducts from fermentation broths. The effect of the anion’s nature and the concentration of the acid in the aqueous solution on the partition coefficients has been evaluated. Two different approaches to recover the organic acid from the ionic liquid – distillation at reduced pressure and pH variation – have been tested.

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P1.9: SYNTHESIS OF NEW TRIAZOLIUM-BASED ILS

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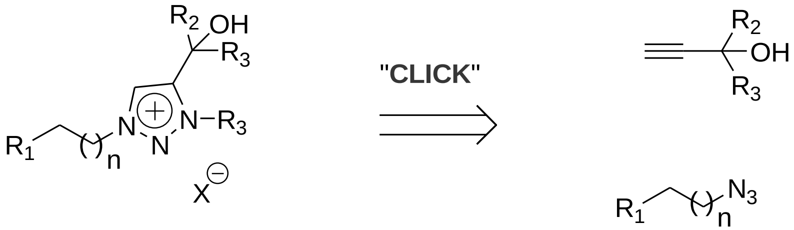
Ionic liquids (ILs) are defined as organic salts, generally consisting of organic cations and inorganic anions, which melt below 100 ºC. A number of cation types of ionic liquids have developed, including imidazolium, pyridinium, ammonium and phosphnium. Imidazolium cations like 1-butyl-3-methylimidazolium are the most commonly used as ionic liquids. However, the C-2 proton of the 1,3-dialkylimidazolium cation is acidic and can be removed even under mild basic conditions [1]. This can represent an advantage in some cases such as the Heck reaction or the Suzuki coupling [2], because the generated carbene can act as a ligand for metal catalysts, however for some reactions such as the Baylis-Hillman, deprotonation at the imidazolium C-2 position is a drawback, leading to indesired side reactions.

Therefore there is a need for chemically inert ionic liquids suitable for reactions involving strong bases [3]. We herein report the synthesis of new 1,2,3-triazolium-based ILs suitable for the Baylis-Hillman reaction using “Click” chemistry [4].



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P1.10: ILS-SUPPORTED TEMPO AS CATALYST IN THE OXIDATION OF ALCOHOLS TO CARBOXYLIC ACIDS

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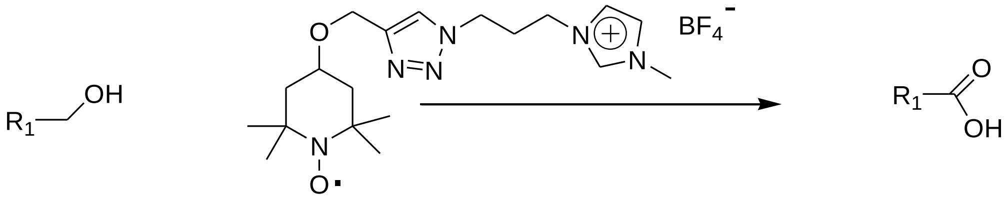
In the last years, ionic liquids (ILs) have attracted considerable interest as environmentally benign reaction media because of their unique properties such as high thermal and chemical stability, negligible vapour pressure, tuneable polarity, nonflammability, friction reduction, antiwear performance, high loading capacity and easy recyclability[1].

An attractive feature of ionic liquids is that their solubility can be tuned readily. Therefore, phase separation from organic solvent or aqueous phase is allowed depending on the choice of cations and anions. This suggests the possibility of using ILs as soluble support for organic synthesis. Substrates anchored on ionic liquids are expected to retain their reactivity, as in solution reactions. One advantage of ILs supported synthesis over solid phase synthesis is that conventional spectroscopic analysis can be carried out during the synthetic process. The feasibility of ionic liquid supported organic synthesis has been demonstrated by many research groups [2].

In this communication we will describe the synthesis of IL supported TEMPO and its use in the oxidation of alcohols to carboxylic acids.



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POSTER PRESENTATIONS, SESSION 2:

Experimental measurements

P2.1: PROPERTIES OF 1-ALKYL-3-METHLYIMIDAZOLIUM BISTRIFLAMIDE IONIC LIQUIDS: EFFECT OF TEMPERATURE AND ALKYL CHAIN LENGTH

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Most of the reported thermophysical and transport properties of ionic liquids are restricted to the 293 K – 353 K intervals, which is only a small part of the large liquid range of these substances. Moreover, there is plenty of ambiguity in the reported data sets from different groups and lack of information regarding the purities. These facts make the task of selecting good quality data rather difficult. Keeping this in mind we undertook a series of high-temperature density, viscosity, surface tension and refractive index measurements of 1-alkyl-3-methylimidazolium bistriflamide, $[C_n mim][NTf_2]$, ionic liquids (with n= 2, 3, 4, 5, 6, 7, 8, 9, 10, 12, and 14), which are commonly studied and known for their high thermal stability and large liquid range. The high temperature surface tensions were measured using the asymmetric drop shape analysis (ADSA) method; densities were measured with a high-pressure cell of Anton Paar vibrating tube densimeter; viscosities were measured using two apparatus viz., rolling ball and Stabinger viscometer; and an Abbe refractometer was employed for refractive index measurements. The results demonstrate that the density, surface tension and refractive index decreases fairly linearly as temperature increases, while viscosity exhibit an exponential decay. Measurements of densities in wide range of temperatures helped us to witness a thermodynamic anomaly in the thermal expanisvity. A correlation has been observed between the molar refraction with dispersive and electrostatic contributions to cohesive energy of ionic liquids. Surface tension exhibit three different segments (C_2-C_4, C_6-C_{12}, C_{14}) with the increase of alkyl chain length in the whole temperature studied. An exhaustive survey of literature indicates that viscosity is the most sensitive property towards the impurities and traces of water present in the samples.

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P2.2: THERMODYNAMICS AND AGGREGATION BEHAVIOUR OF PYRROLIDINIUM-BASED IONIC LIQUIDS IN AQUEOUS SOLUTIONS

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Three pyrrolidinium-based ionic liquids — *N*-dodecyl-*N*-methylpyrrolidinium bromide, *N*-butyl-*N*-octylpyrrolidinium bromide, and *N*-butyl-*N*-dodecylpyrrolodinium bromide — were synthesized and characterized by their decomposition temperatures (T_d) measured by thermogravimetric analysis, and by their melting point (T_m), glass transition (T_g) and crystallization temperatures (T_{cryst}) determined by differential scanning calorimetry. Their self-aggregation properties in aqueous solution were studied and their behavior is compared with that of analogous conventional cationic surfactants, namely tetra-alkylammonium bromide salts. The critical micellar concentration, *CMC*s, were obtained by isothermal titration calorimetry (ITC), which were further validated by meaurements of interfacial tension, fluorescence and NMR spectroscopy. Enthalpies of micellization were measured at three different temperatures using ITC. The Taylor dispersion method and DOSY NMR were used to determine diffusion coefficients of the ionic liquids surfactants in aqueous solution at 298.15 K. Several correlations between structural features of the surfactant species, such as the number and size of their alkyl chains, and the thermodynamic quantities of micellization — expressed by experimental values of *CMC*, counter-ion binding fraction, $\Delta_{\mathrm{mic}}G^{\circ}$, $\Delta_{\mathrm{mic}}H^{\circ}$, and $\Delta_{\mathrm{mic}}S^{\circ}$ — are established. We interpret the different contributions of the two alkyl side chains to the aggregation properties in terms of the balance of interactions in dissolved and micellar phases, contributing to understanding the aggregation behaviour of ionic liquids in water and the parallel between these systems and traditional ionic surfactants.

P2.3: 1-ALKYL-3-METHLYIMIDAZOLIUM CHLORIDE IONIC LIQUIDS ON GOLD SURFACES: ADSORPTION, FRICTION AND MORPHOLOGY

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The adsorption of surfactants on solid surfaces has been the subject of numerous studies because of the widespread technological application of this phenomenon in wetting, adhesion, nano-fabrication, cleaning and degreasing of metal surfaces. Ionic liquid surfactants are a new class of surfactants exhibiting many promising features compare to their conventional counterparts' viz., they can retain the micellar structures up to relatively high temperatures (200 ^{o}C), the versatile nature of their homologous series allows to design novel biodegradable, non-toxic compounds with different head groups and specific features. It would be interesting to exploit their unique properties in various surface science applications. This fact motivates us to study the adsorption, frictional and morphological behaviour of a commonly studied series of 1-alkyl-3-methylimidazolium chloride ionic liquid surfactants at solid surface namely gold. The Quartz Crystal Microbalance studies revealed that ILs readily adsorbed at gold surfaces, the friction coefficient increases as the alkyl side chain grow longer and all ILs show distinct morphology after adsorption at gold surfaces as observed using Atomic Force Microscopy. Moreover, some interesting effects of concentration and surface treatment on the adsorption phenomena and different surfaces (e.g., silicon) on morphologies have also been observed.

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P2.4: EXCESS MOLAR VOLUMES AND VISCOSITY DEVIATIONS FOR BINARY MIXTURES OF THE IONIC LIQUID 1-BUTYL-3-METHYLIMIDAZOLIUM TETRAFLUOROBORATE WITH SOME ORGANIC SOLUTES

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Room-temperature ionic liquids (RTILs) are a class of organic salts that are liquids at or near room temperature in their pure state. RTILs typically consist of a heterocyclic cation based on substituted imidazole or pyridine and an inorganic anion such as $[BF4]^-$, $[NO3]^-$, or $[PF6]^-$. Due to their nonvolatile nature and favourable solvation properties, RTILs have been suggested as green and benign replacements for traditional volatile organic solvents [1]. Also, the RTILs show potential for a wide range of other applications [2]. In spite of their importance and interest, detailed knowledge on the thermodynamic behaviour of the mixtures of ionic liquids with organic molecular solvents is very limited. In this work, we report the densities and viscosities for [BMIM][BF4] with acetone and acetonitrile over several temperatures and at atmospheric pressure. The mole fractions of the mixtures were determined by mass. Density (ρ) measurements were carried out using an Anton-Paar DMA-5000 vibrating tube densimeter. The kinematic viscosities ν were measured with Ubbelohde capillary viscosimeters with a Schott-Gerätte AVS 350 automatic measuring unit. From these data, excess molar volumes V^E and viscosity deviations $\Delta\eta$ values have been calculated and fitted to the Redlich-Kister equation:

$$Y = x(1-x)\sum_{i=0}^{p} A_i (2x-1)^i \qquad (1)$$

where Y is V^E or $\Delta\eta$ and x refers to the mole fractions of [BMIM][BF4]. Assuming that the anions and cations of the ionic liquids formed a strong network with the interstices available in the fluid [3], it is conceivable that the relatively small organic molecules fit into these interstices upon mixing (filling effect). In addition, the non-hydrogen bonding solutes, such as acetone or acetonitrile, interact more strongly with the cation of the ionic liquids by ion–dipole interactions, as it was found from molecular dynamics simulations [4]. These two effects, which lead to contraction in volume, predominate over the expansive effect associated with the breakdown of both the organic solutes dipolar interactions and the ionic liquid ion-pair. This is supported by the negative V^E values obtained for the mixtures studied in this work. As regards to temperature dependence, it is found that V^E becomes more negative with the thermal agitation. The viscosity deviations are negative over the whole composition range, being their values less negative as the temperature increases. The values of $\Delta\eta$ are particularly large due to the high difference viscosity of pure compounds.

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P2.5: DENSITIES AND VISCOSITIES OF 1-BUTYL-3-METHYLIMIDAZOLIUM HEXAFLUOROPHOSPHATE + ACETONE OR ACETONITRILE BINARY MIXTURES FROM (293.15 TO 303.15) K

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In recent years, the ionic liquids (ILs) have been received much attention due to their unusual and interesting properties that make them useful for several applications [1-3]. Some of the more widely studied ILs consist of a heterocyclic cation based on a substituted imidazole and an inorganic anion such as $[BF4]^-$, $[NO3]^-$, or $[PF6]^-$. To design any new processes involving ionic liquids on an industrial scale, it became necessary to know a range of physical properties including viscosity and density. However, the physicochemical and thermophysical properties of ionic liquids have not been studied systematically. Particularly, properties of the mixtures of ionic liquids with organic molecular solutes are very limited. In this work, we determined experimentally the density and viscosity data for the mixtures of the ionic liquid, 1-butyl-3-methylimidazolium hexaflurophosphate [BMIM][PF6] with two non-aqueous solvents (acetone or acetonitrile) over the entire composition range from (293.15 to 303.15) K.

The densities of the pure liquids and their mixtures were measured by a DMA-5000 vibrating-tube densimeter from Anton-Paar. The kinematic viscosities (ν) were determined using an automatic viscosimeter Schott-Gerätte and several Ubbelohde viscosimeters with capillaries of different diameters. The excess molar volumes V^E and viscosity deviations $\Delta\eta$ were calculated from experimental data and fitted to a Redlich-Kister polynomial function [4].

$$Y = x(1-x)\sum_{i=0}^{p} A_i (2x-1)^i \tag{1}$$

where Y refers to V^E or $\Delta\eta$ and A_i are adjustable parameters and can be obtained by least-squares analysis. The V^E values for the mixtures of [BMIM][PF6] + organic solutes are all negative in the whole composition range, and verify an increase of their absolute values with increasing temperature. This indicates that the packing effect and ion-dipole interaction of acetone or acetonitrile molecules with the ionic liquid predominate over those effects associated with breaking of electrostatic attractions between the $[PF6]^-$ anion and $[BMIM]^+$ cation and dipole–dipole interaction in the organic polar molecules in the process of mixing. The viscosity deviations $\Delta\eta$ are negative and very large values due to the big differences between the viscosities of the compounds.

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P2.6: LIQUID-LIQUID EQUILIBRIA OF N-ALKYL-N,N-DIMETHYL-HYDROXYETHYLAMMONIUM BISTRIFLIMIDE IONIC LIQUIDS WITH ALCOHOLS AND WATER

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Choline, *viz.* cholinium chloride, is an essential micronutrient, grouped in B-complex vitamin. Ionic liquids based on the cholinium cation (N,N,N-trimethyl-hydroxyethylammonium) have been investigated as possible environmentally friendly alternatives to conventional ionic liquids in distinct research fields.[1] Nevertheless, most of the ionic liquids based on the cholinium cation show higher melting points than those of common alkylimidazolium based ionic liquids. To overcome this problem, a new family of ionic liquids, N-alkyl-N,N-dimethyl-hydroxylethylammonium, inspired on the cholinium cation, with the alkyl chain ranging from C_2 to C_5, and combined with the bistrisflimide anion was synthesized.

Nockemann *et. al.* [2] reported that cholinium bistriflimide – by the way, probably the most thermally stable ionic liquid ever synthesized[3] - shows an UCST-type phase diagram with water with a critical temperature of about 70ºC. To the best of our knowledge, this is the first example of a totally miscible bistriflimide-based ionic liquid. In the framework of some our previous works [4], we measured the temperature-composition phase diagrams of N-alkyl-N,N-dimethylhydroxylethylammonium bistriflimide ionic liquids ($1<C_n<5$) with water and alcohols (alkyls chains from C_4 to C_8) from about 0ºC to the boiling point temperature of the molecular solvent. The coexistence curves corresponding to liquid-liquid equilibria (LLE) boundaries were visually determined by turbidity methods and the experimental results have been correlated using a set of equations based on the Flory-Huggins principles. The different types of LLE behavior were discussed in terms of the alkyl chain length of the cation and the alkyl-chain length or the ramification of the molecular solvent. Auxiliary simulation data (obtained by ab initio or by molecular dynamics methods) were used to interpret some of the experimental findings.

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P2.7: VAPOR PRESSURES AND OSMOTIC COEFFICIENTS OF BINARY MIXTURES OF 1-BUTYL-3-METHYLIMIDAZOLIUM METHYLSULFATE WITH ALCOHOLS AT 323.15 K

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Ionic liquids (ILs) find a wide range of application as alternatives to the organic solvents for different processes, and they are being used as separation agents with very promising results. Thermodynamic properties of mixtures containing ionic liquids are of great interest, and namely osmotic coefficients. In this work, experimental data of osmotic coefficients together with the vapor pressures of the binary mixtures containing 1-butanol, 2-butanol and 1-pentanol with the ionic liquid 1-butyl-3-methylimidazolium methylsulfate ($BMimMSO_4$) are presented.

The vapour pressure osmometry measurements were performed using a Knauer K-7000 vapour pressure osmometer (VPO). The extended Pitzer model modified by Archer [1,2], and the modified NRTL model (MNRTL) [3] were used to correlate the experimental osmotic coefficients, obtaining standard deviations lower than 0.016 and 0.065, respectively. The mean molal activity coefficients and the excess Gibbs free energy of the studied binary mixtures were calculated from the parameters obtained with the extended Pitzer model modified by Archer.

The vapor pressure depression, Δp, versus molality for the binary mixtures of the different alcohols and the ionic liquid $BMimMSO_4$ is plotted in Figure 1a, while Figure 1b shows the osmotic coefficients versus molality of the studied binary systems at T = 323.15 K.

a) b)

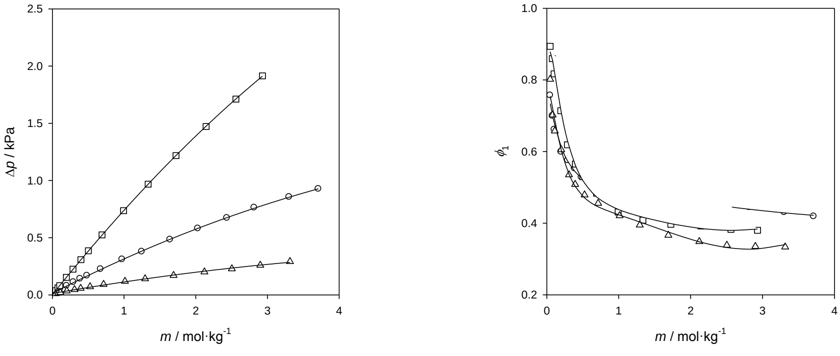

Figure 1: a) Vapor pressure depression, Δp, and b) experimental osmotic coefficients, ϕ_1, plotted against molality at 323.15 K of the studied binary mixtures

(○) 1-butanol, (□) 2-butanol, and (Δ) 1-pentanol with $BMimMSO_4$ at 323.15 K. Solid line (—): a) polynomial fit, and b) Extended Pitzer Model of Archer

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P2.8: EXPERIMENTAL DENSITIES AT HIGH PRESSURES OF 1-BUTYL-3-METHYLIMIDAZOLIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE+2,2,2-TRIFLUOROETHANOL

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In the field of the working fluids for refrigeration by absorption there is a need for new refrigerant/absorbent pairs for domestic and industrial applications. In the case of the absorbents these compounds should be have high heat transfer of heat as well good fluidity.

Shiflett and Yokozeki [1] had thought about H_2O, 2,2,2-trifluoroethanol (TFE), and 1,1,1,2-tetrafluoroethane as refrigerants and ionic liquids (ILs) as absorbents. Kim et al. [2] investigated the TFE + 1-butyl-3- methylimidazolium bromide, [bmim][Br] or TFE + 1-butyl-3-methylimidazolium tetrafluoroborate, [bmim][BF4] systems. Wang et al. [3] determined the vapour pressure of TFE + 1-ethyl-3-methylimidazolium tetrafluoroborate, [emim][BF4]. Currás et al. [4,5] and Salgado et al. [6,7] measured several properties of TFE + some ILs. Some examples are given in the literature. In this work, we have measured the densities of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf2N] with TFE at high pressures in the (283.15-333.15K) temperature range and in all composition range. Thermal coefficients and excess molar volumes of these mixtures were calculated and discussed. Finally, comparison of these results together with those obtained previously could clarify the influence of the cation and anion on the thermophysical properties.

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P2.9: TEMPERATURE AND COMPOSITION DEPENDENCE OF THE DENSITY AND VISCOSITY OF BINARY MIXTURES OF 2,2,2-TRIFLUOROETHANOL + [EMIM][TF$_2$N]

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The present situation of the economy requires the search for alternative energies and the optimisation of current energy technologies with new and clean working fluids. In the recent years, advances in green chemical technology are leading to the development of new compounds among which, ionic liquids (ILs) have special relevancy. An important limitation for the use of ILs is the lack of knowledge about how the structure of the IL may affect its physicochemical properties and the intermolecular interactions, which are the basis for the improvement of their industrial applications or the development of thermodynamic models. In the field of refrigeration industry, absorption refrigeration systems are increasing attention as an efficient and environmentally friendly technology because absorption cycles can use energy provided by low-potential thermal sources and where waste heat is available and cooling is required.

Thermophysical properties of the mixtures of 2,2,2 Trifluoroethanol (TFE) with several ILs have been recently measured in order to propose new refrigerant/absorbent pairs [1-4] which could overcome the problems of the traditional ones, NH_3-H_2O and LiBr-H_2O, such as corrosion, volatility or with the aim to reduce the equipment complexity, which is originally caused by the absorbent fluid volatility.

With the aim of completing this database, we have measured densities and viscosities of the mixture TFE + 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf$_2$N], in the temperature interval of 278.15-333.15 K and in the whole composition range. From these data, excess molar volumes and deviations of viscosity of these mixtures were also calculated and discussed. Finally, the comparison of these results with those obtained previously for other binary systems of TFE and IL with the same cation or anion [1-4] was performed to elucidate the influence of the structure on these physical properties.

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P2.10: SPECIFIC HEAT OF 1-ALKYL-3-METHYLIMIDAZOLIUM (TRIFLUOROMETHANESULFONYL) IMIDE ([CNMIM][TF_2N]) + 2,2,2-TRIFLUOROETHANOL (TFE) MIXTURES (N=2,4)

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Ionic liquids (ILs) have properties wich make them potentially excellent performance fluid for use in a wide range of engineering and material applications. For example as absorbents with several refrigerants. To decide if an ionic liquid could be useful in a large scale industrial applications, the knowledge of their thermophysical properties is needed. In this sense, the specific heat is one of the most important properties to know. The ionic liquid database (IL Thermo) [1] shows the specific heat of the most common pure ionic liquids, but no data of this property for mixtures with another fluids were found.

Due to the difficulty of its experimental determination, the literature of c_p of pure liquids presents values quite different (deviations up to 10%) [2, 3]. In this work, the specific heat of the mixtures of two ILs ([C_2MIM][Tf_2N] and [C_4MIM][Tf_2N]), with 2,2,2-Trifluoroethanol (TFE) has been determined at different temperatures and compositions.

A DSC Q2000 was used and MDSC measurements were performed to obtain the c_p in quasi-isothermal mode. A Sapphire disc was used to calibrate the Kc_p. The amplitude and period used in both, calibration and experiments, was 0.5º C and 100 s, respectively. The pans were hermetic. At each temperature, the modulated heat flow is recorded as the response to the modulated temperature. This method has some advantages over the conventional way to measure the c_p. One of them is that the measurement is made in equilibrium, i.e. the temperature gradients inside the sample are almost avoided. No thermal anomaly was observed or no phase transition took place in the studied temperature interval of 278.15K to 333.15K. The specific heat increases with increasing temperature in all the concentrations for both mixtures. Polynomial equations fit well the c_p values with temperature.

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P2.11: THERMAL STABILITY OF 1-ALKYL-3 METHYLIMADAZOLIUM BIS (TRIFLUOROMETHYLSULFONILIMIDE) [C$_N$MIM] [TF$_2$N] N=2,3,4

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Thermal stability is a significant factor that determines the applicability of ionic liquids (ILs) for high temperature applications. In this work the thermal stability of three ionic liquids, 1-ethyl-3 methylimadazolium bis (trifluoromethylsulfonilimide) ([emim][Tf$_2$N]), 1-buthyl-3-methylimadazolium bis (trifluoromethylsulfonilimide) ([bmim][Tf$_2$N]), and 1-propyl-3-methylimadazolium bis (trifluoromethylsulfonilimide) ([pmim][Tf$_2$N]), was determined. A Perkin Elmer TGA analyzer was used to perform the thermogravimetric analysis.

Firstly, the dinamic method with a temperature interval of 100-900ºC, scanning rate of 10ºC/min on inert atmosphere, was used. Then, the onset temperature was determined as the temperature when the loss weight begins. Figure 1 shows, as example, the TG curve of [bmim][Tf$_2$N] and the onset temperature determination.

Kamavaram and Reddy [1] found that the true stability temperature could be lower than this onset temperature. To obtain the most precise value, which is important for industrial applications, the long-term investigation using isothermal TGA at lower temperatures than onset one, is necessary. Samples of these ILs were exposed at several temperatures lower than the onset temperature, previously determined in order to characterize the long-term stability. Finally, these isothermal TGA studies were used to analyze the kinetics of decomposition of the ILs [2]. In order to evaluate the activation energy of the thermal decompositions, the Arrhenius relation was used [3].

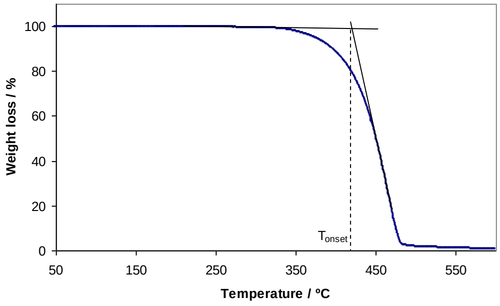

Figure1: Dynamic TG curve and onset temperature of [bmim][Tf$_2$N].

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P2.12: SURFACE TENSION OF BINARY MIXTURES OF IONIC LIQUIDS WITH THE COMMON BISTRIFLAMIDE ANION

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The importance of surface tensions and interfacial properties of diverse mixtures relays on their application in fields like the dried and humidification of cloths, interfacial interactions in membranes of biological cells, dispersion of crude oils, among others. Thus, the determination of the surface tension of a liquid mixture gives us information on the distribution of the molecules between the internal volume of the liquid and the liquid-vapor interface. Here, we present the surface tension of two series of ionic liquids' mixtures. In the first approach, mixtures of the 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, $[C_4mim][NTf_2]$, with other $[NTf_2]$-based ionic liquids for which the cation is a derivative of the 1-alkyl-3-methyl-imidazolium, were studied. The binary mixtures measured were: $[C_4mim][NTf_2]$ + $[C_1mim][NTf_2]$, + $[C_2mim][NTf_2]$, + $[C_4C_1mim][NTf_2]$, + $[C_5mim][NTf_2]$, + $[C_6mim][NTf_2]$, + $[C_8mim][NTf_2]$, + $[C_{10}mim][NTf_2]$. In the second series, the anion $[NTf_2]^-$ was kept while changing the family of the cation: 3-methyl-1-propylpyridinium, $[C_3mpy]^+$, 1-methyl-1-propylpyrrolidinium, $[C_3mpyr]^+$, and 1-methyl-1-propylpiperidinium, $[C_3mpip]^+$. The binary mixtures studied were: $[C_4mim][NTf_2]$ + $[C_3mpy][NTf_2]$, + $[C_3mpyr][NTf_2]$ and + $[C_3mpip][NTf_2]$. All mixtures have been measured using a Dataphysics contact angle system OCA20 at 298.15 K and atmospheric pressure, over the whole composition range. The uncertainty of the surface tension measured is $\pm 1\cdot10^{-2}$ $mN\cdot m^{-1}$. From the data obtained the surface tension deviations were extracted, which provide us with information on intermolecular interactions occurring at the surface for a given mixture. The binary mixture results were fitted with a Redlich-Kister type equation. Finally, we calculated the relative Gibbs adsorption isotherm considering the ideality of the bulk liquid phase accordingly to,

$$\Gamma_2^{(1)} = -\frac{1}{RT}\frac{d\sigma}{d\ln x_2}$$

where $\Gamma_2^{(1)}$ is the relative adsorption of component 2 with respect to component 1.

P2.13: NMR (1D, 2D, DOSY) EXPERIMENTS AND THERMODYNAMICS OF NEW PROTIC LONG-CHAIN IONIC LIQUIDS WITH STEARATE ANION

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In the last few years the amazing growth in ionic liquid investigation has resulted in the development of a huge number of novel ionic liquids, as well as many associated applications. The potential environmentally friendly nature of these substances which results from their negligible vapor pressure, is now under study since it is not possible to guarantee that they will never enter the environment. Toxicity research studies have recently received broad attention and the commonly accepted notion that ionic liquids have low toxicity has been shown to be incorrect, at least for those enclosing heterocycle or halogenated structures. Only now, a growing interest in the socalled protic ionic liquids or Bronsted salts for industrial applications has arisen. A relevant aspect, considering the interest in these substances as more environmentally sustainable solvents, is their low cost and simple preparation. Their real toxicity has not been sufficiently studied until now, especially taking into account the need of this information to fulfil the REACH regulations, allowing the assessment of hygiene and safety issues derived from their manufacture, use, and transport in the industrial sectors in which these substances will be applied. The main objectives of this work are directed towards the development and (1D, 2D, DOSY) NMR and thermodynamic characterization of new protic ionic liquids of low toxicity. The substances enclosed into this work are based on polysubstituted amines and organic anions usually found in nature and easily biodegradable into environment [1]. Previous bibliographic studies of the authors [2-6] have tested different ionic liquids of similar structures and proved wide applicability on different industrial uses.

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P2.14: TEMPERATURE AND PRESSURE DEPENDENCE OF DYNAMIC VISCOSITY OF 1-(2-METHOXYETHYL)-1-METHYL-PYRROLIDINIUM BIS(TRIFLOROMETHYLSULFONYL)IMIDE

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Among the many and ever increasing applications of Ionic Liquids (ILs), it is worth pointing out their use as base oils or lubricant additives [1,2], thanks to their characteristic properties as well as ILs tuneability by appropriate choice of anion and cation. To develop this new kind of base oils, physical properties that affect lubrication, such as viscosity and its dependence with temperature and pressure, should be reliably determined. In this work we focus our attention on the viscosity behavior of 1-(2-methoxyethyl)-1-methyl-pyrrolidinium bis(trifloromethylsulfonyl)imide, for which measurements were performed from 0.1 MPa to 150 MPa. A sample of this IL was kindly provided by Merck with purity higher than 98 %. The sample was treated by vacuum evaporation to remove the residual volatile impurities at room temperature, for at least 30 h. The water content of this sample was determined by volumetric Karl Fischer titration obtaining 28 ppm.

We also present in this work a new falling body viscometer (visLPT1) that has been designed and implemented in our laboratory to study liquids at pressure conditions up to 150 MPa. This device is similar to that previously designed by Daugé et al. [3]. In this viscometer, a cylindrical sinker with a hemispherical end, falls vertically through the sample under study. The equipment has been calibrated by using bis(2-ethylhexyl)phthalate from 313.15 K to 363.15 K and from 0.1 MPa to 150 MPa. The accuracy of the viscometer was verified by comparing experimental results of squalane and diisodecyl phthalate with previous literature data, finding average absolute deviations lower than 3.5 % and 5 %, respectively. We have also used a rotational automated viscometer Anton Paar Stabinger SVM3000 to measure the viscosity at atmospheric pressure in the range 258.15 K to 373.15 K. Over the entire temperature and pressure intervals the experimental viscosities range from 7.3 mPa·s to 620.3 mPa·s. The values obtained were correlated as function of temperature and pressure with a modification of the VFT equation, proposed by Comuñas et al. [4] finding that this equation represents the experimental viscosity values with an average absolute deviation of 1% .

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P2.15: IMPACT OF THE MOLECULAR STRUCTURE OF ALKYLSULFATE IONIC LIQUIDS ON THE SURFACE TENSION

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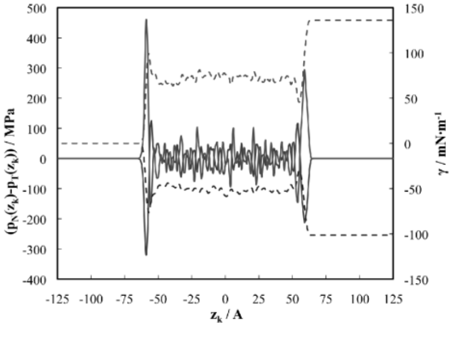
The “bulk” properties of common ionic liquids have received considerable attention, in contrast with the “ionic liquid surface science” [1-2]. The operation of many industrial processes, such as liquid-liquid extraction and gas absorption, relies on the behavior of liquid-liquid or gas-liquid interfaces. A comprehensive study of the surface properties of ionic liquids is then required.

To investigate the influence of the composition on the surface properties, it is helpful to use a homologous series, e.g. changing the aliphatic chain length of the cation, the kind of cation or anion. Molecular dynamics (MD) simulation is a powerful technique for studying interfaces at the molecular level, by giving access to number density profiles of individual atoms or ordering profiles at the interface. Herein, we use molecular simulation to gain access to the surface tension and the structure at the liquid/vapor interface of a set of ionic liquids based on the 1-ethyl-3-methylimidazolium ($[C_2C_1im]^+$) cation and alkylsulfate ($[C_nH_{2n+1}SO_4]^-$) anions, where three different lengths of the alkyl chain of the anion ($n = 2$, $n = 6$ and $n = 8$) were considered. The choice of these liquids was based on the possibility of elucidating the effects of increasing the length of side chain in the surface tension and in the structure of the liquid/vacuum interfaces. The surface tension was calculated using both mechanical and thermodynamic definitions, finding a good agreement between the considered methods.

Figure 1: $p_N(z_k)–p_T(z_k)$ for the Lennard-Jones and the electrostatic part of the potential for $[C_2C_1im][C_2SO_4]$. The dashed lines (surface tension) are the integral of as a function of z_k (right axis).



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P2.16: HOFMEISTER SERIES ON THE PARTITION COEFFICIENTS OF ALKALOIDS IN IONIC LIQUID-WATER SYSTEMS

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Ionic liquids have received significant attention in the past few years mainly due to their negligible vapour pressures, which combined with tailored and favourable properties, grant them the status of powerful solvents for many compounds. Indeed, ionic-liquid-water systems already proved to be potential solvents for the extraction of alkaloids from biological samples, namely caffeine and nicotine, resulting in the alkaloids complete extraction for the ionic liquid-rich phase.[1] Moreover, caffeine and nicotine are natural insecticides and their extraction from natural sources, and subsequent purification, is still a challenging task because of their unexpected low solubilities in common organic solvents and related mixtures.

The aim of this work is to understand the fundamental impact of inorganic salts on the extraction of caffeine and nicotine from aqueous solutions using phosphonium-based ionic liquids. The selected ionic liquids comprise the trihexyltetradecylphosphonium-based cation combined with the following anions: bromide, chloride, bis(trifluoromethylsulfonyl)imide, methanesulfonate, dicyanamide and bis(2,4,4-trimethylpentyl)phosphinate. It was found that the solutes partitioning increases with the ionic liquid hydrophilic character. In addition, both the influence of the aqueous solution ionic strength (ranging from 0.0 $mol \cdot kg^{-1}$ to 3.0 $mol \cdot kg^{-1}$) and the salt nature (with K- and Na-based salts) in the partitioning of caffeine and nicotine were further investigated. The salt nature was evaluated through the course of the solutes partition coefficients where it was found that it closely follows the Hofmeister series.[2]

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P2.17: THERMOPHYSICAL PROPERTIES OF CN-BASED IONIC LIQUIDS

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In the past few years, ionic liquids have earned the epithet of "green solvents" as a result of their unique characteristics, *e.g.*, low melting temperature, negligible vapour pressure, general non-flammability, thermal and chemical stability, and easy recyclability. Most ionic liquids present interesting physicochemical properties, a fact that led to a burgeoning area of research regarding their characterization and possible applications. Due to their structural diversity, there are a nearly unlimited number of potential ionic liquids. A complete database regarding their physical properties is still missing.

In this work, we report on the thermophysical properties —density and viscosity— of ionic liquids containing anions substituted with the cyano group (–CN). These include 1-ethyl-3-methylimidazolium and 1-butyl-3-methylimidazolum cations combined with $[SCN]^-$, $[N(CN)_2]^-$, $[C(CN)_3]^-$ and $[B(CN)_4]^-$ anions. Density and viscosity measurements have been carried out at atmospheric pressure in the 278.15 to 363.15 K temperature range. Results along distinct homologous series will be presented and discussed taking into account the effect of the –CN group addition.

P2.18: INCREASING THE IONICITY IN IONIC LIQUIDS

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This work exploits a new scientific branch of the ionic liquids (ILs) field, one that is almost unexplored. It lays on the significant increase of the Coulombic character of these compounds through the solubilisation of simple inorganic salts (ISs) in their milieu. Therefore, at very low cost, ionicity is increased while the liquid state status is still preserved. A new class of ionic liquids, the Strong Ionicity Ionic Liquids (SIILs) will emerge.

This study includes ILs containing e.g. ammonium or imidazolium cations combined with different anions, such as bis(trifluoromethylsulfonyl)imide, sulfate, or sulfonate. The conventional inorganic salts map the whole Hofmeister series. A screening of the limit of solubility of several inorganic salts in some ionic liquids has been performed. Mixtures in which the IS solubility is greater than 0.2 molar fraction have been chosen. FTIR-ATR has been used to accurately quantify the solubility limits.

A systematic understanding of the complex chemistry behind the SIILs has been achieved by monitoring several thermodynamic and transport properties. The determination of different properties of these mixtures, namely, their ionic conductivity, density, viscosity, refractive index, and thermal stability, have been carried out as a function of the IS content. Walden plots have been used to clarify the role of the inorganic salts in SIILS. These data are paramount for the development of thermodynamic models.

Molecular level insights on the interionic interactions and the liquid structure have been provided by NMR studies. Also, this technique has been used to understand the underlying mechanism of solubilisation. The establishment of preferential interactions simultaneously with functional groups of both the cations and the anions is the cause of this enhancement of the conductivity of these mixtures.

P2.19: ON THE AQUEOUS BIPHASIC SYSTEM BEHAVIOUR OF ALKYLSULFATE AND ALKYLSULFONATE-BASED IONIC LIQUIDS

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Aqueous Biphasic Systems (ABS) have long been considered as an efficient alternative for the development of separation techniques for the extraction of a wide variety of compounds with industrial interest. This separation method consists in adding an inorganic salt (phase promoter) to an aqueous solution of a hydrophilic ionic liquid forming an upper ionic liquid-rich phase and a lower salt-rich phase, both of which are aqueous.

The rationale behind this system is a reflection of the complex competition between the inorganic salt and the ionic liquid for the water molecules and specific interactions between the inorganic salt and the molten salt. This kind of procedure offers inherent advantages both from an economic and environmental standpoint, namely low energy requirements, short process time and absence of traditional organic volatile compounds in the whole process [1, 2].

In this work, the effect of K_3PO_4, K_2CO_3, Na_2CO_3 and $(NH_4)_2SO_4$, as high charge-density inorganic salts on the ABS formed by several alkylsulfate (C_2MIM C_nSO_4, n = 2, 4, 6 and 8), and alkylsulfonate-based ionic liquids ($C_2MIMC_mSO_3$, m = 2, 4, and 6) is assessed at T = 298.15K and analysed in the light of the Hofmeister series. The selected ionic liquids were chosen on the basis of their remarkable characteristics since they can be easily synthesized in a halide-free way, at a reasonable cost, and have relatively low viscosity [3].The influence of different alkyl chain lengths in the anion, together with the ability of the selected salts in inducing the formation of ABS is discussed. Binodal curves are determined through the cloud point method, including tie lines assignment from mass phase ratios according to the lever arm rule. The Merchuck equation is satisfactorily used to correlate the binodal data and the consistence of tie-line data was ascertained by applying the Othmer-Tobias equation.

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P2.20: ACTIVITY COEFFICIENTS AT INFINITE DILUTION IN EMPYESO$_4$

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Using less polluting solvents is an aspect of major interest in the field of "green chemistry". Ionic liquids appear to be an alternative to replace the conventional volatile organic compounds because of their negligible vapour pressure. Our interest in ionic liquids is focused on providing systematic data on activity coefficients of mixtures with organic solvents. Activity coefficients at infinite dilution of a solute can be used to quantify the volatility of the solute as well as to provide information about the intermolecular interactions between solvent and solute or to calculate Henry's constants. They are also useful, in particular, for the selection of solvents for liquid-liquid extraction, extractive and azeotropic distillation, in the prediction of azeotropes and in the calculation of limiting separation factors that are also important in an optimum design of separation processes.

In this work, the activity coefficients at infinite dilution have been measured with the gas chromatography technique for several solutes (ketones, alcohols, and esters) in the ionic liquids 1-ethyl-3-methylpyridinium ethyl sulfate using this solvent as the stationary phase. The measurements were carried out at four different temperatures between 313.15 K and 373.15 K.

P2.21: EXPERIMENTAL DENSITIES AND DERIVED THERMODYNAMIC PROPERTIES OF AQUEOUS BINARY MIXTURES OF [EMIM][C_NS] IONIC LIQUIDS AT SEVEN PRESSURES

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Measurement and interpretation of the physical properties of ionic liquids and its mixtures with water and other solvents are necessary to develop new industrial applications, chemical processes and redesign the ones that had employed molecular solvents for a century, and also to obtain prediction equations and theoretical models.

As a continuation of our studies [1] we present experimental measurements of density for binary mixtures of 1-ethyl-3-methyl-imidazolium alkylsulphate [EMIM][C_nS] (where C_n represents the alkyl chain) with water at 25 ºC and at seven pressure conditions between 0.1 to 30 MPa. Samples were prepared using an inert atmosphere cabin because of ionic liquids are hygroscopic [2]. They were measured using a digital vibrating tube densimeter [3]. From measured data we will extract derived thermodynamic properties such as excess molar volumes and isothermal compressibility.

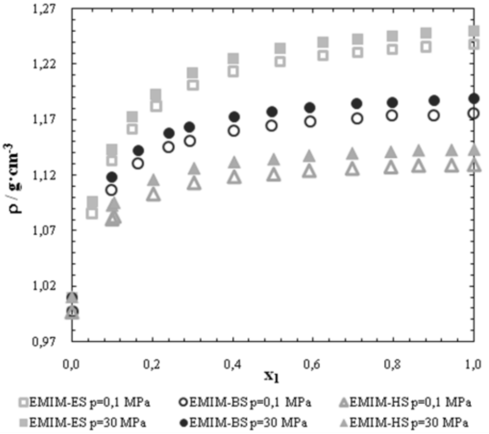

Figure 1: Experimental densities for aqueous binary mixtures of [EMIM][C_nS] ionic liquids with n = 2, 4 and 6 at 25 ºC and with p = 0,1 MPa and 30 MPa.

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P2.22: IONIC LIQUIDS UNDER TENSION

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Absolute negative pressure regimes constitute a specific subclass of superheating [1], one in which $p < 0$. Under such condition, the liquid is under tension and is thermodynamically metastable [2] with respect to the vapour phase. In order to achieve this, it is necessary to define the imposed external thermodynamic constraints to the system, namely, pressure and temperature (p, T) constant or total volume and temperature (V, T) constant. Negative pressure regimes are not forbidden for systems that cannot expand infinitely (condensed phases such as liquids and solids). Absolute negative pressure states can be held for considerable periods of time, in spite of their metastability, permitting the measurement of physical properties of substances[3] and their mixtures, as well as, liquid-liquid equilibria[4].

In this work, several different ionic liquids, 1-alkyl-3-methylimidazolium bis(trifluoro methylsulfonyl)imide, 1-alkyl-3-methylimidazolium alkylsulfonates, 1-alkyl-3-methylimidazolium alkylsulfates and trihexyl(tetradecyl)phosphonium with different anions, were tested at absolute negative pressures to define their practical limit of metastability. Working temperatures ranged from -50ºC to 200ºC and it was possible, for the first time, to achieve values greater than tensions of −1000 bar. Distinct partially immiscible binary mixtures (ionic liquid + conventional solvent) were selected and the liquid-liquid phase diagram − already available for normal, positive pressures − was extended by mapping the negative pressure domain.

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P2.23: EFFECT OF THE CATION ON PHYSICAL PROPERTIES OF TWO TRIFLUOROMETHYLSULFONATE IONIC LIQUIDS

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Ionic liquids (ILs) are relatively new compounds and experimental data on physical properties of pure ILs are scarce. The knowledge of thermophysical and transport properties of ILs, such as density, viscosity, and refractive index, is crucial to achieve a correct design of processes and also for the contribution to the databank of properties.

In this work, a systematic study of density, viscosity, and refractive index of two ILs involving the trifluoromethylsulfonate anion was investigated from (293.15 to 373.15) K. In this case, 1-butyl-3-methylimidazolium trifluoromethylsulfonate, [BMim][TFO], and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate, [BMpyr][TFO] ionic liquids were selected due to both compounds present the same anion and a study of the influence of the cation in the physical properties can be carried out. From the experimental data, the effect of temperature in the physical properties was also analyzed. The variation of density and refractive index with temperature was fitted to a linear equation while dynamic viscosity was fitted using Vogel-Fulcher-Tamman (VFT) equation [1-3].

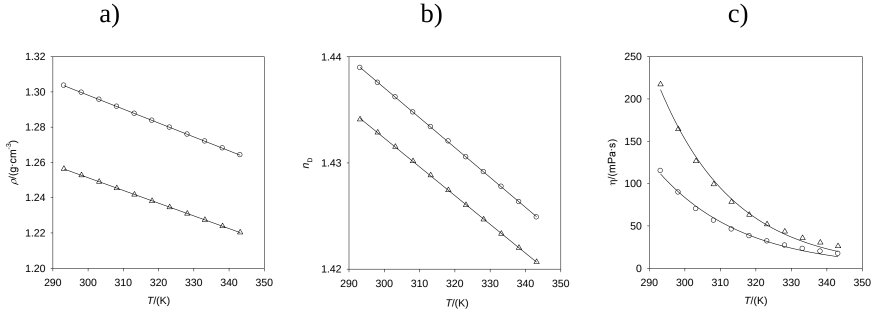

Figure 1: a) Density, ρ, b) refractive index, n_D, and c) dynamic viscosity, η, versus temperature for the ILs: (○) [BMim][TFO], (△) [BMpyr][TFO]. Solid line (□): fitting.

From Figure 1, it is possible to conclude that all studied properties decrease with temperature for the two studied ILs. Moreover, density and refractive index values for [BMim][TFO] are higher than those obtained with [BMpyr][TFO], while for the viscosity the trend is the opposite.

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P2.24: ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR ORGANIC SOLUTES AND WATER IN 1-HEXYL-3-METHYLPYRIDINIUM TOSYLATE, [HM^{3}PY][TOS]

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Pyridinium ionic liquid has been prepared from 1-hexyl-3-methylpyridinium bromide as a substrate. The work includes specific basic characterization of synthesized 1-hexyl-3-methylpyridinium tosylate, [HM^{3}Py][TOS] by NMR spectra, elementary analysis and water content. The basic thermal properties of the pure IL, *i.e.*melting and glass-transition temperatures, as well as the enthalpy of fusion have been measured using a differential scanning microcalorimetry technique (DSC).

As a part of investigation of tosylate - based ionic liquids as a potential solvent in many separation processes application, the activity coefficients at infinite dilution have been determined. The experiment have been done for more than 40 solutes (*n*-alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, ethers, ketones, thiophene and water) in [HM^{3}Py][TOS] over the temperature range from (338.15 to 368.15) K using GLC method. The partial molar excess Gibbs energies $\Delta G_1^{E,\infty}$, enthalpies $\Delta H_1^{E,\infty}$ and entropies $\Delta S_1^{E,\infty}$ at infinite dilution were calculated directly from the experimental γ_{13}^{∞} values. The selectivities for aliphatic/ aromatic hydrocarbon, cycloalkane/ aromatic hydrocarbon and *n*-heptane/ thiophene separation processes were calculated directly from the γ_{13}^{∞} and compared to the literature values for other tosylate – based ionic liquids, NMP and sulfolane [1-5].

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P2.25: PHASE EQUILIBRIA STUDY AND MODELLING OF THE BINARY SYSTEMS {1-HEXYL-3-METHYLPYRIDINIUM TOSYLATE + WATER, OR + AN ALCOHOL, OR + A HYDROCARBON}

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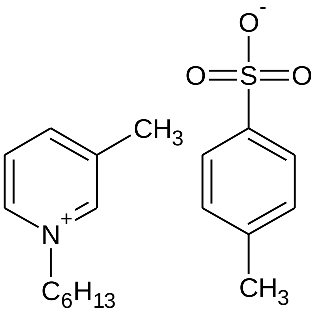
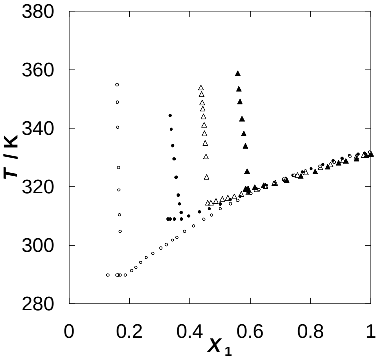
Phase diagrams for the binary systems {[HM^{3}Py][TOS] + water, or + an alcohol (1-butanol, 1-hexanol, 1-octanol, 1-decanol), or + an alkane (*n*-hexane, *n*-heptane, *n*-octane), or + an aromatic hydrocarbons (benzene, toluene, ethylbenzene, *n*-propylbenzene)} have been determined at atmospheric pressure using a dynamic method. (Solid + liquid) phase equilibria with complete miscibility in the liquid phase were observed for the systems involving water and alcohols. The phase equilibria (solid + liquid, or liquid + liquid) for the binary systems containing a hydrocarbon reported here exhibit an upper critical solution temperature (UCST). As usual, with increasing chain length of the solvent, the solubility decreases. The reduction of experimental data has been carried out using the nonrandom two liquid (NRTL) correlation equation. The phase diagrams reported here have been compared with analogous phase diagrams reported previously for systems containing the ionic liquid, 1-butyl-4-methylpyridinium tosylate [1], 1-butyl-3-methylpyridinium tosylate [2], 1-ethyl-methylimidazolium tosylate [3] and 1-butyl-3-methylimidazolium tosylate [4]. The influence of the structure and asymmetry of the cation on the phase behaviour have been tested.





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P2.26: ACTIVITY COEFFICIENTS AT INFINITE DILUTION FOR ORGANIC SOLUTES AND WATER IN PIPERIDYNIUM- BASED IONIC LIQUIDS

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Activity coefficients at infinite dilution for solutes: *n*-alkanes, cycloalkanes, alkenes, alkynes, aromatic hydrocarbons, alcohols, ethers, ketones, thiophene and water in two new ionic liquid (IL): 1-butyl-1-methylpiperidynium thiocyanate, [BMPIP][SCN] [1] and 1-butyl-1-methylpiperidynium bis(trifluoromethylsulfonyl)amide, [BMPIP][NTf$_2$] have been measured using gas-liquid chromatography (GLC) at wide range of temperature from 298.15 K to 368.15 K. The partial molar excess Gibbs energies $\Delta G_1^{\mathrm{E},\infty}$, enthalpies $\Delta H_1^{\mathrm{E},\infty}$ and entropies $\Delta S_1^{\mathrm{E},\infty}$ at infinite dilution were calculated directly from the experimental γ_{13}^{∞} values obtained, over the temperature range. The selectivities ($S_{1,2}^{\infty}$) for aliphatic/ aromatic hydrocarbon, cycloalkane/ aromatic hydrocarbon and *n*-heptane/ thiophene separation processes were calculated from the γ_{13}^{∞} and compared to the literature values for the ionic liquids with the same anions [2-6].

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P2.27: LIQUID-LIQUID EQUILIBRIA OF 1-(3-HYDROXYPROPYL)PYRIDINIUM CATION BASED IONIC LIQUID + HYDROCARBON BINARY SYSTEMS

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Binary liquid-liquid equilibria for 12 systems containing an ionic liquid (1-(3-hydroxypropyl)pyridinium bis(trifluoromethylsulfonyl)-amide, [*N*-C_3OHPY][NTf_2] and 1-(3-hydroxypropyl)pyridinium trifluorotris(perfluoroethyl)phosphate, [*N*-C_3OHPY][FAP]) with a hydrocarbon (hexane, heptane, cyclohexane, benzene, toluene and thiophene) were measured by dynamic method. The influence of anion structure of 1-(3-hydroxypropyl)pyridinium cation based ionic liquids on solubility of thiophene, aliphatic and aromatic hydrocarbons is presented.

The increase of solubility with the increase of temperature is observed for all systems, therefore the liquid-liquid equilibria diagrams have shapes typical for diagrams with upper critical solution temperature (UCST). With the increase of the length of the alkane chain the increase of miscibility gap is observed, accordingly the solubility of heptane is lower than for hexane. In comparison, cyclohexane shows better solubility in the investigated ionic liquids than hexane. This stands that aliphatic hydrocarbons with cyclic structure, analogous to pyridinium structure, reveal better solubility than linear alkanes (*similia similibus solvuntur*). Moreover the molar volume of cycloalkanes is smaller than for linear alkanes, therefore the packing effect additionally increases solubility of cycloalkanes. Thiophene, benzene and toluene have much better solubility in the ionic liquids than aliphatic hydrocarbons due to aromatic nature. Strong interaction between π-delocalized electrons in the aromatic structure with the polar ionic liquids, especially with pyridinium cation, causes better solubility. The solubility is lower for toluene than for benzene because of presence of a methyl group in the toluene structure. More aliphatic character of toluene reduces solubility in ionic liquids. The solubility of thiophene is higher than for benzene for [*N*-C_3OHPY][NTf_2] ionic liquid. For [*N*-C_3OHPY][FAP] ionic liquid the solubility of thiophene and benzene is comparable.

P2.28: EFFECT OF WATER IN THE THERMAL CONDUCTIVITY OF [C_4MIM][TF_2N]

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The presence of water in ionic liquids has been a subject dealt by several authors, because the type of interaction involved (reaction, dissolution) and the understanding of the physical processes that justify a strong variation of the thermophysical properties, namely viscosity with the amount of water present, at ppm levels.

An intensive study of effect of water concentration in the thermal conductivity of 1-butyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide, [C_4mim][Tf_2N], was performed. The thermal conductivity of the ionic liquid, doped with two different concentrations of water (0.5 and 1 % w/w) was measured, between 293 K and 343 K at 0,1 MPa, using a KD2 Pro Thermal Properties Analyzer (Decagon, USA). The principle of measurement is based on the transient hot-wire method, using an electrically insulated probe. The uncertainty of the thermal conductivity was estimated from the standard deviations of experimental and calibration measurements to be 6.6 % (k=2). A careful calibration was performed, using toluene, water, glycerol, one mixture of glycerol + water, and NaCl + water solution, in order to cover the range of thermal conductivities between 0.13 and 0.67 $Wm^{-1}K^{-1}$.

The results are shown in Fig. 1. It is seen that the thermal conductivity of the mixtures is smaller than that of the pure ionic liquid, a fact that was not predicted before, as the thermal conductivity of the pure ionic liquid is much smaller than that of water, and in principle we should expect and increase with increasing water concentration.

An attempt to justify this behavior with the help of recent models on polar-non-polar interactions between the cation and anion of the ionic liquid, and the smaller water molecule will be presented.

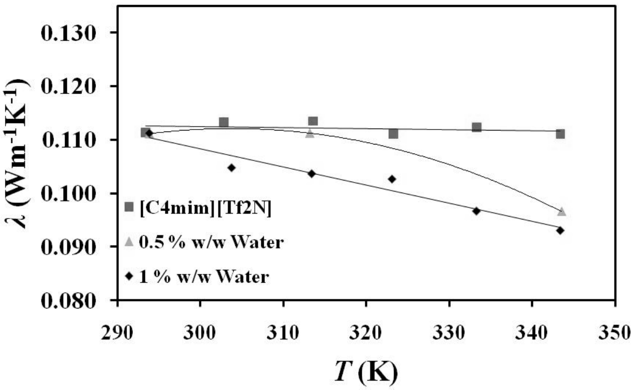

Figure 1: The thermal conductivity of [C_4mim][Tf_2N] and two of its mixtures with water as a function of temperature.

P2.29: DENSITIES OF AQUEOUS BINARY MIXTURES OF EMIM-C_NS IONIC LIQUIDS AT SEVERAL TEMPERATURES

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As a part of our studies on ionic liquids [1-3], we present densities of aqueous binary mixtures containing 1-ethyl-3-methylimidazolium alkyl sulphate, EMIM-C_nS, where the alkyl group (C_n) is ethyl, butyl, hexyl or octyl. Density measurements were carried out at the temperatures of 15, 25, 35, and 45 ºC using an Anton Paar SVM 3000/G2 densimeter, the repeatability of which is 0.0001 g·cm^{-3}. Figure 1 shows the densities obtained for the aqueous mixtures with 1-ethyl-3-methylimidazolium ethyl sulphate (EMIM-ES) as component.

From density data the molar volumes of the mixtures were calculated. They present a quasi ideal behaviour, being the excess molar volume less than a 0.6 % of the molar volume value. The results were fitted with an equation developed by us [4] which only uses a maximum of four fitting parameters.

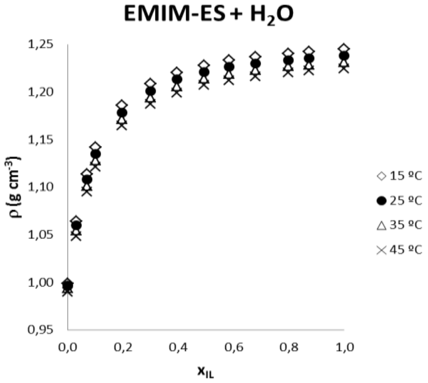

Figure 1.

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P2.30: SECOND ORDER THERMODYNAMIC DERIVATIVES OF RTILS

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A large body of work has been performed in the last decades in order to characterize the thermodynamic behaviour of Room Temperature Ionic Liquids RTILs (see, for details, reviews of Heintz [1] and Marsh et al. [2]). Most of these studies dealt with the experimental measurement of properties under atmospheric pressure conditions, however, little attention was paid in the analysis of these properties as a function of pressure. Particularly scarce is the experimental information on the second order thermodynamic derivatives (also called response functions) such as the isobaric and isochoric heat capacity, the isothermal and isoentropic compressibility, and the isobaric thermal expansivity. This fact traduces in the absence of a global picture of the behaviour of the response functions as a function of temperature and pressure.

Although there are specific experimental methodologies for the determination of theses magnitudes, the common procedure is to determine a set of key properties and to derive them by using thermodynamic relations. It has been proved that density and isobaric heat capacity is the best election for key properties when they are obtained with enough accuracy [3]. Nowadays, the accurate determination of the density and isobaric heat capacity of RTILs is not a problem since difficulties arisen from the high density and viscosity of the RTILs have been solved [4-6]. Therefore, in this work, experimental measurements for [emim] [BF4], [bmim] [BF4], [hmim] [BF4], and [omim] [BF4] were performed in order to obtain the isobaric and isochoric heat capacity, the isothermal and isoentropic compressibility, and the isobaric thermal expansivity in the temperature interval (10-50) ºC an up to 600 bar and to provide for the first time a global picture of the behaviour of the response functions as a function of temperature and pressure. Results have allowed to characterize a RTIL as an alkane under high pressures.

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P2.31: SURFACTANT SELF-ASSEMBLY STRUCTURES IN IONIC LIQUIDS

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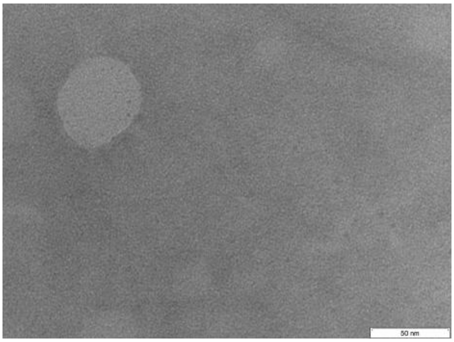
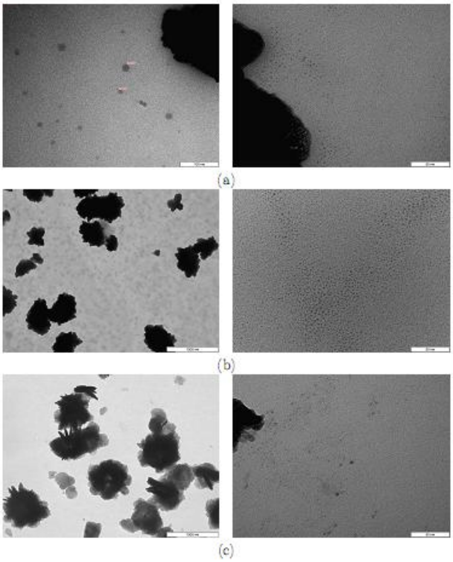
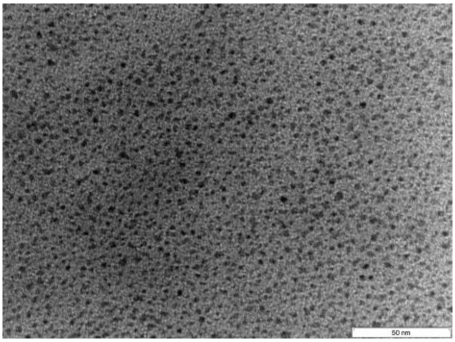
The existence of mesoscopic self-assembly structures formed by surfactants in protic ionic liquids solutions are reported. Micellar aggregates of *n*-alkyltrimethylammonium (*n*=10, 12, 14, 16) bromides, in ethylammonium nitrate (EAN) and propylammonium nitrate (PAN) were observed by means of electron micrography.





TEM images of C_{12}TABr in EAN at concentrations (a) *m*= 0.04 mol kg^{-1}< cmc, and (b) *m* = 0.5 mol kg^{-1}> cmc. The scale bars represent 50 nm in both cases.



TEM images of alkyltrimethylammonium bromides in PAN at concentrations above the cmc’s. (a) $C_{12}TABr$ at m = 0.79 mol. kg^{-1}, (b) $C_{14}TABr$ at m = 0.40 mol kg^{-1}, (c) $C_{16}TABr$ at m= 0.12 mol kg^{-1}. The scale bars on the right represent 50 nm in all cases, 100 nm for the left image in (a) and 1000 nm for images on the left in (b) and (c).

Images for $C_{12}TABr$ in EAN distinctively show spherical aggregates at concentrations above the cmc, and whose diameters have been calculated. While below the cmc no micellar aggregate is observed, at concentrations above the cmc self-association aggregates of the surfactant are clearly visible in great numbers in the bulk solution.

ACKNOWLEDGMENTS: This work was supported by the Spanish Ministry of Science and Innovation in conjunction with the European Regional Development Fund (Grants Nº FIS2007-66823-C02-01 and Nº. FIS2007-66823-C02-02), and by the Directorate General for R+D+i of the Xunta de Galicia (Grants Nº 10-PXI-103-294 PR and 10-PXIB-206-294 PR). T. Méndez-Morales and J. Carrete thank the Spanish Ministry of Education for their FPU grants.

POSTER PRESENTATIONS, SESSION 3:

Theoretical models and numerical simulation

P3.1: UNDERSTANDING THE DISSOLUTION MECHANISM OF NUCLEOBASES IN 1,3-DIALKYLIMIDAZOLIUM ACETATE ILS: *IN SITU* NMR SPECTROSCOPY AND INSIGHTS FROM *AB INITIO* CALCULATIONS

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Neoteric solvents engineering is one of the most promising areas in the evolving field of “green” sustainable technologies, a category which includes supercritical CO2, aqueous biphasic systems, and ionic liquids. Room Temperature Ionic Liquids (RTILs) are revolutionizing the world of solvents due to the unique combination of their many interesting properties. The tunable nature of the solubility of various compounds - including molecules of pharmaceutical and biological interest - in RTILs makes extraction with RTILs attractive for many separation and purification processes. Exploring new applications requires fundamental understanding of phase behavior.

In the present work, we disclose the solvation mechanism of three selected nucleobases, namely, uracil, thymine, and adenine, in RTILs of the 1,3-dialkylimidazolium acetate family. Nucleic acid bases, nitrogenous heterocyclic nucleic acids that form the structural units of DNA and RNA, are ubiquitous in nature, presenting a paramount importance as biochemical compounds. Their chemistry influences different synthetic pathways as well as enzyme systems and dictates the structure and properties of living cells and organisms.

In situ NMR studies of uracil, thymine and adenine dissolved in 1-ethyl-3-methyl-imidazolium acetate ($[C_2mim][CH_3COO]$) and 1-butyl-3-methyl-imidazolium acetate ($[C_4mim][CH_3COO]$) show that hydrogen bonds (HB) command the dissolution mechanism and that both cation and anion participate in the solvation process. For that, the 1,3-dialkylimidazolium acetate RTILs were considered to be bifunctional solvation ionic liquids. The analysis of the solvation sites of the selected nucleic acid bases in 1,3-dialkylimidazolium acetate RTILs were accomplish by DFT methods, corroborating the spectroscopic results.

P3.2: APPLICATIONS OF PC-SAFT EQUATION TO SEVERAL IONIC LIQUIDS USING SPECIFIC ASSOCIATION OR DIPOLAR TERMS

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The PC-SAFT approach [1] is a modification of the SAFT equation by Huang and Radosz [2,3]. PC-SAFT equation depends on three pure component parameters: the segment number m_i, the segment diameter σ_i, and the segment energy parameter ε_i. In compounds with chemical association two more characteristic parameters are introduced [4]: the association energy (ε^{AB}) and the effective association volume (κ^{AB}). Recently we have introduced in PC-SAFT approach a polar term [5] in order to consider dipolar interactions between ionic liquid (ILs) molecules.

The aim of this work was to model densities and to compare both versions of PC-SAFT for the ILs: 1-ethyl-3-methylimidazolium tetrafluoroborate [emim][BF4], 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [emim][Tf2N], 1-butyl-3-methylimidazolium tetrafluoroborate [bmim][BF4], 1-butyl-3-methylimidazolium hexafluorophosphate [bmim][PF6] and 1-ethyl-3-butylimidazolium bis(trifluoromethylsulfonyl)imide [bmim][Tf2N].

The mean deviations obtained for the all compressed ionic liquid densities oscillated between 0.3% using PC-SAFT with the association term and 0.1% using PC-SAFT with dipolar contribution. The version with the association term has captured well the dependence of density with the pressure but not with the temperature for all ILs. Whereas, using the PC-SAFT with the polar term the dependence of density with pressure and temperature was obtained with high precision. Finally, an analysis with the cation and anion was performed with both versions of PC-SAFT.

For the refrigeration by absorption a system with an absorbent solution with higher density is preferred. PC-SAFT model with dipolar term could be useful for practical estimations within refrigeration industry. Nevertheless, it must be reminded that other properties must be examined as well to reinforce the conclusions on their reliability.

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P3.3: THERMOPHIL: AN APPLICATION FOR IONIC LIQUIDS PROPERTY ESTIMATION

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Ionic liquids (ILs) are a class of *neoteric* solvents composed of large organic cations and organic or inorganic anions that cannot form an ordered crystal and thus remain liquid at or near room temperature. The outstanding characteristics of these fluids, and the easy manipulation of their properties due to the possibility of interchange among thousands of cations and anions, make of the ILs “designer” solvents with a wide range of foreseeable applications.

Despite the exponential focus on ILs, both by academia and industry, the availability of thermophysical properties data is still limited and with questionable quality, making difficult the development of correlations and predictive models for these properties. It was however possible after a critical analysis of the available experimental data, complemented with further data measured at our lab to propose a number of predictive methods for the thermophysical and equilibrium properties of ionic liquids.

Based on the correlations and group contribution methods developed at our research group a on-line computer application was developed for the prediction of a number of thermophysical and equilibrium properties such as density, isobaric expansivity and isothermal compressibility, viscosity, surface tension, speed of sound, ionic conductivity, heat capacity, water solubility and carbon dioxide solubility in a wide temperature range.

The application developed will be presented and it will be discussed how it can be used for Computer Aided Molecular Design of Task Specific Ionic Liquids.

ACKNOWLEDGMENTS: Pedro J. Carvalho acknowledges the financial support from Fundação para a Ciência e a Tecnologia through his PhD. (SFRH/BD/41562/2007).

POSTER PRESENTATIONS, SESSION 4:

Industrial applications

P4.1: FRICTION AND WEAR MEASUREMENTS OF STEEL CONTACTS LUBRICATED WITH NEAT IONIC LIQUIDS

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Ionic liquids (ILs) are excellent candidates as lubricants and lubricant additives for mineral and synthetic oils by the combination of their unique properties such as high thermal stability, non-flammability, wide temperature range of liquid, good temperature viscosity behavior, very low vapor pressures and good flame resistance. The high polarity of ILs leads to strong and effective absorption films and tribochemical reactions that contribute to its important antiwear capacity [1-4]. Many studies have been focused on tetrafluoroborate and hexafluorophosphate, but it have been reported that salts of these anions produce corrosive HF in the presence of water that is inevitable in engine operation [5].

In this work we present the tribological behaviour of six ionic liquids. Samples were provided by Merck with 98% purity. Before experiments, all samples were treated by vacuum evaporation to remove the residual volatile impurities at room temperature, at least during 48 h. The water content of each liquid was determined before and after measurements by coulometric Karl Fischer titration using a Mettler Toledo DL32 The friction and wear behavior of a AISI 420 stainless steel plates with a hardness of about 245 HV lubricated with each one of the ILs have been studied using a 100Cr6 ball (hardness 838 HV). Experiments were conducted using a standardized reciprocating sliding test at ambient temperature with a CSM standard tribometer. Tests were performed under loads of 8 N, sliding speed of 0.02 m/s and a total distance of 20 m. Friction coefficients were continuously recorded with sliding distance for each test. Volume loss was determined from wear track width with a DEKTAK^3 profilometer. The specimen surface was characterized by using SEM and XEDS. The presence of undesirable tribochemical reactions in the surface was analyzed by XPS spectra.

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P4.2: PρT BEHAVIOR OF 1-ETHYL-3-METHYLIMIDAZOLIUM ETHYLSULFATE AND 1-(2-METHOXYETHYL)-1-METHYLPYRROLIDINIUM BIS(TRIFLUOROMETHYLSULFONYL)IMIDE

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Ionic liquids (ILs) have been investigated over the last decade for different applications, as lubricants and lubricant additives as well as in biorefining, biotechnology, chemicals and petrochemicals, CO_2-capture, environmental remediation, pharmaceuticals and waste treatment. To develop some of these applications, thermophysical properties, as densities in broad ranges of temperature and pressure, are needed. Moreover, PVT values are fundamental data for developing equations of state and solution theories, which are the main tool used for thermophysical properties prediction for process design purposes. Aparicio et al. [1] have recently analyzed the density data at high pressures for liquids available in the open literature. A high number of density data at high pressures correspond to ILs with tetrafluoroborate and hexafluorophosphate anions which are not very reliable for industrial applications. Data for new or environmentally friendly ILs are almost absent [1].

In this work, we have performed density measurements of 1-ethyl-3-methylimidazolium ethylsulfate, $[C_2C_1Im][C_2SO_4]$ and 1-(2-Methoxyethyl)-1-methylpyrro-lidinium bis(trifluoromethylsulfonyl)imide $[C_1OC_2C_1Pyrr][NTf_2]$. Density measurements were performed from 278.15 K to 398.15 K and pressures up to 120 MPa, using a fully automated vibrating tube densimeter Anton Paar HPM [2]. We should point out that we have not found in the literature density data at high pressures for ILs containing the cation $[C_1OC_2C_1Pyrr]^+$. The ILs samples used in this work were provided by Merck. Their water content was determined by Karl Fischer titration. Density values were correlated as a function of pressure and temperature with the modified Tamman-Tait equation. The isothermal compressibilities (κ_T) and the isobaric thermal expansivities (α_P) were determined and it was also analyzed the pressure effect on the unusual behaviour of α_P (the decreasing value of α_P with increasing temperature).

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ACKNOWLEDGMENTS: Authors acknowledge the advice and samples provided by Dr. Uerdingen from Merck. This work was supported by Spanish Ministry of Science and Innovation and FEDER Program through CTQ2008-06498-C02-01 project. T.R. acknowledges financial support under the FPU program. L.L. acknowledges the financial support of the Ramon y Cajal Program.

P4.3: NEW LONG-CHAIN ALKYLSULFATES IONIC LIQUIDS AS POTENTIAL LUBRICANTS

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The general properties of ionic liquids (ILs) such as non-volatily, non-flammability, chemical and thermo stability and environmentally friendly nature [1], make them ideal candidates for new lubricants [2]. As a part of the european project MINILUBES (**M**echanismis of **in**teractions in nano-scale of novel **i**onic **lub**ricants with functional surfac**es**), we have designed and synthesized nine new ionic liquids derived from ammonium and pyrrolidinium that incorporate long-chain alkanesulfates anions (Scheme 1). Their structures were selected according to the physical properties, toxicity and trybological behavior of previouslly described ILs [3]. The physical properties such us densities, heat capacities and dynamic viscosities of this series of ILs were studied as a function of temperature at atmospheric pressure. Phase transitions were determined by DSC. Studies of friction, wear and corrosion are currently under investigation.

[Et_3MeN][$BuSO_4$], where $R^1=R^2=R^3=Et$, $R^4=Me$, $R^5=Bu$
[Et_3MeN][$HexSO_4$], where $R^1=R^2=R^3=Et$, $R^4=Me$, $R^5=Hex$
[Et_3MeN][$OcSO_4$], where$R^1=R^2=R^3=Et$, $R^4=Me$, $R^5=Oc$
[$BuEtMe_2N$][$BuSO_4$], where $R^1=R^2=Me$, $R^3=Et$, $R^4=Bu$, $R^5=Bu$
[$BuEtMe_2N$][$HexSO_4$], where $R^1=R^2=Me$, $R^3=Et$, $R^4=Bu$, $R^5=Hex$
[$BuEtMe_2N$][$OcSO_4$], where $R^1=R^2=Me$, $R^3=Et$, $R^4=Bu$, $R^5=Oc$

[BuMepyr][$BuSO_4$], where $R^1=Bu$
[BuMepyr][$HexSO_4$], where $R^1=Hex$
[BuMepyr][$OcSO_4$], where $R^1=Oc$

Scheme 1: New ammonium and pyrrolidinium ionic liquids as potential lubricants.

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P4.4: SEPARATION OF SOUR GASES (CO_2 AND CH_4) USING IONIC LIQUIDS

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A class of *neoteric* organic solvents have gained an unprecedented bursting of interest, both by academia and industrial medium, in recent years. Ionic liquids (ILs) large organic cations and asymmetrical organic or inorganic anions compel these molecules to remain liquid at or near room temperature, while presenting, among others properties, negligible vapor pressures, high thermal stability, large liquidus range, nonflammability and high solvation capacity. The tunable properties of ILs, through an endless combination of cations and anions, allow the design of solvents for the development of more efficient and sustainable processes and products.

Nonetheless, and despite of the promising properties of ILs, further research is still required in order to make them solvents feasible candidates for real applications. Being a key parameter in the design of equilibrium stage– and rate–based separations, reliable gas solubility data is of most interest and a fundamental step towards the development of industrial applications, either by the data itself or by developing predictive and simulation tools to aid in the development of such applications.

Using a high pressure cell, previously used for extensive studies of CO_2 solubilities, VLE isotherms up to 363 K and pressures up to 100 MPa were measured for mixtures of CO_2 or CH_4 with several aprotic and protic ionic liquids. A comparison and evaluation of basic, fluorinated and protic ILs in a wide range of pressures and temperatures, aiming at a better understanding of the mechanisms of solvation of CO_2 and CH_4, was performed.

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P4.5: SOLUBILITY OF CARBOHYDRATES IN IONIC LIQUIDS

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ILs have been known as “greener” solvents when compared with volatile organic compounds (VOCs), essentially due to their negligible vapor pressure and high thermal and chemical stability [1]. They have been shown capable of dissolving numerous polar and non-polar compounds. In the past few years several research studies have demonstrated their potential to dissolve carbohydrates, including glucose, cellulose, sucrose, lactose, mannose, xylose, amylose, amylopectin, chitin, chitosan, inulin, pectin, starch, xylan, agarose, dextrin, and cyclodextrin [1, 2, 3, 4, 5]. In this study the solubility of six monosaccharides in different ILs was conducted in a large temperature range. Monosaccharides evaluated were D-(+)-Glucose, D-(+)-Mannose, D-(-)-Fructose, D-(+)-Galactose, D-(+)-Xylose and L-(+)-Arabinose. Solubilities of all monosaccharides in two hydrophilic ILs, 1-butyl-3-methylimidazolium dicyanamide and 1-butyl-3-methylimidazolium dimethylphosphate, were determined in the temperature range between 288.15 K and 348.15 K. Aiming at evaluating the IL anion influence on the solubility of carbohydrates two additional hydrophobic ILs were considered: trihexyltetradecylphosphonium dicyanamide, $[P_{66614}][N(CN)_2]$ and trihexyltetradecylphosphonium chloride, $[P_{66614}]Cl$. In the phosphonium-based ILs the solubility of D-(+)-Glucose was determined in the temperature interval from 298.15 K to 338.15 K. Hydrophilic ILs present solubility values higher than hydrophobic ILs. At lower temperatures dicyanamide-based ILs dissolve more sugars than chloride- or dimethylphosphate-based ILs. For both families it was observed a critical temperature turnover where $[C_4mim][DMP]$ and $[P_{66614}]Cl$ start to dissolve more carbohydrate contents than their dicyanamide-counterparts. From all the results it was observed that the IL anion plays the major goal in the solubility capacity of ILs for carbohydrates. This study showed the high potential of ILs to dissolve carbohydrates and represents a new contribution towards the carbohydrates chemistry.

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P4.6: ELECTROSPUN NANOSIZED CELLULOSE FIBERS USING IONIC LIQUIDS

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Electrospinning is one of the simplest and most effective methods for the production of polymers' nanosized fibers. This process is attractive since it is a cost-effective method capable of producing nanofibers from a large range of raw materials. The most important applications of electrospun fibers convey into fiber-reinforced composites, membranes, biosensors, electronic and optical devices, and enzyme and catalytic supports. However, the range of polymers that can be electrospun is still limited by the availability of common solvents and their limited capability of dissolving polymers. Cellulose, which is one of the most abundant renewable resources, and the main component of lignocellulosic materials, can be effectively dissolved in some ionic liquids (ILs) and further processed by electrospinning. Since ILs present extremely low vapor pressures, the electrospinning of cellulose from ILs would represent a major step towards the development of sustainable cellulose-based materials, while making use of more benign and environmentally friendly solvents than those typically employed.

The main goal of this work is to produce nanosized cellulose fibers from pure ionic liquids by electrospinning. Attempts were carried out aiming at selecting a low viscous ionic liquid at room temperature and with high potential to dissolve cellulose. Such properties will allow the use of a pure IL without requiring the addition of organic co-solvents or high temperature operating conditions. Therefore, the IL 1-ethyl-3-methylimidazolium acetate, $[C_2mim][CH_3CO_2]$, was chosen as the major solvent and electrospun fibers with average diameters within (470 ± 110) nm were obtained. In order to progressively decrease the cellulose fibers diameter, it was further added to $[C_2mim][CH_3CO_2]$ a second IL that could acts as a surfactant, namely, 1-decyl-3-methylimidazolium chloride ($[C_{10}mim]Cl$). Electrospun cellulose fibers from the binary mixture of ionic liquids presented an average diameter of (120 ± 55) nm. Electrospun cellulose fibers were analyzed by SEM (scan electron microscopy), POM (polarized optical microscopy), X-ray Diffraction Spectroscopy, FTIR (Fourier Transform Infra-Red Spectroscopy) and TGA (Thermogravimetric analysis) to evaluate their structural integrity, morphology and crystallinity.

P4.7: AQUEOUS BIPHASIC SYSTEMS COMPOSED OF POLYETHYLENE GLYCOLS AND IONIC LIQUIDS AND THEIR ABILITY TO EXTRACT BIOMOLECULES

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Water-immiscible organic solvents are commonly used in liquid-liquid extractions in industrial applications. However, they have several environmental problems associated with their use, which justify the recent concern on the development of “greener” solvents. In this context, Aqueous Biphasic Systems (ABS) are alternative and biocompatible media due to their predominant aqueous rich phases. In the past few years, ABS have shown to be an improved route for the separation and purification of biomolecules, such as proteins, enzymes, antibiotics, cell organelles and other biological products of interest [1]. Typical ABS are composed of polymer-polymer, polymer-salt, and salt-salt combinations. Nevertheless, recently it was shown that two immiscible aqueous phases could be formed through the concomitant addition of inorganic salts and ionic liquids [2]. Ionic liquids can be chosen from nonhazardous materials which exhibit negligible vapor pressures, non-flammability, and high chemical and thermal stability. Moreover, the possibility of controlling the inherent physicochemical properties of ionic liquids by designed combinations of the cation and/or anion opens a new path in the manipulation of the extraction phase properties for enhanced product recovery.

Recently, in exploratory works [3,4], salting-in/-out effects of inorganic salts *versus* ionic liquids in PEG aqueous media have been compared. In this work, a combination of common polyethylene glycols with ionic liquids is proposed for the formation of novel ABS. Ionic liquids have shown to be potential co-solutes capable of producing polyethylene glycol-based ABS if a careful selection of both polymer and ionic solvent is carried out. These systems, in which the two co-existing phases are aqueous, thus have potential application in novel biotechnological separations. Ternary phase diagrams will be presented at 298 K and several studies of practical application of those systems will be discussed. The partition coefficients of several biomolecules were determined and will be presented. The results obtained indicate improved extraction of different biomolecules using the systems proposed and, therefore, these could be an interesting approach in biotechnological separation processes.

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P4.8: SURFACE HYDROPHOBIZATION OF CELLULOSE NANOFIBERS IN IONIC LIQUIDS

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The rapidly growing quest for renewable resources capable of replacing petroleum based macromolecules, is giving to sources like polysaccharides a major importance [1]. Cellulose, the major component of plant cell walls, is one of the most studied polysaccharides. In addition, nanocellulose fibers have also attracted considerable attention in the last few years, namely, nanofibrillated cellulose (NFC) and bacterial cellulose (BC), and have been extensively explored for the development of new nanocomposites materials [1,2]. However, the extremely hydrophilic nature of cellulose fibers causes a very low interfacial compatibility with less polar polymeric matrices and for overcome this drawback it is necessary to reduce the polar character of the surface of cellulose fibers, for example, by controlled heterogeneous chemical modifications. Most of the chemical approaches described for the surface hydrophobization involve the use of harmful organic solvents like toluene [1,3], which represents an important concern when one considers the scale-up of this process.

In this context, we describe the heterogeneous hydrophobization of NFC and BC fibers with several anhydrides and fatty acyl chlorides in ionic liquids (low-melting-point salts with high stability and easy recyclability [4]) since this approach constitutes an important step on the increase of the green connotation of processes associated with the valorisation of this renewable resource.

The occurence of the surface modification was confirmed by elemental analyses, FTIR spectroscopy, and contact angle measurements. The crystallinity and morphology of the modified cellulose fibers were evaluated by X-ray diffraction and scanning electron spectroscopy, respectively, and the thermal stability was evaluated by thermogravimetric analyses.

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P4.9: ACTIVITY OF *THERMOMYCES LANUGINOSUS* LIPASE IN THE PRESENCE OF DIFFERENT FAMILIES OF IONIC LIQUIDS

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Due to their exceptional solvent properties, ionic liquids (ILs) are emerging as especially promising solvents for biocatalysis. In recent years, the potential of ILs in the field of enzymatic transformations has been highlighted and several reviews tackling this issue can be found. In this sense, ILs provide a new and powerful means for enzymes, in which they can catalyze reactions impossible in commonly used organic solvents. More specifically, in the case of lipolytic enzymes, stability and biocatalysis are the unique areas of research. Commercial lipase from *Thermomyces lanuginosus* (T*l*L) was initially oriented toward the food industry, but nowadays this enzyme has found applications in many different industrial areas, from biodiesel production to fine chemicals [1]. In the frame of our previous work [2] the knowledge of the physical properties of ILs (such as polarity, hydrophobicity and hydrogen-bond basicity) promoting enhanced enzyme activity is of extreme importance [3]. Ionic liquids with various structures and properties have been extensively investigated in many biocatalytic reactions and processes and particularly hydrophilic ILs are able to dissolve many substances that are not quite soluble in common organic solvents [4].

In this work, the lipolytic activity of T*l*L in aqueous solutions of imidazolium-based ILs was measured and several experimental parameters were tested. The results obtained were analyzed in terms of the ILs physico-chemical properties and within the Hofmeister series context.

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P4.10: IONIC LIQUIDS AS CO-SOLVENTS FOR LACCASE FROM *TRAMETES VERSICOLOR*

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There is an increasing interest on biocatalysis in ionic liquids (ILs), specially driven by the interest in replacing traditional volatile organic solvents by nonvolatile ILs. Non-aqueous media are widely used with enzymes, although their natural medium is water. Recent developments with enzymatic catalysis in ILs have mostly investigated enzymatic reactions with lipase [1,2]. However, some works in the field of biocatalysis in ILs or (IL+water) mixtures with oxidative enzymes have been published [3]. In order to develop a green biotechnological solution, the use of ILs as solvents or co-solvents in oxidative enzymatic reactions, such as the degradation of insoluble organic compounds, is a promissory alternative to be developed. Approaches to reduce the traditional solvents will be of great importance in cleaning up industrial effluents and reducing atmospheric emissions.

Results on the use of ILs as co-solvents for laccase-mediated reactions will be presented. ILs derived from the imidazolium ring were used. Laccase was obtained from fermentation broths of *Trametes versicolor* and purified by ultrafiltration and precipitation. A comparison between the fermentation broth and commercial laccase (obtained from Novozymes) will also be made.

The laccase activity was assayed using 2,2´-azino-bis(3-ethylbenzthiazoline-6-sulfonic acid) diammonium salt (ABTS) as substrate [4]. The stability of the enzyme in the ionic liquid aqueous solutions was evaluated after incubation in the reaction media through at least 1 week and up to 3 weeks. The kinetics of the ABTS degradation in these ionic liquid media were also studied experimentally.

The results obtained show that the enzyme stability is reduced with the concentration of the ILs. Besides, it was also found that enzyme is destabilized increasing the length of the alkyl chains in the imidazolium ring. As for the kinetics of the ABTS degradation, the Michaelis-Menten model proved to be inadequate for data correlation. Inhibitory effects of the ILs and of the substrate are reported. Models including these inhibitory effects were able to adequately correlate the experimental data.

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P4.11: IONIC LIQUIDS AND CADMIUM (II) REMOVAL FROM LIQUID EFFLUENTS

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Though cadmium is one of the metals most widely used in various industries, it is also considered as one of the most hazardous for humans, and whereas this element can be found in a series of liquid effluents derived from the industries which used it, its toxicity to humans is due to its carcinogen effect (group I) upon intake, and also to its damaging effects on kidney, bones, etc. Thus, the elimination of this element is a primary target in cadmium-bearing effluents. Removal of metals from liquid effluents is due by several technologies such as precipitation, liquid-liquid extraction, ion-exchange, etc., also in past years, supported liquid membranes-based techniques had gained a great interest due to the practical operational characteristics that they presented. On the other hand, and also recently, the application of ionic liquids in separations technology had gained a prominent position due to the properties that presented these compounds. Based in the above, this work presented results on the removal of cadmium from aqueous solutions using three interrelated technologies such are liquid-liquid extraction, flat-sheet supported liquid membrane (FSSILMs) and pseudo-emulsion membrane based strip dispersion (PEMSD), in which several ionic liquids were tested as extractants or carriers for the metal. Since cadmium(II) can be presented in aqueous solutions both as cation Cd^{2+} or forming a series of successive chloro-complexes $CdCl_n^{2-n}$, with n= 1 to 4, ionic liquids with different transfer properties were properly used according with the metal species to be extracted or transported.

In the case of liquid-liquid extraction operation, experiments on the use of CYPHOS IL101 (quaternary phosphonium chloride) or the quaternary ammonium salt formulated as $(A324H^+)(Cl^-)$, and derived from the tertiary amine Hostarex A324, were carried out on cadmium solutions from neutral or acidic (HCl) media. An extraction percentage of more than 90% was regularly found for both ionic liquids. CYPHOS IL101 system was also implemented in PEMSD technology. In PEMSD, pseudo-emulsion is an emulsion that is formed temporarily between the continuous organic and the dispersed stripping solutions, being both solutions separated when the stirring device is stopped. Removal of the target species from the feed solution is around 90%, whereas the recovery in the ammoniacal strip solution is around 80%.

The liquid-liquid extraction of Cd(II) from aqueous solutions was also successfully carried out using the ionic liquids 1-methyl-3-octylimidazolium tetrafluoroborate, $[omim^+][BF_4^-]$ and methyltrioctylammonium chloride, $[MTOA^+][Cl^-]$ as extraction agents, with extraction percentages around 98%. Flat-sheet supported liquid membrane (FSSILMs) were prepared using these ionic liquids and tested for the recovery of Cd(II). It is worthy to note that recoveries higher than 80% of Cd(II) was achieved with the FSSILMs based on [MTOA$^+$][Cl$^-$] using ammonia 6M as strippant phase.

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P4.12: ON THE USE OF SUPPORTED IONIC LIQUIDS MEMBRANES AS PROTON EXCHANGE MEMBRANES IN MICROBIAL FUEL CELLS

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Technical feasibility of microbial fuel cells (MFCs) has been proven recently so there is great enthusiasm in the scientific community that MFCs could provide a source of "green electricity" exploiting domestic and industrial wastes to generate power. By using organic matter in wastewaters as a fuel, simultaneously to energy generation contaminants are removed from water [1]. So far, MFCs have generated low levels of power using expensive components. The proton exchange membrane (PEM) is a critical component determining the efficiency of MFC. Perfluorinated ionomer membranes such as Nafion® have been widely used as polymer electrolyte membranes of MFCs, because of their high proton conductivities in the fully hydrated state. However, these membranes are still expensive which make their use prohibitive in large-scale application. The immobilization of ionic liquid in polymeric membranes could open up this field of improvement in MFCs. Ionic liquids (ILs) are organic salts that are liquid close to room temperature and possess other unique properties that are interesting in the context of MFCs. For instance, they show high ion conductivity and high chemical and thermal stability. Furthermore, their properties can be varied by alternating the cation or the combined anion which makes ILs a task-specific material [2]. In this work, the potential use of supported ionic liquids membranes based on $[MTOA^+][Cl^-]$, $[omim^+][PF_6^-]$, $[omim^+][BF_4^-]$ and $[omim^+][NTf_2^-]$ were evaluated as proton exchange membranes in one chamber MFCs with cathodes of platinum sprayed on carbon cloth working with a 1 kΩ external resistor. Nafion® and Ultrex® membranes where used as reference PEMs. The maximum voltage (140 mV) was reached using supported liquid membranes based on $[omim^+][PF_6^-]$, which was higher than that obtained with Nafion® and Ultrex®. For the rest of SILMs, this parameter was similar to the reference membranes (~100 mV). Regarding the removal of organic matter from the waster water, more than 80% chemical oxygen demand removal (CODR) was reached using membranes based on $[MTOA^+][Cl^-]$, $[omim^+][BF_4^-]$ and $[omim^+][NTf_2^-]$, which was similar to that obtained with Nafion® and Ultrex®. Therefore, the potential use of supported liquid membranes based on ionic liquids as PEM in MFCs has been demonstrated, reaching COD removal and energy generation similar than that obtained with conventional PEM such as Nafion® and Ultrex®.

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P4.13: SELECTIVE SEPARATION OF ZN^{+2}, CU^{+2} AND FE^{+3} FROM AQUEOUS SOLUTIONS USING SUPPORTED IONIC LIQUID MEMBRANES

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Several technologies can be used to remove toxic metals from liquid effluents, including precipitation, solvent extraction and ion exchange. However, some difficulties are associated with low concentration of the components and heterogeneous mixtures with different amounts of non-desiderable compounds. Membrane-based separation processes have been recognized as an alternative to overcome these drawbacks. Among membrane-based separation processes, the use of supported ionic liquid membranes (SILMs) has received growing attention during recent years [1,2]. SILMs are porous supports whose pores are filled with an ionic liquid.

In this work, the recovery of metal ions from aqueous solution using SILMs is analysed. Flat-sheet supported liquid membranes based on the ionic liquids [MTOA$^+$][Cl$^-$], [omim$^+$][BF$_4^-$] and [omim$^+$][PF$_6^-$] have been used for the selective separation of Zn(II), Cu(II) and Fe(III) from hydrochloride aqueous solutions. These membranes were developed by physical immobilization of the ionic liquid in a Nylon® porous membrane. The transport studies were performed at 30ºC using a glass diffusion cell with two independent compartments, with 30 mL each, separated by the SLM. In each experiment, the initial metal ion concentrations in the feed phase were 0.1 g/L. Milli-Q water, 0.1M sodium carbonate and 6M ammonia were tested as a strip solution. The metal ions concentrations were monitored by AA. It is worthy to note that recoveries higher than 80% of Fe(III) was achieved with a FSSILMs based on [MTOA$^+$][Cl$^-$] and water as strippant. Furthermore, this membrane allowed the selective separation of the metal ion couples Fe(III)/Zn(II), Fe(III)/Cu(II) y Zn(II)/ Cu(II).

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P4.14: NEW PYRIDINIUM IONIC LIQUIDS AS SOLVENTS FOR DESULFURIZATION OF FUELS

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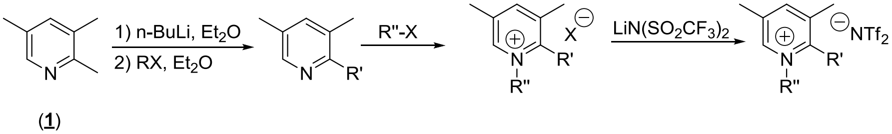
Production of low sulfur fuel has become a main objective of petroleum refining industry. One of the most promising techniques for this proposal is the extractive desulfurization, and researching efforts over the last years are being focused on finding the most suitable solvent for desulfurization purposes.

Because of their good qualities as solvents, such as a negligible vapor pressure, thermal stability, wide liquid range and nonflammability, ionic liquids (ILs) have been proposed as suitable solvents for the extraction of sulfur compounds from transportation fuels [1]. From these salts, highly substituted pyridinium based ILs with high cation size are showing the most promising results [2].

In this work we describe the synthesis of a series of highly substituted pyridinium based ILs from commercial 2,3,5-trimethylpyridine (**1**). The treatment of **1** with *n*-BuLi, followed by addition of an alkylating agent afforded the corresponding 2-alkyl-3,5-dimethylpyridine. Different reaction conditions (temperature, time, reagent concentrations and solvent) were needed to be tested in order to avoid undesirable polyalkylated compounds. Target ILs were then prepared using standard methodology, which involved alkylation of the substituted pyridine with an alkyl halide and subsequent metathesis reaction (Scheme 1).



Scheme 1.- Synthesis of 1,2,3,5-tetralkylpyridinium ILs.

The suitability of $[^1E^3M^5M^5PPy][NTf_2]$ and $[^1B^3M^5M^2PPy][NTf_2]$ as solvents in extraction of sulfur compounds from fuels was analysed by testing the ILs capacity to extract thiophene from heptane. Liquid-liquid equilibrium data for ternary systems were obtained. Composition of the equilibrium phases was analyzed by NMR.

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CURSOS E CONGRESOS
Nº 205

2ndIMIL. 2nd Iberian Meeting on Ionic Liquids

2nd IMIL continues and consolidates the successful tradition started in Aveiro in June 2009 of holding meetings of the Iberian community of researchers on ionic liquids every two years. The main aim of these meetings is to bring together Iberian specialists (as well as contributors from other parts of the world) working in this field in order to share our respective knowledge and expertise in the many fields of research connected to ionic liquids. We aim to create the perfect environment to bring about fruitful synergies among the Iberian Community in this promising, exciting and rapidly evolving field.

The program for 2nd IMIL includes 28 oral and 58 poster presentations. Included among the oral presentations are an opening lecture and four invited plenary lectures regarding the different topics to which the several sessions are devoted: synthesis and extraction, experimental measurements and theoretical and simulation models.

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