IMIL 2015 Madrid

2-3 July 2015

IBEROAMERICAN MEETING ON IONIC LIQUIDS

Book of Abstracts

CENTRO CULTURAL LA CORRALA – MADRID (SPAIN)

UNIVERSIDAD AUTONOMA DE MADRID

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Book of Abstracts of the Iberoamerican Meeting on Ionic Liquids 2015
2nd – 3rd July 2015, Madrid – Spain
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WELCOME MESSAGE

The IMIL2015 Organizing Committee, Scientific Committee and Honorary Committee welcomes you to Madrid, Spain, to this opportunity for the Iberoamerican Scientific Community to share the most recent achievements on their research on Ionic Liquids.

Iberoamerican Meeting on Ionic Liquids 2015 (IMIL2015) continues the spirit of the previous Iberian Meetings on Ionic Liquids, bringing, for the first time, this promising, exciting and rapidly evolving conference to the Iberoamerican Community of specialists. IMIL 2015 attempt to unite research groups starting out in the ionic liquid field with more experienced groups, and to cover the wide variety of disciplines currently being investigated on this subject.

The program for IMIL2015 includes 32 oral and 117 poster presentations evolving different topics on ionic liquid research: synthesis and thermophysical properties, reaction and separation process, biotechnology, advanced materials and electrochemical applications.

The conference IMIL2015 will bring together more than 130 researchers from 13 countries: Brazil, Chile, France, Germany, Italy, India, Japan, Poland, Portugal, Qatar, Spain, United Kingdom and United States of America.

The present IMIL is the fourth in a series of biannual conferences on Ionic Liquids held in Iberian Peninsula since 2009. Previous locations were:

2009 – Aveiro (Portugal)
2011 – Santiago de Compostela – A Coruña (Spain)
2013 – Algarve (Portugal)

We thank you for your participation in the Iberoamerican Meeting on Ionic Liquids 2015, and we wish you a stimulating and rewarding time at the conference and a pleasant visit to our lively city.

On behalf of the IMIL 2015 Organizing Committee,

José Palomar, UAM
Francisco Rodríguez, UCM

IMIL2015 Chairmen

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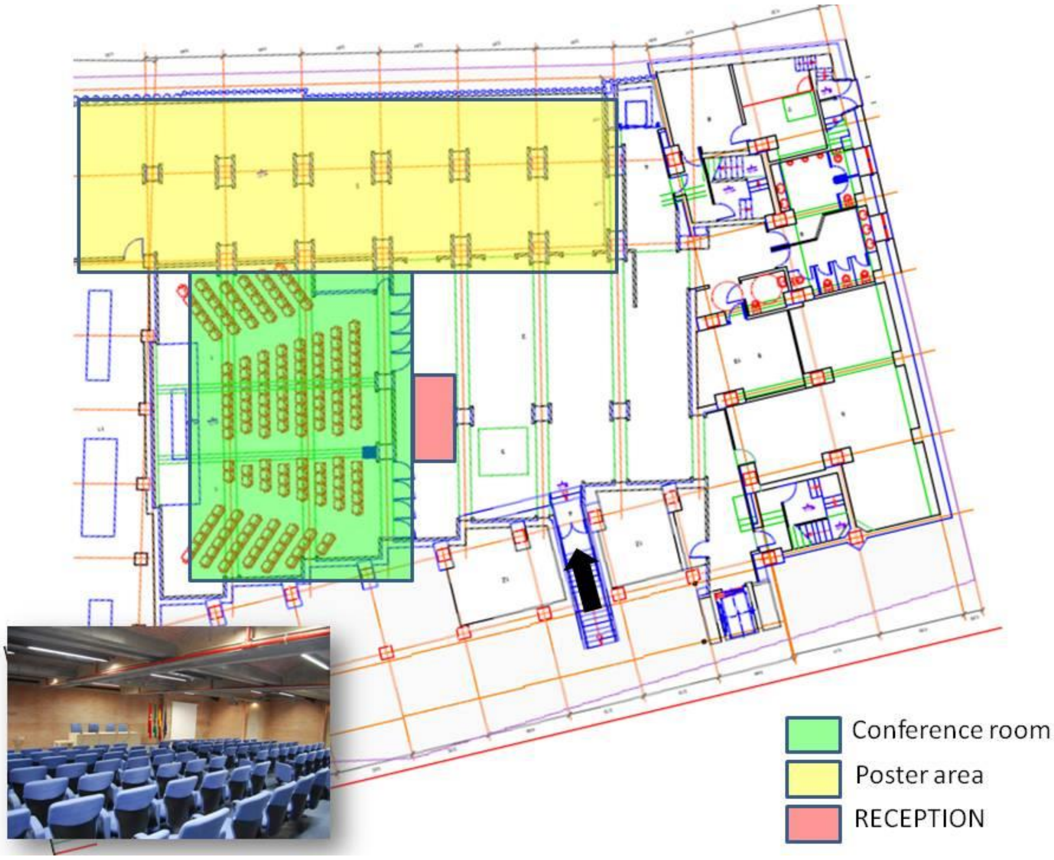
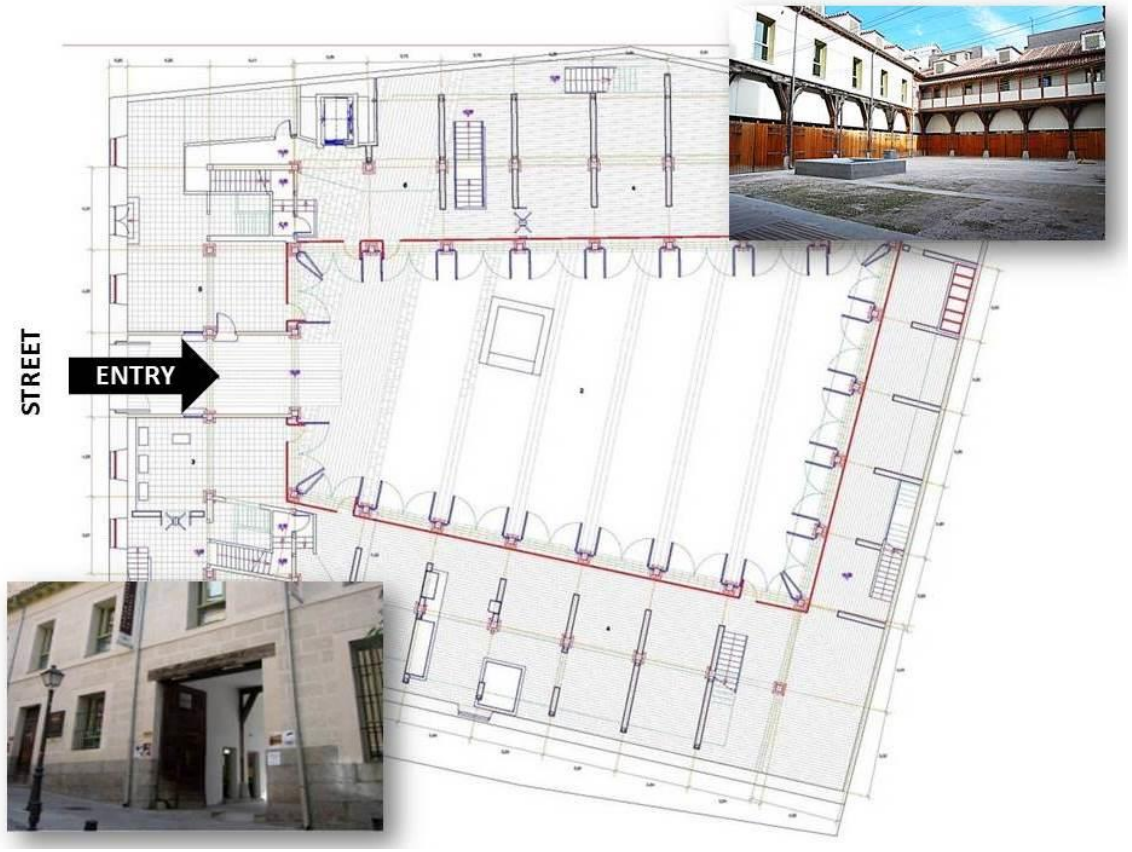
CONFERENCE VENUE

IMIL 2015 meeting will be held in the **"La Corrala" Cultural Center** of the Universidad Autonoma de Madrid, a traditional Madrid-style building located in the historical city center, in a zone where every Sunday El **Rastro**, the most popular open air flea market in Madrid takes place.

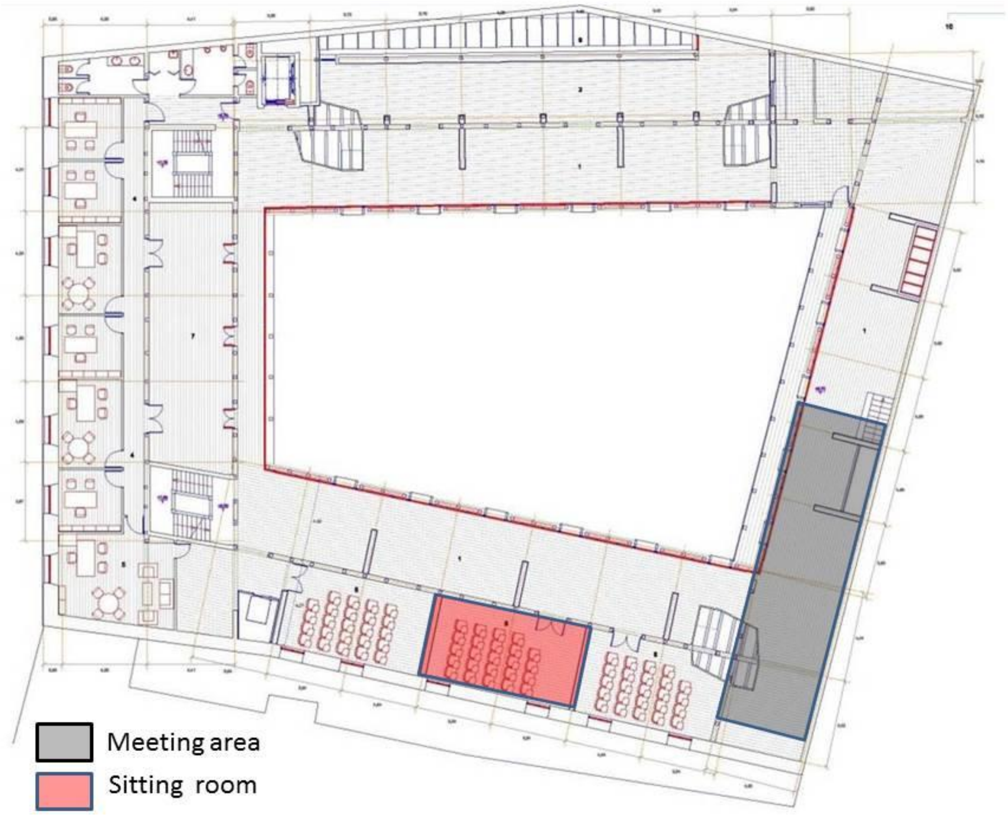
"La Corrala" Cultural Center has the **Museum of Popular Arts and Traditions**, with a collection of more than 8000 pieces of ethnographic and anthropological interest, which can be visited by IMIL2015 participants free of charge.

The **Conference Room** and **Poster Area** of IMIL2015 are located in the basement of the building.





On the second floor of the **“La Corrala”** building are located the **Meeting area** and **Sitting room** with Wifi and electrical outlets for laptops or other devices.



PLENARY LECTURES

Joan F. Brennecke

Keating-Crawford Professor of Chemical and Biomolecular Engineering Department of University of Notre Dame, Indiana (USA).

Presentation Title: Ionic liquids for post-combustion CO_2 capture.

Mara G. Freire

Coordinator Researcher at CICECO, Chemistry Department, University of Aveiro (Portugal).

Principal investigator of a Starting Grant from the European Research Council (ERC).

Presentation Title: Ionic Liquids as Alternative Solvents for the Extraction, Purification and Concentration of High-Value Proteins: from Biopharmaceuticals to Cancer Biomarkers.

Tom Welton

Professor of Sustainable Chemistry at Imperial College of London (United Kingdom).

Dean of the Faculty of Natural Sciences.

Presentation Title: Fine-tuning ionic liquid mixtures.

KEYNOTES

Jairton Dupont – UFRGS (Brazil)
University of Nottingham (United Kingdom)

Pedro Lozano - University of Murcia (Spain)

Rebeca Marcilla - IMDEA Energy (Spain).

Héctor Rodríguez - University of Santiago de Compostela (Spain)

PROGRAM

Thursday, July 2nd 2015

9:00	Registration
9:30	Opening Session
Chair Vice Rector	Jose Palomar, Francisco Rodríguez Rafael Garesse

SESSION I. *Chairman: M. Rodríguez, Universidad Politécnica de Madrid*

10:00 **PL1**	**Ionic Liquids for Post-Combustion CO_2 Capture** J. F. Brennecke
10:45 **O1**	**Utilization of Choline Chloride and Levulinic Acid Based Deep Eutectic Solvents for Efficient CO_2 Capture** M. Atilhan
11:00 **O2**	**Greenhouse and Acid Gases with Ionic Liquids - Predictive Model** L. F. Vega
11:15 **O3**	**Experimental Studies on the Dissolution and Dispersion of Four Indian Coals** T. Banerjee
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SESSION II. *Chairman: S. Aparicio, Universidad de Burgos*

12:00 **KN1**	**Phase Equilibria in Mixtures of Ionic Liquids** H. Rodríguez
12:30 **O4**	**Increasing the Tuneability of Ionic liquids** A. B. Pereiro
12:45 **O5**	**Renewable Lipidic Ionic Liquid Crystals: Cation-Anion Effects on SLcLE** G. Maximo
13:00 **O6**	**Rheological and thermodynamic properties of deep eutectic solvents** I. M. Aroso
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14:30	Coffee + Poster Session I (Meeting venue)

SESSION III. *Chairman: A. G. M. Ferreira, Universidade de Coimbra*

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15:45 **O9**	**Bulk Structure and Transport Properties of Protic-Aprotic Ionic Liquid Mixtures: Imidazoles and Ammonium Nitrates** B. Docampo-Álvarez
16:00 **O10**	**Mechanistic Studies on the Beckmann Rearrangement in Ionic Liquids** E. Tojo
16:15 **O11**	**Organic Reactivity in Ionic Liquids: the Role of the Anion** C. S. Pomelli
16:30 **O12**	**Thermal Stability of Ionic Liquids** J. Salgado
16:45 **O13**	**Process Simulation in the Design/Selection of Ionic Liquids** J. de Riva
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Friday, July 3th 2015

SESSION IV. *Chairman: R. M. Torresi, Universidade de Sao Paulo*

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10:15 **O14**	**Ionic Liquids as Extractive Solvents of Terpenes and Terpenoids** M.A.R Martins
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12:45 **O20**	**Polymer and Ionic Liquids: A Successful Combination** S. Livi
13:00 **O21**	**Novel Aqueous Biphasic Systems Composed of ILs and Copolymers** F.A. e Silva
13:15 **O22**	**Synthesis and Gas Separation Performance of Copper(I)-Containing Poly(RTIL)-RTIL Composite Membranes** G. Zarca
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16:00 **O23**	**Study of Ionic Liquids Electrolytes for Dye-Sensitized Solar Cells** J. M. Vicent-Luna
16:15 **O24**	**Potential Induced Restructuring at Ionic Liquids Electric Double Layer** R. Costa
16:30 **O25**	**Transport Properties in Phosphonium Ionic Liquids and its Lithium Mixtures.- R. M. Torresi** R. M. Torresi
16:45	**Presentation IMIL2017** J. F. B. Pereira
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List of Abstracts

Plenaries

PL 1

Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Ionic Liquids for Post-Combustion CO_2 Capture

Joan F. Brennecke

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Ionic liquids (ILs) present intriguing possibilities for removal of carbon dioxide from a wide variety of different gas mixtures, including post-combustion flue gas, pre-combustion gases, air, and raw natural gas streams. Even by physical absorption, many ILs provide sufficient selectivity over N_2, O_2, CH_4 and other gases. However, when CO_2 partial pressures are low, the incorporation of functional groups to chemically react with the CO_2 can dramatically increase capacity, while maintaining or even enhancing selectivity. We will demonstrate several major advances in the development of ILs for CO_2 capture applications. First, we will show how the reaction stoichiometry can be doubled over conventional aqueous amine solutions to reach one mole of CO_2 per mole of IL by incorporating the amine on the anion. Second, we will show how we have been able to virtually eliminate any viscosity increase upon complexation of the IL with CO_2, by using aprotic heterocyclic anions (AHA ILs) that eliminate the pervasive hydrogen bonding and salt bridge formation that is the origin of the viscosity increase. Third, we will describe the discovery of AHA ILs whose melting points when reacted with CO_2 are more than 100 °C below the melting point of the unreacted material. These materials allow one to dramatically reduce the energy required for CO_2 release and regeneration of the absorption material because a significant amount of the energy needed for the regeneration comes from the heat of fusion as the material releases CO_2 and turns from liquid to solid.

Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Ionic Liquids as Alternative Solvents for the Extraction, Purification and Concentration of High-Value Proteins: from Biopharmaceuticals to Cancer Biomarkers

Mara G. Freire

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In the past few years, novel applications of ionic liquids (ILs) have been proposed in biomedical fields. These include the synthesis of novel ILs with pharmaceutical and antitumor features, as enhanced and alternative solvents for the synthesis of the most diverse drugs, for the enantiomeric resolution of pharmaceutical products, for the separation and recovery of bioproduced antibiotics, as supported materials for drug delivery, among others.[1] Based on these promising results, the development of novel applications involving ILs within the biomedical field is facing a continuous intensification.

In the past few years, our research team has been addressing the use of ILs for the purification of proteins, in particular antibodies from complex media for use in passive immunotherapy, and for the concentration of cancer biomarkers from human fluids envisaging early-stage diagnoses. By virtue of their tunability, ILs can "ideally" cover the whole hydrophilicity–hydrophobicity range, and examples of their successful application as integrated extraction, purification and concentration platforms will be presented. Furthermore, examples of the products recovery and new strategies to guarantee the solvents recyclability will be demonstrated.

Acknowledgements
This work was developed in the scope of the project CICECO-Aveiro Institute of Materials (Ref. FCT UID/CTM/50011/2013), financed by national funds through the FCT/MEC and when applicable co-financed by FEDER under the PT2020 Partnership Agreement. M. G. Freire acknowledges the European Research Council (ERC) for the Starting Grant ECR-2013-StG-337753.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Fine-tuning Ionic Liquids Mixtures

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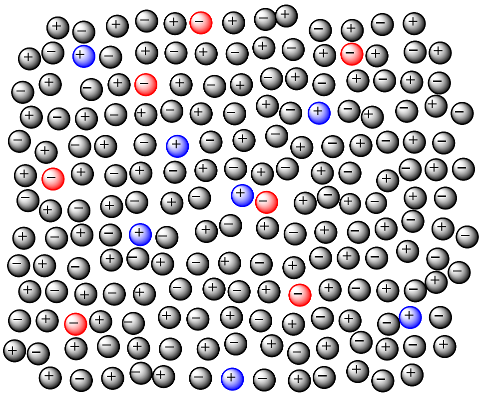
Ionic Liquids (ILs) are by definition liquids composed exclusively of ions. The large range of possible combinations of cations and anions has led to ionic liquids being described as 'designer solvents'.[1] This is even greater when one includes the ability to ionic liquids. [2] However, to realise these advantages it is necessary to understand how ionic liquids behave when mixed.

We have investigated the physicochemical properties [3] of a wide range of mixtures of ionic liquids. The mixing of these ionic liquids has shown itself to be remarkably close to ideal. We have also related this to spectroscopic results that indicate the underlying structural behaviour that leads to these observations. These suggest that the pre-eminence of the Coulomb interactions in ionic liquids is the primary driver of these behaviours, with other interactions only driving secondary effects.



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Keynotes

Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Phase Equilibria in Mixtures of Ionic Liquids

Héctor Rodríguez[a]*, María C. Castro[a], Olga Stolarska[b,c], Alberto Arce[a], Ana Soto[a], Marcin Smiglak[b]

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In recent years there has been a growing interest in the investigation of homogeneous mixtures of ionic liquids for their use in a variety of potential applications.[1] A straightforward option consists of mixing two or more ionic liquids that are already liquid at the temperature of interest. Alternatively, new ionic liquids with three or more different ions can be obtained via the combination of ionic liquids or salts with higher melting points that produce a eutectic system.[2] We have investigated the solid-liquid equilibria in a number of such kind of systems, and we have determined the eutectic composition of the mixture as well as the increment in the liquid range of operation as compared to the parent compounds.[3] For the eutectic compositions, a series of physical properties have been measured, and pertinent comparison with the values for the parent compounds has also been carried out.

Besides the combination to form new homogeneous liquids with unique characteristics, some mixtures of ionic liquids can lead to liquid-liquid immiscible systems, thus generating totally ionic and totally liquid systems with two phases in equilibrium.[4] This kind of systems remains largely unexplored to date. With the aim of increasing the knowledge of the behaviour of this type of systems, we have accurately determined the liquid-liquid equilibrium of binary mixtures of ionic liquids with a common ion, in particular an anion of a basic character (chloride or acetate).[5] Thermodynamic properties of the mixing of these compounds have been analysed.

Research financed in parts by National Science Centre (Poland), project SONATA (No. 2011/03/D/ST5/06200). We acknowledge Xunta de Galicia (Spain) for support through project EM 2012/042, and the Galician Network on Ionic Liquids (REGALIs).

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[4] A. Arce, M.J. Earle, S.P. Katdare, H. Rodríguez, K.R. Seddon, Mutually immiscible ionic liquids, Chem. Commun. (2006) 2548-2550.

[5] M.C. Castro, A. Arce, A. Soto, H. Rodríguez, submitted.

KN 2

Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
July 2-3, 2015 • Madrid • Spain

Sponge-Like Ionic Liquids and Supercritical Fluids, as new platform for Green Chemical Processes

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Chemistry necessitates a paradigmatic shift from traditional concepts of chemical process efficiency, which focus largely on chemical yield, to ones that assign economic value to eliminating waste at source, reusing solvents and avoiding the use of toxic and/or hazardous substances. Enzymes clearly constitute the most powerful green tools for catalyzing chemical processes, because their activity and selectivity (stereo-, chemo- and regioselectivity) for catalyzed reactions are far-ranging. Ionic liquids (ILs) and supercritical fluids (SCFs) are the non-aqueous green solvents which have received most attention worldwide for use in biocatalysis. Research on enzymatic catalysis in ILs was firstly focused on the potential of these neoteric solvents as reaction media, then on understanding the exceptional behaviour of enzymes in some kinds of ILs, and finally on the development of integrated biotransformation / separation systems. In such enzymatic processes, the unique properties of supercritical carbon dioxide (scCO$_2$) to extract, dissolve and transport chemicals, are tarnished by the denaturative effect it has on enzymes. Biphasic systems based on ILs and scCO$_2$ have been proposed as the first approach to integral green bioprocesses in non-aqueous media, where both the biocatalytic and extraction steps are coupled in an environmentally benign and efficient reaction/separation process in continuous operation.**[1]** Several types of continuous reactors based on enzymatic or chemoenzymatic catalysis have been tested with excellent results, *e.g.* dynamic kinetic resolution of *rac*-1-phenylethanol.**[2]**

Alternatively, sponge-Like Ionic liquids (SLILs) are hydrophobic ILs based on cations with long alkyl side-chains, *e.g.* octadecyltrimethylammonium bis(trifluoromethylsulfonyl)imide, ([C$_{18}$tma][NTf$_2$]), which behaves as sponge-like systems by switching from liquid to solid phase with temperature. Based on this new property, the SLILs have been used to develop straightforward and clean approaches for extraction and synthesis of nearly pure compounds of added value (*e.g.* geranyl acetate, anisyl acetate, biodiesel, etc). As liquid phases, the SLILs are able for dissolving (soaking) hydrophobic compounds at temperatures compatible with enzyme catalysis (*e.g.* vegetable oil and methanol mixtures are monophasic in [C$_{18}$mim][NTf$_2$] at 50°C). The resulting monophasic systems showed an excellent suitability for carrying out lipase-catalyzed esterification and transesterification reactions (*e.g*, terpene ester synthesis**[3]**, biodiesel synthesis**[4]**). As solid phases by cooling the reaction mixture under room temperature, the system can be fractionated by releasing (wringing) products from the SLIL using iterative centrifugations, which resulted in two phases: a solid SLIL phase and a liquid phase containing synthetic products, being facilitated by using centrifugal filters (see Fig. 1). For the biodiesel production case, the addition of water into the liquid reaction mixture resulted in a three phase system after the centrifugation/separation step, *i.e.* solid SLIL (bottom), aqueous phase containing glycerol (middle), and pure biodiesel phase (top phase, see Fig. 1), demonstrating the suitability of this green approach for producing biodiesel of easy scaling-up.

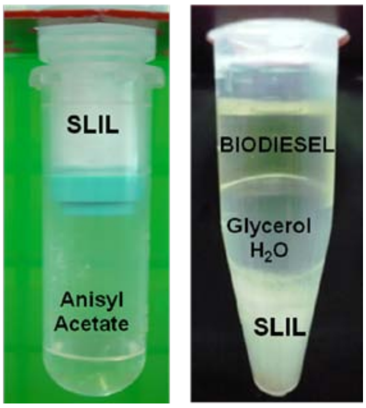

Fig. 1. Phase behavior of SLIL-reaction media after the separation step.

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Acknowledgements. Work partially supported by MINECO, Spain (Ref: CTQ2011-28903), and SENECA Foundation, Spain (Ref: 08616/PI/08) grants.

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Supported Ionic Liquid Phase Nanoparticle Catalysts

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Ionic liquids (ILs), in particular imidazolium-based ILs, have proven to be suitable media for the generation and stabilisation of soluble metal nanoparticles (NPs). Indeed, transition-metal NPs with small sizes, narrow size distribution and different shapes have been prepared by reduction of organometallic compounds with molecular hydrogen, decomposition of transition-metal complexes in the zero-valent state, metal bombardment or simple transfer for previously prepared water- or classical organic solvent-soluble colloids to the ILs. The formation and stabilisation of NPs in these highly hydrogen bonded organised supramolecular fluids occur with the re-organisation of the hydrogen bond network and the generation of nanostructures with polar and non-polar regions, including the NPs. The IL forms a protective layer, which is probably composed of imidazolium aggregates located immediately adjacent to the nanoparticle surface, which provides both steric and electronic protection against aggregation and/or agglomeration. These stable transition-metal NPs immobilised in the ILs have proven to be efficient green catalysts for several reactions in multiphase conditions. The catalytic properties (activity and selectivity) of these soluble metal NPs indicate that they possess a pronounced surface-like (multi-site) rather than single-site-like catalytic properties. In particular, the preparation, stabilisation and catalytic properties of mono and bimetallic NPs in ILs for the partial hydrogenation of benzene will be discuss in details.

Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Application of Ionic Liquids and Their Polymer Electrolytes in Electrochemical Energy Storage

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Ionic liquids (ILs) are organic salts with a low melting point (<100 ºC) which are widely investigated due to their chemical stability, low flammability, negligible vapour pressure, high ionic conductivity and wide electrochemical window.[1] In the last decade, ionic liquids have emerged as one of the most promising candidates as liquid electrolytes in advanced electrochemical devices such as batteries, supercapacitors, fuel cells, electrochromic devices and solar cells.[2] One of most dynamic research topic in the field of electrochemical energy storage is the replacement of the liquid electrolyte by solid or quasi-solid electrolytes in devices such as batteries and supercapacitors. In those cases, solid or quasi-solid electrolytes have important advantages including mechanical stability, safety and simple processing. In the last years, the combination of Ionic Liquids with Polymers has emerged as a hot topic in the field of Polymer Electrolytes since most of the attractive properties of ILs might be translated to the polymer electrolyte that presents higher ionic conductivity, higher thermal stability and improved electrochemical stability than other polymer electrolytes.[3]

In this talk, a general overview of the recent advances in the application of Ionic Liquids and their Polymer Electrolytes in Electrochemical Energy Storage will be reported. Special attention will be paid to the research activities being developed in our group focused on the application of these innovative Ionic Liquid electrolytes in supercapacitors [4] and batteries.

Acknowledgement: R.M. acknowledges financial support from the Spanish Government through the Ramón y Cajal Program (RYC-2011-08093) and ENE2012-31516 Project and from the European Commission though the RENAISSANCE ITN Project (Grant Agreement no. 289347).

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Oral Comunications

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Utilization of Choline Chloride and Levulinic Acid Based Deep Eutectic Solvents for Efficient CO_2 Capture

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Choline chloride ([Ch][Cl]) + levulinic acid [LA] deep eutectic solvent (DES) is studied as a suitable material for CO2 capturing purposes. The most relevant physicochemical properties of this solvent are reported together with the CO_2 solubility as a function of temperature. A theoretical study using both Density Functional Theory and Molecular Dynamics approaches is carried out to analyze the properties of this fluid from the nanoscopic viewpoint and their relationship with the macroscopic behavior of the system and its ability for CO_2 capturing. The behavior of liquid – gas interface is also studied and its role on the CO_2 absorption mechanism is analyzed. The combined experimental plus theoretical reported approach leads to a complete picture of the behavior of this new sorbent with regard to CO_2, which together with its low pricing, and the suitable environmental and toxicological properties of this natural solvent, lead to a promising candidate for CO2 capturing technological applications. Characterization techniques such as TGA, FTIR, viscosity, density, pH, and thermal conductivity analysis have been performed. Both in-situ FTIR and gas solubility measurements have also indicated the suitability of this material for CO_2 and other gases solubility. Rubotherm® sorption apparatus was employed for very accurate gas solubility experiments up to 30 bars and at 25 ºC and 50 ºC. Initial findings are reported in this communication and CO_2 solubility in [Ch][Cl]:[LA] was found to be as 2.12 mmol/g. moreover, corrosive behavior of the DES system have been experimented and compared with the most common amine based system and it has been observed that DES system has order of magnitude less corrosive behavior than the classical MEA CO_2 absorbent system.

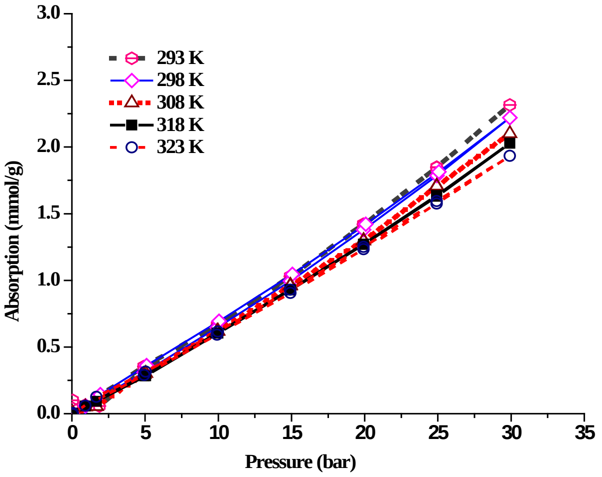

Figure. High pressure CO_2 solubility in CHCL_LEV_1_2 DES system at various isotherms up to 30 bars.

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Greenhouse and Acid Gases with Ionic Liquids – Predictive Model

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One of the ionic liquids (ILs) applications that are raising more interest today is their use as solvents to carry the conversion of CO_2 into more valuable compounds. CO_2 usually comes as a residue from plant effluent streams, mixed with other greenhouse gases (CH_4, CO, etc.) or hazardous pollutants, such as H_2S and SO_2. This process can be seen as an alternative to the conventional technology of using chemical absorption through an aqueous solution of amine, which has important drawbacks, including loss of solvent, corrosion of facility, and high energy demand regeneration of the absorbent [1].

However, there is still a need for a further understanding of the dependence of the gas behavior on the ionic liquid microscopic structure in order to enhance their design for *ad-hoc* applications. Molecular modeling techniques provide an excellent framework to progress on this field. We will present and discuss here results concerning the application of the soft-SAFT equation of state[2] to describe the solubility of greenhouse and acid gases on different imidazolium ILs with different anions, in order to study their feasibility for gas separation and conversion. A simple but reliable molecular model, within the framework of the soft-SAFT equation of state is presented for each IL, based on structural information and molecular simulations, and coarse-grained models are used to model the different gases. The absorption of relevant gases for the separation/conversion process (CO_2, CH_4, CO, H_2, SO_2, H_2S, N_2O) in the ILs is modeled and compared with experimental data using a minimum amount of binary data. From this information, ternary diagrams are predicted, and the selectivity of CO_2 by respect other gases is evaluated, determining the most appropriate solvent and the optimal operating conditions to maximize gas separation [3].

Acknowledgments: *Partial support was provided by a Transbio SUDOE collaborative project (TRANSBIO-BCN-GT2-A1-03), the Catalan Government (2014SGR-1582). M.B. Oliveira acknowledges for her Post-Doctoral grant (SFRH/BPD/71200/2010). This work is financed by FEDER funds through Programa Operacional Factores de Competitividade – COMPETE and by Nacionais funds through FCT – Fundação para a Ciência e Tecnologia through project CICECO - FCOMP-01-0124-FEDER-037271 (Ref. FCT PEst-C/CTM/LA0011/2013).*

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Experimental Studies on the Dissolution and Dispersion of Four Indian Coals

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This work proposes to study the effect of ionic liquids (ILs) for the spontaneous combustion of four Indian coals drawn from the mineral rich eastern part of our country. Five ILs consisting of different cations namely: 1-ethyl-3-methylimmidazolium acetate [EMIM][$COOCH_3$], 1-butyl-1-methylpyrrolidinium methylacetate [BMPYR][CH_3CO_3], 3-methyl-1-propylpyridinium bis(trifluoromethylsulfonyl)imide [MPPY][Tf_2N], tributylmethylphosponium methylsulfate [MTBP][$MeSO_4$] and tributylmethylammonium methylsulfate [TMA][$MeSO_4$] were used for the dispersion and dissolution of Indian coals. All the coals were pretreated with ILs for the fractionation of functional groups. Further the exothermic oxidation of coal using Simultaneous Thermal Analyzer (TGA) was also carried out. The details of functional groups of untreated-coal and ILs pretreated-coals were detected by Fourier Transfer Infrared Spectroscopy (FTIR). The IL treated coal were found to contain lesser amount of carboxyl, hydroxyl and functional aromatic groups as compared to the untreated ones. Thus the ILs pretreated coals are capable of effectively breaking the hydrogen bond which exists between functional groups especially belonging to hydroxyl radical. The TGA analysis further confirmed that the weight loss ratio of IL pretreated-coals were less as compared to ILs untreated-coals during the exothermic oxidation process. From the Simultaneous Thermal Analyzer, it was found that 1-butyl-1-methylpyrrolidinium methylacetate [BMPYR][CH_3CO_3] was capable of fracturing the active oxidative functional groups.

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Increasing the Tuneability of Ionic liquids

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Ionic liquids (ILs) have become recognized as greener media for engineering issues due to their properties, such as almost null volatility, tuneability, null flammability and recyclability. Nowadays, these compounds are being applied at industrial level by different companies e.g. Petronas, BASF, BP, Degussa and Linde industrial gases. One of the most attractive characteristics of ILs is that their physicochemical properties can be fine-tuned through the careful selection of cations and anions leading to the desired properties for each application. An emerging research field of interest in the ILs area is the increment of their tuneability. In this sense, new scientific branches of the ILs field were explored.

Firstly, the significant increase of the coulombic character of ILs through the solubilisation of simple inorganic salts in their milieu was tackled. This simple and inexpensive way to increase the ionicity of an IL was achieved, while preserving the liquid nature of the new ionic media. A new class of ionic liquids, High Ionicity Ionic Liquids (HIILs), emerges because the media is purely ionic and liquid. These new HIILs represent a new promising class of neoteric, "green" engineering liquids for separating processes.[1]

On the other hand, ILs are regarded as nano-segregated fluids, with a polar network permeated by non-polar domains. It is, thus, expected that fluorinated alkyl chains could also control the formation of fluorous nanodomains and may induce the formation of three nanosegregated domains, polar, non-polar and fluorous. Fluorinated Ionic Liquids (FILs) were developed and characterized, and the formation of these three nanosegregated domains was demonstrated.[2] The obtained results clearly show that FILs can be used as "three in one" solvents, increasing the solubilisation power. Playing with the Van der Waals, coulombic and hydrogen bonding interactions and the size of the fluorous domain will allow the development of solvents designed for each specific application.[3]

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Renewable Lipidic Ionic Liquid Crystals: Cation-anion Effects on SLcLE

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Protic Ionic Liquids (PILs) based on lipidic compounds have a wide range of applications in the chemical and pharmaceutical industry (e.g. surfactants, cosmetic creams, lubricants, drug delivery systems) due to their easy preparation, interesting thermophysical properties, and wide liquid phase range[1]. The renewable origin of those PILs synthesized by fatty acids (also considered as industrial byproducts of the oil industry) makes them sustainable because of their low environmental impact. Also, under certain temperature conditions, such PILs are liquid crystals, due to the high self-assembling ability of the long alkyl chain of their chemical structure. This gives them a high applicability, by comprising properties of both, ILs and liquid crystals. A series of mono- and diethanolammonium carboxylates was synthesized in this work through a Brønsted acid-base reaction. The behavior of their Solid-Liquid-crystal-Liquid thermodynamic Equilibrium (SLcLE) (melting temperatures – T_{fus}, and enthalpies) was characterized, and the influence of the alkyl chain length of the fatty acids (C10 to C16), used as the anion, and the ethanolamines, used as the cation, was also evaluated. The melting properties of the new ILs were determined using a DSC8500 calorimeter (PerkinElmer, USA) in a cooling-heating cycle at 1 K min^{-1}. The liquid crystalline mesophases (LCMs) were evaluated using a polarized optical thermomicroscope (Leica, Germany) in a 0.1 K min^{-1} heating run. The SLcLE data indicated that T_{fus} of ILs with diethanolamine as the cation were decreased up to 30°C, in comparison with the fatty acids used for their synthesis, probable due to the increase of the entropic effects promoted by the cation. Notably, diethanolammonium caprate and laurate presented T_{fus} lower than room temperature (298.15 K). However, for those ILs with monoethanolamine as the cation, T_{fus} were increased up to 10°C, in comparison with the fatty acids. In all cases, lamellar structures were observed in the liquid-crystal mesophases, in a temperature range of up to 40°C above T_{fus}, represented by typical marble textures and/or maltese crosses (Figure 1). This is probable due to the size and linearity of the alkyl-chain of the anions whose self-assembly, similar to those observed in organic lipid membranes, could be interesting for the design of active pharmaceutical ingredients or lipid-based food structuration agents.

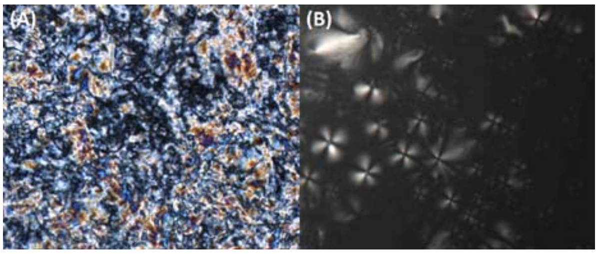

Figure 1. Thermomicrographs showing the mesophases textures of diethanolammonium myristate (A) T=340.55 K and (B) T=345.05 K

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Rheological and Thermodynamic Properties of Deep Eutectic Solvents

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Deep eutectic solvents (DES) and Natural deep eutectic solvents in particular (NADES), are seen as the most promising green alternatives to environmental detrimental solvents, but also to ionic liquids. Moreover, because of its peculiar compositions, NADES can also provide an array of different properties that can be the basis for novel processes. However, such development requires the establishment of a strong knowledge basis on the systems' fundamental properties. In this view, we have developed and characterized NADES based on choline chloride and betaine combined with natural occurring sugars, such as glucose, xylose and sucrose. For each system, the component molar ratios that provide the lowest eutectic points were determined and were further characterized in terms of their rheological and thermodynamic properties. The rheological properties are highly dependent of the nature of the components. Nevertheless, in general, the results obtained have shown that these systems are highly viscous, with typical viscosities higher than 1000Pa.s at 20°C and have Newtonian behavior. The viscosity decreases significantly with both temperature and water content and for temperatures higher than 60°C, the systems with 5 wt% water, the viscosity is typically lower than 1Pa.s. Differential scanning calorimetry (DSC) characterization has shown that for the presence of water in the system up to 5 wt.% does not compromise the single phase behavior of the NADES.

The results obtained demonstrate that the NADES properties can be finely tunned by careful selection of its constituents. The knowledge of these properties will be essential for the development of future sustainable industrial processes.

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On the Ionic Liquids Structure-Property Relationship

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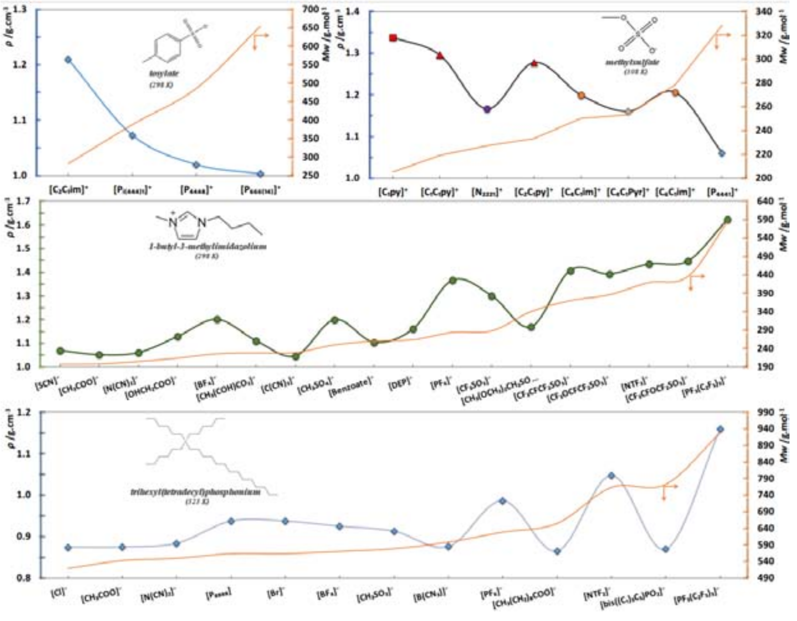
Ionic liquids (ILs) are composed of ions, and as a result there are a large number of potential compounds to be synthesized by simple structural rearrangements. Able to be either inert, acting only as solvents or designed to actively participate in a large range of chemical reactions, these ionic compounds have often been considered as “green solvents” because of their negligible vapor pressures and, in many cases, low flammability, when compared with common organic solvents. Moreover, the ionic nature of ILs is the main characteristic responsible for some of their most outstanding properties, namely a high ionic conductivity, high thermal and chemical stability, and enhanced solvation ability for a large array of compounds. At the same time, the combination of different ions, sustained by a wide chemical diversity, allows the tailoring of their properties, making them quasi specific fluids for a particular application, thus “designer solvents”. Nonetheless and despite the large number of works outing ionic liquids as “designer solvents”, the number of studies dealing with their structural design, besides the simple combination of different cations and anions, is, at this point, surprisingly scarce.

In this work the understanding of the structure-property relationship will be evaluated and discussed beyond the cation-anion combination. In particular the effect of cation isomerism or quasi-isomerism, the presence/absence of the aromaticity and the influence of the cation's central atom in a large range of physical, chemical and biological properties is presented.



Acknowledgments

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Adding Inorganic Salts to Ionic Liquids: Impact on the Properties and Ionicity of the Mixture

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Ionic liquids (ILs) are known for their designing properties, due to the multiple combinations of cations and anions that can be establish. Nevertheless, the mixing of ILs with other ILs or even inorganic salts (ISs) have been recently proposed as a way to expand the range of properties of ILs and to develop new approaches and applications beyond the current limitations of neat ILs.[1]

In this study mixtures of the IL 1-ethyl-3-methylimidazolium acetate with six different ISs were used. The ISs tested combine two different cations, ammonium and sodium, with four different anions, ethane sulfonate, acetate, thiocyanate and chloride. Thermophysical properties, such as viscosity, density, conductivity and refractive indexes of the IL-IS mixtures were measured in the solubility range of each IS.[2] In addition, the ionicity of the IL-IS mixtures was calculated by different methods. Moreover, spectroscopic methods such as Raman and NMR (chemical shifts, diffusion coefficients, NOESY) were used to screen for changes in the molecular environment of the ions in the mixture as compared to their pure state; and MD and Ab Initio calculations were also used to better understand the interactions that occur at a molecular level in the IL-IS mixture.

The results showed that the ammonium based ISs are capable of establishing preferential interactions with the IL, which does not occur for the sodium-based. These interactions were in part a result of the approximation of the IS's cation, the ammonium, to the IL's anion, the acetate, that lead to the establishment of aggregates and to a more detached imidazolium cation. These effects were more pronounced in the case where the IS was the $[NH_4][SCN]$. Furthermore, the ionicity of the IL-IS mixtures calculated by two different methods showed divergent behaviours meaning that the interplay between the interactions of IL and IS is much more complex than in the case of neat ILs or molten salts.

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Bulk Structure and Transport Properties of Protic-aprotic Ionic Liquid Mixtures: Imidazoles and Ammonium Nitrates

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Mixtures of ionic liquids (ILs) have raised academic interest in recent years as a route to take further advantage of their "designer solvent" nature[1]. As a continuation of our group's research into protic alkylammonium nitrates[2] and aprotic imidazoles[3-4], we report results for mixtures involving both families. Classical molecular dynamics simulations of protic-aprotic mixtures of different alkyl chain lengths were performed using the GROMACS 4.5.4 package and the OPLS-AA all-atom force field. Following a similar methodology to our work with molecular cosolvents[2,4], we study the evolution of bulk structure at different concentrations through calculated coordination numbers, average number of hydrogen bonds, and, particularly, the radial distribution function, placing special emphasis on the similarities and differences between cation-cation, anion-anion, and anion-cation interactions. The effects of the alkyl chain length of the IL cations on these properties are also studied and discussed.

As the experimental part of this work, conductivity measurements were made for each of the studied mixtures over the entire concentration range. We detect and discuss the existence of a conductivity minimum and the correlation between its position and the protic IL cation alkyl chain length. Finally, we relate simulation and experimental results in an attempt to understand the relationship between structural changes to the mixtures and their transport properties.

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Mechanistic Studies on the Beckmann Rearrangement in Ionic Liquids

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The Beckmann rearrangement, used to convert a ketoxime to the corresponding amide, is one of the classical and most popular reactions in organic chemistry.[1] It is successfully applied in the industry to produce ε-caprolactam (Figure 1), the basic monomer for manufacturing the synthetic fiber Nylon 6.[2] This reaction, however, requires high reaction temperature and strong acidic media (usually, generated with H_2SO_4), which causes serious corrosion problems and a large amount of by-products. Thus, milder routes are required and alternative methods have been studied.

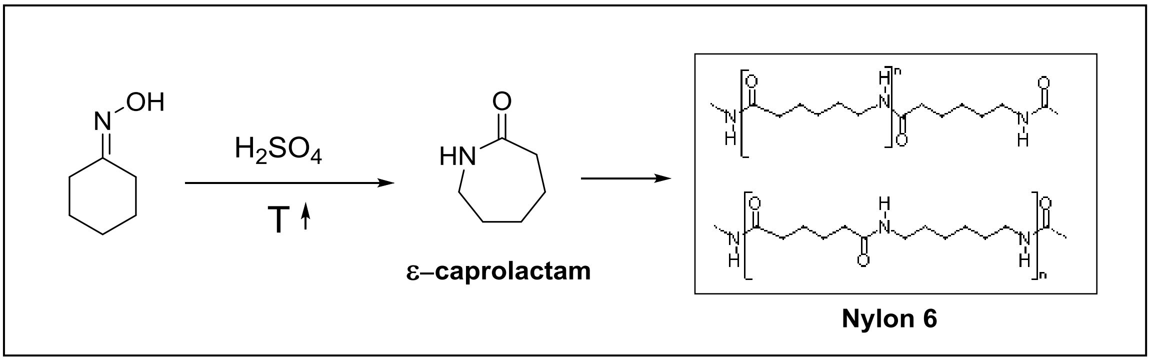

Figure 1. Beckmann rearrangement of cyclohexanone oxime to produce ε-caprolactam.

In a previous work,[3] we have performed the Beckmann rearrangement of several ketoximes by treatment with tosyl chloride, using ionic liquids (ILs) as both solvent and catalyst, without the need of any other promoter. However, no relationships were established between the structure of the ionic liquid and reaction yields, and explanations about the effect of the ionic liquid were not conclusive. Now, we report our recent mechanistic studies on these processes in ILs.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Organic Reactivity in Ionic Liquids: the Role of the Anion

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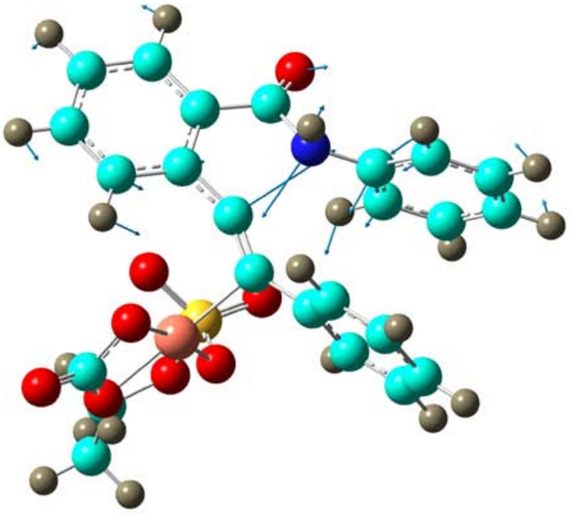
Ionic liquids have been proven as a remarkable media for organic reactions [1]. In this presentation we will present a resume of some integrated computational/experimental studies about organic reactions [2,3] in which the ionic liquid anion has a prominent role. This kind of reactions is fairly less studies with respect to those in which it is the cation that plays a prominent role.

The computational approach used is that of supermolecule [4] that allows us to take account of the specific role that the anion plays in the reaction mechanism.

Anions can play several rolesin reaction mechanisms. Here we consider the roles of complexant of a catalytic metal ion, of proton-transfer agent, of iodonium counterion.



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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Thermal Stability of Ionic Liquids

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Thermal stability, determined by thermogravimetric analysis, is an essential property of ionic liquids (ILs), especially for high temperature applications. But, experimental conditions (heating rate, atmosphere and mass sample) have strong influence on results[1] and disagreements could be found between results of different authors.

In this work, thermal stability of 25 ionic liquids was analysed in the same conditions. Selected ILs have five different cations, imidazolium, pyridinium, pyrrolidinium, choline and phosphonium and combined with 11 different anions ($[C_6SO_4]^-$, $[MeSO_3]^-$, $[C_1C_1PO_4]^-$, $[(C_2F_5)_3PF_3]^-$, $[OTf]^-$, $[NTf_2]^-$, $[BETI]^-$, $[DHPO_4]^-$, $[Ac]^-$, $[B(CN_4)]^-$ and $[(C_4F_9)_3PF_3]^-$).

A Perkin Elmer TGA 7 was used for experimental determinations. Firstly, the atmosphere and heating rate influence was evaluated. Afterwards dynamic studies at 10ºC/min in air atmosphere were carried out for all the selected ILs. Onset temperature[2] was determined from these scans. Although it cannot be considered the liquid range upper limit, this parameter allows establishing a sequence for the ILs thermal stability [2, 3]. Finally, isothermal scans at six temperatures lower than t_{onset} were performed with the aim to know the “real” thermal stability. Additionally isothermal scans allow doing a kinetic analysis of the degradation process by using the Arrhenius equation and an estimation of the degradation time for a given temperature.

The main conclusions of this work can be summarised as follows:

- Anion has stronger influence than cation on thermal stability of ILs, being $[NTf_2]^-$ and $[OTf]^-$ that provides the highest thermal stability and phosphate and sulphate the lowest. For the cation, imidazolium based ILs presented the highest resistance to thermal degradation.

- Onset temperatures cannot be used as maximum operation temperatures, negligible loss weight is only observed at temperatures 200ºC lower, approximately, than onset ones.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Process Simulation in the Design/Selection of Ionic Liquids

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It is well known that the properties of the ionic liquids (ILs) strongly depend on their constituent ions. This, along with the fact that a reduced number of commercially available cations and anions may led to a huge number of ionic liquids (ILs) potentially useable in a specific process, sets out the question of the ions selection. Experimentation with ILs is too expensive to face this challenge only by this way. Consequently, a priori computational procedures to design/select ILs having desired properties have been developed. The key of all the procedures proposed up to now is the "quality" of the descriptors used as inputs of the selection algorithm. Commonly, they are of thermodynamic and kinetic nature. Nevertheless, the development of ILs with real applicability in industrial processes should include parameters related to the operational conditions, energy consumptions, operating and capital costs, etc. This information may be obtained via process simulation. However, this is not a trivial question because: i)- ILs are not available in the process simulators databanks and, ii)- thermodynamic models regularly employed to predict the fluid phase equilibria of mixtures (equations of state, activity models, etc.) demand a large experimental effort in order to obtain their binary interaction parameters. We have developed a computational procedure combining molecular modeling and process simulation, which allows the conceptual design of new processes based on ILs.[1] In our procedure the ILs are introduced in the databank of the Aspen Plus process simulator as pseudo-components and the (already built-in) COSMOSAC property model is used to estimate the activity coefficients of the components in the mixtures. The information required both to create the pseudo-components and to specify the property model is retrieved from COSMO-RS calculations using the COSMO*therm*X software. This procedure has been successfully applied to: the IL regeneration by vacuum distillation[1] and stripping with air; the aromatic compounds separation from aliphatics in naphtha[2] by extraction with ILs; the volatile organic compounds (VOCs) retention from air by absorption[3] with the ILs used as absorbents; the ammonia absorption refrigeration cycles using ILs as absorbents[4]; the desulfurization of naphtha by extraction with ILs; the transport operations of ILs and their mixtures with organic compounds through conductions, etc.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Ionic Liquids as Extractive Solvents of Terpenes and Terpenoids

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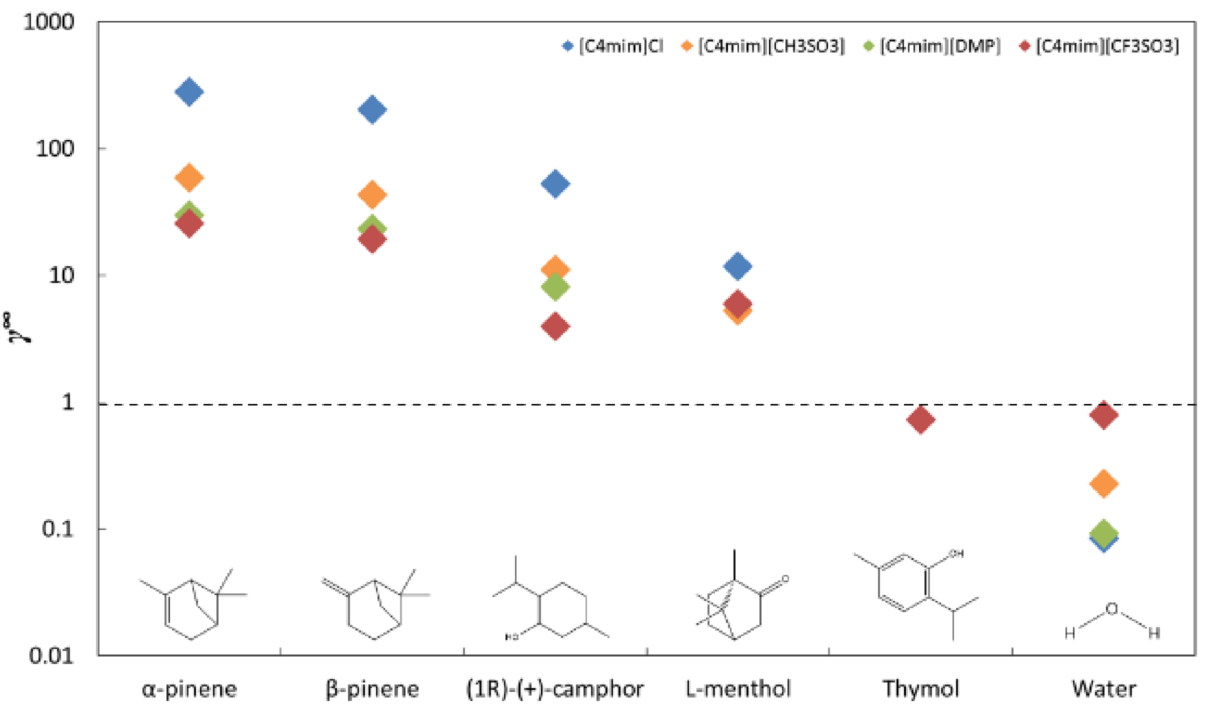
With the new emerging perception of terpenes and terpenoids impact on the environment, rising to implications on a global scale, solutions for their fate in the environment have been sought. One way forward are ionic liquids (ILs), widely proposed as entrainers in the separation processes due their thermal and chemical stability, and high performance extraction abilities. The combination of these two classes of compounds is promising, not only to study the recovery of terpenes and terpenoids from biorefineries effluents, but also for their direct production.

In this work, the interactions of selected terpenes, terpenoids and water with the ILs composed by the 1-butyl-3-methylimidazolium cation, $[C_4mim]^+$, and the anions chloride, Cl^-; dimethylphosphate, $[DMP]^-$; methanesulfonate, $[CH_3SO_3]^-$; and trifluoromethanesulfonate, $[CF_3SO_3]^-$, are measured through gas–liquid chromatography from (398.15 to 448.15) K.

Results show a significant influence of the IL anion, and solute polarities, on the infinite dilution activity coefficients. The highest infinite dilution activity coefficients, which represents the weaker interactions between the solute and the IL, is observed for the pair α-pinene–anion Cl^-, whereas the lowest is observed for water–anion Cl^-, where the interactions are stronger. These data are very important to select the best ionic liquid to capture terpenes and terpenoids from contaminated effluents, enabling also an evaluation of the polarity of the anion.



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Oral Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Organophosphorous pesticides in ionic liquids: reactivity vs selectivity

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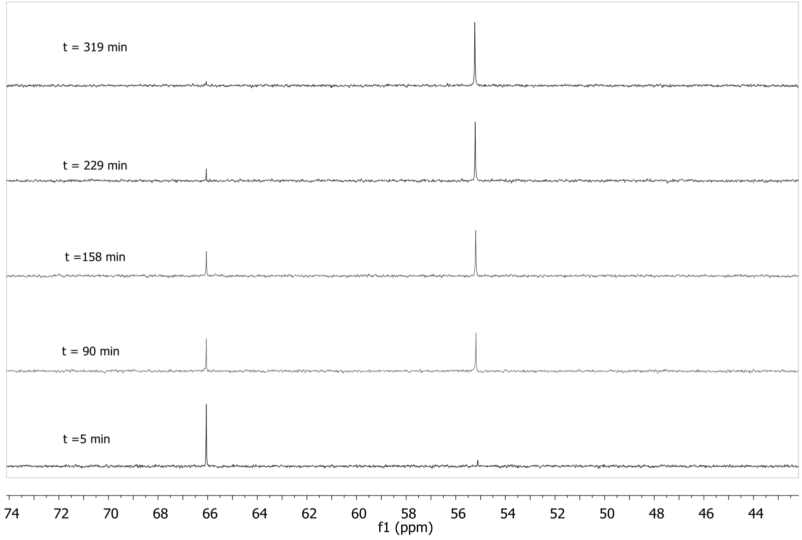
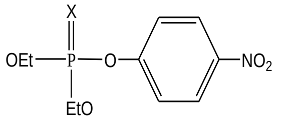
In a previous work, we have studied the effect of ionic liquids (ILs) on the kinetic of the reaction of O,*O*-diethyl *O*-(4-nitrophenyl)phosphate triester (Paraoxon®)with piperidine. It was found that the selectivity changed from exclusive attack at the phosphorus center $S_N2(P)$ in water to attack at aliphatic carbon S_N2(C), to the aromatic C S_NAr and also $S_N2(P)$. [1]

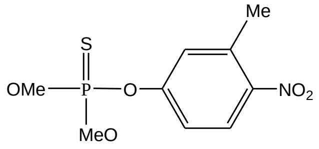
For that reason, and with the aim of finding a “greener” way to degradate pesticides, in this work we will study two other organophosphorates pesticides such as Fenitrothion and Parathion. To achieve this, kinetic study will be carried out by UV-vis and product analyses by ^{31}P-NMR both in ionic liquids and also in conventional organic solvents (COS), and under amine excess (piperidine and n-buthylamine) in order to obtain pseudo-first-order rate coefficients (kobs).

Products analyses showed no changes in selectivity of Fenitrothion with N-amines on going from conventional organic solvents (COS) to ionic liquids. Nevertheless, significant changes in the rate constant were found when ILs were used as solvent.





Paraoxon X=O
Parathion X=S



Fenitrothion

Figure 1. Stacked plots of ^{31}P-NMR spectra of the dregradation of Fenitrothion with piperidine in [Bmim]Ntf$_2$ at room temperature.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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On the Use of Ionic Liquids to Immobilize Biomolecules onto Different Sensing Platforms

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The dissolution of biomolecules and the maintenance of their effective reactivity require the preservation of their highly ordered structure, a condition that is difficult to achieve. Ionic liquids are presented as suitable compounds for this purpose because most of them seem to have ability to solubilize proteins without denaturation[1]. Therefore, many methods are attempted to immobilize proteins using carbon nanotubes, hydrogels, nanoparticles, hybrid compounds, ionic liquids and others[2,3]. Recently, the investigation of room temperature ionic liquids in biosensors has been increasing attention because their unique chemical and physical properties, such as high chemical and thermal stabilities, negligible vapor pressure, good ionic conductivity and ability to dissolve a wide range of organic and inorganic compounds.[2,3]

In the present work the different methods of immobilization of glucose oxidase (GOx) and cytochrome c using the ionic liquid tetrafluoroborate of 1-butyl-2,3-dimethyl imidazolium ($BMMIBF_4$) will be studied showing their electrochemical behaviour and amperometric detections.

Table 1. Comparison of different glucose biosensors

Biosensor	GOx (mg)	Sensitivity (μA mmol^{-1} L cm^{-2})
GC/CuHCNFe/Ppy/Gox/$BMMIBF_4$/Glut	0.05	17.1
nanoCuHCNFe/Ppy/Gox/BSA/Glut (2)	0.07	12.0
Au/Chit/$BMMIBF_4$/Gox (3)	-	5.2

GC: glassy carbon; CuHCNFe/PPy: hybrid of Copper hexacyanoferrate/polypyrrole ; Glut: glutaraldehyde ; Chit: chitosan; Au: gold; BSA: bovine serum albumin

In the case of glucose oxidase (table 1) the method of immobilization is more important than the amount of immobilized protein on the performance of the biosensors. Besides, our results has shown that the use of ionic liquids improve the detection of glucose due the biomolecule stabilization avoiding denaturation; consequently, increasing the sensitivity. Moreover, cytochrome c with chitosan hydrogel studies presented a good electrochemical estabilization in presence of ionic liquid without conformational structural changes and the beneficial effect of ILs on the dispersion of carbon nanostructures will be also shown.

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Tailoring Ammonium-based Bistriflamide Ionic Liquids to Manipulate their Properties and Interactions

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Ionic Liquids (ILs) have been a topic of great interest in the last two decades. During this period, the range of applications expanded mainly due to their “designer solvent” ability. It is generally accepted that aromatic cation head groups, as well as, longer alkyl chains generally exhibit more toxicity than non-aromatic or low lipophilicity cations with short and functionalised side chains. From this perspective, the short chain ammonium based IL, represents a window of opportunity as an environmental-benign and low-toxicity cation for IL design.

In this work, we have synthesized a series of ammonium-based ILs with bistriflimide anion with distinctive number and size of the alkyl chains and number and type of functional groups attached to the cation. The aim of this study is to evaluate the impact of these IL structural changes on the liquid-liquid phase equilibrium with molecular solvents such as ethers, alcohols, diols, and water, and on the thermophysical properties such as density, viscosity, conductivity and refractive index.

The type of phase diagram, Lower critical solution temperatures (LCST) vs upper critical solution temperature (UCST), is controlled by the molecular solvent and not by the functional groups present in the IL. However, the miscibility behaviour of the IL in molecular solvents is strongly dependent on the IL structure. For example, we have obtained a bistriflamide based IL that is soluble in water in all concentration range.

The thermophysical properties of the ILs strongly depend on the functional groups and size of the alkyl chain attached to the ammonium cation. For example, rather surprisingly, using two comparable cations, $[N_{2\,1\,1\,3OH}]$ and $[N_{3\,1\,1\,2OH}]$ the density is not similar, which highlights the distinct effect of increasing an alkyl chain in the apolar group or in the alkyl chain connected to the OH group.

Aknowledgements

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Novel Electrolytes for Supercapacitors based on Ionic Liquids

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Supercapacitors (also known as electric double layer capacitors (EDLCs)) provide several exceptional properties like a remarkable high power density, long operational life, the ability to be charged and discharged within seconds, and a reliable performance even at extreme temperatures. Common supercapacitor electrolytes are using organic solvents, which leads to drawbacks like significant vapor pressure at high temperatures and flammability. Most of these drawbacks can be overcome by using new electrolytes based on ionic liquids (ILs).

The benefits of ILs are large electrochemical stability, which can be directly correlated to the EDLC capacity, combined with high thermal stability as well as negligible vapor pressure. Another advantage of ILs is their incombustibility and being liquid over a wide temperature range. In this regard, new electrolytes based on ionic liquids (ILs) are promising alternatives to organic solvents [1]. In the cases where the viscosity of the pure IL is too high, we can use eutectic mixtures in order to increase performance (Figure 1).

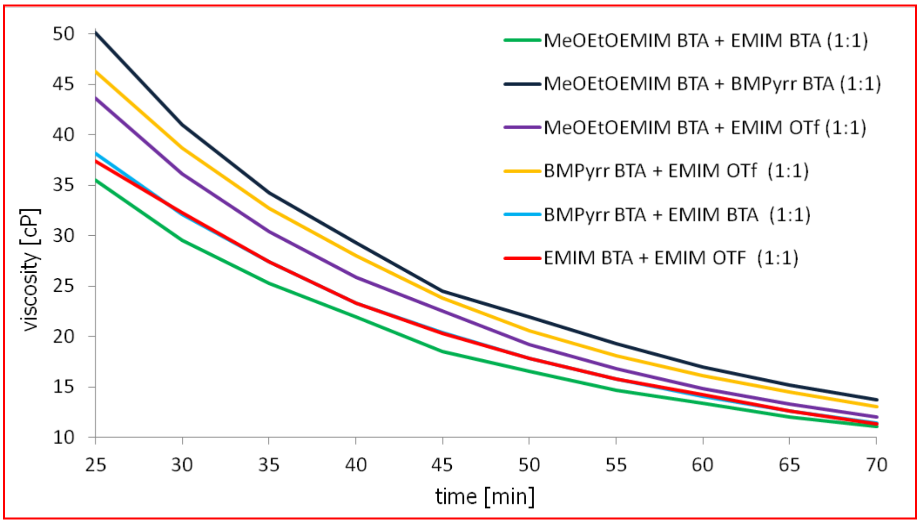

Figure 1 Mixture of ionic liquids and their viscosity.

We will try to present the view of a well established company, specialized in the synthesis and technology development in the field of ionic liquids, which has been on the market for more than 10 years. We would like to present the development of novel ILs as well as on the utilization of eutectic mixtures in order to increase the performance at low temperatures of EDLCs in general and in micro capacitors in particular [2].

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Oral Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Encapsulated Ionic Liquids (ENILs): Carbon Dioxide Capture

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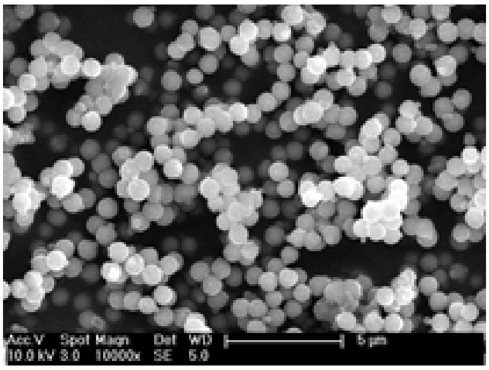
A main disadvantage for the practical applications of ionic liquids (ILs) is the limitation in the transport properties of these solvents, which generally present higher viscosity, density and surface tension than conventional organic solvents. This work presents the preparation, characterization and application of a new material called encapsulated ionic liquid (ENIL), consisting in carbon submicrocapsules filled by IL. These novel materials are based on the idea of moving from continue phase (IL) to discrete fluid phase (ENIL), maintaining the thermodynamic advantages of ILs as solvents, but providing a drastically higher surface contact area respect to the neat IL. As a result, enhanced mass transfer rates are obtained in ENIL systems, as demonstrated in its application to the sorption of ammonia[1].

ENIL is a remarkably versatile functionalized material, which can be prepared using carbon submicrocapsules (Ccap) with different core size, thick shell, porous structure and chemical surface[2]. It was prepared Ccap with a double shell, ABET about 1700 $m^2 \cdot g^{-1}$, particle size up to 400 nm. In addition, ENIL can be prepared by filling the capsule with different amount of solvent (till 80% w/w) and using ILs with very different chemical nature. Then, they were systematically characterized by elemental analysis, adsorption-desorption isotherms of N_2 at 77 K, thermogravimetric analysis, differential scanning calorimetry, scanning electronic microscopy, energy dispersive X-ray and transmission electron microscopy[3], in order to obtain a thoroughly description of their properties as needed information prior their use in gas separation or other applications.

In the present work, these materials have been tested with promising results for the carbon dioxide capture presenting in gas streams, by experiments carried out in gravimetric equipment using ENIL material prepared from carbon submicrocapsules and IL with high affinity toward carbon dioxide.



SEM image of ENIL material

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Polymer and Ionic Liquids: A Successful Combination

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Nowadays, innovation in the materials field, particularly for polymer materials undoubtedly requires the control of their structure at the nanoscale. In fact, the way for significantly improving the functional properties lies at this scale: mechanical performances but also optical, electrical, fire retardant capabilities.

To achieve this objective, several approaches have been considered and studied such as the use of block copolymers, chemical species or nanoparticles. More recently, due to their excellent properties such as their high ionic conductivity, their high thermal and electrochemical stability, their non-volatility and their inflammability, ionic liquids are increasingly used in the polymers as surfactant agent in the field of nanocomposites[1], as plasticizer agent of polymers for medical grade, as building blocks[2] in fluoropolymers where one structuration to the nanometer scale, modulated by the chemical nature of the cation/anion combination, could be generated channels for lithium ion batteries. Moreover, they are also known as compatibilizing agents of polymer blends but also as new additive agent for the preparation of polymer electrolytes[3-4]. For these reasons, our laboratory has multiplied these activities on ionic liquids/polymer research and a research group at the national level with the support of the CNRS was created (GDR LIPS). Thus, in this work, an overview of the potential of ionic liquids in the world of polymers will be presented.

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Novel Aqueous Biphasic Systems Composed of ILs and Copolymers

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With the increased set of natural compounds being adopted by the pharmaceutic, nutraceutic and cosmetic industries, the challenge now is the creation and search for new purification systems capable to selectively extract each specific molecule required by the industry and by the market. If now the extraction is an easier task, the purification of similar structures is being difficult with the purification systems developed, mainly due to their low specificity. As so many times described, one of the main key drivers for the promising status of aqueous biphasic systems (ABS) composed of ionic liquids (ILs) as an extraction technology is their tunable nature. This feature is related not only with the ILs themselves as *designer solvents* but also with the components which ILs can be combined with, such as conventional salts, polymers, carbohydrates and amino-acids [1]. Actually, ILs appeared in ABS domain as a valuable tool to extend the hydrophobic/hydrophylic range of this technology, particularly in polymer-based systems [2]. However, despite the success of ILs in the selective purification of certain molecules, namely enzymes, natural colorants, among others, when there is a need to purify structurally similar compounds, their performance is compromised. Herein, the introduction of copolymers in IL-based ABS is proposed to create even “more tunable” and selective systems, as this component is generated through the polymerization of two (or more) monomers species possessing intermediate properties. The binodal curves of the ternary systems formed by poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) + cholinium-based salts or ILs + water, were firstly ascertained. Then, the developed ABS were applied to the selective extraction of natural flavonoids and their performance compared with the typical copolymer + conventional salts + water systems. These systems introduce an additional degree of polarity within the ABS field and facilitate the recyclability routes as the copolymer is a thermosensitive species.

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Synthesis and Gas Separation Performance of Copper(I)-Containing Poly(RTIL)-RTIL Composite Membranes

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Polymerizable ionic liquids (poly(IL)s) represent a unique and versatile platform that allows for designing stable membranes for gas separation while controlling the chemical structure, i.e. combining the desired cation, anion and functional groups of the RTIL monomer for a particular application.[1] In addition, besides the polymerizable RTIL that forms the polymer network, a certain amount of "free RTIL" may be added to increase both gas pair selectivity and permeability through the membrane.[2] In this work, composite membranes have been prepared including a copper(I) salt as a third component of the polymer matrix: $[C_4vim][Tf_2N]$, $[C_4mim][Cl]$ and CuCl were the RTIL monomer, "free RTIL" and salt, respectively. These three elements were mixed in different proportions and the monomer as then photopolymerized to obtain flexible composite membranes with Cu(I) (as $CuCl_2^-$) concentrations up to 10 mol%, which was only achieved under certain conditions: large excess of $[C_4mim][Cl]$ over CuCl. Portions of self-supported polymer were characterized with FT-IR, DSC and TGA. Our results suggest for the first time that metal ions can be successfully embedded into a poly(IL) matrix what may prove useful for multiple applications including gas separation.

Therefore, the gas permeation properties of the composite membranes prepared with and without CuCl were tested employing a time-lag technique with CO_2, H_2 and N_2. Also, a CO/N_2 mixture was employed to assess whether a CO facilitated-transport mechanism occurs due to selective and reversible complexation reaction with the chlorocuprate(I) species.[3,4] Although all gas permeabilities increased with increasing content of "free RTIL", the contrary effect was observed with the copper salt concentration, i.e. decreasing permeabilities. However, this effect was more significant for the slow diffusing gases thus favoring H_2 separation.

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Study of Ionic Liquids Electrolytes for Dye-Sensitized Solar Cells

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One of the most appealing properties of room-temperature ionic liquids (RTILs or simply ILs) is their use as electrolytes in energy conversion devices such as dye-sensitized solar cells (DSCs).[1] ILs provide a way to increase the long-term stability of DSC because evaporation losses and leakage are minimized. However, this is achieved at the cost of introducing mass transport limitations due to their high viscosity. Therefore, it is crucial to gain insights into the behavior of ILs from the molecular point of view.

In this work we explore the structural and dynamical properties of ILs containing pyrrolidinium cation and bis(trifluoromethanesulfonyl)imide anion as well as their mixtures with the common organic solvent acetonitrile using Molecular Dynamics simulations. Furthermore, we study the transport properties of I^-/I_3^- species (a redox mediator commonly used in solar cells) in IL solution. In addition we analyze the effect of the confinement in a mesoporous media that recreates the morphology of metal-oxide electrodes used in DSCs [Figure 1].

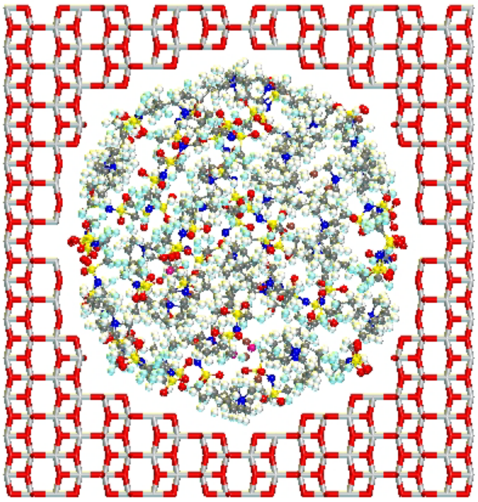

Fig 1. Representative snapshot from MD simulations of structure of DSC electrolyte confined in mesoporous TiO_2 media.

Density and self-diffusion coefficients of constituting ions and solutes in IL systems are depicted and reproduced. We found a deviation of two orders of magnitude between the diffusion coefficient of the redox mediator in pure acetonitrile and in ILs. However, this variation is not linear with respect to the acetonitrile/IL volume ratio. This suggests that a small amount of organic solvent can ensure a significant efficiency of DSC devices without compromising stability. The simulation results are in good agreement with experiments that demonstrate a molecular description that will help to design efficient and stable electrolytes for DSCs and related photoelectrochemical systems that require a liquid medium.

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Potential Induced Restructuring at Ionic Liquids Electric Double Layer

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Electrified interfaces research involving ionic liquids is still intense [1]. The research work focused on the structure of ionic liquids on charged surfaces is technologically-important for the development of new applications particularly for electrodeposition or energy storage and conversion [2]. Recently, a new concept of 'double salt ionic liquids' (DSILs) have emerged from the combination of more than one cation or anion, with mixtures exhibiting distinct properties when compared to their pure ILs [3]. Several theoretical and simulation studies have pointed to the possible occurrence of potential induced restructuring of the double layer [4,5] in pure ionic liquids, but so far, experimental evidence is practically inexistent.

We report for the first time sharp peaks in the differential capacitance data obtained for Hg/ionic liquid mixtures, which we demonstrate to be evidence of structural transitions occurring at the electric double layer. The phenomena occur with mixtures of two ionic liquids with a common cation and within a range of temperature and concentration. This structural singularity is proposed to emerge from the intricate interplay between electrostatic, van der Waals and hydrogen-bond interactions and also introduced by steric effects.

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Transport Properties in Phosphonium Ionic Liquids and Its Lithium Mixtures

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This work presents the physicochemical characterization of two ionic liquids (ILs) with small phosphonium cations, and their mixtures with Li+. Properties as electrochemical window, density, viscosity and ionic conductivity are presented. The diffusion coefficient was obtained by two different techniques, PGSE-NMR and Li electrodeposition with microelectrodes. In addition, the Li+ transport number was also calculated by the PGSE-NMR technique and by an electrochemical approach. Raman spectroscopy and molecular dynamics simulations were used to evaluate the short-range structure of the liquids. The results found in this work suggest that these Li^+ mixtures present outstading have promising potential to be applied as electrolytes in batteries.

Lithium-ion batteries are one of the most popular types of batteries, especially for its high charge density and being rechargeable. These batteries are used extensively in portable devices such as cell phones, laptops, digital cameras. Mixtures of aprotic organic solvents and LiPF6 are used in these batteries. However, the flammability of organic solvents and low thermal stability of LiPF6 makes it prohibitive to build lithium-ion batteries using such systems for large devices. Ionic liquids (ILs) have been widely studied due to the unique properties that they display, such as low vapor pressure, non-flammability, thermal stability.

The polarity and hidrophilicity or lipophilicity can be varied through a suitable choice of the anion. The phosphonium ionic liquids, are thermally stable and they are interesting for use in electrochemical systems. With the strongly electron-withdrawing phosphonium groups, the anion is expected to possess several desirable properties, such as resistance to oxidation and weak cation coordination. In the present study, two ionic liquids, triethylpenthylphosphonium bis(trifluoromethanesulfonyl)imide ($[P_{2225}][Tf_2N]$) and (2-methoxyethyl)trimethyl phosphonium bis(trifluoromethanesulfonyl)imide ($[P_{222(201)}][Tf+N]$) were studied. Properties as electrochemical window, density, viscosity and ionic conductivity are presented. The diffusion coefficient was obtained by two different techniques, PGSE-NMR and Li electrodeposition with microelectrodes. In addition, the Li^+ transport number was also calculated by the PGSE-NMR technique and by an electrochemical approach. Raman spectroscopy and molecular dynamics simulations were used to evaluate the short-range structure of the liquids. The results found in this work suggest that these Li^+ mixtures present outstading have promising potential to be applied as electrolytes in batteries. All liquids are stable till over 400°C and it is observed that adding the lithium salt, there is an increase in the viscosity and density, but surprisingly a slight increase in the ionic conductivity is observed. This result is unusual compared with other ILs derives from other anions and it shows that it is a promising result considering the application as electrolyte for lithium ion batteries.

Poster Presentations

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Second Generation Bioethanol from *Eucalyptus globules Labill* Using 1-N-ethyl-3-methylimidazolium-acetate

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Bioethanol was produced from lignocellulosic residues of *Eucalyptus globules Labill*. Eucalyptus residues as wood-chips were pretreated with the ionic liquid (IL) 1-N-ethyl-3-methylimidazolium-acetate ($[EMIM^+][OAc^-]$) at different temperatures and exposures times, then solids were thoroughly washed with deionized water for IL removal, and subsequently processed under both Separated hydrolysis and fermentation (SHF) and Simultaneous Saccharification and Fermentation (SSF) separately. Enzymatic hydrolysis for SHF process was performed using a commercial cellulase preparation (Celluclast 1.5L and Novozyme 188) at 50°C and stirring at 200 rpm for 72 h, whereas subsequent fermentation of the liquid phase was carried out using *Saccharomyces cerevisiae* strain Red Star at 40°C and stirring at 300 rpm for 72 h. The SSF process was carried out using the same cellulose preparation and microorganism described for SHF process at 40°C and stirring at 300 rpm for 72 h. Fresh and processed Carbohydrate content of Eucalyptus residues were analyzed gas chromatography [1]. The liquid fraction was analyzed for glucose content using a commercial kit, whereas total reducing sugars were analyzed using the dinitrosalicilic acid reagent [2] and ethanol was analyzed by HPLC. Fresh Eucalyptus residues accounted for 40.6 wt-% cellulose and 22.9 wt-% hemicelluloses and pectins. The best pretreatment condition was using $[EMIM^+][OAc^-]$ at 150°C for 30 min, accounting for a 82.2 wt-% glucose yield after saccharification of pretreated biomass. On the other hand, SSF of pretreated biomass accounted for 3.7 g ethanbl $^{-1}$ and yield 0.15 g ethanol/g glucose at 72 h. Analyzes to processed solids demonstrated high cellulose degradation, but partial hemicellulose degradation, mainly xylans. Thereby the results obtained are very promising to give a better use to forestry residues in the Chilean scenario [3]. Further improvements can be obtained in terms of reusability of the ionic liquid and optimization of some operational parameters.

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Separation and Purification of Valued-Added Proteins Using Temperature-Switchable Ionic-Liquid-based Aqueous Biphasic Systems

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The ability to induce reversible phase transitions between aqueous homogeneous solutions and biphasic liquid-liquid systems, at pre-defined and suitable operating temperatures, is of outstanding relevance in the design of separation and purification processes for valued-added proteins. It was already demonstrated that phase transitions in mixtures involving hydrophobic ionic liquids (ILs) and other solvents can be induced by changes in temperature or by reversible reactions with CO_2 forming salts or ILs.[1-3] However, most of the binary liquid-liquid systems comprising ILs typically occur at temperatures far from room temperature and are confined to mixture compositions imposed by the upper or lower critical points of the phase diagrams. Moreover, these systems are composed of an IL-rich phase (typically with hydrophobic characteristics) and a molecular-solvent-rich phase.

In this work, we show that aqueous biphasic systems (ABS), *i.e.*, ternary systems where the major solvent is water, may have their reversible behavior triggered by small changes in temperature (as low as 1 ºC). The applicability of the temperature-induced phase switching is further demonstrated with the complete extraction for the IL-rich phase of two valued-added proteins, namely cytochrome *c* and azocasein, achieved in a single-step. It is shown that the temperature induced phase switching provided by IL-based ABS is significantly more versatile than classical liquid-liquid systems which are constrained by their specific critical temperatures. Instead, this approach allows to combine and to work in a wide range of temperatures and compositions which can be tailored to fit the requirements of a given separation process.

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Ionic Liquids-adapted Microorganisms from Extreme Environments

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From the 90s on, ionic liquids have posed a new inspiration for Green Chemistry as their low vapour pressure may reduce the air pollution with respect to the typical volatile organic solvents. This paradigmatic feature has contributed to the fact that ionic liquids have casted the walls from the research laboratories and had soon covered the pathway from the gram scale to the ton magnitude. This statement is patent for the first family of ionic liquids (imidazolium) applied at industrial scale that was already registered under REACH regulation on chemicals (such as [C_2mim] and [C_4mim] cations combined with Cl, [C_2SO_4], [C_1SO_3], [O_2CMe] and [NTf_2] anions).[1] This regulation indicates that their high chemical and thermal stability suggest potential problems related to their toxicity, degradation and persistence in both the aquatic and the soil environment. Taking into account this fact, their 'green' label is now being questioned by the scientific community. One solution to this problem could be placed in extreme microorganisms, which would play a role as "ionic liquids-metabolizers". The observation that this kind of microbes can thrive under high ionic liquids concentrations would indicate the tremendous technological potential that might surge from the interaction between white biotechnology and green chemistry. [2] Thus, ionic liquids removal could be achieved by using the pathways designed by nature for the metabolism of living beings.

In this work, microbial sources able to resist high concentrations of ionic liquids have been screened. The toxicity data for several fungal and bacterial species from extreme environments in the presence of common families of ionic liquids confirmed that microorganisms from polluted and saline locations were the most adapted to the presence of these neoteric contaminants, reaching minimum lethal concentration values of 1M. The adaptation of *Pseudomonas stutzeri* for 2 months in a stirred tank bioreactor containing a culture medium with 200 mM of an imidazolium-based ionic liquid led to tolerance levels 10 fold higher, as a consequence of the biosynthesis of an extracellular polysaccharide.

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Dissolution and Transformation of Biopolymers in Ionic Liquids

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The inability of common organic solvents to dissolve natural cellulose under mild conditions has significantly delayed the development of large scale applications of this cheap and abundant biopolymer. However, starting from 2002 when Swatloski et al. [1] reported that some ionic liquids could dissolve high amounts of cellulose at moderate temperatures, activity in this field is exponentially increased.

Ionic liquids are actually not only able to dissolve important biomacromolecules such as cellulose and chitin but, due to their negligible vapor pressure and thermal stability, they have been considered as “greener” alternative media to use as solvents and/or catalysts in several fields, including also the industrial processes for generating fuels from renewable feedstock.

Ionic liquids based on acetate or chloride anions, combined with small alkylimidazolium cations, are able in the presence of suitable catalysts to convert initially cellulose in sugars and subsequently into compounds of further oxidative degradation, such as 5-hydroxymethylfurfural (5-HMF), [2] levulinic acid and formic acid.

Herein, we discuss the efficiency of some selected processes based on the use of ionic liquids as media or catalysts in terms of 5-HMF yield and process recyclability. Moreover, the eventual formation of dark-colored solids, generally called humins, [3] will be discussed considering in particular the dependence of the structural features of these latter materials from reaction conditions (temperature, ionic liquid and catalyst structure).

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Analysis of the Advantages of Using CO_2 as a co-solvent in Cellulose Processing in High Melting Point Ionic Liquids

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The capacity of the ionic liquids (ILs) of dissolving high concentrations of cellulose makes them promising solvents for the so called biorefinery process. Nevertheless they present important disadvantages such as extremely high viscosity (especially when the biopolymer is dissolved into it) and high melting points of some of the ILs able to dissolve cellulose (such as those of the imidazolium chloride family). Carbon dioxide presents as a promising co-solvent for the ionic liquid processing of lignocellulose as it is an inert gas without environmental limitation that presents high solubilities in ionic liquids even at low pressures, and can be easily separated of the mixture by depressurization.

In this work, the influence of CO_2 in melting points and other ionic liquids properties of ionic liquids has been experimentally determined. It was found that melting point depressions at pressures of CO_2 up to 10 MPa were experimentally can reach a reduction as high as 33K.

The capacity of CO_2 of effectively increasing the solution rate of cellulose in ILs was evaluated in several ionic liquid at temperatures of 50 and 80ºC, by determining the amount of cellulose dissolved in processing times of 30 minutes in presence and absence of carbon dioxide. Experiments show an average increment of cellulose in the ionic liquids of 10 to 25% using moderate pressures of CO_2 of 0.7 MPa.

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Kinetic Model for Imidazolium-based Ionic Liquids Oxidation by the Fenton Process

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Imidazolium-based ionic liquids (ILs) have huge potential application in many areas of chemical industry due to their interesting physico-chemical properties. However, in recent years the perception of their greenness has dramatically changed since it has been shown that those compounds are highly stable, toxic and non-biodegradable, thus they could become persistent pollutants in the environment.[1] In this context, the development of efficient processes for ILs removal is imperative. Fenton oxidation has proved to be an effective technology for their degradation, achieving complete ILs removal and non-toxic effluents [2, 3] but little is known for the kinetics of this process.

Herein, a kinetic model has been developed to describe the oxidation of imidazolium-based ILs by Fenton treatment. The effect of several operating conditions, including reaction temperature (50-90 ºC), catalyst load (C_{Fe}=10-100 mg/L), initial ionic liquid concentration (100-2000 mg/L) and hydrogen peroxide dose (10-200% of the stoichiometric amount for IL mineralization) on 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) oxidation and mineralization has been investigated. Under the optimum operating conditions (T = 90 ºC; $[Fe^{3+}]_0$ = 50 mg/L; $[H_2O_2]_0$ = 100%), the complete degradation of $[C_4mim]Cl$ (<1 min) and 60% TOC removal (1 h) were achieved.

The developed model is based on a pseudo first order rate equation for hydrogen peroxide consumption and IL oxidation, and includes the temperature dependence. This model is capable of describing accurately the experimental results of IL oxidation. An equation describing the evolution of TOC has been also raised.[4]

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Ionic Liquids for Extraction Antibiotic from Freshwater Surfaces

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In the past few years, the improvement of advanced analytical tools and investigation on wastewater samples confirmed the presence of residual amounts of active pharmaceutical ingredients (APIs) in wastewater treatment plants (WWTPs) and freshwater surfaces. Variable amounts of the taken doses of APIs are metabolized by organisms whereas the remaing is excreted (in a metabolized or unchanged form). Even at low concentrations (ng/L– μg/L), contact with APIs can result in intoxication to the living organisms.[1,2]

In this context, this work addresses the use of liquid-liquid extraction for the removal of antibiotics present in freshwater streams. In particular, aqueous biphasic systems (ABS) composed of ionic liquids (ILs) and aluminium-based salts, usually used in WWTPs, were tested in the extraction of antibiotics. Partition coefficients and extraction efficiency (%EEAntibiotic) of ciprofloxacin, norfloxacin, ofloxacin, enrofloxacin, moxifloxacin and sarafloxacin were determined, providing % EEAntibiotic of 91.6, 88.2, 89.9, 94.7, 96.4 and 96.1 %, respectively. Finally, and envisaging the development of a cost-effective and environmentally benign methodology, the recovery of the fluoroquinolones and reuse of the IL was also addressed. Three antibiotics, ciprofloxacin, norfloxacin and ofloxacin, were used to test this methodology. Overall recoveries larger than 80% were obtained when the IL was reused four times.

In conclusion, IL-based ABS are a very efficient and cost effective method in the removal of antibiotics from freshwater, allowing for the re-use of the IL without significant loss of efficiency.

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Ionic-Liquid-Based Aqueous Biphasic System for Antibodies Separation

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The use of antibodies has become a hot topic of research in passive immunization due to the actual emergence of drug-resistant microorganisms.[1] Traditional antibodies (IgG) are produced by small mammals and are usually collected from repeated bleeding or heart puncture which may frequently result in distress or even death of the animals.[1] An emerging alternative consists on the investigation of antibodies existent in egg yolk (immunoglobulin Y, IgY), that play a similar biological role as mammal IgG.

Several methodologies were investigated aiming at purifying IgY from the complex lipophilic matrix of egg yolk, including multiple precipitation stages with polymers or salts, ultrafiltration or extraction with chloroform. [1] However, these techniques have shown to be time consuming and not provide high purification factors. In this context, ionic-liquid-based-aqueous biphasic systems (IL-based ABS), which fit within the liquid-liquid extraction strategies, can be foreseen as a viable alternative for the extraction and purification of IgY. Traditional ABS display a limited range of polarities at their coexisting phases which have been obstructing selective extractions and improved purifications. One of the main advantages of ILs as phase-forming components of ABS relays on the possibility of tailoring their phases' polarities and affinities by different cation/anion combinations which permits a more efficient selective extraction.[2]

In this work, the extraction/purification of IgY from the water soluble proteins fraction (WSPF) of egg yolk was investigated using ABS composed of several ILs and potassium citrate/citric acid mixtures at controlled and different pH values. According to the obtained results, some systems afford the complete extraction of IgY for the IL-rich phase, in a single-step, with no losses on the antibodies recovery from the WSPF. Yet, future studies are still in need for achieving higher purification factors.

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Supported Ionic Liquids for the Purification of Immunoglobulin Y (IgY)

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Due to the actual emergence of antibiotic-resistant pathogens, the application of antigen-specific antibodies in passive immunotherapy represents an imperative reality in the near future. In addition to the more investigated mammal antibodies, antibodies from egg yolk (IgY) can be obtained in higher titres and by non-invasive methodologies.[1] Up to date, several methods, such as precipitation, dialysis, ultrafiltration and chromatography are available for IgY purification.[1] Nevertheless, the production cost of IgY still remains higher than other drug therapies due to the lack of cost-effective purification techniques. The development of a cost-effective and scalable new strategy for the purification of IgY is thus in high demand and will have an high impact in economics and human health. In this work, a new platform for the purification of IgY using supported ionic liquids (SILs) was investigated. A particular interest has been given to ILs immobilized in silica materials as sorbents in solid-phase extractions (SPE).[2] To this end, silica-functionalized materials were initially synthesised and characterized, based on a wide array of chemically distinct ILs, and their performance for purifying IgY from aqueous solutions of egg yolk was finally investigated.

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Extraction of Phenolic Compounds from *Salicornia ramosissima* Using Polymeric Aqueous Biphasic Systems

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Salicornia ramosissima is a halophyte plant that grows in Aveiro laggon.[1] *S. ramosissima* contains several compounds with commercial added value with pharmaceutical properties: antioxidants, antidiabetic and anticancer. Caffeic acid (CA), ferulic acid (FA) and protocatechuic acid (PA) are the major phenolic acids present in *Salicornia*, from 0.5 - 2.1 g of total phenolic acids *per* 100 g of fresh biomass.[2] Such compounds have a great interest in the pharmaceutical industry, therefore its extraction is economically profitable.[3] Herein, we pretend to find an optimized and selective procedure of extraction and purification of these phenolic compounds from *S. ramosissima* biomass extract. Polimeric-based aqueous biphasic systems, formed by two polymers: sodium polyacrylate (NaPA 8000) and polyethylene glycol (PEG 8000) in which ionic liquids and inorganic salts are used as electrolytes in low concentrations (5.0 wt%) were used as extractive platforms.[4] Distinct proprieties of these polymers and mainly the tailor-made design of ionic liquids used as electrolytes allowed the manipulation of the phase migration behavior of the different phenolic acids, in order to find a selective aqueous biphasic system. The results shows that using different electrolytes (*e.g.* NaCl, Na_2SO_4 and [C_2mim]-based ILs) the phase migration among the phenolic acids (CA, FA and PA) changes and it was possible to create an aqueous biphasic system with high selectivity for the similar-structure phenolic acids.

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On the Evaluation of the Toxicity of Cholinium-based Ionic Liquids

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Based on the fact that the cholinium is a complex B vitamin and widely used as food additive, cholinium-based ionic liquids have been seen as environmentally harmless and thus, accepted as non-toxic, although their (eco)toxicological profile is poorly known [1]. The present communication provides new ecotoxicological data for ten cholinium-based salts and ionic liquids, aiming to extend the surprisingly restricted body of knowledge available about the ecotoxicity of this particular family. Furthermore, insight was gained in counteracting two widely accepted principles ruling ILs ecotoxicity, the side-chain effect until a cut-off level and the decrease in toxicity with the functionalization of the cation. Given the wide range of structures that can be engineered within the same IL family to respond to function and environmental challenges, assessments allowing the establishment of structure-activity relationships such as that performed here are of great use for the proper design of "optimal" ILs from both technical and environmental points of view, minimizing thus the array of final ILs undergoing mandatory and costly prospective risk assessment before licensing. The results show that not all the cholinium tested can be considered harmless towards the test organism adopted [2]. Moreover, data suggest that the cholinium family should have a different mechanism of toxic action as compared to that of imidazolium-based ionic liquids previously described in literature.

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Using Ionic Liquids in the Purification of the Antitumoral Protein R-phycoerythrin from *Gracilaria vermiculophylla*

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In the past few years, there has been an increased demand for natural compound over the synthetic ones. Thus, products extracted from natural sources have gained significant interest among industries and academia. R-phycoerythrin (R-PE) is a protein found in red macroalgae and cyanobacteria and it is recognized for its particular characteristics: high solubility in water, proteinic nature, good stability under different pH values, temperature and time of storage and excellent optical and spectroscopic properties. This protein is being recognized as an antitumoral macromolecule, active against the liver and lung carcinomas, two of the most prevalent forms of cancers reported across the globe (2012: lung cancer led to 1.59 million deaths; liver cancer led to 745000 deaths).[1] One of the major drawbacks associated with the natural molecules is the demand for an effective and non-costly integrated extraction and purification process capable to remove the protein from the biomass, while maintaining its more relevant properties/activities. In this sense, the search for efficient extraction technologies is of extreme importance. In this work, ionic liquids (ILs) were used as alternative solvents being applied in the design of liquid-liquid extraction technologies[2], for the R-PE extraction from the red macroalgae *Gracilaria vermiculophylla*. Different ILs (various families, alkyl chain lengths and anions) were studied considering their capacity to disrupt the seaweed cells and to extract as much as possible the R-PE. The cells' disruption was monitored by Scanning Electron Microscopy and the extraction was followed by the yields of extraction and purity indexes and then compared with those of conventional methods.

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Facing the Complexity of Bioproducts' Purification using PEG-IL-based Aqueous Biphasic Systems: From Antibiotics to L-Asparaginase

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Recently, the large research on applications involving Ionic Liquids (ILs) and the growing search for more sustainable and biocompatible separation and purification processes has headed Aqueous Biphasic Systems (ABS) as a potential solution to conventional liquid-liquid extraction methods frequently using volatile and hazardous solvents.[1] Following these principles, in the last years, we have been pursuing several studies aiming the use of ILs and polyethylene glycol (PEG) as alternative phase-forming promoters of ABS.[2,3] Remarkably, these IL-PEG-based ABS proved to be far more interesting than more conventional IL-salt systems since they allow the adjustment of the intrinsic properties of the phases in equilibrium and the tuning of separation and extraction processes. Nevertheless, some difficulties were found when aiming their utilization as purification systems for the added-value pharmaceuticals, particularly on the bioproducts recovery. In this work, we present some recent advances on previous concerns verified on the recovery of tetracycline from a fermentation broth of Streptomyces aureofaciens[4] and on the extraction of clavulanic acid from Streptomyces clavuligerus media. It was perceived that the presence of impurities in the fermentation broth can change the phase equilibrium leading to a reduction on their extraction efficiencies. These two studies, worked as an initial stage for the recovery of the biopharmaceutical L-Asparaginase (an anti-leukemia compound). Herein, we will show how our previous experiments apply and help in defining IL-PEG-based ABS as effective liquid-liquid extraction systems for the recovery of value-added biopharmaceuticals.

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Cholinium-based Ionic Liquids with Antioxidant Character

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In the past few years, an increasing interest on antioxidants has been observed, particularly as constituents of dermatological pharmaceutical formulations and skin care products[1,2]. However, taking into consideration the high variety of formulations, some antioxidants could present a solubility limitation. In this context, ILs appear as promising tools to synthetize unique antioxidant compounds with specific solubility properties. This *designer* nature is due to their tunable properties, which means that they can be designed for a specific purpose by the selection of the adequate cation/anion combination[3, 4].

In this work, six new cholinium-based ILs with antioxidant nature were synthetized. For this purpose, six antioxidant anions were conjugated with the cholinium cation, an essential nutrient. The chemical structures of these novel ILs were determined by ^{1}H and ^{13}C NMR. Their antioxidant activity was investigated using the 2,2-diphenyl-2-picrylhydrazyl hydrate (DPPH) radical scavenging assay and compared to prototypic antioxidant ascorbic acid. Moreover, their physicochemical properties, namely melting point, decomposition temperature and water solubility were assessed, as well as their (eco)toxicological impact towards a marine luminescent bacteria (standard Microtox® assay). Finally we addressed the impact of the synthesized ILs on mammalian cells, where their cytotoxicity and pro/anti-inflammatory activity were analyzed in relevant human cell lines.

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Micellar Extraction of the Anti-Tumoral Carotenoid Fucoxanthin from *Sargassum muticum*

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Leukemia, prostate and colon tumors are three of the most prevalent forms of cancers reported across the globe[1]. Although the chemotherapy can be quite effective in treating these carcinomas, the chemotherapic drugs do not differentiate the healthy from cancerous cells, and thus there is a crescent demand for new therapeutic agents capable to overcome the drug resistance and reduce the toxicity on the normal cells. Recently, the search for natural molecules is increasing, and several natural compounds have been pointed out, namely fucoxanthin. Fucoxanthin is a well-known carotenoid[2], present in the *Sargassum muticum* brown seaweed (abundant in Portugal), an invasive macroalgae species originally from Japan and whose antitumoral properties have been recognized[2]. The major drawback associated with the natural molecules is the demand for an effective and non-costly extraction/purification method to remove fucoxanthin from the biomass, while maintaining its more relevant properties. In this sense, the search for efficient extraction technologies is of utmost importance. Moreover, and since one of the major limitations of the algae processing is their large water content that often compromises the economic viability of the extraction processes, in this work we will use surfactants to disrupt the cells and extract fucoxanthin with micellar systems. The cell disruption will be characterized by scanning electron microscopy, the micelle morphology by optical microscopy, and the extraction performance will be quantified by the measurement of the fucoxanthin content using HPLC. Conditions such as the time of exposure, type of surfactants (non-ionic, anionic, cationic and zwitterionic) will be tested. An experimental design and sequential extraction processes will be also carried. After the micellar solid-liquid extraction, the fucoxanthin purification will be tested considering the application of common aqueous micellar two-phase systems based in the best surfactants, with and without tensioactive ionic liquids as additives.

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Surface-active Ionic Liquids for the Extraction of Chlorophylls from Spinach Leaves

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Chlorophylls *a* and *b* are the pigments responsible for the characteristic green color of fruits and vegetables. Chlorophylls and their derivatives present unique properties, such as protective features against toxins, the ability to ameliorate some drug side effects in humans, among others[1]. Thus, due to these valued features, chlorophylls are currently used by the food, pharmaceutical and cosmetic industries[2]. However, chlorophylls extracted from natural sources are quite expensive because the traditional methods typically used for their extraction are time- and energetic-consuming, and suffer from low yields and low purity levels[1]. In addition, most of the organic solvents commonly used are hazardous to human health and to the environment. In this context, the use of ionic liquids (ILs) as alternative solvents can be a promising approach.

In this work, aqueous solutions of ILs were investigated as alternative solvents for the extraction of chlorophylls from spinach leaves. In addition, some common organic solvents were also studied for comparison purposes. To improve the extraction yields and purification factors several operational parameters, like concentration, contact time and solid–liquid ratio were further optimized. The results show that aqueous solutions of surface-active ionic liquids are enhanced solvents for the extraction of chlorophylls from biomass. Compared with traditional extraction methods, this new strategy is shown to be capable of providing higher extraction yields, using small amounts of ILs, and water as the major solvent. The gathered results bring new perspectives into the development of a “greener” and cost-effective technology for the extraction of chlorophylls from biomass.

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Pretreatment of Barley Straw with Ionic Liquid for Conversion to Fermentation Sugars

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Ethanol production from biomass has gained considerable interest in order to provide energy security and reduce greenhouse-gas emissions. Lignocellulosic biomass offers many potential advantages in comparison with the traditionally used sugar or starchy biomass, considering it is generated in large quantities and does not compete with food and feed production. Furthermore, lignocellulosic ethanol has shown to involve up to 85% net reduction in greenhouse-gas emissions[1] compared to fossil fuel. Among other lignocellulose feedstocks, the abundance and high carbohydrate content of barley straw make it a good candidate for bioethanol production in Europe [2].

Biomass must be pretreated before enzymatic hydrolysis to improve the digestibility of both cellulose and hemicellulose carbohydrates. The pretreatment consist of breaking the lignocellulose matrix to expose the carbohydrates for enzymatic reaction. Among pretreatment methods, the use of liquid ionic has been proposed as an environmental friendly pretreatment of biomass[3].

In this work, the enzymatic hydrolysis of ionic liquid pretreated barley straw was studied. Different pretreatment conditions (temperature and time) were investigated to determine the effects of the experimental conditions on the sugars yields by enzymatic hydrolysis. The 1-n-ethyl-3-methyl-imidazolium acetate has been selected as ionic liquid, due to its low melting point temperature (liquid at room temperature), its low viscosity and easiness to handle.

At the best conditions an overall yield of 34.8 g glucose per 100 g barley straw and 18.7 g xylose per 100 g barley straw was obtained. These figures are higher than those obtained for barley straw pretreated by steam explosion.

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Optimization of an *In-situ* Ionic Liquids Dispersive Liquid-Liquid Microextraction Method to Determine Endocrine Disrupting Phenols in Water Samples by HPLC-UV

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Ionic liquids (ILs) are the objects of common interest due to their unique physicochemical properties, such as negligible vapor pressure, good thermal stability, tunable viscosity and miscibility or immiscibility with water and in many organic solvents. This outstanding properties make ILs suitable solvents for liquid-phase microextraction (LPME). The utilization of ionic liquids allowed the development of new extraction method such as in-situ ionic-liquid dispersive liquid-liquid microextraction (in-situ IL-DLLME). This microextraction technique is based on dissolution of hydrophilic IL in an aqueous solution containing the analytes of interest followed by addition of an ion-exchange reagent which undergoes an in-situ metathesis reaction forming an insoluble in water IL. Thus, analytes are sedimented and preconcentrated in the separated hydrophobic ionic liquid.

Increasing amount of phenols in household and industrial waste, wastewater, drinking water and natural water reservoirs, raises the need for their continuous monitoring. The fears of excessive amounts of phenol and its derivatives in the environment are associated with the proven high toxicity, ability to bioaccumulation, high stability and cancer-causing properties. It has been shown that even small amounts of phenols in water reservoirs (below mg/L or in some cases µg/L) may cause hazardous environmental effects.

In this work the in-situ IL-DLLME method was used as a new approach for the detection of endocrine disrupting phenols (EDPs) in water samples. The endocrine disrupting phenols determined in this study were Bisphenol A (BPA), 4-tert-Octylphenol (t-OP) and 4-N-Nonylphenol (NP). Project predict use of quat-based ILs with didecyldimethylammonium chloride [DDA][Cl] - hydrophilic ionic liquid as an extractant solvent. During the metathesis reaction [DDA][Cl] was changed into hydrophobic IL, didecyldimethylammonium perchlorate [DDA][ClO_4]. Average relative recoveries of analytes obtained in preliminary studies ranged from 88.2% to 93%. What's more, the in-situ IL-DLLME method appeared to be fast, cost effective and clean method which meets the principles of "green chemistry".

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Extraction of Triterpenic Acids from *Eucalyptus globulus* using Aqueous Solutions of Ionic Liquids

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In order to substitute fossil fuels, the conversion of biomass and its residues into value-added compounds, fuel and energy has been a hot topic of research within an integrated biorefinery scenario. This strategy allows the valorization of biomass residues, and aims the reduction of the environmental impact by using more benign and effective methods towards a sustainable development. Currently, the paper and pulp industries generate significant amounts of residues, namely, leaves and outer barks, which are directly burned for energy production.

This work aims the extraction and recovery (isolation) of added-value compounds from the outer bark of *Eucalyptus globulus,* which is rich in triterpenic acids. These molecules are of special relevance for the cosmetic, pharmaceutical and food industries due to their antioxidant, anti-inflammatory and antitumor properties.[1] To this end, aqueous solutions of ionic liquids (ILs) will be investigated as alternative and more environmentally-benign solvents.[2] Operational parameters (ionic liquid structural features and concentration, contact time, solid–liquid ratio and temperature of extraction) were also investigated aiming at optimizing the extraction process by means of surface response methodologies. The recovery of triterpenic acids from the IL-based solvent, as well as the reusability and recyclability of the IL were also addressed.

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Toxicity Assessment of Imidazolium Ionic liquids by means of Respiration Inhibition Test using Unacclimated Sludge

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Ionic liquids (ILs) are attracting interest due to their unique properties and widespread commercial availability. The group of imidazolium ILs is a family with a great potential for industrial applications, and therefore, the possibilities to find them in the water ecosystems are high[1]. In this study the risks assessment of imidazolium ILs of different aliphatic chain lengths (from 4 to 10 carbon atoms) with the combinative anions: chloride (Cl^-), tetrafluoroborate (BF_4^-) and bis(trifluoromethilsulfonyl)imide (NTf_2^-) has been evaluated.
Toxicity was determined by means of a respiration inhibition test which consisted in short-term respirometric measurements using unacclimated sludge. The toxicity results were expressed as EC_{50}, defined as the effective concentration of a sample that causes 50% reduction of specific oxygen uptake rate[2].

It is assumed that the anion influence on ILs toxicity is subordinated to cation effect. However, our results show a significant effect of the anion group on the ecotoxicity value according to the following trend: $BF_4 < Cl < NTf_2$ (Table 1). The high toxicity of the anion NTf_2^-, the most hydrophobic among the ILs tested in this study, can be related to its affinity to accumulate at the biological membranes that are essentially non-polar interfaces. The presence of fluorine in the anion composition did not provoke an increase of the toxic effect, as has been previously observed using the luminescence bacteria *Vibrio fischeri*[3]. The elongation of n-alkyl chain length in imidazolium ILs gave rise increasing levels of toxicity. Thus, “Bmim” compounds can be classified as “practically harmless” compounds whereas “Dmim” ILs are considered “highly toxic”.

Table 1. EC_{50} values for imidazolium ILs tested.

Compound	Concentration range ($mg\cdot L^{-1}$)	EC_{50} ($mg\cdot L^{-1}$)	Compound	Concentration range ($mg\cdot L^{-1}$)	EC_{50} ($mg\cdot L^{-1}$)	Compound	Concentration range ($mg\cdot L^{-1}$)	EC_{50} ($mg\cdot L^{-1}$)
BmimCl	210-735	419±30	$BmimBF_4$	602-898	> 898	$BmimNTf_2$	665-898	146±16
HmimCl	55-148	67±10	$HmimBF_4$	245-518	299±17	$HmimNTf_2$	30-82	41±5.8
OmimCl	3.5-13	5.4±1.6	$OmimBF_4$	1.9-25	14±1.5	$OmimNTf_2$	3.0-6.0	5.6±0.69
DmimCl	0.15-1.1	0.86±0.28	$DmimBF_4$	0.43-49	2.0±0.33	$DmimNTf_2$	0.24-0.94	1.0±0.53

In summary, although cation and anion contributed to the whole ILs toxicity, when the number of carbons in the alkyl chain length is higher, the effect of the counter anion becomes less important.

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Ecotoxicity of Ionic Liquids

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Ionic Liquids (ILs) are commonly defined as non-conventional solvents. They have been getting increasing attention from the scientific community and industry not only due to their green potential but also to their unique combination of properties. These properties can be manipulated by altering the nature and structure of the composing ions. Characteristics like hydrophobicity, biodegradation or toxicity can be taken into account when designing an ionic liquid to green pharmaceutical and industrial applications.[1]

Nowadays most of the results published in literature are focused in thermophysical and thermal characterization, and there is scarce information about their effects in the environment and human health.[2]

To improve this knowledge distinct ILs based on imidazolium, pyridinium, cholinium cations and some fluorinated and aminoacids anions will be tested. Minimal Inhibitory Concentration (MIC) was determined to define their toxicity for bacterium *Pseudomonas stutzeri*. To complement these data Effective Dose Concentration (EC50) was also measured in different human cells lines (CaCo-2, HepG2). The results obtained allows to select the most "greener combination" for cations and anions.

In conclusion, the ecoenvironmental-friendly nature of these novelty compounds was demonstrated which support their use in diverse industrial applications.

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Cytotoxicity and Partition Coefficients of Fluorinated Ionic Liquids

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Ionic liquids are salts that can be manipulated by choosing the nature and structure of the composing ions according to their properties such as hydrophobicity, solution behaviour, thermophysical properties, biodegradation or toxicity. Although the number of publications in ionic liquids has witnessed an exponential growth, there are still quite unexplored themes. That is the case of the fluorinated ionic liquids family. The solvation of (fully or partially) fluorinated ionic liquids is of particular interest in areas where perfluorocarbons find relevant applications, such as imaging agents, fluorocarbon gels, nanocompartmented supramolecular architectures and colloids, control and stabilization of emulsions, microbubbles and other colloids, pulmonary delivery of drug and genes and oxygen therapeutics, where these compounds are used as gas carriers in liquid ventilation and intravenous formulations.

The nearly null volatility of ionic liquids at atmospheric conditions, their easy recovery, and, therefore, their recyclability, as well as their tuneable toxicity completely justify the application of fluorinated ionic liquids for improving the available oxygen therapeutics. The acute loss of blood is one of the most common problems in the medical community. Every day there is a tremendous demand of blood for accident victims and surgical patients who require rapid replacement of oxygen. There are a lot of benefits for society in the development of novel artificial blood substitutes that can be an alternative for allogeneic blood transfusions or that can improve tissue oxygenation and function of organs with marginal oxygen supply.

In order to evaluate the feasibility of partially replacing perfluorocarbons (PFCs) with fluorinated ionic liquids in PFCs-in-water emulsions, usually used for biomedical purposes, herein the study of the biocompatibility and cytotoxicity of fluorinated ionic liquids were carried out in different human cell cultures types (human colon carcinoma cells, Caco-2; human hepatocellular carcinoma cells, HepG2; spontaneously immortalized human keratinocyte cell line, HaCaT; and human umbilical vein cell line, EA.hy926). A review of these parameters was also performed by determining the octanol-water coefficient (K_{OW}) partition, in order to assess the potential for membrane permeation and cytotoxicity assays. The results may help us predicting whether it is feasible to use these fluorinated ionic liquids for future biomedical applications.

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The Effect of Ionic Liquids on α-amylase Activity

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Processes catalyzed by hydrolytic enzymes such as amylases are at the forefront of enzymatic research in sectors as varied as the petrochemical, pharmaceutical or food industries. The industrial production of biofuel is mainly tackled by fermentation of starchy feedstocks such as rice, wheat and corn. Since starch fermentation to produce bioethanol is not possible, a pretreatment is required, which consist of an acid or an enzymatic-catalyzed hydrolysis. Usually, enzyme-catalyzed hydrolysis is preferred due to economic advantages, because is necessary the use of expensive corrosive-resistant equipment. The effectiveness of the activity of amylases is paramount for the development of more efficient and sustainable technologies for hydrolyzing starch.

Ionic liquids (ILs) are considered greener solvents with appealing physicochemical properties which can be fine-tuned according to the desired application. Moreover, since information about the behaviour of α-amylases in the presence of ILs is scarce, we decided to use a large set of distinct ILs to interpret the effect of both the cation and the anion on the activity and stability of the enzyme.

In this work, ILs belonging to ammonium, pyridinium and imidazolium families were screened in order to elucidate the most biocompatible candidates in terms of the activity of α-amylase from Bacillus amyloliquefacien. Both the structural stability and biocatalytic potential was ascertained and discussed on the basis of the ILs relevant physical properties. Differential scanning fluorimetry and spectrophotometric analysis confirmed higher suitability of ammonium-based ILs to be used as medium for biocatalysis. Besides, carboxylate-based ILs proved to be optimum to avoid typical deactivation and destabilization processes triggered by other hydrophilic ILs families.

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Increasing Lypase Activity Using Ionic Liquids

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Microbial lipases are one of the most widely used class of enzymes in biotechnology, due to their appealing features such as their chemo-, regio- and enantioselectivity, broad substrate specificity and ability to be active in aqueous and organic media. These enzymes are known to perform its catalytic action both in hydrolytic and synthetic reactions like esterifications, transesterifications, alcoholysis, etc. In these latter cases, the pursuit of an optimum non aqueous biocatalytic medium is requested, so ionic liquids (ILs) have been suggested as a viable alternative. One of the challenging trends in this field is the search for ILs able to maintain the enzyme native state.

In this work we designed new environmentally friendly neoteric solvents, more specifically, functionalized ammonium-based cations and amino acids anions. The effect of different concentrations of aqueous solutions of amino acids, cholinium chloride and amino acid-based ILs, synthesised in-house, in the biocatalytic and structural response of TlL was investigated. This work points out that, per se, structural results are not enough to analyze the influence of ionic liquids on the activity of an enzyme. The observed ILs-induced structural changes do not compromise at all the enzyme activity, but reinforce it. This study shows for the first time that new biocompatible amino acid-based hydrophilic ionic liquids can enhance enzyme activity, acting as a special media to be concomitantly used in enzyme extraction and biocatalysis. More specifically, we show that water + hydrophilic ILs mixtures enhance (up to 50%) the enzymatic activity of lipases [1].

Ab initio calculations and MD simulations were performed to obtain information about the structure and thermodynamic properties of these amino acid-based ILs and their aqueous solutions.

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Towards the Use of Ionic Liquids as Bioavailability Promoters for Aromatic Pollutants

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Polycyclic aromatic hydrocarbons (PAHs) are pollutants of concern with potential adverse health impacts that are present in oil, coal or tar and are formed in several industrial processes. One of the most appealing technologies to remove and clean up PAHs from natural environments is bioremediation. Nevertheless, the very low solubility of PAHs in water derails the possibility of using microorganisms to biodegrade them.

Ionic liquids (ILs) can act as solubility enhancers of PAHs due to the formation of micelles/aggregates in water. This surfactant-like behaviour is the solution for the implementation of a bioremediation strategy for PAHs. More specifically, ILs will be used as co-substrates in the culture medium, in order to improve the efficiency of the biodegradation process by distinct organisms, namely bacteria.

In the present work different ILs (imidazolium based, cholinium based and novel biocompatible ionic liquids) possessing surface active properties have been selected to shed light on the implementation of a true remediation strategy for hydrophobic PAHs. Moreover, it also focuses on the study of toxicity of some commonly used ILs and on the elucidation of the metabolic and biodegradation pathway of hydrophobic pollutants and ILs (using phenanthrene as a model compound).

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Ecological Effects of Three Imidazolium Based Ionic Liquid on Microbial Activity of a Soil and on Tree Seed Germination

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Despite the increasing number of papers about the study of ionic liquids (ILs) properties and applications during the last years, the knowledge of their ecotoxicity and biodegradability is still an open question.

In this work the effect of addition of five different doses of three imidazolium based ILs, on the seed germination of different species of pine and eucalyptus, and on the microbial activity of soils under *Pinus pinaster* and *Eucalyptus globulus* was analysed.

The selected ILs are 1-propil-3-methylimidazolium bis (trifluorometilsulfonil) imide, [PMIM][NTF_2], 1-butil-3-methylimidazolium trifluoroborate, [BMIM][BF_4] and 1-butil-2,3-dimethylimidazolium trifluoromethanesulfonate, [BMMIM][OTF]. Four different concentrations of aqueous solutions (10%, 1%, 0.1% and 0.01%) of the IL were prepared.

Seed germination test of species of *Pinus pinaster Aiton, Pinus sylvestris L., Pinus radiata D. Don* and *Eucalyptus globulus* were carried out for all the doses of ILs. Five replies with 25 seeds per Petri dish were incubated for every species and treatments [1]. The seeds were incubated in a Phytotron (Climas AGP890) and were maintained for 16 h under light at 24 °C and in the dark for 8 h at 16 °C. Germinated seeds were counting every Monday, Wednesday and Friday. Germination had been completed in all the species after 45 days of incubation.

On the other hand, the effect of the addition of the same doses of the different treatments on microbial activity of two Galician soils, under *P. pinaster* and *E. globulus* was studied by microcalorimetry. Calorimetric experiments were performed using a microcalorimeter Thermal Activity Monitor (TAM-III) TA-Instruments. Measurements were carried out in hermetically sealed 5 ml stainless steel ampoules. Soil samples of 1 g size at water-holding capacity, treated with 0.2 ml of a glucose solution in water with a concentration of 6.25 g / l to activate the metabolism of soil microorganisms, were used as control [2]. The heat released by the microorganisms was recorded until the total consumption of glucose (at least three days). Three replicates were performed for each case.

Results showed important differences between species and ionic liquids.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Concentration of Prostate Cancer Biomarkers Using Ionic-liquid-based Aqueous Biphasic Systems

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Prostate cancer (CaP) is the second most common diagnosed cancer in men with more than 1.11 million new cases worldwide [1]. However, once diagnosed in its early-stage, CaP can be treated with a successful rate of more than 90% [1]. Thus, in order to increase the lifespan of patients, it is extremely important to invest and to develop new techniques for cancer early-stage diagnoses. Prostate specific antigen (PSA) is a glycoprotein present in human fluids and is well-known as a CaP biomarker. Due to its low content in human fluids, the assays currently employed to identify and quantify PSA require sophisticated analytical equipment and time-consuming methodologies. However, if previous concentration and purification stages are attained, the use of more accessible equipment becomes a possible option. In this context, ionic-liquid-(IL)-based aqueous biphasic systems (ABS) were investigated in this work as viable alternatives to extract and concentrate PSA from human fluids. In order to develop an efficient method for the one-step extraction and concentration of PSA, while allowing the use of more versatile equipment with higher detection limits, a series of ABS composed of potassium citrate and phosphonium-based ionic liquids (ILs) were screened. The respective ternary phase diagrams, as well as the tie-lines and tie-line lengths, were initially determined at 298 K to ascertain on their monophasic/biphasic regimes. Finally, these systems were evaluated through their extraction and concentration performances for PSA. The effects of the IL chemical structure and tie-line length were investigated aiming at reaching and maintaining the complete extraction of PSA for the IL-rich phase in a single-step. Further, several concentration factors were investigated along the same tie-line. This novel technique can be thus envisaged as a new method for the concentration of cancer biomarkers from human fluids, towards an early-stage diagnosis, while allowing the use of more versatile equipment.

Acknowledgements

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Charge Storage on Ionic Liquid Electric Double Layer: The Role of the Electrode Material

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Ionic liquids have revealed to be a new class of solvents with promising new fields of application [1]. The introduction of new anions such as $[FAP]^-$ (tris(pentafluoroethyl)trifluorophosphate) opens new possibilities and a throughout study of their electrochemical properties is required.

In particular, the assessment to how the charge density and the nature of the electrode material influences the structure of ions near the charged electrode is of great importance for the development of new applications of ionic liquids [2,3]. The electronic interactions of 1-butyl-3-methylimidazolium (tris(pentafluoroethyl)trifluorophosphate) $[C_4MIM][FAP]$ ionic liquid with glassy carbon, mercury, gold and platinum were assessed in order to get a fundamental understanding of the electrical double layer microscopic structure and its intrinsic properties at electrode/IL interface.

Ionic liquids containing the (tris(pentafluoroethyl)trifluorophosphate) anion paired exhibit a strong hydrophobic nature and wider electrochemical windows than previously used ionic liquids with simultaneous good electrochemical stability. The magnitude and shape of C(E) curves point to different orientations of the cation when the nature of the substrate is changed.

Acknowledgments

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Chemical and Electrical Characterizations of Polymer Inclusion Membranes and their Constituents: RTIL 336 and Cellulose Triacetate (CTA)

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Polymer inclusion membranes (PIMs) constitute a new class of membranes that have been developed for a variety of applications in separation science and chemical sensors. [1] Base polymer and extractant are the necessary components of the PIMs, but a plasticizer use to be also added to ensure their mechanical stability. However, the use of room-temperature ionic liquids (RTILs) as carriers simplifies PIMs formulation due to their plasticizing abilities. The RTIL Aliquat 336 (a quaternary ammonium salt) is widely used as extractant in PIMs preparation as anion exchanger, since it allows the removal of inorganic anions such as phosphate or toxic species as arsenic, [2-3] among others. Besides the content of Aliquat 336 in the separation efficiency of PIMs, which has previously been demonstrated, [3-4] the role of the other components is also of great importance

This work presents chemical surface and electrical characterizations of PIMs constituents suc
base polymer cellulose triacetate (CTA) and the RTIL Aliquat 336, which were performed by
impedance spectroscopy measurements, respectively, and they are compared with those det
for CTA-based PIMs containing 26 % and 48 % of Aliquat 336. IR spectroscopy, im
spectroscopy and elastic measurements with wet PIM samples (submerged in a 0.01 M NaCl
for 24 h) and electrochemical measurements (membrane potentials with NaCl solutions at
concentrations) were also performed to get significant information on the effect of RTIL conte
behaviour of the PIMs when they are in contact with electrolyte solutions.

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Electrical Characterization of Cellulosic/Aliquat 336 Membranes

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A membrane is a barrier placed between two fluid phases, which restricts the transport of one or various chemical species in a selective manner. Among the different strategies for improving membrane performance, the inclusion of RTILs in the membrane structure by different methods such as injection (under vacuum) into the membrane pores (supported liquid membranes or SLMs), membrane formulation (polymer inclusion membranes or PIMs) or proton/cation exchange mechanism, have been proposed. [1-4] SLMs and PIMs are basically applied in the treatment of metal contaminated waters from industrial effluents or even natural waters, while the membranes obtained by exchangeable cations are proposed for fuel cells application (PEMFC and DMFC). For all these applications, determination of the membranes electrical characteristics can give valuable information.

In this work, cellulose-based membranes were modified with the RTIL Aliquat 336 by dip coating technique, and the effect of IL inclusion in the structure of both porous and dense membranes on electrical parameters is analyzed. Electrical characterization of original and modified membranes was performed by impedance spectroscopy (IS) measurements (electrode/membrane/electrode system), which were carried out with membranes in dry and wet conditions (after 24 h immersion in NaCl solutions), as well as for a mixture of Aliquat 336/water. A comparison of these results and those previously obtained with the IL $BMIMBF_4$ and the dense-membrane/$BMIMBF_4$ [5] is also presented. Moreover, IS measurements have also been used for dynamic analysis of IL inclusion in dense membranes by studying time variation in the values of the electrical resistance. [1]

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Corrosive Properties of Liquid Fractions Issued from Lignocellulosic Biomass Pretreatment with Imidazolium-based Ionic Liquids: Towards a Scale Up of Biorefinery Strategy

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One of the main challenges of the 21st century is to meet the increasing demand for energy requirements by means of a more sustainable energy supply. The use of ionic liquids (ILs) in the lignocellulosic biomass pretreatment necessary to 2nd generation bioethanol production has gained considerable attention in recent years[1],[2]. Indeed ILs present several advantages including high thermal stability and low volatility, which distinguish them from conventional instable and toxic pretreatments, operating at severe conditions[3],[4]. Owing to an imminent scale-up phase, it is necessary to anticipate future problems which could be encountered at industrial scale. Since the annual direct cost of corrosion worldwide is over 3% of the world's Gross Domestic Product[5], prevention and reduction of corrosion in biorefineries of the future is of great scientific and technological interest and of upmost economic importance. However very few reports concerning the evaluation of corrosion due to ILs in biorefineries are available.

Consequently the purpose of the present work was to study the corrosive properties of liquid fractions issued from lignocellulosic biomass valorization into second generation bioethanol after each step of the process: pretreatment with imidazolium-derived ILs (2% w/v biomass-IL, 110°C, 40 min), cellulose regeneration, enzymatic saccharification to release fermentable sugars and alcoholic microbial fermentation. Two industrial metals were tested using mass loss techniques: S235 carbon steel and 316L stainless steel. Corrosion rates measured on 316L stainless steel after 7 days at 100°C were found negligible (below 1 µm/year) whereas rates for S235 carbon steel tested under identical conditions, varied until 400 µm/year depending on the nature of the liquid fraction. Our results indicated that IL anionic moiety played an important role in the IL corrosive properties, as EmimMethylphosphonate (31-390 µm/year) was more corrosive than EmimAcetate (0-100 µm/year), depending on liquid fraction nature. Lignocellulosic biomass components dissolved on ILs after pretreatment did not increase the corrosive power. In contrast, the addition of an anti-solvent (water or ethanol) for the regeneration step seemed to increase the corrosion. Both enzymatic saccharification and microbial fermentation steps did not influence significantly the corrosive properties of the liquid fractions.

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Electrochemistry of Different Noble Metal Nanoparticles in Imidazolium-Based Ionic Liquids. Frequently Asked Questions

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In the last decade, several contributions have been dealing with the use of room temperature ionic liquids (RTILs) as promising solvents for different electrochemical applications (energy production devices, electroanalytical and electrosysntesis purposes, among others) due to their particular physicochemical properties [1]. On the other hand, the employ of metal nanoparticles (NPs) in Electrocatalysis has become the benchmark [2]. However, the use of metal NPs as electrocatalysts in RTILs is still scarce and particularly the influence of key parameters such as temperature and level of humidity (water content) on the resulting electrocatalytic properties still remains unexplored. Consequently, in this communication, we will describe the main electrochemical features of Pt, Pd, Rh and Ir NPs in some particular imidazolium based ionic liquid. Moreover, we will evaluate the effect of i) temperature and ii) water content on the electrocatalytic behavior of these noble metal NPs toward the so-called CO adsorption-stripping reaction [3]. The obtained results show how important are those parameters on the electrochemical response of different metallic nanomaterials.

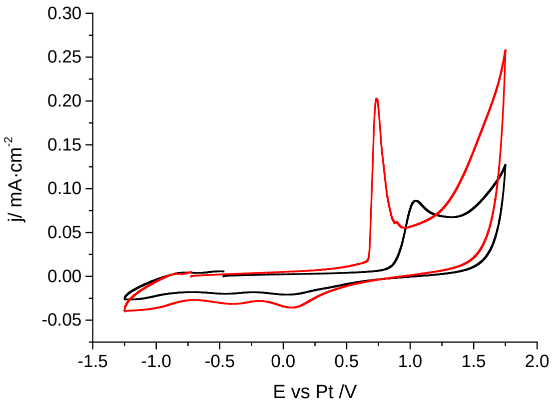

Figure. CO stripping voltammetry on Pt NPs in deareated [BMIm][BF_4] with 190 ppm of water (black line) and 600 ppm of water (red line). Scan rate 20 mV/s.

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P-doped Carbon-CNT Composites Obtained on Deep Eutectic Solvents for Supercapacitor

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Due to its special features (e.g. low flammability and vapour pressure, chemical and thermal stability, and excellent solvation potential)[1], ionic liquids (ILs) have attracted much attention like a media in synthesis of resins. Specifically, the deep eutectic solvent (DES); whose properties can be tailored easily by changes in the components ratio; have been presented as an attractive alternative. DES allows the synthesis of doped-carbon with a lot of heteroatoms (N, S, P, etc.)[2-3], and the dispersion of high amount of nanomaterials, like multiwalled carbon nanotubes (MWCNT)[4] or grapheme flakes[5].

In this poster we present a MWCNT-carbon composite doped with phosphorous. Eutectic mixtures of the monohydrated form of p-toluenesulfonic acid ($pTsOH{\bullet}H_2O$) and triethyl phosphate (TEP) were used to disperse MWCNTs, and to catalyse the polycondensation of furfuryl alcohol. Hierarchically-structured P-doped carbon-CNT composites were obtained after carbonization. The high surface area and the phosphorous functionalization combined with the hierarchical structure and good electrical conductivity exhibited by these composites allow their use as electrodes in supercapacitor cells. Actually, the supercapacitor cell built up with these electrodes provided enough neat energy to turn on an IR LED of 30 mW. This performance surpasses any performance previously reported for electrodes weighing (at least) 10 mg per cm^2 of current collector and using an aqueous electrolyte.

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Selective Aqueous Biphasic Systems Based on Ionic Liquids as Electrolytes

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The selectivity issue on the extraction/purification of a large plethora of common molecules and diverse bioactive compounds is one of the most concerning problems faced nowadays. With the increased concern on the use of more renewable sources of compounds and with the attention focused in more valuable natural raw materials, the definition and design of new and more selective technologies is of utmost importance. Due to the complexity of the new raw materials matrices, it was required to look for more tunable compounds capable to be applied as more manipulative solvents. Ionic liquids (ILs) are one of the classes more focused in the last ten twelve years.[1] In this work we look for ILs as electrolytes used to manipulate the properties of common polymeric aqueous biphasic systems (ABS).[2] These systems were properly designed and then applied in the extraction of two biomolecules with very different structural characteristics, one protein and one dye. After the proper development of the binodal curves using polyethylene glycol (PEG 8000), sodium polyacrylate (NaPA 8000) and distinct ILs, or inorganic salts as electrolytes, the effect of different amounts of ILs (from 0.1 to 5 wt%), the influence of the IL anion nature and the cation core (ammonium and imidazolium) were reported. These systems were characterized regarding the pH condition and the ILs' partition between both phases. The extractive potential of these ABS was evaluated using the protein cytochrome c (Cyt c) and the dye chloranilic acid (CA). The main results on the extraction efficiencies show that these systems are selective in the extraction of both Cyt c ($EE_{Cyt\,c} > 96.13 \pm 3.22$ % in the NaPA-rich phase) and CA (concentrated in the PEG 8000-rich phase $EE_{CA} > 80.13 \pm 1.45$ %), preferentially for lower IL concentrations *i.e.* 0.1 wt%. These results indicate that this class of polymeric ABS may be an advantageous tool in the development of highly selective (the polarity of both phases can be significantly manipulated) and low-cost (possibility of to use very low amounts of ILs – the most expensive solvent used) extractive platforms.

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Aluminium Deposition from Ionic Liquids and LCA Analysis of the Electrolyte

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The reduction of aluminum from organic solutions of Al-halides was shown by Plotnikov for the first time in 1899.[1] Various investigations on electrolyte variations for Al plating have been already described, some of them leading to high purity galvanic depositions, but still some problems persist such as self-ignition of the organo-Al compounds, the flammability of the organic electrolytes and the high cost of the Al-source. In addition, other types of Al-plating electrolytes have been developed, but those drawbacks as well as low film purity and complicated process handling have not been completely resolved. This is now possible with the help of ionic liquids.

Ionic liquids (ILs) are ionic compounds with melting points below 100°C, which have a range of useful properties, among which non-flammability, thermal and chemical stability and very low vapor pressure. Because of those in recent years, the focus was placed more and more on them as potential electrolytes for the deposition of non-noble metals. Further some of them provide also a wide electrochemical window, which is a important feature for the deposition.[2]

Figure 1 Aluminium deposition on a toy car

Current results of Al electroplating (Figure 1) will be shown in our presentation. They have been done at ambient temperature in different electrolytes, where the ionic liquid, the AlCl3 concentration and the additives are varied. So it was possible to deposit Al films of different thickness on substrates with different shapes and composition. Furthermore, a Life Cycle Assessment of the galvanic Al-deposition by using ILs is discussed.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Effect of Electronic Polarizability on the Single-particle Dynamic of Mixtures of Ionic Liquids and Lithium Salts

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In the present contribution we analyze the effect of electronic polarizability on the structure and dynamics of mixtures of the aprotic ionic liquid (ILs) 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([EMIM][TFSI]) with [Li][TFSI]. We report molecular dynamics (MD) simulations of the mixtures at several concentrations with two different optimized force fields, the non-polarizable OPLS-AA and the polarizable APPLE&P. Our analysis focuses on the effect of polarization on the structure (radial distribution functions and coordination numbers) and single-particle dynamics (mean square displacements (MSDs), cage autocorrelation functions (CAFs), velocity autocorrelation functions and densities of states (DOSs) of the different species). Our results indicate that, even when the structure of the mixtures can be adequately described with non-polarizable potentials, the dynamics are deeply affected by the electronic polarization, non-polarizable potential underestimating MSDs of added lithium cations by almost an order of magnitude. This underestimation is undoubtedly associated to the overestimation of the Coulomb coupling in the bulk mixtures that is also reflected in the behavior of the DOSs, whose non-polarizable version are blue-shifted with respect to their polarizable counterparts. This shows lithium cations are more strongly bound inside their cages in the bulk unpolarized mixtures, and therefore in a reduced mobility stat. The CAFs also show this reinforced interactions of [Li^+] with their neighbors, since the non-polarized versions decay much more slowly than the polarized ones.

Acknowledgements

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Charge Transport Mechanism in Ionic Liquids

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Charge transport mechanism in Ionic Liquids (ILs) is far from being a resolved problem. The accepted view assumes that the only mechanism for electrical conductivity is ionic conduction, as it happens in electrolytic solutions[1]. We have recently published results for ionic rigid gels (composed only by an IL and water) that seems to contradict that picture[2]. In order to elucidate the possible role of protons and electrons on ILs conduction, we have measured the temperature behavior of the electrical conductivity on three different ILs which can or cannot generate electronic and/or protonic conduction[3]. First we have studied three compounds with cations 1-ethyl-3-methyl imidazolium (EMIm), 1-ethyl-2-3-methyl imidazolium (EMMIm) and 1-ethyl-1-methyl pyrrolidinium (EMPyrr), all of them with decyl sulfate (DS) anion. Their structures were selected to investigate the influence of the imidazolium H-2 proton (slightly acidic) and the presence of a π system on the cation. Thus the EMIm-DS can protonate (while the other two cannot) and also the EMPyrr has not π electronic cloud (while the two imidazolium based ILs do). Also, we analyze the alkyl chain length effect on the electrical conductivity of a series of seven alkyl (proton, methyl, ethyl, butyl, hexyl, octyl and decyl) sulfate ILs derived from EMIm cation[4].

Results indicate that the main mechanism is certainly ionic conduction (hopping or displacement), as demonstrates the decrease of electrical conductivity with the alkyl chain length increase. In any case, we cannot completely discard protonic and electronic conduction because EMIm-DS presents higher conductivity value than EMMIm-DS and EMPyrr-DS at 100ºC (when all three are liquid). Also, both imidazolium ILs present higher conductivities than pyrrolidinium, which has not aromatic character. More work to completely elucidate the charge transport mechanism in pure ILs and mixed with different solvents is now in progress.

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Poster Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Effect of Na/Li Concentration in Ionic Liquids Electrolytes for Ion Batteries: A Molecular Simulation Study

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The ion transport and structural properties of electrolytes based on Room-Temperature Ionic Liquids (RTILs or commonly ILs) have been investigated by classical and quantum molecular simulation. In this work, we analyze the effect of sodium/lithium salts dissolved in ILs for electrolytes of ion batteries[1-2]. We investigate the behavior of 1-methyl-1-butyl-pyrrolidinium $[C_4PyR]^+$ bis(trifluoromethanesulfonyl)imide $[Tf_2N]^-$ when different concentrations of $[Na]^+[Tf_2N]^-$ or $[Li]^+[Tf_2N]^-$ are dissolved in it. We performed Molecular Dynamics (MD) simulations and quantum calculations to obtain the temperature dependence of the density, diffusion, and conductivity as well as structural information of the systems. The ionic conductivity of electrolytes can be predicted by MD simulations [Figure 1] through its relation with diffusion coefficients thanks to the Nernst-Einstein equation. We provide detailed information about the total conductivity of the systems in addition to the contribution of each individual species (partial conductivity). Both ionic conductivity and diffusion coefficients decrease with increasing concentration of Na/Li salts, due to molecular aggregation or formation of complexes between Na^+, Li^+ cations and anionic species. We study the nature and behavior of these complexes and their impact on the mobility of the components. As most results for density, diffusion, and conductivity are in line with available experimental data, they will help to understand the molecular mechanisms involved in the ionic transport of working electrolytes for novel concepts in batteries.

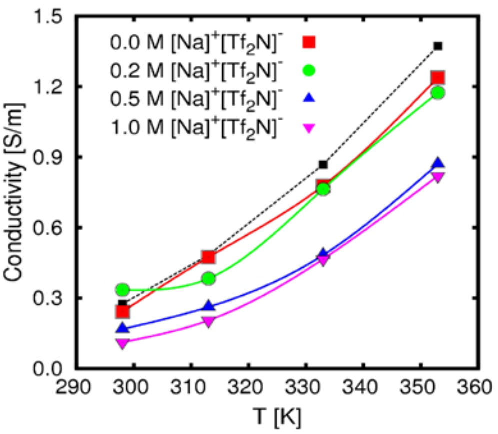

Fig 1. Conductivity vs temperature for $[C_4PyR]^+[Tf_2N]^-$ electrolytes as a function of the concentration of sodium. Black squares represent experimental values for $[C_4PyR]^+[Tf_2N]^-$.

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Corrosion Behavior of Carbon Steel in CO_2 Saturated Amine and Imidazolium-, Ammonium- and Phosphonium- based Ionic Liquid Solutions

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Amine absorption process is considered as the most mature technology for near term CO_2 capture application [1]. However, in addition to the intensive energy requirement of the process, the aggressive corrosive behavior of classical amine solutions is addressed as one of challenges facing the industrial scale carbon capture application [2]. Recent investigations explored the use of amines and room-temperature ionic liquid (RTILs) blends as viable replacement of classical amine solutions [3].This work shows a recent investigation on corrosion behavior of carbon steel CS1018 using novel mixtures of the classical amine, monoethanolamine (MEA) and RTILs. The famously known imidazolium-based RTILs with different fluorinated anions were used in the experiments, namely; 1-butyl-3-methyl imidazolium tetrafluoroborate ([C_4MIM][BF_4]), 1-butyl-3methyl imidazolium trifluoromethanesulfonate ([C_4MIM][Otf]). Phosphonium-based and ammonium-based RTILs with acetate anion, namely tributyl(methyl)phosphonium acetate ([P_{4441}][Ac]) and choline acetate ([Ch][Ac]) were also blended and investigated with MEA amine. Electrochemical polarization techniques were used to determine the absorbent corrosiveness via corrosion rate and polarization behavior. The process parameters of interest were CO_2 loading and test temperature. Results showed that the partial replacement of aqueous phase in MEA solution by hydrophilic imidazolium-based RTILs reduced corrosion rates by 40 to 70% compared to aqueous 30 wt% MEA solution. MEA/[C_4MIM][Otf] solution showed higher corrosivity compared to MEA/[C_4MIM][BF_4] at low test temperatures of 25 °C and 40 °C due to the higher CO_2 absorption loading. At higher temperature, the poor hydrolytic stability of BF_4 anion caused instable polarization behavior and higher steel corrosion rate. MEA/[P_{4441}][Ac] and MEA/[Ch][Ac] solutions showed more promising corrosion inhibition performance compared to imidazolium-based RTILs with corrosivity ranking of MEA/[P_{4441}][Ac] > MEA/[Ch][Ac] > MEA/[C_4MIM][BF_4].

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Theoretical Study on the Behavior of Aminoacid-Based Ionic Liquids Regarding to Carbon Nanostructures

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Molecular dynamics simulations and quantum chemistry methods based on the Density Functional Theory are used for the characterization of aminoacid-based ionic liquids with regard to carbon nanostructures. The dispersion and solvation of C60 fullerenes was considered together with the ionic liquids adsorption on graphene sheets and the confinement in nanotubes. The used theoretical methods allow a detailed nanoscopic characterization of the studied hybrid systems. Adsorption on graphene is characterized by high density layers in the vicinity of the surface, whose properties are analyzed as a function of the ions molecular structures. The behavior of ions when confined between parallel graphene layers and inside carbon nanotubes is also analyzed considering the distance between the sheets and nanotubes diameter with the structural, energetic and dynamic features studied. Likewise, solvation layers around the nanotubes are also analyzed. Structural, dynamic, and energetic factors were analyzed to infer the role of the studied ions on the behavior of fullerenes in ionic liquids with the dispersion mechanism being fully characterized.

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Study of the Interface Pt(111)/ [Emmim][NTf_2] Using Laser-induce Temperature Jump Experiments

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Room Temperature Ionic liquids (RTILs) have attained special attention in the field of the electrochemistry due to their benefits such a wide electrochemical window, low vapor pressure or enough conductivity that make them promising electrolytes. Especially the study of the interface between a metal electrode and RTILs result of great interest as the interface is the region where a reaction takes place. However, the knowledge of the properties of the interface between Pt single crystal electrode and a RTIL is scarce[1].

The use of the laser-induce jump temperature method is a powerful tool to study the interface Pt/solution since it provides a value close to the potential of zero charge (pzc)[2]. In this method the temperature of the interface is suddenly increased by applying short laser pulses and the response obtained while temperature relaxes is the change of the electrode potential measured under coulostatic conditions. This change deals with the reorganization of the solvent network on the surface. The potential where the transient obtained is zero is the potential of maximum entropy (pme), close to the pzc.

In the present work the interface Pt(111)/Emmim[Ntf_2] was investigated by using laser-induce temperature jump experiments[3]. At positive applied potential, positive transients are obtained which means there is major density of anions than cations on the surface. Decreasing the applied potential to enough low values the transient becomes negative which means the density of cations is now higher. The transients obtained show potential dependence and hysteretic behavior with the applied potential.

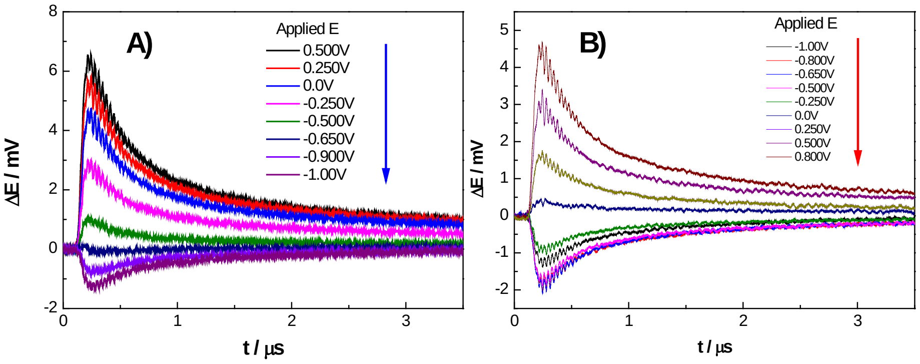

Figure 1: Laser-induced potential transients for a Pt(111) in[Emmim][NTf_2] at different applied potentials.

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Tuning the Porosity of Hierarchical Monolithic Carbons by Dilution of Deep Eutectic Solvents

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Monolithic carbons with hierarchical porous architectures have gained much attention over the past years [1]. However, the improvement of their synthetic method, in order to produce and tune their structure and composition to enhance their performance in different applications (e. g., CO_2 storage or energy storage/conversion electrodes) and make it more sustainable, is still a challenge [1-3].

Ionic liquids (ILs) and deep eutectic solvents (DES) are promising solvents for greener material syntheses due to their physical and chemical properties [4-6]. Our work has been lately focused on the use of DESs playing multiple roles (e.g. reaction medium, monomer precursors, dopping agent and even structure directing agents) in polycondensation reactions [6]. In the present work, DES dilutions with different solvents (i.e. water or organic benzyl alcohol) have been prepared as a way to tune the porosity of the final carbon. The ratio between the eutectic mixture and the solvent was found to be a critical parameter to control the spinodal decomposition and the final internal structure.

In the present work we have added different proportion of solvents (organic and water) as a way to control the internal structure of the final carbon, and observed the change of the final structure when the solvent proportion change.

Acknowledgments

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Removal of Metallic Anions from Aqueous Solutions by Adsorption with Cyphos IL101 Ionic Liquid-impreganted Multiwalled Carbon Nanotubes

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This work analyzed the adsorption of Cr(VI), Au(III), Cr(III), Cd(II) and Au(I) in the form of anions from aqueous solutions of different media: HCl in the case of Cr(VI), Au(III) and Cd(II), alkaline (OH^-) in the case of Cr(III) and cyanide in the case of Au(I). using multiwalled carbon nanotubes impregnated with Cyphos IL101 ionic liquid, being the active substance of Cyphos IL101 (trihexyl-tetradecyl) phosphonium chloride. This reagent was dissolved in Solvesso 100 diluent (aromatic nature) in order to decrease the high viscosity of the undiluted ionic liquid. It was found that the so-impreganted carbon nanotubes, allowed almost complete removal (adsorption >95%) of $HCrO_4^-$, $AuCl_4^-$, $Cr(OH)_4^-$, $CdCl_4^-$ and $Au(CN)_2^-$ from their respective aqueous solutions, though the adsorption is influenced by the stirring speed, temperature and the characteristics of the metal-bearing solution. The adsorption of the different anions onto the impregnated carbon nanotubes may be attributed to an ion-pair adsorption, anion exchange, metal deposition (specially in the case of Au(III)) and simultaneous combination of the above. These results indicate that the use of this ionic liquid impregnating the multiwalled carbon nanotubes as an alternative to pristine carbon nanotubes in adsorption of hazardous and valuable metals is highly promising.

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Propylene Purification in a Hybrid System Using Polymer-ionic Liquid Composite Membranes

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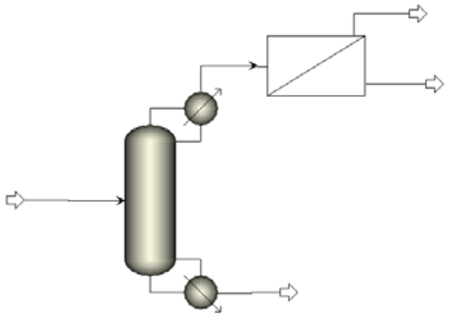
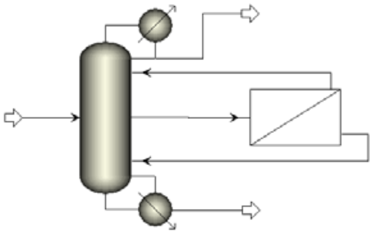
Currently the separation of propylene from propane on a commercial scale is performed almost exclusively by distillation in refineries and petrochemical industries. Since this technology is highly energy intensive, there is a strong economic incentive to explore alternative separation technologies with lower energy consumption. In this study, the combination of membrane and distillation processes to form a hybrid separation system is proposed as an alternative design to replace the current distillation technology.

The use of membranes that play an active role in the olefin/paraffin separation has been extensively reported in the literature.[1] In a previous work by our research group, we proposed the use of a novel polymer/ionic liquid-Ag^+ composite as facilitated transport membrane to carry out the separation of propane/propylene mixtures.[2] Experimental properties of a polymer/ionic liquid composite membrane were used to evaluate a hybrid membrane/distillation process by testing different configurations. Hybrid separations integrate two different unit operations that complement each other to solve a defined separation task. While distillation provides large capacities and simple operation, membranes potentially offer a high selectivity and low energy consumption, as well as a compact and modular design. The membrane modules reduce the loading for distillation columns, and mainly serve as alternative technology for retrofitting the current distillation platform.

We have found that the operating costs associated with a distillation column are closely related to the condenser duty and the reboiler duty. The parallel configuration proved to be more economically advantageous than the top and bottom configurations.





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Polymer Electrolytes: Playing with Natural Polymers and Cyano-based Ionic Liquids

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A solvent-free polymer electrolyte (SPE) is an ionically conductive solid solution of a soft polar polymer host in which a guest salt is dissolved. SPEs have been intensely studied since Wright et al. first reports because of their potential application in solid-state primary and secondary batteries and other electrochemical devices. SPEs have many advantages including high energy density, no risk of leakage, good electrode-electrolyte contact, simple preparation and light weight.[1-3]

Albeit SPEs technological potential, their application in commercial devices has been delayed mainly because SPEs present an ionic conductivity substantially lower than liquid electrolytes.[1,3] To overcome this drawback, in this work the added guest salts were cyano-based ionic liquids (ILs). Also, the increasing environmental regulation and the depletion of petroleum resources are providing the impulse for new materials based on natural polymers. Owing to their biodegradability, low production cost and extraction from renewable sources, biopolymers pose as a great alternative to synthetic polymers.[4] Thus, in this work is described the synthesis and characterization of SPEs based on the natural polymers: chitosan and gelatin, and on the ILSs: 1-ethyl-3-methylimidazolium dicyanamide ([C$_2$mim][DCA]), 1-ethyl-3-methylimidazolium thiocyanate ([C$_2$mim][SCN]), 1-butyl-3-methylimidazolium thiocyanate ([C$_4$mim][SCN]) and 1-ethyl-3-methylimidazolium tricyanomethanide ([C$_2$mim][TCM]).

The samples have been characterized by means of thermal analysis (TGA and DSC), ionic conductivity, cyclic voltammetry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). They presented an amorphous morphology, high thermal stability and high ionic conductivity. The highest conductivity value was 1.28 x 10^{-2} Scm^{-1} at 100 ºC for the sample with [C$_2$mim][SCN].

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New Coatings for Solid Phase Microextraction Fibers Based on Polymeric Ionic Liquids

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Advances in highly efficient detection methods through the development of efficient sample pre-treatment techniques, such as solid-phase-microextraction (SPME), have been playing an important role in metabolomics studies. However, for SPME experiments, only a very restricted number of non-specific sorptive coatings (SCs) are commercially available, thus hampering the great potential of this technique. To overcome this problem, Polymeric Ionic Liquids (PILs) are here proposed as coatings for SPME devices. Ionic Liquids are known by their high solvation capacity for a large number of chemically different compounds [1] and the combination of their properties with the mechanical and thermal properties of polymers is a promising approach to prepare materials with enhanced properties [2]. PILs based on vinyl-alkyl-imidazolium cation, pyrrolidinium and methacrylate cations combined with the bromide anion and bearing different alkyl chain lengths, were synthesized through photopolymerization [3]. In order to increase the prepared PILs thermal stability, the bromide anion was exchanged to the bis [(trifluoromethyl)sulfonyl] imide anion ($[TFSI]^-$). After coating the silica fiber support, the limit of detection, sorption time profiles, specificity, reproducibility and thickness of each fiber were assessed using standard solutions of aldehydes, alkanes, ketones and alcohols. Also, samples of *Eucalyptus* leafs were studied due to their natural complexity.

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Innovative CO_2 Selective Membranes Based on Poly(ionic liquid)s

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The urgent need to take action to prevent irreversible climate change has hugely increased efforts on the development of new efficient and economic technologies for carbon capture and storage. Taking into account the extremely broad range of chemical and structural possibilities of ionic liquid (IL) chemistry, and the undeniable engineering and economical advantages of membrane technology, there has been growing interest in the exploitation of poly(ionic liquid)s (PILs) as membrane materials for CO_2 separation[1] since this new generation of functional materials combines some of the unique properties of ILs with the macromolecular architecture of polymers. Although it has been shown that the endless combination of cations and anions or the incorporation of task-specific chemical groups allow the development of interesting membranes, additional research is still required to realize the full potential of these emerging tuneable materials.

In this communication, we will present a perspective of different approaches to design innovative CO_2 selective membranes based on PILs, ILs and their composites (PIL-IL).[2-5] The aim is not only to show the versatility of these ionic materials in the development of membranes with improved CO_2 separation performance, but also to reveal insights into the relationships between PIL structure and gas transport properties. We here focus on a variety of PILs bearing different polycations and anions having CO_2-phylic groups such as fluorinated or cyano-functionalized groups. Due to the promising data obtained, it is foreseen that the prepared engineered membranes will play a especial role as alternative materials for CO_2 separation.

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Facilitated Transport Composite Membranes Based on Polymer-ionic Liquids-Ag^+ for Propane/Propylene Separation

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Separation of light gaseous olefins from paraffin's of the refinery process off-gasses has been traditionally performed by cryogenic distillation, which is a highly capital and energy intensive operation. This handicap creates an incentive for the investigation of alternative olefin/paraffin separation technologies. In this regard, membrane technology supposes a potential solution for process intensification.

Previous works of our research group reported the use of facilitated transport composite membranes integrating the use of PVDF-HFP polymer, $BMImBF_4$ ionic liquid and $AgBF_4$ silver salt. In this type of membranes, the silver cations react selectively and reversibly with the olefin, allowing the separation via mobile and fixed carrier mechanisms. Ionic liquids were selected as membrane additives because in addition to their negligible vapour pressure that avoids solvent losses by evaporation, they provide stability to the metallic cation dissolved inside, and modify the structure improving the facilitated transport. This technology offers a commercial attractive separation alternative thanks to their modular form of operation, high values of selectivity and permeability and low operational costs.

In the present work, continuous flow propane/propylene permeation experiments, involving the use of different ionic liquids as well as different membrane compositions, were performed. Moreover, basing on the transport and equilibrium parameters previously obtained, a mathematical model description of the system has been proposed fitting the remaining parameters and allowing the design and optimization of the propane/propylene separation process at industrial levels.

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ILs-based Materials as Enabling Tools for the Design of Chemical Processes

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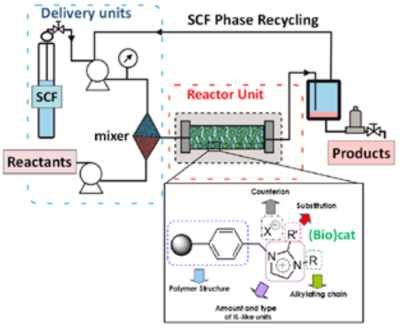
In the last few years, we have developed new functional advanced materials sharing the main properties of the ILs (Supported Ionic Liquid-Like Phases (SILLPs) and Polymeric Ionic Liquids (PILs)).[1] The presence on these materials of IL-like units provide them with the main features of ILs at the molecular level (stability, tunable polarity, etc.), while the presence of the polymeric backbone offers an additional design vector to optimize their macroscopic and process properties. Thus, SILLPs and PILs can be applied for catalytic processes in an analogous way to bulk ILs but simplifying product isolation and recycling of the catalyst-IL-phase.[2-4] Here we will examine and discuss some essential properties of polymer-supported Ionic Liquid-Like Phases (SILLPs), using insoluble matrices as supports, and their behavior to immobilize and stabilize different catalytic species. The use of this type of advanced materials has opened the possibility of performing catalytic and multi-catalytic processes. In general, the adequate design of the corresponding polymer-support for SILLPs/PILS can help not only to advantageously substitute the related bulk ILs but also provides additional design elements to optimize the final characteristics and performance of the related supported ionic liquids-catalyst composites.



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Extraction of Neodymium from Aqueous Phase to Preselected Ionic Liquids – Insights from Quantum Chemical Calculations

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Recently, we proposed simple theoretical procedure for selection of efficient ionic liquid (IL) extraction solvents for Nd(III) and Dy(III) chlorides[1] using a conductor-like screening model for real solvents (COSMO-RS). The results obtained in that study indicated that the rare earths reveal strong affinity to ILs based on three specific anions, namely of [bis(2,4,4-trimethylpentyl)phosphinate], [decanoate], [benzoate], and one specific cation, namely of [dodecyl(dimethyl)-3-sulfoethylammonium].

Experimental tests[2] confirmed very high efficiency of extraction of Neodymium by ILs containing the preselected IL-anions (the cation based-IL is currently being synthesized for the test).

In the present study we use density functional theory (DFT) to investigate the mechanism of $NdCl_3$ extraction by all of the preselected ILs.

For this purpose, the optimized lowest energy structures of the individual ions of: [Nd^{3+}], [Cl^{1-}], [$NdCl_4^{1-}$], [IL-cation^{1+}] and [IL-anion^{1-}], were used to construct possible ion pairs. To identify the most possible geometries of the ion pairs, the partners were arranged at 16 different dihedral angles around the axis of the centers of mass of the two compounds (with COSMO*thermX* C30_1301) and then optimized with Turbomole V6.5 package, at B3LYP/def2-TZVP level of theory with Grimme-D3-dispersion.

To the optimized lowest energy structures of the ion pairs, additional counter ions were gradually added and optimized, using the method described above.

Binding energies (BEs) of the lowest energy structures of the ions pairs were then calculated using the minimum-energy geometries of the individual ions, and the corresponding ion pairs[3].

The above procedure was repeated until highly positive values of calculated BEs indicated on low probability of any further bonding.

The most possible interactions between dissociated $NdCl_3$ and the ionic liquids were thus identified, and were used to explain mechanism of the metal extraction.

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Study of the Application of [BMpyr][DCA] and $[N_{4441}][NTf_2]$ as Solvents in the Extraction of Benzene from Octane and Decane at 298.15 K

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In the petroleum refining industry, the availability of practically sulphur-free blend stocks having very low aromatics content and high isoparaffin content is an essential criterion for maximizing profit in the production process of engine gasoline, diesel fuels and lube base oils. For this reason, the development of aromatic/aliphatic hydrocarbons extraction techniques is crucial in order to improve the industry process. Ionic liquids (ILs) are a good alternative to actual volatile organic solvents due to their unique properties, like negligible vapor pressure, non-flammability, high thermal stability and large liquid-state temperature range.

In order to properly design aromatic/aliphatic hydrocarbons separation processes and select the most suitable IL to perform the extraction, the knowledge of liquid-liquid equilibrium (LLE) data of multicomponent mixtures containing aromatic compounds is required, since real petrochemical streams consist of a wide variety of compounds. Following this aim, quaternary systems involving benzene, octane and decane as hydrocarbons and the ILs 1-butyl-1-methylpyrrolidinium dicyanamide, [BMpyr][DCA], and tributylmethylammonium bis(trifluoromethylsulfonyl)imide, $[N_{4441}][NTf_2]$, have been investigated in order to evaluate the capability of these ILs as extraction solvents. The effectiveness of the extraction of benzene from octane and decane was evaluated in terms of the solute distribution ratio, β, and selectivity, S, and the experimental LLE data were correlated using the non-random two-liquid (NRTL) thermodynamic model[1]. A comparison of the obtained parameters for both quaternary systems were performed, obtaining higher values of S for the quaternary system in which the solvent was [BMpyr][DCA], as displayed in **Figure 1**.

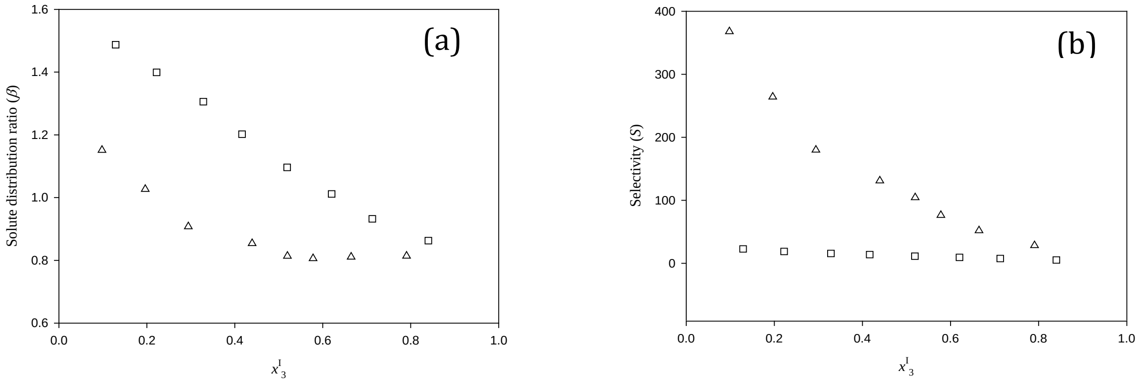

Figure 1. (a) β and (b) S as a function of mole fraction of benzene in the upper phase for the quaternary systems {Octane (1) + Decane (2) + Benzene (3) + IL (4)} being (△) [BMpyr][DCA] and (☐) $[N_{4441}][NTf_2]$.

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Deep Eutectic Solvents Based Synthesis of Hierarchical Carbons Tailored for Different Applications

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Carbon materials are a promising alternative for very different applications ranging from energy devices to gas adsorbents. Very different approaches have been made to develop carbonaceous materials with well define porous structures and different chemical compositions. [1] Recently, Ionic liquids (ILs) have emerged as a new family of carbon precursors.[2] Deep eutectic solvents (DESs) are a related class of ILs obtained by complexión of quaternary ammonium salts with hydrogen-bond donors. DESs share many characteristics of conventional ILs (e.g. nonreactive with water, nonvolatile and biodegradable) while offering certain advantages (e.g. high purity and low cost, among the most significant). Our work has been lately focused on the use of DESs playing multiple roles (e.g. reaction medium, monomer precursors and structure directing agents) in resorcinol-formaldehyde polycondensation reactions. [2] Monolithic resins were obtained after gelation of the DES (containing a carbon precursors, e. g., resorcinol) with formaldehyde. Carbonization of the gels in a nitrogen atmosphere leads to hierarchical carbon monoliths. Depending on the initial DES composition, both pore structure and chemical composition (e. g. introduction of heteroatoms such as nitrogen or sulfur) of final carbon monoliths can be modified.

In this poster we present the versability of DES based synthesis to produce tailored carbons suitable for different applications. Depending on the initial DES composition, non-doped as well as N-doped and S-doped hierarchical carbons were synthesized. Depending on the composition of the monoliths, they were tested as supercapacitors, CO_2 adsorbents [4] and as supporting carbons for fuel cells electrodes [5].

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Ionic Liquids Mixtures as an Alternative Approach to Boost the Formation Ability of Aqueous Biphasic Systems and their Polarity

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Aqueous biphasic systems (ABS) are commonly used as liquid-liquid separation processes, and consist on two immiscible aqueous-rich phases created by the mixture of two polymers, a polymer with a salt or two salts dissolved in aqueous solutions above specific concentrations. Due to the aqueous nature of their phases, ABS are ideal media for the separation of biologically active molecules. The identification of ionic liquids (ILs) as ABS phase-forming components created a plethora of novel separation systems with additional advantages when compared to polymer-based ABS, such as low viscosity, quick phase separation and high and tailored extraction efficiencies.[1,2]

The phase diagrams of ternary systems composed of ILs, salts and water are widely studied and reported in the literature.[2] It is also well-known that the polarity of their coexisting phases is essentially dependent on the IL anion.[2] In the present work, the possibility of manipulating the polarities of the ABS' phases, was investigated through mixtures of ILs (with very distinct polarities in different molar proportions: [C_4mim][CF_3SO_3] and [C_4mim]Cl). Novel phase diagrams of ABS constituted by mixtures of the two ILs in different molar proportions, K_2CO_3 and water were initially determined and characterized. Moreover, the relative hydrophobicity of the equilibrium phases was quantified through the partition coefficients of a series of dinitrophenylated (DNP) amino acids. The results obtained were compared with the relative polarities of simple ABS composed of imidazolium-based ILs, K_2CO_3 and water.

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"All-in-One" DESs, a Great Instruments in the Search and Development of Sustainable Processes for Preparation of Biodegradable Polyesters

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Deep Eutectic Solvents (DESs) are molecular complexes typically formed by mixing a quaternary ammonium or phosphonium salt with hydrogen-bond donor agents. DESs, that were first reported in 2003,[1] appeared as a new class of ionic liquids (ILs) since exhibit similar physico-chemical properties to the traditionally ILs while being much cheaper and environmentally friendlier.[2]

Our work has been lately focused on the use of DESs playing multiple roles (e.g. reaction medium, monomer precursors,...) for preparation of biodegradable polyesters.[3] We have successfully prepared biodegradable poly(octanediol-co-citrate) polyesters with acquired antibacterial properties. In this synthetic approach, DESs play a multiple role providing not only most of the ingredients required for the synthesis (as one of the polymer precursors or the quaternary ammonium or phosphonium salts that inhibits bacterial growth), but also the synthetic media where the second polymer precursor (e.g. citric acid) is solubilized and the reaction subsequently proceeds.[4] We also prepared polycaprolactone polymers under physiological conditions (at 37 ºC) by ring opening polymerization of ϵ-caprolactone catalyzed by a DES in the absence of further organic solvents and even initiator. This eutectic mixture, played multiple roles as bifunctional catalyst and reaction media.[5]

The use of DESs act as all-in-one systems offers an interesting green alternative to conventional syntheses in materials science,[6] and become a great instrument in the development of sustainable processes in the field of materials chemistry, according to the 12 principles of the green chemistry.[7]

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Ionic-Liquid-based Aqueous Biphasic Systems as an One-Step Extraction/Concentration Technique for a Suitable Monitoring of 17α-ethinylestradiol in Wastewaters

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The synthetic hormone 17α-ethinylestradiol (EE2) is classified as a priority substance with a significant risk to or *via* aquatic environment.[1] EE2 displays the most potent estrogenic activity amongst the estrogens currently existent, being thus a prominent endocrine disruptor in water cycles. However, due to the low content of EE2 in the wastewaters (usually in $ng \cdot L^{-1}$), its identification/quantification is unfeasible and a complete assessment of its persistence and environmental impact is far from being established.[1]

Aqueous biphasic systems (ABS) composed of ionic liquids (ILs) are here proposed as a new promising technology for the one-step extraction/concentration of EE2 from wastewater matrices.[1] ABS composed of various hydrophilic ILs and $KNaC_4H_4O_6$ were initially tested and optimized, reaching extraction efficiencies of EE2 from 92 to 100% for the IL-rich phase. The improved systems that led to the complete extraction of EE2 were further investigated by a proper manipulation of the concentration of the phase-forming components, while controlling the concentration factor achievable. An outstanding concentration of EE2 up to 1000-fold (from $ng \cdot L^{-1}$ to $\mu g \cdot L^{-1}$) in a single extraction and concentration step was achieved.[1] IL-based ABS are here envisaged as a novel and promising strategies for wastewater analysis of a wide range of micropollutants as one step extraction-concentration routes, allowing thus a proper evaluation of the environmental impact of pollution tracers by conventional analytical equipment.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Development of a Reactive Absorption Process for Sulfur Dioxide Based on Ionic Liquid as a Solvent and Catalyst

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Sulphur Dioxide (SO_2) being extensively produced by industry (fossil fuel; mineral processing by pyrometallurgy, among other), its emissions are a precursor to particulates in the atmosphere and "acid rain" and therefore environmental regulations for this gas are severe. Large productions of SO_2-streams usually are leading up to a sulfuric acid plants, while low flow or diluted streams it may be absorbed and chemically neutralized. In this field the existing processes have operative limitations related to the solvent utilized, mainly solvent loss by volatilization and chemical/thermal degradation.

On the other hand, state-of-the-art studies on catalytic oxidation of sulphur dioxide have demonstrated that catalytic reaction of SO_2 oxidation occurs in a eutectic melt composed by a poly-oxygenated metal (Vanadium oxide) and an alkaline metallic pyro-sulphates (K, Na, and Cs). Moreover, the ionic liquids are actually low temperature molten salts and furthermore, these ionic liquids could be functionalized with a polyoxymetalate anion (an oxidation catalyst).

In the present communication the selection criteria of both ionic liquid and catalyst and experimental absorption results are presented, as a first stage of a project intended to demonstrate the technical feasibility of operate a continuous process based on functionalized ionic liquid or a metal oxide catalyst slurry in ionic liquid that allow intensive absorption and conversion of SO_2 to SO_3 with no degradation of both solvent nor on the catalyst active agent.

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Extraction of Phenol Compounds Using [BMim] [NTf_2]

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The development of industrial activity has associated a considerable increase in the volume of wastewater that, depending on their source, may contain large amount of organic and / or inorganic substances in concentrations which are harmful to the environment. Among these substances are the phenols, highly polluting substances and present in a large number of industrial activities (paper, food, photography, paints and explosives industries, synthesis of pharmaceuticals, petrochemical processes...). The removal of these compounds from wastewater streams before discharge is fundamental to the environmental protection. In this way, the Spanish legislation on industrial emissions limits the content of phenols in the wastewater to a maximum of 1 mg / l. Actually, the ionic liquids are an attractive alternative to replace classic organic solvents while improving performance and causing less damage to the environment and reduce associated health.

The ionic liquid 1-ethyl-3-methylimidazolium ethylsulfate bis(trifluoromethylsulfonyl)imide [BMim][NTf_2] has been tested as solvent for the separation of phenolic compounds (phenol, o-phenol) from water. Liquid-liquid equilibria data have been determined for the ternary systems containing this ionic liquid, phenol or o-phenol and water at T = 298.15 K and at atmospheric pressure.

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Under the Development of Aqueous Micellar Extraction Systems using Ionic Liquids as Co-surfactants

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Aqueous micellar two-phase systems (AMTPS) using surfactants are advantageous extraction systems due to their main aqueous component, emerging as an appellative type of liquid-liquid extraction (LLE). A plethora of biomolecules has already been separated and purified using these systems with several surfactants. AMTPS composed of two surfactants enhanced the extraction of biomolecules, hence exploiting the advantage of introducing ionic liquids (ILs) as a new class of co-surfactants came as an attractive alternative owing to their unique properties. The alkylmethylimidazolium [$C_n$mim] family has been widely studied and demonstrated to self-aggregate in micelles, having also reports on their incorporation in mixed micelles. Thus, the objective of this work is to develop a new technology to be applied into the extraction field.

Herein, two families of ILs, namely the [$C_n$mim] and phosphonium were applied in the design of new AMTPS, based on Triton X-114 as the main surfactant. To evaluate the potential of this new LLE system, the partition and purification of different (bio)molecules is analyzed, considering the effect of the ILs as co-surfactants in the coexistence curves and their impact upon the solutes partition. Therefore, two model (bio)molecules, cytochrome c (Cyt c) and Rhodamine 6G (R6G), are used in order to study their partition coefficients (K) and selectivities ($S_{R6G/Cyt\ c}$)in the mentioned AMTPS. The obtained results clearly demonstrate that ILs have an important effect on the T_{cloud}. The presence of ILs as co-surfactants is able not only to enhance the $K_{Cyt\ c}$ (indicated as log $K_{Cyt\ c}$) from -0.587 ± 0.117 up to -1.510 ± 0.139, but also to improve the $S_{R6G/Cyt\ c}$ from 925.25 up to 3418.89.[1]

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Selective Purification of Natural Red Colorants Employing Ionic Liquid-based Aqueous Two-Phase Systems

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The use of colorants as additives in the industry is a significant factor for manufactures to determine the products acceptability. Natural colorants have been extracted directly from plants or animals, but microorganisms such as fungi are a promising source of these compounds[1]. Besides the production step, it is of great interest the screening of alternative methods for the colorants purification. Ionic Liquid-based Aqueous Two-Phase Systems (IL-ATPS) do not suffer from high viscosity as other ATPS systems[2] and one of the main advantages of the application of ILs to ATPS formation is their tunable nature accomplished by the proper cation/anion combination[3]. This work aims to extract red colorants from fermented broth of *Penicillium purpurogenum* DPUA 1275 using IL-ATPS. Two different ILs' families were investigated (imidazolium and quaternary ammonium) using a potassium citrate buffer, as the salt component. The conditions investigated were the IL and salt concentrations, the IL chemical structure and the pH. The results suggest that the red colorants were properly isolated by the appropriate manipulation of the process conditions under study, i.e. low concentrations of quaternary ammonium-based ILs with short alkyl chains, alkaline pH media and lower tie-line lengths (systems with lower IL concentrations). High partition coefficients for the red colorants (K_{red} = 24.4 ± 2.3), protein removal (60.7 ± 2.8 % of protein removed) and selectivity parameters ($S_{red/prot}$ = 10.05) were achieved. The results obtained shows that it is possible to envisage the potential application of these systems as a first step towards the purification of natural colorants from fermented broth.

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Poster Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Aqueous Biphasic Systems Composed of Ionic Liquids and Amino Acids as Remarkable Selective Extraction Approaches

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Aqueous biphasic systems (ABS) based on ionic liquids (ILs) emerged, in recent years, as suitable alternatives to traditional polymer-based ABS [1]. The major advantages of IL-based ABS comprise a lower viscosity of the coexisting phases and the possibility of tailoring their polarities and affinities so that more effective and selective extractions can be achieved. IL-based ABS formed by ILs, water and inorganic salts are the most studied [2]. However, there are some concerns associated with the use of inorganic salts. Previously, we demonstrated that IL-based ABS can also be formed with amino acids [3]. Amino acids are excellent alternatives to inorganic salts since they decrease the ionic strength of the overall solution and may prevent or minimize the ion exchange between the coexisting phases.

Based on the possibility of using amino acids as phase-forming components of IL-based ABS, in the current work, we investigated the ability of ABS formed by the combination of phosphonium-based ILs with hydrophilic amino acids to selectively separate the aromatic phenylalanine, tyrosine and tryptophan amino acids. The liquid-liquid phase diagrams were firstly determined at 25ºC, through the cloud point titration method, as well as the tie-lines and tie-line lengths of the ABS, and then used for the design of aqueous two-phase extraction routes envisaging the selective separation of amino acids. Based on the gathered results, $[P_{4444}]Br$ + Lysine reveals to be the better system to selectively separate lysine from the three aromatic amino acids for opposite phases. The results obtained reveal that IL-based ABS are promising approaches for the selective extraction of mixtures of amino acids, being the selectivity highly dependent on the IL employed.

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Removal of Textile Dyes from Aqueous Media using Aqueous Biphasic Systems Composed of Ionic Liquids

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Dyes are used in different industries for coloring purposes. The textile industry is one of the main industries which discharges a heavy load of chemicals during the dying process[1]. The release of large contents of dyes for aqueous effluents leads to both environmental and economic concerns. Most of the textitle dyes are carcinogenic, mutagenic, allergenic and toxic. As a result, in the past few years, new environmental laws were implemented[2], and the development of novel techniques for the removal of textile dyes from wastewater streams has been a subject of great interest.

As an alternative approach for removing dyes from aqueous effluents, ionic-liquid-based aqueous biphasic systems (IL-based ABS) were investigated in this work. The studied ABS are composed of several ionic liquids (ILs) and distinct inorganic salts to evaluate the influence of the IL structural features, the nature and salting-out ability of the salt employed, and the pH of the aqueous medium toward the efficiency of a given ABS to remove textile dyes from aqueous solutions. The extraction efficiencies of several dyes, namely sudan III, indigo blue and chloranilic acid using different ABS were experimentally determined at 298 K. The results obtained reveal that a proper selection of the IL and of the inorganic salt can lead to a remarkable complete extraction of the three dyes in a single-step[3]. After selection of the best systems for the extraction of dyes, their recovery and recycling was finally addressed aiming at a reduction in the environmental footprint and economical issues[3].

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Aqueous Biphasic Systems Composed of Two Ionic Liquids as Novel Extraction Platforms

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The introduction of aqueous biphasic systems constituted by ionic liquids (IL-ABS), which fit within the liquid-liquid extraction strategies, has led to improved and tailored extraction efficiencies of a wide range of value-added biomolecules.[1,2] In particular, in these systems and contrarily to the typical polymer-based ABS, there is the possibility to tune the polarity and affinity of the coexisting phases by a thoughtful combination of the chemical structures of the IL ions. [3] However, most IL-based ABS investigated are formed by imidazolium-based ILs and inorganic salts [2]. Therefore, their tailoring ability is limited to the IL-rich phase since the opposite phase is normally enriched in strong salting-out salts. Thus, the implementation of ABS formed by two ILs will certainly enable the expansion of their tailoring ability at both aqueous phases.

In this study, the possibility of forming ABS composed of two ionic liquids is demonstrated. Several combinations of ILs were tested, and the respective binodal curves, tie-lines and tie-line lengths, were determined at 25ºC. The extent of ionic exchange between the coexisting phases was also evaluated. Moreover, the extraction and selectivity ability of these systems was explored with mixtures of high-value proteins, by the proper choice of the ILs phase-forming components. It will be demonstrated that ABS formed by two ILs are new extraction platforms with improved selectivity and extraction ability.

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Solubility of Lignin Precursors in Aqueous Solution of Deep Eutectic Solvents

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Deep eutectic solvents (DES) are a new generation of solvents with attractive cost and unique physicochemical properties. These solvents have been emerging as an alternative to ionic liquids (IL) regarding biomass processing methodologies. Recent studies have reported that lignin and cellulose, which are the most abundant renewable polymers in lignocellulosic biomass, can be selectively dissolved by this new kind of solvents.[1,2] However, and due to the fact that this process is still poorly understood, it becomes imperative to evaluate its potential as a new delignification procedure for *Eucalyptus globulus* wood.

In this context, the solubility of lignin precursors selected models (syringic acid and syringaldehyde) using aqueous solutions of DES was evaluated. To achieve this goal we studied the effects of DES chemical structure, concentration and solubility temperature of these precursors, in their whole composition range, from pure water to pure DES. DES were prepared by a combination of renewable hydrogen bond acceptors (choline chloride, amino acids, etc.) with hydrogen bond donors (carboxylic acids, sugars, urea, glycerol and amino acids) in equimolar ratio to form a novel DES with melting point lower than 100°C. The underlying molecular phenomena responsible for the solubility were investigated by Dynamic Light Scattering, NMR spectroscopy and molecular dynamics simulations. This work has contributed to a greater knowledge of DES aqueous solutions role in the solubility of lignin precursors providing a new perspective for the delignification process.

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Novel Aqueous Biphasic Systems Formed by Carbohydrates and Fluorinated Ionic Liquids and Their Use in Dyes Extraction

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Aqueous biphasic systems (ABS) formed by ionic liquids (ILs) have been the focus of increasing attention due to the high extraction efficiencies and the selectivity they provide in separation and purification procedures.[1] Most studied systems combine ILs with inorganic salts, but the inherent high values of ion concentrations may pose environmental concerns, and hence there is a need to develop more environmentally friendly IL-based ABS to improve the manufacturing and/or the separation processes.

This work aimed the formation of more biocompatible and environmentally friendly ABS using carbohydrates as potential alternatives to the salts commonly used. To this end, ABS formed by perfluoroalkylsulfonate-based ILs and a large number of small molecular weight carbohydrates (monosaccharides, disaccharides and polyols) were studied. The respective ternary phase diagrams (solubility curves and tie-lines) were determined at 298 K and atmospheric pressure. In general, the aptitude of carbohydrates to induce phase separation closely follows their hydration extension and/or hydrogen-bonding ability towards water. Moreover, only the more hydrophobic and fluorinated ILs are able to undergo liquid-liquid demixing.

To evaluate the potential of these systems in downstream processing, a few were tested in the extraction of sulphonated dyes mostly used in the food and in the textile industries. The food dyes E102, E124, E133 and E142 were investigated, and the results showed their extensive partition to the carbohydrate-rich aqueous phase, contrarily to the most conventional IL-salt ABS. [1] Extraction efficiencies values up to 94% were achieved using these novel systems.

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Evaluation of a Binary Mixture of Ionic Liquids as Mass Agent in the Separation of *n*-Heptane from Toluene

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The research of ionic liquids (ILs) as solvents in the liquid-liquid extraction of aromatics from their mixtures with aliphatics has been a relevant field in the last years. The use of ILs instead of now-used solvents such as sulfolane would imply a high reduction in both operational and capital investment costs, mainly because of the reduction in heating and purification steps.[1] The use of binary mixtures of ILs has allowed the development of solvents with extractive properties higher than those of sulfolane and with similar physical properties.[2] Specifically, the binary IL mixture involving 1-ethyl-4-methylpyridinium bis(trifluoromethylsulfonyl)imide ([4empy][Tf_2N]) and 1-ethyl-3-methylimidazolium dicyanamide ([emim][DCA]) showed similar performance than that of sulfolane.[2]

Nevertheless, the purification section required to separate selectively the aromatics, the aliphatics, and the IL-solvent has not been deeply investigated yet. In our previous work, the performance of [emim][DCA] as mass agent in the *n*-heptane separation from toluene was evaluated, achieving high values of *n*-heptane relative volatilities from toluene.[3] As a result of the high efficiency observed in the case of [emim][DCA], the aim of this contribution was the evaluation of the efficiency for the {[4empy][Tf_2N] + [emim][DCA]} IL mixture as mass agent over the whole range of compositions of the IL mixture and at several temperatures. Moreover, the Yalkowsky and Roseman mixing rule was used in order to predict the {[4empy][Tf_2N] + [emim][DCA]} performance from the results using the pure ILs forming the mixture.[4]

The results showed high values of *n*-heptane relative volatilities from toluene under the presence of the IL mixture at all temperatures. The best results were obtained at the lowest temperature studied and with the highest presence of [emim][DCA] because of its high aromatic/aliphatic selectivity. Hence, low temperatures and ILs with high aromatic/aliphatic selectivity should be used to separate selectively the extracted hydrocarbons. In addition to this, the experimental results for all compositions of the binary IL mixture were correctly predicted using the Yalkowsky and Roseman mixing rule at all temperatures.

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Extraction of Benzene, Toluene, and *p*-Xylene from Pyrolysis Gasoline Using the {[4empy][Tf_2N] + [emim][DCA]} Ionic Liquid Mixture

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The liquid-liquid extraction of aromatic hydrocarbons currently is based pm organic solvents, such as sulfolane. Due to its non-volatile nature, ionic liquids (ILs) could reduce the environmental impact and energy consumption of the aromatic separation unit.[1] In our recent researches, we have studied the use of binary IL mixtures, obtaining aromatic solvents with intermediate extractive and thermophysical properties between those of the pure ILs.[2-4] In this work, we have used an IL mixture formed by the [4empy][Tf_2N] and the [emim][DCA] ILs in the extraction of benzene, toluene, and *p*-xylene (BTX) from a pyrolysis gasoline obtained from severe cracking.

Liquid-liquid equilibrium experiments were made using the {[4empy][Tf_2N] + [emim][DCA]} mixture with a [4empy][Tf_2N] mole fraction (ϕ_1) of 0.3 and sulfolane as solvents at 303.2 K, 313.2 K, and 323.2 K to study the temperature effect on the extraction. At each extraction temperature, vials were gravimetrically prepared at solvent to feed ratios in mass basis between 1.0 and 5.0 to determine the influence of the solvent to feed ratio on the extraction. To evaluate the performance of both extraction solvents, values of yield of extraction of aromatics (Yld_{arom}) and the relative purity of extracted aromatics in the extract phase (P_{arom}) were calculated.

Values of Yld_{arom} for the sulfolane were substantially higher than those using the IL mixture. Because of this, the IL mixture could require a higher number of equilibrium stages to achieve the extraction yield of aromatics than those using sulfolane in a countercurrent extraction column. By contrast, the IL mixture showed higher values of purity of the extracted aromatics than those using sulfolane. A higher purity of BTX obtained would imply a lower number of extraction stages in the aromatic extraction unit, simplifying the further purifications. Employing both solvents, the highest values of P_{arom} were achieved at the lowest temperature. A temperature of 303.2 K and a solvent to feed ratio of 5.0 were selected as the optimal conditions to extract BTX from pyrolysis gasoline obtained from severe cracking using the IL mixture, considering the influence of temperature and solvent to feed ratio on the values of Yld_{arom} and $P_{\text{arom.}}$

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Facilitated CO_2 Separation through Supported Liquid Membranes of Cyano and Amino Acid-based Ionic Liquid Mixtures

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Due to environmental concerns and consequent legislative constrains, great effort has been put on the development of energy efficient processes and high selective materials to capture and separate carbon dioxide from light gases. Membrane-based technologies, in particular, supported ionic liquid membranes (SILMs) have attracted considerable attention in the past few years not only due to the low volatility of ionic liquids (ILs) but also to their highly tunable nature, which makes them absolutely unique when compared to other conventional solvents.

Although a broad diversity of ILs has already been used to prepare SILMs,[1] their CO_2 permeability and selectivity is not enough for highly efficient industrial applications. In order to increase the flexibility in tailoring permeability and selectivity of SILMs for flue gas separation (CO_2/N_2), we have recently proposed the use of IL mixtures.[2],[3] The results showed that a proper balance combining both the most CO_2 selectivity and the less viscous anions is crucial to achieve improved CO_2 separation performances. These aspects motivated us to further explore the use of binary IL mixtures with specifically tailored properties as a mean to design new liquid phases with fine-tuned gas permeation properties and consequently enhanced CO_2 separation performances. Taking into account that ILs with amino acids present “reactive” amino groups that can work as CO_2 carriers,[4] and considering that ILs combining cyano-functionalized anions show remarkably low viscosities,[5] mixtures of these ILs were explored.

In this study, five ILs based on a common imidazolium cation ($[C_2mim]^+$) and different amino acid anions such as glycinate ($[Gly]^-$), L-alaninate ($[L\text{-}Ala]^-$), taurinate ($[Tau]^-$), L-serinate ($[L\text{-}Ser]^-$) and L-prolinate ($[L\text{-}Pro]^-$) were mixed with $[C_2mim][C(CN)_3]$ and SILMs of these mixtures were prepared. The gas permeation properties (permeability, diffusivity and solubility) of CO_2 and N_2 were determined at a fixed temperature and different trans-membrane pressure differentials using a time-lag apparatus. Since IL viscosity and molar volume are significant parameters that impact the gas permeation properties of SILMs, the thermophysical properties of the pure ILs and their mixtures, namely viscosity, density and refractive index, were also measured so that trends could be evaluated.

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Gas Separation by Supported Liquid Membranes Using Ionic Liquids Containing Novel Fluorinated-based Anions

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The use of supported liquid membranes for gas separation has been widely studied during the last 20 years. In these membranes, the selected solvent is immobilized into the pores of a solid membrane by capillary forces. Unfortunately, their long-term stability can be affected by solvent depletion through evaporatin at specific temperature and pressure operating conditions. One of the most interesting strategies to circuvent this drawback is the use of ionic liquids (ILs). Supported ionic liquid membranes (SILMs) have been studied owing to the intrinsic properties of ILs such as negligible vapor pressure, high thermal stability, and highly tuneable nature, making them ideal liquid phases for supported liquid membrane applications. In the past few years, a broad diversity of ILs has been used to prepare SILMs and investigate the effect of the IL structure on the gas permeation and separation performance of these membranes.[1] Since someSILMs have shown potential for industrial applications, particularly for low pressure systems such as the treatment of bio-methane from anaerobic digesters and CO_2 separation from flue gases, many efforts are being putted on developing new task-specific ILs to enhance the already advantageous combination of gas permeability and selectivity of SILMs.[2-4]

In this study, novel ILs based on the 1-ethyl-3-methylimidazolium ([C_2mim]) cation and different low viscous fluorinated anions such as 2,2,2-trifluoromethylsulfonyl-N-cyanoamide ([TFSAM]), 2,2,2-trifluoro-N-(trifluoromethylsulfonyl) acetamide ([TSAC]), bis (fluorosulfonyl) imide ([FSI]), and bis(trifluoromethylsulfonyl) imide ([TFSI]) were synthesized [5]. Moreover, ILs containing the nonafluorobutanesulfonate ([$C_4F_9SO_3$]), the tris(perfluoroalkyl)trifluorophosphate ([FAP]), and the bis(perfluoroethylsulfonyl)imide ([BETi]) anions, were also prepared in order to explore the effect of the fluorinated chain. The gas permeation properties (permeability, diffusivity and solubility) of CO_2, CH_4, N_2 and O_2 through the prepared SILMs were determined using a time-lag apparatus. The thermophysical properties of the IL phases, namely viscosity and density, were also measured so that trends could be evaluated. This communication will provide results for the understanding of the effect of different fluorinated anion species on the gas separation performance of SILMs.

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Ionic Liquids as Adjuvants to Pluronic-based Aqueous Biphasic Systems

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In last decades, investigation has been stimulated to reduce the ecological footprint, developing more sustainable alternatives to the current processes and fossil-based chemical products. Separation and purification processes play a central role in the chemical industry not only due to their impact in the quality of the final product but also due to the high level of energy and solvents used. In this context, aqueous biphasic systems (ABS), largely applied in bioseparation processes have been proposed as alternative to liquid-liquid extraction techniques, owing their many advantages, such as high effectiveness, high yield, high purity degree, low cost and technological simplicity. [1] These systems usually result of the mutual incompatibility in aqueous solution of two polymers, one polymer and one salt, or two salts above a certain concentration. [2] However, the commonly used polymers (e.g. polyethylene glycol - PEG) present a limited range of applicability, due to their low polarity. To overcome this limitation, ionic liquids (ILs) can be used as adjuvants in ABS, enlarging the polarity range of these systems. [3] In the last twenty years, the exponential interest on ILs as non-volatile and tuneable fluids scattered their application to a wide range of disciplines, including separation processes. [4]

In this work, several ILs are used as adjuvants in the formation of ABS based on pluronics and inorganic salts. Pluronics are triblock copolymers composed of one PPO (poly(propylene oxide) block connected to two PEO (poly(ethylene oxide) blocks and are used in the formation of ABS for the first time. Phase diagrams and tie-lines will be presented. The role of the polymer structure as well as the IL structural features in ABS formation will be discussed.

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Characterization and Interfacial Properties of Surfactant Ionic Liquids for Enhanced Oil Recovery

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Ionic liquids (ILs) are often considered "designer solvents" because of the large variety of interactions and physicochemical properties that can be combined in these components [1]. In the last decade, "surface-active ionic liquids", SAILs, have been prepared attaching long alkyl chains to the ions [2]. Self-aggregation and complex structures in the micro- or nano-domains are then produced. Moreover, the addition of long alkyl chains in both ions, termed "biamphiphilic" or "catanionic" surfactants, produces more complex structures and behavior [3].

A promising application of SAILs is in Enhanced Oil Recovery. There are several methods to improve oil extraction, but addition of surfactants to the extraction fluid has proved highly efficient from the technological viewpoint. Amphiphilic compounds reduce oil/water interfacial tension and therefore capillary forces entrapping petroleum also decrease [4]. SAILs bring important advantages over common surfactants: easier handling due to its liquid state, higher viscosity that may avoid addition of polymers to improve the mobility ratio, "design" of ILs for specific operation conditions, and in some cases the use of co-surfactants can be avoided because ILs form stable aggregates due to their strong cohesive forces [5].

In this work, several SAILs with phosphonium and imidazolium cations have been synthesized. Surface-active character is introduced adding one or more long alkyl chains in the cation, or in both anion and cation. Their self-assembly behavior in aqueous solution was evaluated experimentally by means of surface tension and electrical conductivity. The dynamic interfacial tensions between the aqueous solutions of the surfactant ionic liquid and crude oil were evaluated by spinning drop method. The effect of different variables, such as concentration of SAIL, presence of other electrolytes (NaCl) and alkalis (NaOH, Na_2CO_3), and operation temperature has been analyzed.

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Separation of *n*-Heptane and Toluene using [EMim][SCN] and [EMim][SCN]/salt Mixtures as Entrainer

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The use of ionic liquids (ILs) as potential solvents in liquid extraction of aromatics hydrocarbons from their mixtures with aliphatic compounds has been extensively documented in the last years.[1] Nevertheless, in order to apply these ionic compounds in an industrial process, the selective separation of the aromatic obtained and the regeneration of the ILs should be also investigated.

In a previous work, a high efficiency of the ionic liquid 1-ethyl-3-methylimidazolium dicyanamide, [EMim][DCA], as mass agent in the separation of *n*-heptane and toluene was observed.[2] The obtained vapor-liquid equilibrium (VLE) data showed high values of *n*-heptane relative volatilities from toluene. In view of these satisfactory results, the study is now extensive to the use of 1-ethyl-3-methylimidazolium thiocyanate, [EMim][SCN], and [EMim][SCN]/salts mixtures in order to analyze the effect of the anion and the presence of salts on the phase behavior. For this, isothermal VLE data for the ternary mixtures {*n*-heptane (1) + toluene (2) + IL or IL/salt (3)} were experimentally measured at $T = 323.2$ K through the analysis of the phases by Static Headspace Gas Chromatography (HS-GC). All the salts used in this work are thiocyanate based-salts (AgSCN, $Co(SCN)_2$ and CuSCN). The temperature selected to carry out this work is intermediate between the maximum operation temperature of [EMim][SCN] ($T = 360$ K) [3] and the common equilibrium temperature used in the liquid-liquid equilibrium ($T = 313.2$ K).

The obtained results showed that [EMim][SCN] improves the efficiency obtained with [EMim][DCA]; nevertheless, the presence of thiocyanate-based salts doesn´t improve the values of *n*-heptane relative volatilities from toluene. The best results were obtained using high concentrations of [EMim][SCN] which confirms ILs with high aromatic/aliphatic selectivity, as is the case here, should be used to separate selectively the extracted hydrocarbons. In addition to this, the experimental VLE for the ternary mixture {*n*-heptane (1) + toluene (2) + [EMim][SCN] were satisfactorily fitted using the Non-Random Two Liquids (NTRL) thermodynamic model.[4]

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Solubility Modeling of High-Pressure (CO_2 + Toluene + IL) Systems by Combination of COSMO-RS and Equations of State

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Application of ionic liquids (ILs) in the liquid-liquid extraction of aromatics from aliphatics has been widely identified as a promising alternative to the conventional sulfolane-based solvent for petroleum processing. However, the removal of the aromatic compounds from the IL after the extraction process remained a major issue. Recently, the use of high-pressure CO_2 as an anti-solvent to induce a liquid-liquid phase split has proven effective to recover and recycle the IL after the extraction process. [1,2]

Modeling the phase behavior of the systems is critical for efficient simulation, optimization and design of novel Chemical Engineering Processes. This is even more challenging in the case of IL-containing systems for which experimental and thermodynamic data are still limited. In this regard, the quantum-chemical based COSMO-RS (COnductor-like Screening Model for Real Solvents) method allows predicting the thermodynamic equilibria of fluid mixtures from structural information of the compounds, without the need for previous experimental data. In fact, COSMO-RS has demonstrated to be a sensible method for estimating the thermodynamics of mixtures containing ILs, including (CO_2 + ILs) and (organic compounds + ILs) at near ambient conditions. [3-5] Nevertheless, a key limitation of COSMO-RS is the capability to predict the solubility behavior of high-pressure systems and small gases close to their critical point.

In this work, COSMO-RS modeling is combined with Soave-Redlich-Kwong (SRK) Equation of State (EoS) to estimate the solubility of CO_2 in toluene and ILs mixtures at high pressures. The predicted results are compared against the available experimental data, which support the suitability of the aforementioned approach to predict the behavior of (CO_2 + toluene + ILs) systems up to near critical conditions. This may be useful for further design and optimization of separation systems based on ILs for aromatics recovering and solvent recycling.

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Recovery and Reuse of AmimCl as Solvent for the Cellulose Regeneration from *Pinus Radiata* Wood

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Lignocellulosic biomass is a renewable energy with a worldwide production of around 1.1×10^{11} tons/year able to produce liquid fuels [1]. The rigid structure of lignocellulosic biomass that provides resistance, makes them difficult to process, being necessary a pretreatment to fractionate these resources [2, 3]. The remarkable properties presented by ionic liquids (ILs) as solvents have meant that numerous research studies are focused on their use for processing biomass in general. However, the high ILs cost and toxicity difficult their use at large-scale. The recovery and reuse of ILs could solve some of these inconveniences [4].

The aim of this work is to study the recovery of AmimCl, widely used for wood dissolution and subsequent regeneration of cellulose with an antisolvent, analyzing the reuse of the recovered IL in the process [5]. The presence of dimethyl sulfoxide (DMSO) to reduce the viscosity of the dissolution is a factor to be considered in the recovery and reuse of the IL. The wood is dissolved in AmimCl 4 % wt/wt in a microwave oven, adding DMSO as cosolvent and the subsequent cellulose regeneration using methanol as antisolvent [5]. The liquid phase (AmimCl-Methanol-DMSO) obtained after separating the regenerated cellulose is distilled in a rotary evaporator, recovering AmimCl impurified with DMSO. The recovered impurified IL is reused in the process and the yields of cellulose regenerated are compared with those obtained employing the fresh AmimCl. Furthermore, the influence of adding DMSO before and after the microwave step is studied. The results show that due to the high boiling point of DMSO (189 °C at atmospheric pressure), obtaining a 100 % pure IL is energetically unachievable. However, it is able to get a mixture of LI/DMSO in a ratio 90/10. Regarding the reuse process, the absence of DMSO improves the wood dissolution being more advisable to add DMSO after the microwave radiation step.

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Desulfurization of Hydrocarbon Streams: from COSMO Ionic Liquid Selection to Process Simulation

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The increasing society concern about environmental affairs, related with both city pollution and climate change, has pushed governments to restrict sulphur compound contents in hydrocarbon products, since 2011, to levels below 10 ppm. Such restrictions have been translated into new development in hydrocarbon refineries, as new catalysts or process schemes for the hydrodesulfurization unit (HDS). It is well known that HDS is very efficient in tiols, sulfides and disulfides reduction to H2S. However, it is not so effective for the removal of aromatic sulphur compounds such as tiophene, benzotiophene or dibenzotiophene.

On the other hand, the use of ionic liquids for the desulfurization of hydrocarbon streams has been widely studied from experimental [1], molecular dynamics [2] and quantum chemistry methods (COSMO-RS).[3] The last ones have shown great results for the selection of the best ionic liquid for a specific separation.

In this work, we use COSMO models, such as COSMO-RS and COSMO-SAC, evaluating how good they are for the prediction of thermodynamic properties of ionic liquids mixtures such as excess enthalpy or activity coefficient. Then we go forward, implementing ionic liquid physical property parameters in commercial process simulation software, i. e. Aspen Plus to improve ionic liquid screening. It is carried out by simulating the liquid-liquid extraction process where ionic liquid efficiently remove sulphur compounds from the hydrocarbon stream.

The work is structured as follows: first, a short introduction and computational details are briefly presented. Then bibliographic systems of liquid-liquid equilibria with ionic liquids are reviewed and compared with results from both COSMO-SAC and COSMO-RS predictions. Finally, a description of the liquid-liquid extraction process and simulation results are presented and the main points of the work are discussed.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Enhancing Integrated Biorefineries Performance Using Ionic Liquids

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Fossil fuels are estimated to be exhausted in 60-80 years due to the increase in human population and living standards. Finding a new source of energy environmentally friendly and sustainable is a crucial challenge to be solved. Biofuels, energy from biomass is one of the most promising alternatives. Depending on the type of feedstock, biofuels have been classified as first generation (food crops), second generation or non-edible biomass (some crops, forest residues, animal fat, waste) and third generation biomass (microorganisms as microalgae). Recently, different research projects have been funded by the European Commission like: Eurobioref (European Multilevel Integrated Biorefinery), Biocore (Biocommodity Refinery), Suprabio (Sustainable Products from Economic Processing of Biomass in highly Integrated Biorefineries), Miracles (Multiproduct Integrated Biorefinery of Algae). From these projects it is clear that the biorefinery of the future will be highly integrated, flexible to allow the conversion of different feedstock (2nd and 3rd generation biomass) and multi product (biofuels, chemicals, polymers, energy, etc.)

One of the bottlenecks of biorefineries is the use of solvents, organic solvents are generally used in different stages of the production process. These solvents are usually non-environmentally friendly, and its separation and recovery increase the overall cost significantly.

Ionic liquids are salts that are liquid at room temperature. Their properties make them a more environmentally friendly and less costly alternative to conventional species. Ionic liquids are usually used as substitutes of solvents but they can be also used as catalysts or catalyst supports among other uses. One of the main benefits of using ionic liquids, that makes them green solvents, is that they can be recovered almost completely.

In this work we present the process flowsheet of a whole integrated biorefinery, showing for each section the different options (processes or operating units) and indicating where the use of ionic liquids is an alternative to consider. This biorefinery treats lignocellulosic biomass (non-edible plants, forest residues and municipal solid waste) as well as microalgae to produce multiple products: chemicals like the antioxidant astaxanthin, polymers like PHB (polyhydroxybutyrate), specialty chemicals from levulinic acid and esters, biodiesel (mainly jet fuel), bioethanol, etc. Ionic liquids can be used in many parts of the process: as solvents for lignocellulosic biomass, for the deconstruction of lignin, as catalysts in the transesterification reaction, in the enzymatic hydrolysis of sugars, as extraction agents of lipids from algae or other biomass, as entrainers in azeotropic distillation. A comparison of the use of ionic liquids with the existing approaches in each section is made establishing the benefits and drawbacks of their use. Finally, the process biorefinery process flowsheet is completed adding the ionic liquids recovery process.

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Predicting the Surface Tension of Phosphonium-Based Ionic Liquids

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In phosphonium-based ionic liquids (PBILs) the core phosphorous atom allows a larger variety at the structures of cations. This increases the number of possible cation/anion combinations and consequently their range of physicochemical properties. The PIBLs are more stable and of less expensive manufacture than other ionic liquids (ILs) and present a low toxicity. [1] As a result their applications have increased as well as the interest in the research on these ionic liquids properties. One of these is the surface tension, an important and less reported property, with only some data available in literature for PIBLs. In the IL Thermo Database [2], which gathers data on the thermophysical properties of 1060 pure ionic liquids, only about 200 can be found in measurements at the air–ionic liquid interface and 83% of these are imidazolium ILs. This work reports the determination of surface tension of: tributyl(methyl)phosphonium methylsulfate, [(C4)3PC1][C1SO4], trihexyltetradecylphosphonium chloride, [(C6)3PC14][Cl], trihexyltetradecylphosphonium bis((trifluoromethyl)sulfonyl)imide, [(C6)3PC14][NTf2], and trihexyl-tetradecylphosphonium bis-2,4,4-(trimethylpentyl)phosphinate, [(C6)3PC14][Phosph]. The surface tension was measured over the range T= (293.16 to 350.89) K with maximum uncertainty of ±0.3 $mN.m^{-1}$. The data obtained compare well with the known literature values, when existent.

The lack of experimental data on surface tension turns the determination of this property by estimation into a valuable approach. In order to predict the surface tension of ILs an equation derived by Sanchez (1983) [3] for liquids was used. This equation relates the surface tension to the isothermal compressibility and the density and includes a constant, A, which shown to be an invariant for a large class of nonpolar and polar organic liquids [3]. Therefore, after determining this invariant for ionic liquids, and if the density and isothermal compressibility is known for a particular ILs, the surface tension can be determined straightforwardly. A group of several ILs was selected, which comprised the PIBLs studied in this work and other phosphonium, imidazolium, pyridinium, piperidinium and pyrrolidinium ILs. This method (INV) was tested in parallel with other two approaches for the surface tension prediction: a QSPR correlation method (PCH) proposed by Gardas & Coutinho (2008) [4], which makes use of the parachor number calculated from a QSPR correlation and the density, and a group contribution neural network method (GMDH) implemented by Atashrouz (2014) [5], which requires extensive calculus involving the critical properties, density and boiling temperature. The overall average deviation (AAD) of the INV method was found to be 5,93%, for 250 surface tension data points from 26 ILs, a result close to the values of other estimation methods. For the GMDH and the PCH methods the AAD obtained were 6,21% and 16,71%, respectively. The latter value clearly states the inadequacy of the PCH method for PIBLs surface tension prediction.

A sample of the applicability of the INV method is illustrated in Figure 1, where the PBILs surface tension measured data is represented by markers and the lines represent the predicted values. The proposed invariant method proved to be a simple and reliable method for surface tension prediction.

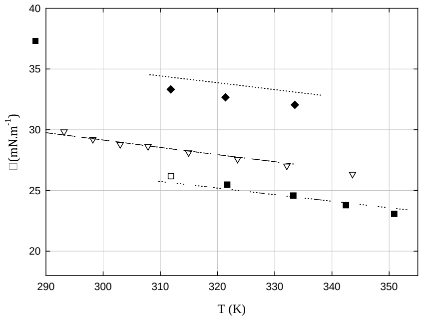

Figure 1. Surface tension, γ, as function of temperature, T. The symbols represent experimental data and the solid lines the predicted values from the invariant method. Legend: ■, (—··) [$(C_6)_3PC_{14}$][Phosph]; ▽, (- - ·), [$(C_6)_3PC_{14}$][NTf_2]; ◆,(—) [$(C_4)_3PC_1$][C_1SO_4];

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Assessment of the Equilibrium in Ionic Liquid/Salt Aqueous Biphasic Systems: Modeling of the Binodal Curve

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Ionic Liquid-based Aqueous Two Phase Systems (ILATPS) are considered the common alternative to extracting biomolecules with ionic liquids and they have been widely used in the separation, concentration and purification of many types of compounds such as proteins, amino acids, antioxidants, among others.[1] Most of these systems are based on ionic liquids and salts, and form two aqueous phases (ionic liquid-rich and salt-rich phases). The equilibrium in these ionic liquid/salt systems is described by the binodal curve, which is required to determine the composition of the two liquid phases.[2] An empirical, exponential equation with 5 parameters (2 fixed and 3 adjusted) that was proposed by Merchuk and collaborators[3] is often used to model the binodal curve of ILATPS. Despite its relatively high number of parameters and mathematical complexity, its accuracy should be improved for some specific applications, namely in the recyclability of the ionic liquid.[4]

The aim of this work is thus, the analysis of the binodal curve of ionic liquid/salts systems so that it can be modeled by means of equations that provide higher accuracy or lower mathematical complexity. For this purpose, and in order to obtain sound conclusions, the binodal data of 100 ionic liquid/salt systems have been used in the analysis. The assessment of the models proposed is based on different statistical criteria (e.g. the R^2 values; the residual mean squared error, RSME; the Akaike Information Criterion, AIC). Results show that, on the one hand, an additional adjusted parameter (instead of a fixed one) clearly improves the quality of adjustment (RSME decreases more than 25%) without losing the statistical significance of the parameters. On the other hand, the binodal curve can be simplified using an explicit equation with only 2 adjusted parameters keeping the R^2 value higher than 0.99. Moreover, the estimation of parameters based on relative errors is also performed to enhance the accuracy at high salt concentrations, because this region of the binodal curve is crucial for a correct analysis of the recyclability of the ionic liquid.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Marriaging Non-Ionic Surfactants and Ionic Liquids for Aqueous Splitting

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Since 2003, when Rogers and collaborators [1] have first addressed the ability of ionic liquids to be salted out in aqueous solutions by high charge density inorganic salts, a booming interest has been devoted to ionic liquid-based aqueous biphasic systems (ABS). [2] Miscibility control in aqueous solutions of ionic liquids has been basically tackled by using different inorganic and organic salts, although they often entail biocompatibility concern with some kind of biological metabolites. These handicaps have made us to hypothesize that the use of non-ionic surfactants, widely employed in bioprocessing operations, could be a suitable strategy for achieving phase separation in the presence of ionic liquids, the latter acting as salting out agents. In this way, liquid-liquid equilibrium is yielded after a complex competition between the non-ionic surfactant and the ionic liquid for the water molecules.

In this study, given the advantages provided by surfactant-based ABS such as lower interface tension, economical reasons (low cost of the reagents and rapid phase segregation), greater immiscibility windows, null flammability, and commercial availability of all components at bulk quantities, we have bet in Triton family, due to its relevance in different biotechnological applications. Thus, Triton X-100 and Triton X-102, composed by an 8-carbon tertiary alkyl chain and 9-10 ethylene oxide units or 12-13 ethylene oxide units, respectively, have been cherry-picked for this work. In relation to the salting out agent, we have selected 1-ethyl-3-methyl imidazolium ethylsulfate since it is already produced at an industrial scale (more than one ton per annum), which ensures its availability when implemented at high scale. Besides, it can be easily synthesized in an atom-efficient and halide-free way, at a reasonable cost, it shows high chemical and thermal stabilitiy, low melting points and relatively low viscosities.8 Its biocompatibility with enzymes has also been reported in previous works for the separation of lipases.9 Moreover, 1-ethyl-3-methyl imidazolium butylsulfate and 1-ethyl-3-methyl imidazolium hexylsulfate were selected in order to evaluate the influence of the hydrophobicity of the ionic liquid at 25ºC.

Acknowledgements

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Experimental Determination of Melting Point Depression Induiced by CO_2 in High Melting Temperature Cellulose Dissolving Ionic Liquid. Modeling with GC-EoS

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Ionic liquids (ILs) of the alkylmethylimidazolium chloride family are able to solubilize high amount of cellulose and other natural polymers and have very good characteristics for their processing. Nevertheless, they present important disadvantages related to high melting points and viscosities. Dissolution of carbon dioxide can reduce melting point of these ionic liquids as well as other ILs presenting the same problems. In this work the effect of pressurized carbon dioxide on the melting point depression of some ionic liquids (ILs) able to dissolve biopolymers was experimentally determined using the forst melting point method. Five different ionic liquids (ILs) were studied in contact with carbon dioxide using a high-pressure visual cell, up to 10 MPa. The ILs studied were four ILs with chloride anion coupled with 1-butyl-3-methylimidazolium, $[C_4mim]^+$, 1-ethyl-3-methylimidazolium, $[C_2mim]^+$, 1-allyl-3-methylimidazolium, $[Amim]^+$ and 1-(2-hydroxyethyl)-3-methylimidazolium, $[C_2OHmim]+$ and one ammonium-based cation choline $[C_5H_{14}NO]^+$ combined with dihydrogen phosphate anion, $[H_2PO_4]^-$. Melting point depression (MPD) effect observed for these groups of ionic liquids were around 10ºC for chloride ILs and went as high as 33.2ºC for choline dihydrogen phosphate. To correlate the melting point depression of imidazolium chloride ILs, parameters for the Group Contribution Equation of State of Skold-Jorgensen were adjusted using literature data of liquid vapour and activity coefficient and infinite dilution. Melting point depression was calculated with an average deviation of ±0.4 and a maximum deviation of ±1.9.

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Experimental Densities and Viscosities for concentrated water + cellulose dissolving ionic liquids. Viscosity correlation

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Alkylimidazolium ionic liquids with chloride and acetate anions are susceptible to dissolve cellulose and other natural polymers allowing their green processing [1]. Nevertheless high viscosities of ionic liquids in general and those with a chloride anion in particular is a limitation for this processes, and this viscosity is increased with cellulose or other polymer is dissolved in the IL. Nevertheless for many of this process other molecular solvents are added to the mixture: i.e. water and sometimes acids for hydrolysis process are added in amounts low enough to prevent cellulose precipitation[2]. And it is known that viscosity of ionic liquids is in general decreased with increasing concentrations of molecular solvents such as water or organic solvents [3].

In this work the density, and dynamic viscosity, of different binary mixtures of water and the ionic liquids 1-ethyl-3-methylimidazolium acetate (EmimAc) and 1-allyl-3-methylimidazolium chloride (AmimCl) up to 35% water mol and from 298 to 373 K at atmospheric pressure were experimentally determined using a an Anton Paar (model SVM 3000) automated rotational Stabinger viscometer-densimeter. Water content was measured before and after the measure finding significant changes in the water composition. AmimCl present viscosities almost one order of magnitude higher than EmimAc. For both ILs viscosities decrease when increasing temperature and water concentration as described in literature with viscosities of molecular solvents + ionic liquids. Previously existing correlations were modified in order to calculate viscosity in all the temperature and concentration range.

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Theoretical-Experimental Study of Aqueous Fluorinated Ionic Liquids

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The fluorination of ILs (FILs) is of particular interest in areas where perfluorocarbons (PFCs) find relevant applications, such as in the biomedical field, where PFCs are used as in vivo gas carriers in liquid ventilation or artificial blood substitute formulations.[1] This work is based on the possibility to design and develop FILs to replace, partially or totally, the PFCs present in the emulsions used as oxygen therapeutics.

A combined theoretical-experimental approach has been followed to characterize these compounds. For this purpose, the phase equilibria of FILs containing anion fluorinated chains equal to four carbons with water has been studied to evaluate the feasibility of partially replacing PFCs-in-water emulsions usually used as oxygen carriers. The phase equilibria of aqueous [$C_n$mim][$PFBuSO_3$] has been studied in a temperature range from 298.15 to 353.15K. Furthermore, the critical aggregation concentrations (CACs) for these FILs in water at 298.15K (which present cations and anions with surfactants properties) have been also performed by measurements of the ionic conductivity and surface tension. Finally, the self-assembled structures of FILs in aqueous solutions have been evaluated using transmission electron microscopy and the critical packing parameter determined from surface tension measurements. This experimental information has been modeled using the soft-SAFT equation of state (EoS).[2] Soft-SAFT is a molecular-based EoS where the different molecular effects of the molecule are considered in a coarse-grained model, keeping the basic physical information of the molecule. Based on their chemical structures, preliminary ab-initio calculations and the experimental evidences, a molecular model has been built and a characteristic set of molecular parameters has been fitted to density data. The model is later tested to describe the liquid-liquid equilibrium of (water + FILs) binary mixtures. Additionally, a critical study on the aggregate formation is carried out with the equation and compared to experimental observations.

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On the Interfacial Properties of Deep Eutectic Solvents Regarding to CO_2 Capture

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The interfacial properties of deep eutectic solvents based on choline chloride plus urea, glycerol or malonic acid in contact with gas phases composed by pure CO_2, pure SO_2 and a model flue gas, along with the liquid-vacuum interface, were studied using molecular dynamics simulations. The works provides insights on the mechanisms of acid gases capture at relevant interfaces and at nanoscopic level. The structural rearrangements on the molecules and ions composing the solvents at the interfaces upon contact with the studied gas phases are studied together with the initial adsorption of gas molecules at the surface, the diffusion rates across the surface boundary and the strength of intermolecular forces in the surface. The work provides a detailed analysis on the interfacial mechanism controlling acid gases capture by deep eutectic solvents.

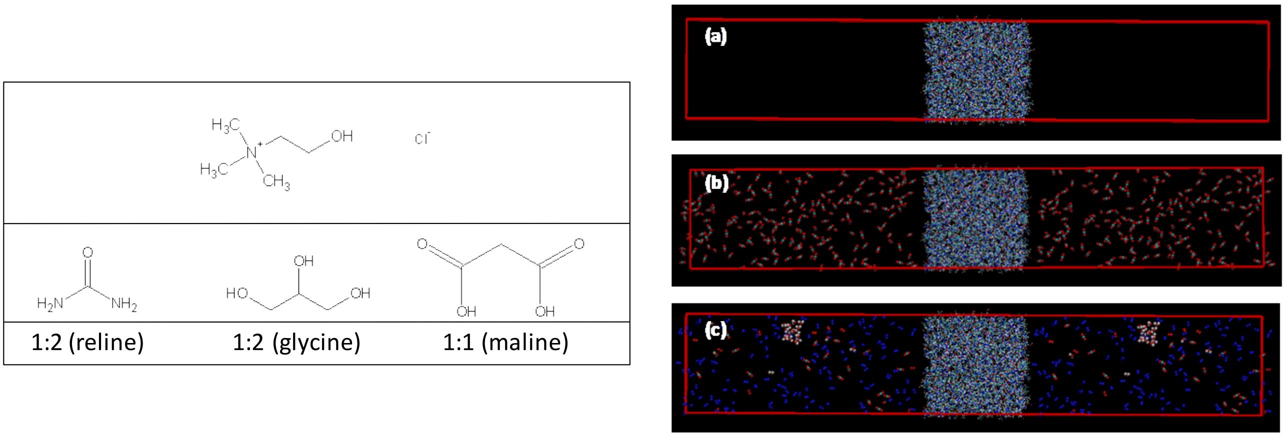

Figure. Deep eutectic solvents studied in this work and models for molecular dynamics studies of solvent - gas interfaces.

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1-Allyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide as a New Stationary Phase for Capillary Gas Chromatography

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Ionic liquids (ILs) are organic salts utilized for various industrial applications. Their unique and tunable physicochemical properties are unlike any other solvent. They typically remain liquid over wide temperature ranges, and tend to exhibit low melting points, good thermal stability, negligible vapor pressure, and high viscosity. These properties also make them ideal candidates as stationary phases (SPs) for gas chromatography (GC). A quick literature search reveals a great deal of development aimed at preparing columns with IL stationary phases (a few of them commercially available), in order to achieve better analytical separations or to obtain thermodynamical parameters of the net IL.

In both cases, the quality of the columns prepared in terms of efficiency, inertness and film thermal stability is fundamental. When non-ionic SPs are used, a sequence of surface preparation steps of the fused-silica capillary tube is commonly employed before coating it by the static method. These steps result in improved reproducibility, film stability, column efficiency and reduced adsorption of polar compounds. However, when ILs are employed, this key process generally receives much less attention. Columns are simply coated without a previous treatment or just after depositing a layer of sodium chloride on the inner wall, not considering if it is the optimum method for column preparation. In fact, there is a lack of systematic studies on wall tube preparation processes and their effect on column quality.

In the present work, several methods of capillary column preparation with 1-allyl-3-methylimidazolium bis[(trifluoromethyl)sulfonyl]imide ([AMIM][NTf_2]) as a new stationary phase have been evaluated. For the first time, the retention properties of [AMIM][NTf_2] have been characterized by means of the solvation parameter model (SPM), comparing its separation characteristics to those of other commercially available columns with ionic and non-ionic SPs in capillary GC.

The results revealed that the static coating method without any pre-treatment of the inner tube wall was the most adequate for [AMIM][NTf_2] column preparation. According to the SPM results, [AMIM][NTf_2] can be considered a highly cohesive and moderately hydrogen-bond acid SP, and on which the dominant contributions to retention were the dipolar-type and hydrogen-bond base interactions, while π-π and n-π interactions were barely significant. A principal component analysis for the conventional SPs in GC clearly showed that IL columns fill an empty area of the available selectivity space.

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Eutectic Mixtures of Pyrrolidinium-based Ionic Liquids, and Their Physical Properties

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Ionic liquids are often called "designed solvents" due to the possibility of tuning their properties by suitable selection of the cation and anion.[1] However, properties modification can be obtained not only by changing the component cations or anions of the salt, but also by formulating mixtures of different ionic liquids instead of pure salts.[2] A particularly attractive case is that in which the mixed substances present a eutectic behavior, with a eutectic composition presenting a maximum depression in melting temperature. Thus, the eutectic composition is utilizable in liquid state at lower temperatures than any of the parent compounds, expanding the catalogue of ionic fluids to be potentially considered for many applications.[3] Such eutectic mixtures can be easily achieved by mixing two ionic liquids or organic salts at proper molar ratios.

The aim of the research presented was to develop a better understanding of the eutectic behavior of ionic liquid mixtures, in particular of those with a cation derived from pyrrolidine. Five of these mixtures were prepared, comprising a total of either three different ions (if the parent compounds had an ion in common) or four different ions. For all five tested systems a eutectic behavior was found via characterization of the corresponding solid-liquid equilibria. Their eutectic compositions and temperatures were determined through the analysis of changes in the melting point depression, and relevant physical properties of these eutectic mixtures were measured and compared to the properties of the parent salts.[3]

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Characterization of Novel Mixtures of Fluorinated Ionic Liquids

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Nowadays, we are facing a wide number of already available ionic liquids (ILs), with most of them already characterized in terms of their properties and applications. One of the major advantages of ILs conveys on their tailoring ability by a proper cation/anion rearrangement. This feature can be even more enlarged if mixtures of ILs are considered.[1] Moreover, in the past few years, a large interest has been devoted to fluorinated ILs due to their outstanding physical-chemical properties and further potential applications, *e.g.*, as refrigerants, surfactants, fire retardants, lubricants, among others.[2] The goal of this work consists on the expansion of the advantageous features afforded by fluorinated ILs by the characterization of some selected (binary) mixtures. The melting behavior or solid-liquid equilibrium of four mixtures of fluorinated ILs, comprising the cations 1-butyl-1-methylpyrrolidinium, 1-ethyl-N-methylpyrrolidinium and (2-hydroxyethyl)trimethylammonium combined with the anions bis(nonafluorobutylsulfonyl)imide, perfluorobutanesulfonate and trifluoromethanesulfonate, were determined by differential scanning calorimetry (DSC). The gathered phase diagrams also allow to ascertain on the (non)ideality of mixtures of ILs. The Conductor like Screening Model for Real Solvents (COSMO-RS) was additionally investigated for describing the solid-liquid phase behavior. The thermophysical properties of some mixtures which present an eutectic-like behavior were additionally determined.

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Molecular Dynamics Simulations of Mixtures of Protic Ionic Liquids and Long-chained Alcohols

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The microscopic details of the solvation of molecular cosolvents and inorganic salts in ionic liquids (ILs) are currently under intense scrutiny, and the specific features of nanostructured solvation have been recently reported.[1,2] Specifically, MD simulations of mixtures of ILs and alcohols with short alkyl chains (methanol and ethanol) have been reported by our group for both protic and aprotic ILs. [3,4] In this contribution, we report MD simulations of bulk mixtures of protic ILs (ethyl- and butylammonium nitrates, EAN and BAN) with propanol, butanol and pentanol at 298.15 K and 1 atm, and we analyze the effect of the alkyl chain length of the alcohol molecules on the structure and single-particle dynamics. For that, we calculate the radial distribution functions, coordination numbers and effect of the addition of alcohols on the number of hydrogen bonds of the mixture, and the dynamic behavior is analyzed by means of the velocity autocorrelation functions and densities of states (DOSs) of the different species. Neither cluster formation nor caging effect of alcohol molecules is observed, and the increase of the alkyl chain length of the alcohol molecules scarcely modifies the structure of the mixtures. The local environment of the anions is seen to be less modified than that of the cations. All these evidences are indicative of alcohol molecules mixing homogeneously with the ILs, being solvated in the interface between the polar and apolar regions of the IL, in line with previously reported results for nanostructured solvation. [4,5]

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Aqueous Biphasic Systems Formed by Phosphonium-based Ionic Liquids and Polyvinylpyrrolidone

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Aqueous biphasic systems (ABS) formed by two immiscible aqueous-rich phases have emerged as environmentally friendly and economically feasible procedures for the extraction and purification of several substances[1]. In the past decade ionic liquids (ILs) have emerged as a green alternative in industrial applications due to their low volatility, null flammability and "tailoring" amenability that make them unique and have led to remarkable results in the separation and purification of a wide diversity of compounds[1]. To this aim, ABS composed of ILs and inorganic and organic salts have been investigated[1]. However, the inherent high values of ionic strength and charged species concentrations may be deleterious to some (bio)molecules. To ameliorate the separation techniques, different solutions must be employed and new biocompatible processes, environmentally and economically sustainable, must be developed.

In this work, new ABS combining phosphonium-based ILs with polyvinyl pyrrolidone (PVP) were investigated. Phosphonium-based ILs were chosen since they are chemically and thermally more stable than the more commonly used imidazolium-based ILs[1], and the polymer PVP is considered a safe substance by FDA. The results obtained in this work demonstrated, for the first time, that ABS can be formed when PVP is combined with phosphonium-based ILs in aqueous media.

Ternary phase diagrams of several phosphonium-based ILs, PVP and water were determined at 298 K; the respective tie-lines and tie-line lengths were also obtained. From the gathered data, the effects of the nature and structural characteristics of the ILs on the ability to form ABS are discussed. To evaluate their potential in extraction processes, a few systems were tested in the extraction of antioxidants. The results reveal that the novel ABS formed by phosphonium-based ILs and PVP are a promising alternative to conventional liquid-liquid systems.

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Structural Properties of Mixtures of Ionic Liquids and Divalent Salts with a Common Anion

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Following previous works of our group, regarding the structure of mixtures of ionic liquids (ILs) (both protic[1] and aprotic[2] ones) and univalent salts with common anion calculated using classical molecular dynamics (MD) simulations, in this work we report MD calculations for the same kind of mixtures, but introducing 1:2 salts in the system instead of 1:1 ones. The simulated aprotic ILs were 1-butyl-3-methyl ammonium tetrafluoroborate [BMIM][BF_4] and 1-butyl-3-methyl ammonium hexaflurophosphate [BMIM][PF_6], while as protic IL we simulated ethylammonium nitrate (EAN). Selected 1:2 salts were magnesium and calcium ones with the corresponding anion of the IL. Simulations were performed using the Gromacs 4.5.4 package and a standard MD all-atom force field, OPLS-AA, and we test our predictions with experimental measurements of the densities of the mixtures. All simulation details have been reported elsewhere [1, 2].

The effect of the addition of divalent cations to the pure ILs is analyzed and compared to the effect caused by monovalent cations. For this purpose, we calculated coordination numbers, hydrogen bond fractions, radial and spatial distribution functions, and velocity autocorrelation functions, as well as densities of states of the salt cations in the bulk. The main conclusions are the presence of solid-like structures placed in polar domains of the IL, which are stronger than in lithium mixtures due to higher cation valence. The behavior of these same mixtures in presence of an interface is also briefly reported and compared to that of mixtures with Li salts [3].

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Hydrogen-bond Acidity and Basicity of Mixtures of Ionic Liquids: Experimental and COSMO-RS Approaches

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In the past decade, ionic liquids (ILs) have been the focus of intensive research regarding their use as potential and alternative solvents in many chemical applications[1]. Targeting their effectiveness, recent investigations have attempted to establish polarity scales capable of ranking ILs according to their chemical behaviors[2]. However, mixtures of ILs can broaden the tailoring ability of these fluids aiming at tuning their polarity behavior, and thus their effectiveness as potential solvents for the most diverse applications.

This works aims at determining the solvatochromic parameters of mixtures of ILs and to evaluate the ability of adjusting their polarity. Various mixtures with different proportions of each IL (in the whole composition range) were investigated by the determination of their Kamlet–Taft solvatochromic parameters, namely hydrogen-bond acidicity, hydrogen-bond basicity and dipolarity/polarizability. Since polarity scales only report relative ranks because they depend on the set of probe dyes used, we additionally addressed the COSMO-RS (COnductor-like Screening MOdel for Real Solvents) capability as an alternative tool to estimate the solvatochromic parameters of mixtures of ILs. This theoretical approach allows to classify mixtures of ILs according to their chemical behavior and opens the possibility to pre-screen appropriate mixtures for a given task or application.

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Partition Data of Protic Ionic Liquids Based on N-methyl-2-hydroxyethyl Amine in Butanol-Water

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Ionic liquids (ILs) have interesting properties that include wide temperature range in the liquid state, negligible vapor pressure and high solubility of organic and inorganic components. This indicates that ILs are excellent solvents to use for different process. Due to their negligible volatility they can replace organic solvents causing less damage to the environment. Protic ILs based on N-methyl-2-hydroxyethyl ammonium cation and short chain carboxylate anions have simple synthesis and purification, and therefore has a low production cost [1,2,3] moreover initial research on similar cations indicates that they have low toxicity.[4] In order to investigate the partition of these substances in alcohol-water, the objective of this work is to determine experimentally liquid-liquid equilibria data of three ionic liquids (formed by the cation N-methyl-2-hydroxyethyl ammonium and the anions propionate (m-2HEAPr), butanoate (m-2HEAB) and pentanoate) with butanol and water. Ternary solubility data were obtained using the cloud point method.[5] Mass differences were measured in an analytical balance (Shimadzu AX200, accuracy of ± 0.001g. Ionic liquid water content was measured in a volumetric Karl-Fisher tritator from Mettler-Toledo and this value was taken into account to calculate compositions. The system temperature was controlled with the aid of a water jacket connected to a thermostatic bath and recorded in a calibrated glass thermometer. Temperature uncertainity is determined as better than 0.1K. Mixtures with compositions in the region of immiscibility were prepared weighting known masses of each component, and placed in a glass cell with a stopper. The prepared mixtures were placed in a thermostatic bath, stirred for 40 minutes, and left to rest for 24 hours to guarantee the equilibrium achievement. The organic phase was carefully collected and weighed. With this value, and following the approach by Merchuck et al. [6], the parameters required for the calculation of tie-lines were obtained. Data for liquid-liquid equilibria of the protic ionic liquids m-2HEAPr, m-2HEAB and m-2HEAP in water-butanol system were collected at 293.15K, 313.15K and 333.15K. The data were well correlated by the NRTL model and the results confirms the high hidrophilicity of these ionic liquids, as their butanol-water partition coefficient are lower than 1.

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Effect of Water Content and Temperature in Viscosity and Conductivity of Pehaa (Pentaethylenehexammonium Acetate) and its Application in Construction of a Bioelectrode

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This work presents the synthesis of the protic ionic liquid pentaethylenehexammonium acetate (PEHAA). Furthermore, the effect of water contents and temperature were evaluated in viscosity and conductivity of PEHAA. With this information one Walden Plot was built with which it was possible to analyze the ionic character liquid synthesized to discuss electrochemical behavior of built bioelectrode. Finally, we obtained promising results with a good synergistic mixture for the construction of a bioelectrode based on the enzyme catalase.

The pentaethylenehexammonium acetate (PEHAA) was synthesized from simple reaction between acetic acid and pentaethylenehexamine basis[1]. The walden plot gave information about the ionic character of PEHAA, finding same general behavior of an ionicity of 10% for all analyzed compositions[2]. The PEHAA was electro-oxidation with the enzyme catalase through to electrodeposition based to Saadati's methodology[3].

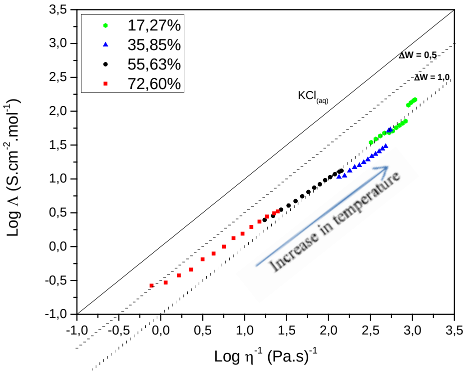

Figure 1. Walden plot for different compositions HEPAA in water (percentage by weight)

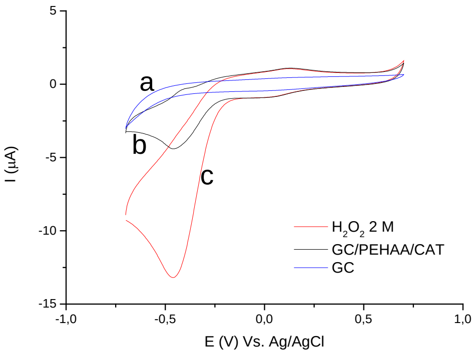

Figure 2. Cyclic Voltammograms of a) glass carbon (GC) electrode, GC/HEPAA/CAT in b) PBS (pH 7) e c) in H_2O_2 2 mol L^{-1} in PBS (pH 7), v = 50 mV s^{-1}.

This result shows the possibility of built bioelectrode based in catalase using PEHAA like intermediate of electronic transference in the reaction with hydrogen peroxide.

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Study of Temperature and Water Content Effect on Viscosity, Density and Speed of Sound for Protic Ionic Liquids Based on Acetate Anion

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Currently, Ionic Liquids have been extensively studied because of its unique features. Variations in cation, anion or substituents result in significantly different properties between species. [1–3] In fuel cells, the IL have been used as electrolytes as much in form of composite, combined with the polymeric membranes, [4] as materials which themselves are participants polymer generation.[5] They are employed principally aiming the operation of electrochemical devices at temperatures above 100 ° C, where aqueous electrolytes are not applicable. In addition, high temperatures contribute significantly to the increase of catalyst reaction rates, and in the increasing of the catalyst tolerance to fuel impurities, including the presence of CO. [6–8] So, the objective of this study was to evaluate the influence of the variation of the cation (alkanolammonium based) in the physicochemical properties: density, sound velocity, viscosity and conductivity, as well as the influence of water content in these organic salts. It was observed that all the LI are denser than water, their density and speed of sound majorly decreases with increasing temperature following this order between themselves: BHEAA > 2HEAA > m-2HEAA. The viscosities of the pure ionic liquids were relatively high, and as in the other analyzed properties, they followed this order to viscosity: BHEAA > 2HEAA > m-2HEAA. With the addition of water, the viscosity decreases exponentially as well as with increasing temperature. Finally, the results of conductivity analyzes performed between the three LI evaluated, revealed the following order to conductivity: m-2HEAA > 2HEAA > BHEAA. However, with the reduction of IL concentration in binaries with water, the conductivity order of m-2HEAA and 2HEAA was reversed. Thus, for use in enhanced fuel cell electrolyte membranes, m-2heaa was the most qualified LI between 3 LI evaluated by presenting a conductivity of 6.0 mS.cm^{-1} at a temperature of 343 K and degree of purity of 99.74% wt.

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Microscopic Assembly of Water in Presence of Ionic Liquids

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Ionic Liquids (ILs) have attracted special attention as a promising alternative for environmentally unfriendly traditional solvents due to its appealing properties[1]. Among them, of especial interest is the behavior in aqueous solution due to their amphiphilic characteristics[2]. One of the crucial molecular-level interactions affecting the macroscopic behavior is hydrogen-bonding[3]. In this work, we performed Molecular Dynamics (MD) simulations to analyze the nanostructural organization of water/IL mixtures. We investigate systems containing different low concentrations of ILs for different lengths of the alkyl chain of imidazolium-based cations, $[C_nMIM]^+$ (n=2,..,20) and a variety of anions, namely $[Br]^-$, $[NO_3]^-$, $[SCN]^-$, $[BF_4]^-$, $[PF_6]^-$, and $[Tf_2N]^-$. The hydrogen bond network of water was found sensitive to the amount of IL and to the anion-type. In particular, among the considered anions, $[SCN]^-$ and $[Tf_2N]^-$ showed the most hydrophilic and hydrophobic characters, respectively [Figure 1]. Conversely, the effect of the cation chain length on the structure of liquid water was almost negligible. These results suggest that interactions with anions break more hydrogen bonds in water than the steric effect by the presence of long cation chains. The microscopic information provided in this work is useful for the design if ILs for given applications involving water.

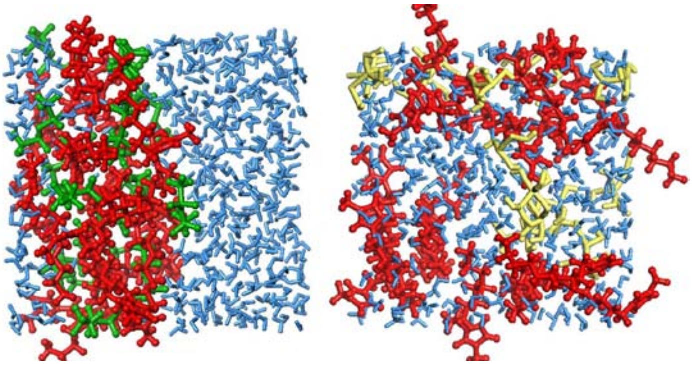

Fig 1. Representative snapshot from MD simulations of mixtures of water (blue), cation $[C_{10}MIM]^+$ (red), and either $[Tf_2N]^-$ (green) or $[SCN]^-$ (yellow) anions.

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Modeling of Mass Transfer through Asymmetric [bmim][Tf$_2$N]-based Membranes for Pervaporation of Biobutanol

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Biobutanol is a second-generation biofuel produced from ABE fermentation process. This process produces mainly acetone, butanol and ethanol in a ratio equal to 3:6:1, respectively. Current researches are focused on the three steps of biobutanol production: the pretreatment of raw materials, the fermentation process itself and the product separation techniques [1]. Among the novel separation techniques, liquid-liquid extraction using ionic liquids and pervaporation are two operations that could be used for the selective recovery of butanol from ABE fermentation broths with energy requirements lower than distillation [1].

In this work, these separation processes are combined through the analysis of a pervaporation system, which uses an ionic liquid-based membrane [1,2]. Thus, this study describes the transfer of butanol through an asymmetric pervaporation membrane, which is formed by three layers: PDMS/[bmim][Tf2N]/PDMS. The ionic liquid layer placed between two PDMS layers is mechanically stabilized by a gelation procedure described in literature [2].

Pervaporation tests were done in order to extract butanol from model ABE solutions. The extraction efficiency and butanol transfer flux obtained from these experiments were compared with predictions obtained from a mass transfer model based on a resistance-in-series approach in order to correlate the values of diffusion coefficients of butanol in each membrane layer. This model was solved using Matlab® by means of the Regula falsi method [3].

A first set of pervaporation tests was carried out with single PDMS layer membranes in order to obtain the distribution coefficient of butanol between the aqueous ABE mixture and the PDMS membrane as well as the diffusion coefficient of butanol in the PDMS layer. A second set of pervaporation tests with the PDMS/[bmim][Tf$_2$N]/PDMS membrane was done in order to estimate the distribution coefficient of butanol between PDMS and ionic liquid as well as to correlate the value of the diffusion coefficient of butanol through the ionic liquid layer.

Average transfer fluxes obtained from experiments were $2.8*10^{-3}$, $3.8*10^{-3}$ and $9.5*10^{-5}$ kg m^{-2} h^{-1}, for acetone, butanol and ethanol, respectively. These values can be considered high compared with the reported ones in literature for a membrane with a thickness close to 900 µm. Meanwhile, the flux of water can be considered negligible. The solution of the mathematical model explains the mass transfer process through the asymmetric membrane with errors lower than 5%. The diffusion coefficients of butanol in PDMS and ionic liquid were $4.23*10^{-11}$ and $4.05*10^{-10}$ m^2 s^{-1}, respectively.

Moreover, this model allows obtaining the distribution of mass transfer resistances where the PDMS layers represent more than 90% of the overall resistance and the selectivity is mainly explained by the higher solubility of butanol in the ionic liquid layer.

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Binary Systems Composed of Cholinium- and Phosphonium-based Ionic Liquids

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Ionic liquids are organic salts with melting temperatures below 100°C. Their unique properties, such as a negligible vapour pressure, high chemical and thermal stabilities, wide liquidus temperature range, and the possibility of fine tuning their properties through appropriate cation/anion combinations make them viable candidates to replace the common organic and volatile solvents currently used in an extensive range of industrial applications.[1] In fact, there are circa to 600 different organic solvents used by industry while there are one million of possible combinations of ions or different ionic liquids.[1] In particular, ionic liquids have been designated as potential solvents for "clean" liquid-liquid extractions.[2] Therefore, the search on novel biphasic systems composed of two ionic liquids, while comprising the determination of their liquid-liquid equilibrium, allows the creation of a new plethora of separation processes constituted only by non-volatile solvents. In this work, mixtures of cholinium- and phosphonium-based ionic liquids were investigated and their phase diagrams were determined from 40°C to 150°C. Nuclear Magnetic Resonance (NMR) and Electrospray Ionisation - Mass Spectrometry (ESI-MS) were used as analytical techniques for the quantification of each ion/ionic liquid and for the evaluation of the ionic exchange extension in such mixtures.

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Physical Properties of Mixtures of Ionic Liquids and Inorganic Salts

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Ionic liquids (ILs) are novel materials with many well-known peculiar properties, which are widely reputed as green designer solvents and used in many electrochemical devices for energy conversion and storage. For this purpose, an accurate knowledge of the bulk and surface properties of solutions of electrochemically relevant salts in ILs is essential. In this presentation, and extending previous results of the group for pure ILs [1], we report systematic experimental measurements of the solubility and physical properties of bulk and surface properties of mixture of a protic ionic liquid (IL), ethylammonium nitrate, and several monovalent (Li, K), divalent (Mg, Ca) and trivalent (Al, Fe, Cr…), leading to a complete macroscopic and microscopic characterization of equilibrium and transport properties of these systems: density, sound velocity, surface tension, viscosity and electrical conductivity [2]. The results are interpreted in terms of the microscopic mechanisms of the nanostructured solvation of ions in the polar regions of the IL [3, 4], and the impact of ionic concentration on the main physical properties of the ILs explicitly analyzed. The effect of temperature and IL cation chain length on some of these properties is also considered.

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Characterization of Fluorinated Ionic Liquids: A New Family of ILs

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The Europe 2020 strategy establishes a sustainable growth based on the adoption of greener policies, thereby the development of greener products and technologies became one of the most challenging goals for the science. Due to their properties like practically nonvolatile nature, null flammability, low melting point and thermal stability, among others, ionic liquids (ILs) have become a popular green media for industrial applications, as separation and extraction techniques. However, the plethora of novel applications is expanding in areas such electrochemistry, physical chemistry, analytics, engineering and biomedical industry, among others.[1] Ionic liquids are salts entirely composed of ions, usually an organic cation and an organic or inorganic anion. Characteristics like hydrophobicity, biodegradation or toxicity can be manipulated by altering the nature and structure of the composing ions taken into account the final desired product. But also the thermophysical properties could be “previous selected” accordingly to the nature of the cation and the anion.

Although the number of publications in ionic liquids had grown tremendously, there are still quite unexplored themes. That is the case of the fluorinated ionic liquids (FILs) family. This specific family of ionic liquids is characterized by having fluorine tags longer than four carbons.[2] They are a viable option to be used in extraction processes to separate perfluoroalkyl acid contaminants from industrial effluents due to the presence of a fluorinated domain. With this aim in mind we show how the balance between the three domains (polar, nonpolar and fluorinated)[3] in FILs influences the thermal and thermophysical properties, namely density, viscosity, iconicity, conductivity and melting and decomposition temperature. With that purpose we compare a series of compounds based on imidazolium cation and carboxylate and sulfonate anions. The final aim of this study is to create knowledge that allows the design of fluorinated ionic liquids with desired properties for a specific application.

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Dimethyl Sulfate Ionic Liquid Based Aqueous Biphasic Systems

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Aqueous biphasic systems (ABS's) are formed when polymer/ polymer, polymer/salt, and salt/salt mixtures are dissolved in water above critical concentrations. The most of the aqueous solutions of the phase-forming polymers present high viscosities, form opaque systems, and present a limited range of polarities at their coexisting phases. The ionic liquids seem be a new alternatives to polymers in the composition of ABS's. Ionic liquids (ILs) show enormous advantages such as negligible vapor pressure, non flammability, high thermal stability, and high solubility for both polar and non-polar organic and inorganic compounds and easiness of recovery.

This work addresses the evaluation of the ability of Dimethyl Sulfate (DMSO$_4$) Ionic Liquid on the formation of aqueous biphasic systems (ABS's), with K_2HPO_4, Na_2CO_3, K_2SO_4, or CH_3COONa. All binodal curves were determined by the cloud-point titration method at 298 K and atmospheric pressure. A known amount of salt was added to the different IL aqueous solutions until detection of turbidity was achieved. Then, dropwise addition of ultra-pure water until a clear monophasic region was reached.

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Physical Properties and Thermal Behavior of Natural Deep Eutectic Solvents

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Natural deep eutectic solvents (NADES) have been shown to be promising, sustainable media for a wide range of applications. Nonetheless, very limited data is available on the properties of these solvents. NADES based on choline chloride, organic acids, amino acids and sugars, were prepared, and their density, thermal behavior, conductivity and polarity were assessed, for different NADES compositions. The NADES studied are stable over a wide range of temperatures up to 170 ºC, depending on their composition. Thermal characterization revealed that all the NADES are glass formers and some exhibit crystallinity. It was also observed that water has a plasticizing effect on NADES, with a decrease of the glass transition temperature with the addition of water. The morphological characterization of the crystallizable materials was done by polarized optical microscopy that provided also evidence of homogeneity/phase separation. The conductivity of the NADES was also assessed from 0 to 40 oC. The more polar, organic acid-based NADES presented the highest conductivities. The conductivity dependence with temperature was well described by the Vogel-Fulcher-Tammann equation for most of the NADES studied. It is crucial to characterize the fundamental physicochemical properties of NADES to provide data for more complex molecular simulation studies. To tailor the most suitable combination of compounds for a given application, the development of models able to predict their properties and the mechanisms that allow the formation of the deep eutectic mixture will be hereafter of utmost value. Only using computer simulation models it is possible to evaluate the 106 possible combinations within a reasonable time frame and to truly produce tailor-made solvents.

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Solubility of Polycyclic Aromatic Hydrocarbons in Ionic Liquids

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Ionic liquids are being explored as solvents and electrolytes for chemical systems and devices that use carbon-nanomaterials. The stabilization of carbon-nanomaterials in suspension is still not sufficiently well understood, in terms of the fundamental physical-chemistry of colloids and interfaces, thus hindering the development of large-scale applications. Moreover, in ionic liquids there is a balance between electrostatic and van-der-Waals interactions, due to the presence of non-polar groups such as alkyl side chains, which leads to structured liquids with persistent heterogeneities at nanometer-length scales that offer distinct salvation environments.

In this work, we use polycyclic aromatic hydrocarbons (PAHs), which are compounds consisting of two or more fused aromatic rings, as models to understand deeper the interactions that govern their solubility in ionic liquids. A large variety of ionic liquids was used to understand how the type of cation or anion would interfere in PAHs solubility. Moreover, the effect of the alkyl chain length or the functional groups attached to both cation and anion were also studied. The model compounds chosen were benzene, naphthalene, anthracene, phenanthrene, pyrene and coronene.

A new HPLC protocol was used to measure the solubility of the PAHs in pure ionic liquid.

Ab-initio calculations and Molecular Dynamics simulations have also been used as valuable tools to unravel the interactions between the aromatic moieties and the selected surface active ionic liquids.

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Towards a Higher Hydrophilicity in Bistriflamide Based Ionic Liquids

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The bistriflamide anion (NTf_2) became a commonly-used anion in ionic liquids (ILs) due to some important advantages, such as chemical stability, increased thermal decomposition and low melting points. However, ILs holding a bistriflamide anion are also known to form hydrophobic ILs. Only recently it was shown that bistriflamide based IL with the choline cation is miscible with water in the entire composition range, although in a temperature range above approximately 70 ºC.[1]

The motivation that has driven this work was the development of bistriflamide-based ILs completely miscible with water at room temperature by manipulation of the ammonium cation. The natural step was to functionalize the alkyl chains connected to the ammonium cation making it much more hydrophilic. We were able to obtain low melting point and high thermal stability ILs completely miscible in water at room temperature. To the best of our knowledge, this is the first successful attempt to synthesize a bistriflamide based IL that comprises such characteristics. Moreover, using such a cation will keep the ionic liquid's toxicity as low as possible despite the use of a bistriflamide anion. Moreover, we also relate distinct thermophysical properties, such as density, viscosity and conductivity, with the size of the alkyl chains and type of functional groups attached to the ammonium cations.

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Natural Deep Eutectic Solvents for Dissolution of Raw Materials

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Recently, many studies concerning the environmental impact of ionic liquids (ILs) have shown that despite their unique properties and clear advantages in an ever wide range of applications and processes, ILs are not universally green.[1] In the search for biodegradable and low toxicity ILs, a new type of ILs have been developed, the Deep Eutectic Solvents (DES). These compounds are fluids composed of cheap, non toxic and biodegradable salts, nature derived, that self-aggregate by H-bond interactions, resulting in an eutectic mixture that presents a lower melting point than the starting materials, ideally liquid at room temperature.[2, 3] Inspired by this novel advanced class of green ILs, the aim of this work is to prepare DES from cheap, non-toxic, biodegradable compounds using cholinium chloride, acetylcholine chloride and benzoylcholine chloride as hydrogen bond acceptors (HBA) and a wide variety of naturally occurring carbohydrates which will act as hydrogen bond donors (HBD). The prepared DES will be analyzed using NMR spectroscopy and FTIR in order to check their structures and purities. DSC will be used to accurately determine the solid-liquid equilibrium and to detect the eutectic composition. Thermophysical properties, such as densities and viscosities, at atmospheric pressure and in a large range of temperatures and with variable water contents will be measured. The application of these new deep eutectic solvents as solvents to the dissolution for straw rice was investigated.

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New Natural Deep Eutectic Solvents for Azeotrope Breaking

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The separation of azeotropic mixtures is of particular interest in modern sustainable chemical engineering, especially in what concerns the recycle of solvents. Liquid extractions are among the industrial processes used for this kind of separation, in which organic solvents such as sulfolane, dimethyl sulfoxide, and ethylene glycols are used.These solvents are harmful to the environment because of their volatility and toxicity or do not offer the required efficiency, and therefore, their substitution for greener alternatives has been a topic of interest over the past several years.[1] Recently, many studies concerning the environmental impact of ionic liquids (ILs) have shown that despite their unique properties and clear advantages in an ever wide range of applications and processes, these fluids are not universally green. Thereby, in a search for biodegradable and low toxicity ILs, a new greener class of solvents has been emerging, the Deep Eutectic Solvents (DES).

The most popular DESs synthesized so far are those based on cholinium chloride because of its low cost, low toxicity, biodegradability, and biocompatibility. DES can present several advantages to ILs, since they can be easily synthesized and can also present lower viscosities than their ILs counterparts, as shown previously by us.[2] In addition, we also shown that DES can be efficient extraction solvents for the separation of n-heptane + ethanol azeotropic mixtures.[3]

The main goal of this work is to evaluate the performance of benign ILs and deep eutectic solvents in the separation of common azeotropic mixtures, where liquid-liquid separation is the most common extraction process. Liquid-liquid equilibria for the following ternary systems: toluene + heptane + [C_2MIM][OAc] and toluene + heptane + DES were measured at 298.15K and the obtained results were compared to the usual solvents described in the literature. Both the selectivity and the distribution coefficient parameters were used in the assessment of the extraction solvent feasibility for these systems.

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Production of Lysozyme Nanofibers using a Deep Eutectic Solvent

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Amyloid fibrils have gained increased attention because of their association with several pathological medical disorders, such as Alzheimer's and Parkinson's diseases. However, while many studies focus on how to prevent protein fibrillation, others focus on promoting the formation of protein nanofibers, since they present excellent mechanical properties. A range of technological applications, such as bioactive membranes and tissue engineering scaffolds, rely on protein nanofiber-based materials. Hen egg white lysozyme (HEWL) has been widely used for this purpose and a variety of conditions have been tested *in vitro* to induce protein fibrillation, including acidic solutions [1], high temperature[2], the addition of ethanol[3], among others. Nevertheless, the time required to obtain fibrils can take days, weeks and even months. Consequently, new fibrillation methods that might leverage this limitation have been put forward. In particular, Bae *et al.*[4] demonstrated that the presence of small amounts of specific ionic liquids (ILs) induces the formation of amyloid fibrils at mild conditions, in 20mM glycine buffer (pH 2.0) with constant shaking at room temperature, opening up a new range of possibilities just by changing the solvent. Very recently, deep eutectic solvents (DES), obtained by mixing a salt/IL and an hydrogen bond donor in certain amounts, have been gaining much attention as versatile alternatives to ILs.[5] In this work, we explore the possibility of using these solvents as fibrillation adjuvants. DES based on cholinium chloride and acetic acid was studied as a possible promoter of HEWL fibrillation, and protein nanofibers were obtained within few hours. The influence of experimental variables such as temperature (RT, 50, 70ºC) and pH (2, 7.4) in the process of fibrillation was also addressed, as well as the role of DES in the production of protein nanofibers.

Acknowledgments

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Poster Communication abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Characterization of Choline and Pyridinium Based ILs

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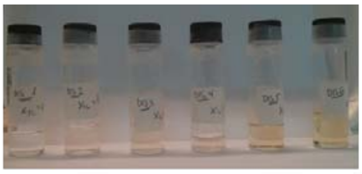
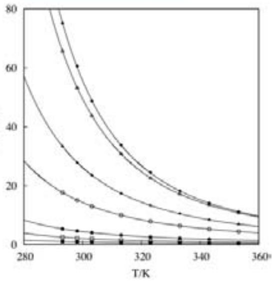
Physical characterization is a critical issue to develop industrial applications involving ionic liquids. Therefore what we have tried to do with this work is, on one hand, obtained useful data for the particular application we are working on, and on the other hand, improve the understanding about how ionic liquids and their water mixtures behave. Analyzing anion and cation structures and their effect over physical properties we will be able to select among the massive amount of ionic liquids[1] those which have suitable properties for any given application[2]. Since some physical properties are strongly influenced by impurities, it seems very important to identify and quantify them as accurately as possible, not only to avoid undesirable effects but also as another way of "tuning" ILs properties, with that goal ionic chromatography (IC) and Karl Fischer tritation were used.





In this work, several physical properties are presented and compared with literature results. Temperature and composition effect will be analyzed. Finally, relations between these properties will be also commented.

Acknowledgements

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Behavior of Ternaries IL+Water+Alkanol. Experimental Information on Thermodynamics Properties of Volumetric and Energetic Nature

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This work shows the results obtained in the experimentation carried out with three ternary system formed by hexyl-3-methylimidazolium chloride, $[\text{hmim}]^+[\text{Cl}]^-$, water, and the first three alkanols, $C_uH_{2u+1}(OH)$ (u=1-3), as well as those for corresponding binaries. Interaction energies that arise in the mixing processes and the volumetric effects produced were determined to interpret the behavior of the final solution in order to develop a structural model explaining the effects of ionic liquid (IL) in the water+alkanol solutions. These binaries are sufficiently studied in the bibliography, in most cases the properties are measured at 298.15 K. It was also found a study on the ternary of this work containing ethanol [1] and their corresponding binaries [1], with experiments conducted at the same temperature, but only about interpretation volumetric from densities; there is no information concerning on the energetic effects. In this work, in order to facilitate the handling of solutions containing IL, $[\text{hmim}]^+[\text{Cl}]^-$, measurements were carried out at 318.15 K, using the above reference for comparison.

To help the data representation, the experimental values were modeled with an equation developed by our team using the so called *"active fraction, z"* as variable, given by:

$$y^{\text{E}}_{2,\text{N}} = \sum_{p=2}^{N}\left[\sum_{i_1 i_2 \dots i_p \in CR^*(2,p)} a_{\text{i}_1\text{i}_2\dots\text{i}_p} z_{\text{i}_1} z_{\text{i}_2} \dots\ z_{\text{i}_p}\right] \qquad z_{\text{i}} = x_{\text{i}} k^{\text{i}1} \Big/ \left[\textstyle\sum_{\text{j}=1}^{\text{n}} x_{\text{i}} k^{\text{i}1}\right] \tag{1}$$

Particularly for the ternary, the particular expression of eq (1) is written as sum of the binary contributions i-j, $y^{\text{E,ji}}$, and the corresponding term to the synergistic effect in each property, due to the joint action of the three compounds, indicated by $\Delta y^{\text{E,123}}$, giving as result,

$$y^{\text{E,123}}(x_1, x_2) = y^{\text{E,12}} + y^{\text{E,13}} + y^{\text{E,23}} + \Delta y^{\text{E,123}} \tag{2}$$

Graphical representations of the three studied ternaries are summarized in Figure 1.

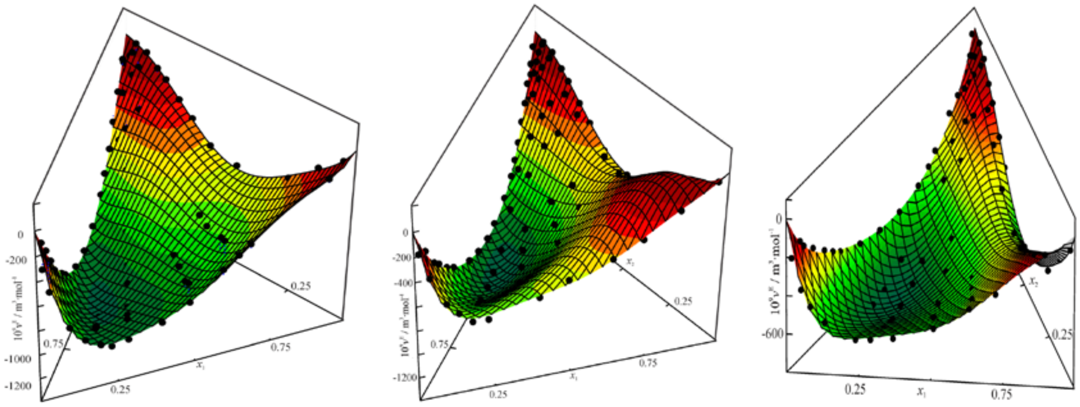

Figure 1. 3D-Plot of experimental v^E data and the corresponding surfaces $v^E=\varphi(x_1,x_2)$, obtained with eqs (1,2), for the ternaries $\{[\text{hmim}]^+[\text{Cl}]^- + C_uH_{2u+1}(OH) + H_2O\}$, being: (a) for u=1, (b) for u=2, (c) for u=3

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
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Using Pyridinium-Based Ionic Liquids as Entrainer in Distillation Processes. Results Obtained in an Experimental Application

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Ionic liquids (ILs) have been used by several researchers [1,2] as entrainers in some processes of extractive distillation for separating certain compounds in azeotropic solutions. It is known that the ILs offer some advantages over other solvents when they act in the separation processes mentioned, highlighting its almost null volatility and the influence on the conditions of singular points (azeotrope). Our group has worked for years on ester+alkanol solutions [3,4], whose interest is currently focused on the field of biofuels. Furthermore, we have also done some studies [5,6] using pyridinium-derived ILs. In this work we have analyzed the impact of a series of ILs isomers [b*X*mpy][BF$_4$] *X*=2,3,4, on the azeotropic conditions of the binary methanol+methyl ethanoate whose singular point has the following coordinates (p=101.32 kPa; x_{az}=0.34; T= 326.82 K). Therefore, the characteristic variables of the isobaric (p=101.32 kPa) vapor-liquid equilibria were determined for the binary solutions involved (methanol+methyl ethanoate, methanol or methyl ethanoate+[b*X*mpy][BF$_4$] *X*=2,3,4) resulting an experimentation on seven binaries, six of which have not been studied previously. The position of the methyl group, *X*, is important.

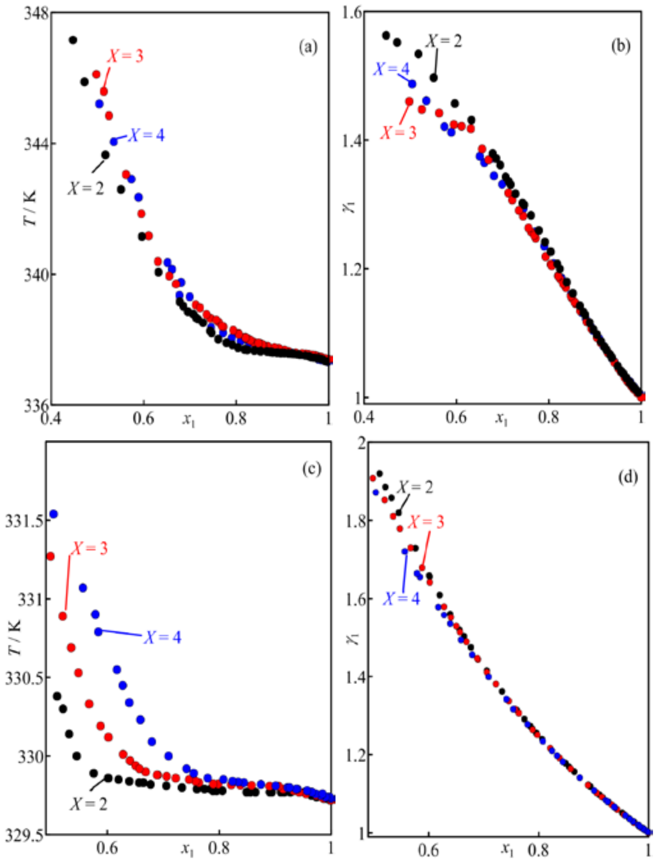

Figure 1. Results of *iso*-101.32 kPa VLE for binaries: (a), (b): methanol+[b*X*mpy][BF$_4$]; (c), (d): methyl ethanoate + [b*X*mpy][BF$_4$], being *X*=2,3,4

In Figure 1 (a-d) the characteristic values obtained in the isobaric vapor-liquid equilibrium for the six binaries containing ILs are shown. From experimentation can be observed that the presence of the ILs raises the temperature of methanol significatly, a fact that does not happen with ester, which favors the displacement of the azeotropic point. The mobility of the singular point depends of the isomer, but when *X*=2 the separation of the compound should be more effective.

An own model [3,5] was used to correlate the VLE data comparing the results obtained with those obtained by NRTL.

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Measurement and Modeling of the Solubility of Ammonia in some Ionic Liquids

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Ionic liquids (ILs) are low-melting-point salts composed entirely of ions.[1] One of their most important characteristic is that their thermophysical properties can be easily tuned for a specific application using simple anion-cation combinations. Therefore, studies related to ILs as potential alternatives to the original restraints imposed by the use of conventional substances in several processes have increased recently. In the case of the absorption refrigeration, ILs are presented as a very interesting alternative to the conventional absorbents, which present some drawbacks, as the case of the conventional working fluid ammonia + water that requires the use of a rectification column due to the low relative volatility of the compounds affecting to the efficiency of the system. By replacing water for a suitable IL, this problem could be solved. Some thermophysical properties of the ILs and their mixtures with refrigerants, such as solubility, density, viscosity and heat capacity, are essential to have a first insight and to understand the use of these fluids as working pairs.

In this work, solubility of ammonia in four ILs has been experimentally determined. Two of the ILs (1-(2-hydroxyethyl)-3-methyl imidazolium tetrafluoroborate [hemim][BF_4] and choline bis(trifluoromethyl sulfonyl) imide [choline][NTf_2][2]) have been reported in the literature as very suitable for this purpose, based on a combination between a computational tool (COSMO RS) and experimental work (notice that the absorption experiments are limited to T= 293.15, 313.15 K). The remaining two are new ammonium based ILs designed as potential absorbents for ammonia, considering both the presence of hydroxyl group in the cation to facilitate the solubility, and the use of anions that allow the reduction of viscosity and the increase of thermal stability.[3] This was achieved by incorporating the common cation N-ethyl-N-(2-hydroxyethyl)-N,N-dimethyl, [$EM_2N(CH_2)_2OH$], and two different anions: bis(trifluoromethylsulfonyl)imide [NTf_2] and trifluoromethanesulfonate [TfO].

To determine the solubility, the vapor pressure of the mixtures of ammonia with each IL has been measured by the static method at several compositions and a range of temperature from 293.15 K to 373.15 K. Liquid phase composition was determined using the Barker's method, with the Redlich-Kister equation to calculate the liquid activity coefficients and the virial equation of state to describe the vapor phase. Additionally, an Antoine-type equation and the Non-Random-Two-Liquids model (NRTL) were used to fit the data. The solubility of the mixtures was compared with data reported in the literature for other mixtures in order to elucidate relationships with the IL chemical structure, which will help in the design of new more efficient absorbents.

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Protonic Ammonium Nitrate Ionic Liquids and Their Mixtures: Insights into Their Thermophysical Behaviour

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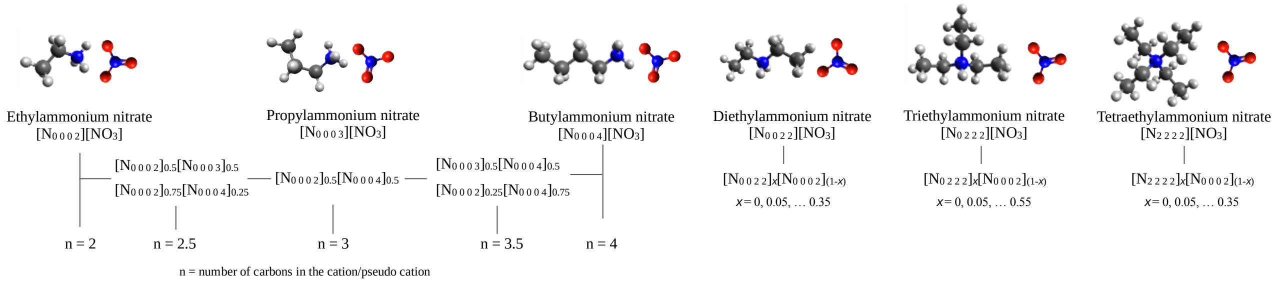
Protonic ionic liquids are generally conceived as a particular class of ionic liquids due to the fact that one or more protons are effectively available for strong hydrogen bonding, leading to hydrogen exchange. Thus, protonic ionic liquids may not be neat liquid salts; instead they may be a mixture of ionic species and molecular ones. Together with the presence of Coulombic and van der Waals interactions, hydrogen bonds are regarded as key forces that determine many of the peculiar physico-chemical properties of protonic ionic liquids.

In this work, the density, viscosity and conductivity of pure protonic ionic liquids have been studied, as well as two different sets of binary mixtures, *viz*: (i) selected binary mixtures of monoalkylammonium nitrate ionic liquids (ethyl-, propyl- and butyl-ammonium nitrate); and (ii) binary mixtures composed of ethylammonium nitrate (three hydrogen bond donors) and different homologous nitrate ionic liquids with a distinct number of hydrogen bond donor groups: di- (two hydrogen-bond donors), tri- (one hydrogen-bond donor) and tetra-ethylammonium nitrate (no hydrogen-bond donor). The results show a *quasi*-ideal behaviour for all monoalkylammonium nitrate mixtures. In contrast, the other mixtures show deviations from ideality, namely when the difference in the number of carbon atoms present in the cations increases or the number of hydrogen-bond donors decreases. Moreover, the results clearly show that besides the length and distribution of the alkyl chains present in a cation such as alkylammonium, there are other structural and interaction parameters that influence the thermophysical properties of both pure compounds and their mixtures.



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Thermal Behavior of Dialkyl Pyridinium Bis(trifluoromethylsulfonyl)imide Ionic Liquids

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The thermal behavior of the new dialkyl pyridinium bis(trifluoromethylsulfonyl)imide ionic liquids was studied by differential scanning calorimetry (DSC), exploring the effect of the alkylation, chain length increase and symmetry of the cation.

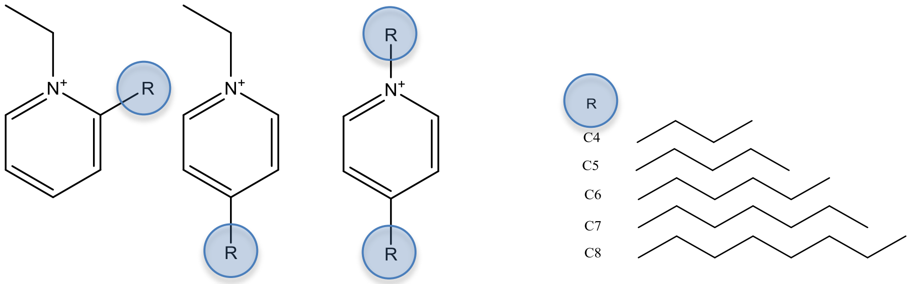

Figure 1. Schematic representation of the three dialkyl pyridinium NTf2 ILs Series.

Glass temperatures, *T*g, crystallization behavior, (solid- solid and fusion) transitions temperatures and standard molar enthalpies and entropies of fusion for the ionic liquids were measured in a power compensation differential scanning calorimeter, PERKIN ELMER model Pyris Diamond DSC. A comparative analysis of the alkyl chain length in the dialkyl pyridinium bis(trifluoromethylsulfonyl)imide base ionic liquids isomers will be presented focused in the symmetry effect and on the alkyl chain length trends.

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DFT Calculations on Fe Containing Ionic Pairs

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The interest in Magnetic Ionic Liquids (MIL) has increased since the discovery of the first MIL in 2004 by Hayashi and Hamaguchi [1]. Several experimental studies have been performed in order to determine the behaviour of these systems and their properties when magnetic fields are applied to the system. However, there are just a few theoretical studies in this field, and most of them are focused in the solid state [2].

In this work we have used Density Functional Theory (DFT) methods to determine the electronic structure and structural properties of a set of ionic pairs containing iron ($FeCl_4$, Fe_2Cl_7, Fe_2OCl_6). We have tested the influence of the functional and basis set in the determination of the coupling magnetic constants and interaction energies between cation and anion. In addition COSMO-RS method was used to determine bulk properties as density and viscosity.

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Estimation of Properties of Amino Acid-based Ionic Liquids

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Ionic liquids are substances of interest due to their remarkable properties as disolvents, which make them a good green alternative to the organic solvents. The N,N,N-trimethylethanolammonium cation (choline) is an essential nutrient [1] and, therefore a good candidate for combining with appropriate anions to produce ionic liquids of relatively low toxicity. [2] The carboxilic acid functional group of amino acids may act as anion. Cholinium amino acid ionic liquids (ChAA-ILs) are ionic liquids resultant from the combination of choline as cation and amino acids as anions.

In this work, ChAA-ILs have been considered for a theoretical analysis of their molecular structure and a prediction of physicochemical properties like hydrophobicity and polarity have been made within the COSMO model framework. All geometries have been optimized using DFT calculations at the B3LYP/6-311+G** level, checking for the absence of imaginary frequencies. All calculations have been performed with Gaussian09 package, and stabilization energies have been corrected from the basis set superposition error by using the CounterPoise method. Physicochemical properties have been estimated by COnductor-like Screening MOdel for Realistic Solvation (COSMO-RS) at room temperature. Chemical behavior of twenty ionic liquids have been analyzed, and the results of physicochemical properties obtained with COSMO-RS method have been compared with those of other methods. [3]

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Advances in Imidazole-derived RTILs Synthesis

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Room Temperature Ionic Liquids (RTILs) can be designed for every kind of application due to the fact that the selection of their ions will determine their physical and chemical properties. Certain interest has been aroused in our group in studying the synthesis of these ionic liquids using modern instrumental methods that enable us to optimise the quality of the product. Synthesising RTILs, such as 1-butyl-3-methylimidazolium bromide (BMIMBr), represents a highly exothermic alkylation and the kinetics (S_N2) are too fast. The high temperature has a detrimental effect on the quality of the RTILs obtained. So it is crucial to eliminate the heat released by the reaction efficiently to enhance the purity of the product. One way of controlling the temperature in a highly exothermic reaction is to do it slower. The traditional solution was to dilute the reagents with solvents and/or slowly add one of the reagents in Batch reactors with heating/ cooling systems. Solvents that are ideal for the S_N2 reaction are usually used, such as acetone or chloroform. The use of large volumes of solvents increases costs and also pollution, and slowly adding reagents sometimes leads to very slow reactions (hours or days) with a progressive loss of the alkylating reagent from evaporation. A solvent-free synthesis system with optimised thermic transfer was therefore advisable. This was made possible by synthesis in a continuous channel micro-reactor.[1,2] So, Iolitec Ionic Liquids Technologies (Io-li-tec) designed a modular continuous micro-reactor system for producing ionic liquids, specifically by reactions of amines (e.g. 1-methylimidazole) with alkylating agents like alkyl chlorides, bromides, iodides and sulphates. The system is a self-confined unit with peripherals that have to be attached in the form of power supply, substrate supply and product outlet. The system was designed to perform alkylating reactions in tube reactors (PFTE or stainless steel).

This study addresses different aspect concerning the synthesis of the following RTILs: HMIMCl, HMIMBr, BMIMCl, BMIMBr, $DMIMMSO_4$ and EMISE, together with a study of the fine-tuning and validation of the aforesaid Io-Li-Tec modular apparatus by NMR and physical-chemical constant quality control of the product.

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Poster Presentation abstract for the Iberoamerican Meeting on Ionic Liquids- IMIL 2015
July 2-3, 2015 • Madrid • Spain

Synthesis of a New Series of Dicationic Ionic Liquids

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Room Temperature Ionic Liquids (RTILs) are a new class of substances that are considered potential substitutes for many traditional organic solvents in reaction processes and others of a different nature.[1,2] Because of their low vapour pressures and thermal stability, ILs are strong candidates, at least a priori, for using in certain sustainable processes from an environmental point of view. Most of the current research is conducted using ILs based on pyridinium and imidazolium, which constitute the central nucleus of the cation of the corresponding compound. However, the use of many of these substances has not reached the expected levels. Therefore, the search for new compounds has become one of the research objectives of many groups.

In our laboratory, we have synthesised a series of imidazolium-derived di-cationic compounds belonging to the aprotic ionic liquids (AILs) group, using several halides as an anion[3]. Specifically, we refer to organic 1,ω–bis-(3-metilimidazolium-1-il)- alkane (ω=1-6) chloride, bromide or iodide salts. This communication details the synthesis of the different sets, indicating the most significant physical characteristics and the identification results obtained by ^{1}H-NMR and HRMS. One advantage that ionic liquids present a priori, is that they have lower vapour pressures than the corresponding mono-cationic because of the duplicity of the ion concentration, giving rise, also a priori, to less environmental contamination. Fundamental aspects of the synthesis of seventeen substances (ILs) are presented, indicating some of their physical properties and some aspects of their toxicity. Other questions that could be useful in the field of so-called green-chemistry are also considered in this work, such as biological activity.

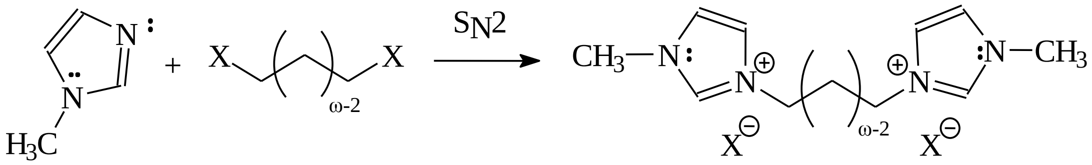

Figure 1.- Bi-molecular nucleophilic substitution reaction (S$_N$2)

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Effects of the Ionic Liquids on the Rates and Selectivity of the Reaction of *O*,*O*-Diethyl 2,4-dinitrophenylphosphate with Amines

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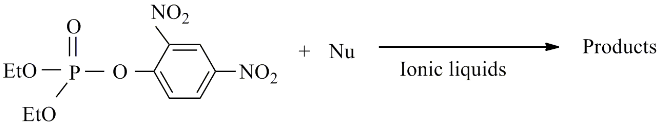
Ionic liquids (ILs), which are typically composed of organic cations and inorganic anions, have been considered as a new class of solvents for different organic reactions.[1] It is know that modifications in the ILs nature can induce radical changes in rates or even in the selectivity of one reaction.[1] Recently, we have demonstrated that the reaction of Paraoxon® with piperidine in ILs occurs via three simultaneous reaction paths, whereas the same reaction in aqueous solution proceeds with exclusive phosphoryl attack.[2]

Bearing in mind these precedents, our particular interest is focused on the possibility that ILs may substantially alter the reactivity in parallel nucleophilic substitution reactions of phosphate esters. To improve our understanding of the effect of ILs as solvents on rate and product distribution, we perform a kinetic study and analysis of product of the reaction of *O*,*O*-diethyl 2,4-dinitrophenyl phosphate triester (**1**) with primary amines in ionic liquids and some conventional solvents (Scheme 1). By ^{31}P-NMR analysis, when 4-methoxyaniline was the nucleophile only one attack pathway was detected: at the C-1 aromatic carbon of the substrate **1**. Nevertheless, two pathways were detected when butylamine was the nucleophile: nucleophilic attack at the phosphoryl center (pathway $S_N2(P)$) and at the C-1 aromatic carbon (pathway S_NAr), except when [Bmim][DCA] was the reaction solvent. The total second-order nucleophilic constant (k_N^T) was separated into two microconstants, which are the rate constants for each attack pathway. These results show that the rates and selectivity of the reactions are dependent on the nature of the IL used. Good correlations of rate with solvent acceptor capacity to form hydrogen bonds (β) were observed. In both cases the anion is the most important factor, while the effect of the cation is relatively modest.



(1)

Nu: 4Methoxyaniline, Butylamine

Scheme 1

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Mechanism of the Aminolysis Reaction of 4-nitrophenyl Acetate and *O*,*O*-diethyl *O*-(2,4-dinitrophenyl)phosphate Trimester in Ionic Liquids

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Herein we describe the effect of the nature of ionic liquids (ILs) on the kinetics of the reactions of 4-nitrophenyl acetate (NPA)[1] and of O,*O*-diethyl *O*-(2,4-dinitrophenyl) phosphate triester (DNPP)[2] with piperidine. In order to determine the mechanism of the title reactions we study the kinetics of both compounds with 1-(2-hydroxyethyl) piperazine, morpholine and formilpiperazine.

In the reactions of DNPP with the amines in [Bmim]BF_4 and [Bmim]DCA, plots of the observed rate constant against the amine concentration were linear, except for the reactions of DNPP with formilpiperazine which were curved; these results are in accordance with a stepwise mechanism with formation of two intermediates. On the other hand, linear Bronsted plots with β values 0.3 and 0.4 were obtained for the reactions of NPA in [Bm_2im]NTf_2 and [Bmim]NTf_2, respectively; these values are borderline between a concerted and a stepwise mechanism with the formation of the tetrahedral intermediate as rate determining step.

To understand more about the effect of ILs as solvents on the mechanism of the title reactions, the activation parameters were obtained. Figure 1 shows the Eyring plots for the reactions of NPA with piperidine in different ILs solution. These results are consistent with a concerted mechanism for the reactions in all ILs, except in [Bmim]PF_6 where a stepwise mechanism is proposed.

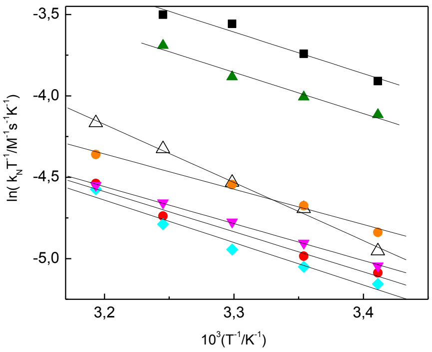

Figure 1.- Eyring plots for the reaction of NPA with piperidine in different solvents:
Acetonitrile (▼), [Bmim]PF_6(Δ), [Bmim]BF_4(■), [Bmim]OTf (▲), [Bmim]NTf_2 (●), [Hmim]NTf_2(♦), [Bm_2im]NTf_2 (●)

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Are There Two Pathways in Hydrogen Redox Reaction in Ionic Liquids?

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Hydrogen oxidation and proton reduction are one the most important and simple reactions in electrochemistry. However, the behavior observed in ionic liquids seems to be more intricate than in aqueous media[1-3]. The H_2 oxidation observed in the ionic liquid 1-ethyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [Emmim][NTf_2], showed a dependence of the surface structure used, being less reversible in Pt(100) than in Pt(111) and Pt(110). The electrochemical behavior of the H^+/H_2 redox system shows that both solution and adsorbed species are involved[4]. Besides, the addition of some organic acids like methanesulfonic acid (MSA) produces a new redox signal at lower potentials. This behavior can be explained if two pathways for the H_2 oxidation are considered, one dissociative at lower potential and one non-dissociative at higher potentials. Finally the change on reactivity at potential higher than 0.4 V can be due to changes on the structure of the electric double layer.

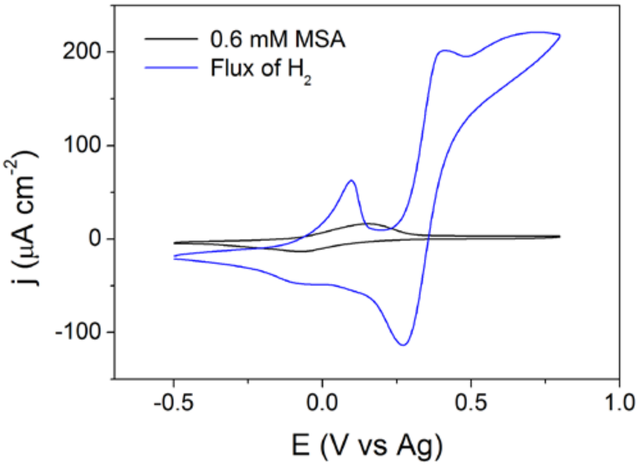

Figure 1. Cyclic voltammograms of 0.6 mM MSA in [Emmim][NTf_2] on Pt(111), before and after a flux of hydrogen passing through the cell. It was used a scan rate of 50 mV s^{-1}.

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