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ILMAT 2023

7TH INTERNATIONAL Conference on Ionic Liquid Based Materials

21st to 24th November 2023

Porto, Portugal
Instituto Pernambuco

Book of Abstracts

Editors:
José C. S. Costa
Luís M. N. B. F. Santos

University of Porto,
Faculty of Science

Book of Abstracts of the 7th International Conference on Ionic Liquid-Based Materials
ILMAT 2023
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FOREWORD

The **ILMAT 2023** | **7th International Conference on Ionic Liquid-Based Materials** held in Porto, Portugal, from November 21st to November 24th, 2023, is organized by the Faculty of Science of the University of Porto in partnership with the Portuguese Society of Chemistry (SPQ). The technical sessions for **ILMAT 2023** take place at the **Instituto Pernambuco – Porto**, providing an ideal venue for fruitful discussions and knowledge exchange among researchers and industry professionals in the field.

The International Conferences on Ionic Liquid-Based Materials (ILMAT) are well-established European conferences that focus on the properties and applications of ionic liquids. Previous conferences were successfully held in Vienna (2011), Montpellier (2013), Berlin (2015), Santiago de Compostela (2017), Paris (2019), and Alsace (2021). This European conference is dedicated to the study of ionic fluids, with a strong emphasis on ionic liquids. It comprehensively covers a wide range of topics, including the physicochemical and biological properties of these substances, as well as their potential applications. In recent years, the remarkable potential applications of ionic liquids have captured the interest of researchers from various multidisciplinary fields such as chemistry, physics, biology, and materials engineering. These versatile substances possess exceptional properties that stem from their unique dual character as both ionic and molecular entities. As a result, they have emerged as ideal advanced materials for a diverse range of energy applications. The extensive research and utilization of ionic liquids in various domains have made significant contributions to the advancement of knowledge in this field.

ILMAT 2023 presents an unparalleled opportunity for researchers worldwide who specialize in ionic liquids to showcase their latest achievements and exchange valuable experiences. By bringing together academic scientists from diverse regions of the world, this conference aims to provide a forum for discussing a wide range of materials and their properties and applications, with a particular emphasis on ionic liquids. The overarching goal is to foster scientific discussions and collaborations in a socially dynamic and intellectually stimulating atmosphere that will inspire new applications in the field of sustainable development.

The current Abstracts Book encompasses all contributions submitted to the Conference, comprising **5 Plenary Lectures**, **5 Keynote Lectures**, **54 Oral Communications**, and **48 Poster Communications**. **ILMAT 2023** is attended by 122 participants from 15 countries (12 from Europe, 1 from South America, and 2 from Asia).

The conference takes place in two rooms at **Instituto Pernambuco – Porto**: Room A and Room B. Plenary and Keynote Lectures are held in Room A, while Oral Communications take place concurrently in both Room A and Room B.

This book includes the following abstracts and codes:
Plenary Lectures (PL);
Keynote Lectures (KL);
5 sessions of **Oral Communications (O)**;
2 sessions of **Poster Communications (P)**.

Authors are exclusively responsible for the accuracy, style, and quality of their abstracts, faithfully reproduced from the originals. The contributions of all authors are sincerely acknowledged.

University of Porto, November 2023

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POSTER COMMUNICATIONS

PLENARY LECTURES (PL)

PL_1 to PL_5

Plenary 1 (PL_1)

Maximizing solubilities in aqueous solutions of ionic liquids

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The nanostructuration of ionic liquids, resulting from their amphiphilic character, is one of the defining characteristics of ionic liquids that, to some extent, remain, or can be recreated, when these are dissolved in aqueous solutions. This lecture discusses the mechanism of solvation of hydrophobic compounds in aqueous solutions of ionic liquids. It will be shown that the dissolution of hydrophobic solvents in aqueous solutions of ionic liquids is distinct from their solvation in pure solvents and micellar dissolution. Molecular dynamics simulation and light scattering techniques, showing the formation of large and loose aggregates with a hydrophobic character around the solutes, allowed us to establish that hydrotropy is the leading mechanism of solvation in these systems. Hydrotropy enhances the solubility of hydrophobic solutes by orders of magnitude and makes these mixed solvents far more powerful than pure water or neat ionic liquid to dissolve some target compounds. The modeling of these systems using a thermodynamic statistical model based on Kirwood-Buff integrals and COSMO-RS is discussed. Finally, we will address the advantages of ionic liquids when compared with conventional ionic hydrotropes.

Plenary 2 (PL_2)

Ionic liquids at interfaces with 2D and porous materials

Agilio Padua[1,*], Zheng Gong[1], Mirella Simões Santos[1], Leila Bou Tannous[1], Audrey Steinberger[2],
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The interfaces of ionic liquids with materials are essential for the design and performance of devices and processes, with examples including batteries and capacitors with ionic liquids as electrolytes, or separations using porous solids in contact with ionic liquids. These interfaces are dominated by Coulomb forces and are highly structured, with features that depend strongly on the nature of the ions, composition, and the surface charge and geometry of the materials. This talk will illustrate how a detailed, molecular-level view of the interfaces can be obtained by experimental and computational methods.

We present a study of alkylimidazolium dicyanamide ionic liquids at the interfaces with 2D materials, including MoS_2, using atomic force microscopy in an electrochemical cell allowing for a potential to be applied and using all-atom molecular dynamics simulations with polarization effects explicitly represented. The charge density at the surface greatly affects the ordering of the ions in the interfacial layers near atomically flat surfaces, but the water content also has a drastic effect.[1]

On very different surfaces, namely those of porous metal-organic frameworks (MOF), which contain cavities, pore entries, and various chemical groups exposed, ionic liquids adopt peculiar arrangements, resulting from geometric features of the exposed surface of the MOF. The systems we study are suspensions of porous particles in bulky ionic liquids, with ions too voluminous to enter the pores. The way in which the ions occupy surface features determines the permeability to small molecules and the stability of the suspensions. Using molecular simulation, we characterize the ordering and dynamics of the interfacial layers for various cation and anion structures on ZIF-8 and other MOF materials.

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Plenary 3 (PL_3)

Protic ionic liquids. Structure, dynamics, and new cations!

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Protic ionic liquids are a subclass of the broader family of ionic liquids, known for more than 100 years now.[1] Differently from their aprotic counterparts, protic ionic liquids possess an exchangeable proton, typically on the cation. This chemical structure results in specific properties, such as the ability to form hydrogen-bonded networks and to hypothetically assist the transfer of protons. Yet, protic ionic liquids still provide a high ion density and decent ionic conductivities, they can dissolve Li-salts and in many cases are compatible with polymers to form self-standing polymer electrolytes, even based on biopolymers.[2] Hence, protic ionic liquids are interesting materials for use in a number of energy relevant devices, including capacitors, Li-ion batteries, and fuel cells.[3] Nevertheless, in order to best use them, a knowledge of the structure-property correlation is needed,[4] which can be achieved by use of appropriate methods. These can include vibrational spectroscopy (IR and Raman), NMR spectroscopy (diffusion and solid-state NMR), calorimetric methods (DSC), and dielectric spectroscopy.[5] Moreover, to make progress in this scientific field, new molecular structures need to be explored,[6] which could come with improved desired properties. In this oral contribution, I will share some of the work done in my research group on how changes in the molecular structure affect the transport properties of the resulting protic ionic liquids. The dynamics and orientation of protic ionic liquids inside mesopores will also be touched upon, as well as I will present protic ionic liquids based on new cations never explored before. Welcome!

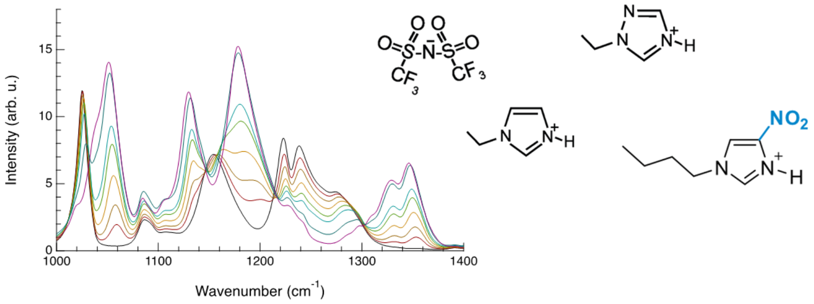

Figure 1: Infrared spectra recorded for mixtures of protic ionic liquids based on different anions (left) and a selection of alternative cationic structures (right).

Acknowledgements
The financial support through the years from the Swedish Research Council, the Knut & Alice Wallenberg Foundation, the Swedish Foundation for Strategic Research, and the Chalmers Areas of Advance is kindly acknowledged.

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Plenary 4 (PL_4)

Nanoscience and engineering of ionic liquids with vacuum technology

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Amongst a number of unique properties of ionic liquids (ILs) is their huge stability in liquid even in vacuum due to their extremely low vapor pressures. This background is the motivation that has driven us to develop vacuum science and engineering with ionic liquids during the last decade. At that time when we embarked on such a new frontier of ILs, the key process was “Infrared laser deposition”, a new vapor deposition method that is purposefully tuned for nano thin film ionic liquid [1].

My presentation will include the following topics:
(1) Ion conduction of ultra-thin IL films [2]
(2) IL-assisted vapor deposition for high-quality and unique crystal film growth [3, 4]
(3) EDL-OFET with thin film nano IL-gel as a gate electrolyte [5]

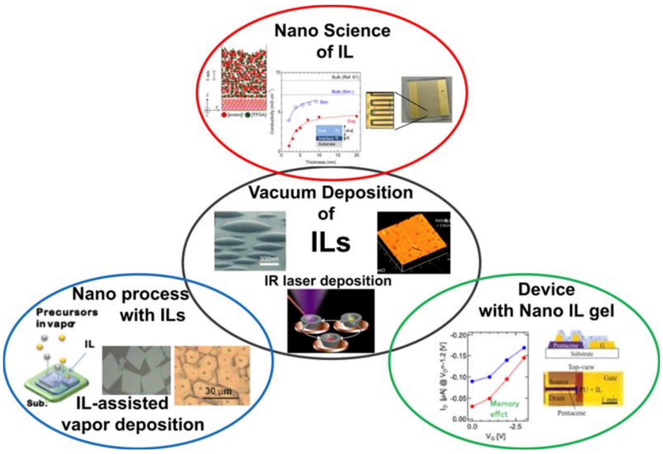

Figure 1: Research fields of nanoscience and engineering of ILs with vacuum technology [6, 7]

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Plenary 5 (PL_5)

The mesoscopic landscape in Ionic liquid-based materials

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Ionic liquid materials, encompassing conventional ionic liquids as well as more complex systems, such as water in salt (WiS) or (deep) eutectic media (DES), keep on attracting a high level of academic and industrial attention, with the research focus progressively shifting towards applications.

The inherent amphiphilicity of a large fraction of these media led to a wealth of studies addressing the nature and the role of their mesoscopic spatial and temporal features. Nowadays it is acknowledged that nm-scale structural heterogeneities represent one of the most outstanding features in ionic liquid materials morphology and, as such, they manifest into specific bulk performances.

In this presentation, an overview of the evolution of the awareness of the mesoscopic landscape in ionic liquid materials will be provided, highlighting the nature of mesoscopic organization under different conditions, including temperature, pressure, and chemical composition effects.[1,2]

Moreover, recent results on novel media, including WiS[3], water-based hydrophilic[4,5] and hydrophobic[6] DES, supramolecular eutectic media[7–9], will be presented, rationalizing the role of different interactions in determining morphology and solvation features, by means of the synergy between experimental techniques and computational tools.

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KEYNOTE LECTURES (KL)

KL_1 to KL_5

Keynote 1 (KL_1)

Hydrophobic eutectic mixtures and eutectogels: structural and dynamic features

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In the evergrowing set of eutectic mixtures created and investigated as sustainable alternatives to conventional molecular solvents, the molecular, hydrophobic type V eutectic solvents (ES)[1] gained the scene for their versatility and the broad spectrum of potential applications, ranging from liquid – liquid extraction[2] to solvometallurgic recovery of critical materials from battery waste.[3]

The ES components are often natural products, among them terpenes and carboxylic acids. The main driving force for the local structuration is still the H-bond donor (HBD) – H-bond acceptor (HBA) interaction. However, the presence of large apolar fragments in the molecular frame of both HBD and HBA calls for a deeper understanding of how the dispersive interactions concur with the overall network of interactions within the ES.

In the present communication, two paradigmatic case studies will be presented, both involving two of the most popular molecular components of type V ES, menthol and thymol.[4,5]

In the first case, the intensity of the H-bond network has been modulated by changing the steric hindrance at the HBD site of the phenolic components. The results of 1H-NMR spectroscopy, Raman spectroscopy and MD simulations allowed us to highlight the relative contribution of H-bonds and dispersive forces.

In the second case study, a collection of menthol- and thymol-based ES have been studied via diffusion NMR. The transport properties of the ES' components in the pure liquid and in the gel stat after gelification with DBS show counterintuitive trends, which will be discussed in terms of the network of intermolecular interactions.

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Keynote 2 (KL_2)

Charge and proton transfer in polarizable molecular dynamics simulations of ionic liquids

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Although non-polarizable molecular dynamics simulations successfully modeled the structure of various ionic liquids, the simulated dynamics tend to be one order of magnitude too slow compared to the experiment. Scaled charge methodologies can expedite these dynamics, albeit at the expense of neglecting hydrogen bonding interactions and the potential introduction of simulation artifacts [1].

Employing polarizable molecular dynamics simulations, although computationally demanding, confers multiple advantages [1]. Firstly, these simulations closely approximate experimental dynamical data. Secondly, they permit the induced molecular dipoles to respond instantaneously to their local environments, thereby unveiling mechanistic pathways not accessible via fixed charge methodologies. Thirdly, the induced dipoles act to modulate the Coulombic energy landscape during non-equilibrium processes such as charge and proton transfer.

Despite these advantages, classical molecular dynamics simulations remain constrained by the immutable nature of charge assignments and the inability to facilitate the formation or dissociation of chemical bonds. Our innovative polarizable molecular dynamics simulations circumvent these limitations by incorporating both charge [2] and proton transfer [3-5] events. These mechanisms are indispensable for a comprehensive understanding of protic ionic liquids. In addition to evaluating the concomitant effects of reduced charge and polarizability [2], the incorporation of proton transfers facilitates the exploration of diverse conductivity mechanisms, including Grotthus and vehicle-mediated transport [4,5].

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Keynote 3 (KL_3)

Computational modeling of ionic liquids in nanoconfinement

Trinidad Méndez-Morales[1,2*], Hadrián Montes-Campos[1,2,3], Luis M. Varela[1,2]

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Ionic liquids (ILs) are organic salts composed of anions and cations that exist as liquids at room temperature. They have been widely investigated in several fields including energy storage, lubrication, and pharmaceutics due to the attractive properties they exhibit. However, the local structure and physicochemical properties of ILs are strongly modified compared to the bulk when they are confined in restricted spaces, which leads to the appearance of physical phenomena such as molecular layering, overscreening, crowding, and superionic state.

Thus, having a deep understanding of the confined effect as a function of the correlations between pore structure, surface chemistry, and IL nature is fundamental to designing novel nanoconfined ILs for task-specific applications.

In this presentation, I will review the main recent advances in the computational modeling of the structure and dynamics of ILs under nanoconfined environments in different porous hosts.

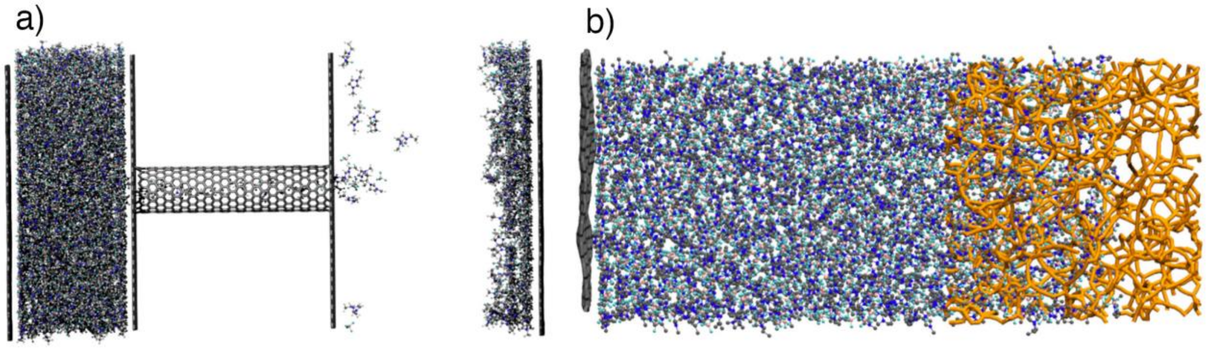

Figure 1: Snapshots of an IL nanoconfined inside a carbon nanotube (left) and a zeolite-templated carbon (right).

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Keynote 4 (KL_4)

Metal-based ionic liquids: a highly flexible toolbox for materials design

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Metals and ionic liquids (ILs) have a long history both in terms of fundamental questions and in terms of rather applied questions. The Taubert group has been researching metal-based ILs for roughly 20 years and has mainly focused on these ILs for materials synthesis. The key aspect is that metal-based ILs are rather easy to make and that the can be tailor-made to contain certain metals, exhibit certain phases (including liquid crystalline phases, and that the transformation of these ILs towards a variety of materials can be achieved via a number of different strategies. For example, transition metal-based ILs have been reacted to form CuCl, CuO, ZnO, Mn_3O_4, a series of Spinells, and other oxides and oxyhydroxides.[1] Moreover, the same ILs can also be used to form porous carbides lik Fe3C, porous Fe-doped silica, or also metal sulfides such as CuS_{1-x} or $CuCo_2S_4$.[2] Overall, therefore, metal-based ILs are highly flexible and viable precursors for a rather large variety of different materials with interesting properties and the presentation will highlight some examples from this work.

Furthermore, metal-based ILs are interesting material in their own right and the presentation will also highlight some of the investigations into the ILs themselves. For example, we have recently shown that 1D $[AgI_2]^-$ infinite chains can be formed in crystalline Ag-I-ILs below the melting points and that a large number of transition metal-based ILs also exhibit rather interesting solid state ionic conductivities at temperatures below 70 ^oC.[3] Again, some of these result will be presented.

Overall, the presentation aims at demonstrating that metals-based ILs are a partially overlooked but rather interesting ub-class of materials with highly interesting and easily adjustable properties with high application potential but also very variable fundamental properties.

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Keynote 5 (KL_5)

Choline chloride thermophysical and phase change studies: relevance for the representation of eutectic systems

Simão. P. Pinho

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The ubiquitousness of choline chloride as a component of eutectic systems, either deep or not, is indisputable. The primordial work from Petrouleas and Lemmon[1] shed light on a well-defined solid-solid transition, but the same level of reliability is yet to be found concerning other properties, such as the melting temperature and enthalpy, among others. In 2017, we first proposed a methodology to estimate the melting properties of choline chloride,[2] allowing to model (deep) eutectic systems containing choline chloride and opening a line of research, as demonstrated by the works of Pyykkö[3] or Alhadid et al.[4]
Following these first significant efforts to characterize choline chloride thermal properties, we were able to contribute much by measuring the enthalpy and temperature of the solid-solid transition, the heat capacities of both solid phases, estimating solid-liquid heat capacity change at 298.15 K, and thermal decomposition of choline chloride.[5] Additionally, the solid-liquid phase diagram of the choline chloride + water binary system was measured in the whole composition range (Figure 1). A detailed analysis of all data is shown in this communication, comparing and checking different sources and highlighting challenges still to pursue for full characterization of that compound and systems.

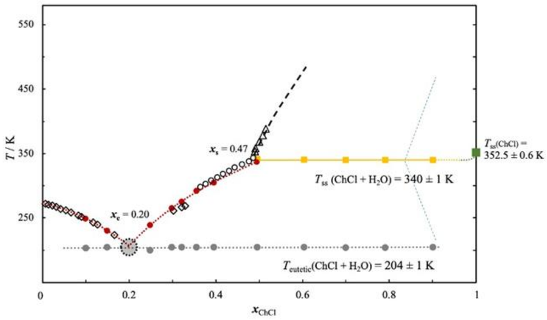

Figure 1: Solid-liquid phase diagram (*p* = 0.10 ± 0.01 MPa) for the binary system choline chloride (ChCl) and water: ◇ – liquidus line (DSC NETZSCH); ○ – liquidus line (shake-flask)[35]; △ - liquidus line (shake-flask); ● – liquidus line (DSC PERKIN ELMER); ■solid–solid transition of binary mixtures (ChCl + H_2O); ■solid–solid transition of ChCl; ● – eutectic transition.

Acknowledgements
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ORAL COMMUNICATIONS (O)

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Session 2: O_A2.1 to O_A2.6
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O_B5.1 to O_B5.4

Oral O_A1.1*

Electrical double layer in ionic liquids: structures, potentials, and applications

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Ionic liquids (ILs) remain a focal point in research due to their unique properties and potential in various applications.[1] While specific interactions have been central to many studies, recent insights suggest that the steric effect – much like how toys of various shapes pack in a toy box – plays a significant role at interfaces.[2]

This talk highlights the role of ion shapes in ion packing at interfaces and how it translates into practical applications. We introduce a hypothetical structure-determined reference potential – The potential of Monolayer Charge (PMC)[3,4] – to offer a fresh perspective on classifying packing regimes of the potential scale. Namely, the PMC distinguishes between two well-known packing regimes – overscreening and crowding[5,6] – and offers a new tool for interpreting empirical data. For instance, we examine the capacitance-potential dependence (relevant for supercapacitors) as a demonstration of the practical implications of the PMC.[7,8] Besides supercapacitors, the role of steric effects is explored using examples from batteries, sensors, actuators, and lubricants, where (despite complex structure-properties relations) distinguishing between packing regimes can help optimize these applications.

We encourage the community to validate and expand upon the presented perspective, starting from the meta-analysis of past empirical data and proceeding with hypothesis-driven experiments and simulations.

Acknowledgments

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* highlighted talk

Oral O_A1.2

Immobilization of lipases with the hydrophobic ionic liquids as effective biocatalysts in the resolution of ibuprofen ester

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Many commercially available drugs are a racemic mixture of enantiomers of a given active pharmaceutical ingredient. However, it often happens that only one of the enantiomers is responsible for the therapeutic effect, whereas the other may provide different properties and in extreme cases cause or intensify side effects. Therefore, it seems highly justified to use asymmetric synthesis methods, which will allow obtaining only one desired enantiomer.[1] For this purpose, enzymatic biocatalysts may be helpful and are increasingly used in the synthesis of active pharmaceutical ingredients (API). The use of enzymes in synthesis has many advantages, including chemo-, regio- and stereoselectivity as well as mild process conditions compared to traditional methods of organic synthesis. An addition of ionic liquids can provide a suitable environment for enzymes, increasing their activity, compared to classic immobilization routes. Due to their properties such as biocompatibility can provide a stabilization effect on enzymes during organic synthesis.[2] Biocatalysis can be successfully used in the synthesis of non-steroidal anti-inflammatory drugs, including ibuprofen - one of the most popular drugs known and widely used around the world. It occurs in the form of a racemic mixture in which (S)-ibuprofen is more responsible for the therapeutic effect, therefore methods of selective synthesis of this enantiomer are being sought. [3]

Due to the hydrophobic environment that ionic liquids can provide, different ILs were tested, such as 1-butyl-3-methylimidazolium hydrogen sulfate, as the stabilizing agent during the immobilization of lipase on a hydrogel support. The obtained results showed a great increase in the enzyme activity but also the amount of the deposited enzyme on the support's surface was increased. Compared to the immobilization conducted without ILs, the amount of enzyme supported by hydrophobic ionic liquid was almost 3 times higher, significantly increasing the activity of produced biocatalysts. Prepared biocatalysts with the addition of ILs were further applied in the synthesis of API. During synthesis the influence of reaction time was checked, the importance of the type of organic solvent was assessed, and an attempt was made to demonstrate differences in the case of pH change and the addition of DMSO (kinetic separation/dynamic kinetic separation). It was shown that the tested parameters have a significant impact on the substrate conversion and, to a lesser extent, on the enantiomeric excess of the obtained (S)-ibuprofen over (R)-ibuprofen. The increase in the pH of the reaction and the addition of DMSO turned out to be important, which enabled dynamic kinetic separation of ibuprofen methyl ester and included in situ racemization of the unreacted (R)-ester to (S)-ester and resulted in an increased conversion rate. For the process carried out in isooctane, the use of the $NaHCO_3$-NaOH buffer at pH 9.5 instead of the phosphate buffer at pH 7 allowed the substrate conversion rate to increase from 48% to 83%. Moreover, the addition of DMSO improved the conversion of ibuprofen methyl ester to 95%.

Acknowledgements
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Oral O_A1.3

Advancing membrane-free batteries: A COSMO-RS analysis of viologen derivatives

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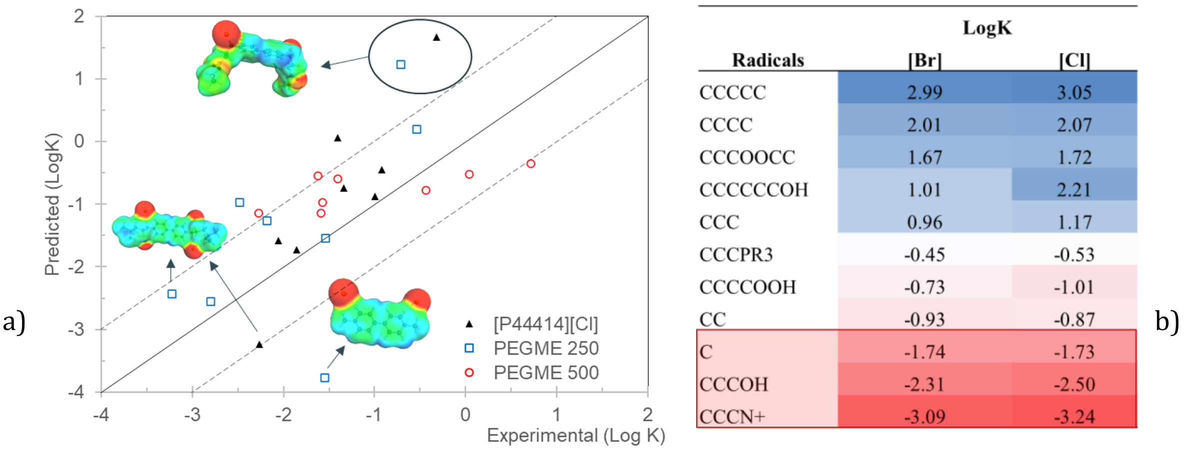
The transition to renewable energy is essential for combating climate change and achieving energy security. Despite renewables making up 22% of the EU's energy consumption, energy storage remains a hurdle due to the intermittent nature of wind and solar power. Redox Flow Batteries (RFBs) offer a compelling solution but face issues like the high cost of ion-selective membranes and the volatility of vanadium prices. In response, membrane-free batteries using aqueous biphasic systems (ABS) and organic molecules as redox-active compounds offer a sustainable alternative.

In this study, COSMO-RS thermodynamic modeling is used to assess suitable viologen derivatives as anolyte compounds for ABS-based, membrane-free batteries. Specifically, we employ the COSMO-BP-TZVPD-FINE template on TmoleX 4.5 software with a def-TZVPD basis set and B-P86 DFT. Despite being time-intensive, this method offers high-quality results and is superior for partition coefficient (K) estimations. After optimization, COSMOthermX 21 software is used for thermodynamic calculations at 298 K. Figure 1 validates the model's effectiveness in representing partition coefficients and highlights promising viologen derivatives with reduced partition coefficients due to substituents like short alkyl chains, hydroxyl groups, and tertiary ammonium cation. This study advances our understanding of viable material selection for membrane-free batteries and contributes to sustainable energy storage solutions.



Radicals	LogK [Br]	LogK [Cl]
CCCCC	2.99	3.05
CCCC	2.01	2.07
CCCOOCC	1.67	1.72
CCCCCCCOH	1.01	2.21
CCC	0.96	1.17
CCCPR3	-0.45	-0.53
CCCCOOH	-0.73	-1.01
CC	-0.93	-0.87
C	-1.74	-1.73
CCCOH	-2.31	-2.50
CCCN+	-3.09	-3.24

Figure 1: Validation with experimental data (a), and viologen's radical influence on partition coefficient (b) in three different ABS.

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Oral O_A1.4

Structural characterization of the $NiCl_2 \cdot 6H_2O$:urea 1:3.5 metal-based deep eutectic solvents: a combined experimental and theoretical study

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Deep eutectic solvents (DESs) are formed by two or more compounds that melt upon contact at a precise molar ratio and produce a mixture with a melting point (MP) that is not only lower than those of the single constituents but also lower than the ideally predicted one. DESs show interesting properties such as negligible volatility, non-flammability, high solvating capability, and low toxicity.[1] Common components of DESs are biocompatible and for this reason, they have been proposed as sustainable solvent media in different applications including extraction processes, purification, and catalysis.

DESs are usually classified into five categories according to the chemical nature of the components, and most of these eutectics fall into the so-called "type I - IV" classes, being formed by at least one ionic compound.[2] In recent years, interest has been directed towards the study of the so-called "metal-based deep eutectic solvents" (MDES). Thanks to the high concentration of ionic species these solvents exhibit important chemical-physical properties such as high polarity and conductivity, making them ideal candidates as new electrolytes and media for electrodepositions and catalytic processes.

Here, a structural characterization of the $NiCl_2 \cdot 6H_2O$:Urea 1:3.5 MDES is presented. Particular attention has been put on the role of water in the MDES formation since the eutectic could not be obtained with the anhydrous form of the metal salt.[3] With this purpose, X-ray absorption spectroscopy (XAS), small- and wide-angle X-ray scattering (SWAXS), and UV-visible absorption spectroscopy, integrated with molecular dynamics simulations (MD), were employed. This combined approach allowed us to reconstruct the structural arrangement of the MDES on both short- and intermediate-scale levels, highlighting how the eutectic formation was achievable thanks to the close packing of Ni^{2+} ion clusters, only possible because of the mediation of bridging chloride anions and water molecules (Figure 1).

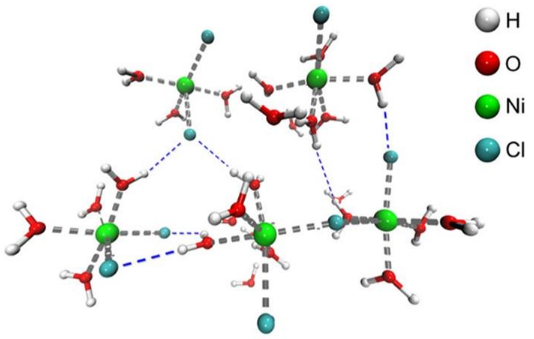

Figure 1 Selected MD snapshot showcasing the close contacts between the Ni^{2+} ion clusters in the $NiCl_2 \cdot 6H_2O$:urea 1:3.5 MDES (gray dashed lines: coordination interactions, blue dashed lines: H-bonds).

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Oral O_A1.5

Bridging chemistry and biology: synthesis, characterization, and biological profile of fluoroquinolone-based GUMBOS

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Antimicrobial resistance (AMR) has been prioritized by international health institutions as a global public health threat worldwide[1]. Strategic therapies are under development to help replace ineffective antibacterials, such as the use of well-known antibacterials as active pharmaceutical ingredients, along with adjuvants[2]. These adjuvants possess non-antibiotic properties but can extend the lifespan and enhance the effectiveness of the treatment, while also improving the suppression of resistance[3]. In this regard, ionic liquids (ILs)[4] and a group of uniform materials based on organic salts (GUMBOS)[5] present an alternative to this problem allowing the combination of antibacterials with adjuvants. Resistance rates of fluoroquinolones, a family of antibacterial agents with major clinical relevance used to treat respiratory and urinary tract infections, are increasing[6]. Fashioning these compounds with different anions and thus different chemical structures may improve their properties and antimicrobial performance. Organic salts based on ciprofloxacin and moxifloxacin were produced via anion exchange reactions with lithium and sodium salts. Structural characterization was performed using NMR, FTIR, and ESI-MS. Thermal stability of the GUMBOS was assessed by TGA and DSC with compound dehydration in the range of 130-150 °C, and their oxidative decomposition between 250-350 °C. Octanol/water partition ratios were assessed to evaluate relative hydrophobicity with a log $K_{O/W}$ range of -1.110 to 1.086. Antibacterial activities against *S. aureus* and *E. coli* were evaluated through a micro-broth dilution method at concentrations of 0.25 and 25 $mg.L^{-1}$. Antibacterial activity of GUMBOS was not statistically different from cationic counterparts, however, some of the synthesized GUMBOS were less cytotoxic to L929 mouse fibroblasts and non-hemolytic on human red blood cells. Therefore, GUMBOS exhibited remarkable performances and showed potential to be further investigated as an alternative approach to combine drugs for treating infections caused by resistant bacteria. This strategy aims to contribute to the ongoing fight against the increasing threat of AMR.

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Oral O_A1.6

Water-based DES.

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The kaleidoscopic richness of potential DES ingredients prompts for exploring a variety of opportunities for optimization of formulations and resulting performances. The chances offered by DES tunability in design ought to be exploited to decrease the environmental impact associated with their use. In this respect, a steady path towards exploitation of natural, sustainable, and low-cost chemicals to develop DES can be recognized in the recent literature. In this scenario, the exploitation of water as a genuine hydrogen bonding donor species in the DES formulation, rather than either a contaminant or an added component to an already existing formulation, is recently attracting great attention.

In this presentation, we will report on recent results on the use of water as a major component in the formation of different hydrophilic[1,2] as well as hydrophobic DES [3]. The experimental solid-liquid equilibrium data of various water-based DES were modeled to get insights into the intermolecular interaction in the liquid phase, in particular, taking advantage of the recently determined fusion properties of choline chloride[4]. (Figure 1).

We also exploit the synergy between experimental data, including the phase equilibria behavior, and Molecular Dynamics simulations, to provide an atomistic-level overview of the structural features in a series of water-based DES, aiming at extracting common features in the behavior of the eco-sustainable, natural DES.

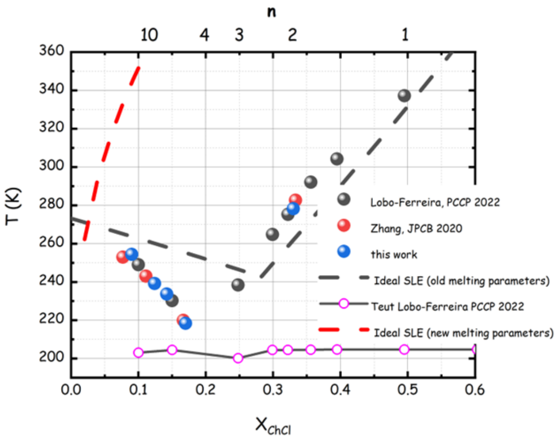

Figure 1: Solid-liquid equilibrium data for the choline Chloride: water system, highlighting the existence of a DES at X_{ChCl}=0.2.

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Oral O_A2.1*

Tools for screening solubility and understanding interactions in ionic liquids

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Ionic liquids have firmly established their presence in diverse research areas and industrial sectors, spanning catalytic processes, mercury capture, biomass deconstruction, and chromatography.[1] Despite these successes, there is still relatively less understanding of the behavior of gases absorbed in ionic liquids, in part due to the intrinsic complexities of working with these mixtures. In the first segment of this presentation, we will introduce the first fast experimental screening method available for determining gas uptake/solubility and real separation selectivity. This user-friendly method, based on headspace gas chromatography, boasts versatility across a wide range of sorbents. It enables the screening of up to 264 sorbents per day, post-equilibration (Figure 1).[2]

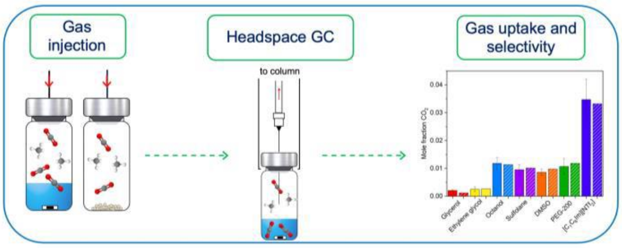

Figure 1: Simplified representation of the screening method for gas uptake and separation ability.

The second part of our presentation will focus on how we are using insights into ionic liquid-gas and ionic liquid-water interactions to steer the design of liquids for gas separations and water desalination applications. Notably, we explore the nuanced differences in the absorption of ethane and ethylene by employing neutron diffraction and spectroscopic techniques. Equipped with these insights we designed ionic liquids and mixtures with the potential to enhance interactions with ethylene.[3,4] Finally, we are actively investigating a series of ionic liquids exhibiting lower critical solution temperature (LCST) in water, harnessing them as drawing fluids for water desalination. Our approach integrates techniques that include calorimetry, single-crystal X-ray diffraction, and surface tension measurements.[5]

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* highlighted talk

Oral O_A2.2

Functionalization of imidazole with electron-withdrawing groups for the synthesis of new acidic protic ionic liquids

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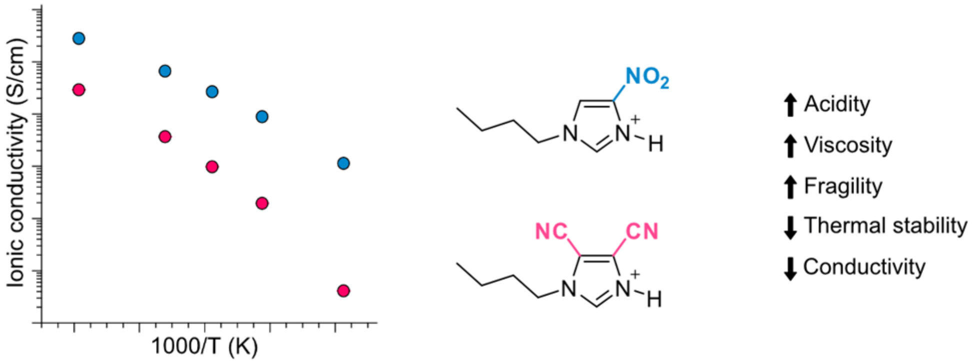
Acidic ionic liquids have proved to be useful in a variety of applications, such as for the transformation of lignocellulosic[1] and marine biomass,[2] catalysis,[3,] and as proton conductors in proton-exchange membrane fuel cells.[4] However, their synthesis is currently limited to a few strategies, with either acidic anions like HSO_4^- or $H_2PO_4^-$ or sulfonic acid moieties on the cation commonly being used as the Brønsted acidic sites. Here we present an alternative strategy, that is the functionalization of the cation with an electron-withdrawing group, showcased by the functionalization of imidazole with nitro- or cyano-groups. Combining the modified bases with HTFSI, two new room temperature Brønsted acidic protic ionic liquids were formed whereby the effect on acidity was studied by molecular modeling and spectroscopic methods. These modifications resulted in substantial changes in their physicochemical properties, including thermal stability, viscosity, ionic conductivity, and fragility. Here I will present the synthesis of these new acidic ionic liquids, and the difficulties that we faced during the process, as well as an overview of their properties.



Scheme or Figure 1: The imidazolium cation functionalized with nitro-(blue) and cyano-groups (pink) as well as the Arrhenius plot of ionic conductivity for the ionic liquids formed upon neutralization with HTFSI. An indication of changes in physicochemical properties is also given.

Acknowledgements
The support from the competence Centre Tech$_4$H$_2$ with all its partners as well as from the Area of Advanced Materials Science at Chalmers University of Technology is kindly acknowledged.

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Oral O_A2.3

Enthalpy of solvation of alkali metal salts in a protic ionic liquid: Effect of cation charge and size

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The current technology market demands the development of better energy storage systems. The efficiency and safety of current energy storage systems electrolytes still present shortcomings. These disadvantages create the need for new alternatives to current electrolytes, ionic liquids (ILs) and ILs doped with salts appear as promising alternatives to conventional electrolytes in energy fields. However, the behavior of the IL and the salt in this solution is still unknown. Interactions among the ions in electrolyte solutions are of high interest and will help in understanding the nature of the solvent. An experimental study of solution and solvation of mono- and divalent alkaline metal cations in the ethylammonium nitrate IL is reported.

The thermodynamics of solvation of alkali metal cations in a protic ionic liquid (PIL) ethylammonium nitrate (EAN) was analyzed through high-precision solution-reaction calorimetry to obtain the heat of solvation. Enthalpy of solvation for the exchange of Li$^+$ for M^{v+} in EAN solution was obtained according to the scheme in Figure 1. A close relation between the structure of the salts in the crystalline phase and its solvation enthalpy in the IL is reported. The analysis of the energetics and structure of solvation confirms the well-known water-like solvation properties of EAN. Furthermore, the results show that it is energetically more favorable to solvate smaller cations with higher valence.[1]

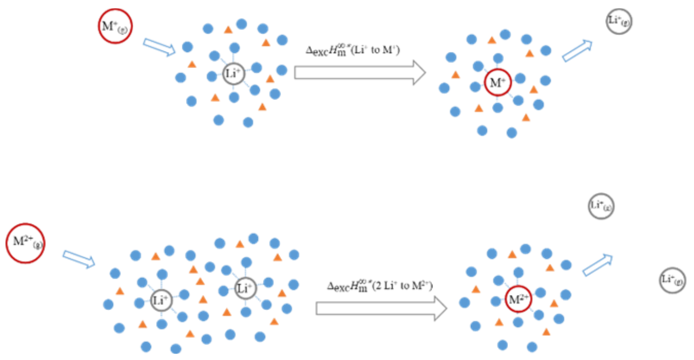

Figure 1: Exchange of M+ (top) or M2+ (bottom) for Li+ into a solution of Li+ in EAN(l).

Acknowledgements

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Oral O_A2.4

Hydrophobic low melting mixtures for biogas upgrading

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Biogas is a carbon-neutral energy source produced from the anaerobic digestion of organic waste. Its major components are methane (CH_4) and carbon dioxide (CO_2) with other impurities present in smaller quantities such as volatile organic compounds (VOCs). Upgrading of biogas to biomethane can be carried by pressure and temperature swing adsorption, liquid scrubbing, membrane separation, and cryogenic methods. However, in general, these methods involve large facilities with multi-step, energy-intensive processes that often incorporate hazardous materials [1]. Alternative low-energy purification processes would make biogas significantly more attractive as an energy source of methane for small-scale widespread application. Changing from multiple steps to a single technology for multiple contaminants would lead to a process that could be implemented on a much smaller geographical footprint ideal for smaller agricultural purposes.

Low melting mixtures (LMMs) offer alternatives to traditional biogas upgrade sorbents such as alkanolamines, however, lower CO_2 capacities coupled with high viscosities of physisorbant LMMs have limited their application scope. Here we report the study of hydrophobic LMMs based on trioctylphosphine oxide (TOPO) [2,3] that couple lower viscosities and a high tolerance to environmental water with high CO_2 capacities. Experiments carried out utilizing both single gasses and CO2/CH4 mixed gasses have shown that these materials have both comparable capacities and selectivity's for CO2 over CH4 when compared to fluorinated ILs (figure 1). Partition coefficients of VOCs in these same LMMs are also lower than that of many standard sorbents which could enable them to be implemented as a "one pot" upgrading method for biogas. These measured properties along with the relatively low viscosity make these materials seem like a viable new technology for biogas upgrading in the future.

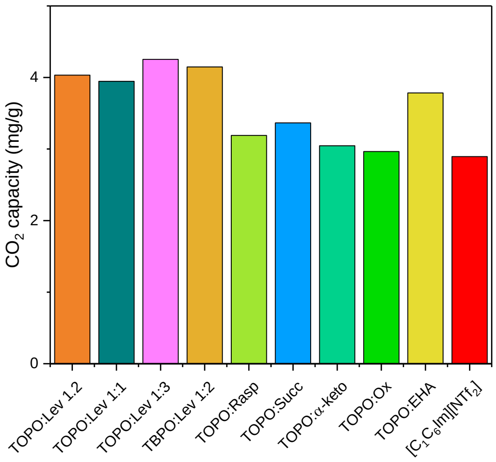

Figure 1: Screened CO_2 capacities of phosphine oxide-based LMMs compared to $[C_1C_6Im][NTf_2]$ at 1 bar and 308 K.

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Oral O_A2.5

Transport and mechanical properties of methacrylate-based ionogels designed for use as structural battery electrolyte

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Structural batteries have emerged as promising composites in the field of Li-ion batteries. They mainly consist of interpenetrated multifunctional components: (*i*) carbon fibers that enable lithium ions insertion and electrical conductivity and (*ii*) a polymer network providing the mechanical load transfer while confining (*iii*) the liquid electrolyte responsible for ion transport.[1-2] This unique design enables the storage of electrical energy within load-bearing components of a device or a part of a vehicle. One of the key challenges to achieving multifunctionality in structural batteries is the design of a suitable structural battery electrolyte (SBE), exhibiting simultaneous high ionic conductivity and mechanical stiffness.

To date, known SBEs consist of a methacrylate-based polymer network and organic solvent electrolyte. However, the use of an organic solvent is usually accompanied by safety issues. A promising approach to address this safety concern is their substitution with ionic liquids.

In this work, we focused on the design and investigation of phase-separated SBEs, where the liquid electrolyte phase consists of a protic imidazolium-based ionic liquid doped with a lithium salt. Raman spectroscopy is employed to study the nature of interactions established between cations and anions and the compositional homogeneity, whereas dielectric spectroscopy is used to get an insight into the local dynamics of the ions and to estimate the ionic conductivity of the systems. The phase behavior of the synthesized SBE is investigated by calorimetric methods that allow the identification of characteristic temperatures associated with crystallization (T_c), melting (T_m), and glass transition (T_g). The mechanical stability and the estimated storage modulus of the SBEs are determined using rheology methods. Our results suggest that SBEs composed of a phase-separated copolymer electrolyte, particularly a methacrylate-based polymer matrix and a protic imidazolium-based IL doped with LiTFSI, have the potential to serve as structural electrolytes in weightless structural batteries of the future.

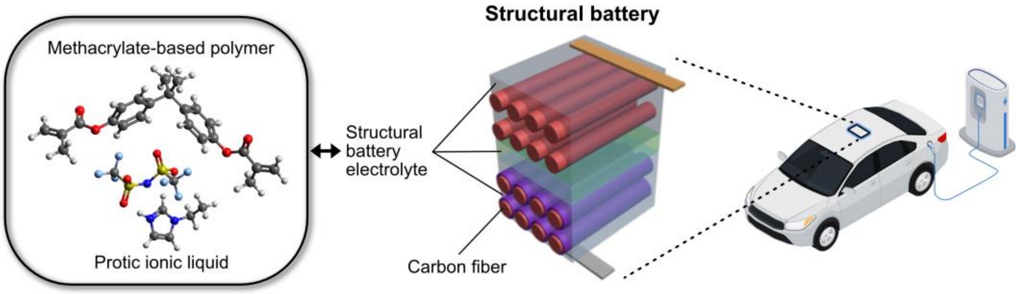

Figure 1: Illustration of the structural battery concept and its components.[3]

Acknowledgements
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Oral O_A2.6

Strange behavior of the transport properties of ethyl ammonium nitrate (EAN) binary mixtures with organic solvents

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As it is well known, mixing ionic liquids with organic solvents increases electrical conductivity and decreases viscosity, in some cases by more than one order of magnitude[1]. Thus, water is the solvent that generates the much higher conductivity increase[2], but other ones, including alcohols[3], dimethyl sulfoxide (DMSO), γ-butyrolactone (GBL), acetonitrile (AN), carbonates..., also increase conductivity[4]. This behavior, that seemed to be universal, is due to the fact that solvent molecules break the pseudo-lattice formed by anions and cations in the pure IL[5], liberating fixed anions to hoop to a neighbor hole, and thus increasing hopping frequency and consequently conductivity, while decreasing viscosity. That increase reaches a maximum value for conductivity at the molar percentage of solvent usually higher than 80 %.

In contrast, we have found that ethyl ammonium nitrate (EAN), the first synthesized IL, does not increase its conductivity when mixed with many solvents, although the viscosity of the mixture is lower than that of EAN. Thus, we present novel measurements of the electrical conductivity and dynamic viscosity of binary mixtures of EAN with methanol, propanol, propanediol, GBL, or DMSO, which are compared with those containing AN[6] or nitromethane[7] from the literature. For some of those solvents, its addition to EAN decreases conductivity respecting its value when pure for all solvent concentrations, while decreasing viscosity (except that with propanediol, which presents a minimum at equimolar concentration). In Figure 1 we plot the electrical conductivity and the dynamic viscosity of 8 different EAN binary mixtures at 25 ºC in all ranges of concentrations. A theoretical discussion will be given to explain these results.

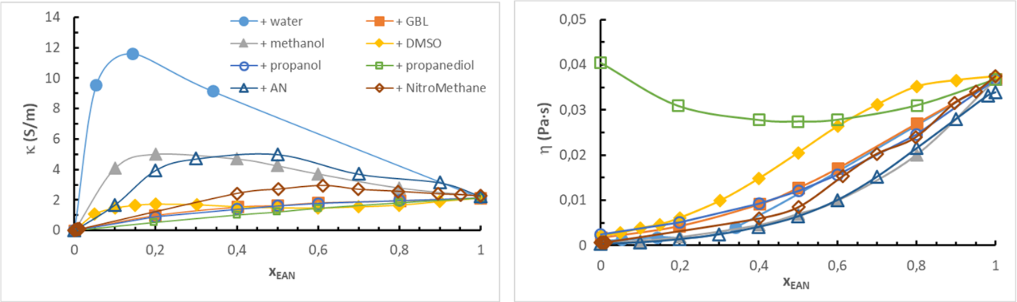

Figure 1: Electrical conductivity and dynamic viscosity at 25 ºC and 1 atm. of binary mixtures of EAN with eight different solvents in all ranges of concentrations. Data for mixtures with AN[6] and nitromethane[7] were taken from the literature.

Acknowledgements
To our technician M.R. Cabanas for his excellent measurements.

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Oral O_A3.1*

Luminescent ionic materials for use as tools in biology and for physics to detect Neutron radiation

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Light and associated phenomena, such as luminescence, have proven to be powerful tools with great sensitivity for exploring the infinitely small, physical processes (energy and electron transfer, polarity, pressure, etc.) and physicochemical processes (concentration, visualization, localization of species, ...). In this context, molecular salts, in particular those based on imidazolium units, have attracted the attention of the scientific community due to their original properties and structural versatility. In this presentation, we will describe the synthesis and design of new families of highly luminescent materials in the three states of matter (liquid, liquid crystal, crystalline) in a minimum of steps and without rare, expensive, and strategic chemical elements.[1-2] Once functionalized with fluorophores, these saline materials; where the amphipathic character can be adjusted; we will present that these platforms are efficient and highly bioavailable for DNA detection and cell imaging, opening the way to theranostics (therapy and diagnosis).[3] The crystal structures obtained by R-X will be used to shed light on the photo-physical properties of these materials. Finally, we will present the shaping of some luminescent imidazolium into centimetric photonic single crystals and their properties to detect neutrons of any energy. In the near future, these luminescent salts could replace helium(3) in detector the low energy neutrons (see Figure 1).

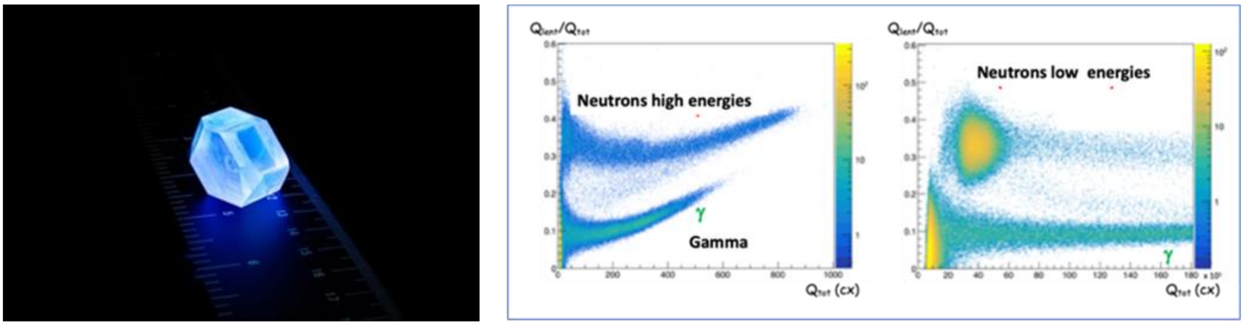

Figure 1: luminescent centimetric single crystal (left), fast and slow neutron detection (right).

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* highlighted talk

Oral O_A3.2

Switchable adhesive films loaded with a deep eutectic solvent-photosensitizer formulation for the treatment of drug-resistant skin infections

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Antimicrobial resistance is a major threat to global health.[1] The emergence of multi-drug resistant pathogens like methicillin-resistant *Staphylococcus aureus* (MRSA) has narrowed the number of effective treatment options to tackle this demanding challenge.[2,3] Antimicrobial photodynamic therapy (aPDT) is a potent tool to surpass the rise of antimicrobial resistance; still, the effective topical administration of photosensitizers remains a difficult task not only due to the low-water solubility of many of these but also their difficult incorporation in delivery systems.[4] Hydrogels and films benefit from the ability to act both as bandage material and delivery systems, while providing a moist healing environment, and can be seen as promising options for the incorporation of these compounds.[5,6] However, their application is narrowed by their limited water absorption capacity and gel strength.[7] In this study, we explored pullulan, a biocompatible biopolymer, for the development of films with a switchable character (from a solid film to an adhesive hydrogel) for application in aPDT. The switchable behavior was achieved by the incorporation of a betaine-based deep eutectic solvent (DES) formulation containing curcumin (used as a model photosensitizer) into the pullulan films. This combination resulted in transparent films and allowed tuning the films' skin moisture absorption ability, and therefore they switch into an adhesive hydrogel when topically applied, being capable of delivering the photosensitizer to the infected skin area. This modification, enabled to improve in the extensibility of pullulan-based films (elongation at break up to 338.2%) compared to its counterparts (6.08%), at 54% of relative humidity. The corresponding hydrogels with the DES present a 4-fold higher adhesiveness than commercial hydrogels used for topical application. These non-cytotoxic adhesives have shown to be effective in the inactivation of multi-drug resistant strains, such as MRSA (~5 log reduction), down to the detection limit of the method, in ex vivo skin samples. Overall, these materials are promising for aPDT in the treatment of resistant skin infections, while being easily removed from the skin with water, and being gentle to the sensitized skin area.

Acknowledgements

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Oral O_A3.3

Innovative oxalatoborate-based ionic liquids for electrochemical applications: greener synthesis and combined experimental-theoretical characterization

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Lithium-ion batteries are a vital energy storage system for portable electronic devices. To improve their energy density the use of new cathode materials capable of working at higher potentials (5V) is a crucial request. However, the commonly employed electrolytes based on organic solvents are not stable at such high potentials. Ionic liquids (ILs) have been proposed as additives to them to improve their thermal and electrochemical stabilities. Despite this, the application of ILs on an industrial scale is hindered by their high cost and environmentally unfriendliness of synthesis[1]. In this study, four ILs containing oxalatoborate anions – known to form a protective layer on the cathode surface[2] - have been synthesized: specifically, *N*-ethoxyethyl-*N*-methylpiperidinium bis(oxalato)borate ($PIP_{1,2O2}BOB$), *N*-ethoxyethyl-*N*-methylpiperidinium difluoro(oxalato)borate ($PIP_{1,2O2}DFOB$), *N*-propyl-*N*-methylpiperidinium bis(oxalato)borate ($PIP_{1,3}BOB$) and *N*-propyl-*N*-methylpiperidinium difluoro(oxalato)borate ($PIP_{1,3}DFOB$) (Figure 1a). To address the problem of ILs synthesis, a new synthesis method, involving mostly water as solvent, is proposed. The thermal behavior of the synthesized ILs has been studied by differential scanning calorimetry, confirming the presence of oxygen in the lateral chain of the cation totally suppresses the crystallization. Furthermore, $PIP_{1,2O2}DFOB$ shows a lower glass transition temperature than $PIP_{1,2O2}BOB$ (Figure 1b). To explain these observations a computational approach has been used, combining both molecular dynamics (MD) simulations and density functional theory (DFT) calculations. The simulations highlight an increase in the degree of freedom of the lateral chain of the cation when oxygen is present. Comparing instead $PIP_{1,2O2}DFOB$ and $PIP_{1,2O2}BOB$, it is observed a notable anion-anion interaction in the former, ascribable to the charge-delocalization induced by the fluorine atoms, which causes the formation of a relatively positive charge on the boron atom. The stronger anion-anion interaction is well correlated with a weaker anion-cation interaction and reduced segregation, which hinder the glass transition of $PIP_{1,2O2}DFOB$. Finally, preliminary results regarding the use of these ILs as additives to the electrolyte in high-voltage lithium-ion batteries will also be reported.

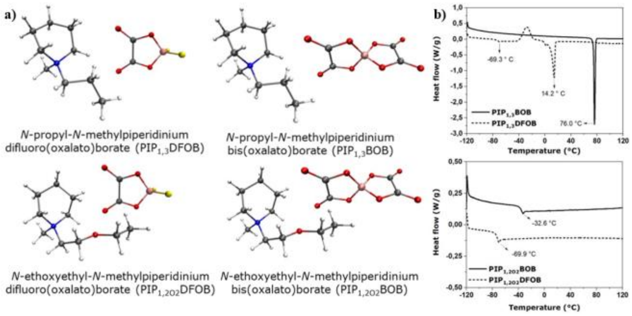

Figure 1: a) The four synthesized ILs. b) Thermal behavior of the four ILs.

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The present work is developed in the framework of a doctoral position funded by MUR (DM 1061/2021, PON 2014-2020).

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Oral O_A3.4

Selective precipitation of gold from an aqua regia leachate of e-waste using a quaternary ammonium ionic liquid

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E-waste is a source of valuable base and precious metals, making its exploration a key step in reducing the environmental impact of modern electronics and establishing a circular market for critical and rare materials. Gold is one such material present in e-waste in greater concentrations than the primary ores from which it is mined, providing a strong justification for its recycling. In this work, the use of a quaternary ammonium ionic liquid (IL) as a precipitating agent for the selective recovery of gold from an aqua regia leachate of printed circuit boards was investigated. A suitable IL was selected considering the cation's apolar volume and geometry as well as counter-anion selection. The precipitation was optimized in regard to time, the IL to Au molar ratio, temperature, and aqua regia dilution. IL to gold ratio and dilution were found to be the key factors driving the precipitation. Optimized conditions were applied to a real leachate sample, resulting in a gold salt with a metallic content of over 90% gold and a yield of 64%. The same IL was used to establish an acidic aqueous biphasic system for the recovery of Au for higher acid concentration, demonstrating two possible avenues of Au recovery depending on the leachate condition. The technique presented herein allows for the selective separation of gold using relatively simple materials and techniques with a lower reagent use than what is required with other gold separation techniques employing ILs.[1]

Acknowledgements

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Oral O_A3.5

Combination of Ionic liquids and polymers for designing new generation of ionomers

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In polymer science, developing pathways to design and tune the properties of existing materials is a major challenge. The main routes to modify such properties involve either the physical structuration provided from phase separation or the formulation with additives generating additional physical or chemical interactions with the polymer. The use of ionic liquids (ILs) represents a novel route to modify the structure and properties of polymers. Ionic liquids have already shown promising capabilities to generate a nanoscale structuration in polar polymers such as fluorinated copolymers[1] or bio-based polymers[2] in which a tunable effect on the crystallization behavior, on the resulting morphology, and the crystalline phase structure have been reported. LIonomer is a new generation of ionomer designed by combining polypropylene grafted maleic anhydride (PPgMA) and ionic liquids[3]. The short-range interactions limit the movement ability of polypropylene chains and lead to an increase in melting viscosity. This continuum of interactions COO-/cation is all the more promoted than cation is less sterically hindered and can ionically interact with carboxylic anions. The morphology in relation to mechanical property was systematically investigated by exploring the effect of COO- content, IL concentration, and the nature of ionic liquid. The ability of ionic liquids to change the morphology and the rheology paves the way for processing new materials like films or foams. This talk will illustrate the dual role of ionic liquids as structuring agents either i) through phase separation phenomena or ii) via the establishment of short-range ionic interactions in LIonomers.

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Oral O_A3.6

Ionic liquids as healing agents for polymer-based materials

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Improving properties of epoxy polymer networks which are used as high-performance materials, will be detailed in this lecture. The strategy deals with microencapsulated ionic liquids (ILs) dispersed in such polymers. Based on this concept, different microcapsules were synthesized. Meanwhile, different combinations of ionic liquids and epoxy show the various roles of ionic liquids for different purposes in epoxy composite materials.
First, phosphonium ionic liquid (tetradecyl(trihexyl)phosphonium bis-(2,4,4-trimethylpentyl)phosphinate, IL 104) was encapsulated in silica microcapsules from the water-based ionic liquid emulsion and using a sol-gel process. IL@SiO_2) microcapsules have good thermal stability and high strength due to the silica shell, *i.e.* these ones could act as filler and IL reservoirs. In fact, IL@SiO_2 microcapsules can improve the fracture toughness and mechanical properties without damaging the thermal properties of epoxy-amine matrices and bring self-healing functionality. In the second part, the conventional epoxy monomer was encapsulated by a poly(urea formaldehyde) shell to obtain EP@UF microcapsules combined with ILs in order to bring self-healing ability to epoxy polymer networks In order to endow this self-healing behavior for a broader range of materials, a different phosphonium ionic liquid, *i.e.* IL169, having a high thermal stability and able to initiate epoxy monomer polymerization at high temperature, was added in the bulk of the epoxy matrix in which EP@PUFs are added. As the epoxy monomer is released from broken EP@PUF microcapsules during fracture propagation, this one could react with IL169 to heal the cracks. The addition of 10wt% of EP@PUF microcapsules into the epoxy matrices can bring a self-healing ability to the resulting materials. Thus, this study has put forward that using IL and epoxy-containing microcapsules allows to achieve self-healing for epoxy including for high-temperature cured epoxy systems.
In the third part, an ionic liquid epoxy monomer (ILEM) was synthesized as a new core material of microcapsules having a poly(melamine-formaldehyde) (PMF) shell (ILEM@PMF). It was shown that ILEM@PMF microcapsules are promising additives to allow self-healing. In fact, ILEM@PMF microcapsules were added in different epoxy-amine networks and demonstrated their performances for self-healing purposes.

Acknowledgements
The authors thank the China Scientific Council for supporting this research via Dr. Shi Ting's PhD grant.

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Oral O_A4.1*

Sustainable pathways to develop porous ionic liquids from common materials

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We report innovative pathways for the creation of porous ionic liquids with a primary focus on reducing environmental impact. Although recent literature highlights the employment of surface deposition techniques for the production of stable porous suspensions,[1] we propose the fabrication of porous ionic liquids utilizing readily accessible materials. We present evidence that suspensions of porous solids show permanent porosity and maintain stability when incorporated into eutectic mixtures, highlighting their potential in the preparation of porous ionic liquids.[2]

We also show that porous suspensions exhibit large electrochemical windows, analogous to their precursor pure ionic liquids, making them well-suited for environmentally friendly electrochemical reactions, particularly those involving gases as reactants. Furthermore, their capacity as gas-enriched media suggests promising prospects in sustainable biomedical and pharmaceutical applications provided non-toxic, biocompatible ionic liquids and porous solids are used.

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* highlighted talk

Oral O_A4.2

Encapsulated amino acid-based ionic liquid for CO_2 separation membranes

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Energy-efficient separation of gases has attracted intensive attention in research and industry. Among several approaches proposed for improving carbon dioxide (CO2) absorption for suitable industrial implementation, chemical absorption using amino-acid-based ionic liquids (AA-ILs) has attracted special interest because of the great affinity of the amino acid anion or cations in ionic liquids with CO2 finally contributing to high adsorption selectivity.[1] Unfortunately, the use of AA-ILs alone presents several disadvantages that need to be addressed before their scape-up and ultimately industrial applications, as their high viscosity and regeneration energy demand, lead to high operational costs and make the process unfeasible. Membrane-based gas separation technology through gas-liquid membrane contactors has been reported as one of the alternative methods to efficiently and economically separate carbon dioxide from the flue gas of fossil fuel combustion. Separating gases by membranes is more effective and energy-saving with lower production and equipment costs than traditional gas separation methods, such as adsorption or distillation. However, most polymeric membranes suffer from the trade-off between mass transport rates and separation efficiency. Polymeric membranes show high gas permeation flux but low selectivity, and vice versa. Moreover, the membrane gas-liquid contractors based on MMMs themselves do not provide any selectivity properties but only act as a barrier for separating the liquid phase from the gas phase and provide a large gas-liquid contact area for mass transfer. To overcome such weakness, mixed matrix membranes (MMMs) can provide promising potentials in high-performance gas separation, by combining the high separation properties of the inorganic filler with the low cost and flexibility of the polymers.[2] For filler selection, carbon sub-micro carbon capsules are promising adsorbents for gas storage and separation due to their high surface area and porosity, adjustable pore sizes, and controllable surface functionality. The use of absorbents on a membrane contactor improves the separation selectivity and the mass transfer driving force, allowing high membrane fluxes and low gas outlet CO2 concentration, highlighting the potential of the technology to take advantage of the green solvents discussed here.[3,4]

This work focuses on developing and characterizing novel encapsulated AA-ILs-based MMMs for gas separation with high permeability and selectivity and good thermal and chemical stability. The studies include fabrication and optimization of dense membranes and spinning coats of hollow fiber membranes with encapsulated amino acid-based ionic liquids, designing MMMs with goof filler/include interaction and good interfacial morphology, as well as evaluating the permeation and selectivity performance of all the prepared membranes for gas capture and separation.

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Oral O_A4.3

Novel technology for indoor air quality: ionic liquids in carbonaceous sub-microcapsules into polymeric hollow fiber membranes

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According to the World Health Organization (WHO), around 2.4 billion people are exposed to dangerous household air pollution levels[1], and more than 3,2 million deaths worldwide were related to domestic air pollution in 2022[2]. Furthermore, the National Institute for Occupational Safety and Health (NIOSH) estimates that deaths from work-related respiratory diseases account for about 70% of all occupational disease mortality[3]. Indoor air pollution is caused by several types of contaminants, including inorganic gases (such as CO, CO_2, O_3, NO_x, and SO_x), particulate matter (PM_x), volatile organic compounds (VOCs), and emerging pollutants. Various technologies could be foreseeable to tackle the problem, such as filtration, adsorption, ionization, ultraviolet disinfection, and UV-photocatalytic oxidation. Nonetheless, they are limited to target pollutants, can generate more harmful degradation products than their precursors, have energy- and size-demanding setups, dispose of hazardous residues to the environment, and stand unfeasible. Innovative technology and emerging self-claimed green solvents have been proposed, but none has reached a development level fit for deployment at an industrial level. Among those, ionic liquids (ILs) have attracted special interest due to their high capacity and selectivity. However, using ILs alone presents significant drawbacks mainly related to their transport properties. To overcome this limitation, we proposed encapsulating ILs in carbon sub-microcapsules (ENILs) to achieve virtually instantaneous absorption kinetics. Nonetheless, the size and weight of ENILs inhibit their direct implementation, hindering their direct application in conventional separation units. But, combining encapsulation of the ILs and its subsequent support in membrane matrices allows taking advantage of the green solvent absorption capacity and selectivity with the modularity, compactness, and easy scalability of membrane technology, envisioning a sustainable separation technology. Here, we propose the development of ENILs supported in membranes as a new technology to tackle the problem mentioned above. The polymeric coating thin layer containing ENILs supported on membrane matrices makes the absorption kinetics faster due to improved gas transport properties related to the higher surface area, tunable permeability, and selectivity of ILs while removing the need for regeneration steps and units. The hollow fibers with ENILs show higher permeation and selectivity than other technologies and present compactness necessary for easy allocation to different sites, making this hybrid material promising for absorbing contaminants in indoor air environments.

Acknowledgments

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Oral O_A4.4

Tuning of the CO_2 absorption by reactive phosphonium-carboxylate ionic liquids (ILs)

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Imidazolium acetate ionic liquids (ILs) are known to chemically react with CO_2[1, 2] leading to improved low-pressure gas capacities compared to non-reactive ILs. A similar CO_2 absorption mechanism has been recently identified for tetrabutylphosphonium ILs with linear carboxylate as counteranions. The acidic proton of the α-carbon (C_α) of the phosphonium is abstracted by the negatively charged oxygen atom of the carboxylate leading to the formation of a ylide which is able to react with CO_2.[3,4]
A series of phosphonium carboxylate ILs, with different types of substituents linked to the anion, has been synthesized. Their physico-chemical properties as well as their CO_2 absorption capacities have been thoroughly explored by experimental and *in silico* studies.
The design of a new family of ILs permits to control of their reactivity towards CO_2 to reach either large or very low capture capacities. CO_2 absorption is reversible under mild conditions even with the more reactive phosphonium carboxylate ILs which represents a major advantage compared to other absorbents. *Ab initio* calculations provided valuable insights and enhanced comprehension of the energetic aspects of the chemical absorption reaction, while molecular dynamic simulations helped to understand the physical absorption process and its influence on the microscopic structures of the ILs.
Surprisingly, CO_2 absorption in the phosphonium carboxylate ILs led to an increase in the self-diffusion coefficients of both the cation and the anion of the IL revealing that the dynamic properties are improved upon the capture of this acidic gas. This result overcomes the dramatic increase of viscosity that many ILs suffer from upon CO_2 absorption.

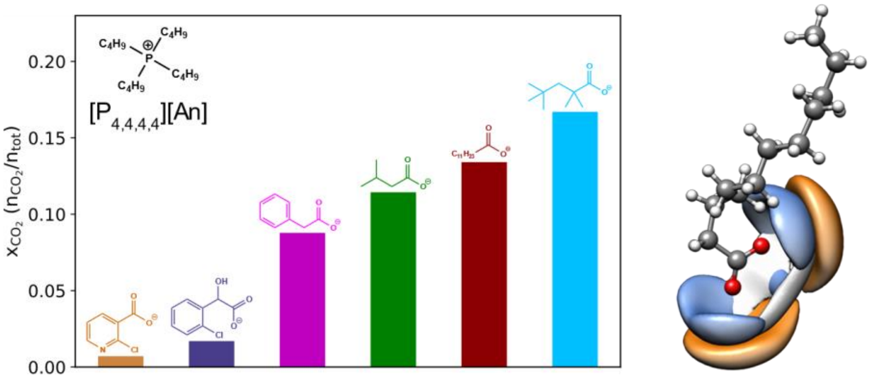

Figure 1: (Left) CO_2 absorption capacity of a few ILs under study at 1.0 bar and 343.15 K. (Right) The SDFs of P^+ (in orange), of the acidic protons H_α (in white) and of C_{CO2} (in blue) around the O_{COO-} of the $[C11COO]^-$ anion in $[P_{4,4,4,4}][C_{11}COO]$ at 343 K. Isodensity contours at 11.6, 14.1 and 0.8 times the average density around the central anion, respectively.

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Oral A4.5

New setup for the measurement of the electrical conductivity of ionic fluids: exploring the nanostructuration in ionic liquids

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This work presents the development and test of a high-precision apparatus, based on a Precision LCR meter (20 Hz - 500 kHz) from Keysight (model E4980AL), for the measurement of electrical conductivity of ionic fluids. Two measuring cells were specially designed and developed: I) a dip-in cell based on an adapted Metrohm electrical conductivity cell (model MTO-6.0908.110), a sample glass vessel (7 mL), and a customized holder designed to insure the vacuum, gas-tight, and chemical inertia of the sample container; II) a coin cell with flow-type injection (sample volume of 250 µL) and switchable electrode disks. The temperature control is ensured by a customized air bath thermal chamber based on Peltier heat and cooling that is prepared to adapt both cells. A dedicated software application was developed for data acquisition and analysis as well as to configure the setup for the measurements. The results are evaluated in terms of resistance, reactance, impedance, and phase angle as functions of frequency. The resistance of the solution was derived from the extrapolation to infinite frequency in order to correct the polarization effects[1].

The Vogel-Fulcher-Tammann (VTF) equation was used to fit the conductivity – temperature data, $\sigma(T)$ as well as to derive the pre-exponential coefficient and energy barrier. The effect of the increase of the alkyl chain on the electrical conductivity of imidazolium ionic liquids was studied $[C_nC_1im][NTf_2]$, $[C_nC_1im][OTf]$, $[C_nC_1im][PF_6]$, $[C_nC_1im][BF_4]$. For all series, the increase of the alkyl chain highlights the presence of two regimes which is likely associated with the intensification of the nanostructuration of the ionic liquids as the nonpolar regions become larger [2,3]. The comparison between the different anionic series provides insight into the impact of the shape and nature of the anion on the electrical conductivity of the ILs, which is mainly reflected in the cohesive energy (energy barrier) and temperature dependence. To further evaluate this effect this study was extended to other 1-butyl-3-methylimidazolium based ILs with different anions ($[C_4C_1im][Ac]$, $[C_4C_1im][TFA]$, $[C_4C_1im][DCA]$, $[C_4C_1im][FAP]$, $[C_4C_1im][FSI]$, $[C_4C_1im][BETI]$).

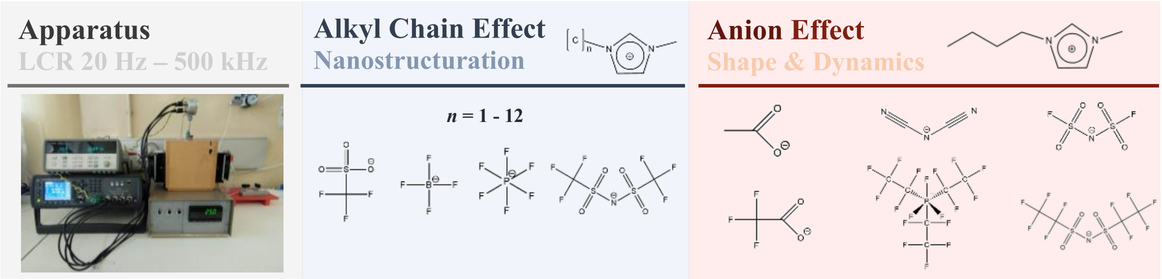

Figure 1: Image of apparatus and structural representation of the studied imidazolium ionic liquids.

Acknowledgements

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Oral O_A5.1*

Recovering valuable and critical metals from e-waste through innovative hydrometallurgical systems

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The rapid expansion of the electronics industry has led to a surge in global metal demand, contributing significantly to metal scarcity. Despite reaching historic mining rates for most metals, the average ore quality has declined over the past century. The dearth of mineable deposits, coupled with their concentration in a few countries, has disrupted the balance between supply and demand, rendering current practices unsustainable.

E-waste has emerged as the fastest-growing waste stream worldwide, posing a substantial challenge in waste management due to its value, heterogeneity, and toxicity. Certain e-waste streams contain higher concentrations of valuable metals than primary ores, presenting an opportunity as a secondary source. However, conventional hydrometallurgical processes for e-waste recycling prove inefficient, requiring aggressive digestion methods, generating significant waste streams, and utilizing flammable, volatile, and toxic solvents. Consequently, there is an urgent need for more efficient and sustainable alternatives.

Liquid-liquid extraction processes using hydrophilic ionic liquids (ILs) and hydrophobic eutectic solvents (HES) have demonstrated promising outcomes in the separation and recovery of metals from solutions spanning a wide concentration range. The versatile and tunable nature of these alternative solvents has significantly expanded the field of metal processing in both aqueous and non-aqueous media. In recent years, our research has been dedicated to the development, characterization, and application of these systems as integrated hydrometallurgical processes, encompassing the entire spectrum from leaching to metal recovery. Valuable and critical metals, such as transition metals, rare earth elements, platinum group metals, and gold, have been successfully recycled from e-waste streams, including nickel-metal hydride batteries, Li-ion batteries, CPUs, and spent automotive catalytic converters.[1-4] The dynamic behavior of these systems enables the development of innovative and cost-effective strategies for metal recovery from secondary sources, contributing to more sustainable and efficient practices in metals recycling.

Acknowledgements

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* highlighted talk

Oral O_A5.2

Design for disassembly of composites and thermoset by using cleavable ionic liquid monomers as molecular building blocks

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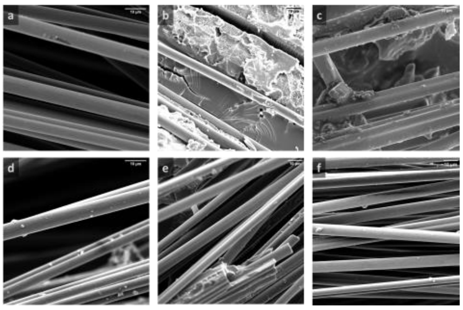
Nowadays, advanced polymeric materials are at the forefront of tackling global challenges such as environmental issues while pursuing research into high-performance materials. Thus, the development of new synthetic methods is critical for designing innovative polymer materials and proposing sustainable solutions to meet the requirements of the circular economy, *i.e.* to be durable, reusable, and recyclable. Scientists must thus propose through a '*Functional materials by design*' approach to develop molecular brick platforms allowing the integration at the molecular scale of the required functions in the initial synthesis steps. Simultaneously, scientists must think about the End-of-Life of these functional materials by the concept of '*design to recycle*', mainly by chemical recycling to be reused in a closed-loop supply chain. Very recently, the pioneering work of our research group developed an efficient route to design polyfunctional imidazolium ILs bearing two, three, or four glycidyl groups without the use of toxic and carcinogenic compounds such as bisphenol A and epichlorohydrin[1-4]. These new IL-based monomers have been designed at a multi-grams scale (up to 200 grams) and they have been incorporated as a molecular brick platform into conventional epoxy-amine networks in order to tailor the physical properties as well as the end-of-life of the resulting networks. Thus, all the networks designed in this work presented high thermal stability (>350 °C), with higher Tg included between 180 and 230 °C combined with hydrophobic behavior. Most importantly, the use of epoxidized ILs led to the development of degradable networks under mild conditions (4.5 h) and allowed to recovery of the carbon fibers (see **Figure 1**).



Scheme or Figure 1: Carbon Fibers recovery after solvolysis process.

Acknowledgements
This work was carried out with the financial support of IDEXLYON (ANR-16-IDEX-0005).

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Oral O_A5.3

The challenge of recovering superbase ionic liquids from aqueous solution

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There is a global trend toward promoting environmental awareness and social responsibility in the textile industry's supply chain, focusing on green and sustainable approaches. Cellulose is a valuable renewable resource with unique structural characteristics and is widely used in the textile industry. However, the solvent systems used to produce artificial cellulose fibers (rayon, lyocell, acetate) often rely on harmful chemicals, despite the high performance of the resulting fibers. To address this issue, green solvents such as ionic liquids (IL) are considered a sustainable alternative. While many ILs have been reported in the literature to have the potential to dissolve cellulose, only a small portion possess the necessary characteristics to produce regenerated cellulose fibers. Recently 5-methyl-1,5,7-triaza-bicyclo[4.3.0]non-6-eniumacetate ([mTBNH][OAc]) has been identified as a promising solvent.[1] Typically, after fiber spinning, the spinning bath solution undergoes several purification steps to remove particulates and precipitates. From then onwards, the water is removed to restore IL's solvating power. Several separation methods are available for removing water from ILs, such as adsorption, thermal evaporation, membrane processes, two-phase aqueous extraction, and others. However, only a few of these methods are economically viable and can be adopted in the Ioncell process. Thus, this work investigated the recovery and purification of ILs from the spinning bath using different approaches (membrane filtration, aqueous two-phase system, and liquid-liquid extraction). Firstly, aiming to gather knowledge to recover and recycle superbase-ILs, the physicochemical characterization of the binary systems water + [mTBNH][OAc] was obtained. The physicochemical characterization results show a formation of complexes or special organization between water and IL molecules, revealing a strong interaction between the ILs and water. Using membrane filtration (nanofiltration and reverse osmosis) allowed a three-fold ionic liquid concentration for a maximum concentration of 14 wt % of the ionic liquid. From these results, it is possible to remark that membrane filtration can hardly be used as a single step for separating IL from water because the maximum IL concentration obtained (14 wt %) is lower than the desired (80 wt %) for IL reuse. In the two-phase aqueous extraction (ATPE), the use of potassium carbonate (K2CO3) allowed concentrating of the IL present in the stirring bath (xIL = 20.0 wt%), obtaining an IL-rich-phase (xIL = 64.0 wt%) and with a small amount of salt (xK2CO3 = 3.6 wt%). The results demonstrate that the ATPE separation method can be considered one of the alternative ways to remove water. The liquid-liquid extraction of superbase ILs with hydrophobic allowed an efficiency of 70% and 37% using dichloromethane and butanol as extractants, respectively. However, it was found that dichloromethane reacts with the IL anion, acetate, leading to the production of methylene diacetate and chloromethyl acetate.

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Oral O_A5.4

Emerging photoswitchable materials based on ionic liquids

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While the first documented utilization of ionic liquids (ILs) dates back to the previous century, it was only in the last two decades that the ILs field has experienced exponential growth in publications. And just when it seemed that scientific interest in ILs might start to decrease, a resurgence has occurred, driven by the development of new generations of ILs that are less toxic and biodegradable, expanding the applications of ILs beyond the realm of biology to various other domains. Our research team has contributed to this trend[1,2] and also developed magnetic ILs with low toxicity.

ILs are desirable materials not only due to their adaptable properties but also because they can be easily integrated into other materials, particularly polymers, enabling the creation of smart materials[3,4]. For instance, photo-responsive properties can be integrated into ILs through the incorporation of photochromic moieties into either cations or anions and further attached to the final polymer[4].

Gelatin, a cost-effective, water-soluble form of denatured collagen with inherent biocompatibility, has some limitations in terms of its suitability as a hydrogel material due to its inadequate mechanical properties. To enhance its applicability, gelatin is often combined with other polymers, such as alginate, chitosan, or hyaluronic acid, to bolster the structural integrity of the resulting hydrogel. Alternatively, derivatization methods, typically involving the addition of methacrylate groups to the amine-containing side chains of gelatin, are employed to create photopolymerizable hydrogels[5].

In this work, we describe a new generation of materials that combines the chemical versatility of ILs with the morphological flexibility of biopolymers with photochromic properties.

Acknowledgements

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Oral O_B1.1*

Chirality transfer and enantiomeric recognition in chiral ionic liquids

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Chiral ionic liquids (CILs) exhibit potential utility both as solvents in asymmetric synthesis and as selectors in the enantiomeric recognition of small molecules. The effective use of CILs in these applications requires a comprehensive understanding of the dynamic phenomena and molecular architecture. Due to their sensitivity to molecular conformations and conformational changes, chiroptical spectroscopy methods such as vibrational circular dichroism (VCD) offer unique opportunities to study the structure of CILs and in particular the occurrence of chirality transfer effects.

In this talk, we present the combined results of two studies on CILs. The first study[1,2] involves ab initio molecular dynamics (AIMD) simulations applied to the CIL 1-ethyl-3-methylimidazolium L-alaninate ([C_2C_1Im][L-ala]), elucidating the transfer of chirality from the anionic to the cationic moiety, thereby inducing a perturbation within the conformational landscape of the cation. Capitalizing on these findings, we investigate two prototypical molecular arrangements involving (R)- or (S)-butan-2-ol solutes within [C_2C_1Im][L-ala] to uncover chiral recognition mechanisms. VCD spectra and structural analyses reveal discriminative interactions between the CIL and the enantiomers of butan-2-ol.

While the focus of the first study is on the chiral induction in the IL cations, the second investigation[3] examines plausible effects on the anionic components. Using AIMD simulations of (R)-propylene oxide dissolved in the achiral IL 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([C_2C_1Im][NTf_2])[4], we observe a preferential transfer of chirality from propylene oxide to the anion, monitored by VCD spectroscopy. These results are remarkable as the cation is less involved in the chirality transfer, but the conformational landscape of the anion is strongly influenced by the chirality of the dissolved molecule.

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Oral O_B1.2

Effect of DMSO concentration in the bulk and interfacial molecular dynamics of protic and aprotic ionic liquid-lithium salt mixture electrolytes

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Finding stable electrolytes for novel battery chemistries is crucial for the development of the ongoing energy transition. Mixture electrolytes based on ionic liquids with lithium salts and a solvent stand as a promising option for the next generation of lithium batteries.[1,2] This contribution summarizes the differences found between ternary mixtures of a protic (ethylammonium nitrate) and an aprotic (1-Ethyl-3-methylimidazolium tetrafluoroborate) ionic liquid, lithium salts with common anion and dimethyl sulfoxide as a solvent. Several properties were studied in the whole solvent concentration range via Molecular Dynamics simulations of bulk and interfacial systems, such as conductivity, coordination numbers, densities, and orientation profiles.[3,4]

Acknowledgements
The financial support of the Spanish Ministry of Science and Innovation (PID2021-126148NA-I00 funded by MCIN/AEI/10.13039/501100011033/FEDER, UE) is gratefully acknowledged. H. M. C. thanks the USC for his “Convocatoria de Recualificación do Sistema Universitario Español-Margarita Salas” postdoctoral grant under the “Plan de Recuperación Transformación” program funded by the Spanish Ministry of Universities with European Union’s NextGenerationEU funds. This work was supported by the Fundacão para a Ciência e Tecnologia (FCT) funded by national funds through the FCT/MCTES (PIDDAC)) to CIQUP, Faculty of Science, University of Porto (Project UIDB/00081/2020), IMS-Institute of Molecular Sciences (LA/P/0056/2020). T. M. M. acknowledges her contract funded by the pilot program of the USC for the recruitment of distinguished research personnel—call 2021 under the agreement between the USC and the Santander Bank for 2021–2024. M. O. L. and P. M. C. wish to thank the Xunta de Galicia for their “Axudas de apoio á etapa predoutoral” grants (ED481A 2022/236 and ED481A 2022/045).

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Oral O_B1.3

Elucidating ion-pairing in ionic liquids and their salt mixtures from theoretical calculations

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In the energy storage field,[1,2] the IL mass and charge transport combined with its electrochemical stability are the key points to developing a high-performance IL-based electrolyte. Therefore, we have used theoretical and simulation methods to investigate the ion dynamics in IL-based systems, focusing on understanding the structure effects and ion-pairing in the transport properties. To reach our goals, we first carried out a series of molecular dynamics (MDs) simulations to characterize the performance of different force field sets in the transport properties description, and also, evaluated the analysis protocols to compute reliable quantities from the MD trajectories. With that, we observe that it is possible to obtain reasonable results for transport properties, i.e., with satisfactory deviations from experimental data, using a nonpolarizable force field with 0.8 scaling charge. However, polarizable force fields present a more accurate reproduction of the transport properties and densities of the experimental data, which also comes with higher computational costs. Then, when choosing a force field, it is necessary to consider the trade-off between model accuracy and computation costs. Although simple force fields do not have high accuracy, their low computational costs make room for the usage of more rigorous MD simulation protocols, e.g., longer simulation times, and better sampling using independent replicas, which also contribute to the quality and accuracy of the result.[3,4]

Once we identified the most suitable force field for our goals, we evaluated how ion pairing affects the ion dynamics in IL-based electrolytes. As expected, the local environment of the ions plays a crucial role in their transport. For example, an increase in the mole fraction of sodium ions in IL leads to ion aggregation and, consequently, to an increase in the dynamics heterogeneity due to the presence of different ion-ion arrangements. Furthermore, changes in system composition or molecular structure of the ion have a direct effect on the pairing of the ions,[5] indicating that although the overall behavior of transport properties is similar between different systems based on IL, their microscopic dynamics must be carefully evaluated, considering all particularities of the ions and a more accurate analysis may be needed.[6]

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Oral O_B1.4

Molecular dynamics simulation of surface charge screening in Ionic liquids mixtures: competition of ions

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How do ions compete in screening charged surfaces? This question of fundamental and practical importance we addressed in this study. Indeed, understanding the screening mechanism is the way to enhance the energy storage efficiency in electrochemical devices, such as supercapacitors, via controlling the structure–capacitance–potential dependence. We focus on mixtures of ionic liquids, as these electrolytes extend the advantages of ionic liquids with higher tunability towards desired properties.[1-2] As shown recently, the ions' interplay in such mixtures can result in differential capacitances up to three times higher than those for pure ionic liquids, depending on the combination of ion size and asymmetry.

In previous work, we elucidated the intricate relationship between structure, capacitance, and potential at Au(hkl)–[C_4mim][PF_6] interfaces,[4-6] also exploring [C_4mim][PF_6]-[C_4mim][FAP] mixtures in bulk.[7] This investigation infers the impact of [FAP]$^-$ concentration rises on interfacial structure, potential drop, and capacitance. Molecular dynamics simulations were conducted on mixtures of 1-butyl-3-methylimidazolium hexafluorophosphate [C_4mim][PF_6] & 1-butyl-3-methylimidazolium tris(perfluoroethyl)trifluorophosphate [C_4mim][FAP] ionic liquids confined between gold Au(100) electrodes.

Consistent with both earlier experiments and simulations, we validate the dominance of smaller [PF_6]$^-$ ions over their larger [FAP]$^-$ counterparts. Specifically, smaller ions replace larger ones in the contact layer, where ions (over)screen. Notably, under low and moderate electrode charges, the symmetric [PF_6]$^-$-anion, with its stronger charge concentration, displaces the larger and asymmetric [FAP]$^-$-anion. Conversely, higher electrode charges foster [FAP]$^-$-anion adsorption on the electrode surface. However, the precise factors underpinning the superior electrode charge screening abilities of certain ions remain unclear. In sharing our findings with the ionic liquid community, we aim to engage in insightful discussions and collectively advance our comprehension of this intriguing phenomenon.

Overall, our study provides new insights into the interfacial behavior of ionic liquid mixtures and can potentially inform the design of novel energy storage devices that use these promising solvents.

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Oral O_B1.5

NeuralIL, a neural network-based force field for ionic liquid simulations

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In this contribution, we present pioneering results of ionic liquids simulation using Neural network-based force fields. Specifically, we report results for several ionic liquids using the last version of NeuralIL.[12] This force field allows the simulation by molecular dynamics without any *a priori* functional for neither a definition of atom bonding. NeuralIL allows the simulation of hundreds of ionic pairs with *ab initio*-like accuracy without the enormous computational cost of DFT calculations. The results are compared with the results of classic force fields focusing on the structure and the ability of the force field to replicate the molecular structure.

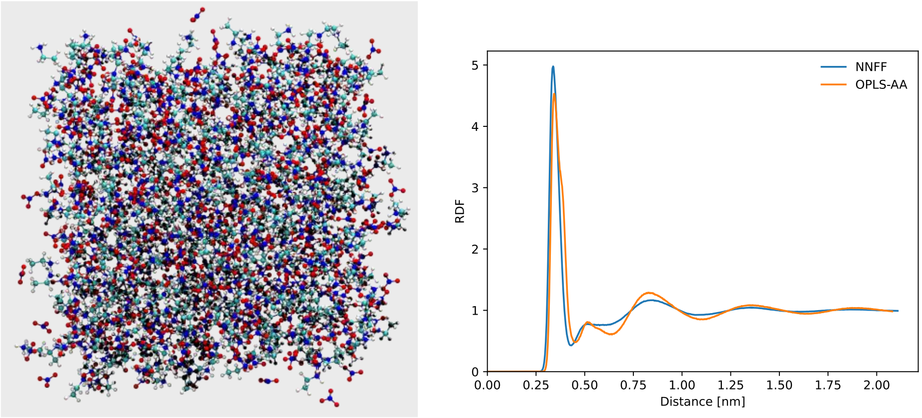

Figure 1: Left, a snapshot of a system simulated with NeuralIL. Right, comparison between the radial distribution function calculated with NeuralIL and a classical force field (OPLS-AA).

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Oral O_B1.6

Nanostructure and solubility of carbon dioxide in ionic liquids

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Human activities, including the combustion of fossil fuels and deforestation, have led to a significant increase in greenhouse gas concentrations in the Earth's atmosphere, resulting in substantial climate change and its associated consequences. Among these greenhouse gases, carbon dioxide (CO_2) stands out as a major contributor, playing a pivotal role in regulating the planet's temperature and climate conditions[1]. Effective management and reduction of CO_2 emissions have become imperative in addressing these challenges. Ionic liquids (ILs) have emerged as a promising solution in the quest for effective CO_2 capture and storage methods. These remarkable compounds possess a diverse array of properties, with their exceptional solvation capabilities being of particular interest. ILs have demonstrated the ability to solvate polar solutes with significant dipole and quadrupole moments, including CO_2, making them attractive candidates for addressing greenhouse gas issues[2]. However, the solubility of gases in ILs is profoundly influenced by the specific characteristics of the IL, particularly the nature of the anion. This IL's features can be tailored by selecting appropriate ion combinations, providing an avenue for precise control over gas solubility. In this context, Molecular Dynamics (MD) simulations have proven to be a valuable tool for investigating the molecular-level properties and interactions of ILs. This work aims to contribute to our understanding of the structural behavior of imidazolium-based ILs in the presence of CO_2 through a systematic MD study. By exploring various IL compositions and configurations, it strives to uncover insights into how the structural properties of ILs can be strategically adjusted to enhance their capacity for capturing and storing greenhouse gases. Ultimately, our research endeavors to provide valuable guidance for the development of advanced CO_2 capture and storage technologies, contributing to the ongoing efforts to mitigate the impacts of climate change.

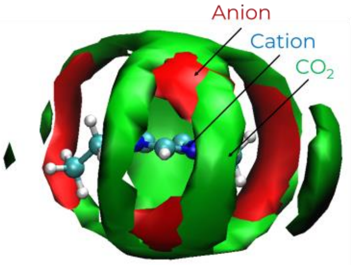

Figure 1: Selected spatial distribution function around the imidazolium cation ring in a mixture of 30% mole fraction of CO_2 and [C2C1im][BF4], calculated from MD trajectories. The red color represents the B atoms of the anion, while the green color represents the C atoms of the CO_2 molecule. The isosurface value corresponds to 70% of the maximum number density.

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Oral O_B2.1*

Development and application of task-specific ionic liquid crystals

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Ionic liquid crystals (ILCs) are considered new functional soft materials, which combine the properties of ionic liquids (negligible vapor pressure, high chemical and thermal stability, and designer functional properties) and liquid crystals (anisotropy, optical birefringence, anisotropic electrical and magnetic properties, and fluidity).[1] Recently, our group reported a new series of ILCs based on pyridinium and picolinium cations synthesized through sustainable methods and further characterized by thermal, microscopic, and spectroscopic techniques.[2,3] Herein, an overview of the influence of the methyl group position[2] and the alkyl chain length[3] impact on their mesomorphism and conductive behavior is provided, allowing the design of new functional materials.

In this context, it is discussed the potential applications of the selected ILCs include the fundamental studies regarding modifications at the molecular level and their use as smart materials for chromogenic applications.

In general, smart materials are known for their ability to stimuli-responsive environmental variations, usually reversibly, by the activation of the material's specific functions.[4] In particular, chromogenic materials are capable of changing their coloration when induced by light, electrical potential, temperature, pressure, or pH variations, originating, respectively, photo-, electro-, thermo-, piezo-, and halochromic responses.[5]

The two most promising ionic liquid crystals were used as intrinsically chromogenic materials as well as task-specific media to dissolve responsive probes.

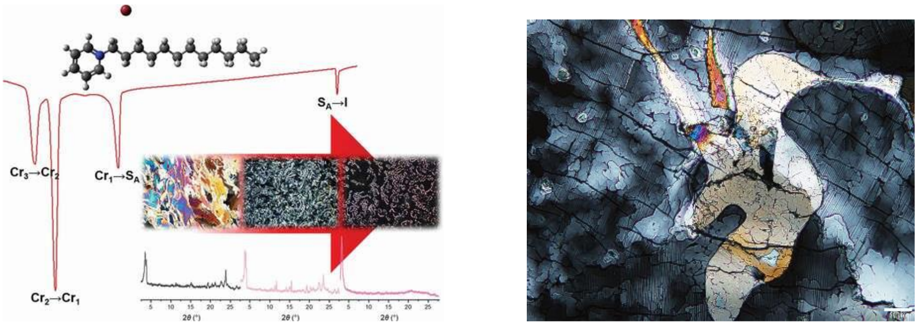

Figure 1: Illustration of Ionic Liquid Crystals behavior based on substituted pyridinium cations.

Acknowledgements

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* highlighted talk

Oral O_B2.2

Understanding the 1:2 CAGE analogs properties

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Ionic liquids and deep eutectic solvents have been both largely studied for their potential utilization and one of the most challenging possibilities is their use in biomedical applications. Particularly, in recent years, it has been shown that the system composed of an equimolar mixture of a cholinium cation, a geranate anion, and a geranic acid molecule, the so-called 1:2 choline-and-geranate (CAGE), can be successfully used for transdermal and oral drug delivery[1, 2].

However, its industrial-scale preparation and its long-term storage present several difficulties in order to make it really applicable on a large scale. Possible alternatives can be found, looking for more suitable candidates while maintaining its advantageous properties. With this aim, following the targeted modification[3] approach already successfully used for ionic liquids, some analogs can be synthesized, changing targeted functional groups. To achieve good results a complete understanding of the structure-property relationship is fundamental.

In the present work, we present an extensive characterization of several CAGE analogs, obtained by substituting the choline with 2 butyltrimethylammonium and the geranic acid (and the relative anion) with either citronellic or octanoic or 2-octenoic acid.

In particular, we exploited several experimental techniques like differential scanning calorimetry, dynamical mechanical analysis, and infrared spectroscopy, comparing the measured data with results provided by DFT calculations. We obtain information about their thermal properties, the occurrence of phase transitions and the presence of dynamical processes. The analysis of the far infrared range provides indications about the intermolecular interactions and the hydrogen bonding network.

The properties observed for the synthesized analogs are studied against those observed in the starting CAGE mixtures, providing insights into the role played by the different species in the mixtures.

Acknowledgements

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Oral O_B2.3

Ionic liquids as extraction solvents for citrus oil deterpenation

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Deterpenation of citrus essential oils consists of separating (totally or partially) the terpenes in the composition of the oil, leaving it enriched in other, more stable, volatile components, namely oxygenated compounds. These oxygenated compounds are actually responsible for the attractive organoleptic properties of the essential oil.[1] This deterpenation process is of key relevance due to the easy degradation of terpenes and subsequent reduction of the shelf-life of the essential oil. Most researchers evaluate the separation techniques for deterpenation assuming that the essential oil is a binary mixture of limonene and linalool, the biggest fraction in all citrus oils.[2-4] But this neglects the separation effect on other components that are also relevant for the organoleptic properties of the oil. In the context of liquid-liquid extraction, the partitioning of all key components of the essential oil should be evaluated to decide on the best extraction solvent.

In this work, we have assessed imidazolium-based acetates for the extraction of oxygenated components of citrus oil, including linalool, citral, octanal, and geranyl acetate. Limonene is assumed as major component (diluent) of the essential oil, and the effect of other terpenes such as pinene and terpinene has also been considered. Linalool and 1-octanal proved to be more efficiently extracted than citral, while geranyl acetate was not efficiently extracted. On the other hand, terpenes were mostly not extracted. The effect of the length of the alkyl substituent of the imidazolium cation on the partitioning has been studied, and it has proven to be a key parameter in the partitioning, affecting the balance between oxygenates' extraction and terpenes co-extraction, that is, controlling the selectivity of the extraction process. Full liquid-liquid equilibria of ternary systems of the type (terpene + oxygenated compound + ionic liquid) have also been experimentally determined, and the corresponding data have been modeled to obtain the binary interaction parameters that will enable an extension to multicomponent systems that reproduce more realistically the authentic essential oil.

Acknowledgements

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Oral O_B2.4

Ionic liquids as mass separation agents in terpenes separation processes

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Terpenes and terpenoids can be abundantly found in nature and have extensive applications in the cosmetics, pharmaceuticals, and food areas. These compounds are often found in complex multicomponent mixtures at low concentrations, making their separation and purification challenging. This work summarizes our findings[1–4] on the potential of ionic liquids (ILs), and their mixtures, as entrainers in the separation and purification of terpenes using both experimental and COSMO-RS methodologies. The main goal is to understand the solute-solvent interactions and to identify suitable ionic liquids for terpene extraction and separation. To do so, the activity coefficients at infinite dilution of terpenes and terpenoids in ILs were measured by inverse gas chromatography. Selectivities, capacities, and solvent performance indices were then calculated. Overall, the results show that ILs have the potential to isolate the main components present in important essential oils and highlight the importance of tailoring their polarity. It was also shown that COSMO-RS is a useful predictive tool for the screening of ILs for essential oils processing.

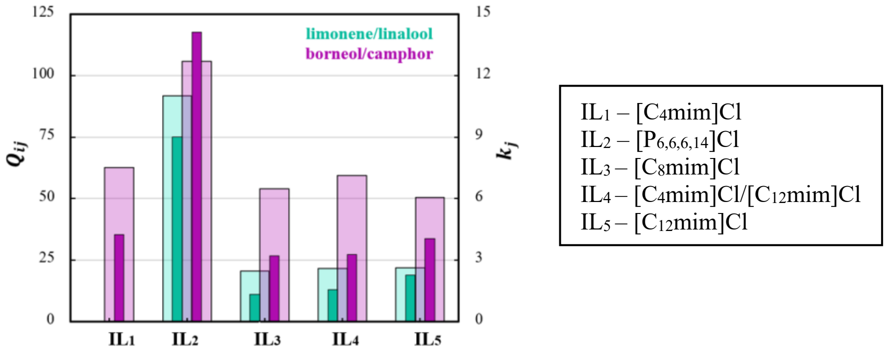

Figure 1: Solvent performance indices, Q_{ij}^{∞}, (light-colored bars) and capacities, k_{ij}^{∞}, (dark-colored bars) at infinite dilution.

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Oral O_B2.5

Solubility enhancement of hydrophobic compounds in aqueous solutions using eutectic solvents or ionic liquids

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Aqueous solutions of eutectic solvents (ES) or ionic liquids (IL) have been proposed to enhance the solubility of different biomolecules that are poorly soluble in water.[1-2] When compared, ES are frequently described as alternative solvents to IL with some advantages regarding their preparation, as no synthesis steps are required. Nevertheless, the molecular mechanisms controlling the significant increases in solubility are still unclear, which makes the selection of the best family of hydrotropes difficult. Aiming to achieve a fairer comparison between IL and ES, the solubility of benzoic acid, hesperetin, and tryptophan was measured in aqueous solutions of two structurally similar ionic liquids (choline glycolate and choline malonate), and eutectic solvents (choline chloride:glycolic acid and choline chloride:malonic acid).

The results showed that the pH of the aqueous solutions played a dominant effect on the increase in solubility of the studied ionizable solutes. More interestingly, when the pH effect was subtracted, a hydrotropy mechanism was in some cases identified, supporting the idea that both IL and ES can act as hydrotropes in aqueous solutions. The results here reported (exemplified in Figure 1 for L-tryptophan) show that the solutes speciation and co-solvation/hydrotropy molecular mechanisms may have complementary effects and should be considered in the selection of the best solubility enhancer (ILs *versus* ES).

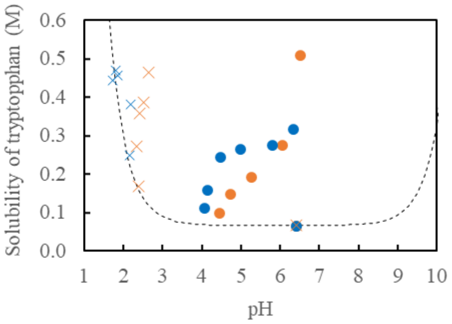

Figure 1: Solubility profiles of L-tryptophan, at 303.2 K, in aqueous solutions of: × choline chloride:malonic acid (1:1); × choline chloride:glycolic acid (1:1); • choline malonate; • choline glycolate. The dashed line is the predicted solubility-pH profile.[3]

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Oral O_B2.6

In silico COSMO-RS predictive screening of green solvents for lupin debittering

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Andean lupins (*Lupinus mutabilis*) have been widely cultivated in the Andean highlands for the enrichment of the soil, animal feeding, and as a food crop. Their seeds are nutrient-rich in terms of their high content of protein (about 50%) and oil (about 20%). However, the presence of toxic quinolizidine alkaloids, including sparteine, lupanine, and 13-OH-lupanine, in the seeds limits their industrial applications.[1,2]

Conventionally, alkaloids are removed from the lupin beans via water leaching (which consumes a large amount of water) or solid-liquid extraction using toxic organic solvents. As an alternative, supercritical fluid extraction, namely supercritical carbon dioxide (scCO$_2$) extraction, has been proposed for lupin debittering. [1,2] Nevertheless, so far, the alkaloids removal from the bean samples is still limited and can be attributed to the limited modifiable property of the scCO$_2$, since there is a lack of miscibility of the commonly applied co-solvents (typically ethanol or water-ethanol mixtures) to scCO$_2$. Therefore, finding a suitable co-solvent may be the key to enhancing the performance of the extraction by addressing the miscibility issue. Another possible approach is to perform a multi-step extraction, combining the use of environmentally friendly solvents for extraction, followed by selective isolation of alkaloids or non-alkaloids by scCO$_2$.[1,2]

Several ionic liquids (ILs) and eutectic systems (ESs) have been reported in the literature to extract alkaloids from plant materials with the advantages of sustainability, biodegradability as well and adjustable polarity to dissolve polar and non-polar compounds.[3] However, identifying an optimal IL or ES from a large number of possible combinations is quite challenging. To address this issue, the COSMO-RS (COnductor-like Screening MOdel for Real Solvents) model has emerged as a reliable computational tool that can screen numerous compounds or mixtures based on different thermodynamic properties.

The current study demonstrates the dissolution behavior of quinolizidine alkaloids in ILs and ES using the COSMO-RS model. Several combinations were attempted and evaluated by predicting the logarithmic activity coefficient ($\ln(\gamma)$) of typical quinolizidine alkaloids (sparteine, lupanine, and 13-OH-lupanine) in conventional solvents, ionic liquids, and natural-based eutectic solvents at 1:1, 1:2, 2:1 molar proportion.

Through this research, we aim to develop a novel separation method, based on the use of both scCO$_2$ and green solvents, to separate alkaloids from the Andean lupin beans, and to unveil efficient and environmentally conscious strategies for maximizing the use of Andean lupins.

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Oral O_B3.1*

Copper-catalyzed click reactions in ionic liquids

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Since 2002, when Meldal[1] and Sharpless[2] independently unveiled the copper-mediated enhancement of the azide-alkyne cycloaddition, commonly referred to as the Huisgen reaction, the copper(I) catalyzed azide-alkyne cycloaddition (CuAAC) reaction has attracted significant attention and popularity among scientists from diverse fields. In recognition of this pivotal discovery, Bertozzi, Meldal, and Sharpless were jointly awarded the Nobel Prize in Chemistry in 2022.

In this study, we have expanded the scope of the CuAAC reaction by employing ionic liquids (ILs) as reaction solvents. Within this investigation, we systematically explore the influence of IL structure and composition on the kinetics of the CuAAC reaction between benzylazide and phenylacetylene. Specifically, we investigate the effects of coordinating and non-coordinating IL anions on reaction kinetics. Furthermore, we assess the significance of water content, the structural characteristics of the Cu(I) catalyst, and the introduction of a base within the reaction medium. Our findings reveal profound alterations in reaction kinetic profiles and relative reaction rates, highlighting the diverse role ILs can play in modulating the CuAAC reaction rates.

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* highlighted talk

Oral O_B3.2

An ionic element in lubricating greases: what are the implications?

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Greases are widely used for the lubrication of machine components: with rolling element bearings being an obvious example[1]. In fact, grease is a vital machine component and should be designed accordingly. A lubricating grease is composed of a base oil, a thickener, and additives[2]. There are many different thickener systems to choose from. They range from soaps to polypropylene. A polypropylene thickener is non-polar and thus does not interfere with the surface protection mechanisms of the additives. In contrast, soaps are ionic materials and thus surface active. This may create a problem for the additive expression. There are of course many other design and operational parameters to consider. For example, the rapid development of e-drives has led to additional requirements for lubricating greases such as electric conductivity. Should it be high or low? This is still debated.

A way to tune the conductivity of greases is to use ionic liquids. Ionic liquids are composed entirely of ions but liquid under the conditions used. A great variety of cations and anions and their combinations is possible, opening up the potential to efficiently tune not only ionic conductivity but also tribochemical reactions responsible for the formation of wear and friction-reducing boundary films[3,4].

In this talk, we show how ionic species, coming from the ionic liquids, the thickener, or both, influence grease lubricating performance in sliding and rolling contacts[5,6]. Bulk nanostructure effects on lubricating performance will be highlighted[7]. Results from the single contacts as well as component level contacts will be presented and discussed.

Acknowledgements
The Swedish Foundation for Strategic Research (project EM16-0013), the Knut and Alice Wallenberg Foundation (project KAW2012.0078), and the Swedish Research Council (project 2018-05017) are gratefully acknowledged for financial support.

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Oral O_B3.3

Green energy storage: supercapacitors with sustainable solid-state electrolytes and marine waste biocarbon electrodes

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The fast progress of flexible wearable electronic devices makes it crucial to develop stretchable power supplies[1]. Supercapacitors offer several advantages, such as high-power density and excellent charge-discharge cyclability, compared to batteries. However, it is also essential to develop flexible electrolyte materials with appropriate conductivity and elasticity to produce flexible energy storage materials.

An ion gel based on an eco-friendly deep eutectic solvent (DES) was developed using a free radical polymerization on acrylamide monomer in a choline chloride-based system with several hydrogen bond donors (ethylene glycol, glycerol, urea). The obtained gel is flexible with excellent mechanical properties, which can be attributed to the formation of a coherent hydrogen bond network between the DES and the polymer matrix. The different gels were electrochemically characterized in a three-electrode cell using a glassy carbon as a working electrode through cyclic voltammetry and electrochemical impedance spectroscopy. Promising preliminary studies led to increased capacitance compared to the non-solid-state DES. The gels were also applied as a solid-state electrolyte in a symmetric supercapacitor configuration, using a high surface porous carbon material as electrodes fabricated from biocarbon obtained by considering one-step carbonization of glycogen isolate purified from mussel cooking effluents (biomass recovered from marine waste). These prototypes delivered a maximum capacitance of 703 F g^{-1} at a 1 A g^{-1} of current density, showing a 75% capacitance retention over 1000 cycles, delivering the highest energy density of 0.335 W h kg^{-1} and power density of 1341 W kg^{-1}. An upgrade on the developed prototype was obtained with the attachment of anodized TiO_2 to the glycogen-based carbon matrix, increasing the surface area of the composite (x1.45), thereby enhancing the specific capacitance (x2) of the electrode/electrolyte system, with a consequent increase of the capacitance retention.

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Oral O_B3.4

Exploring the unique extraction behaviors of critical metals by hydrophobic eutectic solvents: comparison with diluted systems

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Solvent extraction, one of the representative methods for separating metal ions, raises concerns about environmental impact due to the release of organic solvents. In recent years, deep eutectic solvents (DES), which turn liquid at room temperature by mixing hydrogen bond donors (HBD) and acceptors (HBA) as alternative solvents to organic solvents, have gained attention. DES exhibits various functions not present in conventional solvents, owing to the hydrogen bond network formed by HBD and HBA. In this study, we investigate the use of hydrophobic DES for extracting platinum group metals which face significant geopolitical risks in terms of resource supply among precious metals. Through comparison with dilution systems using conventional organic solvents, we attempt to elucidate the unique extraction and separation capabilities demonstrated by hydrophobic DES.

A series of eutectics composed of trioctylphosphine oxide (TOPO) as a hydrogen bond acceptor, and lauric acid (LauA) or lauryl alcohol (LauOH) as hydrogen bond acceptors were prepared. The liquid-liquid extraction experiments were carried out by contacting the mixed metal solutions with known HCl concentrations as aqueous phases and the DESs or their diluted solutions as organic phases. The effect of HCl concentration on the extraction efficiency of metals into 500 mmol/L TOPO diluted by toluene and LauOH/TOPO(1:1) is shown in **Figure 1**. The extraction efficiency of Pt and Pd was enhanced, while the extraction of typical impurities Fe and Cu was comparable to the diluted system. Therefore, the use of DES is beneficial for the separation of previous metals from base metals.

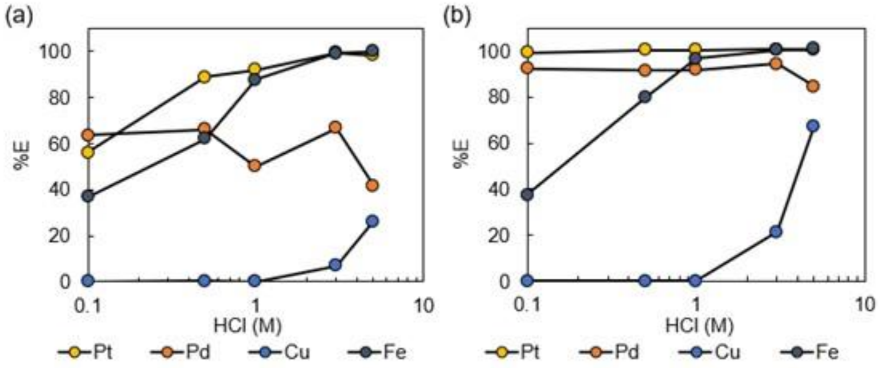

Figure 1: Liquid-liquid extraction of Pt, Pd, Cu, and Fe with (a) 500 mmol/L TOPO and (b) LauOH/TOPO(1:1).

Acknowledgements

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Oral O_B3.5

The importance of applying different characterization methods for studying organic adlayers at the electrode | ionic liquid interface

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Self-assembled monolayers (SAMs) have significant importance in many modern applications[1-2]. The properties of SAMs depend on many aspects, such as the characteristics of individual molecules, forming the monolayer; the interactions between these molecules; SAM interactions with the electrolyte; the crystalline surface of the substrate; etc[3]. Therefore, the fundamental studies of these systems are crucial in determining the function of SAMs in various applications[4-5].

The current work focuses on the adsorption characteristics of 4,4'- bipyridine (4,4'-BP) from ionic liquid media at different electrodes[6].

Cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and in situ scanning tunneling microscopy (STM) experimental measurements were conducted to characterize the electrochemical behavior of the self-assembled 4,4'-BP layers at the Sb(111) and Cd(0001) | 4,4'-BP+1-ethyl-3-methylimidazolium tetrafluoroborate (EMImBF$_4$) interface. In addition to experimental methods, density functional theory (DFT) calculations were used to characterize the adlayer structure.

CV is the most widely used technique for acquiring qualitative information about electrochemical processes. In this study, the potential region for Sb(111) is from −0.9 V to 0.0 V, and for Cd(0001) from −2.1 V to −0.8 V for vs. Ag|AgCl. The current values increase rapidly at the more negative end of the studied potential region, indicating that reduction processes started at the Sb(111) and Cd(0001) | 4,4'-BP+EMImBF$_4$ interface. Different from the data measured in EMImBF$_4$, where the system shows ideal polarizable behavior in the whole potential range.

EIS is a powerful tool for investigating the mechanisms and kinetics of electrochemical reactions. Interfacial capacitance (C_s) values depend on the composition of the electrolyte (i.e., on the concentration of 4,4'-BP), electrode material as well as on applied potential. C_s values are lower in the mixture than those measured in pure EMMImBF$_4$ at a certain potential region in the case of both electrode materials. This effect is caused by the adsorption of 4,4'-BP molecules at the electrode surface.

In situ, STM is a very informative and versatile method to study organic adlayers' structural and electronic properties that provide resolution on the atomic and molecular level in real space. The in situ STM images of the 4,4'-BP adlayers confirm the adsorption process on the electrode surface.

Acknowledgments:
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Oral O_B3.6

Mixtures of ionic liquids and natural organic acids as an example of deep eutectic solvents: experimental and computational characterization

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In the last two decades, many alternatives to traditional solvents have been proposed: among these, we can certainly include ionic liquids (ILs) and deep eutectic solvents (DESs). The idea behind this compelling research is to obtain stable liquid phases with an improved eco-compatibility concerning traditional solvents [1]. The eutectic mixtures are in general composed of two or more natural and low-toxic organic or inorganic compounds: the preparation of DESs in general consists of the mixing of two solid (or liquid) compounds, that lead to the formation of a liquid mixtures. The depression of the melting point of the eutectic mixtures can be primarily attributed to the formation of strong secondary interactions between the components: the most important one is hydrogen bonding. To accurately predict and model the macroscopic behavior of the DESs, in order to develop possible technological applications, it is essential to have a deep understanding of the microscopic arrangement of the components in the liquid phase.

With the aim to investigate the molecular mechanisms governing the formation of the DESs we proposed several binary mixtures obtained by two hydrogen bond acceptors (HBA), Choline Acetate (ChAc) and Tetrabutylammonium Acetate (TBAAc), and three different natural organic acids, namely Ascorbic Acid (AA), Citric Acid (CA) and Maleic Acid (MA), acting as hydrogen bond donor (HBD): the different number and type of OH group in the HBD molecules should influence the capability of each acid to form H-bonds with different strength.

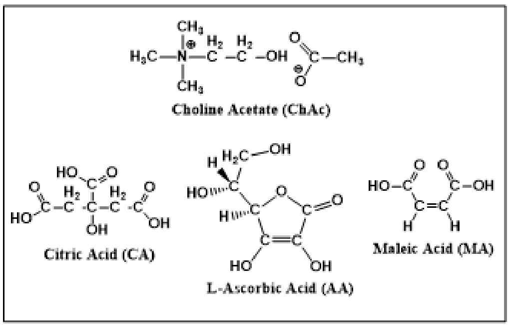

Figure 1: Chemical structure of the starting materials.

The starting materials and the mixtures were studied by IR spectroscopy at AILES beamline of the SOLEIL synchrotron in Paris, as a function of temperature, covering both far and medium IR ranges. The spectra obtained were assigned by means of DFT calculations and the bulk structure was also investigated by classic molecular dynamics simulations. All techniques reveal the formation of a strong H-bond network between HBA and HBD. The FIR spectra (30-600 cm^{-1}) show the bending and the stretching of the H-bond. The MIR region shows the coordination between the components, observing in particular the bands of $\nu_{C=O}$ and ν_{OH}. All the computational results agree with the spectroscopic interpretation.

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Oral O_B4.1*

The role of quantum capacitance in capacitive energy storage with nanoporous electrodes: Can less be more?

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Low-dimensional electrode materials become increasingly important in capacitive energy storage and conversion.[1] A characteristic signature of such electrodes is quantum (or space-charge) capacitance, which appears due to a finite density of states of electrons in an electrode, as opposed to ideally metallic electrodes where it is infinite. Gerisher[2] demonstrated that quantum capacitance, rather than an electrical double-layer capacitance, determines the total (measured) capacitance of an electrolyte at graphite electrodes. Since this pioneering work, several studies have indicated that quantum capacitance is generally detrimental and lowers the total capacitance.[3-6] However, these studies have focused on flat electrodes and carbon nanotubes (CNT) with an electrolyte outside CNTs. In this talk, I discuss how quantum capacitance affects the capacitive properties of electrolyte-filled narrow nanotubes. We use analytically solvable, computationally inexpensive but realistic models,[7,8] allowing us to investigate the effects of quantum capacitance systematically.[9] In line with previous work, we find that the total capacitance is lowered by the quantum capacitance compared to the capacitance due to ideally metallic nanotubes, but only at low potential differences applied to a nanotube with respect to the bulk electrolyte. At intermediate and high potential differences, at which a CNT is saturated with counter-ions, a low quantum capacitance can enhance energy storage, providing even a few-fold enhancement in the stored energy density. Our results[7] suggest exciting opportunities for boosting capacitive energy storage by rationally engineering the electronic properties of low-dimensional electrodes.

Acknowledgements
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* highlighted talk

Oral O_B4.2

Charging and discharging of supercapacitors in molecular simulations

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Supercapacitors are a promising technology for fulfilling the demand for advanced energy storage in, *e.g*. electric vehicles and buffers on electric grids. Molecular Dynamics (MD) simulations give insight into the processes in supercapacitors at the molecular level, which can help optimize supercapacitors. However, these simulations are computationally very demanding. In the constant potential method (CPM), the electrode atoms are traditionally endowed with narrow Gaussian charge distributions, which require a dedicated electrostatic solver. We show that identical results are obtained when point-like electrode atoms are endowed with hardness, *i.e*. an internal energy penalizing the gain or loss of charge by an atom.[1] It then becomes possible to maintain a potential difference between two conducting electrodes using any off-the-shelf electrostatic solver. As an example, we present simulations of supercapacitors combining this generalized constant potential method (GCPM) with particle-particle particle-mesh (PPPM) in LAMMPS. GCPM and CPM yield identical results for a properly selected hardness, while the time complexity of GCPM is similar to that of traditional simulations with fixed charges.[1] This gain in speed opens new possibilities to simulate the dynamics of ionic liquids in supercapacitors.

A disconnected supercapacitor does not maintain a constant voltage difference between the electrodes but rather conserves the total charges on both electrodes (in an ideal world). To simulate this situation we developed the constant sum charge method (CSCM), which again works with any off-the-shelf electrostatic solver.[2] The small fluctuations in the voltage are related to the differential capacitance. Charging and discharging of a supercapacitor are simulated by introducing an equation of motion for the sum charges, taking into account the electronic properties of the elements in the external circuit (Figure 1). Simulations of a model supercapacitor with an aqueous electrolyte show double-exponential relaxation, with a one-time scale set by the internal resistance to the flow of ions and the other time scale governed by the external resistance to the flow of current. We propose an equivalent circuit model that captures these characteristics.[2]

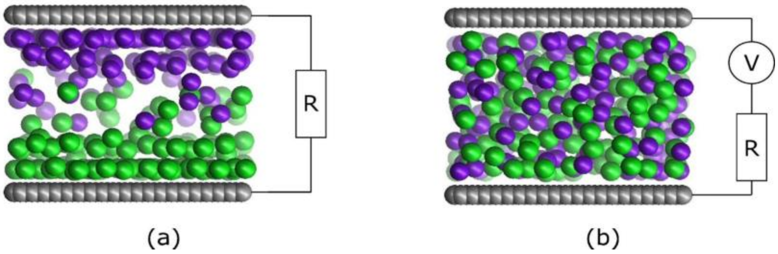

Figure 1: Setups to simulate (a) discharging and (b) charging of a supercapacitor. The capacitor (co-)determines the current in the external current, the external current co-determines the dynamics within the supercapacitor.

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Oral O_B4.3

Hybrid water-in-salt electrolytes: A computational study

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In this era of profound global change, energy harvesting and storage are considered to be one the most crucial challenges that humanity is facing. The global energy system must be transformed into a more efficient and sustainable one, so it is not surprising the amount of scientific and technological efforts that are devoted to the development of new affordable, reliable, and advanced energy devices. This effort led to the proposal of a new "water-in-salt" based electrolyte (WiSE) in 2015 by Suo *et al.*[1] This pioneering electrolyte (a system in which mass and volume ratios of salt-to-solvent are greater than 1) exhibits an electrochemical stability window (ESW) up to 3V by using aqueous solutions of LiTFSI. Besides, the fraction of free H2O molecules in these systems is too low, as these molecules are taking part of the solvation shell of metal ions. As a result, the decomposition of salt anions led to the formation of protective solid-electrolyte interphase, which prevents the reduction of water and expands the ESW. To enhance the kinetic protection of WiSEs, increasing salt concentration is suggested. However, most WISEs are already near their saturation point. One of the approaches followed to further increase the amount of salt that can be added to the system was to dilute WiSEs by adding organic co-solvents to form superconcentrated hybrid aqueous/non-aqueous electrolytes, promoting ionic motion by decreasing cation-anion interaction.

In this contribution, a computational study of these hybrid systems by adding different types of organic co-solvents (such as acetonitrile or ethylene carbonate) at different concentrations to the traditional WiSE (21 m LiTFSI/H2O) was performed by means of molecular dynamic simulations. A detailed comparison between their physicochemical properties at 298.15K was performed by analyzing different thermodynamic (density), structural (radial function distribution, free water fraction, hydrogen bonding…), and dynamic (velocity autocorrelation functions and conductivities) properties.

Acknowledgements

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Oral O_B4.4

Size Matters: A computational study of hydrogen solvation in ionic liquids

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In recent years, due to the advances of climate change, the need for an energy transition towards a greener model capable of both meeting the needs of the population and reducing our carbon footprint has become a global priority. Because of this, there is a great demand both for new methods of producing renewable energy and techniques or materials to store it. In this context, hydrogen has recently gained popularity as a clean alternative to fossil fuels. However, a key aspect of the “hydrogen economy" is the safe and efficient storage of this gas, and porous liquids such as ionic liquids (ILs) have been proposed as potential candidates[1].

In this contribution, a computational study of hydrogen sorption in a wide variety of ionic liquids is presented. As a first approach, the solvation properties were studied by means of both classical molecular dynamics (MD) and density functional theory in the context of bulk ILs, and it was found that the main mechanism behind gas solvation is the structural voids present in the IL, and whether they are big enough to host a hydrogen molecule, rather than the specific interaction between the solute and the solvent. Moreover, it was found that correctly tuning the cation-anion pair can have a big impact on hydrogen solubility as well as on the dynamics that hydrogen molecules undergo within the system.

Finally, recent results regarding the absorption of gases in ILs when these are confined within carbon nanotubes, by means of MD and hybrid MD - Grand-Canonical Monte Carlo simulations will be presented and compared with their bulk counterparts.

Acknowledgements

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Oral O_B4.5

Ternary solid polymer electrolytes at the electrochemical interface: a computational study

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The large increase in consumption of electrochemical devices that has taken place in recent years demands a corresponding improvement of the capabilities of the batteries they are based on. As an alternative to traditional Li-ion batteries, solid polymer electrolytes (SPEs) have emerged as attractive candidates to solve the safety and environmental issues of the former. The presence of the polymer allows for enhanced mechanical rigidity and wider electrochemical stability, although Li ion mobility is hampered.[1] Ternary SPEs, which are constructed by adding an ionic liquid (IL) to the binary mixture, avoid this issue thanks to the plasticizing effect of the IL, which enhances the Li ion dynamics.

In this contribution,[2] we perform a computational study of ternary SPEs through molecular dynamics simulations. Polyethylene oxide and [Li][TFSI] were selected as the model polymer and salt species for the binary mixture. The effect on the properties of ternary SPEs due to several factors will be discussed. Specifically, how the presence of a layer of graphene, acting as a solid interface, or its charge state (neutral, positive, or negative) influences the structure of the mixture. This interface-electrolyte interaction mimics that of batteries or capacitors. The effect of changing the cation that composes the IL and the relative concentration of the IL to the binary mixture will also be discussed.

Acknowledgements

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Oral O_B5.1*

Enthalpy of mixing of an alcohol + IL binary mixture - the signature of the different structuration regimes

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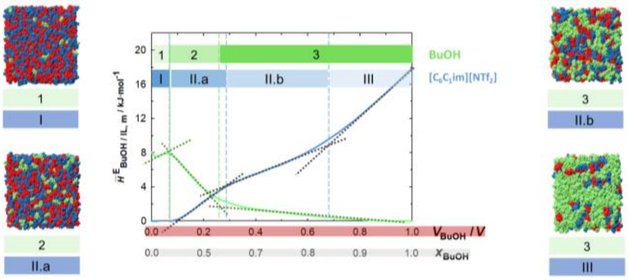
In recent works[1,2] addressing the study of solution and solvation of alcohols in ionic liquids, at infinite dilution, we demonstrated that the alcohols are preferentially located at the IL polar domain, showing a preferential interaction by hydrogen bond of the hydroxyl group of the alcohol with IL anions. Nevertheless, a significant role of the cation in the solvation process was found in ionic liquids with poor basicity. These insights are valid at infinite dilution conditions. As the content of the alcohol in the ionic liquid increases forming binary mixtures, different structuration and interaction profiles are expected.

In this work are presented the results of the excess molar enthalpy of the binary mixture 1-butanol (BuOH) + 1-hexyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_6C_1im][NTf_2]$), obtained in µFlowCal[3], at T = 298.15 K and in the molar fraction range 0.15 < xBuOH < 0.95. The µFlowCal[3] is a new heat conduction twin microcalorimeter, designed and constructed in our laboratory for the measurement of high-resolution heat of mixing of small sample size (200 µL) in all ranges of composition in isothermal mode.

The experimental data was fitted with the Redlich-Kister equation, and the partial molar excess enthalpy of BuOH and the partial molar excess enthalpy of $[C_6C_1im][NTf_2]$ were derived. Given the similarities found between the alcohols and the ionic liquids, the obtained results were compared with the binary mixture BuOH + HexOH[4]. The results evidence a difference of a factor of 100 in the enthalpy values, which we believe to be due to the different nature of the species and molecular interactions established, deviating the mixture from the ideality. In addition, we have noticed a different shape of the curves of partial molar excess enthalpy, which may be the signature of the nanostructuration of the ionic liquids and their ability to solvate the added alcohol molecules, until a certain amount, preserving their structure. Based on the presented results we venture to propose that the different structuration regimes already described in the literature[5] for alcohol-IL binary mixtures are expressed in the partial molar enthalpy of both components (BuOH and $[C_6C_1im][NTf_2]$) as it can be seen in scheme 1.



Scheme 1: Partial molar excess enthalpy of the binary mixture BuOH + $[C_6C_1im][NTf_2]$ as a function of the BuOH volume fraction, with the division of the diagram into different regimes illustrated with representative simulation boxes. (figure created using the simulation boxes of the molecular dynamics simulations of the alcohol-IL mixture BuOH (colored in green) + $[C_4C_1im][NTf_2]$ (cation colored in red, anion colored in blue) [5].

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* highlighted talk

Oral O_B5.2

Ultrasound-assisted extraction of bacteriorhodopsin from *halobacterium salinarum* using superbase ILs: a green and efficient approach

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Bacteriorhodopsin (BR) is a membrane protein that plays an essential role in a wide variety of physiological functions and has the potential to be used in biotechnological, bioelectronic, and photoelectrical sectors due to unique qualities such as its photochemical activity, biological compatibility, and high structural, chemical and thermal stability[1]. However, the complicated extraction techniques have hampered its wider implementation. The goal of this study was to develop a simplified and long-term approach for extracting BR from *Halobacterium salinarum*. In this work, an ultrasound-assisted extraction (UAE) technique with aqueous solutions of a superbase IL (SBIL) - [mTBNH][OAc] was used to induce cell disruption. UAE has been successfully used in the extraction of several substances, including proteins, making it suitable for a wide range of industrial applications. UAE coupled with SBIL, in particular, has shown efficiency in dissolving the purple membrane of *Halobacterium salinarum*, allowing the SBIL to obtain high BR extraction yields. The ideal extraction conditions were determined by testing with different concentrations of [mTBNH][OAc] in an aqueous solution. After, a purification process after extraction was required to improve protein purity. This was accomplished through induced protein precipitation, a process in which a precipitating agent lowers protein solubility in water, causing precipitation and separation from the solvent. Notably, because of its simplicity, this technology has great industrial prospects, with a low carbon footprint and economic implications. Finally, a dialysis and drying step was used to remove any excess salts, resulting in a pure solid extract of bacteriorhodopsin. This novel approach has the potential to transform bacteriorhodopsin recovery, setting the framework for future studies and diverse applications.

Acknowledgements

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Oral O_B5.3

Are ionic liquids key materials in the development of controlled drug delivery systems?

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The development of controlled drug delivery systems with high drug efficacy and safety is one of the major concerns of the Pharmaceutical Industry. Nonetheless, there are several drawbacks to surpass when trying to formulate new delivery systems, such as poor drug solubility or loading, inflexible drug release profiles, and low stability of the produced systems. With this in mind, finding new functional excipients that improve these systems' performance to overcome some of these challenges is vital. Ionic liquids (ILs) may be potential candidates as key materials, since their chemical structure can be tailored to achieve the most suitable properties, according to the desired applicability, and they may be introduced in various solutions, thus improving the chances of successfully incorporating these salts into different types of delivery systems[1,2].

Thus, in this study, several ILs were synthesized and their applicability as functional excipients, at non-toxic concentrations, was evaluated in different delivery systems. Five ILs were prepared: 3 choline-aminoacid ILs, (2-hydroxyethyl)–trimethylammonium-L-phenylalaninate [Cho][Phe], (2-hydroxyethyl)–trimethylammonium-L-glutamate [Cho][Glu] and (2-hydroxyethyl) trimethylammonium glycinate [Cho][Gly], and 2 imidazole-based ILs, 1-ethyl-3-methylimidazolium bromide [C2mim][Br] and 1-ethyl-3-methylimidazolium glycinate [C2mim][Gly]. Their cytotoxicity in human keratinocytes (HaCaT) was first evaluated. Then, considering these results, two types of delivery systems — lipidic implants and TransfersomILs (a new class of nanovesicles containing ILs)— were prepared with and without the ILs. Each IL was incorporated at the upper concentration of these salts allowing the maintenance of cell viability, according to the cytotoxicity results obtained. The results showed that the ILs promoted a significantly higher drug loading, with the choline-based ILs displaying better results. Regarding the lipidic implants, the incorporation of the ILs showed that they seem to modulate the release profile of the drug. The new TransfersomILs presented higher association efficiency with higher total amount of drug release, and better colloidal and storage stability when compared with the transfersomes produced in the absence of the ILs.

Thus, our results indicated that the incorporation of ILs, at non-toxic concentrations, allowed the development of more efficient controlled drug delivery systems, showing that these salts may be multifunctional and valuable materials to upgrade the performance of controlled delivery systems.

Acknowledgements

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Oral O_B5.4

Supported ionic liquid materials as portable colorimetric sensors for L-asparagine detection

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L-asparaginase (ASNase) is an amidohydrolase enzyme applied in the pharmaceutical industry as an anticancer agent in the treatment of lymphoproliferative disorders.[1] ASNase is also used in biosensors for the detection of L-asparagine in blood serum samples of acute lymphoblastic leukemia (ALL) patients.[2] However, the high cost of non-portable and sensitive L-asparagine detection techniques, being mainly carried out by chromatography, reinforces the need to develop portable and low-cost colorimetric sensors for L-asparagine detection.[3]
Supported ionic liquid (SIL) materials comprise ionic liquids (ILs) covalently attached to the support, enabling distinct interactions to be established among the target compounds and the support.[4] SIL materials with quaternary ammonium cations and Cl^- as the counterion have been successfully applied in the immobilization of ASNase.[1]
In this work, SIL materials based on silica fabric functionalized with quaternary ammonium cations and the Cl^- anion, viz. silica fabric functionalized with dimethylbutylpropylammonium chloride ([SF][N_{3114}]Cl) and silica fabric functionalized with triethylpropylammonium chloride ([SF][N_{3222}]Cl), were synthesized and characterized through elemental analysis, Attenuated total reflectance-Fourier-transform infrared (ATR-FTIR) spectroscopy, and scanning electron microscopy (SEM). These SIL materials ([SF][N_{3114}]Cl and [SF][N_{3222}]Cl) were investigated as portable colorimetric sensors for L-asparagine detection in aqueous samples, i.e., aqueous solution of L-asparagine or commercial blood serum spiked with different L-asparagine concentration levels (10^{-1} M - 10^{-5} M). The developed low-cost and portable SIL allows the fast and accurate detection of L-asparagine at different concentration levels.[5]

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POSTER COMMUNICATIONS

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P_A3.1 to P_A3.4
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Poster P_A1.1

Solvent-catalyst optimization of ionic liquid-based CO_2 conversion to propylene carbonate: Laboratory validation and techno-economic analysis

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Ionic liquids (ILs) have been widely suggested as efficient catalysts to produce propylene carbonate (PC) from CO_2 and propylene oxide (PO). Recently, the use of liquid-liquid extraction (LLE) has been proposed to efficiently separate ILs from PC since it reduces energy consumption, with fatty alcohols when selecting hydrophobic ILs. However, the study of this reaction-separation system at the experimental level is scarce. In addition, the solvent-catalyst system design to improve the global process performance is a current challenge. This work develops an integrated experimental-computational multiscale approach to improve the PC production process by CO_2 cycloaddition to PO using the IL [P_{66614}][Br] as the catalyst. Reaction yield and liquid-liquid equilibrium measurements were carried out for the experimental validation of the proposed catalytic/separation systems using different solvents (fatty alcohol and water). Process modeling and techno-economic analysis were performed using Aspen Plus for solvent-catalyst optimization, proceeding with an integrated iterative experimental-computational approach to decrease energy requirements and operating costs. It was found that the presence of solvents in the reaction affects conversion and selectivity of the reaction, with fatty alcohols increasing PC yield and enabling IL/PC separation, while water reduces PC selectivity. On the other hand, the presence of water in the process allows reducing electricity demands as well as vacuum requirements. It was possible to modulate fatty alcohol and water dosages to minimize energy consumption, vacuum requirements, and utility costs. Optimal configurations have an energy consumption of approximately 0.6 kWh/kg_{PC} and utility costs of 6.6 $\$/t_{PC}$.

Poster P_A1.2

Efficient recyclability of amine-free CO_2 sorbent based on a solid-supported ionic liquid

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Nowadays, research on direct CO_2 capture is a hotspot topic due to the critical impact it has on both the environment and energy. Amine-based sorbents are widely used owing to their high CO_2 solubilities. However, they cause serious adverse issues such as volatility losses, thermal degradability, and high energy costs for regeneration. Therefore, it is important to chase alternatives. Hydrated carboxylate-based ionic liquids (ILs), as non-volatile materials that can capture 1 eq(CO_2) per carboxylate hydrate unit at equimolar IL/H_2O ratio, are appropriate and promising for low-energy regeneration due to their reduced enthalpies of absorption as compared to those of amines. In this work, hydrated tetrabutylphosphonium acetate was impregnated onto silicon dioxide to overcome mass transfer limitation due to the high viscosity of ILs and to maximize sorbent-gas contact area, giving rise to $[P_{4\,4\,4\,4}][AcO]\cdot H_2O/SiO_2$ (IL-100/SiO_2) as an efficient CO_2 sorbent material. Several short CO_2 sorption-desorption experiments at a moderate temperature were performed in a fixed-bed setup and compared with polyethyleneimine impregnated onto silicon dioxide as a competitor amine sorbent material. IL-100/SiO_2 showed complete and rapid CO_2 release, while the release of CO_2 was inefficient and incomplete for the amine sorbent under the same conditions.[1]

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Poster P_A1.3

Improving CO_2 solubility using [C_4C_1im][DMP] + carboxylate-based protic ionic liquids mixtures

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According to the World Health Organization (WHO), access to clean air is an essential human right and a necessity for human health.[1] However, air pollution is a serious threat to human health, being responsible for around 7 million deaths per year.[1] This mortality is associated with several pollutants with both ambient and household emissions, such as gases, particulate matter, and volatile organic compounds (VOCs).[1] As such, because poor air quality is responsible for various diseases, improving indoor air quality (IAQ) must be a priority.[1] Despite the existing guidelines to guarantee IAQ, other strategies should be employed whenever possible, including the reduction of pollutants at their source, air ventilation, and, if necessary, indoor air treatment.[2] Although several technologies can be considered for indoor air treatment, generally these possess some disadvantages such as high energy consumption, waste generation, and harmful by-product production.[2] Therefore, new indoor air technologies are required to overcome these limitations. Among several new technologies and solvents that can be considered, ionic liquids and eutectic solvents have gathered special attention due to their high sorption capacity, unique thermophysical properties, and are easily tuneable by the simple combination of anions and cations.[3] On top of their inherent characteristics, one can further enhance gas physisorption by preparing mixtures with positive deviations to ideality and, therefore, positive excess volumes.[4] Furthermore, the absorption capacity of the selected non-volatile solvents (NVS) can be improved by immobilizing and encapsulating them in microcapsules, and afterwards by using physical support for the immobilization of said encapsulated solvents in the form of membranes.[5] Therefore, the main goal of this work is to consider NVS that can remove indoor air pollutants, like gases and VOCs, taking advantage of their properties through the combination of absorption with membrane technology, thus creating a new and viable solution for the improvement of IAQ. To achieve this goal, the experimental work focuses on gas solubility measurements in different NVS mixtures using the isochoric method and gas membrane separation. Parallelly, optimizations are performed regarding the encapsulation of NVS, as well as the characterization of NVS that can show promising potential for gas absorption and, ultimately, be considered as an option for the treatment of indoor air.

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Poster P_A1.4

Use of polysulfone and n-methylpyrrolidone for preparation of polymeric membranes

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Large-scale production requires sustainable alternatives in all procedures used in the industry, in order to minimize the negative consequences for the environment. Due to the large volume of pollution of the effluents from the industry, it is necessary to take treatment measures for the reuse or correct disposal of the material[1]. The objective of this work is to produce a polysulfone (PSU) membrane with zinc oxide (ZnO) for potential use in cleaning industrial effluents. To produce pure and hybrid membranes[5], the phase inversion technique was used. The membranes produced were analyzed by FTIR and XRD. The results of the diffractogram of the membranes showed peaks characteristic of the PSU. The spectrum in the infrared region of the hybrid membranes showed characteristic polysulfone bands superimposed on the characteristic ZnO bands[4]. Finally, the production of hybrid membranes of PSU was successful and possibly has potential for use in cleaning effluents due to the antibacterial properties of ZnO together with PSU[2,3].

This study presents the production of polymeric membranes with solutions of 13% polysulfone and its effectiveness in industrial filtrations. To form the membrane, a solution was prepared with 13% polysulfone dissolved in 87% N-methylpyrrolidone. The solution was continuously stirred for 24 hours and then spread with the aid of a glass rod onto a glass plate that had three layers of adhesive tape on its edges to create a boundary for the membrane and maintain a regular thickness. The membranes in this research were prepared using the phase inversion method, which involves immersing the glass plate containing the solution in a non-solvent liquid, accelerating polymer precipitation, and causing the solidification of the polymeric matrix with a porous structure. For membrane characterization, XRD, FTIR, and contact angle analyses were employed[4]. The 13% polysulfone membrane exhibits characteristic peaks of pure polysulfone polymer in its XRD, with reduced crystallinity due to the addition of the solvent N-methylpyrrolidone during its production. The FTIR data confirm the characteristic peaks of the polymer in the 13% polysulfone membrane. The average contact angle of the produced membrane is 62.63°, indicating a hydrophilic nature. Analyses by XRD, FTIR, and contact angle confirmed the presence of polymer characteristics in the produced membrane, such as low crystallinity and high wettability provided by the polymer percentage used. The average flux of 33.958 L/m^2 indicates possible industrial application.

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Poster P_A1.5

Liquid crystalline phases in fluorinated ionic liquids with surfactant-based anions

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The concepts of ionic liquids and ionic surfactants have a high degree of overlap. Both are usually characterized by a carbon chain attached to a charged head that sits next to its counterion. It is no surprise that these two classes of compounds present many of the same types of mesophases, such as micelles, vesicles, and liquid crystalline phases. The incorporation of typical surfactant ions in the formulation of ionic liquids confers these types of compounds to the activity of ionic detergents and, due to their wide availability, also decreases the cost of production of these surfactant-based ionic liquids. It is a common occurrence in the ionic liquid scientific community to focus on the apolar chains in the cationic moiety but in this work, it is shown that there is an appreciable potential to tailor the properties of the anionic component coupled with some soft-charged cations such as the imidazolium family to produce compounds with interesting properties. Furthermore, the influence of fluorination, which is known to add to the hydrophobicity and rigidity of the apolar region, should also be assessed. Mukai et. al. have shown that the compounds containing perfluorooctanosulfonate anions and varying sizes of n-alkylimidazolium cations, $[C_n\text{im}][C_8F_{17}SO_3]$, where n=1-10, all display smectic-A type liquid crystalline phases in temperature ranges that can go up to 60 degrees[1]. These results seem to show that fluorination seems to increase the liquid crystalline phase stability, which can be of tremendous importance in applications where a wide range of operability is crucial. In this work, fluorinated and hydrogenated ionic liquids containing long-chained anions have been assessed as candidates to form liquid crystals, showing that molecular dynamics simulations can be a powerful tool to scan and predict the supramolecular organization of real systems.

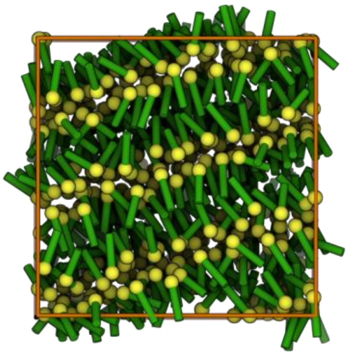

Figure 1: Snapshot from MD simulation of $[C_2\text{mim}][C_8F_{17}SO_3]$ forming a Sm-A LC phase.

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Poster P_A2.1

Biosorbents modified with deep eutectic solvents for biogas purification

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Biogas has considerable potential as a viable substitute for traditional fossil fuels. Its primary composition comprises methane and carbon dioxide and various organic and inorganic volatile contaminants. Although the concentration of volatile organic compounds (VOCs) in biogas is notably lower than that of its principal constituents, their presence can have adverse environmental consequences. Furthermore, burning biogas containing VOCs can lead to corrosion and substantial harm to engines and facilities designed to convert biogas into usable energy. To make biogas suitable for energy applications, thorough purification is required [1,2].
This study introduces an innovative technique for enhancing biogas purity using lignocellulosic biosorbents impregnated with deep eutectic solvents (DES). This study primarily concentrated on the elimination of volatile organic compounds (VOCs) and carbon dioxide (CO_2) from a model biogas sample. The biosorbents employed in the study included *Prunus mahaleb, Secale L., Fagus L., and Populus L.,* which differed in terms of their lignin and hemicellulose content. Given the numerous possible combinations of DES components, the appropriate impregnation layers were carefully chosen using the COSMO-RS (COnductor-like Screening Model for Real Solvents) computational model. This model was utilized to predict the solubility and interactions between DES and individual pollutants. Based on this preliminary selection, a DES formulation comprising quaternary ammonium salts and glycols was selected. The fundamental physicochemical characteristics of this new DES, such as its viscosity, density, and melting point, were assessed. Subsequently, the prepared, purified, and shredded adsorbents were infused with the new DES. The biosorbents' characteristics before and after modification were analyzed using thermogravimetric analysis (TGA), scanning electron microscopy (SEM), and X-ray diffraction (XRD). Subsequently, the adsorption of VOCs from the biogas was investigated. This study demonstrated the strong competitiveness of the new sorbents compared to commercially available ones. Furthermore, the utilization of an impregnation layer based on deep eutectic solvents led to a significant enhancement in the efficiency of VOC removal from the gas phase compared to pure biosorbents. This improvement exceeded 50%. The utilization of both absorption and adsorption processes is attributed to the elevated efficacy in removing volatile organic compounds from gas streams.

Acknowledgements
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Poster P_A2.2

Optimization of collagen extraction, purification, and scale-up via DES

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In recent years, collagen as a valorized biomolecule, has been one of the most studied biomaterials extracted and purified from different biomass. Due to the biocompatibility, biodegradability, low cell toxicity - antigenic properties, and the significant role of collagen in tissue structure and function, along with the current environmental pollution policy toward waste management, and biomedical applications of collagen concerning the low risk of transmission of zoonotic diseases along with religious restrictions, and moral concerns for biomedical, and cosmetic applications, marine collagen is considered a desirable alternative for collagen obtained from terrestrial animals. On the other hand, fish processing industries deal with considerable fish waste due to the procedures that are among the top waste-producing industries. Fish skin, as a mass-produced waste product, has a high content of proteins, mainly collagen type I which could be extracted and purified in its native form via Deep Eutectic Solvents (DES) known as the environmentally friendly solvents. Due to the low imino acid content of collagen extracted from marine sources, lower thermal stability, and general gel-forming properties of collagen obtained from marine sources, optimizing the material and methods, along with other parameters during the extraction procedure, and the downstream process is associated to the purity, biological activity, and total yield of the extracted collagen. In this study, we aim to investigate innovative solutions toward optimizing the extraction procedure, materials, and methods commonly used for collagen extraction from cod fish skin via DES as the green solvent.

Acknowledgements
This work was developed within the scope of the project CICECO-Aveiro Institute of Materials, UIDB/50011/2020, UIDP/50011/2020 & LA/P/0006/2020, financed by national funds through the FCT/MEC (PIDDAC).

Poster P_A2.3

A green separation of rare-earth elements from spent NdFeB permanent magnets using organic acid and eutectic solvent

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The production of neodymium-iron-boron (NdFeB) magnets consumes around 30% of rare earth elements (REE) from primary sources, contributing to a rapid shortage of these elements and considerable environmental impacts. Adding to this, the high amount of waste generated in the manufacture of this type of magnet and its short lifespan cause the disposal of critical metals essential for different sectors. Therefore, understanding the REE extraction mechanism in a two-phase system (TPS) will allow us to develop green, economical, and efficient processes to recover critical metals from secondary sources. The partitioning behavior of Nd, Pr, and Dy was investigated in different TPS consisting of an aqueous phase (diluted organic acid) and a hydrophobic eutectic phase. Figure 1 shows the extraction percentage (E%) of Nd in a TPS consisting of organic acid (citric, acetic, lactic, levunilic, or formic acid) and hydrophobic eutectic solvent (decanoic acid (DA) + trioctylphosphine oxide (TOPO) or DA + thymol (THY). TPS with acetic and levulinic acid at a concentration of 0.10 mol L^{-1} was best for Nd extraction, whose E% was 77 and 74 %, respectively. The similarity in E % in the presence of these two acids can be explained by the similarity in their pKa 4.76 and 4.59, respectively. Figure 2 shows the influence of the presence of Pr, Dy, and Fe (element predominant in the NdFeB magnet, about 62 %) on Nd extraction. In the presence of Pr, there is a decrease in the Nd extraction. Conversely, in the presence of Pr, Fe, and Dy, the extraction of Nd is favored. In this case, it is believed that the Nd partition was influenced by an increase in the amount of nitrate resulting from adding each metal salt to the TPS.[1] To verify the extraction of metals from NdFeB magnets' residues without nitrate's influence. One liquor was obtained by dissolving the magnet with levulinic acid. This liquor was mixed proportionally with a eutectic phase of TOPO+DA and another THY+DA. Figure 3 shows the E% of REE, transition elements, and boron in two TPS. The extraction and separation of REE was more efficient using the TPS consisting of THY+AD. The best extraction and separation for REE occurs because, under these pH conditions, the formation of the REE-DA complex is favored.[2]

Using levulinic acid, less harmful to health and the environment, in the dissolution stage associated with HES THY + DA, efficiently separated REE from the transition elements and boron.

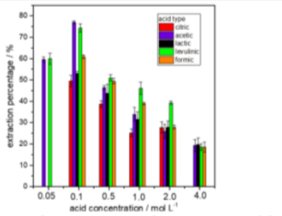

Figure 1. Element extraction versus acid concentration

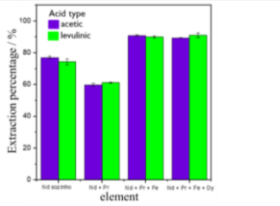

Figure 2. Nd extraction in the presence of other elements

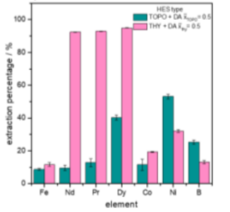

Figure 3. Element extraction in different TPS

Acknowledgements
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Poster P_A2.4

Ultrathin films of $[C_1C_1Im][Tf_2N]$ on Au(111) and Pt(111) – adsorption and thermal behavior studied by ARXPS

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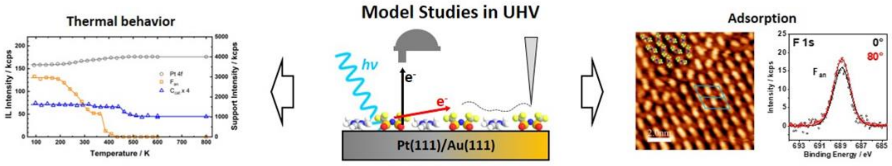
Solid Catalyst with Ionic Liquid Layer (SCILL) is a catalytic concept using the advantageous properties of Ionic Liquids (ILs) coated onto a solid catalyst to improve its catalytic performance such as selectivity and long-term stability.[1] Despite the successful application of SCILL in industrial processes, like the selective hydrogenation of acetylene,[2] fundamental knowledge on how these systems work on a molecular scale is still lacking. In this context, our group focuses on the study of model systems to get insights into the IL-metal interface properties.

In this work, the IL 1,3-dimethylimidazolium bis[(trifluoromethyl)sulfonyl]imide – $[C_1C_1Im][Tf_2N]$ – was investigated on the less reactive Au(111) and the more reactive Pt(111) surface under ultra-high vacuum (UHV) conditions (Scheme 1). Ultrathin films (d < 1 nm) of the IL were prepared in situ via physical vapor deposition (PVD) and characterized by angle-resolved X-ray photoelectron spectroscopy (ARXPS). Complementary information is gained by scanning probe microscopy (AFM/STM).

On Au(111), the IL forms an intact wetting layer with the imidazolium-cations lying flat on the surface and the anions being adsorbed in *cis*-conformation with oxygen pointing towards the surface and the CF_3-groups towards the vacuum.[3] At room temperature, this IL shows 2D growth in the wetting layer regime, and also at higher coverages. Heating the IL initially leads to structural changes,[4] then at 350 K desorption of multilayers followed by desorption of the strongly bound wetting layer at 429 K. Switching to the more reactive Pt(111) surface, an intact wetting layer can be obtained at 200 K with the ion pairs in a similar orientation as on Au(111). Initially, the growth behavior is similar to Au(111) (almost perfect 2D), but it switches to moderate 3D at coverages higher than 2 layers.[5] Heating a wetting layer to room temperature leads to partial decomposition, where the anion decomposition products partly desorb, while cation-derived products form a carbon residue stable up to 800 K. Interestingly, these carbon residues partially seem to passivate the platinum surface, resulting in co-adsorbed intact IL remaining stable even up to room temperature.[5]



Scheme 2: Model studies of $[C_1C_1Im][Tf_2N]$ on Au(111) and Pt(111).

Acknowledgements

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Poster P_A2.5

Interfacial nanostructure and wetting behavior of ionic liquid mixture films on solid surfaces

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Ionic liquids (ILs) have been widely used for energy storage and conversion devices due to their negligible vapor pressure, high thermal stability, and outstanding interfacial properties. In particular, the unique characteristics exhibited by ILs under vacuum conditions have attracted considerable interest in their study.[1] Understanding the interaction between ILs and solid supports is of principal importance for thin film applications.[2] While numerous researchers have extensively investigated the adsorption, growth, and stability of ultra-thin films of different IL classes on metal surfaces in recent years, the focus has primarily been on pure ILs.[3-6] In this study, our objective was to broaden the scope by exploring IL mixtures. These systems offer a greater potential for targeted applications of ionic liquid films and present a whole new set of fundamental scientific inquiries.[6]
In this work, we investigated the co-evaporation of two ILs, $[C_2C_1im][OTf]$ and $[C_8C_1im][OTf]$, by varying the film composition and thickness. The formation of an ionic liquid mixture film was achieved through simultaneous deposition of the pure ILs using a customized physical vapor deposition (PVD) technique.[7,8] The film morphology (micro- and nanodroplets and coalesced films) was evaluated by high-resolution scanning electron microscopy (SEM). We examined the adsorption, nucleation, and growth of the mixture film on different substrates, including glass surfaces coated with indium tin oxide (ITO), ITO/glass coated with silver (Ag), and ITO/glass coated with gold (Au). Our findings revealed that enrichment of C_8C_1im in the mixture enhanced droplet coalescence mechanisms on ITO and Ag/ITO surfaces, while also contributing to the formation of compact and coalesced films on Au/ITO surfaces. Furthermore, the ionic liquid mixture film demonstrated superior capabilities in inducing crystallization of organic semiconducting films under vacuum when compared to the use of pure ILs.

Acknowledgments
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Poster P_A3.1

Anion effect on the thermophysical behavior of alkylsilane-based ionic liquids

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The use of an alkylsilane chain, in substitution of the more common *n*-alkyl chain in ionic liquids (ILs), has been revealed as an efficient way to reduce the viscosity of this kind of substance. It has also been shown that depending on the used anion, the magnitude of this viscosity decrease is different[1,2]. In this work, we studied some of the thermophysical properties of ILs composed by the [(SiCSiC)C_1im] cation, paired with different anions. The structures of the cation and the different studied anions are represented in Figure 1.

The studied thermophysical properties include the glass transition, melting point, thermal decomposition, heat capacity, and volatility. Differential scanning calorimetry (DSC) was used to study the glass transition and the melting properties (melting point, enthalpy, and entropy of melting). The thermal decomposition of the ILs was studied by thermogravimetric analysis (TGA). Two different techniques were used to determine the heat capacity of the liquid phase of these ILs: differential scanning microcalorimetry was used to determine the heat capacity in the temperature range from T = 283 K to T = 333 K, and a high-precision drop microcalorimeter[3] was used to determine the heat capacity at the temperature of T = 298.15 K. When possible, Knudsen effusion apparatus coupled with quartz crystal microbalance (KEQCM)[4] was used to study the volatility of the ILs.

Glass transition was obtained for all ILs, with [NTf_2] and [OTf]-based ILs having, respectively, the lowest and highest Tg. The [$N(CN)_2$]-based IL presented the highest melting point. The thermal stabilities of the [$N(CN)_2$] and [$C(CN)_3$]-based ILs were found to be significantly lower than those of the other studied ILs. The volatilities of the [$B(CN)_4$] and [OTf]--based ILs were found to be lower than that of the [NTf_2] based IL. The difference in heat capacity found between the various ILs is identical to that found in the conventional *n*-alkyl-based ILs.

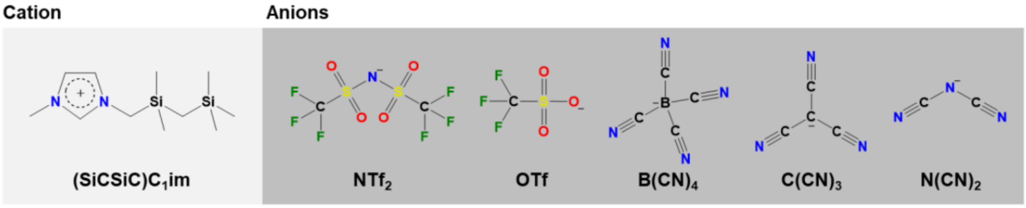

Figure 1: Structures of the cation and different studied anions.

Acknowledgements

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Poster P_A3.2

Calorimetric and crystallographic phase-behavior study of selected 1-butylpyridinium ionic liquids

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The applicability window for ionic liquids (ILs) is limited by their melting or glass transition temperatures and their decomposition temperatures. The mentioned temperatures and other phase behavior data are thus the basic building blocks for the compounds' successful introduction to industrial use.

As a follow-up to our previous efforts to thoroughly characterize the phase behavior of ionic liquids,[1-4] commercially available ILs based on 1-butylpyridinium cation coupled with eight different anions were chosen. Even though pyridinium ILs are generally less stable than imidazolium ones,[5] they act as promising, high-efficiency separation agents for alkane mixtures.[6] Nevertheless, the lack of solid thermodynamic data for the selected ILs prevails, as melting points are known only for three of them[7-10] as well as heat capacities.[7, 9, 11] Of all the studied ILs, crystal structures are available only for 1-butylpyridinium hexafluorophosphate in the Cambridge Structure Database (CSD) (identifiers LOFQOP and LOFQOP01) suggesting the existence of two polymorphic structures of this compound.

The compounds were provided by vendor with sufficient purity and therefore the samples were only vacuum dried to reduce their water content, transferred to, and handled under a dry nitrogen atmosphere. For the phase behavior study, a differential scanning calorimeter (DSC) was used. Three of the studied compounds did not crystallize during any of the experiments, while four exhibited polymorphic behavior. Where appropriate, temperature variable X-ray powder diffraction was employed to confirm the phase behavior deduced from the DSC experiments. Crystal structures were successfully determined for two ILs. 1-Butylpyridinium hexafluorophosphate exhibited a rare second-order lambda transition with a maximum of 272.7 K, which was in detail described by DSC and X-ray powder diffraction leaving no ambiguities about its nature. Finally, the heat capacities of the crystalline and liquid phases were measured by means of Tian-Calvet calorimetry.

Acknowledgements

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Poster P_A3.3

On thermal stability of amine and carboxylic acid-based protic ionic liquids

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Due to well-known advantageous properties as well as a theoretical possibility of property design ionic liquids (IL) potential phase change materials (PCM) for latent heat thermal energy storage.[1] For the development of a PCM a clear understanding of thermal behavior of different ILs is needed. Protic ionic liquids (PIL) based on amines and carboxylic acids have various properties according to the data found in the literature. PILs are generally synthesized by a one-step proton transfer reaction and since carboxylic acids are classified as weak acids the proton transfer energy is not considered high enough to form a highly thermally stable compound[2]. Low thermal stability has been observed for acetate PILs[3]; however, it is not systematically studied how this property changes when ammonium cation is combined with other carboxylate anions.

To get a better understanding of the thermal stability of this type of PILs a list of amine and carboxylic acid-based PILs with different structures and ΔpK_a range of 3.91-6.88 were synthesized (Figure 1) and studied with nuclear magnetic resonance spectroscopy (NMR) and thermogravimetric analysis (TGA). The first results from dynamic TGA suggested that PILs synthesized from reagents with higher boiling points and/or higher ΔpK_a values are more stable, e.g., ethylammonium acetate extrapolated onset temperature (T_{onset}) of the TGA curve was 100.1°C compared to T_{onset} of ethylammonium glycolate of 146.7°C. Additionally, the mass change was not in a clear single step in the case of glycolate PILs. NMR results of samples heated up to 110°C and held at this temperature for 15 minutes showed no change in structures and chemical shifts. Calculated molar ratios from NMR peak integrals changed at most 2% outside calculation uncertainty. Overall, to better understand the thermal behavior and stability of synthesized PILs and estimate this to new combinations of amines and carboxylic acids differential scanning calorimetry will be applied. In addition, for identifying evaporation products headspace technique will be used. Further NMR investigations for liquid structures will be held.

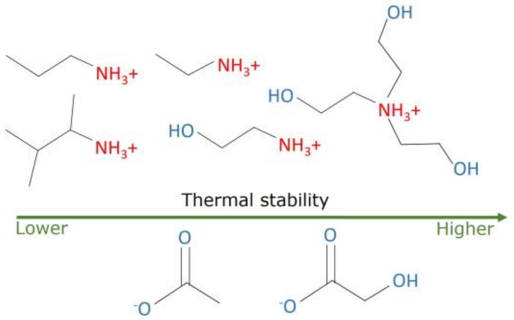

Figure 1: General trend in thermal stability among cation and anion combinations studied according to dynamic TGA onset temperatures.

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Poster P_A3.4

Thermodynamic study of a mixture of two tertiary alcohols - A pathway for the design of type V deep eutectic solvents

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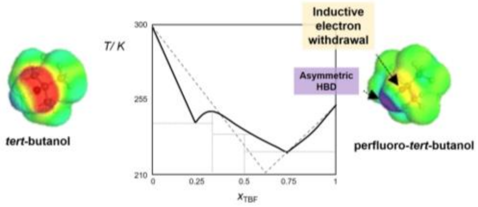
Contrary to what sometimes is found in literature, deep eutectic solvents (DESs) are not a type of ionic liquid (IL) or a similar compound.[1] In true, DESs are not pure compounds as ILs but liquid systems originated by the mixture of pure compounds for which the eutectic point temperature is lower than the one expected from ideal behavior.[1–3] Despite the fact that many DESs have ionic constituents and many properties in common with ILs, they can also be constituted solely by molecular compounds such as type V DES.[4,5] As in ILs, their properties can be tailored or fine-tuned, in this case by judiciously selecting their constituents and varying the molar ratios. The selection of constituents that interact through strong cross-intermolecular interactions favors the existence of negative deviations to the thermodynamic ideality and the existence of a lower eutectic point temperature. Especially for type V DESs, this usually translates into the existence of strong HBD–HBA interactions and weak HBD–HBD or HBA–HBA association.[4,5]

In this work, the excess molar enthalpies and volumes for the *tert*-butanol + perfluoro-*tert*-butanol binary mixture (TBH + TBF system) are presented and discussed. The interpretation of these results and its insight into the comprehension of the SLE diagram of the TBH + TBF system (scheme 1) is supported by the use of MD simulations. The results show significant negative deviations in the excess molar enthalpies, as in thesolid–liquid phase transitions, as well as positive deviations in the excess molar volumes.[6] Overall, the results evidence the major effect of the changes in hydrogen bonding behavior from the pure compounds to the mixtures (with the formation of a “strong” cross hydrogen bond between the oxygen of TBH and the hydrogen of TBF) and the secondary role of the phobicity between the hydrogenated and fluorinated parts.[6] The effects of acidity, stereochemical hindrance, and phobic effects in these binary mixtures are discussed, providing indications of interesting strategies to design and fine-tune type V DES.



Scheme 1: Sold-liquid equilibrium phase diagram of the TBH+TBF binary system and illustration of its constituents.

Acknowledgements

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Poster P_A4.1

Deposition and surface dynamics of ionic liquids in confined spaces

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This study employed vapor deposition, utilizing a customized apparatus[1,2], to coat various surfaces with distinct morphologies and physicochemical properties using ionic liquids (ILs). The surfaces included organic semiconductor materials (OSCs), particularly TCB and TDAB[3,4] (Figure 1), as well as pentacene and perylene[5], in addition to indium-tin-oxide (ITO), gold-coated quartz crystals and anodic aluminum oxide (AAO) porous membranes. Surface treatment with argon plasma was used to manipulate the positioning and morphology of the ILs. The study compared the effects of long and short-alkyl-chained imidazolium ILs[5,6]. The ILs studied demonstrated a significant affinity for the OSCs and were found to assist their crystallization under vacuum. In the case of the gold-coated quartz crystal microbalance, the research revealed that the ion pairs moved into confined spaces but, upon filling these spaces, formed droplets on the surface, ultimately rendering the balance non-functional[7,8]. The pore arrangement on the AAO membranes was shown to be of significance to the surface interaction with ILs. Overall, these findings provided insights into the dynamics of ionic liquids on both porous and non-porous surfaces. This knowledge could be useful for engineering nanostructures consisting of ionic liquids in nanoconfined spaces.

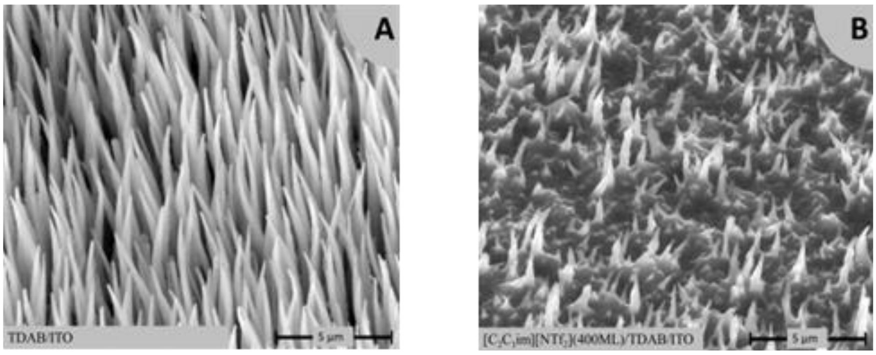

Figure 1: Micrographs of 1,3,5-tris(diphenylamino)benzene (TDAB) films, both without (A) and with (B) ionic liquid confinement.

Acknowledgments
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Poster P_A4.2

EMI TFSI effects on structural and mechanical properties of a composite material based on graphene oxide aerogels

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A few years ago, a synthetic technique to produce Sn nanoparticles in an ionic liquid (IL)[1] was reported by our group. Nanoparticles (NPs) exhibited a 10 nm mean diameter with a very narrow size distribution. Results obtained from electrodes which were prepared using tin NPs as active material in Li-ion batteries were found interesting, but wanting as common binders and additives limited the accessibility of the nanoparticles and failed to prevent their structural damage during the cycling of the batteries. We could establish through relaxometry measurements privileged interactions with the cation, the 1-methyl-3-ethylimidazolium, at the surface of NPs that could explain NPs uniformity as their growth during reduction could be controlled by the IL playing both solvent and capping agent parts. This was our starting point to produce more elaborated systems, in order to improve containment, using graphene-based structures.

Graphene and its derivatives can organize in several different types of 3D structures with varying and tunable characteristics.[2] These structures are active as Li hosts, flexible and conductive, and they can adapt to the expansion and contraction in the composites all the while maintaining the electrical contact throughout the electrode. Considering the fact that the morphology of the material has a large impact on the improvement of its properties, we investigated various conductive graphene-based scaffolds such as membranes and aerogels obtained by freeze casting techniques[3] EMI TFSI could be combined with graphene-based matrix and we performed some preliminary experiments. The mixed aerogels were subjected to thermal annealing at 200°C for 2 h under vacuum. The obtained aerogel monoliths exhibited noticeably enhanced mechanical properties and a capacity much higher than graphite in coin-cell batteries. We decided to further study several binary composite materials made of graphene oxide (GO) aerogels and EMI TFSI and more specifically the influence of the graphene oxide concentration and the mass percentage of ionic liquid on the structural and mechanical properties of the material. The GO aerogels and composite materials before and after annealing were examined via several techniques and characterized at each stage. Mechanical tests were also performed to quantify the relationship between stress and axial strain allowing to extract the Young's modulus.

Acknowledgements
Authors acknowledge José Gomes, Sandrine Leclerc, and Katsuya Komiyama.

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Poster P_A4.3

Unlocking plastic recycling: exploring eutectic solvents for selective polymer dissolution by COSMO-RS

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The widespread use of plastics (polymers) has played an important role in promoting global economic progress in recent years, with annual production exceeding 350 million tons. Nevertheless, the recycling of mixed waste and multi-layered materials remains a major challenge, primarily due to the complicated nature of the separation process. As a result, only 18% of these materials are currently recycled.[1] One promising approach to solving this problem is the use of a selective dissolution-precipitation technique, although the use of conventional organic solvents is still the most common choice. Recently, the use of alternative solvents has attracted some attention due to the search for more environmentally friendly alternatives, and some of them have already been shown to selectively dissolve and precipitate polymers.[2,3] In this context, eutectic solvents (ES) have been mentioned as a promising option for dissolving and recycling polymers, but they pose a particular challenge due to the large number of hydrogen bond acceptors (HBA) and hydrogen bond donors (HBD) and their possible combinations.

Therefore, the aim of this work was to identify some selective and effective ES for polymer dissolution of petroleum-based polymers such as high-density polyethylene (HDPE), polypropylene (PP), polyethylene terephthalate (PET), and polyvinyl chloride (PVC), as well as bio-based polymers such as polylactic acid (PLA) and polyethylene 2,5-furandicarboxylate (PEF), using the COndutor-like Screening Model for Realistic Solvents (COSMO-RS) thermodynamic calculation tool for this purpose.

First, a total of 2360 combinations of 40 HBAs and 59 HBDs were evaluated for each polymer, and solvent-polymer affinity was assessed by predicting logarithmic activity coefficients at 100˚C. After in-silico pre-selection of ES, wet tests were performed dissolving the polymers in ES, which had the most negative logarithmic activity coefficient, to evaluate the accuracy of the results from COSMO-RS. The results showed that hydrophobic ES with long-chain alkyl alcohols (decanol, dodecanol, tetradecanol, hexadecanol) as HBD were effective for dissolving HDPE and PP. Monoterpenes such as thymol and carvacrol as HBA were effective for the dissolution of PET, PLA, and PEF. Thymol:formic acid dissolved PET, but not HDPE and PP, which is a method for selective separation of polymer mixtures. It was also found that different temperatures selectively dissolved PLA, PET, and PEF. Further studies for PVC are underway. Overall, this work suggests that the selection of appropriate ES for efficient and selective dissolution of complex polymer blends, typically found in municipal waste streams and multilayer films, may represent an advance in polymer recycling and recirculation.

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Poster P_A4.4

The adsorption and self-assembly of organics' from ionic liquid electrolyte

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The formation of adlayer of molecules on a well-defined solid surface is at the heart of numerous applications such as sensors, single-molecule junctions, and corrosion protection[1]. The structure of the adlayer is determined by the interplay of forces acting between the electrode, adsorbate, and the surrounding environment. Furthermore, the adlayers can be controlled by applying electric potential, which alteration can lead to the reorganization of the interfacial structure.

A significant number of adlayer studies have been carried out in a vacuum, providing insights into the driving principles behind self-organization. It has been shown that the adsorbed nanostructures can form aggregates, wires, and densely-packed networks by selecting proper adsorbates and electrodes[2–4]. In addition to the solid-vacuum interface, the adlayers can be also formed at the solid-liquid interface. In this regard, ionic liquids are an excellent medium due to low vapor pressure and good electrochemical stability[5]. While advantageous, there have been only a limited number of studies investigating the adsorption of organic molecules at the solid-ionic liquid interface.

In the given presentation, we will discuss our latest studies, investigating the bipyridine adsorption and adlayer formation from EMImBF$_4$ ionic liquid at Bi(111), Sb(111)[6], and Cd(0001)[7] surfaces. In these studies, we have combined different electrochemical characterization techniques (*in situ* scanning tunneling microscopy and electrochemical impedance spectroscopy) with density functional theory calculations to provide insights into the formed adlayer structures. The results highlight the complex nature of the adsorption and organization processes, as the findings observed in aqueous solution cannot be straightforwardly carried over to ionic liquid electrolyte-based interfaces.

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Poster P_A5.1

Poly(ionic liquid) compounds as multifunctional cement additives

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The intensive development of cement additives pushed the research toward designing new task-specific materials aimed at enhancing cement strength, workability, and durability. Introduction of ionic species into cement composition can offer the consistent dispersion of inorganic oxides featuring both micrometric and nanometric structures within the cement matrix, consequently leading to modifications in the structural, mechanical, and bactericidal characteristics of the composite.[1] According to the literature coordination of imidazolium type poly(ionic liquid) (PIL) with $CuCl_2$, $FeCl_3$ or $ZnCl_2$ increases the antibacterial effect of the ionic materials.[2] The advantageous approach is to combine metal-containing ionic liquid's features with polycarboxylate plasticizing properties to achieve multifunctional cement admixture.

In this study, we have developed ionic polycarboxylate materials by atom transfer radical copolymerization of selected ionic liquid monomers based on choline and imidazolium cations with poly(ethylene glycol) methyl ether methacrylate (PEOMA) of different molecular weights. Ionic polycarboxylate materials were synthesized in various IL:PEOMA monomers molar ratios, such as 85:15, 50:50, and 15:85. To mimic the commercially available plasticizers, we designed copolymer including methacrylic acid as the next unit of ionic polycarboxylate admixture (Figure 1). The structures of new copolymers, degree of polymerization, and conversion, were confirmed by ^{1}H NMR. The absolute molecular weight and dispersity values of the novel ionic polycarboxylate derivatives were determined by size exclusion chromatography with light scattering detection, and the thermal behavior was investigated using thermogravimetric analysis. The developed ionic polycarboxylate copolymers can be expected to increase the affinity of the admixture to new cement binders. Additionally, their plasticizing properties will enable a reduction in the water–cement ratio, leading to an increase in compression strength and improvement in the tightness and durability of the cement matrix over a long-life cycle, making it a more sustainable material.

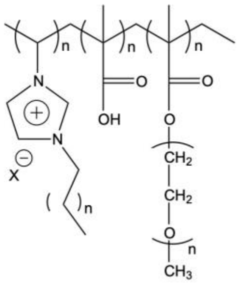

Figure 1: Structure of ionic polycarboxylate copolymer.

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Poster P_A5.2

Triblock copolymers as versatile constituents of double stimuli-responsive ionic-liquid-based aqueous biphasic systems

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As an alternative to conventional liquid-liquid extraction, Albertsson proposed aqueous biphasic systems (ABS)[1]. ABS is formed by combinations of polymer-polymer, polymer-salt, or salt-salt, with a third component, water, and these systems have shown successful application for the extraction, separation, and purification of (bio)molecules[2]. The integration of ionic liquids (IL) in ABS amplified the system design ability and improved the conventional ABS characteristics. Also, the addition of compounds with reversible characteristics allows the increase of applications of these systems. This work proposes the use of triblock copolymers as structurally versatile constituents to develop double stimuli-responsive aqueous biphasic systems (ABS) comprising ionic liquids (ILs). In this study, phase diagrams of ABS comprising cholinium acetate ([Ch][Ac]) and triblock copolymers composed of polyethylene oxide (PEO) and polypropylene oxide (PPO) with adjustable compositions of PEO, 20% (PE 6200), and 40% (PE 6400), were determined by the cloud point titration method at several temperatures (25 - 45 °C) and pH (5 - 7). The results allowed to conclude that the systems present a response to both stimuli, temperature, and pH simultaneously. These ABS present, for all the tested pH conditions, a Lower Critical Solution Temperature (LCST)-like behavior. Therefore, the developed systems can be applied as adaptable separation and purification systems, with great relevance for the industry.

Acknowledgements

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Poster P_A5.3

Novel ionic liquid-based aqueous biphasic system for the selective recovery of platinum group metals from spent automotive catalytic converters

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In the Critical Raw Materials (CRM) list of the European Union, Platinum Group Metals (PGM) - platinum, palladium, rhodium, osmium, iridium, and ruthenium - are recognized as materials with a notably high supply risk[1]. One of the most prominent applications of PGM is in the production of automotive catalytic converters (CC)[2], playing a crucial role in neutralizing pollutants generated through combustion processes. Over the past few decades, driven by the rising global vehicle production rates and the enforcement of more stringent environmental regulations, there has been a rapid and substantial increase in the number of spent automotive catalytic converters (SACC)[3]. Consequently, SACC poses both a substantial waste management challenge and a potential secondary source of strategic and critical materials. However, the recycling rate of PGM from SACC within the EU reaches only around 50%[4]. PGM can be recovered from SACC through a hydrometallurgical process comprising three main steps: leaching (dissolution), purification (isolation of metals), and refining (recovery of purified metals). In this work, an alternative leaching step is applied, using aluminum salts to dissolve the metals instead of the traditional hazardous highly acidic solutions. For the purification, multistep solvent extraction is proposed using ionic-liquid-based aqueous biphasic systems (IL-based ABS). ABS consists of two water-rich phases that are immiscible and created by combining hydrophilic ILs with salts, polymers, or even acids. The high salt concentration in the leachate is the key to the ABS phase formation and the presence of IL is of special interest since they can stabilize metal complexes not typically available in water. In the first instance, the target is to separate PGM from other metals exploiting the anionic chloro-complexes formed between them and the IL. Next, the extraction targets the separation between the PGM, namely platinum, palladium, and rhodium. Prominent results are being obtained with IL containing phosphonium cations, such as tetrabutylphosphonium chloride ($[P_{4444}]Cl$) and tributyltetradecylphosphonium chloride ($[P_{44414}]Cl$). Their capacity to create stable complexes with platinum facilitates an effective extraction of this element while also indicating the possibility of recycling the leaching solution due to the non-extraction of aluminium.

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Poster P_A5.4

Association and coacervation of stimuli-responsive host-guest complexes driven by ionic interactions

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Host-guest (or inclusion) complexes are supramolecular assemblies composed of a macrocycle (the host) with a guest molecule inserted in its cavity. Their formation is driven by non-covalent interactions, and among them, ionic interactions may play a pivotal role. These complexes may in turn self-organize into more complex nano or micro-scale structures that are easily tunable and often stimuli-responsive, which offers the opportunity to construct a diversity of functional soft materials, useful for example in solubilization, biosensing, and drug delivery [1, 2]

Strong associative phase behavior in host-guest complexes may lead to coacervation, a type of liquid-liquid phase separation where one phase is enriched in the solvent and the other in the solute.[3] Coacervate nano and microdroplets, containing the host-guest complexes, can be used for encapsulation and controlled release of molecules (including the guest). Herein, we present a host-guest complex system, the formation of which is driven by electrostatic interactions, that originate coacervates able to disassemble through a pH-gated photochemical reaction (Figure 1a). The ionic components of this inclusion complex are a penta-anionic calixarene (SC$_4$), as the host molecule, and a cationic 2-hydroxychalcone derivative (C$_6$NCh), as the guest and photosensitive molecule (Figure 1b).[2, 4] Initial phase screening shows that coacervates are formed when [SC$_4$]/ [C$_6$NCh] = 1/3-1/5. Under these conditions, the coacervates consist of dispersed particles in solution with an average diameter of ~250 nm and an overall negative ζ-potential of -35 mV. Upon near-UV irradiation under acidic conditions, which leads to the conversion of the chalcone into a flavylium ion, the complex is disturbed and the coacervates are dissolved in solution. Hence, we have at hand a dual light and pH-responsive coacervate system that can be exploited for molecular encapsulation and release.

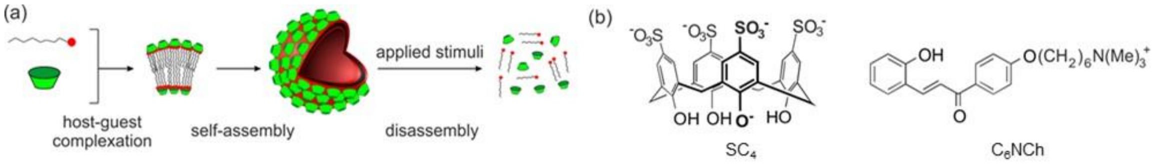

Figure 1: (a) Self-assembly and disassembly of host-guest complexes. (b) Macrocycle and amphiphilic guest used in this work.

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Poster P_A5.5

Efficient decontamination of chemical warfare agents by ionic liquids

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Chemical warfare agents (CWAs) are still being used as destruction weapons, posing danger not only to military personnel but also to civilian populations, as witnessed in numerous terrorist attacks across different nations. Although the World’s first multilateral disarmament agreement, Chemical Weapons Convention (CWC), prohibited the development, production, and storage of CWAs, there are still occasional reports of their use in certain countries.

In the event of a CWA attack, swift response actions are imperative to mitigate casualties. In such scenarios, the ability to promptly detect and identify CWAs is crucial but equally pivotal is the thorough decontamination of materials, personnel, equipment, and the entire affected area. Numerous decontamination methods have been reported, however, the use of bleach-based decontaminants in the field is still prevalent due to their cost-effectiveness and broad-spectrum efficacy against different CWAs. However, the drawback of these systems include their potential corrosiveness to surfaces, toxicity to human health, and harm to the environment.[1,2]

This work reports an innovative approach to CWAs decontamination, centered on novel materials based on Ionic Liquids (ILs). These materials display the capacity to adsorb and absorb CWAs from contaminated surfaces or from the atmosphere into their interior. As proof of concept, several ILs were synthesized and rigorously tested as sorbents for CWAs simulants, yielding not only remarkably high sorption rates but also high degradation efficiency.

Acknowledgements

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Poster P_B1.1

Optimal cationic structure of acidic ionic liquids for synthesis of porphyrins

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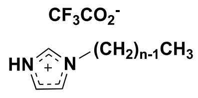
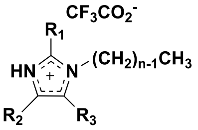
Porphyrins are attractive substances for a wide range of applications, including electroluminescence devices, metal catalysts, and the development of organometallics. Among various porphyrins, tetraphenylporphyrin, TPP, has been widely synthesized because of its simple synthetic procedure. Refluxing propionic acid containing benzaldehyde and pyrrole followed by filtration of precipitated TPP obtained in 20% yield (Adler method). However, this method generates a large amount of waste acid after the reaction. Therefore, we have reported several green synthesis methods for TPP using acidic ionic liquids (ILs) instead of propionic acid used in this method.[2] We have developed a method for the preparation of TPP using acidic ILs composed of 1-alkylimidazoles and strong acids such as CF_3COOH, HBF_4, and CF_3SO_3H. In the case of using $[HC_4im][CF_3CO_2]$, TPP was obtained in 15% yield, which was comparable to that obtained with propionic acid. Furthermore, we focused on the anion structures of acidic ILs, $[HC_4im][X]$ to determine the optimal structure for TPP synthesis.[1] This study revealed that the optimal structure of the anion is $[CF_3CO_2]^-$. However, no study has been reported evaluating the correlation between the cationic structure of acidic ILs and their ability to generate porphyrins in the Adler modified method using acidic ILs. Herein, we investigated the optimal acidic ILs structure for the modified Adler method, focusing on their cationic structures.

(a) Effect of alkyl chain length of acidic ILs on TPP synthesis



$[HC_nim][CF_3CO_2]$
(n = 1, 4, 6, 8, 10, 12)

(b) Effect of outer substituents on the imidazolium ring of acidic ILs on TPP synthesis

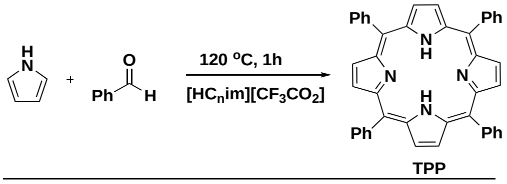


$[HC_1mim][CF_3CO_2]$: n = 1, $R_1 = CH_3$, R_2 = H, R_3 = H
$[HC_1m_3im][CF_3CO_2]$: n = 1, $R_1 = CH_3$, $R_2 = CH_3$, $R_3 = CH_3$
$[HC_1(CN)_2im][CF_3CO_2]$: n = 1, R_1 = H, R_2 = CN, R_3 = CN
$[HC_8mim][CF_3CO_2]$: n = 8, $R_1 = CH_3$, R_2 = H, R_3 = H

Figure 1 Structures of acidic ILs used in this study.

The investigation in $[HC_nim][CF_3CO_2]$ (n=1-12) with different lengths of alkyl groups at the N(1) position of imidazolium showed that the highest yield of tetraphenylporphyrin (20%) was obtained when the alkyl chain length was C8, which indicated that $[HC_8im][CF_3CO_2]$ is the optimal ionic liquid for the tetraphenylporphyrin synthesis (Table 1). In addition, we also investigated the influence of electron-withdrawing and electron-donating substituents at the C(2), C(4), and C(5) positions of the imidazolium cation of the acidic ionic liquids on the synthesis of tetraphenylporphyrins. The highest tetraphenylporphyrin yields were obtained in $[HC_8mim][CF_3CO_2]$, which suggested that the imidazolium cation with an octyl group at the N(1) position and a methyl group at the C(2) position was the optimal structure. We are currently continuing to investigate the structure of acidic ILs that produce TPP even more effectively in order to achieve green and efficient TPP synthesis.

Table 1 Effect of alkyl chain length on TPP synthesis using acidic ILs.



Entry	n	Yield / %
1	1	4.7
2	4	13
3	6	15
4	8	17
5	10	14
6	12	14

Acknowledgements
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Poster P_B1.2

Selective extraction of naringin and rutin from orange peels using aqueous solutions of biobased ionic liquids

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Due to the growing population around the world, there is an increasing food demand. In this situation, businesses are straining their food supply chains to the maximum, generating a lot of byproducts that could be potential sources of added-value compounds. The scientific community is currently working to develop sustainable extraction platforms to produce high-value bioactive compounds (HVBCs) from food waste, within the circular economy concept as a result of the growing socioeconomic awareness. The development of novel integrated processes is a priority to address contemporary bioeconomy concerns. This research aims to boost the value of orange peels, a food industry waste, by isolating high-value phenolic compounds using novel biobased ionic liquids derived from glycine-betaine, able to increase the solubility of rutin and naringin by several orders of magnitude. Rutin and naringin were efficiently and selectively extracted, enabling the reuse of the solvent, using experimental design to optimize extraction conditions. The created method is a competitive replacement for established procedures using volatile solvents.

Acknowledgements

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Poster P_B1.3

Ionothermal syntheses of cluster-based tellurido mercurates

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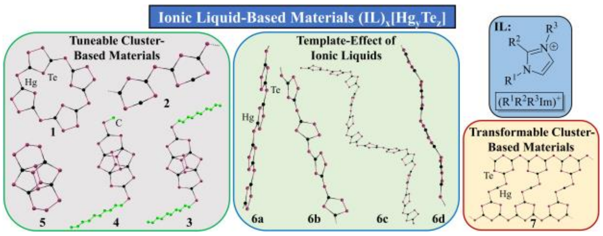
The synthesis of compounds containing chalcogenido metalates has been the subject of active research in recent years. Chalcogenido metalate-based compounds exhibit a wide range of particular chemical and physical properties, including photoluminescence, (photo)conductivity, and photocatalytic potential. This can be attributed to their large variety of structural motifs and the diverse dimensionalities of the latter. Corresponding research activities include the development of various synthetic approaches.[1,2] In our group, we are focusing on ionothermal synthesis using imidazolium-based ionic liquids (ILs, general form: $(C_m(C_n)C_oIm)X$; m, n, o = alkyl chain length at positions 1, 2, or 3 of the Im = imidazolium ring, respectively; X = anion), which have several advantages, such as usage at moderate temperatures, high efficiencies, and modifiability.[2,3] In addition, this technique enables facile fine-tuning of heavy-element structures in metalate materials.[3,4] Here, we present four related studies in the context of cluster-based materials from ILs, which are summarized in Scheme 1.

First, by reactions of $Na_2[HgTe_2]$ or $K_2[Hg_2Te_3]$ with $(C_xC_1Im)[BF_4]$ (x = 10, 12, 14, 16), we received $(C_xC_1Im)_8[Hg_8Te_8(Te_2)_4]$ (**1**), a family of compounds with an inorganic anionic homolog of the porphyrin structure, and $(C_xC_1Im)_2[Hg_3Te_4]$ (**2**), comprising a one-dimensional six-membered ring as its metalate substructure. The chain length of the alkyl groups attached to the Im rings served to fine-tune the optical absorption and electrical conductivity properties.

Second, ILs can act as non-innocent reaction media. Treatment of $Na_2[HgTe_2]$ or $Na_2[Hg_3Te_4]$ with $(C_{10}C_1Im)[BF_4]$ afforded decylation in $(C_{10}C_1Im)_6[Hg_6Te_6(Te_2)_2(TeDec)_2]$ (**3**), methyl-/decylation in $(C_{10}C_1Im)_6[Hg_6Te_6(Te_2)_2(TeMe)(TeDec)]$ (**4**) and the formation of $(C_{10}C_1Im)_4[Hg_4Te_2(Te_2)_2(Te_3)_2]$ (**5**), comprising two Te_3^{2-} fragments instead of two $[HgTe_3C_{1/10}]^{3-}$ units. The latter led to a narrowing of the optical band gap. These compounds exhibit lamellar crystal structures caused by the long alkyl chains of the ILs used.

Third, further modification on the alkyl chains at the Im cation led to a series of compounds with one-dimensional chains based on five-membered rings: $(Cat)_2[Hg_2Te_2(Te_2)]$ (**6**; Cat = C_2C_1Im, C_4C_2Im, C_2C_2Im, $C_4C_1C_1Im$). The template effect of the cations induced structural differences in the anionic chains.

Finally, ILs can also be used for structural transformations. $(C_2C_1Im)_6[Hg_7Te_{10}]$ (**7**) consists of a one-dimensional anionic substructure based on two distorted six-membered rings that are connected by a linear $[HgTe_2]^{2-}$ unit. It was synthesized from $K_2[Hg_2Te_3]$ with $(C_2C_1Im)[BF_4]$ at room temperature. Transformation of **7** in the same IL at 80 °C for 20 h yields $(C_2C_1Im)_2[Hg_2Te_2(Te_2)]$ (**6a**).



Scheme 1: Overview of tellurido mercurate-based material compounds $(IL)_x[Hg_yTe_z]$ (**1**–**7**), prepared in ionic liquids (ILs).

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Poster P_B1.4

Solvent recovery in the process of deterpenation of citrus essential oils by liquid-liquid extraction with the ionic liquid 1-ethyl-3methylimidazolium acetate

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Essential oils obtained by cold pressing from citrus fruit processing waste are complex mixtures containing dozens of chemicals. Most components correspond to the categories of terpenes and oxyterpenes, while the other constituents are low molecular weight organic compounds (aliphatic alkanes, alcohols, aldehydes, ketones, esters, and acids) and non-volatile substances such as waxes and pigments. Although these essential oils are often used without further refinement in a varied number of applications in the food, cosmetic, and other industries, an important improvement in their chemical stability and preservation of their organoleptic properties can be achieved by the removal of the terpenes. The latter, albeit representing the largest percentage in the composition of the citrus essential oils, are responsible for the mentioned undesired effects. Thus, a concomitant advantage of a so-called deterpenation stage to improve the concentration of the oxygenated fraction would be a drastic reduction in the essential oil volume, with little or negligible effect on the organoleptic properties of interest of the product. Among different approaches, promising results have been obtained for the deterpenation of these oils by liquid-liquid extraction with ionic liquids (ILs).1-3 The efficient recovery of the solvent, critical for the viability of any liquid-liquid extraction process, is typically claimed as easy by distillation in the case of using an IL, due to its non-volatile character (as opposed to the volatile compounds mixed with it in the outlet streams of the extractor). However, such a statement must be validated only through knowledge of the corresponding phase equilibrium data, required for the appropriate engineering design of the recovery units.

In view of the important lack of data on the above-mentioned phase equilibrium data to assess the viability of the IL recovery from the extract of the liquid-liquid extractor in a citrus essential oil deterpenation process, the vapor-liquid equilibrium (VLE) of binary mixtures of a representative IL and a representative oxygenated compound (that is expected to leave the extractor in the extract along with the IL) has been investigated. In particular, the VLE data for 1-ethyl-3-methylimidazolium acetate (commonly abbreviated as [C2mim][OAc], and one of the ILs for which better liquid-liquid extraction results have been obtained to date) plus linalool, citral, or octanal have been experimentally determined under isobaric conditions at reduced pressure. From the results, it can be highlighted that the vapor phase is obviously constituted by just the oxygenated compound, and the bubble temperature increases significantly with an increase in IL concentration. Equilibrium temperatures could not be reached at high concentrations of IL, due to its limited thermal stability (5%-onset decomposition temperature: 154 ºC).4 The VLE data have been satisfactorily correlated by means of the NRTL model, enabling their implementation in the Aspen Plus process simulation software for the simulation of the corresponding solvent recovery flash distillation unit. This simulation has evidenced an important energy cost associated with this flash unit operation, which should be offset by an excellent deterpenation capacity of the IL in the extractor.

Acknowledgements
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Poster P_B1.5

Synthesis and physicochemical characterization of antimalarial surface-active ionic liquids

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Ionic liquids are a particular class of compounds that attract interest in medicinal chemistry due to the simplicity of their preparation. Novel structures with biological activity can be achieved through simple, cost-effective reactions.[1] Reusing old ionizable drugs and improving their characteristics can be achieved economically and simply by mixing them with molecules of opposite charge. This approach is attractive for reviving old antimalarials, not only because of the prevalence of malaria in low- to middle-income countries, but also because several of these drugs are associated with malaria parasite resistance. In this context, our work has been focusing on synthesizing ionic liquids with potential antimalarial activity by mixing antimalarial aminoquinolines, specifically chloroquine, and primaquine, with natural lipids.[2, 3] More recently, using an acid-base reaction between chloroquine and bile acids (Figure 1), we synthesized surface-active ionic liquids (SAILs), which proved to possess significant antiplasmodial activity *in vitro*. The presence of an amphiphilic anion in the ionic pair confers surface-active and self-aggregation properties to the ionic liquids. The interfacial and aggregations properties of these SAILs have been characterized by surface tension, electric conductivity, dynamic light scattering, and differential scanning microcalorimetry. Moreover, the interactions of SAILs with micelles of the block copolymer F127 have been studied with the aim of designing an efficient, robust, and biocompatible nanocarrier system for the encapsulation and *in vivo* release of these antimalarial ionic liquids.

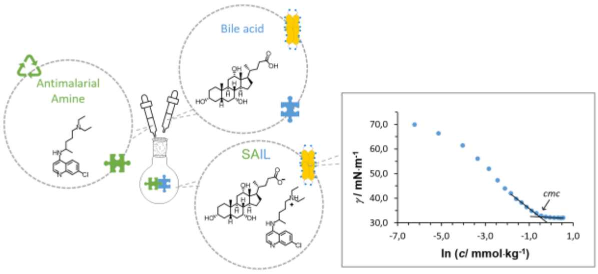

Figure 1: Synthesis and surface tension assays of a SAIL derived from the antimalarial drug chloroquine and cholic acid.

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Poster P_B2.1

Influence of deposition rate on the nucleation and growth of ionic liquid films

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The wetting behavior of ionic liquids (ILs) on the mesoscopic scale significantly impacts a wide range of scientific fields and technologies.[1-4] This study aimed to investigate the influence of deposition rate on the nucleation and growth of IL films fabricated through vacuum thermal evaporation on different solid substrates.[5] We examined four ILs comprised of an alkylimidazolium cation ($C_nC_1$im) paired with either bis(trifluoromethylsulfonyl)imide (NTf_2) or triflate (OTf) as the anion. The deposition was performed on indium tin oxide (ITO) and silver (Ag) surfaces. Additionally, the research focused on the co-evaporation of [C_2C_1im][OTf] and [C_8C_1im][OTf], with variations in the film composition and thickness. These systems hold substantial promise for tailored applications of ionic liquid films and open an entirely new realm of fundamental scientific investigations. Thin films of ILs were obtained through a customized physical vapor deposition (PVD) technique[6-7], based on the Knudsen effusion system, enabling precise control of the mass flow rate. Scanning electron microscopy (SEM) was utilized to analyze the morphology of the films.

Modifications in the mass flow rate were observed to exert a substantial influence on the wettability of the examined substrates by the pure ILs. More specifically, the findings suggested that increasing the deposition rate heightened the droplet coalescence mechanisms on the ITO surface, indicative of increased surface diffusion. In contrast, a relatively minor effect was noted on the Ag surface due to the better adhesion between the ILs and the metallic film. Notably, droplets originating from long-chain ILs exhibited enhanced coalescence on ITO surfaces, regardless of the deposition rate.

Acknowledgments

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Poster P_B2.2

Ultrathin ionic liquid films tailor the selectivity of 1,3-butadiene versus 1-butene adsorption on Pt(111)

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Ionic Liquids (ILs) have promising applications in catalysis: In Solid Catalysts with Ionic Liquid Layer (SCILL) systems, IL thin films are used to coat the catalytically active metal, and thereby modify the reactivity, selectivity and/or stability of the catalyst. Particularly, the SCILL concept is a promising approach to enhance the selectivity of hydrogenation reactions, like the selective hydrogenation of 1,3-butadiene to 1-butene using transition metal catalysts.[1] In this context, we combined experimental and theoretical methods to study the adsorption dynamics of 1,3-butadiene and 1-butene on a Pt(111) surface modified with ultrathin layers of the IL 1,3-dimethylimidazolium bis(trifluoromethanesulfonyl)imide ($[C_1C_1Im][Tf_2N]$). The sticking coefficients of both olefins were measured using a supersonic molecular beam applying the method of King and Wells. Both hydrocarbons show pronounced precursor-mediated dynamics on clean Pt(111) and the IL-modified surface. Increasing the IL coverage leads to an increased blocking of adsorption sites for the incoming olefins. Interestingly, a smaller IL amount is needed to block 1-butene adsorption in comparison to 1,3-butadiene (see Figure 1). Indeed, molecular dynamics simulations show IL film densification/relaxation as the key mechanism to allowing/excluding olefin adsorption on the metal. Being a function of IL coverage, the energy of film penetration is used to control the effective olefin adsorption energy – and thus creates an operation regime for permitting 1,3-butadiene adsorption, while accounting for a squeeze-out of 1-butene. We propose that this effect is directly related to the IL's influence on selective hydrogenation in SCILL catalytic systems.

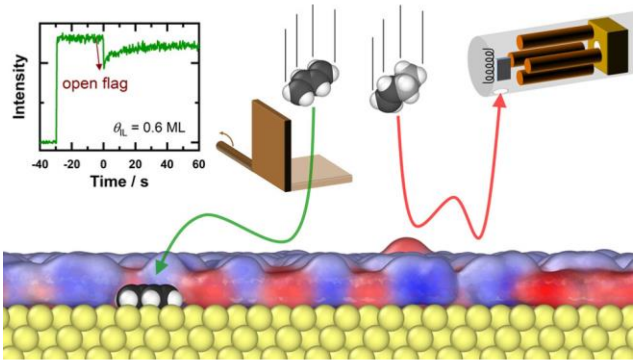

Figure 1: Sticking coefficient measurements show that a smaller IL amount is required to block the adsorption of 1-butene in comparison to 1,3-butadiene. These experimental findings are in line with our QM/MM calculations showing that in this coverage regime, the energy required for film penetration is different for both olefins. Reproduced from ref. [2] under license CC BY-NC-ND 4.0.

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Poster P_B2.3

Enhancing solubility of hydrophobic compounds: exploring zwitterionic compounds as alternative hydrotopes

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The limited water solubility of drugs poses a challenge to the pharmaceutical industry. While hydrotropes have traditionally been used as solutions, new, highly efficient hydrotropes with low toxicity are needed. Recent advances suggest that zwitterionic compounds analogous to ionic liquids (ZILs) are a promising option for improving the solubility of poorly water-soluble compounds due to their lower cytotoxicity[1] and ecotoxicity[2].

In this study, we investigate the use of (i) sulfonate-based ZILs, (ii) carboxylate-based ZILs, and (iii) ILs analogous to ZILs to improve the solubility of two model molecules (syringic acid and ibuprofen).

The results provide three important findings: (i) ZILs with longer alkyl chains and spacers exhibit higher hydrotropic activity, especially in the case of carboxylate-based ZILs; (ii) the observed hydrotropic effect is more pronounced for solutes with higher hydrophobicity; and (iii) ZILs exhibit lower hydrotropic behavior compared to their analogous ILs. The results here presented are particularly important for pharmaceutical formulations because, although ZILs exhibit somewhat lower hydrotropic behavior among the ZIL/IL pairs studied, their low toxicity profile makes them a desirable option.

Acknowledgements

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Poster P_B2.4

Exploring DASA stability in ionic liquids

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Ionic Liquids (ILs) are a unique class of versatile and "greener" solvents, compared with classic organic solvents, with customizable properties, including polarity. Due to the variety of combinations between anions and cations, it can show a high capacity for dissolving a variety of polar and non-polar compounds.[1,2] Deep Eutectic Solvents (DES) considered also as green solvents, similar to IL, result from a mixture characterized by a melting point depression, due to the formation of robust hydrogen bonds between the hydrogen bond donors (HBDs) and acceptors (HBAs). Compared to ILs, DES has the advantage of being cheaper and readily available from nature.[3] Molecular photoswitches are small molecules containing a chromophore that, when exposed to light, can reversibly switch between two isomers with different physicochemical properties.[4] Current research has shown significant interest in these molecules due to their wide-ranging applications in light-mediated catalysis, photoresponsive materials, selective drug delivery within biological systems, molecular electronics, and more.[5] Most common photoswitches include azobenzenes, stilbenes, spiropyrans, and diarylethenes among others.[4,6] The switching process usually involves reversible electrocyclization of a p-system (spiropyran, diarylethene) or*cis*–*trans* isomerization (azobenzene). Azobenzenes, for example, are well known for their use as dyes, because of their strong color. However, these photoswitchable compounds have limitations, such as their reversible isomerization being highly dependent on the solvent used and the requirement of high-energy UV light to trigger their photochemical reactions, which can be potentially harmful for biological applications [7]. Donor-acceptor Stenhouse adducts (DASA) are a novel class of photoswitchable molecules reported by Alaniz *et al.*[7], capable of displaying photochromism under visible light, which overcomes a limitation observed in the other photoswitchable compounds. Moreover, the synthesis of DASA through Knoevenagel condensation takes advantage of furfural, obtained from plant products so, readily available.[8] DASA proposed mechanism for their switching process is via a reversible Nazarov-type 4π electrocyclization.[7] Given the potential benefits of their use in smart applications, a study was conducted to understand the stability of molecular photoswitches in different ILs. The aim was to evaluate the behavior of the equilibrium between the two isomers in different ILs and DES.

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Poster P_B2.5

New protic ionic liquids as lubricant additives for nano and microelectromechanical systems

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Nano and microelectromechanical devices (NEMs and MEMs) are miniaturized devices made of silicon, which have a great impact on our day-to-day lives. In 2018, the global total value in the market for these devices was 10 billion euros and that value is expected to reach 50 billion by 2024. There is a high demand for efficient lubrication for NEMs and MEMs, particularly in terms of more efficient and greener alternatives in comparison to commercial lubricants.

Ionic Liquids (ILs) are task-specific organic salts with interesting physicochemical properties such as high chemical and thermal stability, almost negligible vapor pressure, high ionic conductivity, non-flammability, and ease in dissolving organic, inorganic, and polymeric materials. Another very interesting property if the fact that these compounds allow tuning of their properties, through the choice of an adequate cation-anion combination, according to the final desired application.

One of the potential applications of ILs is in the lubricants field, in which they have shown very interesting properties, namely for NEMs/MEMs lubrication.1 ILs are conductive fluids, so they lead to the minimization of the contact resistance between sliding surfaces, which is an important parameter for various electrical applications. However, ILs are still too expensive to be applied as neat lubricants, so a viable alternative is to use them as additives to commonly used base oils.

Protic Ionic liquids (PILs) are a subclass of ILs that have recently been considered as potentially good lubricants. The PILs composed of protonated ammonium cations have the advantage of being prepared by simple protonation, with low cost and toxicity. Besides that, they exhibit low viscosity when compared to conventional aprotic ionic liquids, making them potentially good lubricant candidates.

In this work, we report the use of protic ILs based on different organic cations combined with two anions (hydrogen sulfate and methyl sulfate) as additives to the commonly used base oil polyethylene glycol MW 200 (PEG 200).2 All the prepared lubricants were characterized in terms of their water content, viscosity, wettability, and tribological properties. Two different tribological pairs were tested: steel and silicon spheres against Si surfaces. Friction and wear were determined, and the worn sliding surfaces were imaged and chemically analyzed in order to give insight into the wear mechanisms. The most promissory PILs containing the protonated cation 4-picolinium showed good tribological performance, both in terms of friction and wear reduction compared to commercial lubricant PEG 200, making them very good candidates for future applications in electronic devices.

Acknowledgements

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Poster P_B3.1

Systematic study on the electrical conductivity and viscosity of imidazolium and pyrrolidinium-based ionic liquids

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This work presents a study on the viscosity and electrical conductivity of ionic liquids (ILs), focusing on the comparison between imidazolium and pyrrolidinium-based cations. The approach of the study was centred on the homologue 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, $[C_nC_1im][NTf_2]$ (n = 1 – 12)[1], and 1-alkyl-1-methylpyrrolidinium, $[C_nC_1pyr][NTf_2]$ (n = 3, 4, 6 and 8) series. The aim was to evaluate the effect of the nature of the cation and understand the impact of the differentiation of the cationic structure on the dependence of the transport properties with the length of the alkyl chain. This study was then extended to four other 1-alkyl-3-methylimidazolium and 1-alkyl-1-methylpyrrolidinium ILs based on the trifluoromethanesulfonate, $[C_4C_1im][OTf]$ and $[C_4C_1pyr][OTf]$, and tris(perfluoroalkyl)trifluorophosphate, $[C_4C_1im][FAP]$ and $[C_4C_1pyr][FAP]$ in order to account for different anion-cation relations.

The electrical conductivity measurements were performed between 283 and 333 K using a multi-frequency impedance methodology and were based on the scanning of resistance, R, and reactance, X, from 20 Hz to 500 kHz. The resistance of the solution was derived from the extrapolation to infinite frequency in order to avoid polarization effects[2]. The viscosity and density were measured between 273 and 373 K using an automated SVM 3001 Stabinger viscometer-densimeter based on the concentric cylinders and vibrating tube methods.

The dependence of electrical conductivity, $\sigma(T)$, and dynamic viscosity, $\eta(T)$, with the temperature, was found to be well represented by the Vogel-Fulcher-Tammann (VFT) equation, which was consequently used to derive the energy of barrier for the respective processes. Based on the conductivity, viscosity, and density results, the Walden plots for the studied ILs were constructed to evaluate their ionicity. The combination of the $\sigma(T)$ and $\eta(T)$ data, along with the derived VTF coefficients, energy barrier, Walden plots, and the resistance-reactance spectra were used to elucidate the effects of: a) the size of the alkyl chain; b) the nature of the cation; c) the nature of the anion on the dynamics and structuration of these ionic liquids systems.

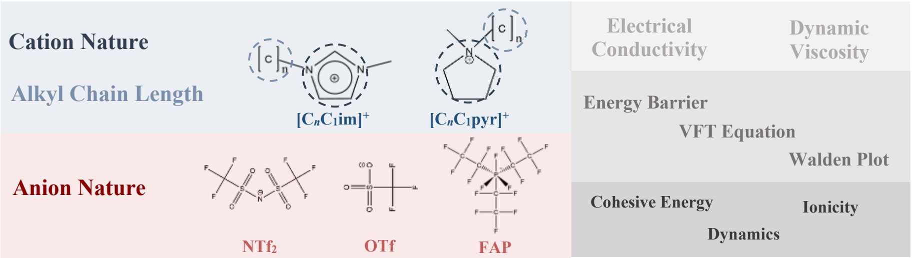

Figure 1: Structural representation of the studied imidazolium and pyrrolidinium ionic liquids.

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Poster P_B3.2

How electrode and membrane thicknesses affect capacitive energy storage with nanoporous supercapacitors

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Understanding charge storage in nanoporous electrodes is crucial for developing novel ecologically friendly devices for capacitive energy storage and conversion, water desalination, etc.[1] The effect of impurities and solvent combined with asymmetry in the ion's radii or charge has attracted much attention in this respect.[2-4] However, most modeling studies treated an electrolyte-filled membrane of a supercapacitor as an infinite reservoir of anions, cations, and solvent molecules, while typically, it is comparable in size to the electrodes. In this contribution, we analyze the effect of the supercapacitor geometry on the charge and energy storage. Using a computationally efficient numerical model based on an analytical solution for ion densities in single-file pores[5] and the scaled-particle theory[6] and mean countershell approximation[7] for the bulk electrolyte, we investigate how the interplay between the membrane and electrode thicknesses affects pore filling and charge accumulation and discuss the role of impurities in capacitive energy storage.

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Poster P_B3.3

Self-assembly phenomena in deep eutectic solvents: a systematic molecular simulation study

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Micellization is a crucial process in numerous industrial applications, including drug delivery, oil recovery, and wastewater treatment, and, at the same time, it is also an interesting topic of research from a fundamental point of view. Traditionally, micellization has relied primarily on aqueous solutions which, despite the obvious advantages of availability and non-toxicity, might limit their efficiency and applicability. The utilization of non-aqueous solutions, particularly deep eutectic solvents (DES) can unveil new phases and morphologies that are not observed in aqueous solutions. Moreover, the tunability of the solvent, which is possible by combining different compounds, is crucial to adapting the properties for specific applications where water is not suitable. As such, it is important to have a better understanding of how several factors, such as temperature, concentration, charge density, or hydrophobicity, can have an impact on the structure and properties of the supramolecular assemblies formed in non-aqueous solutions.

Despite the relevance of this topic, the availability of experimental data is still scarce, but nonetheless showcases the potential of DES to alter the self-assembly mechanism when compared to water-based colloids[1]. Still, a more systematic approach to the factors that govern the self-assembly in non-aqueous solutions is needed, at a more fundamental level. Moreover, there is also a lack of theoretical approaches to DES-based self-assembly; while simulations have been performed on the self-assembly in non-aqueous ionic systems[2], to the best of our knowledge, no simulation work on DES-based colloids has been attempted. As such, in an effort to systematically understand what drives the self-assembly of surfactants in DES mixtures, we performed molecular dynamics (MD) simulations on an array of ionic surfactants with different properties in deep eutectic mixtures containing glycerol and choline chloride under different conditions, such as concentration, surfactant chain length and type of polar group. The simulations are able to reproduce the experimentally observed mesophases, from micellar to hexagonal and lamellar phases (Figure 1) and a thorough structural analysis is used to correlate the observed structures with the molecular morphology of the surfactants.

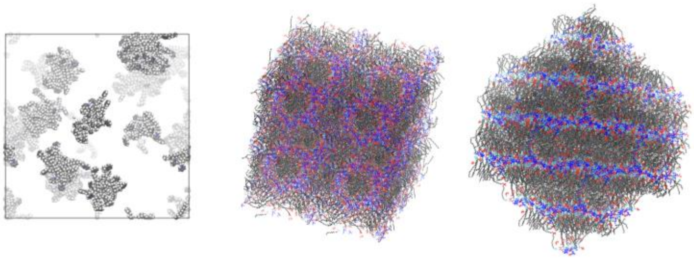

Figure 1: MD simulation snapshots showcasing the mesophases formed for the system containing choline chloride, glycerol, and cetylpyridinium bromide: left – micellar, middle – hexagonal, right – lamellar.

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Poster P_B3.4

Exploring the impact of sodium salts on the hydrotropic solubilization

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Some ionic liquids (IL) were shown to display a strong ability to enhance the solubility of phenolic compounds through hydrotropy. However, evidence shows that salt ions in hydrotropic aqueous solutions may change the behavior of molecules by promoting possible interactions between the components of the system, thus causing changes in solubility. Herein we study the impact of sodium salt anions on the hydrotropic dissolution of syringic acid using 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) as hydrotrope, with a focus on the dicyanamide $Na[N(CN)_2]$ and thiocyanate Na[SCN] salts. Dynamic light scattering, Raman, and nuclear magnetic resonance spectroscopy were used to investigate how the mixture of IL-salt affects the solvation. The results obtained show that $[C_4mim]Cl$ is able to increase the solubility of syringic acid 80-fold. Despite their structural similarities, the presence of $Na[N(CN)_2]$ or Na[SCN] in an aqueous solution of $[C_4mim]Cl$ induced opposite solubility trends. The addition of $Na[N(CN)_2]$ promotes a higher ability to solubilize syringic acid than in the corresponding IL system due to a pH buffering effect, resulting in the deprotonation of the solute. The addition of Na[SCN], on the other hand, induces a relative decrease in syringic acid solubilization at higher concentrations of IL due to the negative contribution of the NaCl formed by anion exchange. These results emphasize the often overlooked pH contribution provided by ILs for biomolecule solubilization whilst providing experimental insights as to the structure of aqueous solutions of ionic liquids and the role they play in the formation of IL-salt aggregates.

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Poster P_B3.5

Exploring chain length mismatch and structural isomerism on thermotropic ionic liquid crystals from lysine-based surfactants

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Thermotropic liquid crystals (TLCs) are temperature-driven structures that possess an intermediate degree of order between the crystalline solid and the isotropic liquid phases. Some systems are capable of changing their optical properties (e.g. birefringence and color) in response to external stimuli such as mechanical stress or electrical fields).[1,2] Beyond their fundamental interest, e.g. assessment of structure-behavior-performance relationships, TLCs find a wide variety of applications in electric-optical devices, sensors, liquid crystals displays, and medical applications. In the last two decades, ionic liquid crystals have also been subject to intense research, due to the combination of properties of conventional uncharged TLCs and those of ionic fluids.[3] In this context, the thermotropic phase behavior of amino acid-based surfactants was addressed in the past, and it was observed that these compounds typically form smectic phases for C12 chain lengths.[4] In this work, we undertake a systematic investigation of the thermal phase behavior of lysine-based amphiphiles (sodium salts) having two asymmetric tail lengths, designated as *m*Lys*n*, where *n* and *m* = 8, 10, 12, 14, and 16, represent the number of carbon atoms in alkyl chains. Previous studies have also demonstrated that these compounds have a rich lyotropic phase behavior, with the formation in water of different aggregates, such as micelles, vesicles, tubular structures, and lyotropic liquid crystals.[5] Here, we focus on the thermotropic phases. The experimental toolbox includes DSC, TGA, polarized light microscopy, and XRD. Structural isomerism (*m*/*n* vs. *n*/*m*) and total chain length (*n* + *m*) have a significant impact on the ionic TLCs formed and their optical properties. All the compounds show several thermal phase transitions denoting a complex melting process. When the charge is located on the same side as the longer chain, Figure 1a), the phase behavior of the surfactant is much more complex than for its respective isomers. Furthermore, high-temperature smectic phases, characterized by focal conics textures (Figure 1b), dominate the mesomorphism.

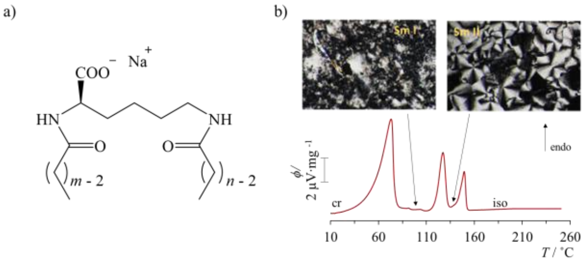

Figure 1: a) molecular structure of the *m*Lys*n* lysine-based surfactants; b) DSC thermogram of the surfactant 16Lys10 and micrographs of the birefringent smectic phase textures (Sm I and Sm II) obtained by polarized light microscopy.

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Poster P_B4.1

Size effects of binary cation ionic liquid mixtures on capacitive energy storage

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Room-temperature ionic liquids (RTILs) are environmentally friendly molten salts playing an increasingly important role as electrolytes in nanoporous electrical double-layer capacitors (EDLCs).[1] Recent studies show that mixtures of two or more RTILs can be advantageous over pure RTILs in improving the EDLC performance, particularly its capacitive properties.[2-4] In this contribution, we investigate theoretically and experimentally the effect of cation size in a mixture of two RTILs sharing a common anion. We consider ultranarrow cylindrical pores and combine molecular dynamics simulations with the previously developed analytical model,[5] having an exact solution for the voltage-dependent in-pore ion densities, allowing us to investigate the effect of cation size systematically. To better model our experimental system, we account for pore polydispersity by averaging single-pore results over the distribution of pores in an electrode. Our calculations show that binary-cation RTIL mixtures can enhance the capacitance of single nanopores and nanoporous electrodes but provide only moderate enhancements for two-electrode EDLCs. In agreement with these theoretical predictions, we observe the comparable electrochemical performance of EDLCs based on neat [EMIM][TFSI] ionic liquid and on its mixture with [K][TFSI]. Investigating the origin of this result, we reveal subtle effects of how the distribution of pores relates to charge storage and discuss possibilities to enhance stored energy density with RTIL mixtures.[6]

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Poster P_B4.2

Using aqueous biphasic systems as membrane-free redox flow batteries

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In 2021, 22% of the energy consumed in the Europe Union was generated from renewable sources, mainly solar and wind power. However, a deeper transformation of the energy system, such as increasing efficiency, is required to achieve the 2030 target of 40%. Energy storage devices are essential to enhance efficiency, reducing the mismatch between the continuous production of energy from renewable sources and consumers' needs. Redox flow batteries (RFB) are a kind of electrochemical energy storage device. However, the high costs of the ion-selective membranes and the toxicity and availability of metallic compounds hinder their vast application. To overcome these problems, the Membrane-Free RFB appears as a promising strategy. Through aqueous biphasic systems (ABS), it is possible to replace metallic substances with organic redox molecules and optimize the separation of the species, which improves the difference between the redox potential of the immiscible phases without a physical membrane. So, in this work, the partition coefficients (K) of redox-active compounds, used in Membrane-Free RFB, in ABS formed by ionic liquids (IL), salt, and water were determined. First, different binodal curves with ammonium sulfate salt and different ionic liquids with thiocyanate anion were determined. Then, the partition coefficient of the redox pair methyl viologen (MV) dichloride hydrate and 2,2,6,6-tetramethylpiperidine-1-oxyl radical (TEMPO) were determined. The results obtained showed that MV preferentially migrates to the salt-rich phase, and the partition coefficient to this phase increases with the hydrophobicity of the ionic liquid-rich phase. On the other hand, TEMPO preferentially migrates to the ionic liquid-rich phase. The gathered results show that those systems are promising to be applied in the Membrane-Free RFB, and can be used to validate predictive models, namely COSMO-RS, for the prediction of new and more effective systems.

Acknowledgements

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Poster P_B4.3

Electric double-layer structure of salt-in-protic ionic-liquid ethylammonium nitrate doped with lithium

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Ionic liquids (ILs) mixed with inorganic salts have shown high potential as highly conductive electrolytes in electrochemical storage devices. A systematic prediction of the effect of alkali metal salts on the electrolyte-electrode interfacial structure is needed to achieve the most promising electrolyte mixture formulation with the best electrochemical performance. Differential capacitance, the potential of zero charge, and charge density curves were obtained at the Hg/pure ethylammonium nitrate (EAN) interface. The C(E), the PZC relative position, and ⍰(E) curves allowed to propose a valid EDL structure using a Hg electrode as a metal model for the pure IL. The trend was interpreted as a baseline to better understand the contribution/absorbability of the inorganic ions in shaping the electrolyte binary mixture structure at charged surfaces[1,2]. The EDL model selected to describe the interfacial properties of the IL adjacent layer to the electrode was the Helmholtz model, which, although very simple, provided an accurate estimation of the EDL thickness that was validated independently. The dopant effect of the metal ions on the IL network was assessed by evaluating the impact of the lithium nitrate ($LiNO_3$) salt at different molalities on the shape/magnitude of the capacitance-potential curves and charge density curves obtained at the Hg/pure EAN interface. A detailed picture of the molecular environment in the EDL resulting from the metal salt addition is provided by means of classical molecular dynamics simulations. The computational analysis shows a slight reorientation of IL cations and a modification of dipole relaxation when varying the salt concentration.

Acknowledgements

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Poster P_B4.4

Formation and stabilization of metal nanoparticles in ionic liquid films

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This study aimed to investigate the sputter deposition of metal nanoparticles (silver and gold) onto thin films of different imidazolium-based ionic liquids (ILs). A diverse range of ILs with different anions, including acetate, trifluoroacetate, triflate, and bis(trifluoromethylsulfonyl)imide, was explored. Additionally, it was studied the impact of modifying the alkyl chain length and symmetry of the cationic moieties. The specific combinations of ILs included $[C_2C_1im][Ac]$, $[C_2C_1im][TFA]$, $[C_2C_1im][OTF]$, $[C_2C_1im][NTf_2]$, $[C_4C_1im][NTf2]$, $[C_8C_1im][NTf_2]$, $[C_2C_2im][NTf_2]$, and $[C_5C_5im][NTf_2]$. The ILs served not only as media to capture the metal atoms but also as stabilizers during the formation of nanoparticles, as they tended to form aggregates of small and uniform sizes.[1-3]

Ionic liquid (IL) films of different thicknesses were obtained in the form of microdroplets through vacuum thermal evaporation. The IL films were deposited onto glass substrates coated with indium tin oxide (ITO). The process of thermal evaporation was conducted by carefully controlling the effusion temperature, deposition rate, and deposition time. The use of Knudsen cells as evaporation sources provided a means to achieve precise and reproducible control over the mass flow rate.[4,5] The sputtering process of the metals onto ILs when conducted simultaneously with argon plasma promoted the coalescence of microdroplets of ILs and the incorporation and stabilization of silver (AgNPs) and gold nanoparticles (AuNPs) in the coalesced IL films. The formation/stabilization of metal nanoparticles into the ionic liquid (IL) films was confirmed through high-resolution scanning electron microscopy (SEM) and UV-Vis spectroscopy.[1]

Based on the experimental findings, the investigated IL films exhibited higher suitability as capture media for the formation and stabilization of AgNPs. On the other hand, controlling the conditions to favor the formation of AuNPs proved to be more challenging. The gold particles tended to aggregate and form a thin film on the surface of the IL film. On the other hand, it was observed that IL films with greater thicknesses provided a more favorable environment for the formation of small silver particles. Among the ILs investigated, those containing longer alkyl chains in the cation and the anion NTf_2 demonstrated better results in terms of AgNPs formation. Additionally, ILs containing the acetate anion were found to be particularly conducive to the formation of large silver aggregates. Of all the ILs studied, $[C_5C_5im][NTf_2]$ showed particular promise for the stabilization of AgNPs. When exposed to argon plasma and Ag bombardment, larger IL droplets acted as confining agents, preventing the aggregation of AgNPs and facilitating their stabilization within the IL films.[1]

Acknowledgments
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Poster P_B4.5

Ionic liquids-carbon scaffolding materials for fluids exchange

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Ionic liquids (ILs) are a category of compounds that have a number of distinctive properties, including chemical stability, minimal volatility, and task-specific properties that can be altered. These characteristics make ILs promising materials for numerous applications, including water purification and carbon capture. Ionic Liquids-Carbon scaffolding materials (ILs-CSMs) are a novel form of ion exchange system that combines the exceptional properties of ILs with the high porosity and structural flexibility of CSMs. ILs-CSMs are produced by immobilizing ILs on carbon scaffolding materials using various techniques, including physical adsorption, chemical bonding, and encapsulation.

In this work, we synthesized a variety of task-specific ionic liquids, including imidazolium sulfonate and triethanol ammonium acetate. We also prepared carbon scaffolding structures of varying porosities and aspect ratios. We have shown that imidazolium sulfonate-based CSMs can be used as sorbents for capturing CO_2. We designed ILs-CSMs ion exchange systems for water treatment by physically adsorbing ILs onto porous membranes. These ion exchange systems can be used to selectively remove specific ions from water, such as heavy metals and organic pollutants [1]. The development of CSM-based ion exchange systems is a promising step towards developing sustainable, scalable, and cost-effective methods for water treatment and carbon capture.

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Poster P_B5.1

Vesicles from cationic/anionic (catanionic) surfactant mixtures based on lysine derivatives: self-assembly and encapsulation of a bioactive molecule

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Cationic/anionic surfactant mixtures, often referred to as catanionic mixtures, are capable of spontaneously forming a diversity of self-assembled structures such as micelles, vesicles, liquid-crystals, and crystalline solids owing to the headgroup electrostatic interactions between the oppositely charged amphiphiles, mediated by packing (hydrophobic) interactions. Catanionic vesicles have a wide range of potential applications such as membrane models, nanoreactors, nanotemplates, and, especially, nanocarriers for bioactive molecules. The physicochemical properties (namely size, polydispersity, surface charge, and pH) of the vesicle can be tuned by controlling its composition, e.g., by changing the cationic/anionic surfactant ratio or varying hydrocarbon chain length.[1,2,3]

Herein, we employed different (in-house synthesized) anionic surfactants based on the amino acid lysine, designated as *m*Lys*n*,[4] in a mixture with a varying molar fraction (x_+) of either cationic gemini (12-*n*-12) or cationic single-tailed surfactants (DTAB or CTAB), aiming to spontaneously form robust catanionic vesicles for encapsulation and release (Figure 1). Phase behavior of the *m*Lys*n*/gemini and *m*Lys*n*/single-tailed surfactant systems was determined to select the most suitable vesicular systems. All catanionic mixtures exhibit strong synergism, having reduced critical aggregation concentration compared to the neat surfactants. The 10Lys12/12-3-12 (x_+=0.50) and the 14Lys8/CTAB (x_+=0.60) yield the largest vesicles, while the 12Lys8/single-tailed systems have the smallest and least polydisperse ones. Lastly, encapsulation efficiency and loading capacity of the vesicles was evaluated using cynaropicrin as the bioactive target, from which we concluded that the systems 10Lys12/12-3-12 (x_+=0.50) and 14Lys8/CTAB (x_+=0.60) have the highest encapsulation capabilities.

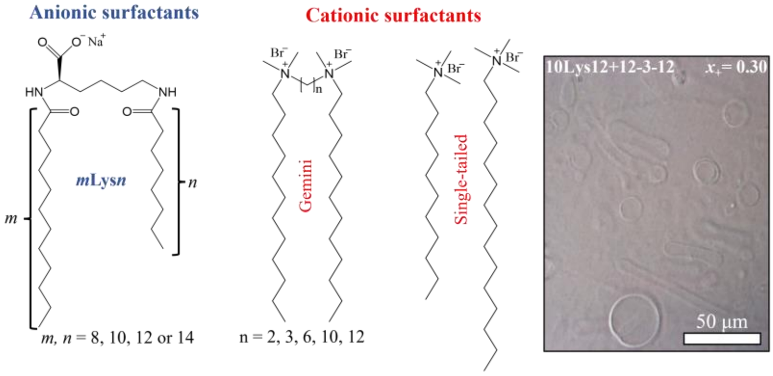

Figure 1: Structure of anionic and cationic surfactants used in the mixtures and micrograph of the resulting nanostructures.

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Poster P_B5.2

Keratin recovery using ionic liquids and its application for biofilm processing

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A large amount of chicken feather waste is generated by the poultry-processing industry, corresponding to up to 10 % of the total weight of an adult chicken. This waste is typically disposed of through incineration or landfilling, not only contributing to environmental pollution but also decreasing the industry's economic worth. Regarding chicken feather valorization, this waste contains around 90 wt % keratin, which is one of the most abundant biopolymers in the environment. Nevertheless, keratin dissolution is challenging due to the presence of disulfide bonds present in the amino acids chain. From this perspective and considering the high dissolution capability of ionic liquids (ILs), we explored its use as an alternative and greener solvent for feather dissolution. By adding a coagulant solvent, we can achieve a keratin recovery yield of up to 93 wt % under optimal conditions. Concerns regarding the high cost of ILs led us to investigate IL recovery and reuse. Our findings indicated that ILs can be effectively reused for at least four cycles without compromising the keratin recovery yield. The proposed process' technical-economic assessment was also conducted, demonstrating that the minimal selling price of keratin is appropriate for biomedical applications. In order to explore the potential applications of keratin in the biomedical field, biofilms were developed, and their biological properties were investigated. The keratin films exhibited interesting biological properties (*e.g.* antioxidant and anti-inflammatory) and effectiveness in promoting wound healing. Overall, the results obtained in this work highlight the valorization of chicken feather waste using ILs while also contributing to the development of biofilms for biomedical applications.

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Poster P_B5.3

Application of ionic-liquid-based aqueous biphasic systems in the extraction and purification of prostate-specific antigen from human serum

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The early detection of prostate cancer can be assisted by the quantification of serum biomarkers, such as the prostate-specific antigen (PSA), improving disease management. However, high abundance serum proteins, mainly immunoglobulin G (IgG) and human serum albumin (HSA), may interfere with PSA analysis, often providing low-accurate results. To reduce these interfering effects while improving the accuracy of analysis, serum pretreatment steps are a necessary part of the analytical setup. While solid-phase extraction using affinity resins/columns and protein precipitation are the most widely adopted serum pretreatment techniques, there is still a lack of high yield/high selectivity strategies matching simple operations and reduced costs. To address such performance and technological requirements, this work investigates the versatility of ionic liquids (ILs) in the formation of aqueous biphasic systems (ABS) for the pretreatment of human serum and PSA extraction. In the proposed ABS, ILs are used either as main constituents or adjuvants, and their structure is finely tuned to achieve the simultaneous depletion of high-abundance serum proteins and PSA extraction. If well-designed, ABS composed of ILs as adjuvants is better suited to perform the proposed task in a single step, yielding depletion efficiencies of HSA and IgG higher than 95% along with extraction efficiencies of PSA of 97%. Overall, IL-based ABS can be considered promising tools to assist the analysis of PSA, supporting a timelier and more accurate detection of prostate cancer.

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Poster P_B5.4

Design of ionic liquids as solvents for the materialization of biopolymers

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DNA double helix, which is a genetic material, has been expected for its application in chiral material science and electrochemistry as a natural chiral supramolecule. However, it is difficult to use DNA double helix as a material due to its insolubility in organic solvents. We focused on the high substrate solubility of ionic liquids, which can dissolve polymers such as cellulose.[1] In this study, we systematically investigated the construction of DNA double helices in ionic liquids and the formation of complexes between them and functional molecules using porphyrins.

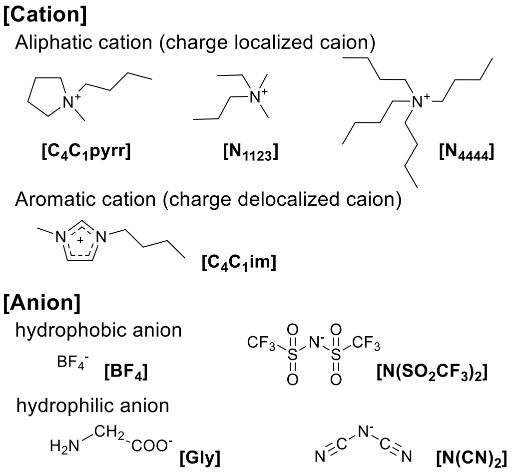

Figure 1: Structure of ionic liquids using in this study.

The ionic liquids employed in this study are shown in Figure 1. Although the DNA could not be dissolved with the ionic liquids alone regardless of their polarity and their affinity to water, the -dissolution of DNA was observed in the hydrophilic ionic liquids containing water. The formation of DNA double helix and its helical structures were experimentally determined by CD spectroscopy. Figure 2 shows the CD spectral changes of the DNA double helix with the addition of $[N_{4444}][Gly]$ as an example. With the addition of the ionic liquid, the DNA double helix was converted from the general right-handed B-form to the C-form which is a right-handed twist tightly. Formation of C-form DNA was observed in other hydrophilic ionic liquids with the aliphatic ammonium cations, while the DNA double helix could not retain in the ionic liquid with the aromatic imidazolium cation $[C_4C_1im][BF_4]$. It is reasonably surmised that the base of DNA with aromatic ring and the aromatic imidazolium cation of $[C_4C_1im][BF_4]$ formed π-π stacking interaction because DNA, which is an anionic super-molecule, can strongly interact with cationic molecules. In order to demonstrate the usability of the DNA double helix construction in ionic liquids, we examined the formation of complexes with functional molecules and the induction of DNA chirality. Experiments were performed using THPP, a water-insoluble porphyrin that cannot interact with DNA in aqueous media. THPP was dissolved in ionic liquid solutions capable of constructing DNA double helices. The CD signals induced by the chiral DNA double helix indicated that THPP can interact with DNA in different modes depending on the structure of ionic liquids.[2]

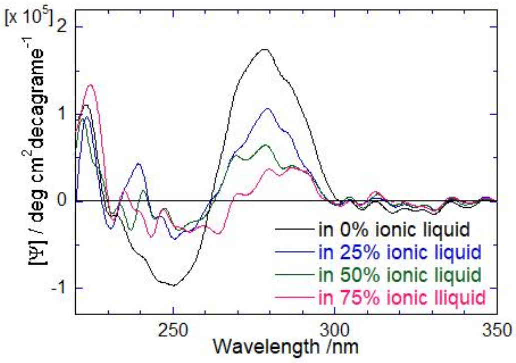

Figure 2: CD spectra of DNA in $[N_{4444}][Gly]$ solution ($[[N_{4444}][Gly]]$ = 0, 25, 50, 75% (v/v) in 20 mM MOPS-NaOH buffer (pH 7.0)), [DNA] = 15.0 mg L^{-1}, *T* = 25°C, Path length = 1 cm)

In this study, we investigated the functional complexation of DNA double helices in ionic liquids. This approach can be applied to other biopolymers, and it is expected for a wide range of applications such as chiral catalysts, chiral fluorescent dyes, and material production.

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Poster P_B5.5

Removal of estrogens in an enzymatic membrane reactor using ionic liquids as reaction stabilizers

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Considering the common problem of difficulties in metabolizing certain drugs, such as estrogens, sewage contamination with pharmaceutically active substances stands out. There are four estrogens in sewage, three of them are natural steroids produced by living organisms: estrone (E1), 17β-estradiol (E2), and estriol (E3), while the fourth one is classified as synthetic: 17α-ethinyl estradiol (EE2).[1] Monitoring should mainly focus on 17β-estradiol, which has the greatest stability and toxicity. Concerns include endocrine disruption and negative effects on the reproductive and sexual functions of wild animals, fish, and humans. Due to the resistance of some active pharmaceutical ingredients' resistance to classic forms of pollutant removal commonly introduced in sewage treatment plants, hence the search for new alternative environmentally friendly solutions plays an important role.[2] Enzymatic degradation of estrogens can be considered a promising method compared to the conventional physical and chemical oxidation process. Introducing ionic liquids in the immobilization of enzymes can influence enzymatic reactions by altering the structure, activity, enantioselectivity, and stability of the enzymes, providing higher conversion rates.[3]

In the presented work, electrospun fibers made of polystyrene, polystyrene (PS) with the addition of MOF (PS+MOF), poly(methyl methacrylate) (PMMA) and poly(methyl methacrylate) with the addition of MOF (PMMA+MOF) were used as a carrier for laccase immobilization by adsorption for use as a biocatalytic membrane in a continuous flow reactor. Then, a proof of concept was presented for the use of the produced biocatalytic system for the biodegradation of two estrogens: naturally produced 17β-estradiol (E2) and synthetic 17α-ethinyl estradiol (EE2) at a concentration of 0.1 mg/L. An important part of the work was the use of ionic liquids as surface modifiers to bind the enzyme to the material surface more permanently and effectively. Additionally, differences in flow and permeability were examined between the tested membranes, both the clean membrane, the membrane after immobilization, and after estrogen degradation by the produced biocatalyst. It was found that the proposed biocatalysts produced on various polymer matrices should be considered a promising alternative for the efficient degradation of E2 and EE2 under various process conditions. Additionally, membranes with immobilized enzymes with the addition of ionic liquid were characterized by higher activity compared to the other tested systems, indicating the importance of using ionic liquids during the fabrication of the biocatalytic systems.

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