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Abstract Book

Solvay Workshop on
‘Ionic Liquids:
from fundamentals to applications’

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Ionic liquids
A(n) (Hi)story

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Considering the now very large variety of ionic liquids, it is fundamental to understand the role of the solvent and to establish the general methodology and laws allowing the prediction of chemical reactions.

In general, many chemical properties of the solvents are primarily related to the formation of complex species and much effort was applied in this field with main goal to better understand the relationship which exists between the nature and structure of the solvent with the chemical and structural properties of a solute.

It is in this context that I would like to tell a few stories in honor of three persons who have played a major role in the ionic liquids community and also in my life: Gleb Mamantov, Bob Osteryoung, and Yves Chauvin.

The first comprehensive studies on the so called “inorganic chloroaluminates” were made last century mainly in the late sixties and early seventies by Gleb mamantov. These solvents were made of mixtures of $AlCl_3$ with an inorganic chloride and their melting points ranged from 110 to 160 °C, depending on the composition. Despite experimental handling difficulties (such as an extreme moisture sensitivity) they exhibit a very interesting property: the acidity (expressed in terms of chloroacidity) can be varied quantitatively by several order of magnitude in the range of the equimolar composition, a property which has led to many investigations.

During a postdoctoral stay with R. Osteryoung (1976-1977), I was fortunate to show, that $AlCl_3$, mixed with an organic halide (butyl-pyridinium chloride) forms a bath liquid at room temperature in a broad range of composition. Since it is still liquid around the 1:1 composition, it was possible to observe that its Lewis acidity can be varied by more than 16 orders of magnitude in the vicinity of the equimolar composition, a discovery which has opened a large number of analytical studies. This work together with the work of J. Wilkes and C. Hussey (Air Force Academy) was at the origin of the development of a new field of molten salts, the “Room temperature molten salts” which is now expanding with the advent of “Ionic Liquids” associated to the concept of “Green Chemistry”.

More recently, in collaboration with Y. Chauvin and the Institut Français du Pétrole, we have shown that various Ethyl-Chloroaluminium, mixed with the same organic halides, also form ionic melts with properties close to the preceding salts. Moreover, they proved to be excellent solvents for a biphasic catalysis process, for example for the dimerisation of propene into dimethyl-butene. A detailed study of this type of liquids has lead to the Difasol process.

With this same institution, we also participated to the development of applications of the non-chloroaluminate ionic liquids for the petroleum industry. It indeed appeared that the marked acidic character of the chloroaluminates was not always desirable in catalysis. The salts mixtures based on the BF_4^-, SbF_6^{3-}, PF_6^- or Ntf_2^- anions form ionic liquids at ordinary temperature, in principle non acidic while remaining very weakly solvating. Our contribution mainly consists in developing methods which make it possible to characterize, quantitatively if possible, the respective capacity of solvation of these solvents and to propose a comparison among them and with other solvents. In this context, much interest was devoted to the evaluation of the Brønsted acidity level which can be reached by adding a strong acid in such systems.

All these topics will be illustrated by published and unpublished examples.

MONDAY 20 FEBRUARY 2017

EVERYTHING YOU ALWAYS WANTED TO KNOW ABOUT IONIC LIQUIDS, BUT WERE AFRAID TO ASK

Kenneth R. Seddon

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"The most erroneous stories are those we think we know best and therefore never scrutinize or question."

S.J. Gould, in *Full House: The Spread of Excellence from Plato to Darwin* (1996)

Well, in 45 minutes (including questions), perhaps not everything! But, in this short introductory talk, I will follow on from Bernard Gilbert's *histoire*, and discuss some of the issues facing all practitioners in the field today. What **IS** an ionic liquid? Is the literature reliable? Is the quality of published papers dropping as their number increases? Truth or post-truth? Useful or overhyped? Green or toxic? These questions, *inter alia*, will be posed – and will hopefully settle within the minds of the audience to ponder and discuss throughout the week.

TUESDAY 21 FEBRUARY 2017

Ionic liquids from theoretical considerations

R. Elfgen, M. von Domaros, S. Gehrke, P. Ghosh, O. Hollóczki, R. Macchieraldo, F. Malberg, E. Perlt, P. Ray, and Barbara Kirchner*

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Ionic liquids (ILs) possess many unique properties making them a promising material class. Utilizing state of the art theoretical methods, such as molecular dynamics (MD) simulations and ab initio calculations [1], helps understanding these liquids on the atomic level. By examining the fundamental interactions, the solvents' nanostructure and the complex behaviour with different materials can be explored more accurately. The side chain aggregation of ILs, i.e. microheterogeneity, showed a significant effect with respect to gas absorption [2]. Within our program TRAVIS, we present alternative ways to obtain dipole moments and thus spectroscopic information, as well as new analysis tools such as domain analysis and structure factor tool [3]. Applying these tools to a newly suggested mixture from alkyl- and fluoroalkylimidazolium ILs, the formation of a tri-phillic nano-system [4] is seen. As shown by Schulz and coworkers [5] and many others, the formation and morphology of nanoparticles within highly structured ILs is affected by the choice of the IL, e.g., the side chain or the anion can play a role [6]. In order to shed light on this behaviour, the interactions with the ILs are investigated and results are being presented. Mixtures of ionic liquids with and of molecular liquids [7] are also in the scope of this talk.

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TUESDAY 21 FEBRUARY 2017

“Ionic Liquids Under Harsh Reactive Conditions”

Claudio J. Margulis, The University of Iowa

Ionic Liquids (ILs) are, for the most part, pursued and used for their excellent stability under thermal and electrochemical conditions. For example when used as solvents for chemical reactions or as electrolytes in batteries and capacitors we seek that the solvent be inert. However, many real-life practical processes of interest to energy applications certainly involve IL reactivity. When harvesting light for energy applications an excited state chromophore may be able to donate or accept an electron from the solvent. In lithium-ion or sodium-ion battery problems the solid-electrolyte interface (SEI), a key component to the device function, is a result of solvent degradation at the anode interface. In the nuclear fuel recycling problem, we may sometimes seek a radiation resistant IL or diluent.

Combined with our more traditional work on statistical mechanics, structure and dynamics of ILs, in this talk I will present work our group has pursued and is currently pursuing to understand short-time patterns of reactivity of ionic liquids in the condensed phase. This includes understanding the nature of HOMO and LUMO bands for different ILs, and their time dependent behavior in the presence of excess electrons and holes. I will also discus systems in which anions or cations can act as electron donors, and ions that are particularly suitable to protect from radiation damage.

TUESDAY 21 FEBRUARY 2017

Evaluating the valence electronic structure of [C_4C_1im][SCN] gas vs liquid phase.

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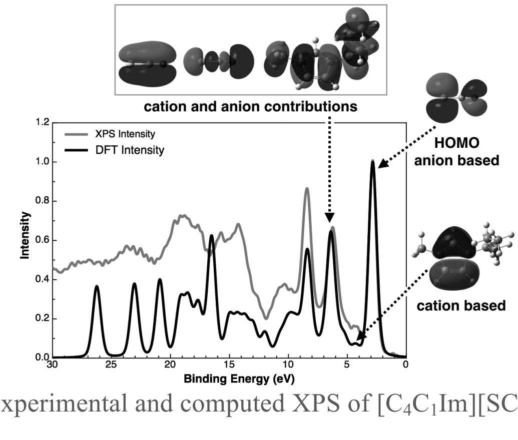
The majority of chemical reactions occur in liquids and to fully understand these processes knowledge of the liquid-phase electronic structure is required. Typically it is assumed that individual liquid state orbitals delocalize over the whole liquid. The liquid state energies also clump together, forming energy bands. Nevertheless, delocalized states can often be related to the molecular orbitals (MOs) of the individual solvent molecules. Typically, when relating a single molecule MO to the liquid state electronic structure, a curve is fitted to each MO energy level to represent the liquid state broadening. Thus, knowledge of the liquid phase electronic structure can be built up from an understanding of the molecular electronic structure.

We are interested in establishing how well gas phase or continuum solvated molecular quantum chemical methods recover the electronic structure of the liquid state. In particular, we want to identify a low cost methodology that will allow for *a-priori* prediction of ILs and modeling of ILs *in-silico* prior to synthesis and characterization.

DFT (B3LYP-D3BJ/6-311+G(d,p)) calculations have been performed on six model systems of increasing complexity. The models consist of the individual ions, ion pairs and ion-pair dimers of [C_4C_1im][SCN], both in the gas phase and using a continuum solvation model (SMD) specifically parameterized for [C_4C_1Im][SCN]. Experimentally, variable source valence XPS and RAESX-ray spectroscopy techniques have been employed to determine band energies and atom based contributions to the liquid phase orbitals. Electronic structure calculations are essential to enabling a proper interpretation of spectra, identifying the orbitals that give rise to each peak.

Thus we have used molecular electronic structure methods to enable interpretation of the experimental spectra and then we have used the experimental spectra to determine which of the six model systems provides the best representation of the liquid phase electronic structure. Moreover, we are able to quantify the fit for each method, and to provide information on the importance of explicit ion-ion interactions (such as covalent H-bonding and charge transfer) and multiple conformer analysis. Overall, this combined study has offered significant insight, that neither technique could achieve alone, into the electronic structure of [C_4C_1Im][SCN].



Experimental and computed XPS of [C_4C_1Im][SCN]

TUESDAY 21 FEBRUARY 2017

Ionic Liquid Dynamics in Electrical Fields

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Ionic liquids are liquids composed entirely of ions. These ions are in constant motion. Ionic liquids have found use in a wide range of electrochemical applications, such as batteries, fuel cells and solar cells. In these applications ionic liquids are exposed to electric fields. It is, therefore, surprising that the dynamics of ions in ionic liquids has been hardly studied.

In this paper we report the diffusion of solutes in ionic liquids using Fluorescence Correlation Spectroscopy (FCS). We show that the diffusion of these ions slow on the application of an electric field. Further to this, we show that the relaxation of this motion after discharge of the cell is remarkably slow – on the timescale of tens of minutes.

We also report a study of the rotation of molecular rotors by Fluorescence Lifetime Spectroscopy, which can be correlated with the viscosity of the solvent in the cybotactic region. These results show that the slower motion of ions is associated with an increase in this viscosity.

TUESDAY 21 FEBRUARY 2017

Functional design of highly thermoresponsive phase changes in ionic liquid/water mixed systems

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After energetic development of functional ionic liquids, there are some spread research areas on the ionic liquids. One of them is the science of ionic liquid/molecular liquid mixtures, especially mixtures with water. There are three groups of these mixtures based on the phase behavior, such as totally miscible (hydrophilic) ionic liquids, totally immiscible (hydrophobic) ionic liquids, and their intermediates. Among the ionic liquids with intermediate hydrophobicity, some of ionic liquids showed highly temperature-dependent phase changes after mixing with water. Furthermore, a few of them showed very interesting phase changes, i.e., miscible with water by cooling and immiscible by heating so-called lower critical solution temperature (LCST) type phase change. We have been working vigorously on this interesting phase change and proposed some applications based on this LCST-type phase change.

We have synthesized many ionic liquids to evaluate their phase behaviors after mixing with water, and found that these ionic liquid/water mixture showed the LCST-phase behavior only when the hydropbobicity/hydrophilicity balance of the ionic liquids is in between hydrophobic and hydrophilic ones. Furthermore, we found that the water content of these ionic liquids should be more than seven water molecules per ion pair. According to these data, we succeeded to design freely the ionic liquid to show the LCST-type phase change after mixing with water. The phase transition temperature between homogeneous mixture and phase separated mixture was found to be the function of total hydrophobicity of the ion pair.

According to this interesting phase behavior, we have prepared polyelectrolytes from polymerizable ionic liquid having suitable hydrophobicity. These new polyelectrolytes showed the LCST-type phase change similarly to those of monomeric ionic liquids in aqueous media. These polyelectrolytes were further cross-linked to form hydrogels to realize reversible water absorption/desorption by small temperature change. This was used as a chemical water pump driven by small temperature change.

Other interesting applications will be delivered at the talk.

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A New Basicity Scale for Ionic Liquids

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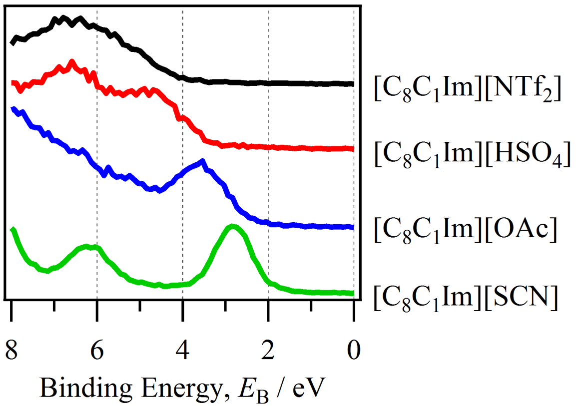
Understanding chemical reactivity of ionic liquids (ILs) is a major challenge. Basicity scales play a key role in overcoming this challenge. The most commonly accepted definition of a Lewis base is the ability to donate an electron-pair.[1] The ability to donate an electron-pair is controlled primarily by the highest occupied molecular orbital (HOMO), and in particular the HOMO energy, E_{HOMO}.[2, 3] To date, all basicity scales for ILs, and indeed for all liquids, rely on the use of a solute probe, *e.g.* Gutmann donor numbers, Kamlet-Taft parameters.[1, 4] The use of probes brings a set of challenges in itself, *e.g.* solubility, specific interactions.

X-ray spectroscopy is routinely used to study the valence and conduction bands of solids. Ionic liquids are sufficiently involatile that standard apparatus can be used to study the liquid phase at room temperature.[5]
Studying the valence bands of volatile liquids,
e.g. water-ionic liquid mixtures, is far more
challenging, and a liquid microjet is usually used.[6]
We used X-ray photoelectron spectroscopy (XPS) to
probe the electronic structure of both neat ionic
liquids and ionic liquid-water mixtures.
Experiments were carried out on both lab- and
synchrotron-based XPS apparatus.

We directly measure E_{HOMO} for a wide range of
ILs. We use these values to produce a new basicity
scale for ILs that does not require the use of any probe
molecules. We compare our basicity scale to those
developed from probes dissolved in ILs, and also make
comparisons to basicity scales for anions dissolved
in water. Furthermore, we demonstrate the difference
in basicity for an $[SCN]^-$ anion dissolved in water
versus an $[SCN]^-$ anion forming part of an IL. Finally, we compare our experimental results to DFT calculations, demonstrating that relatively cheap and simple DFT calculations have the potential to predict IL basicity.



photoelectron spectra for four ILs. E_{HOMO} ranges from small ($[C_8C_1Im][SCN]$) to large ($[C_8C_1Im][NTf_2]$).

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TUESDAY 21 FEBRUARY 2017

Ionic Liquids and Wavefunction in DFT embedding

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Quantum embedding methods have long been known to provide an efficient method of including environmental effects in an otherwise intractable quantum problem. A prominent example is Quantum Mechanics/Molecular Mechanics (QM/MM) embedding where the electron density of the environment is represented by atomic point charges. On a technically higher lever, the quantum problem can be embedded in an environment wherein the electron density is represented by Density Functional Theory (DFT). This allows for explicit representation of the electron density thereby including important effects such as polarization. While the computational costs of DFT are indeed greater than MM they are highly advantageous when compared to a full treatment with advanced wave function (WF) methods. Following the recent development of an efficient WF in DFT method by Manby et al.[1,2] we are developing a stand-alone software package which acts as intermediary between standard WF and DFT software packages. In this presentation I cover the main points of WF in DFT and introduce the software we are developing. Finally, test cases illustrating the useful application to the study of Ionic Liquids will also be presented.

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Reactivity in ionic liquids from the point of view of an electrochemist

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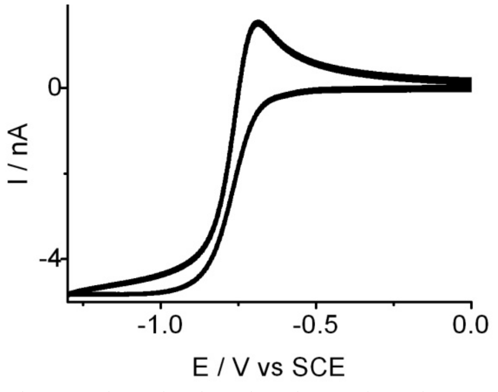
A (general) definition of reactivity is the ability of a system to respond to a perturbation. If this perturbation is an electron transfer, Molecular Electrochemistry provides powerful tools and concepts to study and understand the associated reactivity and its dynamics.

In the last two decades, most works in electrochemistry have been devoted to highlight the possible performance of ionic liquids in different electrochemical applications, namely batteries and electrodeposition. Fundamental electrochemical studies have been much less developed. Not only the classical cyclic voltammetry on millimetric electrode, but also more sophisticated techniques (e.g. SECM, voltammetry with ultramicrolelectrodes) are efficient for probing the physical chemistry and the chemical reactivity of reaction intermediate that are electrogenerated in ionic liquids.[1,2,3] Generally, the main reactivity patterns involving electrogenerated species in ionic liquids, are for the most part maintained when passing from a conventional solvent to a ionic liquid. However, specific interactions with the ionic liquids in relation with their charged nature play a major role on the transport properties processes (mass transport or electron transfer) and on reaction kinetics. We will exemplify these phenomena with different examples. A better basic understandings of the electrochemical processes is critical and allows a clean domestication of the processes, useful for many applications.



Electrochemical reduction of O_2 in $[Et_3BuN][Ntf_2]$ at a 5 µm Pt ultramicroelectrode

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TUESDAY 21 FEBRUARY 2017

Azolium Ionic Liquids in Electro-organic Chemistry

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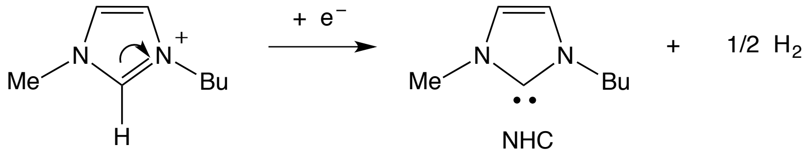
Electro-organic chemistry allows to carry out oxidation and/or reduction reactions under heterogeneous conditions, using the electrons as reagents. In this way, no by-products from the oxidant/reductant are generated. In order to have a good charge transport within the solution, an ionic species is necessary, the *supporting electrolyte*. Azolium ionic liquids are ionic species liquid in a large range of temperatures, and thus they can behave as both solvent and supporting electrolyte in an electrolysis, avoiding the use of two different compounds. Moreover, the immiscibility of some azolium salts with diethyl ether allows a simple separation of the electrolysis products from the reaction mixture and thus the easy recycling of the ionic liquid.

When using an azolium ionic liquid in electrosynthesis, it should be kept in mind that both anion and cation can react at the electrodes. In particular, the cathodic reduction of an imidazolium cation can yield the corresponding carbene (NHC), via monoelectronic cleavage of the C2-H bond:



This NHC is a singlet carbene, in which the two nonbonding electrons occupy the s-orbital as a lone pair. The presence of the two adjacent nitrogen atoms stabilizes the singlet state by p-donation. The presence of NHC in a solution (molecular solvent or ionic liquid) can be pointed out by cyclic voltammetry (NHC oxidation peak).[1]

Electrogenerated NHC can behave as a base and/or as a nucleophile, depending on the reaction partner. In both cases, if the azolium ionic liquid is used as both solvent-supporting electrolyte system and precatalyst, particular care should be devoted to the experimental conditions, in order to avoid the simultaneous cathodic reduction of the substrates.

Numerous examples of the use of azolium ionic liquids in electro-organic chemistry will be described, in which the azolium salt is pure solvent, or also precatalyst. In particular, the use of NHC as a base or as nucleophilic catalyst in classical organic reactions will be reported, with emphasis on umpolung reaction of aromatic aldehydes.

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Electrochemical Reduction of Carbon Dioxide in Room Temperature Ionic Liquids, at Gold and Copper Electrodes

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The electrochemical reduction of carbon dioxide to valuable products is a potent strategy for CO_2 remediation. Carbon monoxide, formic acid, oxalate and hydrocarbons can be formed depending on the electrode material and on the reaction medium. In this context, Room Temperature Ionic Liquids (RTILs) are promising solvents to overcome some known limitations of conventional aqueous and organic media.

This work reports on the influence of the ionic liquid on the electrocatalytic performance and selectivity of the CO_2 electroreduction. RTILs composed of a common anion, bis(trifluoromethanesulfonyl)imide (NTf_2^-), known to solubilize fairly large amounts of CO_2 and different cations such as imidazolium, ammonium and pyrrolidinium were employed. The electrochemical behavior of CO_2 in these media was studied by voltammetry, while the liquid and gas products formed during electrolysis were analyzed by chromatographic techniques and NMR spectroscopy.

The cathodic stability of the ionic liquids at gold electrodes has a tremendous impact on the CO_2 electroreduction process. In [BMIm][NTf_2], the reduction of the imidazolium cation is concurrent with the reduction of CO_2, decreasing the faradaic efficiency for the formation of CO, but also producing an adduct with CO_2. The reduction of pyrrolidinium and ammonium-based ionic liquids is shifted to more negative potentials and does no longer appear as a competitive reaction.

Owing to its wide accessible potential window, [BMPyrro][NTf_2] is ideally suited to investigate various strategies for the electrochemical use of CO_2. Besides the potential, it is shown that the nature of the electrode (copper instead of gold), the controlled addition of protons or the presence of electroactive co-reactants (bipyridines) have an influence on the generated products and on the overall efficiency of the reduction process. In particular, formic acid, methane and glyoxylate are detected with appreciable faradaic efficiency at copper electrodes in the presence of protons.

Energy Applications of Ionic Liquids: From Global Perspectives to Computational Approaches

Douglas R. MacFarlane

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Ionic liquids offer a unique combination of properties that are particularly valuable as electrolytes in electrochemical processes and devices.[1] Their low vapour pressures, extended electrochemical stability and unusual solvent properties creates new possibilities in electro-synthesis, as well as device operation. In this presentation we discuss some recent examples in the field of sustainable energy generation and storage, highlighting the important role of computational studies in supporting these developments.

Efficient production of hydrogen from water would represent a significant step towards truly sustainable supplies of energy. However, water electrolysis is currently too low in efficiency to be practical, due mainly to energy losses at the water oxidation electrode, but also due to losses in the electrolyte. In this context we describe novel, high efficiency catalyst material based on earth abundant metal oxides prepared by electro-deposition. To carry this out under controlled conditions at elevated temperatures, an ionic liquid electrolyte medium is used to control the water activity in the electrolyte. The catalyst supports high rates of water oxidation and exhibits a light stimulation effect such that water oxidation rates are higher under illumination – a feature of interest in solar driven water splitting. We have also shown recently that certain protic ionic liquid based electrolytes tend to produce hydrogen peroxide (the two electron oxidation) rather than oxygen (the four electron oxidation) during water oxidation. The result is a very significant improvement in the energy efficiency of the water oxidation process.

In other contexts, ionic liquids are having an impact as energy device electrolytes. Important recent example of this are merging in the fields of (i) sodium batteries, where inorganic-organic salt mixtures[2] are supporting impressively long cycle life in the battery (ii) magnesium batteries where ionic liquids offer a finely balanced co-ordination environment[3] and (iii) thermo-electrochemical devices – power generating devices based on a temperature gradient and an electrochemical Seebeck effect – where nique combinations of redox couples and the unusual solvation environment offered by certain ionic liquids are producing record-high Seebeck coefficients and thermopower.[4]

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Energy harvesting and storage with ionic liquids: the essential physics at the nanoscale

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The renewal of interest to fundamental mechanisms of energy storage in electrochemical supercapacitors was boosted by the progress in development of novel materials (mainly carbon based) for nanostructured electrodes. It was also affected by the booming research in room temperature ionic liquids that offers virtually unlimited number of new electrolyte combinations. Some of them have large potential windows that allow to charge capacitors to higher voltages and thereby store more energy. This material-science based progress had to be matched with detailed investigation of performance of such systems. In particular, exploiting ultrananoporous electrodes, with pores just about to accommodate one layer or one row of ions, can increase the interfacial area and thereby the stored energy, but what will be the capacitance-voltage dependence and the dynamics of charging of such electrodes? What are the laws of population of such pores with ions subject to applied potential, and the conditions for maximizing stored energy and power?

There was a considerable progress in this area over the last five years. Basic mechanisms of charge equilibria in ultrananoporous electrodes have been understood based on statistical theory of ion-ion and ion interactions in nano-confinement. The modes of charging dynamics have also been revealed based on kinetic theory and simulations. The talk will overview these advances, with a focus on the effects that theory explains or predicts, as well as highlight pressing questions for future experiments and theory.

Sister systems to supercapacitors are electroactuators. These can be and are being used for the conversion of time dependent applied voltage into mechanical motion, or other way around – for the conversion of the applied force into the AC current. Such harvesters of mechanical work, draw currently attention in the context of AC-current generation from walking. Physics of this class of systems will also be briefly reviewed.

With intention to overview this research area, the talk will still be majorly based on a series of joint works of the *theoretical chemical physics* team at Imperial College and our partners at University of Strathclyde (UK), University of Drexel, Virginia Tech, ORNL, FZ-Juelich (Germany), University of Tel Aviv, LPTL CNRS (France), HUST (China) and other groups, highlighted and acknowledged in the talk. Some papers of this series are cited below.

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Ionic liquids for supercapacitor applications

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The electric double layer is generally viewed as simply the boundary that interpolates between an electrolyte solution and a metal surface. Contrary to that view, recent studies have shown that the interface between ionic liquids and metallic electrodes can exhibit structures and fluctuations that are not simple reflections of surrounding bulk materials [1]. The charge of the electrode is screened by the interfacial fluid and induces subtle changes in its structure, which cannot be captured by the conventional Gouy-Chapman theory.

In recent years, this topic has been more intensively addressed in order to develop more efficient supercapacitors [2]. The latter are electrochemical devices that store the charge at the electrode/electrolyte interface through reversible ion adsorption. In order to understand the molecular mechanisms at play, we have performed molecular dynamics simulations on a variety of systems made of ionic liquids and electrodes of different geometries ranging from planar to nanoporous. A key aspect of our simulations is to use a realistic model for the electrodes, by allowing the local charges on the atoms to vary dynamically in response to the electrical potential caused by the ions and molecules in the electrolyte [3].

These simulations have allowed us to gain strong insight on the structure and dynamics of ionic liquids at electrified interfaces. From the comparison between graphite and nanoporous carbide-derived carbon electrodes, we have elucidated the microscopic mechanism at the origin of the increase of the capacitance enhancement in nanoporous carbons [4]. The simulations also provide us the diffusion coefficients of the ions and the charging times for the full supercapacitor device [5]. More recently, we have focused on the determination of redox reaction rates in nanoporous carbons.

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Electrical double layer structure at metal electrodes and electrochemical characteristics of supercapacitors based on ionic liquids

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Cyclic voltammetry, electrochemical impedance spectroscopy, in situ STM and surface enhanced infrared adsorption (SEIRA) spectroscopy have been applied for the study of the electrical double layer at magnetron sputtered thin film Bi, Sb or Pb or single crystal Bi(hkl) , Sb(hkl) or Cd(0001) electrodes in the room temperature ionic liquids. A wide potential range of ideal polarizability has been established for the different electrode | ionic liquid systems from -1.6 to -0.1 V (vs. Ag|AgCl in the same ionic liquid).

For Pb electrode, the shape of differential capacitance plots depends noticeably on the single crystal plane used. For (the magnetron sputtered thin film Pb electrode, the differential capacitance vs. potential curve shows two maxima with a minimum at the perceived potential of zero charge. Asymmetric shape of the capacitance vs. potential curves for other metal electrodes has been observed. The first application of the in situ SEIRA technique for the study of Pb electrodes in an electrolyte solution is shown and the results are put into context of the latest developments concerning screening of different metal interfaces in ionic liquid medium. Slow kinetics of faradic reactions including oxide reduction reaction is demonstrated, which may limit the application of dry ionic liquids in various electrochemical devices including lead-acid batteries.

A wide selection of ionic liquids has been tested. In situ synchrotron radiation based XPS studies have been conducted and influence of chemical composition of ionic liquid on the region of ideal polarizability has been tested. The role of specific adsorption of anions on the in situ XPS data will be discussed. Applicability limits of various ionic liquids, their mixtures and solutions of ionic liquids in non-aqueous solvents as electrolytes in supercapacitors will be discussed. The role of surface active anion on the energy and power densities of supercapacitors will be analysed.

WEDNESDAY 22 FEBRUARY 2017

Enhancement of energy storage efficiency by tuning the composition of ionic liquids mixtures

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Evolution from fossil fuel energy to renewable energy sources and technologies is in the spotlight towards an accelerated energy transition process. One of the challenges of the intermittent renewable energy production is related with the existence of an appropriate energy storage technology in order to effectively consume the renewable energy generated.

Stemming from the results of studies aiming to understanding of the role of ionic species components of ILs on the electrical double layer structure and capacity, recent research efforts have been focused on the possibility of increasing the energy and power densities of EDL capacitors by combining actions upon the electrode surface [1] and tailoring the electrolyte composition by using ionic liquids mixtures [2,3]. ILs mixtures formulation revealed to be a promising strategy to tune EDL capacitors performance by regulating the both ions concentration near the electrode surface. According to the results obtained, it was possible to demonstrate the existence of an optimal IL mixture composition and an electrode potential at which the differential capacitance of the mixture increases approximately 3 times comparatively with their pure stating materials.

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BIREDOX IONIC LIQUIDS: NEW OPPORTUNITIES TOWARD HIGH PERFORMANCE SUPERCAPACITORS

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Kinetics of electrochemical reactions are several orders of magnitude slower in solids than in liquids as a result of the much lower ion diffusivity. On the other hand, the solid state maximizes the density of redox species, which is at least two orders of magnitude lower in molecular solutions because of solubility limitations. For such devices the ideal system should endow the liquid state with a density of redox species close to the solid state. Here we report an approach based on biredox ionic liquids (ILs) to achieve towards bulk like redox density at liquid like fast kinetics, Fig. 1a. The cation and anion of these biredox ILs bear moieties that undergo very fast reversible redox reactions.[1] As a first demonstration of their potential for high-capacity / high-rate charge storage, we used them in supercapacitors with specific capacitance of 200 F/g and 370 F/g respectively for 0.5 M of biredox ILs in BMimTFSI and for pure biredox ILs at 60°C (Fig. 1b). [2] This new class of functional materials opens up a wide new field in redox materials and their applications in energy storage and beyond.

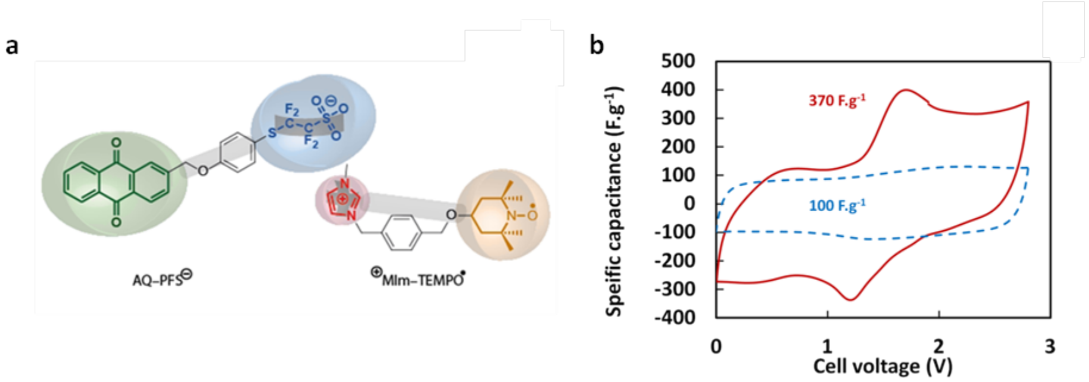

Figure 1| charge storage in EDLC with the biredox IL enhanced supercapacitor. a, Structure of the biredox IL comprising a perfluorosulfonate anion bearing anthraquinone (AQ–PFS$^-$) and a methyl imidazolium cation bearing TEMPO (MIm$^+$–TEMPO$^\bullet$). **b**, Cyclic voltammetry at 5 mV·s^{-1} with pure biredox IL at 60°C (red solid line) and pure BMImTFSI (blue dashed line) made with PICA activated carbon as electrodes.

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DEEP EUTECTIC SOLVENTS - TOWARDS THE CONCEPT OF LIQUID ACTIVE INGREDIENTS

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Deep eutectic solvents, DESs, are mixtures of quaternary ammonium salts and hydrogen bond donors such as urea or glucose [1, 2]. There are in excess of 10^5 binary liquid mixtures possible and an almost limitless number of ternary and quaternary mixtures. Inclusion of hydrophobic and hydrophilic groups in the same liquid enables novel solvent properties to be blended. The concept of producing active ingredients as part of the DES will be explained using a variety of pharmaceutical and natural product examples. Many quaternary ammonium salts and hydrogen bond donors are naturally occurring and some food grade examples are demonstrated in this presentation. DESs have been used for a wide variety of applications including metal processing, biocatalysis, leather processing and material preparation [3]. The concept of how these materials can be safely used in consumer products is shown together with the theory of why they can selectively dissolve solutes from a complex matrix.

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Electrodeposition from Deep Eutectic Solvents: A nucleation study

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The electrodeposition of metals and alloys from aqueous electrolytes is limited by operational (the narrow electrochemical window and hydrogen evolution) and environmental (use of hazardous chemical) constrains. To surpass these disadvantages, in recent years Ionic Liquids (ILs) have attracted a significant attention and are expected to be promising alternatives for various electrochemical processes, including electrodeposition. [1]

Although the increasing number of ILs in the market and research in this subject, the industrial application of ILs is still limited due to high price and water sensitive properties of some of the liquids. A new kind of solvent was introduced by Abbott and co-workers [2] which consisted on mixtures of substituted quaternary ammonium halide cations (such as hydroxyethyltrimethylammonium chloride) with metal chlorides [2] and/or suitable hydrogen-bond donors such as carboxylic acids, alcohols and amides [3]. These new solvents named Deep Eutectic Solvents (DES) have proved to be a good solvent to metal [4] and alloy [5] electrodeposition or to metal surface treatments [6].

In this work we will present a thorough study of the nucleation process in the preparation of metallic films and a comparison with the electrodeposition from aqueous electrolytes will be made.

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Fundamental studies on the early stages of electrochemical nucleation and growth from Deep Eutectic Solvents

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Fundamental understanding of the early stages of electrochemical nucleation and growth is important in a wide variety of applications that make use of nanostructured surfaces (electroanalysis, electrocatalysis, etc.). Although studied since decades, the process is not fully understood yet. Moreover, Room Temperature Ionic Liquids (RTILs) in general and Deep Eutectic Solvents (DESs) in particular have generated great enthusiasm as a new generation of non-aqueous electrolytes. They offer several advantages, such as high stability at higher temperatures and broad electrochemical window compared to aqueous solutions. Particularly, DESs are easier to prepare, less toxic and much cheaper than room temperature ionic liquids (RTILs) [1]. However, the use of these non-aqueous electrolytes as electroplating media adds a further level of complexity to the already intricate electrodeposition field.

On the one hand, we investigate the electrodeposition of nickel on different substrates (glassy carbon, low-carbon steel) from 1:2 choline chloride – urea (1:2 ChCl-U) DES. By combining electrochemical techniques, with ex-situ FE-SEM, XPS, HAADF-STEM and EDX, we aim to better understand the electrochemical processes occurring during nickel deposition. Special attention is given to the interaction between the solvent and the electrodeposited nickel phase. This is of high relevance when using DESs as electrolytes, since these interactions have shown to be substantially different from these in aqueous solutions [2,3]. In this regard, the effect of residual water in the DES is highlighted [4] as suggested in recent studies [5].

On the other hand, the effect of residual water in electrodeposition from non-aqueous solvents is also studied by Finite Element Simulation using Multi-Ion Transport and Reaction Model (MITReM). The model takes into account the transport of all relevant species driven by convection, diffusion and migration together with chemical/homogeneous reactions (HR) in the electrolyte and electrochemical reactions (ER) at the electrode surface [6]. The effect of competitive reduction and temporary adsorption of water on the surface of the growing metallic phase is related to the transition [6] from kinetic to diffusion controlled growth.

These ongoing studies indicate how the combination of experiments and numerical modelling provides an interesting platform to study the early stages of the electrochemical nucleation and growth in non-aqueous solvents.

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Electroless deposition of metals on silicon in ionic liquids and its application for lithium ion batteries

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Silicon is an essential material in electronics and photonics industries. Deposition of metals onto silicon is important for electrical contact for various devices. Electrodeposition and electroless deposition are simple routes for deposition of metals onto silicon[1], [2]. However, for electroless deposition, HF is necessary for the galvanic displacement reaction to take place. As HF is a hazardous acid, a HF free electroless deposition would be advantageous.

Here, we show that metals such as antimony (Sb) and silver (Ag) can be directly deposited onto electrodeposited silicon at room temperature from ionic liquids containing $SbCl_3$ and silver bis(trifluorosulfonyl)amide (AgTFSA). Fig 1a shows the SEM of electrodeposited Si. On addition of ionic liquid containing AgTFSA, Ag could be directly deposited which changed the microstructure considerably. The EDX confirms the presence of both Si and Ag (fig 1b). Fig 3 and 4 shows the microstructure and EDX spectra of electroless deposited Sb on Si, respectively.

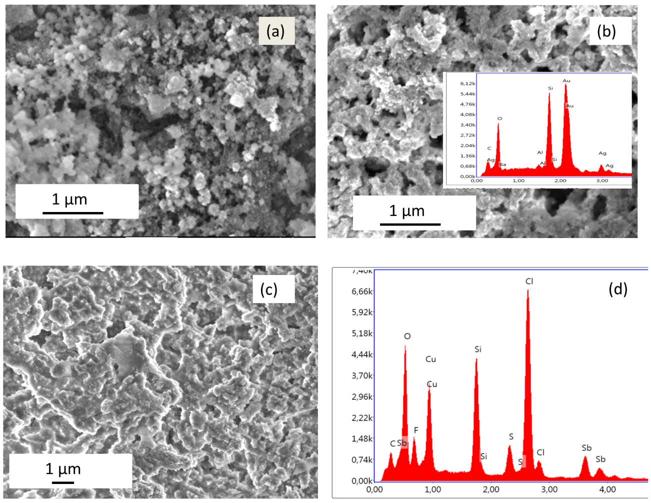

Fig 1 (a): Microstructure of electrodeposited Si (b) Electroless deposition of Ag on Si. Inset showing the EDX spectra showing the presence of both Si and Ag (c) microstructure of electroless deposited Sb on Si (d) EDX spectra of deposited Sb on Si

Quartz crystal microbalance (QCM) and in situ AFM was also used to evaluate the reaction kinetics of the electroless deposition process. Finally, the electroless deposited Sb on Si was used as an anode for lithium ion battery. It was observed that compared to electrodeposited Si, the Sb modified silicon resulted in a higher Li storage.

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Ionic liquid technology for recovery and separation of rare earths

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End-of-life neodymium-iron-boron and samarium-cobalt permanent magnets, fluorescent lamps and metal hydride batteries are valuable secondary resources of rare earths. These resources are characterised by relatively small volumes, but high concentrations of rare earths.[1] On the other hand, industrial process residues such as bauxite residue (red mud) and phosphogypsum contain low concentrations of rare earths, but are available in huge volumes.[2] Recovery of rare earths from end-of-life consumer goods by urban mining and from industrial process residues by landfill mining can partly mitigate the supply risk of these critical metals. Efficient recovery of rare earths from these resources is a technological challenge, even though many pyrometallurgical and hydrometallurgical processes have been described in the literature. At KU Leuven (Belgium), we are developing new breakthrough technologies for recovery and separation of rare earths based on the use of ionic liquids. Ionic liquids are solvents that consist entirely of ions.[3] These solvents have properties that are quite different from those of conventional molecular organic solvents. Ionic liquids can find applications as lixiviants for selective leaching of rare earths from solid materials, as organic phase in solvent extraction processes for separation of rare earths, and as electrolytes for the electrodeposition of rare earths and alloys. During this talk, several new ionic liquid processes will be discussed: (1) recovery of yttrium and europium from end-of-life fluorescent lamps,[4] (2) recovery of rare earths from neodymium-iron-boron magnets,[5] (3) separation of rare earths from transition metals by extraction with undiluted ionic liquids,[6] (4) separation of rare earths by homogeneous liquid-liquid extraction (HLLE),[7] (5) efficient recovery of scandium from leachates of bauxite residue.[8]

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THURSDAY 23 FEBRUARY 2017

SAIL away - Exploring the potential of surface active ionic liquids: From phase diagrams to the extraction and purification of biomolecules

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Most people think of ionic liquids as molten salts but, if the nanostructuration is what makes an ionic liquid distinct, they are closer to structured fluids such as surfactants and block copolymers than to molten salts or conventional liquids.

Much can be gained from the study of the surface of ionic liquids, and some interesting phenomena of surface structuration, including surface crystallization, will be addressed.

If their surface shows a broad range of interesting and unique features, the bulk of these fluids, or their aqueous solutions, can be even more surprising. From the self-assembly in liquid crystals to the interfacial behavior and formation of complex aggregates, alone or in interaction with other surfactants and block copolymers they can produce a rich variety of phase diagrams, and be used to manipulate the CMCs and cloud points of a range of compounds. Yet these surfactant ionic liquids are more than just curiosities, and applications from the superactivation of enzymes to the extraction of biomolecules, such as fluorescent proteins, from biomass will be presented.

Like common surfactants, for which small chain lengths prevent the formation of micelles but allow them to act as solvents and hydrotropes in aqueous solution, the nanostructure, even if incomplete, produces dramatic changes in the properties of their aqueous solutions, allowing the solvation of many different compounds and the appearance of novel mechanisms of dissolution, intermediate between the conventional solvation and micelle dissolution: the poorly understood hydrotropic realm. The action of ionic liquids as hydrotropes will be presented for a variety of molecules, from simple phenolic compounds to alkaloids, complex drugs and polymeric lignin, and the hydrotropic dissolution mechanism discussed phenomenologically, and by Molecular Dynamics and the Kirkwood-Buffer theory.

It is expected that this overview of the work developed in our laboratory, covering from the basic molecular phenomena to applications with industrial potential, may prompt a swerve in the view of ionic liquids from molten salts to ionic structured fluids more akin to surfactants, and instill the desire for novel studies and approaches in the use of ionic liquids.

Biomass processing with ionic liquids: Off the beaten track

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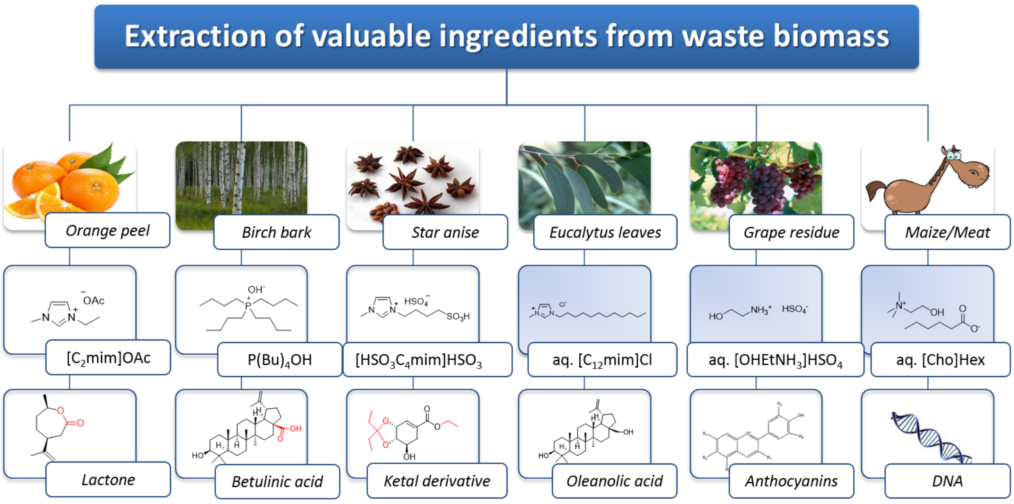
While the growing research on ionic liquids as solvents for lignocellulosic biorefinery is mostly related to the production of biofuels, relatively little attention is paid to the extraction of valuable ingredients from plant materials [1]. Yet there are several aspects of ILs that are potentially advantageous for the extraction of valuable natural products: Apart from their unique solvent properties and potential environmental benefits, the ability of ILs to dissolve biomass can lead to a better access to valuable ingredient embedded in the biopolymers [2]. This offers a range of novel applications of the beaten track varying from a value-added biorefinery to drug manufacturing or food analysis.



In here, we present novel strategies towards the isolation of valuable components, including pharmaceutically actives, essential oils or biomacromolecules from biomass such as tree bark, maize or grape residues [3],[4],[5]. We will not only discuss ionic liquids as mere extraction media, but focus on the design and role of functionalized ionic liquids, e.g. surface-active, biodegradable or Brønsted acidic ionic liquids that provide novel and unique possibilities for fine chemical production, drug synthesis or bioanalytics [6],[7].

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THURSDAY 23 FEBRUARY 2017

Ionic liquids unforeseen values in fungal biology and biotechnology

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Ionic liquids discovery has just celebrated 100 years. These liquid salts consist solely of ions, one of which is typically organic and asymmetrical. Matchless physical and chemical properties stirred their use as alternative solvents in many chemical processes. The recent demonstration of ionic liquids occurrence in nature (probably as part of widespread chemical-base defensive mechanisms)[1] might boost their interest in biological sciences. In the search of mechanistic understandings of ionic liquids eco-toxicological impacts in fungi,[2] we have collected data on the fungal proteome,[3] transcriptome and metabolome[4] upon exposure to this chemical stress. Data illuminated new hypotheses altering the paradigm of our research – exploit ionic liquids as tools to guide discovery of pathways and metabolites in fungi that may impact their development and pathogenicity. As our group gets closer to understanding the primary effects of each ionic liquid family and move towards the identification of their specific gene targets,[5-6] the vision of developing antifungal ionic liquids and materials, by taking advantage of elegant progresses in this field, might become a reality. Moreover, task-designed ionic liquid can be used to isolate naturally occurring antifungal plant polymers.[7-8] We are confident that the frontier research in the cross-disciplinary field of ionic liquids may provide us unforeseen means to address the global concern of mycotic diseases.[9] Pathogenic and opportunistic fungi are responsible for numerous infections and are emerging as causative agents in a broad diversity of clinical conditions. They kill annually nearly 1.5 million immunocompromised individuals worldwide, a similar rate to malaria or tuberculosis. In my lecture I will review our major findings and current hypothesis, contextualizing how they might bring us closer to efficient strategies to prevent and fight mycotic diseases.

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Ionic liquid ion exchange: exclusion from strong interactions leaves cations to the most weakly interacting anions

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It is well established that for a fixed cation, varying the anion of an ionic liquid determines its physicochemical properties and its activity as solvent or catalyst for chemical processes. Although ion exchange is an acknowledged phenomenon, it is often overlooked on the level of applications, resulting in poor process design and interpretation. Our recent work on the application of trihexyl(tetradecyl)phosphonium ionic liquids for processing of fermentation products demonstrated a change in appearance, properties and reaction outcome after contact with a high salinity fermentation broth, and a change in aqueous anion composition. This urged us to look into ion exchange and its implications on ionic liquid-mediated processes. We propose here a framework to describe and predict ionic liquid ion exchange with the ion pair binding energy as quantitative parameter for the ion couple's strength and its tendency to exchange. In a given system of two cations and two anions, the most strongly interacting cation and anion will couple, to strive for the highest ion pair binding energy, and leave the remaining cation and anion to match. The typical low charge density cations in ionic liquids display relatively weak electrostatic interactions with anions and thus have a lower ion pair binding energy compared to conventional high charge density cations, making that they can only engage in interactions with the most weakly interacting anions in the system, after all stronger couples have formed. Ion exchange will proceed if an added cation interacts stronger with the native ionic liquid anion than with its initial counterion, leaving the latter to couple with the ionic liquid cation to maintain electric neutrality. This was demonstrated both for phosphonium and imidazolium ILs, with and without solvation effects of water. The importance on processing is demonstrated for the esterification of acetic acid as model organic reaction. The conversion of acetic acid into ethyl acetate is determined by the amount of acetate that exchanges for the native ionic liquid anion and the availability of protons to catalyze the reaction, and can be increased or decreased depending on the added anion. This study intends to be a stepping stone towards a generalized, quantitative rationale for ionic liquid ion exchange, to predict and understand the outcome of ionic liquid-mediated processes with ionic substrates and catalysts, where their availability for reaction is dictated by the extent of ion exchange.

Impact of ionic liquids on the extraction and purification of phycobiliproteins from red seaweeds

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A highly efficient and low cost extraction and purification process to recover proteins, namely the green fluorescent protein from fermentation broth and phycobiliproteins from *Gracilaria* sp., highly available worldwide (and in Portugal) and a promising phycobiliproteins' source, is being developed. Phycobiliproteins are photosynthetic proteins recognized for their high solubility in water, great photoluminescence efficiency, and stability under different pH values, temperatures and time of storage. These are important as fluorescent biomarkers due to their outstanding fluorescent properties, and as natural colorants in health, cosmetic and food industries. Their global market is still small, but estimated to growth 20%/year, because it is limited by the high prices of the pigments' extraction/purification processes available. The applications of bio-based marine pigments require different purity levels; low purity for the energy sector, high purity for food and cosmetic, and very high purity for pharmaceutical and medical applications. For all these applications, processes for the efficient extraction and adequate purification of phycobiliproteins from algae are required. The common practice is the precipitation by ammonium sulfate, followed by chromatography and gel filtration, or enzymatic processes[1]. However, these approaches are costly, with a poor selectivity and do not guarantee an adequate purity of the final product.

Technological innovation on algae processing is thus required, to contribute for the creation of new products fostering the emergence of new markets. An effective and economically viable method for the proteins extraction and purification from water-rich extracts is the use of aqueous biphasic systems (ABS) based in ionic liquids (ILs)[2]. In this context, this work focuses the use of aqueous solutions of ILs[3] as alternative and more performant solvents to develop integrated processes of extraction and purification by applying ABS to recover pure phycobiliproteins from wet seaweed. In this context, different ILs structural features and process conditions have been investigated considering their capacity to disrupt the biomass cells and to extract as much as possible the phycobiliproteins. In a second task, the optimization of the purification step by applying IL-based ABS is assessed. By this optimization, preliminary results of extraction of the green fluorescent protein are assessed.

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Synthesis of 7-azoniabicyclo[2.2.1]heptane-based dicationic liquids

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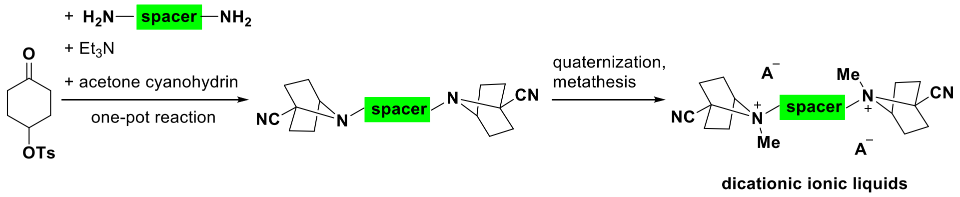
This abstract presents the synthesis of a new class of dicationic ionic liquids based on two 7-azoniabicyclo[2.2.1]heptane moieties and a variable spacer. The construction of the 7-azabicyclo[2.2.1]heptane skeleton and formation of the two- up to ten-atom spacer occurred concurrently in a one-pot reaction. Quaternization and subsequent metathesis afforded the dicationic ionic liquids consisting of two linked quaternized bicyclic moieties and bis(trifluoromethylsulfonyl)imide and dicyanamide as counterions.



Ionic liquids mixtures as an alternative approach to enhance the tunability of aqueous biphasic systems

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In the past decade, ionic liquids (ILs) were introduced as phase-forming components and as promising replacements of polymers in aqueous biphasic systems (ABS).[1] Due to the wide variety of their chemical structures, the introduction of ILs in ABS allows to overcome the narrow hydrophilic-hydrophobic range of the more typical polymer-based ABS. As a result, IL-based ABS have provided higher extraction performance and increased selectivity for a wide variety of compounds.[2] Phase diagrams and possible applications of ABS composed of ILs and salts were extensively investigated and it is now accepted that the phases' demixing ability and polarities of the coexisting phases are largely dependent on the IL anion hydrogen-bond basicity.[3] Thus, the tuning of ABS phases properties is frequently achieved by the IL anion change.

Taking into account the potential of binary mixtures of ILs to improve their tunable ability, the present work aims the evaluation on the use of mixtures of two imidazolium-based ILs, with opposite hydrogen-bond basicities, in the preparation of ABS. Novel phase diagrams of ABS constituted by mixtures of two ILs ($[C_4mim][CF_3SO_3]$ and $[C_4mim]Cl$) in different molar proportions, K_2CO_3 and water were initially determined and characterized. The obtained results were compared with simpler ABS composed of only one imidazolium-based IL, K_2CO_3 and water. Moreover, the partition coefficients of a series of dinitrophenylated (DNP)-amino acids in these systems were determined to infer on the relative hydrophobicity of the coexisting phases. The gathered results confirm that ABS composed of two ILs and one salt behave as quaternary systems and that the polarity range of their coexisting phases is further enhanced if compared with simpler IL-based ABS.

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Acknowledgments

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Study of the Electrochemical Stability of Ionic Liquids at Gold Electrodes

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During the last decades, ionic liquids have received increasing attention within the scientific community and in particular amongst the electrochemists. Indeed, due to their high ionic conductivity and wide electrochemical window, many ionic liquids appear to be good electrolytic supports for various electrochemical processes such as metal deposition or electrocatalysis.

Voltammetric experiments reveal that, in some cases, the reduction of the ionic liquid takes place concomitantly with the process of interest. It is surprizing to note that little is known on the cathodic decomposition of current ionic liquids such as imidazolium and pyrrolidinium-based ionic liquids.

In this work, we investigated in detail the electrochemical stability of [BMIm][NTf_2] ($BMIm^+$ = 1-butyl-3-methylimidazolium NTf_2^- = bis(trifluoromethanesulfonyl)imide) and [BMPyrro][NTf_2] ($BMPyrro^+$ = 1-butyl-3-methylpyrrolidinium) at negative potentials in relation with the electroconversion of CO_2 at a gold electrode.

Long-time electrolysis experiments were performed at controlled potential under nitrogen atmosphere and the ionic liquid was analysed afterward by ^1H and ^{19}F NMR spectroscopy. Additional information was obtained by chromatography techniques. Modifications of the ^1H NMR signals of the $BMIm^+$ cation and several new NMR signals ascribable to the reduction of the ionic liquid were detected. The structure of the electrogenerated products was elucidated thanks to various one- and two- dimensional NMR experiments and the outputs could be quantified as a function of the consumed charge. Additional experiments were conducted in order to examine the reactivity of the electrogenerated $BMIm^+$ products in contact with CO_2.

The study of the electrochemical stability at gold electrodes was extended to the pyrrolidinium based-ionic liquid [BMPyrro][NTf_2], in which the cathodic limit is shifted to more negative potentials. The reduction of the pyrrolidinium cation has been evidenced by ^1H spectroscopy while the reduction of the anion is here also occurring as indicated by the analysis of the chromatographic data.

Acknowledgement: This project is supported by a PDR-FNRS grant (BE) n° T.0090.130. R. Michez thanks the FRIA for his PhD fellowship.

Influence of the Electrode Material on the Electrochemical Stability of an Imidazolium-Based Ionic Liquid

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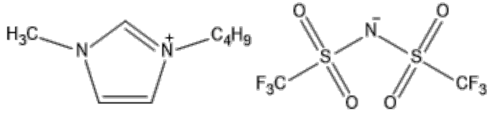
Imidazolium-based ionic liquids, which are known for their high ionic conductivity, their wide electrochemical window and relatively low viscosity at room temperature, are promising electrolytic media. For most applications, a high electrochemical stability of the RTILs is necessary to achieve a good efficiency of the process. It has been hypothesized that the electroreduction of the imidazolium cation gives rise to a radical which can further decompose to produce a carbene and a hydrogen atom adsorbed at the electrode surface. Additional products formed by recombination or disproportionation of these intermediates have also been predicted but only few experimental evidence for these conversion products has been provided.

In this work, the electrochemical stability of [BMIm][NTf_2] has been examined at various electrodes (Au, Cu, Pt, Hg) by performing long-duration electrolyses under potential control. The gas and liquid phases were analysed by chromatographic techniques and the composition of the catholyte was investigated by ^{19}F and ^{1}H NMR spectroscopy.



Chemical structure of the ionic liquid [BMIm][NTf_2]
$BMIm^+$ = 1-butyl-3-methylimidazolium, NTf_2^- = bis(trifluoromethanesulfonyl)imide

Carbene formation could be indirectly evidenced because of its implication in a proton exchange with the $BMIm^+$ cation. Besides, several signals ascribed to reductive decomposition products of the $BMIm^+$ cation were detected.

The proportions of these conversion products were found to be correlated with the hydrogen-atom adsorption ability of the electrode material, providing valuable information on the mechanism of cathodic decomposition of [BMIm][NTf_2].

Acknowledgement: This project is supported by a PDR-FNRS grant (BE) n° T.0090.130.
R. Michez thanks the FRIA for his PhD fellowship.

POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Biodegradation studies of a series of novel L-Phenylalanine derived Ionic Liquids by a modified Closed Bottle Test

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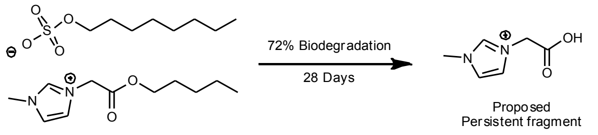
The association of Ionic Liquids (ILs) with green chemistry has increased substantially over the past decade concurrent with the upsurge in their use in industrial and academic applications. The properties that make ILs attractive for performance applications and candidates for green chemicals include the potential for high recyclability, low-volatility, low-flammability, low-toxicity, biodegradability and the potential for synthesis from renewable resources. However, early generations of ILs such as the butyl-methylimidazolium [bmim] class, have shown to be recalcitrant to biodegradation, [1] calling for the need to examine ILs for biodegradability.

The biodegradability of ILs has become increasingly more important as a point of characterisation of ILs. Information gained from biodegradation studies allows for rational design of performance chemicals and should help prevent the synthesis of persistent organic pollutants (POP's) - the "**Benign by Design**" concept (Scheme 1). [2] Biodegradation can be measured by a number of prescribed test methods including the Closed Bottle Test (CBT) and the CO_2 Headspace Test. Modifications to the prescribed test methods allow results to be obtained from biodegradation screening that were not initially accommodated for. [3] In this presentation the results of the biodegradation screening of a series of novel L-Phenylalanine derived ILs (and predicted transformation products) using a modified CBT will be presented along with analysis, synthesis and structural elucidation of transformation products detected by LC/MS after the test. [4] The ILs synthesised are the culmination of the design lessons learned within the Gathergood and Kümmerer research groups from previous generations of ILs studied. [5-7]



Scheme 1: Readily Biodegradable Imidazolium Octyl Sulphate IL

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Influence of additives on the electrochemical behaviour of BMImDCA at a gold electrode

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Due to their unique physical properties Room Temperature Ionic Liquids (RTILs) are interesting media to study at fundamental level and in novel electrochemical devices.

Since modifications of the double layer structure and composition may lead to important variation of the electrochemical reaction rates and mechanisms it is essential to investigate at the fundamental level the characteristics of RTIL|metal interfaces, which are still poorly understood in comparison with conventional electrolytes.

Cyclic voltammetry and electrochemical impedance spectroscopy methods were used to characterize the interfacial behavior of 1-butyl-3-methylimidazolium dicyanamide (BMImDCA) at an Au(poly) electrode in the presence of water and 2-thiouracil (2-TU), respectively, used as additives.

The experiments with the addition of 2-TU were all carried out in in a glovebox under a nitrogen controlled atmosphere while experiments with water were performed outside the glovebox. Cyclic voltammetry was used to determine the domain of ideal polarizability in the absence and presence of the additives and impedance measurements to obtain interfacial capacitance values.

The results show that the addition of water affects the electrochemical response of the electrolyte at both the negative and positive potential limits. Under oxygen atmosphere, the addition of water also affects the cathodic peak related to the superoxide ($O_2^{\bullet -}$) formation.

Differential capacity measurements were performed under nitrogen atmosphere by alternating current (ac) voltammetry at a constant ac frequency (f = 113 Hz). Capacitance values ($C_s = -Z''(2\pi f)^{-1}$) depend on the applied potential and on the composition of the electrolyte. Addition of 2-TU to the BMImDCA liquid leads to a significant decrease of the capacity values. The constant low capacity observed in a wide potential range evidences the adsorption of 2-TU molecules that displace the RTIL cations and anions by interacting strongly with the gold surface through sulfur- and nitrogen-gold bonds.

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Halides in Ionic Liquid Mixtures Electrochemical and in situ Characterization

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Ionic liquids are composed of entirely organic cations and organic or inorganic anions with a melting point close to room temperature. Liquid state makes possibilities to use these salts as electrolytes without any solvent addition. However, creating much more complicated interfacial structures.

For the detailed investigation of electrode | electrolyte interface Bi(111) monocrystal was used as electrode materials. Different ILs have been used for the investigation of adsorption characteristics of I^-, Br^- and Cl^- anions. 1-ethyl-3-methylimidazolium tetrafluoroborate was used (as less-active salt at the electrode surface) to prepare the mixture of ionic liquids. $EMIm^+$ cation and halide anions based salts have shown very good thermal stability, i.e. they are suitable electrolytes for higher temperatures devices as well.

Our recent studies have shown that the addition of specifically adsorbed halide ions in the mixture influences strongly the electrochemical double layer parameters and increasing remarkably the differential capacitance values of the system. We have also established to visualize the ion arrangements with in situ STM measurements and find conformation of the results by applying computational methods.[1–4]

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Electrochemical recovery of platinum from spent proton exchange membrane fuel cells using ionic liquid melts

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Proton Exchange Membrane Fuel Cells (PEMFC) are made of a membrane electrode assembly (MEA), constituted by two electrodes separated by a polymer membrane. The electrodes consist of a carbon substrate on which platinum nanoparticles are immobilized with a platinum loading ranging from 0.15 to 4 mg.cm-² [1]. The amount of platinum used in MEA represents 25 % of the MEA's price. With the future emergence of PEMFC, platinum used in MEA should represent a very important industrial market - approximately 20 % of platinum production- for platinum recovery. At the moment, only extractive pyro-hydro-metallurgical processes are known for the recovery of platinum contained in PEMFC [2]. Typically, in these processes, MEA are calcinated to eliminate the carbon substrate and the polymer membrane. Ashes obtained from this calcination are then leached by aqua regia, in order to recover the platinum. Calcination step leads to a high consumption of energy and induces the use of a fume treatment system. Moreover, the use of aqua regia, a highly corrosive solution, induces NOx emission and tight working conditions. It is then very important to find a new treatment pathway which can be more friendly environmental.

The aim of this work is to develop an electrochemical route for platinum recovery from MEA using ionic liquids (ILs). ILs are interesting solvents for hydrometallurgical treatments purposes due to their low vapor pressure and their chemical stability leading to safer/greener processes. As the platinum of MEA's electrodes is already immobilized on carbon substrates, the leaching of platinum can be achieved by electrochemical dissolution. The leached platinum can then be recovered by electrodeposition. For this purpose, ILs are particularly promising due to their wide electrochemical window allowing the electrodissolution and the electrodeposition of numerous metals [3].

Our results show that simultaneous electroleaching and electrodeposition of platinum is achievable in ionic liquids melts containing chloride ions. The leaching rates are comparable to those obtained by chemical dissolution in aqua regia without the use of any oxidant in the ionic liquid medium. The influence of applied potential or current was studied, as well as the influence of temperature and chloride content. The leaching efficiency and rate were evaluated by Atomic Absorption Spectrometry. By modulating the composition of the ionic liquid medium, we show that it is possible to recover platinum by electrodeposition at the counter electrode simultaneously to its electroleaching. This single cell process was then successfully applied to the recovery of platinum from MEA's electrodes, in ambient atmosphere.

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Exploration of different ionic liquid electrolytes for zinc electrodeposition

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Zinc is an interesting material for energy storage devices, as it is inexpensive, abundant and nontoxic material. Electrodeposition of zinc from the aqueous solutions has been studied for many years. The major impediments in the aqueous electrolytes are the evaporation of the electrolyte and dendritic zinc structure. Therefore, it is of interest to find alternative electrolytes for zinc electrodeposition to overcome these issues. Ionic liquids have some favorable advantages over aqueous electrolytes, making them suitable for metal electrodeposition. In this study, two different ionic liquids such as [EMIm]OAc and $[Py_{1,4}]TfO$ have been employed to investigate the electrodeposition of zinc film, macroporous and nanowires structures.

The environmentally friendly ionic liquid 1-ethyl-3-methylimidazolium acetate ([EMIm]OAc) was used as an electrolyte for Zn electrodeposition. The electrochemical behavior of various concentrations of zinc acetate and water were studied in this ionic liquid. The solvation of zinc ions was investigated with Raman and IR spectroscopy as a function of concentration. It was found that the increasing of $Zn(OAc)_2$ and water concentrations change the species of Zn(II) and the morphology of the electrodeposited zinc[1].

The highly ordered macroporous zinc was electrodeposited on the brass substrate covered by polystyrene spheres as template in the ionic liquid 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate $[Py_{1,4}]TfO$ and subsequently the cycling behavior of a zinc/polystyrene composite electrode in the same ionic liquid was investigated. The results show that zinc grows uniformly within the voids of the polystyrene spheres with no hints of dendritic growth before and after cycling process[2]. Furthermore, the template-free zinc nanowires were synthesized by electrochemical deposition from two different electrolytes, $Zn(TfO)_2/[Py_{1,4}]TfO$ and $ZnCl_2/[Py_{1,4}]TfO$ at 125 °C on the gold and indium tin oxide (ITO) substrates[3].

Finally, a new class of electrolyte was synthesized with a mixture of 1-butylpyrrolidine and different ratios of $ZnCl_2$ to investigate the feasibility of Zn electrodeposition from these electrolytes at 60 °C and room temperature without and with the presence of toluene, respectively. Contrary to the conventional ionic liquids, where the anionic species are responsible for the electrodeposition of metals, in this new ionic liquid, the metal containing cationic species are responsible for electrodeposition[4].

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Template-free electrodeposition of 1D Te nanostructures in ionic liquids

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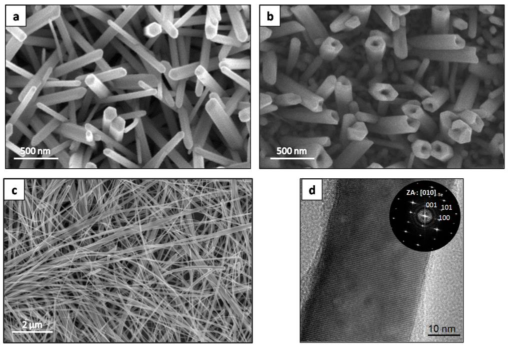
Electrodeposition of nanowires is usually performed in a porous template and involves multiples fabrication steps, like the preparation of the template and its removal. A single step template-free electrodeposition would in some cases be more convenient, for example to synthesize core@shell structures. It has been shown in literature that ionic liquids, in addition to have high electrochemical and thermal stabilities, can act as capping agents allowing the formation of nanostructures without using a template [1].

We will present here the template-free electrodeposition of Te nanostructures in a piperidinium ionic liquid. A systematic study of the influence of synthesis parameters Te(IV) concentration, applied potential, nature of the cation and of the anion of the ionic liquid and the halide content in the electrolyte) was conducted and revealed that the deposits morphology mainly depends on mass transport conditions and Te(IV) speciation. Under diffusional control, nanowires are deposited (Figure a), whereas by applying high overpotential values and then severe mass transport conditions, hollow nanostructures are formed due to a limitation by species supply (Figure b) [2].



The electrolyte composition determines the Te(IV) speciation that also strongly influences the morphology of the nanostructures. Specifically, the addition of a small amount of bromide ions in the electrolyte allows to synthesize 70 µm long hair-like nanowires with a mean diameter of 50 nm (Figure c) [3]. High Resolution Transmission Electron Microscopy analyses show that the nanostructures are single crystalline and grow along the *c*-axis, with a smooth interface and no external surface layer (Figure d).

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Aluminium Chloride – Trimethylphenyl Ammonium Chloride Ionic Liquid for Aluminium Electrodeposition

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Room temperature ionic liquids (RTIL) are used for many applications, because of their non-volatile and non-flammable character, as well as their high thermal and chemical stability and their wide electrochemical window (up to 5 V) [1]. All these advantages, especially the last one make RTIL very suitable as solvents for electrodeposition of strongly reducing species, such as aluminium [2,3].

The aluminium electroplating on carbon steel is carried out potentiostatically and galvanostatically from the inexpensive aluminum chloride - trimethylphenylammonium chloride room temperature ionic liquid (RTIL). The electrochemical conditions and temperature are studied in terms of coating composition, morphology and resistance to corrosion. For each condition, the coatings are composed of metallic crystalline aluminum, contain a small amount of chlorine and some RTIL cations remain weakly adsorbed on their outer surface. It is shown that the temperature increase favours growth but at the expense of nucleation, leading to less covering coatings at higher temperatures. The corrosion inhibition ranges from 34% to 98%.

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Use of secondary hydrogen bond donors and group 1 salts for the tailoring of chloride free DES

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Deep Eutectic Solvents (DES) and ionic liquids (ILs) have the potential to become important industrial solvents for synthesis, catalysis, extraction, and purification, as they have a low vapor pressure and unusual catalytic properties[1].DES are room temperature ILs created by complexing a Hydrogen bond Acceptor(HBA), typically a quaternary ammonium salt, with a hydrogen bond donor (HBD) to lower its melting point. In addition DES also show the potential for applications in electrochemistry due to their high ionic conductivity and electrochemical stability[2]. Physical properties such as melting point, density, viscosity, and ionic conductivity can be adjusted through variation of both the HBD and HBA with an ever increasing list of possible combinations of amino acids, carboxylic acids, amines sugars and polyols being reported[1].

However, most DES have a high halide concentration[2], which makes them aggressive towards metals like aluminium and magnesium. Therefore, our goal is to establish the potential of chloride free Natural DES (NaDES) as an alternative electrochemical medium maintaining the low cost and environmental compatibility that characterize DES[3].

We report the synthesis and characterization of a novel NaDES with a large charge diffuse anion instead of the commonly used large, charge diffuse cation (Choline chloride). Furthermore, we evaluate the role of methanol and sodium citrate salts on the conductivity and viscosity of the system. The purpose of the tailoring was to obtain similar conductivity and viscosity as those of more established DES[4,5] and ILs electrochemical baths. The molecular kinetics for viscosity and ion mobility were modelled to determine the effect of the additives on charge and mass transport. Furthermore, the changes in ionicity were tracked via the Walden plot. We determined the potential window of the NaDES to be between -0.8 V to 1 V. The electrochemical data is reported against a ferrocene internal reference.

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Comparative Spectroscopic Study of Chromium(III) Coordination Compounds in Deep-Eutectic Solvents and Water

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For the protection of steel from harsh condition, those products are generally coated with a **hard chromium layer** which is electrodeposited from an aqueous solution containing the toxic, mutagenic and carcinogenic Cr(VI). Powered by the quest to a **sustainable** production process and by the incentive of new European legislations, OCAS NV has already been working for 6 years on a patented Cr(VI)-free alternative. This new hard chrome-plating process is established by the electrodeposition from a Cr(III) containing deep-eutectic solvent (DES) on a steel substrate. Advantages include the presence of the more sustainable Cr(III) as alternative for Cr(VI), the lack of sulfuric acid and hydrogen embrittlement, the broader potential window of the DES with regard to water, and the intrinsically more efficient reduction process of Cr(III) to Cr(0).

Due to the **lack of fundamental knowledge** of the deposition mechanism, it is far from straightforward to predict the in-use properties of the layer. Therefore, this project focusses on the elucidation of the **coordination chemistry of the Cr(III) species** in the DES as a function of composition and the presence of additives, and the link of this knowledge with the properties of the eventual hard chromium layer.

Hence, the deep-eutectic solvent is analyzed by means of several spectroscopic techniques such as single crystal XRD, UV-Vis, and Extended X-Ray Absorption Fine Structure (EXAFS) measurements.
Since 1957, the generally used reference for the analysis of chloroaquachromium(III) UV-Vis spectra has been the work of Elving et al[1]. However, since all possible Cr(III) species are in equilibrium, their statement that each of the compounds could be isolated separately without interference of some of the other species could be questionable. Therefore, the spectroscopic data were analyzed by means of a high-end chemometric method called **Multivariate Curve Resolution – Alternating Least Squares (MCR-ALS)**[2]. This technique is used to unravel the spectra of the different coordination species which are present in the DES and to obtain information about their relative concentration in each possible DES composition. These data were compared with similar experiments in aqueous solutions and with literature[1]. Consequently, new state-of-the-art reference spectra could be obtained for the possible Cr(III) species in both aqueous and DES mixtures.

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Electrodeposition of Nickel Nanostructures from Deep Eutectic Solvents: Passivation and Self-Limiting Growth

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Supported nickel nanoparticles (NPs) are widely used as catalysts for fuel cells and electrosynthesis, as well as for biosensors and supercapacitors. These nanomaterials can be fabricated by multiple methods. However, electrodeposition offers several advantages since it permits the growth of the NPs directly on the support of interest and allows obtaining highly electroactive nanostructures [1]. In order to produce highly electroactive nanostructures, the electrochemical processes on the nanoscale need to be understood. In this context, Deep Eutectic Solvents (DESs) have generated great enthusiasm as a new generation of non-aqueous electrolytes. They offer plenty of advantages, such as high stability at higher temperatures and broad electrochemical window compared to aqueous solutions. Furthermore, DESs are easier to prepare, less toxic and much cheaper than room temperature ionic liquids (RTILs) [2].

The electrodeposition of nickel nanostructures on glassy carbon was investigated in 1:2 choline chloride – urea (1:2 ChCl-U) DES. By combining electrochemical techniques, with ex-situ FE-SEM, XPS, HAADF-STEM and EDX, the electrochemical processes occurring during nickel deposition were better understood. Special attention was given to the interaction between the solvent and the electrodeposited nickel phase. A passivation phenomenon attributed to the presence of residual water in the DES was disclosed. In the frame of this investigation, a large population of small crystalline nickel nanostructures was obtained at different deposition potentials. Interestingly, we have found evidence that supports the presence of an interaction between the DES and the growing nickel NPs that leads to a self-limiting growth mechanism. This phenomena was attributed to the presence of residual water in the DES and the formation of a mixed layer of $Ni/Ni(OH)_2$ [3]. Moreover, by adding small fractions of water to the DES, the electrolyte quality could be remarkably improved as it was proved in some recent studies [4]. In this way, the beneficial use of water, as additive, will be discussed.

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Simulation of the Effects of Impurity in the early stages of Electrochemical Growth of Nanoparticle in acetonitrile solution

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Fundamental understanding of the early stages of electrochemical nucleation and growth is important in research areas as diverse as electrochemical sensors, catalysis, fuel-cells, etc. Although studied since decades, the process is not fully understood yet. In this presentation, we show a new and generic numerical modeling approach to study the effects of impurities on the early stages of the growth of a silver nanoparticle from an acetonitrile. The electrolyte contains 1 mM of AgNO3 as source of Ag+ cations, 0.1 M of LiClO4 as a supporting electrolyte and different amounts of H_2O. This model takes into account the transports of all relevant ions/species driven by convection, diffusion and migration of all species together with chemical/homogeneous reactions (HR) in the electrolyte and electrochemical reactions (ER) on the surface of the electrode/active surface. We used Multi-Ion Transport and Reaction Model (MITReM) [1] to solve the transport equations of all species and electrolyte potential in the solution. In addition, the effect of competitive reduction and temporary adsorption of water on the surface of the silver nanoparticle are modeled by using the Langmuir equation. The level set method is used to track the interface of the activated hemispherical nanoparticle. First, the modeling approach has been validated by showing that the MITReM simulations of linear sweep voltammetry and chronoamperometry experiments, by considering diffusion, convection and migration are in good agreement with experimentally obtained data. The simulation results considering an isolated hemispherical silver nanoparticle show that, when water molecules are added to the solution, the transition time [2] of the growth from kinetic to diffusion control at sufficiently negative electrode potential takes place at a longer time when the water concentration increases. Moreover, when we consider the water equilibrium reaction in the solution linked to high electrode potentials, we show that water molecules hinder the surface reactions of silver; hence, the transition time is more pronounced. These results show that Finite Element Simulation provides an interesting platform to study the effects of impurity on the early stages of the electrochemical nucleation and growth of nanoparticles from room temperature ionic liquids.

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Electrodeposition of thin solid films on gold from a choline chloride-urea electrolyte

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Electrodeposition is as a promising technology to decrease the fabrication costs in thin-film technologies involving metal or semiconductor deposition. Electrodeposition often proceeds from complex and toxic electrolytes. To satisfy sustainable requirements, non-conventional electrolytes such as ionic liquids are promising alternatives.

Present research in the CHANI group is focused on the electrodeposition of metal and of inorganic semi-conductors from deep eutectic solvents (DESs). More specifically, the deposition of silver and the formation of copper-selenide binary compounds in the 1:2 choline chloride-urea medium (ChCl-U) is presented in this communication.

The electrochemical behaviour of silver at gold electrodes has been investigated by cyclic voltammetry at various temperatures and silver concentrations. Beside the main peaks due to the bulk silver electrodeposition (overpotential deposition - opd) and dissolution, we have highlighted, for the first time in deep eutectic solvents, additional peaks at potentials more positive than the potential of silver bulk deposition. These peaks are limited by a surface process step and can be related to an underpotential deposition (upd) of Ag(I) on gold.

The electrodeposition of copper-selenium binary compounds from a SeO_2/Cu_2O mixture in choline chloride-urea has been realised at 110°C. This deposition is based on the electrochemical behaviour of selenium in this DES, which can be electrodeposited at 110°C under the conductive "grey" allotrope rather than in the non-conductive "red selenium". In the presence of metal precursors, the cathodic dissolution of selenium proceeds at less negative potentials, being coupled with the formation of a metal selenide deposit. Binary metal-selenium compounds can thus be electrodeposited in one step by a proper choice of the deposition potential. The chemical composition of the copper-selenium binary compounds film and its photoelectrochemical response will be discussed.

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POSTER PRESENTATION - TUESDAY 21 FEBRUARY 2017

Use of deep eutectic solvent in a cyanide-free silver plating process for connectors

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Silver electroplating on copper-based substrates for electronic devices is still widely performed nowadays in cyanide-containing baths. This very efficient process nevertheless suffers from the risks encountered by the workers, the cyanide waste treatment and the specific authorization required for the possession and use of cyanide products. Many studies aimed to replace the cyanide ligand by non toxic complexing agents such as thiosulfate, succinimide, hydantoin,… But none was totally efficient, often due to the poor stability of the bath or the lack of adhesion of the silver deposit, especially in the presence of a nickel coating.

An aqueous cyanide-free formulation was developed as part of the EDILCO project to perform silver electroplating on copper and nickel-coated copper substrates for connector applications. Adherent silver coatings were achieved without a first silver strike on copper but this failed on nickel. In this work, a choline chloride - oxalic acid deep eutectic solvent was used as first silver strike bath for silver deposition in the presence of a nickel coating. The thin silver deposit obtained was found to be a very good bonding layer and to ensure the adhesion of the subsequent silver coating. The cyanide-free process was successfully scaled up to a several liters pilot scale.

Early stage mechanisms of Ni electrodeposition on low carbon steel from chlorine chloride based Deep Eutectic Solvents

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Electrodeposition of nickel is commonly performed in aqueous solutions due to its relative simplicity and cost-effectiveness. However, the use of these media has several disadvantages such as hydrogen formation, that causes a decrease of the current efficiency and morphological problems in the coatings (hydrogen formation, presence of cracks and pores). In order to avoid these issues, non-aqueous alternatives such as Deep Eutectic Solvents (DESs) are being sought and explored[1,2].

The feasibility of electrodepositing Ni from choline chloride (ChCl) based DESs has been proven by several research groups[1]. In order to improve the morphology of the deposits and solve structural problems, it is necessary to understand the mechanisms underlying the electrodeposition process. Such studies have been previously performed on non-reactive substrates such as Pt, Au or glassy carbon (GC). Nonetheless, it is also highly relevant from the application point of view to investigate the early stage mechanisms of electrodeposition on steel. This work focuses on understanding Ni nucleation and growth process on low carbon steel from ChCl – urea (1:2) DESs.

First, the electrochemical behavior of steel in DESs was investigated, which later allowed us studying the mechanisms of Ni electrodeposition. The effect of temperature, applied potential, and composition was studied by cyclic voltammetry and chronoamperommetry, combined with surface analysis techniques, such as scanning electron microscopy and X-ray photoelectron spectroscopy. The obtained results highlight the complex electrochemical processes occurring at the electrode surface and their influence on the nucleation and growth. This is of high relevance when using DESs as electrolytes, as the interactions of these solvents with the substrate and the growing metallic phase have shown to be very different from these in the aqueous solutions[3,4].

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Ionic Liquids: a smart platform to synthesise naked metallic nanoparticles

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The controlled synthesis of metallic NPs in the range of 1 to 10 nm is an on-going challenge, as is the understanding of their stabilisation and ag- glomeration. Unlike traditional solvents, ionic liquids (ILs) readily stabilise NPs. ILs are molten salts, generally liquid at room temperature, com- posed of an organic cation and an inorganic or organic anion. They are non-volatile and ther- mally and electrochemically stable.

ILs can dissolve organometallic (OM) precur- sors, which precipitate into metallic NPs by de- composition under dihydrogen. This reaction was studied in 1-alkyl-3-methylimidazoliumbis-trifluoromethylsulphonylimide ILs (abbreviated as $C_1 C_n ImNTf_2$). Stable suspensions of metal- lic NPs were obtained with accurate size control and high stability.[1–4]

Interestingly enough, upon mixing two dif- ferent OM precursors, bimetallic NPs can be obtained with improved size control. [5–8] In $C_1C_4ImNTf_2$, Ru-core Cu-shell NPs were formed, as shown by EELS. It could be unambiguously demonstrated that the core-shell NPs are pro- duced by fast decomposition of the Ru precursor, followed by decomposition of the Cu precursor by reaction with hydrides present at the surface of the Ru clusters.Similar size reduction has been observed for other bimetallic systems and is cur- rently studied for CoPt and CoRu.

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