EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

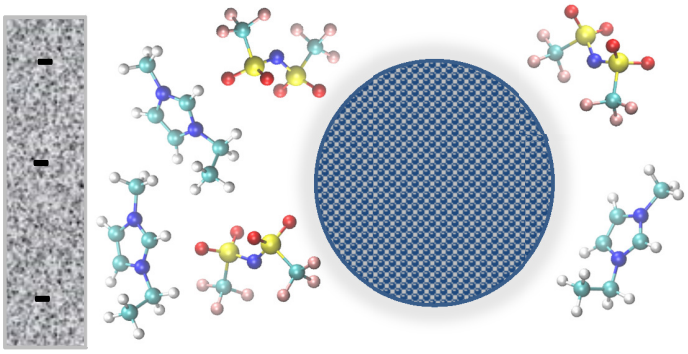
Joint workshop of WG 2 and 3: „Ionic liquids at interfaces“
3rd -5th October 2015 in Belek (Turkey)

Objectives:

This workshop explores and focuses on overlaps between physicochemical, theoretical and practice-oriented research in our COST action CM1206 and acts as a base for future joint project applications on international level as well as bilateral STSM applications.

Sessions:

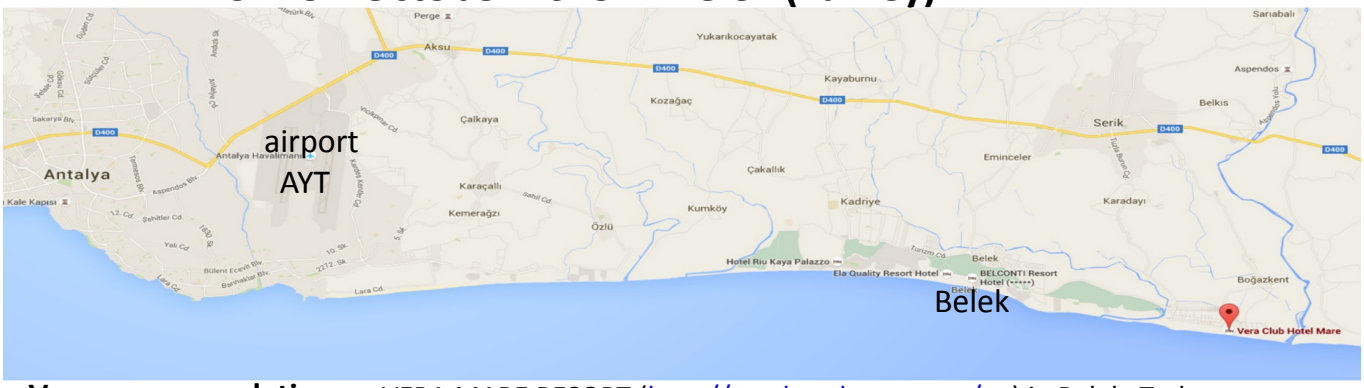
Solid-liquid interfaces: Electrolytes and electrodes
Solid-liquid interfaces: Nano- and supported materials
Liquid-liquid interfaces: Solutions
STSM presentations



EUROPEAN COOPERATION IN SCIENCE AND TECHNOLOGY

EXIL

Joint workshop of WG 2 and 3: „Ionic liquids at interfaces“
3rd -5th October 2015 in Belek (Turkey)



Venue, accomodation: VERA MARE RESORT (http://verahotelmare.com/en) in Belek, Turkey

Belek is located near Antalya airport (AYT) which offers daily flight to most European cities.
The transfer from the airport to the resort can be booked in combination with the hotel room.
For booking details, please contact Mrs. Selma Yagci (selma.yagci@verahotels.com).

Organizing committee:

Katharina Schröder (nee Bica)	katharina.bica@tuwien.ac.at
Christian Schröder	christian.schroeder@univie.ac.at
Susanne Mossin (STSMs)	slmo@kemi.dtu.dk
Lotte Jespersen (administration)	losk@kemi.dtu.dk

Contents

Time table **4**

Speakers on Saturday, October 3rd **5**
R. Costa . . . 5
C. Merlet . . . 6
B. Gollas . . . 7
L. Varela . . . 8
B. Esat . . . 9
I. Billard . . . 10
A. Rivera-Calzada . . . 11
O. Cabeza . . . 12

Speakers on Sunday, October 4th **13**
A. Lahiri . . . 13
P. Verpoort . . . 14
L. Magagnin . . . 15
R. Zirbs . . . 16
I. Szilagyi . . . 17
A. King . . . 18
M. Haumann . . . 19
E. Garcia-Suarez . . . 20
J. Palomar . . . 21
M. Mezger . . . 22
P. Lobotka . . . 23
A. Martinelli . . . 24
S. Verevkin . . . 25

Speakers on Monday, October 5th **26**
G. Hantal . . . 26
L. Santos . . . 27
Short term scientific mission reports . . . 28
M. Hübner . . . 28
M. Martins . . . 28
D. Patinha . . . 28
I. Rodriguez . . . 28

Solid-Liquid Interfaces: Electrolytes and electrodes	Saturday, Oct. 3rd			Title
	13:00:00	13:10:00	K. & C. Schröder	Welcome and introduction
	13:10:00	13:40:00	R. Costa	Ionic liquids at electrified interfaces: Current and future challenges
	13:40:00	14:10:00	C. Merlet	NMR study of the electrode/electrolyte interface in supercapacitors
	14:10:00	14:30:00	Coffee break	
	14:30:00	15:10:00	B. Gollas	Electrochemistry and in situ PM-ORRAS of Electrode/Deep Eutectic solvent interfaces
	15:10:00	15:40:00	L. Varela	Interfacial behaviour of mixtures of ionic liquids with water and inorganic salts
	15:40:00	16:10:00	B. Esat	Organic Electrodes For Rechargeable Batteries
	16:10:00	16:30:00	Coffee break	
	16:30:00	17:00:00	I. Billard	Ils interfaces: diffusion and kinetics
	17:00:00	17:30:00	A. Rivera-Calzada	Electrostatic doping of strongly correlated systems with ionic liquids
	17:30:00	18:00:00	O. Cabeza	Self organization in alkyl sulfate based IL hydrogels
Solid-Liquid Interfaces: Nano materials	Sunday, Oct. 4th			
	8:30:00	9:10:00	A. Lahiri	Exploring the interfacial nanostructures of LiTFSI in ionic liquids on different substrates
	9:10:00	9:40:00	P. Verpoort	Towards understanding the anodic reactions in plating from DES
	9:40:00	10:10:00	L. Magagnin	Electroplating from Deep Eutectic Solvents
	10:10:00	10:30:00	Coffee break	
	10:30:00	11:00:00	R. Zirbs	Novel Pathways for the Synthesis of Superstable Nanoparticles by the use of Ionic Liquids
	11:00:00	11:30:00	I. Szilagyi	Effect of Ionic Liquids on Aggregation of Latex Colloids
	11:30:00	12:00:00	A. King	Processing and analysis of nanocellulose using ionic liquids
Solid-Liquid Interfaces: Supported ionic liquid phases	12:00:00	14:00:00	Lunch	
	14:00:00	14:40:00	M. Haumann	Surface influences on catalytic performance of supported ionic liquid phase (SILP) materials
	14:40:00	15:10:00	E. Garcia-Suarez	Continuous flow ethylene methoxycarbonylation by supported ionic liquid phase (SILP) catalysts
	15:10:00	15:40:00	J. Palomar	Encapsulated Ionic Liquids (ENILs) applied to gas capture
	15:40:00	16:00:00	Coffee break	
	16:00:00	16:30:00	M. Mezger	Surface-layering of ionic liquids at interfaces
	16:30:00	17:00:00	P. Lobotka	IL-based nanocolloids prepared by vacuum sputtering
	17:00:00	17:30:00	A. Martinelli	Local structure and dynamics in water-added and nano-confined ionic liquids
	17:30:00	18:00:00	S. Verevkin	Energetics of liquid-gas interfaces in imidazolium based Ils with PF6 and NTf2 anions
Liquid-Liquid interfaces	Monday, Oct. 5th			
	8:30:00	9:00:00	G. Hantal	Intrinsic analysis of liquid/liquid interfaces involving ionic liquids
	9:00:00	9:30:00	K. Schröder	
	9:30:00	10:00:00	L. Santos	Interfacial Thermodynamics and Morphology of Ils
	10:00:00	10:30:00	Coffee break	
Short term scientifc missions	10:30:00	10:50:00	M. Hübner	Extraction of proteins using IL-containing aqueous biphasic systems (ABS)
	10:50:00	11:10:00	M. Martins	Ionic liquids as extractive solvents of terpenes and terpenoids
	11:10:00	11:30:00	D. Patinha	Polymeric ionic liquids for sample preparation techniques
	11:30:00	11:50:00	I. Rodriguez	Surfactant Ionic Liquids for Enhanced Oil Recovery
	12:00:00	13:30:00	Lunch	

Ionic liquids at electrified interfaces: Current and future challenges

Renata Costa, Carlos M. Pereira, A. Fernando Silva

CIQUP – Physical Analytical Chemistry and Electrochemistry group

Faculdade de Ciências da Universidade do Porto, Chemistry and Biochemistry department

Rua do Campo Alegre, s/n 4169 – 007 Porto, Portugal

e-mail: renata.costa@fc.up.pt

Research on ionic liquids (ILs) at electrified interfaces are receiving increasing experimental and theoretical attention due to their enormous potential for energy applications, such as, capacitive energy storage devices [1]. The understanding of the mechanisms of electric double layer (EDL) formation involving ILs is far from being accomplished and much more experimental studies are required. Molecular simulations and most of the experimental studies of electrode-electrolyte interfaces have been focused on IL EDL at solid surfaces certainly due to be closer to potential practical applications.

The electrochemical properties of the interface are assessed through the interpretation of differential capacity curves based on an acceptable model that accurately may describe such structure, namely the effect of the size of the ions on the EDL thickness.

Simple systems composed by monocationic [2], dicationic [3] and binary mixtures of ionic liquids [4] are focus of our attention, never disregarding the role of the electrode material [5] and the temperature effect on the EDL structure.

References:

[1] M. Fedorov, A. Kornyshev, Chem. Rev. 2014, 114, 2978–3036.
[2] R. Costa, C. Pereira, A. Silva, Phys. Chem. Chem. Phys., 2010, 12, 11125-11132.
[3] R. Costa, C. Pereira, A. Silva, Electrochim. Acta, 2014, 116, 306-313.
[4] R. Costa, C. Pereira, A. Silva, Electrochem. Commun., 2015, 57, 10-13.
[5] R. Costa, C. Pereira, A. Silva, Electrochim. Acta, 2015, 167, 421-428.

Acknowledgments

This research was carried out with financial support of FCT – CIQUP – Physical Analytical Chemistry and Electrochemistry group (Pest-C/QUI/UI0081/2013) and Renata Costa acknowledges a Pos-Doc scholarship awarded by FCT with reference SFRH/BPD/89752/2012 under the QREN - POPH - Advanced Training, subsidized by the European Union and national MEC funds.

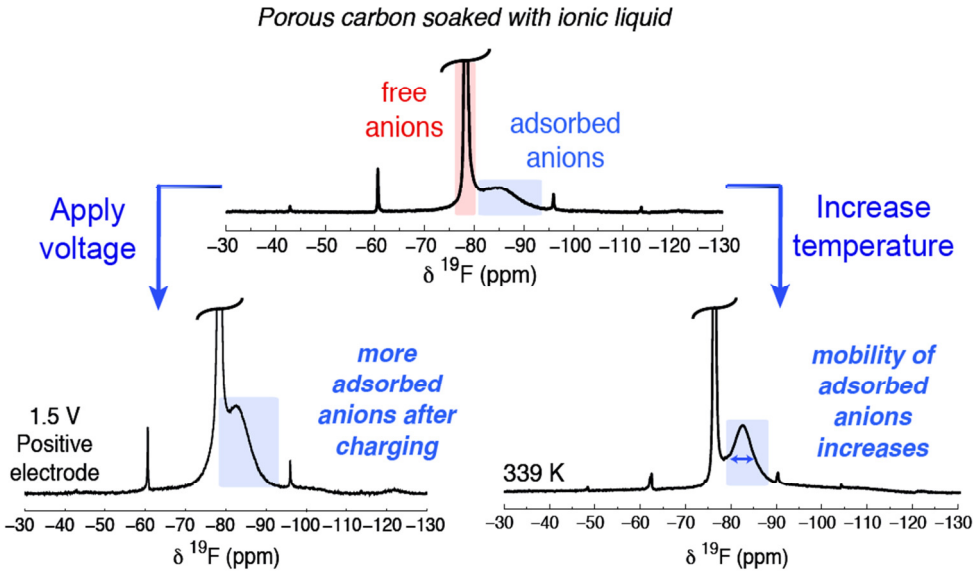
NMR study of the electrode/electrolyte interface in supercapacitors

C. Merlet, A. C. Forse, J. M. Griffin, D. Frenkel, C. P. Grey

Department of Chemistry, University of Cambridge, Lensfield road, Cambridge CB2 1EW, UK

Email: celine.merlet.fr@gmail.com

Nuclear magnetic resonance (NMR) spectroscopy is a powerful tool for studying electrochemical systems due to its element specificity, sensitivity to dynamics and its applicability to crystalline as well as amorphous systems. In this talk, we first focus on the characterisation of the electrode/electrolyte interface through NMR experiments on ionic liquid based supercapacitors. We find that ionic liquids wet the micropores even in the absence of an applied potential, and use NMR spectra at various applied potentials to investigate the charge storage mechanism. In the second part of the talk, we explore the possibility of predicting NMR spectra for ions diffusing in carbon particles via a combined density functional theory (DFT) and lattice model approach. The original lattice method we develop shows great promise for the interpretation of temperature and carbon structure effects on the NMR spectra lineshapes.



References:

[1] A. C. Forse, J. M. Griffin, C. Merlet, P. M. Bayley, H. Wang, P. Simon, C. P. Grey, *J. Am. Chem. Soc.* **137**, 7231 (2015)

[2] C. Merlet, A. C. Forse, J. M. Griffin, D. Frenkel and C. P. Grey, *J. Chem. Phys.* **142**, 094701 (2015).

Electrochemistry and *in situ* PM-IRRAS of Electrode/Deep Eutectic Solvent Interfaces

Luciana Vieira[1,2], Robert Schennach[3], Bernhard Gollas[1]

[1]Graz University of Technology, Institute for Chemistry and Technology of Materials, Stremayrgasse 9, 8010 Graz, Austria, [2]Competence Centre for Electrochemical Surface Technology GmbH, Viktor-Kaplan-Str. 2, 2700 Wiener Neustadt, Austria, [3]Graz University of Technology, Institute of Solid State Physics, Petersgasse 16, 8010 Graz, Austria

bernhard.gollas@tugraz.at

Since their discovery some ten years ago deep eutectic solvents have been advocated as cheap and environmentally benign alternatives to classical room temperature ionic liquids [1]. For a more widespread use of these types of electrolytes in electrochemical applications a better understanding of their interfacial behavior is required. In our search for hydrogen-free zinc plating we have studied the electrodeposition of zinc from a deep eutectic 1:2 molar mixture of choline chloride and ethylene glycol containing $ZnCl_2$ [2]. Unusual electrochemical behaviour has been observed in cyclic voltammetry at static and rotating glassy carbon (GC) disc electrodes and in chronoamperometry. Raman spectroscopy confirmed the tetrachlorozincate ion $[ZnCl_4]^{2-}$ as the main zinc species in this strongly Lewis-basic electrolyte [3]. We suggested a reaction pathway that involves the reduction of solvent components under formation of hydrogen. The study has been extended to Zn, Pt, Au, Cu and steel electrodes and the results support our mechanistic hypothesis. The electrochemical behaviour of the electrolyte on these electrode materials indicates that – apart from the formation of surface alloys – adsorption of the electrolyte components also plays a role in this electrode reaction. The first *in-situ* polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS [4]) studies of a GC/deep eutectic solvent interface show the extremely slow formation of an adsorbate at open circuit potential [5]. Below –0.4 V vs. Zn/Zn^{2+}, presumably adsorbed hydrogen and/or choline blocks the electrodeposition of zinc. The spectroelectrochemical results indicate a potential-dependent rearrangement of the interfacial architecture.

References:

[1] F. Endres, D. MacFarlane, A. Abbott (Eds.), *Electrodeposition from Ionic Liquids*, Wiley-VCH, Weinheim 2008.

[2] A.H. Whitehead, M. Pölzler, B. Gollas, *J. Electrochem. Soc.* **2010**, *157*, D328.

[3] L. Vieira, A.H. Whitehead, B. Gollas, *J. Electrochem. Soc.* **2014**, *161*, D7.

[4] V. Zamlynny, J. Lipkowski in R.C. Alkire, D.M. Kolb, J. Lipkowski, P.N. Ross (Eds.), Diffraction and Spectroscopic Methods in Electrochemistry, Wiley-VCH, Weinheim **2006**, Vol. 9, pp. 315.

[5] L. Vieira, R. Schennach, B. Gollas, *Phys. Chem. Chem. Phys.* **2015**, *17*, 12870.

Interfacial behaviour of mixtures of ionic liquids with water and inorganic salts

L. M. Varela,[1] V. Gómez-González,[1] B. Docampo-Álvarez,[1] V. Ivaništšev,[2] T. Méndez-Morales,[1] O. Cabeza,[3] M. Fedorov,[4] L. J. Gallego,[1] R. M. Lynden-Bell[5]

[1]Departamento de Física da Materia Condensada, Universidade de Santiago de Compostela, Campus Vida s/n E-15782, Santiago de Compostela, Spain
[2]Institute of Chemistry, University of Tartu, Ravila 14a, 50411, Tartu, Estonia,
[3]Facultade de Ciencias, Universidade da Coruña, Campus A Zapateira s/n E-15008, A Coruña, Spain
[4]Department of Physics, Scottish University Physics Alliance (SUPA), University of Strathclyde, John Anderson Bldg., 107 Rottenrow, Glasgow, G4 0NG United Kingdom
[5]Department of Chemistry, University of Cambridge, Lensfield Road, Cambridge, UK CB2 1EW

e-mail: luismiguel.varela@usc.es

In the present contribution we demonstrate results of molecular dynamic simulations of mixtures of ionic liquids (ILs) with water, mono- and divalent salts of electrochemical interest near neutral and charged graphene walls. We focus on the main trends that determine solute–electrode interactions in ILs and we show how the layered structure of the IL at the electrolyte–electrode interface imposes potential energy barriers that the ions must overcome in their way to the electrodes, therefore limiting the efficiency of redox reactions. The effect of salt concentration and of the size and valence of the salt cations on the barriers' parameters is analysed, by comparing the interfacial behaviour of Li^+ and K^+ [1,2] at charged graphene surfaces in a room temperature IL, 1-butyl-3-methylimidazolium tetrafluoroborate. We show that the stronger solvation of Li^+ in the ionic liquid leads to formation of significantly higher interfacial free energy barriers for Li^+ to come to the electrode than for K^+. Some preliminary results for divalent salts of Mg^{2+} and Ca^{2+} will also be discussed. Finally, we will consider the interfacial behaviour of mixtures of ILs with water [3], studying the effect of the latter on the structure of the interface under normal and nanoconfined conditions.

We acknowledge the supercomputing support from the EPSRC funded ARCHIE-WeSt High Performance Computer centre (www.archie-west.ac.uk). EPSRC grant no. EP/K000586/1. VI acknowledges support from the Estonian Materials Technology Program Project SLOKT12180T, Estonian Institutional Research Project IUT20-013 and Estonian Centers of Excellence in Science Project: High-technology Materials for Sustainable Development TK117. The financial supports of the Spanish Ministry of Economy and Innovation MAT2014-57943-C3-1-P and MAT2014-57943-C3-3-P and of the Ministry of Science and Innovation (Grant No. FIS2012-33126) are gratefully acknowledged. All the Spanish research projects were partially supported by FEDER. Funding from the European Union (COST Action CM 1206) and by the Galician Network on Ionic Liquids, REGALIs (CN 2014/015) is also acknowledged. Facilities provided by the Galician Supercomputing Centre (CESGA) are also acknowledged.

References:

[1] T. Méndez-Morales et al. Phys. Chem. Chem. Phys. 2014, 16, 13271-13278.
[2] V. Ivaništšev et et al. Energy &Environmental Science. Submitted for publication.
[3] B. Docampo-Álvarez et al. In preparation.

Organic Electrodes For Rechargeable Batteries

Sumeyye Bahceci Sertkol[±], Burak Esat[±], Anton Momchilov[¥]

[±]Fatih University, Buyukcekmece 34500 Istanbul-TURKEY

[¥] Institute of Electrochemistry and Energy Systems (IEES), Bulgarian Academy of Science, Sofia-BULGARIA

besat@fatih.edu.tr (presenting author)

The ever-increasing demand for high-performing, light weight, economical, and safe power storage for high–tech portable devices and electric vehicles leads to augmented research efforts in the field of organic or organic/hybrid materials to be used as electrodes in energy storage devices. There has recently been an increasing number of studies toward the development of novel pure or composite materials containing redox polymers with pendant organic electro-active groups. These efforts may eventually lead to totally organic batteries with improved properties such as light weight, flexibility, improved environmental safety, low cost of manufacturing.

We hereby represent novel polymers and reduced graphene oxide materials with pendant electro-active groups such as TEMPO, benzimidazole-1-oxyl-3-oxides and quinones.

The first example of polymers with pendant anode-active groups studied in our group is a polymethacrylate derivative carrying anthraquinone moieties (pMAntrq). This anthraquinone based anode-active material has proven to show a quite good reversible electrochemical reduction behavior in both aqueous and non-aqueous electrolytes in our studies. A battery which utilizes a composite material made of this compound mixed with carbon conductivity agent against lithium metal has been constructed and analyzed (AQ|1M $LiClO_4$ in EC:DEC=1:1|Li). The initial discharge capacity of the cell obtained was 151 mAh/g when cycled between 4.2 and 1.2V at 0.25C rate. This material was also used in an aqueous battery (AQ|5M KOH aq.|$LiMn_2O_4$). However although an initial discharge capacity of 37.7 mAh/g was obtained, it deteriorated quickly due to the solubility of the reduced form of the polymer in this electrolyte system. This is the first reported example of such organic-inorganic hybrid battery. An anode material based on reduced graphene oxide (rGO) functionalized with anthraquinone is also investigated. The initial studies against Li metal revealed that a quite reversible capacity of 200 mAh/g was obtained based on the weight of electro-active anthraquinone moieties when cycled between 3.2 and 1.8 V at 0.3C rate. The energy density was found to be around 450 mWh/g. We have also synthesized and characterized some polymers with pendant nitroxide radicals, such as TEMPO, which are electrochemically oxidizeable in a reversible manner at around 3.5-3.6V vs. Li.

ILs interfaces: diffusion and kinetics

Isabelle Billard[a,b], Maria Boltoeva[c], Sylvia Georg[c], Céline Bonnaud[a,b], Nicolas Papaiconomou[a,b], Eric Chainet[a,b]

a) Univ. Grenoble Alpes, LEPMI, 1130 avenue de la Piscine, 384000 Grenoble, France
b) CNRS, LEPMI, F-38000 Grenoble, France
c) IPHC, CNRS, 23 rue du Loess, 67037 Strasbourg Cedex, France

Isabelle.billard@lepmi.grenoble-inp.fr

This presentation is divided in two parts: First, studies that are conducted at IPHC, (Strasbourg, France), aiming at the study of interfacial phenomena during liquid/liquid extraction[1]. Second, on-going studies at LEPMI, (Grenoble, France) dealing with electrochemistry in IL media.

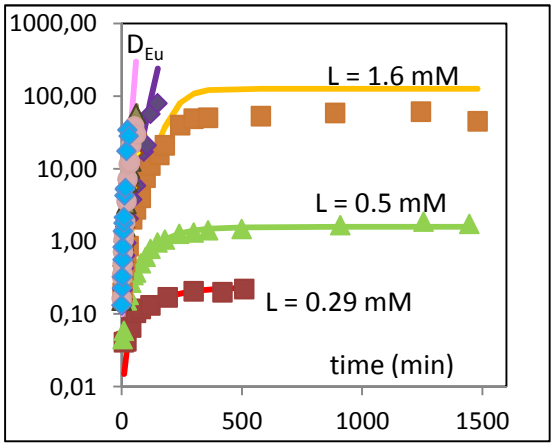


Fig.1 : D_{Eu} vs time, TODGA from 0.3mM To 10 mM. C1C4imTf2N

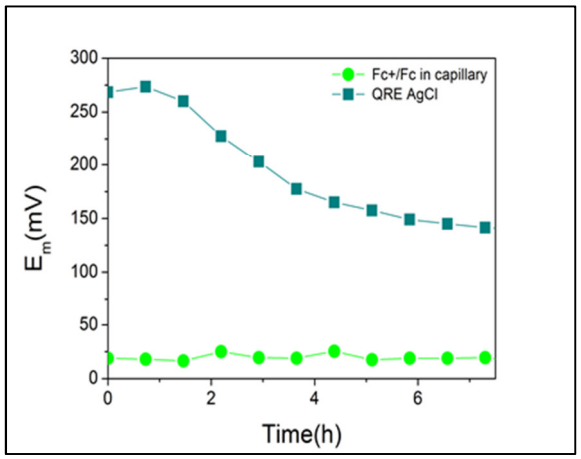


Fig. 2: deleterious effect of Fc+/Fc diffusion on the average potential for pseudoref and ref, as a function time. 10 mV s^{-1}. BMPyrTf2N

Liquid/liquid interface. We investigated the kinetics of Eu(III) extraction from nitric aqueous solution towards $C_1C_4imTf_2N$ by use of TODGA, as a function of ligand concentration (fig. 1). Data analysis evidences a change in the TODGA stoichiometry of the extracted complex from one ligand at short times to three ligands at longer times. This is discussed under the frame of interfacial reactivity.

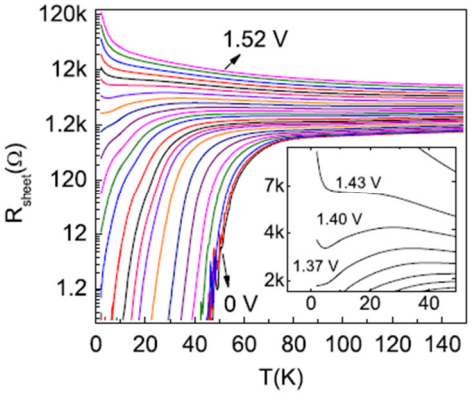
Electrochemistry in IL media: We illustrate technological bias arising from the use of pseudoreferences in IL media. The effect of scan rate and type of references (pseudo or not) is investigated (fig. 2) and a cell design is proposed.

[1] Project leader : Dr. Maria Boltoeva, IPHC. Financial support from CNRS, mission interdisciplinaire.

Electrostatic doping of strongly correlated systems with ionic liquids

A.M.Pérez-Muñoz[1,2],P. Schio[2,3], R. Poloni[4], A. Rivera-Calzada[1,2], J. C. Cezar[3], E. Salas[5], G. Castro[5], N.M.Nemes[1,2],M.Clement[1,6], E.Iborra[1,6], C.León[1,2], J.Santamaría[1,2], J.García-Barriocanal[1,2]

[1] CEI Campus Moncloa, UCM-UPM Madrid, Spain
[2] GFMC, Universidad Complutense de Madrid, Madrid, Spain
[3] PGM beamline at the LNLS (National Laboratry of Synchrotron Light), Campinas, Sao Paulo, Brasil
[4] SIMaP, Laboratoire Science et Ingénierie des Matériaux et Procédés (SIMaP), Grenoble-INP, France
[5] SpLine, BM25 beamline at the ESRF (European Radiation Syncrhtron Facility), Grenoble, France
[6] GMME, ETSIT, Universidad Politécnica de Madrid, Madrid, Spain
e-mail: alberto.rivera@fis.ucm.es



The Field Effect Transistor (FET) is a well-known technology to artificially modify the concentration of carriers in the surface of semiconductors, using a gate electrode to apply an electrostatic doping by an external electric field through a thin dielectric.

The use of ionic liquids as gate dielectrics in the so called Electric Double Layer Transistors (EDLT) was recently proposed as an alternative to minimize the thickness of the dielectric, since the liquid to sol id interface forms a capacitor in the surface of the material with around one nanometer separation. Higher electric fields than in the case of solid dielectrics can be applied in a controlled way to the surface of the material, up to 10^7 V/cm, which enables the study of the fundamental physical properties of materials in this doping range.

Strongly correlated electron systems are oxides characterized by a complex phase equilibrium that is critically influenced by the charge carrier concentration, which ultimately determines their physical properties. Electrostatic charge doping experiments allow the control of such carrier density in a reversible manner avoiding the alteration of the level of disorder associated with conventional chemical substitution.

Several examples of studies of high Tc superconducting cuprates will be presented in which the physical behavior of the material is changed from superconductor to insulator in a controlled and reversible way. Large changes of the doping concentration allow exploring wide regions of the phase diagram of these materials, which appear as model systems for the electrostatic doping.

References:

[1] A. T. Bollingeret, G. Dubuis, J. Yoon, D. Pavuna, J. Misewich, I. Bozovic, Nature (London) 472, 458 (2011)
[2] X. Leng, J. Garcia-Barriocanal, B. Yang, Y. Lee, J. Kinney, and A. M. Goldman . Phys. Rev. Lett .108, 067004 (2012)
[3] X. Leng, J. Garcia-Barriocanal, S. Bose, Y. Lee, and A. M. Goldman . Phys. Rev. Lett.107, 027001 (2011)

Self organization in alkyl sulfate based IL hydrogels

Oscar Cabeza[1], Esther Rilo[1], Luisa Segade[1], Luis Miguel Varela[2], Emilia Tojo[3]

1 Univ. da Coruña. Dpt. de Física, Fac. de Ciencias. 15071 A Coruña, Spain
2 Univ. de Santiago de Compostela. Dto. de Física de la Materia Condensada. 15782 Santiago de Compostela. Spain
3 Univ. de Vigo, Dpt. de Química Orgánica. 36310 Vigo, Spain
e-mail (oscabe@udc.es)

We have discovered that some ionic liquids (ILs) containing octyl [OSO_4] or decyl [DSO_4] sulfate as anion (liquid at room temperature) jellied when they are left open to the atmosphere [1]. The cation nature seems not to be important in the process, because we observe the same phenomena for 1-ethyl-3-methyl imidazolium [EMIm], 1-ethyl-2,3-dimethyl imidazolium [EMMIm] and 1-ethyl-3-methyl pyrrolidinium [EMPyrr] cations, all of them with [DSO_4]. In contrast, we have not observed that isotropic-mesomorphic transition for any IL with other anions. The gelation process takes place because the sample adsorbs water from the moisture up to a given quantity, which depends on the relative humidity grade (and being about a 25% of weight in water for the saturated sample both for [EMIm][OSO_4] and [EMIm][DSO_4]). Thus, the sample is continuously interchanging water molecules with the atmosphere, as we observe from FTIR experiments on gelatine samples prepared with heavy water. If the sample is exposed to a dry atmosphere (with relative humidity grade below 10%) it loses completely the absorbed water (as it also happens to many hygroscopic ILs) [2] and it goes to liquid (isotropic) state. The mesomorphic state ranges a temperature interval higher of 50 K, and in this state the solidification temperature is much lower than expected for an equivalent liquid aqueous mixture. Below that solidification temperature the sample crystallizes in a Pmmm orthorhombic unit cell, as observed from powder diffraction X-ray analysis. We have measured some physical properties of some of these compounds around the mesomorphic-isotropic transition temperature: electrical conductivity, viscosity and density. In addition, we present DSC measurements of the compound for all temperature range. These ILs are very promising to apply them in electrochemical devices (due to its relatively high electrical conductivity in jelly state) [3] and also as lubricants for low temperature.

References:

[1] O. Cabeza et al., J. Chem. Thermodyn. 75 (2014) 52-57.
[2] S. Cuadrado et al., Fluid Phase Equilibria 278 (2009) 36-40.
[3] A. Noda, M. Watanabe. Electrochimica Acta 45 (2000) 1265-1270.

The financial supports of the Spanish Ministry of Economy and Innovation MAT2014-57943-C3-1-P and MAT2014-57943-C3-3-P are gratefully acknowledged. All the Spanish research projects were partially supported by FEDER. Funding from the European Union (COST Action CM 1206) and by the Galician Network on Ionic Liquids, REGALIs (CN 2014/015) is also acknowledged.

Exploring the Interfacial nanostructures of LiTFSI in Ionic Liquids on different substrates

Abhishek Lahiri, Timo Carstens, Natalia Borisenko, Andriy Borodin, Frank Endres

Institute of Electrochemistry, Clausthal University of Technology, Arnold Sommerfeld Str 6, D-38678, Clausthal-Zellerfeld, Germany

e-mail: abhishek.lahiri@tu-clausthal.de

Ionic liquids are potential electrolytes for both Li-metal and Li-ion batteries [1]. As the solid-liquid interface governs the electrochemical reactions, it is important to evaluate the interfacial structure. For ionic liquids (ILs), it has been shown that the interfacial structure depends on both the cation and anion which affects the electrochemical processes [2].

Here we will show the interfacial nanostructure of lithium bis(trifluoromethylsulfonyl)amide in 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide (LiTFSI-[$Py_{1,4}$]TFSI) on Au (111) and on electrodeposited Ge. *In situ* AFM studies on Au (111) showed that on addition of LiTFSI in the IL, the interfacial structure changed considerably wherein Li^+ ions replaced the [$Py_{1,4}$] cation on Au (111) surface, figure 1a. In case of Ge, with applied potential, Li intercalation took place along with the formation of a solid electrolyte interface (SEI) layer (figure 1b). AFM and XPS studies revealed that the SEI layer was inhomogeneous and changed during lithiation/ delithiation processes.

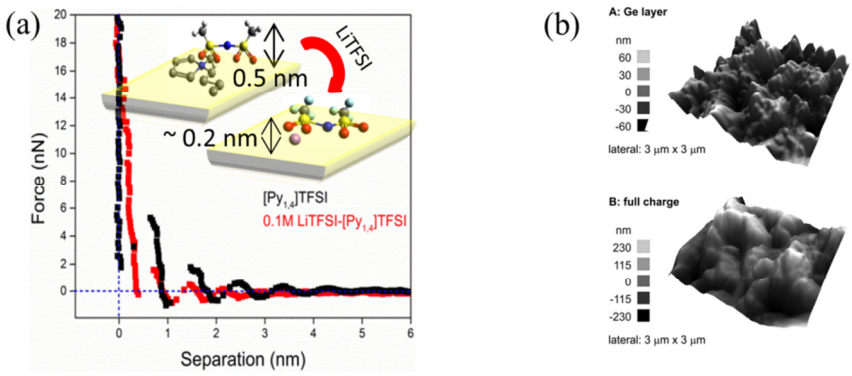


Figure 1 (a): Force-separation curves of [$Py_{1,4}$]TFSI and LiTFSI-[$Py_{1,4}$]TFSI at open circuit potential. (b) AFM images of electrodeposited Ge at various charge-discharge potentials

References:

[1] M. Armand, F. Endres, D.R. MacFarlane, H. Ohno, B. Scrosati, Nat. Mater. 2009, 8, 621-629

[2] F. Endres, O. Höfft, N. Borisenko, et al. Phys. Chem. Chem. Phys. 2010, 12, 1724-1732

Towards understanding the anodic reactions in plating from DES.

Philippe VERPOORT, Eva Diaz Gonzalez

OCAS NV (Pres. JF Kennedylaan 3, B-9060 Zelzate, Belgium)

philippe.verpoort@ocas.be

OCAS NV is upscaling a hexavalent chromium free alternative electrodeposition technology, which is based on a deep-eutectic solvent containing a trivalent chromium salt. During this upscaling from lab scale (1-10 liter baths) to semi-industrial scale (1000 liter baths), it was observed that the level of evolving hazardous gases may require adding an industrial gas scrubber. Therefore a more fundamental mass balance study was performed on the use of soluble versus inert anodes, with a focus on anodic side reactions occurring during deposition. The use of soluble anodes leads to a dramatic decrease in gas formation. However bath composition has to be carefully monitored, as soluble anodes can induce large variations in the bath composition.

Electroplating from Deep Eutectic Solvents

Luca Magagnin

Dip. Chimica, Materiali e Ingegneria Chimica Giulio Natta – Politecnico di Milano – Via Mancinelli, 7 – 20131 Milano (Italy)

luca.magagnin@polimi.it

Among the air and water stable ILs, deep eutectic solvents (DESs) based on quaternary ammonium salts have been selected recently due to their moisture stability, low price, biodegradability, non-toxicity, and ease of synthesis and handling. The synthesis of these solvents can be done simply by mixing quaternary ammonium salts with hydrogen bond donors (such as amines or carboxylic acids) [1,2], and the most studied electrolytes belonging to this category are based on choline chloride (ChCl) as ammonium compound. Electroplating of alloys, i.e. samarium-cobalt alloys, for magnetic applications in choline chloride based electrolytes will be discussed as an example of difficult to plate alloys in water based baths. The use of DES electrolytes in plating on reactive substrates, e.g. magnesium, will be also presented. The present work investigates for the first time the influence of the physical properties of electrolytes based on choline dihydrogencitrate (CDHC) mixed in different ratios with a hydrogen bond donor such as ethylene glycol (EG) on the deposition of copper on a nickel substrate. In particular the relation between chemistry, viscosity, conductivity of the solutions and the quality of the Cu layer obtained is evidenced. The actual possibility of good quality metal deposition from the new electrolytes is demonstrated as well. CDHC/EG 1:4 is suitable for copper deposition, as the coatings produced present comparable quality with respect to their equivalents from ChCl/EG. This demonstrates the possibility of metal electrodeposition in chloride free organic mixtures for applications presenting critical issues towards aggressive baths. A new generation of ionic liquids will be also discussed, presenting preliminary results about electroplating of aluminum coatings.

References:

[1] A.P. Abbott, G. Capper, D.L. Davies, R. Rasheed, V. Tambyrajah, Novel Solvent Properties of Choline Chloride/Urea Mixtures, Chem. Commun. (2003) 70-71

[2] A.P. Abbott, D. Boothby, G. Capper, D.L. Davies, R. Rasheed, Deep Eutectic Solvents Formed between Choline Chloride and Carboxylic Acids: Versatile Alternatives to Ionic Liquids, J. Am. Chem. Soc. 126 (29) (2004) 9142-9147

Novel Pathways for the Synthesis of Superstable Nanoparticles by the use of Ionic Liquids

Ronald Zirbs, Tanja Zwölfer, Katharina Schröder, Erik Reimhult

Department of Nanobiotechnology; Institute for Biologically inspired materials
University of Natural Resources and Life Sciences Vienna
Muthgasse 11-II; A-1190 Vienna, Austria

ronald.zirbs@boku.ac.at

Superparamagnetic iron oxide nanoparticles (NPs) are used in a rapidly expanding number of applications in e.g. the biomedical field, for which brushes of biocompatible polymers such as poly(ethylene glycol) (PEG) have to be densely grafted to the core. Grafting of such shells to monodisperse iron oxide NPs has remained a challenge mainly due to the conflicting requirements to replace the ligand shell of as-synthesized NPs (commonly oleic acid) with irreversibly bound PEG dispersants. Using ionic liquids for the particle stabilization during the synthesis provides a new pathway to prepare particles that are stabilized strong enough to prevent aggregation during the synthesis (by the ionic liquid) but is easily removed in a subsequent ligand exchange step.

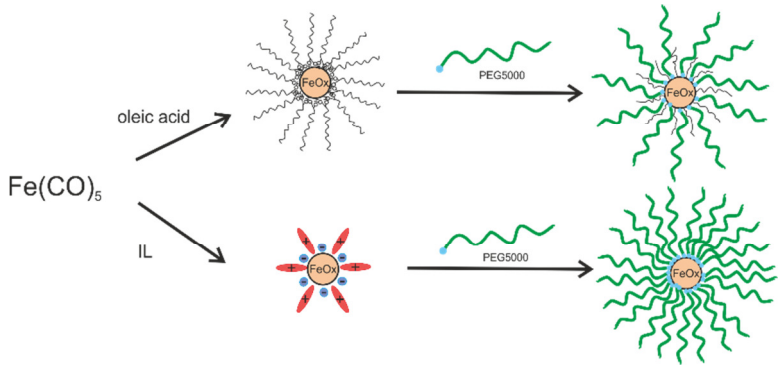


Figure 1: Conventional synthetic pathway for the synthesis of iron oxide core-shell nanoparticles involving oleic acid as stabilizer in comparison to the usage of different ionic liquids.

Effect of Ionic Liquids on Aggregation of Latex Colloids

Istvan Szilagyi, Tamas Szabo, Anthony Desert, Tamas Oncsik, Gregor Trefalt, Michal Borkovec

University of Geneva, Department of Inorganic and Analytical Chemistry, 30 Quai Ernest-Ansermet, 1205 Geneva, Switzerland

istvan.szilagyi@unige.ch

Colloidal stability of polystyrene latex particles in water miscible ionic liquids (ILs) was studied by light scattering techniques. Upon systematically varying the IL-to-water ratio, we observed slow aggregation at low IL concentration while the aggregation becomes fast as the IL content increases indicated by high aggregation rates (Figure 1). The dependence of the rates on IL concentration in the diluted regime was similar to simple salts and can be qualitatively explained with the classical theory developed by Derjaguin, Landau, Verwey and Overbeek (DLVO). At higher IL-to-water ratios, the aggregation takes place again slowly and very stable colloidal suspensions were obtained in ILs containing only little percent of water. Taking the increased viscosity at higher IL concentrations into consideration, one finds that the aggregation of particles can be described by two mechanisms. In highly viscous ILs, the stability originates from the slowdown of the diffusion controlled aggregation rate due to slower diffusion in a viscous liquid. Although smaller absolute aggregation rates were determined in this regime, the rate coefficients normalized by the viscosity indicate that the aggregation is still governed by the diffusion of the particles. Solvation stabilization mechanism gave rise to a dramatic slowdown of the aggregation rate in pure ILs. This mechanism is most likely related to repulsive solvation forces due to strong layering of ILs close to the surfaces. These two stabilization mechanisms are found to be generic, accordingly, ILs containing dicyanamide or thiocyanate anions together with imidazolium, pyridinium or pyrrolidinium derivatives tend to stabilize suspensions of negatively and positively charged latex particles by both mechanisms.

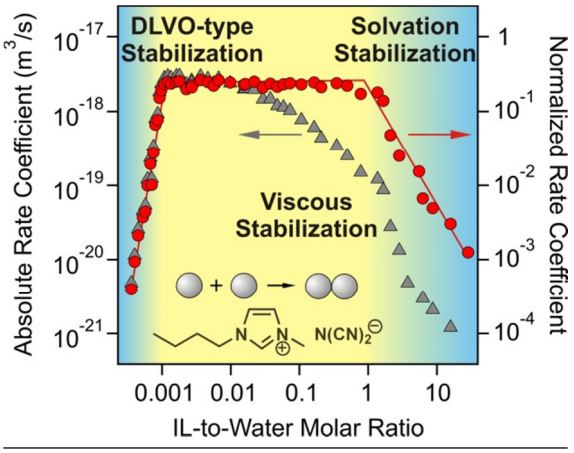


Figure 1. Absolute and normalized aggregation rates of amidine latex particles at different IL-to-water molar ratios.

References:

[1] Szilagyi, I.; Szabo, T.; Desert, A.; Trefalt, G.; Oncsik, T.; Borkovec, M., Particle aggregation mechanisms in ionic liquids. *Phys. Chem. Chem. Phys.* 2014, **16**, 9515-9524.

Processing and Analysis of Nanocellulose using Ionic Liquids.

A. J. Holding,[1] J. K. J. Helminen,[1] L. Lemetti,[1] V. Mäkelä,[1] S. Kedzior,[2] E. D. Cranston,[2] E. I. Filpponen,[3] I. Kilpeläinen,[1] A. W. T. King[1]*

[1] Laboratory of Organic Chemistry, Department of Chemistry, University of Helsinki, A.I Virtasen Aukio 1, FIN-00014, Finland, e-mail: alistair.king@helsinki.fi
[2] Department of Chemical Engineering, McMaster University, 1280 Main St. West, Hamilton, Canada.
[3] School of Chemical Technology, Department of Forest Products Technology, Aalto University, P.O. Box 16300, 00076 Aalto, Finland.

Nanocellulose is intensively researched for its industrial potential, mainly for the bulk formation of composites, films and fibres. The main reasons for this are due to the added strength and barrier properties imparted by the high aspect ratio and H-bonding cohesion between particles, on the nano-scale. However, this presents two major drawbacks when processing nanocellulose and optimising processes: 1) current industrial preparation of nanocellulose is as a viscous aqueous dispersion (~1-10 wt % cellulose). Dewatering these materials down to low water contents is very energy intensive, and 2) no non-destructive solution-phase analytical techniques are available for accurate process optimisation. Consequently, we would like to present our research on the application of ionic liquids in 1) the dewatering of nanocellulose, and 2) high-resolution solution-state NMR analysis of chemically modified nanocellulose.

For the first point we have developed a new process, which takes advantage of the low volatility and cellulose stabilising properties of basic ionic liquids. We will show that aggregation of nanocellulose can be avoided by using ionic liquid additives to the process and allowing simple water removal in a rotary evaporator.

For the second point we will show that it has been possible to run high-resolution solution-state qualitative and quantitative NMR on polymethylmethacrylate (PMMA)-grafted cellulose nanocrystals (CNCs), allowing for more accurate understanding of structure and possibly affording new methods of process optimisation over existing solid-state or destructive techniques.

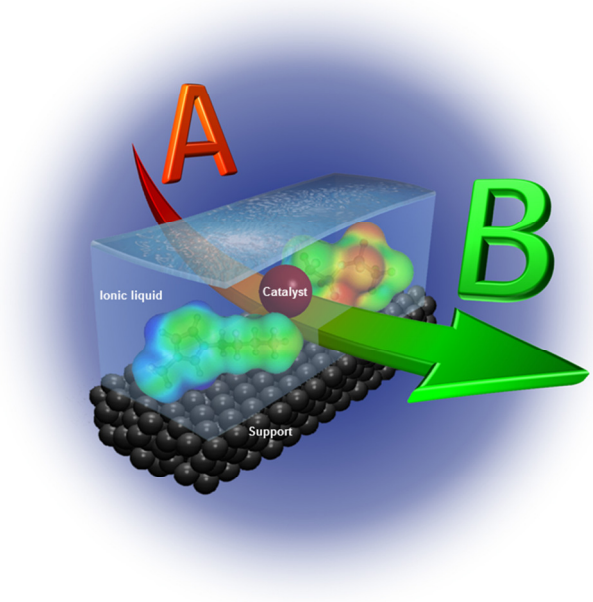
Surface influences on catalytic performance of supported ionic liquid phase (SILP) materials

Marco Haumann

FAU Erlangen-Nürnberg, Chemische Reaktionstechnik, Egerlandstr. 3, 91058 Erlangen, Germany

marco.haumann@fau.de

The supported ionic liquid phase (SILP) technology is a fundamental, new approach to achieve the goal of long-term stable, immobilized homogeneous catalysis, involving surface modification of a porous solid by a thin film of an ionic liquid catalyst solution.[1] Due to the extremely low vapor pressure of ionic liquids, the surface of SILP materials remains coated permanently even in contact with a continuous gas stream or at elevated temperature.



By variation of anions and cations, solubility, reactivity and coordination properties of the ionic liquids can be modified according to the special requirements of the given process. By an appropriate choice of the IL ions, it is possible to transfer specific properties of the fluid onto the surface of a solid material by simply confining the fluid onto the surface. Thus, the SILP concept allows tailor making of solid surfaces resulting in uniform and well-defined surface topologies with defined and uniform properties and controlled chemical reactivity. Importantly, the SILP concept thereby constitutes an attractive methodology to circumvent the lack of uniformity of solid surfaces in traditional heterogeneous catalysis at least for continuous gas phase reactions.

In this presentation the latest results from SILP material design are presented. By appropriate modification of the surface it is possible to improve the catalytic performance of the SILP material significantly.

References:

[1] Supported Ionic Liquids – Fundamentals and Applications (Eds. R. Fehrmann, A. Riisager, M. Haumann), Wiley-VCH, Weinheim, 2014.

CONTINUOUS FLOW ETHYLENE METHOXYCARBONYLATION BY SUPPORTED IONIC LIQUID PHASE (SILP) CATALYSTS

Eduardo J. Garcia-Suarez, Santosh G. Khokarale, Rasmus Fehrmann, Anders Riisager

Centre for Catalysis and Sustainable Chemistry, Technical University of Denmark, Lyngby, Denmark.

edgar@kemi.dtu.dk

Polymethyl methacrylate (PMMA) is a highly world demanded transparent thermoplastic polymer with many useful applications such as alternative to glass, medical technologies, etc. [1] One of the routes to prepare PMMA includes the use CO, ethylene and methanol as raw materials to give methylpropanoate (MP) as key material in the production of PMMA in a reaction known as ethylene methoxycarbonylation. Tipically, the methoxycarbonylation of ethylene is carried out homogeneously in the presence of Pd-phosphine complex catalysts and a strong Brønsted mineral acid.[2] Due to the problems associated to the use of an strong acid at industrial level the searching for an alternative is still a challenge. In this sense, we have published recently a work where Brønsted acidic ionc liquids are used as both alternative to the mineral acid and reaction media yielding a biphasic system affording excellent results being the only backdraw the high amount of ionic liquid required to generate the biphasic system and the diffusion problems associated to it.[3] An elegant alternative to overcome these problems is the use of the supported ionic liquid phase technology (SILP). The SILP technology consists in an ionic liquid (IL) film immobilize on a porous solid material and a homogeneous catalyst dissolved in a supported IL layer. The resulting ionic liquid catalyst film is only a few nanometers thick minimazing mass transport resistance from the gas into the liquid phase. SILP catalysis has potential for efficient catalyst recycling and it makes possible the application of homogeneous catalysis in fixed-bed reactor technology.

In this work, it is reported the application of the SILP catalysis technology to the continuous gas-phase methoxycarbonylation of ethylene for methylpropanoate (MP). A screening of the influence of different reactions parameters such as, ionic liquid loading, nature of the support, metal loading, temperature, GHSV (h^{-1}) etc, in both catalyst activity and selectivity has been performed.

References:

[1] Kirk-Othmer Encyclopedia of Chemical Technology, Wiley

[2] W. Clegg, G.R. Eastham, M.R.J. Elsegood, R.P. Tooze, X.L. Wang, K. Whiston, Chem. Commun., **1999**, 1877

[3] E.J. Garcia-Suarez, S.G. Khokarale, O.N. van Buu, R. Fehrmann, A. Riisager, Green Chem., **2014**,16, 161.

Encapsulated Ionic Liquids (ENILs) applied to gas capture

Jose Palomar, Cristian Moya, Noelia Alonso, Jesus Lemus, Miguel Angel Gilarranz, Juan José Rodríguez

Universidad Autónoma de Madrid, Chemical Engineering Section, 28045 Spain

e-mail: pepe.palomar@uam.es

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

ENIL is a remarkably versatile functionalized material, which can be prepared using Ccap with different core size, shell thickness, pore structure and surface chemistry. In this work, Ccap were prepared with a single and double shell, ABET ~1400 m2·g-1 and particle size up to 800 nm. On the other hand, ENIL can be prepared by filling the Ccap with different amount of IL solvent (up to 85% w/w) and using ILs with very different chemical nature (hydrophobic/hydrophilic; acidic/basic, etc), to promote inter or intramolecular interactions between the components of the system and, consequently, enhance the physical or chemical capture of the solute by the ENIL separating agent. In this work, a number of ENIL materials were designed by for the selective capture of gaseous solutes of interest. The new ENIL materials were prepared using selected ILs with adequate absorption capacity and systematically characterized by elemental analysis, N2 adsorption isotherms, thermogravimetric analysis, differential scanning calorimetry, energy dispersive X-ray, scanning and transmission electron microscopy [3], in order to obtain a thoroughly description of their properties. Finally, ENIL materials were evaluated as potential sorbents of different gases (NH_3, CO_2, acetone and toluene.) by gravimetric measurements to analyse the thermodynamics and the kinetics of the process and, later, carrying out fixed bed experiments to evaluate their performance in a more realistic scenario. In addition, the successfully regeneration of the exhausted ENIL sorbent and, consequently, the recovery of the gaseous components were also experimentally demonstrated at mild operating conditions.

X-Ray Reflectivity Studies of Ionic Liquids at Interfaces

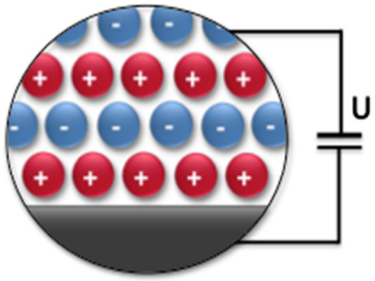
M. Mezger[1,2], P. Reichert[2], J. Mars[2], D. Pontoni[3]

1. Institute of Physics, Johannes Gutenberg-University Mainz, Germany
2. Max Planck Institute for Polymer Research, Mainz, Germany
3. European Synchrotron Radiation Facility, 38043 Grenoble, France

mezger@mpip-mainz.mpg.de

Ionic Liquids (ILs) are promising electrolytes for electrochemical double-layer capacitors with high energy storage densities. To understand and optimize their capacitance as well as charging and discharging processes, detailed information of the IL's molecular scale structure at interfaces, i.e. the spatial density profiles of the ions near an electrode, is highly desirable. Using high-energy x-ray reflectivity we get access to deeply buried solid-liquid interfaces and gain structural information with molecular scale resolution. At dielectric sapphire substrates, our experiments revealed interfacial profiles comprised of alternating anion and cation enriched regions decaying gradually into the bulk liquid [1].

For our in-situ x-ray reflectivity study at electrodes under potential control a novel sample chamber was developed. Experiments were carried out at the High-Energy Micro Diffraction instrument at ID15, ESRF. Reflectivity curves vs. angle at fixed potentials as well as time-resolved signals upon potential variation were recorded in the anodic and cathodic regime. Quantitative analysis of the experimental XRR data revealed potential induced changes in the ion distribution near the interface. The molecular scale structure at the solid-liquid interface is compared with complementary electrochemical measurements.



References:

[1] M. Mezger et al., Science 322, 424 (2008).

[2] M. Mezger et al., *J. Chem. Phys.* 131, 094701 (2009).

[3] M. Mezger et al., Proc. Natl. Acad. Sci. USA 110, 3733 (2013).

IL-based nanocolloids prepared by vacuum sputtering

P. Lobotka[1], G. Radnóczi[2], M. Sojková[1]

[1]Institute of Electrical Engineering Slovak Academy of Sciences, Bratislava

[2]Centre for Energy Research, Institute for Technical Physics and Materials Science, Budapest

eleklobo@savba.sk

We shall report our very preliminary results on two-component nanocolloid containing Ni and C nanoparticles prepared by vacuum sputtering of both materials on the surface of an IL. Our goal is to prepare double-purpose colloid: superparamagnetic nanoparticles (e.g. Ni) would enhance the contrast in magnetic imaging by MRI and simultaneously the luminescent nanoparticles could be used in optical imaging.

In addition we shall try to review attractive application of ILs or ionogels in semiconductor physics. It was revealed by two groups [1-2] that the anions and cations are stratified in the vicinity of IL/solid interface. In the research of physical properties of novel semiconductors like graphene or MoS_2 this feature is of great importance since the electric double layer formed at the interface (with the intensity of electric field in the range of MV/cm) allows to form in an easy way a field-effect transistor. A drop of IL on the semiconductor surface plays the role of a gate electrode. When the liquid gate electrode is not applicable, the ionogel can be used.

References:

[1] Takashi Ichii et al., 19th Int. Vacuum Congress, Paris 2013

[2] Markus Mezger et al., Science **322** (2008) 424

Local structure and dynamics in water-added and nano-confined ionic liquids

Negin Yaghini[1], Moheb Nayeri[2], Mounesha Garaga Nagendrachar[1], Brad F. Chmelka[3], A. Martinelli[1,*]

[1]Chalmers University of Technology, Gothenburg, Sweden
[2]CIT (Chalmers Industriteknik), Gothenburg, Sweden
[3]University of California Santa Barbara, CA 93106-5080, USA

E-mail: anna.martinelli@chalmers.se

The interest in understanding the physico-chemical properties of ionic liquids is still increasing and new scientific areas have grown. More and more studies are being devoted to binary systems based on two ionic liquids or on water-added ionic liquids, and a few are focused on understanding the effect of nano-confinement on transport properties such diffusion or conductivity. In particular, the incorporation of ionic liquids into a solid matrix would render them interesting for real applications since leakage problems would be overcome.

In this contribution, we present our most recent results on how added water influences the ion-ion coordination as well as the self-diffusion of the individual ions in ionic liquids based on either the imidazolium or the ammonium cation [1]. The role of the ion pair's structure on the observed results is emphasized. We also show some results on how nano-confinement in porous silica influences both the structural and dynamical properties of the ionic liquid. In this context we investigate two different types of gels, those prepared *in situ* using the ionic liquid as a co-solvent during a non-aqueous sol-gel synthesis [2], and those based on filling the pores inside nano-textured silica micro-particles [3]. In all cases we employ 1D ^{1}H NMR spectroscopy, 2D ^{29}Si{^{1}H} solid-state NMR spectroscopy, and vibrational spectroscopy (complementing Raman with Infrared) to understand the degree and site of inter-molecular interactions as well as the ion-ion coordination scheme. Pulsed field gradient NMR spectroscopy is, on the other hand, used to estimate the self-diffusion of the individual ions and, when compared with the measured conductivity, to estimate the ionicity. These results will be presented in the perspective of using these ionic liquid based materials in next-generation proton exchange membrane fuel cells, for which fast proton conductivity is expected to occur at temperatures higher than 120 °C.

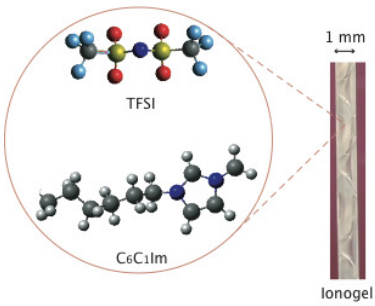


Figure 1. Picture of an ionogels prepared with the ionic liquid C_6C_1ImTFSI.

References

[1] N. Yaghini et al., PCCP 16(2), 9266-9275, 2014; and J Phys. Chem. B 119(4), 1611-1622, 2015.
[2] M. Nayeri et al., *Soft Matter*, 10 (30), 5618-5627, 2014.
[3] M. G. Nagendrachar et al., in preparation for Advanced Functional Materials, 2015.

Energetics of Liquid-Gas interfaces in imidazolium based ILs with [PF6] and [NTf2] anions

Sergey P. Verevkin, Dzmitry H. Zaitsua

(University of Rostock, Chemical Department, Dr-Lorenz-Weg 1, 18059 Rostock, Germany)

e-mail (sergey.verevkin@uni-rostock.de)

The determination of vaporization enthalpies of extremely low volatile ionic liquids is challenging and time consuming due to the low values of vapor pressure. In addition, these liquids tend to decompose already at temperatures where the vapor pressure is still low. Conventional methods for determination of vaporization enthalpies are thus limited to temperatures below the decomposition temperature. Here we present a new method for the determination of vaporization enthalpies of such liquids using differential fast scanning calorimetry (DFSC). We have developed and proved this method using $[C_2mim][NTF_2]$ at temperatures up to 750 K and in different atmospheres. It was demonstrated by us that evaporation is still the dominating process of mass loss even at such highly elevated temperatures. In addition, since the method allows one to realize very high heating rates (up to 10^6 K s^{-1}). We discuss the advantages and limits of this new method of vaporization enthalpy determination and compare the results with data obtained from established methods. The DFSC and the quartz crystal microbalance method were applied for a series of extremely thermally labile ionic liquids $[C_nmim][PF_6]$ with n = 2-18. The absence of decomposition of ILs during investigations was proved by a spectroscopy. New experimental results have revealed a clear trend shift (percolations) on the dependence of ionic liquid vaporization enthalpies on the chain length of the alkyl group on the cation. Energetics of $[C_nmim][PF_6]$ and $[C_nmim][NT_2]$ families on the liquid-gas interface as well as mesoscopic structures were discussed in terms of CH_2-contribution to vaporization enthalpy.

Intrinsic analysis of liquid/liquid interfaces involving ionic liquids

György Hantal[1,2,3], Marcello Sega[1], Christian Schröder[2], Sofia Kantorovich[1] and Miguel Jorge[4]

[1]Dept. of Comput. Physics, University of Vienna, Sensengasse 8/9, 1090 Wien, Austria.
[2]Dept. of Comput. Biological Chemistry, University of Vienna, Währinger Str. 17, 1090 Wien, Austria
[3]Dept. of Chemistry, Eszterházy Károly College, 3300 Eger, Leányka út 6, 3300 Eger, Hungary
[4]Dept. of Chemical Engineering, University of Strathclyde, James Weir Building 75 Montrose Street Glasgow, G1 IXJ, United Kingdom
e-mail: gyorgy.hantal@gmail.com

Since the early 2000's, extensive research has been dedicated to understanding ionic liquid (IL) properties which resulted in an offspring of novel applications of ILs in a broad range of chemical technologies. Although most of the emerging applications rely on properties of ILs at interfaces with other liquids, our knowledge on these interfacial systems is still very limited which strongly restrains further developments. Due to the inherent complexity of interface systems molecular simulations come in very handy as they can probe the interface at the molecular level. Novel intrinsic analysis techniques have recently made it possible to decouple thermally activated capillary waves from fluid interfaces leading to structural information free from the random noise of capillary waves.

Recently we performed the first intrinsic analysis of liquid/liquid interfaces of two popular ionic liquid species: BMIM PF_6 and BMIM NTf_2. The main goal was to understand how interface properties (intrinsic density profiles, lateral ordering in the surface layer and molecular orientations at the surface) change as the vapor phase is replaced either with apolar cyclohexane or polar water. The results show a strong effect on the structural properties as the opposite phase is varied – this effect being weak in the case of cyclohexane, but very pronounced in the case of water. The other liquid phase has, in general, the tendency to decrease structural correlations at the surface of the IL rich phase. We observed a decrease of intrinsic ordering along the surface normal, but also a loss of preference of the anions at the surface to associate with the most acidic imidazolium ring H with respect to the other ring H atoms. The orientational preferences of the cations and the anions at the IL/cyclohexane interface were found to change only slightly, and the most preferred orientation is still where the apolar "chains" (butyl or CF_3 groups) stick out to the cyclohexane phase. However, water induces drastic changes in the orientational preferences: the cations prefer an orientation where their butyl chains point inwards while the methyl substituents point outwards. Anion orientations were also found to change in a way that allows to maximize the number of contacts between its polar moieties and water.

Interfacial Thermodynamics and Morphology of ILs

José C.S. Costa[1], Ana F. S.M. Coelho[1], Ana C. P. Aguas[2], Guilherme N. M. Ferreira ,[2] Rui M. Borges dos Santos,[2] Luís M. N. B. F. Santos[1]

[1]CIQ, Faculdade de Ciências da Universidade do Porto, P4169-007 Porto, Portugal.
[2]Universidade do Algarve, Campos Gambela, P8005-007 Faro, Portugal
lbsantos@fc.up.pt

The increasing interest in Ionic liquids (ILs) are due to their unique features resulting from the type of cohesive interaction, charge distribution, structuration, polar network and apolar domains, which leads to many interesting and unusual, physical and transport properties at the bulk and interface. The molecular structure and supramolecular organization of an ionic liquid is complex and is reflected in their thermodynamic complexity, interface morphology and properties.

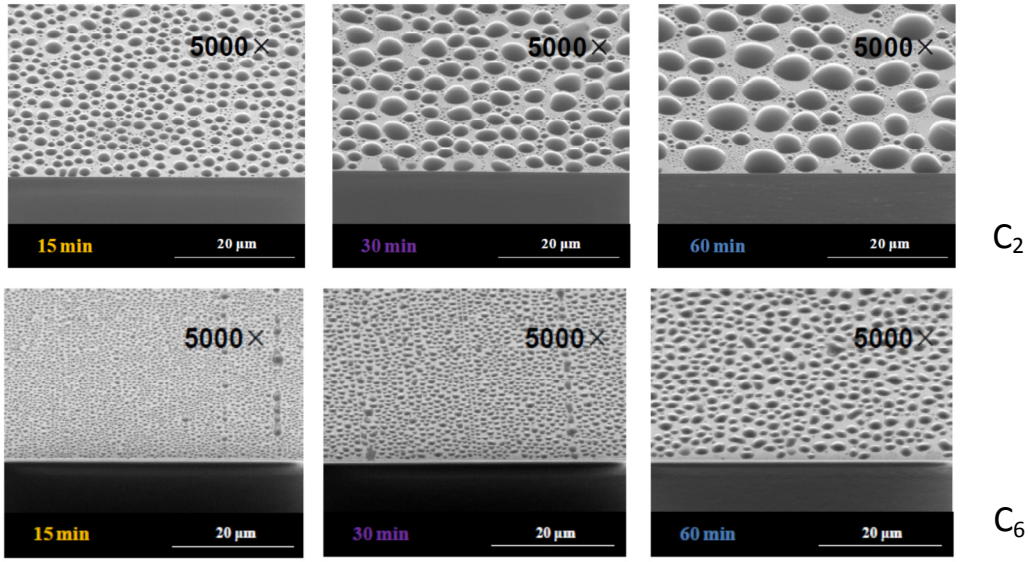


Figure 1. Thin film morphology of Ionic liquids ($C_n$mimNtf$_2$ series) fabricated by vapour deposition.

This presentation will be focused in the analysis of experimental interfacial thermodynamics and morphology of ILs, including their chain length and temperature dependence: surface tension; thin film fabrication and morphology, XPS spectral analysis and contact angle in ITO and Gold surfaces.

Short term scientific mission reports

M. Hübner	Extraction of proteins using IL-containing aqueous biphasic systems (ABS)
M. Martins	Ionic liquids as extractive solvents of terpenes and ternoids
D. Patinha	Polymeric ionic liquids for sample preparation techniques
I. Rodriguez	Surfactant ionic liquids for enhanced oil recovery