

Molten Salt Discussion Group

2011 Summer Research Meeting

Programme & Abstracts

5 - 6 July 2011
Fitzwilliam College, Cambridge

Programme

Tuesday 5th July

12:00 - 12:30 Arrival and Registration

12:30 – 13:25 Lunch

13:25 – 13:30 MSDG's Chairperson's welcome

13:30 – 15:25 Technical Session 1

(Chairperson : Dr Peter Licence)

13:30 – 14:00 Qing Huang¹, Xianbo Jin¹ and **George Z. Chen^{1,2}**
1 College of Chemistry and Molecular Sciences, Wuhan University
2 Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, University of Nottingham
Interactions of CO₂ and MEA in hydroxylated ionic liquids

14:00 – 14:30 **Ali Kamali**, Carsten Schwandt and Derek Fray
Department of Materials Science and Metallurgy, University of Cambridge, UK.
The electrolytic preparation of carbon nanostructures in molten salts

14:30 – 15:00 **Robert Watson**
AWE, Aldermaston, UK.
Electrochemical adventures in CaCl₂

15:00 – 15:25 **Moira Lewis**, Paul Nancarrow, Quan Gan and Lizhe Liang
School of Chemistry and Chemical Engineering, Queen's University, Belfast.
Predicting and Designing the Properties of Ionic Liquids

15:25 – 16:00 Tea/coffee break & poster session

16:00 – 17:30 Technical Session 2

(Chairperson : Dr Kevin Murnaghan)

16:00 – 16:25 **Manabu Tokushige**
Institutt for Materialteknologi, NTNU, Sem Salands vei 12, Trondheim, Norway, NO-7491
Nanoparticle Size Control by Plasma-Induced Cathodic Discharge Electrolysis using Rotating Disk Anode

16:25 – 16:50 **Peter L. Licence**
University of Nottingham, Nottingham, UK.
XPS as a probe of solvent-solvent and solvent-solute interactions in ionic liquids

16:50 – 17:20 **Trevor Griffiths**
Redston Consulting Ltd., Leeds, LS17 8RF, UK.
A Description, History and Anecdotes concerning the Oak Ridge National Laboratory Molten Fluoride Reactor -and does it have a future?

17:20 – 17:30 **MyRSC** presentation

17:30 – 18:00 MSDG Committee Meeting

18:00 – 19:00 Drinks reception

19:00 – 20:00 Banquet in Walter Grave Room

After Dinner Lecture
(Chairperson : Dr Stuart Mucklejohn)

Professor Doug Inman
Imperial College, London, UK.
My life in ionic liquids, from one lab to another

Wednesday 6th July

08:00 – 09:00 Breakfast (for residential attendees only)

09:00 – 09:35 Invited Lecture

(Chairperson : Professor Derek Fray)

Professor L P N Rebelo
Universidade Nova de Lisboa, Instituto de Tecnologia Química e Biológica, Portugal
Stretching ionic liquids to the limit

09:35 – 10:35 Technical Session 3

(Chairperson : Dr Robert Watson)

09:35 – 10:05 **Mohd Azri Ab Rani**, J. Hallet, P. Lickiss, T. Welton
Chemistry Department, Imperial College, London, SW7 2AZ, UK.

Synthesis, Characterization and Physical-Chemical Properties of Room Temperature Ionic Liquids (RTILs) With Siloxane Containing Cations

- 10:05 – 10:35 **Geir Martin Haarberg**
Norwegian University of Science and Technology, Trondheim, Norway
Electrodeposition of titanium from molten chloride electrolytes by using titanium oxycarbide anodes
- 10:35 – 11:05 Tea/coffee break and poster session
- 11:05 – 12:30 Technical Session 4

(Chairperson : Professor George Chen)
- 11:05 – 11:35 **Eimutis Juzeliunas**, Antony Cox and Derek Fray
Department of Materials Science and Metallurgy, University of Cambridge.
Black silicon from Molten Salts
- 11:35 – 12:05 **Simon Puttick** and Peter Licence
University of Nottingham, Nottingham, UK.
NMR as a Probe of Nanostructure in Ionic Liquids
- 12:05 – 12:30 **Kevin Murnaghan**
Henkel Ireland, Dublin, Republic of Ireland.
Ionic Liquids in Industry: Processable, Functional & Task-Specific
- 12:30 -13:30 Lunch
- 13:30 – 14:00 Free discussion and networking
- 14:00 Close of meeting

Authors' Abstracts

Abstracts presented on the following pages are compiled by the MSDG for the sole purpose of distribution amongst attendees of the 2011 MSDG Summer Research Meeting and are based on the submitted versions from the authors who are responsible for issues related with the scientific correctness and copyright.

Interactions of CO₂ and MEA in Hydroxylated Ionic Liquids

Qing Huang¹, Xianbo Jin¹ and George Z. Chen^{1,2,*}

¹ College of Chemistry and Molecular Sciences, Wuhan University. ² Department of Chemical and Environmental Engineering, and Energy and Sustainability Research Division, University of Nottingham. *
Email: george.chen@nottingham.ac.uk

There is an ongoing global effort to tackle the challenge of climate change by developing the so called carbon capture and storage (CCS) technologies.¹⁻³ Although being a passive approach, the outcome of CCS does present an unprecedented opportunity for commercial utilisation of CO₂ as a cheap carbon sources for securing both materials and energy supplies. This is because CO₂ is in fact very rare on the earth as a trace component of air (340 ppm).⁴ It may be produced from liquefied air at high pressures, or from carbonate based minerals, but the energy input is not negligible. More importantly, with the fast exhaustion of fossil resources on the earth, it will inevitably become increasingly challenging to maintain our carbon based civilisation if new methods are developed for producing carbon related materials. In the current industry, CO₂ capture is achieved via absorption by aqueous solutions of monoethanolamine (MEA). This aqueous amine process has however a number of technical drawbacks, of which the high heat capacity of water is the main factor for high energy consumption in MEA regeneration. With a heat capacity of about 1/3 of water, ionic liquids are promising media to accommodate the MEA-CO₂ reactions at a lower energy cost.

This presentation reports the preliminary findings from an investigation of the absorption of CO₂ by MEA in hydroxylated ionic liquids (HILs) under different conditions.⁵ The absorption and desorption of CO₂ in these liquids were particularly studied in the absence and presence of halide ions, such as the difference shown in **Fig. 1**. The findings confirm that halide ions, particularly Cl⁻, are capable of stabilising the absorbed CO₂ in the HIL-MEA mixture at elevated temperatures, even under vacuum. Other aspects of this research include conductivity and viscosity changes in the mixture upon CO₂ absorption, and results from electrolytic treatment of CO₂ saturated MEA-HIL. It is hoped that this ongoing work may help establish a new and **affordable** strategy for CO₂ capture and reclamation (CCR).

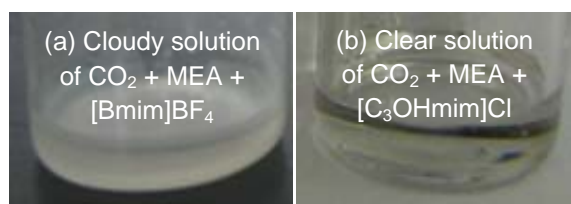


Fig. 1. Photos of equimolar mixtures of MEA with (a) [Bmim]BF₄ or (b) [C₃OHmim]Cl after CO₂ bubbling for 30 min at 25 °C.

References

1. P.M. Cox, R.A. Betts, C.D. Jones, S.A. Spall, I.J. Totterdell, *Nature*, 408 (2000) 184.
2. Y. Malhi, P. Meir, S. Brown, *Phil. Trans. R. Soc. Lond. A*, 360 (2002) 1567.
3. N. MacDowell, N. Florin *et al.*, *Energy Environ. Sci.*, 3 (2010)1645.
4. http://en.wikipedia.org/wiki/Carbon_dioxide
5. H. Huang, Y. Li, X.B. Jin, D. Zhao, G.Z. Chen, *Energy Environ. Sci.*, 4 (2011) 2125.

Acknowledgement

This research received partial support from each of the 973 (2007CB613801), 863 (2009AA03Z503) and 111 Projects, NSFC (20973130), EPSRC (EP/F026412/1), and Fundamental Research Funds for the Central Universities.

The electrolytic preparation of carbon nanostructures in molten salts

Ali Kamali, Carsten Schwandt and Derek Fray

Department of Materials Science and Metallurgy, University of Cambridge, UK.

Electrochemical adventures in CaCl₂

Robert Watson

AWE Aldermaston Reading. RG7 4PR, UK.

AWE © Crown Owned Copyright (2011)

Predicting and Designing the Properties of Ionic Liquids

M. Lewis¹, Dr. P. Nancarrow, Dr. Q. Gan

¹Queen's Univ. Belfast, Dep. Chemistry and Chemical Engineering, David Keir Building, Stranmillis Rd.,
Belfast, BT9 5AG, Northern Ireland;
e-mail: mlewis09@qub.ac.uk;

Ionic liquids and their application in both industry and academia has become an area of great interest in recent years ^[1]. Their unique properties such as negligible vapour pressure, wide melting point range and wide thermal stability, give them many advantages over traditional materials for commercial use such as, solvents, gas separation membranes and for use in nanochemistry and catalysis ^[2].

However, the main attraction of ionic liquids is the ability to change the physical properties by simply altering the anion/cation combination. As a result, ionic liquids can potentially be designed for any application. With the number of possible pure ionic liquids being estimated at 10^6 ^[2], experimental measurement of the physical properties of these liquids is unfeasible and, without this information, ionic liquids cannot be easily incorporated into industry.

Group contribution methods are a tool widely used in industrial design for predicting the physical properties of compounds. To date, there are few group contribution models for the prediction of ionic liquid properties.

Here, group contribution models based on a universal parameter set, are presented for the prediction of heat transfer properties of ionic liquids:

- Heat capacity
- Melting point
- Viscosity
- Thermal conductivity
- Thermal decomposition.

The models developed have been incorporated into a reverse design framework enabling the user to design ionic liquids with high heat capacities.

^[1] Heat Capacities of Ionic Liquids as a Function of Temperature at 0.1 MPa.: Measurement and Prediction, Ge, R., Hardacre, C., Jacquemin, J., Nancarrow, P., Rooney, D.W. *J. Chem. Eng. Data*, **2008**, 53, 2148

^[2] Applications of ionic liquids in the chemical industry, Plechkova, N.V., Seddon, K.R., *Chem. Soc. Rev.*, **2008**, 37, 123-150

Plasma-Induced Cathodic Discharge Electrolysis to Form Metallic Nanoparticle by the Use of Molten Salt System

M. Tokushige^a, T. Nishikiori^b, and Y. Ito^c

^aGraduate School of Engineering, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan (tokushi@iis.u-tokyo.ac.jp)

^bR&D Division, I' MSEP Co., Ltd., D-egg 310, Kyotanabe, Kyoto 610-0332, Japan (nishikiori@imsep.co.jp)

^cEnergy Conversion Research Center, Doshisha University, Kyotanabe, Kyoto 610-0321, Japan (yasito@mail.doshisha.ac.jp)

Introduction

As compared to their bulk counterparts, metallic nanoparticles have attracted considerable interest owing to their superior electronic, catalytic, optical, and magnetic properties. In order to realize these properties, the production of fine and uniform nanoparticles is crucial; however, no such production process has been established thus far. The authors and their collaborators have investigated plasma-induced cathodic discharge electrolysis in a molten salt electrolyte to form metallic nanoparticles [1]. In this study, to obtain smaller and more uniform nanoparticles, a rotating disk anode having a high rotation speed was utilized for plasma-induced cathodic discharge electrolysis and its availability was confirmed. Smaller nanoparticles can be obtained by decreasing the residence time and number density of the early-formed nanoparticles in the melt. In a molten LiCl-KCl-CsCl electrolyte, Ni nanoparticles (diameters, ~5 nm) were obtained at rotation speeds higher than 2,500 rpm; however, there was a slight aggregation of these nanoparticles. The dependence of the aggregated particle size on both the rotation speed of the disk and the electrolysis current were investigated using dynamic light scattering (DLS) measurements.

Results and Discussion

The dependence of the aggregated particle size on the rotation speed is shown in Fig. 1, which confirms that the particle size significantly decreased above 1,500 rpm; this dependence decreased at rotation speeds higher than 2,000 rpm. The hydrodynamic consideration suggests that the rotation speed of the disk significantly affected on the residence time of the melt at around 1,000 rpm (Table 1). These results and considerations could semi-quantitatively explain the effect of the rotating disk anode type electrolytic cell in shortening the residence time of the early-formed particles just under the discharge.

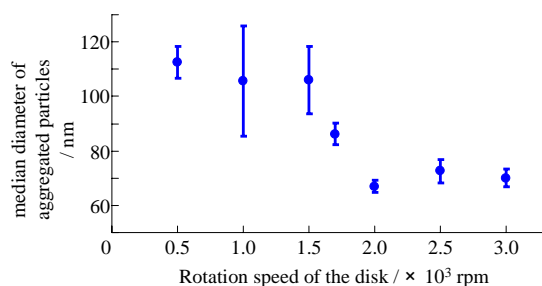


Fig. 1 Dependence of aggregated particle size on

Table 1 Velocity components and residence time

of the melt just under the discharge estimated from Navier-Stokes equations.

N / rpm	v_r / m·sec ⁻¹	v_ϕ / m·sec ⁻¹	t_r / msec
500	2.7	2.1	0.58
1,000	6.2	4.2	0.27
1,500	11	6.3	0.15
2,000	13	8.4	0.13

[1] M.Tokushige, T.Nishikiori, and Y.Ito, *J.Electrochem.Soc.*, 157, pp.E162-E166 (2010).

Ionic liquids in-vacuo

Men Shuang, Kevin Lovelock and Pete Licence
The University of Nottingham, UK
pete.licence@nottingham.ac.uk

Ionic liquids are, in general, organic based salts with melting points below 100 °C. This lecture describes a series of completely new experiments that are only made possible because these liquids are composed entirely of ions and consequently have *almost zero vapour pressure*, *i.e.* they do not evaporate even under vacuum. We have recognised that this lack of volatility allows ionic liquids to be used in a whole range of analytical instruments that require high vacuum for their operation. We have obtained high quality X-ray photoelectron spectroscopy (XPS) data of the pure liquids as well as the liquids doped with simple metal salts. XPS provides information about the electronic structure of different elements within a compound and has sufficient sensitivity to distinguish between atoms of the same element situated in chemically distinct environments.¹⁻⁴

The lecture will give an overview of general charge referencing methods^{4,5} and the extraction of data pertinent to both anion-cation and solvent-solute interactions.⁶ The impact of both anion and indeed ligand selection will be investigated with selected examples from homogeneous catalysis in ionic liquids.

¹ *Chem. Commun.*, **2005**, 5633-5635.

² *Chem. Commun.*, **2009**, 5817-5819.

³ *Phys. Chem. Chem. Phys.*, **2010**, 12, 1982-1990.

⁴ *Chem. Rev.*, **2010**, 110, 5158-5190.

⁵ *Phys. Chem. Chem. Phys.*, **2011**, 13, 2797-2808.

⁶ *Phys. Chem. Chem. Phys.*, **2011**, DOI:10.1039/C1CP21053J

The First Molten Salt Nuclear Reactor: A Description, History and Anecdotes concerning the Oak Ridge National Laboratory Molten Fluoride Reactor

Trevor R. Griffiths

Redston Trevor Consulting Ltd., Leeds LS17 8RF

The Oak Ridge National Laboratory in Tennessee, USA, was built to be one of the major sites for the Manhattan Project to build the world's first atomic bomb. The lab's main contribution, as most know, was to develop techniques for enriching U235 and then to produce it in quantity. What is less well known is that ORNL was shortly thereafter, in the 1950s, also chosen to be the site for developing and testing various designs for nuclear reactors.

The basic principle is that a nuclear reactor, maintained at criticality, generates heat and this heat must and could be taken away and usefully employed to generate steam to drive turbines, thereby providing electricity. Thus a crucial feature was the effective removal of this heat energy. Water and gas cooling are obvious candidates but are not the best conductors of heat. It was recognised that molten salts are amongst the best candidates, being good heat conductors; stable to radiation; thermally stable and of low viscosity at 700°C; and fission products formed can be controlled and readily removed.

A description of the Oak Ridge Molten Salt Reactor will be given, with pictures, and indications of considerations and problems encountered in designing and bringing the reactor into being in a pre-computer era. Personal reminiscences will be included.

Synthesis, Characterization and Physical-Chemical Properties of Room Temperature Ionic Liquids (RTILs) With Siloxane Containing Cations.

Mohd Azri Ab Rani, Jason Hallett, Paul Lickiss and Tom Welton

Department of Chemistry, Imperial College London, London SW7 2AZ, UK

email: m.ab-rani08@imperial.ac.uk

Ionic liquids (ILs) can be defined as salts that melt at or below 100 °C to afford liquids composed solely of ions. ILs have been classified as “designer solvents” because it is possible to tune the physical and chemical properties by varying the combination of cations and anions. Research has been stimulated into Ionic liquids as potential solvents because they are good solvents for a wide range of organic and inorganic compounds, since they are composed of poorly coordinating ions, non-volatile and stable at high temperatures.

Siloxanes find widespread use in a variety of applications such as antifoams, lubricants, hydraulic fluids and detergents, but their potential as solvents has been unexplored until recently. Having siloxane functionalities in ionic liquids would allow their use as solvents while maintaining the good properties of siloxanes: they neither oxidize nor hydrolyze readily.

We have successfully synthesized ILs containing cations with alkane, ether and siloxane side chains and paired with a bis(trifluoromethylsulfonylimide), [N(Tf)₂] anion. The ILs that have been synthesized are 1-methyl-3-pentylimidazolium bis(trifluoromethylsulfonylimide), [C₅C₁im][N(Tf)₂], 3-(2-ethoxy-ethyl)-1-methylimidazolium bis(trifluoromethylsulfonylimide), [C₂OC₂C₁im][N(Tf)₂], 1-methyl-3-pentamethyl-disiloxymethylimidazolium bis(trifluoromethylsulfonylimide), [(SiOSi)C₁C₁im][N(Tf)₂], 1-methyl-3-heptamethyl-trisiloxyimidazolium bis(trifluoromethylsulfonylimide), [(SiO)₂SiC₁C₁im][N(Tf)₂], 1-methyl-1-pentylpyrrolidinium bis(trifluoromethylsulfonylimide), [C₅C₁pyrr][N(Tf)₂], 1-(2-ethoxy-ethyl)-1-methylpyrrolidinium bis(trifluoromethylsulfonylimide), [C₂OC₂C₁pyrr][N(Tf)₂], 1-methyl-pentamethyl-disiloxy-1-methylpyrrolidinium bis(trifluoromethylsulfonylimide), [(SiOSi)C₁C₁pyrr][N(Tf)₂] and 1-methyl-1-hepta-methyl-trisiloxy-methyl-pyrrolidinium bis(trifluoromethylsulfonylimide), [(SiO)₂SiC₁C₁pyrr][N(Tf)₂].

Polarity measurements show the siloxy-ionic liquids have lower dipolarity/polarisability (π^*) values compared with those containing alkyl and ether side chains. The thermal stability of the ionic liquids follows the order of alkyl > ether > disiloxy > trisiloxy side chains for both imidazolium and pyrrolidinium based-ILs. The results also show that conductivity is proportional to diffusion of ions which is proportional to viscosity⁻¹. This suggests that the faster movement of the ions, the lower the viscosity of the liquids and that the flexibility of the siloxane bonds has no effect on viscosity.

Electrodeposition of titanium from molten chloride electrolytes by using titanium oxycarbide anodes

Geir Martin Haarberg^a, Ole S. Kjos^b, Ana Maria Martinez^b, and Karen S. Osen^b

^a Department of Materials Technology, Norwegian University of Science and Technology,

NO-7491 Trondheim, Norway

^b SINTEF Materials and Chemistry, NO-7465 Trondheim, Norway

The use of an anode consisting of titanium oxycarbide combined with a liquid cathode is an alternative method to produce pure titanium by electrolysis. This approach was studied in order to overcome problems related to carbon contamination and to reduce the influence of disproportionation reactions involving various oxidation states of titanium.

The anode material was prepared by mixing and compacting powders of TiO₂ and graphite before heat treatment in inert atmosphere at temperatures from 1350 - 1600 °C.

Cyclic voltammetry and electrolysis experiments were carried out in molten equimolar NaCl-KCl containing dissolved TiCl₃ at 800 °C. Promising results from using liquid electrodes of Zn, Sn and Bi were obtained.

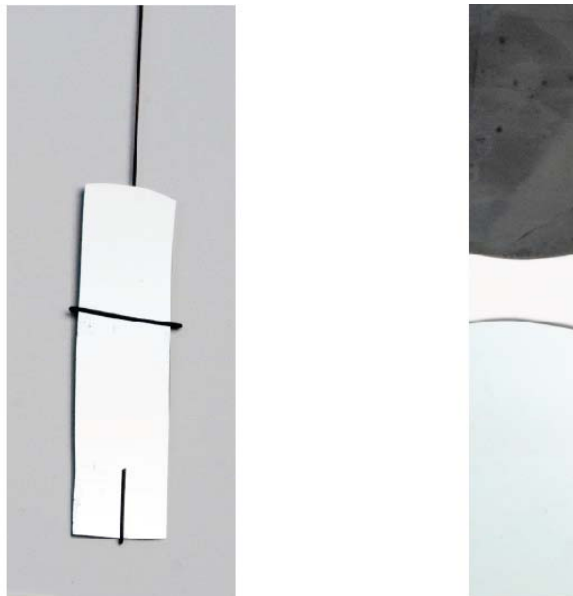
Black silicon from Molten Salts

Eimutis Juzeliunas, Antony Cox and Derek Fray
Department of Materials Science and Metallurgy
University of Cambridge

Photovoltaic (PV) electricity generation is a rapidly expanding industry with the goal of reaching 12% of the total EU electricity market by 2020. However, solar energy conversion still remains relatively expensive and cost reduction is high on the agenda of PV engineers and Materials Scientists. The vast majority of solar cells are produced from silicon but bare silicon reflects more than 30% of the incident light and, in some cases, the surface is textured to reduce the light reflection losses and increase efficiency.

Black silicon is a material with a nano-structured surface, which effectively absorbs light and, therefore, has the capability of increasing the efficiency of solar cells. Various surface engineering techniques have been used to obtain black silicon and these include femtosecond laser engineering, coating with thermal oxide chloroalkylsilane layers and numerous etching procedures. Most of the techniques are too expensive and technically sophisticated to be applied in silicon mass production. Furthermore, etching usually involves toxic and aggressive chemicals, such hydrofluoric acid and, in certain cases, expensive catalysts.

The simple method, proposed in this presentation, is to remove the oxygen in the silica film that is found on silica, by making the silicon the cathode in bath of molten calcium chloride at 850°C. The oxygen in the silica ionises and, as there are two oxygen atoms for every silicon atom, these leads to vacancies which can diffuse to form various micro-architectures. The figures below show a silicon sample coated with 2µm thermal SiO₂ (on the left) and the effect of electrochemical deoxidation of the surface of the silicon (on the right).



NMR as a Probe of Nanostructure in Ionic Liquids

Simon Puttick^a, Adrienne L Davis^a, Kevin Butler^a, Lynette Lambert^c, Jaouad El Harfi^{a,b}, Derek J Irvine^{a,b}, Andrew K Whittaker^{c,d}, Kristofer J Thurecht^{c,d} and Peter Licence^a

^a School of Chemistry, The University of Nottingham, Nottingham NG7 2RD, UK.

^b Process and Environment Research Division, The University of Nottingham, Nottingham NG7 2RD, UK.

^c Centre for Advanced Imaging, The University of Queensland, St Lucia, Q 4072, Australia

^d Australian Institute for Bioengineering and Nanotechnology (AIBN), The University of Queensland, St Lucia, Q 4072, Australia
email: pete.licence@nottingham.ac.uk

As the field of ionic liquids has progressed, it has become apparent that a solvent environment very different to that in conventional molecular solvents exists within room temperature ionic liquids. Recent theoretical and experimental data suggests that a nanostructured environment consisting of polar and non-polar domains exists in the liquid state¹ conferring elements of order upon the overall solvent matrix.

The nuclear Overhauser effect (NOE) has long been used to investigate spatial relationships via the dipolar interactions of neighbouring spins. It has previously been shown that various Overhauser spectroscopies (NOESY, ROESY, HOESY) can be applied to the mapping of intermolecular interactions in ionic liquids.²

The aim of this investigation was to use oligomeric species of methyl methacrylate (MMA), of increasing molecular mass as probe molecules to investigate the affinity of reactant species for the different domains in an ionic liquid. We show that domain specific solubility of molecular solutes can be observed by the use of ROESY spectroscopy and that, through the use of a model reaction, this domain segregation can influence both the kinetics and products of a reaction. Furthermore we show that domain segregation is highly influenced by functionality on the solute.³

1. J. N. Canongia Lopes and A. A. H. Pádua, *J Phys Chem B*, 2006, **110**, 3330-3335.

2. A. Mele, *Chim. Oggi-Chem. Today*, 2010, **28**, 48-55.

3. S. Puttick, A. L. Davis, K. Butler, L. Lambert, J. El harfi, D. J. Irvine, A. K. Whittaker, K. J. Thurecht and P. Licence, *Chemical Science*, 2011, 10.1039/c1sc00207d

Ionic Liquids in Industry: Functional, Processable and Task-Specific

Kevin Murnaghan, Henkel Ireland

Molten Salt Discussion Group, Summer Meeting July 5th & 6th 2011

In this short presentation, an overview of some large scale and potentially large scale industrial processes that use room temperature ionic liquids (RTILs) will be presented. This study will show that powerful, simple solutions using these salts can be found, which when combined with enabling process and engineering technology, can result in efficient, clean and high yielding chemical processes.

Examples discussed include the BASF acid scavenging process, Eastman's 2,5-dihydrofuran process, and the application of functionalized RTIL technology to hydrogen peroxide production.

Cohesive Energy of Ionic Liquids: Evaluation of the Dispersive and Electrostatic Components through Molecular Dynamics Simulations and Molar Refraction Data

K. Shimizu¹, J. Araújo², A. J. L. Costa², I. M. Marrucho², L. P. N. Rebelo², J. N. Canongia Lopes¹

1. Instituto Superior Técnico, Centro de Química Estrutural, Lisbon, Portugal, 1049 001, Portugal

2. Universidade Nova de Lisboa, Instituto de Tecnologia Química e Biológica, Oeiras, 2780 901, Portugal

karina.shimizu@ist.utl.pt; jnlopes@ist.utl.pt

Recently, the density and the cohesive molar internal energy calculated by molecular dynamics simulations were correlated with previously reported experimental density and molar refraction data for seventeen different ionic liquids.[1] The link between the dispersive component of the total cohesive energy of the fluid and the corresponding molar refraction was established in an unequivocal way. The results have shown that the two components of the total cohesive energy (dispersive and electrostatic) exhibit different trends and ratios along different families of ionic liquids, a notion that may help explain their diverse behavior toward different molecular solutes and solvents.

The contributions from the dispersive and electrostatic interactions to the total energy markedly depend on the nature of the ions. Very large ions such as tetraalkylphosphonium cations originate disproportionate dispersive contributions. These different dispersive/electrostatic energy ratios are directly related to the polar/nonpolar character of ionic liquids [2] and can explain the diverse behavior toward different solutes or solvents of this class of compounds.[3] Towards a better understanding of this behavior, molecular dynamics simulations were carried out to calculate the density and the cohesive molar internal energy of nine ionic liquids in the liquid phase. The ionic liquids studied here have in common the cation (cholinium) combined with anions belonging to the carboxylate series, with varying length of the alkyl side chain, from a number of carbon atoms $n = 2$ to 10, in steps of one $-CH_2$ group, *i.e.*, all even and odd numbers n have been considered.

References:

[1] Shimizu, K.; Tariq, M.; Costa Gomes, M. F.; Rebelo, L. P. N.; Canongia Lopes, J. N. *J. Phys. Chem. B* **2010**, *114*, 5831–5834.

[2] Canongia Lopes, J. N.; Pádua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.

[3] Canongia Lopes, J. N.; Costa Gomes, M. F.; Pádua, A. A. H. *J. Phys. Chem. B* **2006**, *110*, 16816–16818.

How do non-coordinating anions in ionic liquids coordinate to metal centres?

Nur Hasyareeda Hassan, Prof Tom Welton, Dr. Jason P. Hallett

Department of Chemistry, Imperial College London, London SW7 2AZ, UK

Green Chemistry aims to modify chemical processes so that they are more friendly to the environment. The 9th principle of Green Chemistry emphasises the use of catalytic reagents in chemical processes. One way in which ionic liquids can implement this principle is in two-phase catalytic processes. A major drawback of homogenous catalysis processes is associated with the separation of the catalyst from the products. This can be solved by the use of biphasic catalysis, in which the catalyst can be reused several times without any significant changes in its catalytic performance.

However, it is vital to understand how catalysts interact with the solvents in a biphasic solvent system. On one hand, it is advantageous to use an ionic form of catalyst (e.g Cu^{2+}) because this improves the retention time of the catalyst in the ionic liquid. However, using charged ions affect their catalytic performance, because their coordination characteristics are changed. Many catalysts are transition metal complexes. Therefore, solvatochromic transition metal is an ideal probe to study the behaviour of ionic liquid specifically how do the non-coordinating anions in ionic liquids coordinate towards metal centre.

A set of solvatochromic copper complexes with different charges were synthesised and characterised. The monocationic complex had the form $[\text{Cu}(\text{acac})(\text{tmen})]\text{X}$ where X were Cl^- , $[\text{NO}_3]^-$, $[\text{OTf}]^-$, $[\text{N}(\text{Tf})_2]^-$ and $[\text{PF}_6]^-$. The neutral complex was $\text{Cu}(\text{hfac})$ and $[\text{Cu}(\text{en})(\text{tmen})][(\text{ClO}_4)_2]$ was used for dicationic complex. A set of non-functionalised ionic liquids and functionalised ionic liquids (FIL) varying from hydroxyl, nitrile, ketone, and ether were also synthesised and characterised. A UV-Vis absorption spectra of the complexes were measured in solid state, dichloroethane and ionic liquid solutions and combined with the crystal structures. Analysis of these spectra suggested all these weakly coordinating anions coordinate with the copper centre in a different manner depending on the coordinating ability of the anion and also the charge of the copper centre. The coordination mode and the order of binding strength for the individual of these complexes were fully studied and analysed. The correlation between ν_{max} and solvent donor number was investigated by measuring UV-vis spectra in a range of molecular solvents, and was used to predict the donor numbers of the ionic liquid solvents. The apparent donor number of ionic liquids was also predicted using the value from the spectrum measured in ionic liquids. The effect of functionalised group in ionic liquids on donor ability has also been investigated by comparing the results from non-functionalised and functionalised ionic liquids.

Pyrochemical treatment of calcium chloride electrorefining salt – an initial study

Sharon Slade, Tim Paget and Robert Watson

AWE, Aldermaston, Reading, Berkshire, RG7 4PR, UK

AWE © Crown Owned Copyright (2011)

Delegates

Ali Kamali	University of Cambridge
Andrew Doherty	Queen's University Belfast
Carsten Schwandt	University of Cambridge
Daniel Jewell	University of Cambridge
David Jones	Manchester University
David Kerridge	
Derek Fray	University of Cambridge
Diem-Hang Tran-Nguyen	University of Cambridge
Doug Inman	Imperial College
Eimutis Juzeliunas	University of Cambridge
Geir-Martin Haarberg	Trondheim
George Chen	University of Nottingham
Georgios Photiadis	University College London
Karina Shimizu	Universidade Nova de Lisboa
Kevin Murnaghan	Henkel Ireland, Dublin
L Rebelo	Universidade Nova de Lisboa
Louise Graham	Queen's University Belfast
Manabu Tokushige	Trondheim
Mohd AzriAb Rani	Imperial College
Moir Lewis	Queen's University Belfast
Nur Hassan	Imperial College
Peter Licence	University of Nottingham
Rasheed Sheikh	University College London
Robert Watson	AWE Aldermaston
Sharon Slade	AWE Aldermaston
Simon Puttick	University of Nottingham
Stuart Mucklejohn	Ceravision
Trevor Griffiths	Redston Trevor Consulting

NOTES

NOTES