

# Molten Salts Discussion Group

## Newsletter September 2011

### Summer Meeting 2011

The MSDG met at Fitzwilliam College, Cambridge for the 2011 Summer Meeting on 05 and 06 July. During the tea interval the Group celebrated the 80th birthday of both David Kerridge and Doug Inman with a specially prepared cake and some stories of their involvement with the MSDG. After two busy scientific sessions and the traditional glass of Pimm's, the participants took their places for the banquet which was followed by Doug Inman's informal presentation 'My life in ionic liquids, from one lab to another'.

### Papers

#### *Interactions of CO<sub>2</sub> and MEA in hydroxylated ionic liquids*

Qing Huang, Xianbo Jin & George Z. Chen

This is a Wuhan-Nottingham joint study on the absorption of CO<sub>2</sub> by monoethanolamine (MEA) in hydroxylated ionic liquids (HILs). The CO<sub>2</sub> – MEA interactions were investigated under the influence of chloride ion by thermodynamic analysis, NMR spectroscopy, viscosity, conductivity and cyclic voltammetry. In addition to enhancing CO<sub>2</sub> absorption capacity and stability, the chloride ion assisted the electrolysis of the CO<sub>2</sub>-MEA-HIL mixture to produce hydrogen, chlorine gases and carbamate, promising the development of a low energy route for carbon capture and reclamation (CCR).

#### *The electrolytic preparation of carbon nanostructures in molten salts*

Ali Kamali, Carsten Schwandt & Derek Fray

There is a pressing need for a low cost method for the production of carbon nanotubes, the current methods are very expensive and worldwide capacity is limited to approximately 20 tonnes per annum. This research has shown it is possible to produce carbon nanotubes from the electrolysis of graphite in molten LiCl. The crystalline size of the product is proportional to the crystalline size of the graphite reactant. The reaction is thought to proceed by intercalation of the graphite into graphene sheets which then roll into nanotubes. Cathodic erosion of the graphite can lead to intercalation of LiCl into the nano-structures.

#### *Electrochemical adventures in CaCl<sub>2</sub>*

Robert Watson

Available impurity separation data from the electrorefining of plutonium suggests there is a subtle cathodic shift in the reduction potentials of U, Np and Am relative to Pu between NaCl-KCl and CaCl<sub>2</sub>. Attempts to investigate the electrochemistry of PuCl<sub>3</sub> in CaCl<sub>2</sub> were complicated by the difficulty in obtaining pure PuCl<sub>3</sub>. An electrochemical method was proposed and was investigated using Ce as a surrogate for Pu. CV of the electrolysis product showed CeCl<sub>3</sub> had been formed, but this may react over time with the ceramic crucible to form CeOCl. An alternative chemical process was proposed using CuCl<sub>x</sub> to oxides Pu metal.

#### *Predicting and designing the properties of ionic liquids*

Moira Lewis, Paul Nancarrow, Quan Gan & Lizhe Liang

If ionic liquids are to be widely used in industrial processes, their physiochemical properties must be known so that plant can be correctly designed and the process controlled. However, the main attraction of ionic liquids is the ability to change the physical properties by simply altering the anion/cation combination but this leads to approximately  $1 \times 10^6$  possible pure ionic liquids from the currently known cations and anions. Measurement of the physical properties of such a large number of materials is not feasible but calculation methods are being developed to predict the properties. Group contribution methods, widely used in industrial design for predicting the physical properties of compounds, have now been extended to ionic liquids. These models have been used to predict the heat transfer properties of some ionic liquids. The properties include: heat capacity; melting temperature; viscosity; thermal conductivity; thermal decomposition.

*Nanoparticle size control by plasma-induced cathodic discharge electrolysis using rotating disk anode*Manabu Tokushige, T.Nishikori & Y.Ito

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 but no such production process has been established to date. The authors have investigated plasma induced cathodic discharge electrolysis in a molten salt electrolyte to form metallic nanoparticles. To obtain smaller and more uniform nanoparticles, a rotating disk anode with a high rotation speed was used for the plasma - induced cathodic discharge electrolysis. 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 (diameter ~5 nm) were obtained at rotation speeds higher than 2500 rpm. 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 measurements.

*XPS as a probe of solvent - solvent and solvent - solute interactions in ionic liquids*Peter Licence, Kevin Lovelock & Men Shuang

This presentation was on using X-ray photoelectron spectroscopy to study ionic liquids (ILs) under vacuum, focusing on the influences of the molecular structures of, and the interactions between the cations and anions in the ILs. Particularly, it was observed that positive charge on the imidazolium ion could only extend the influence to a few -CH<sub>2</sub>- groups along the alkyl chain.

*A description, history and anecdotes concerning the Oak Ridge National Laboratory Molten Fluoride Reactor - and does it have a future ?*Trevor Griffiths

A molten salt reactor was operated briefly at Oak Ridge National Laboratory in the US in 1954 as part of the Aircraft Reactor Experiment. This used fluoride salts to contain the fuel and operated at high temperatures. The Molten Salt Reactor Experiment, also at ORNL, ran for 4 years from 1965 with a LiF-BeF<sub>2</sub>-ZrF<sub>2</sub>-UF<sub>4</sub> salt at up to 650°C. The output was 7 MW (thermal). A Molten Salt Breeder Reactor was designed at ORNL between 1970-1976. This would use a LiF-BeF<sub>2</sub>-ThF<sub>4</sub>-UF<sub>4</sub> salt at up to 705°C. Molten salt reactors are being considered as part of the Generation IV programme for new nuclear power plants.

*MyRSC*Adam Turner (Royal Society of Chemistry)

MyRSC is the online professional networking tool of the Royal Society of Chemistry and has been in place since 2009. It is open to members and non-members. A key objective of MyRSC is to increase interaction between members and to further support their work. 2010 saw more than 57000 visits to the site with over 460000 page views, these values have already been surpassed in 2011 by the end of June. Currently available tools include: file sharing; discussion pages; calendars; blogs. Future plans will add Chemistry Connections, Talk Chemistry and a careers service.

*Stretching ionic liquids to the limit*L.P.N.Rebelo - Invited Lecture

Acknowledging the absence of a negative "absolute pressure" in the gas phase, this presentation described the concept and feasibility of negative absolute pressure in liquid state. With unique properties in a wide temperature range, ionic liquids are therefore interesting objects for studying and understanding the negative absolute pressure. At the end of this presentation, the audience was reminded the COIL-5 conference in Portugal in 2013.

*Synthesis, characterization & physical - chemical properties of room temperature ionic liquids (RTILs) with siloxane containing cations*Mohd Azri Ab Rani, J.Hallet, P.Lickiss, & T. Welton

New ionic liquids with siloxane side chains of different lengths were synthesised and characterised for molecular structure, and other physicochemical properties. In particular, the polarity, thermal stability, viscosity and conductivity of the synthesised siloxy-ionic liquids were found to be comparable with their alkyl counterparts, which were thought to be due to the highly flexible siloxane bonds.

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

Geir Martin Haarberg, Ole S.Kjos, Ana Maria Martinez &amp; Karen S.Osen

The use of a titanium oxycarbide anode combined with a liquid cathode was investigated as an alternative method to produce pure titanium by electrolysis. The anode material was prepared by mixing and compacting powders of TiO<sub>2</sub> and graphite before heat treatment in inert atmosphere at temperatures from 1350 to 1600°C. Cyclic voltammetry and electrolysis experiments were carried out in molten equimolar NaCl-KCl containing dissolved TiCl<sub>3</sub> at 800°C. Promising results were obtained from using liquid electrodes of Zn, Sn and Bi.

*Black silicon from molten salts*

Eimutis Juzeliunas, Antony Cox &amp; Derek Fray

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. 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, increases the efficiency of solar cells. Various surface techniques have been used to obtain black silicon but these techniques are too expensive for mass production. A simple electrochemical method for the production of black silicon is to remove the oxygen in the silica film that is found on silicon 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 lead to vacancies which can diffuse to form various micro-architectures.

*NMR as a probe of nanostructure in ionic liquids*

Simon Puttick, Adrienne L.Davis, Kevin Butler, Lynette Lambert, Jaouad El Harfi, Derek J.Irvine, Andrew K.Whittaker, Kristof J.Thurecht &amp; Peter Licence

Oligomeric species of increasing molecular mass were synthesised and used as the probe molecules to study the molecular functions of different regions in the cations and anions of ionic liquids. The study was carried out in conjunction with NMR spectroscopy and the nuclear Overhauser effect, confirming domain segregation different ionic liquid ions can influence both the kinetics and products of a reaction. The MSDG Conference bursary was acknowledged at the end of this presentation.

*Ionic liquids in industry: Processable, functional & task - specific*

Kevin Murnaghan

A number of industrial processes which involve ionic liquids were identified. Typically these are not using the ionic liquid as the solvent medium for the process. Examples included the BASF BASIL process where 1-alkylimidazole scavenges acid from an existing process and forms an immiscible ionic liquid phase which can be separated; this gives significant process benefits. Eastman have also operated a process to synthesise 2,5 - dihydrofuran between 1996 and 2004 which utilised an ionic liquid.

Posters (Abstracts reproduced in full)*Cohesive energy of ionic liquids: Evaluation of the dispersive and electrostatic components through molecular dynamics simulations and molar refraction data*

K. Shimizu, J. Araújo, A. J. L. Costa, I. M. Marrucho, L. P. N. Rebelo, J. N. Canongia Lopes

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 behaviour 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 behaviour

toward different solutes or solvents of this class of compounds.[3] Towards a better understanding of this behaviour, 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, Tom Welton & Jason P. Hallett

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 the metal centre.

A set of solvatochromic copper complexes with different charges were synthesised and characterised. The monocationic complex had the form  $[Cu(acac)(tmen)]X$  where  $X$  were  $Cl^-$ ,  $[NO_3]^-$ ,  $[OTf]^-$ ,  $[N(Tf)_2]^-$  and  $[PF_6]^-$ . The neutral complex was  $Cu(hfac)$  and  $[Cu(en)(tmen)][(ClO_4)_2]$  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. 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  $\nu_{max}$  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 & Robert Watson

Electrorefining of plutonium can produce a  $CaCl_2$  salt containing 5 - 10 wt% plutonium as  $PuCl_3$ . To make the salt suitable for potential disposal via encapsulation the plutonium content needs to be reduced to about 0.5%. A calcium reduction process with a salt containing 3.9% plutonium, using a small excess of calcium, resulted in a salt mass containing up to 0.4% plutonium with about 67% of the plutonium recovered as a coalesced metal product. Some black material was present in the bottom of the salt mass, suggesting incomplete reaction. The process shows potential as a treatment of electrorefining salts for disposal via encapsulation.

**Forthcoming conferences**

18th Int. Symp. molten salts & ionic liquids as part of 220th meeting of The Electrochemical Society  
09 - 14 Oct 2011, Boston, MA, USA  
See: [www.electrochem.org/meetings/biannual/220/220.htm](http://www.electrochem.org/meetings/biannual/220/220.htm)

Fray International Symposium  
27 Nov - 01 Dec 2011, Cancun, Mexico  
See: [www.flogen.com/FraySymposium](http://www.flogen.com/FraySymposium).

MSDG Christmas Meeting  
19 December 2011, 15 Hatfields, London, UK  
See: <http://www.ch.qub.ac.uk/msdg/201112.html>

Ninth International Conference on Molten Slags, Fluxes and Salts (MOLTEN12)  
27 - 30 May 2012, Beijing, China  
See: <http://hy.csm.org.cn/MOLTEN12/en/>

MSDG Summer Meeting  
10 - 11 Jul 2012, Fitzwilliam College, Cambridge

EUCHEM conference on molten salts & ionic liquids  
05 - 10 Aug 2012, Celtic Manor, Wales  
See: [www.euchem2012.org/](http://www.euchem2012.org/)

**MSDG Support Fund**

Members are reminded that bursaries to help towards the cost of attending meetings on molten salts and/or ionic liquids are available from the MSDG. Those interested in applying for a bursary should contact the Chairman, Derek Fray (E-mail: [djf25@cam.ac.uk](mailto:djf25@cam.ac.uk)).

G.Z.Chen, S.A.Mucklejohn & R.F.Watson 31 Jul 2011  
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