Molten Salts Discussion Group

Newsletter January 2010

Christmas Research Meeting 2009

The MSDG returned to 15Hatfields for the Christmas Meeting held on Monday 14 December following a highly successful introduction to the venue in 2008. 15Hatfields is the conference centre at the Chartered Institute of Environmental Health.

The meeting was opened by the Director of Policy, Andrew Griffiths (brother of Trevor Griffiths) who welcomed the MSDG and described some of the recent work conducted by the Institute and gave a stout defence of health and safety legislation and pointed out some of the many misconceptions that abound about this often misunderstood topic.

The meeting was attended by 36 participants, the ten oral presentations were accompanied by a new innovation for the MSDG, electronic posters that were displayed during the lunch and tea breaks. The scientific part of the meeting was followed by the traditional wine & cheese party. The AGM was held between lunch and the start of the afternoon scientific session. The afternoon tea break proved the ideal opportunity to present Derek Fray with a magnificent cake to celebrate his 70th birthday.

The MSDG thank Trevor Griffiths for arranging to have the meeting hosted at 15Hatfields.

The next MSDG gathering will be the Summer Meeting 06 to 08 July 2010 at Fitzwilliam College, University of Cambridge.

Papers

Catalysis in Molten Ionic Media

Rasmus Fehrmann (Invited speaker) - Technical University of Denmark

This paper opened with a review of the use of molten salts in catalytic processes used by industry. For some of these processes the precise role of the molten salt was established only after several detailed fundamental studies. A good example is the mechanism of the catalytic processes used in the production of sulfuric acid. This story evolved over the period 1933 to 1990 and a full account can be found in *Topics in Catalysis*, 19, 323 (2002). The use of ionic liquids in industrial scale catalytic processes is still evolving, the potential is enormous when one considers that the typical time to take a process from a laboratory scale to an industrial scale is 10 years. Promising examples of ionic liquid based catalytic processes include alkene hydroformylation, ethylene methoxycarbonylation and the production of biodiesel from fatty acids.

The FFC Cambridge Process for Production of Low Cost Titanium and Titanium Powders

Kartik Rao, Bertolini, Lee Shaw, Lucy England, James Deane & James Collins - Metalysis Ltd

The team at Metalysis is taking the FFC Cambridge Process from laboratory scale through the development phase to pre-production scale during 2010. The development phase involves production of metal on the kilogram scale by a batch process. During this phase, many of the limitations of the present equipment will be addressed leading to a semi-continuous process for the pre-production stage. It is anticipated that processes to make Ta and Ti powders will be operational by late 2010. The FFC Cambridge Process has the potential to enable manufactures to make Ti sheet via a powder metallurgy route thus avoiding the extremely expensive process of melting the metal.

Carbonylation in Ionic Liquids

Anders Riisager, O.N.Van Buu, C.Hanning, J.Xiong & R.Fehrmann - Technical University of Denmark

The hydroformylation of C2-C5 alkenes and the methoxycarbonylation of ethylene, both industrially important reactions, have recently been accomplished in ionic liquid media. The former reactions were efficiently conducted in fixed-bed, continuous flow reactors with heterogenised supported ionic liquid-phase (SILP) catalysts compromised of an ionic liquid solution of catalytically active Rh-phosphine complexes distributed as a thin film on a high surface area inert support. The methoxycarbonylation of ethylene was

performed with Pd-phosphine complexes dissolved in a Bronsted acid functionalised ionic liquid solvent where the low solubility of the product facilitates spontaneous phase-separation and hence facile product recovery and re-use of the catalyst.

Depolarised Gas Anodes for Aluminium Electrowinning
Geir Martin Haarberg, Eirin Kvalheim, Arne Petter Ratvik & Saijun Xiao - Norwegian University of Science & Technology
Consumable carbon electrodes are used in the Hall-Heroult process for the electrowinning of aluminium. Emission of CO_2 from this process could be eliminated by the use of inert anodes but this would require a higher anode potential. An alternative approach is to use a natural gas or hydrogen gas anode to reduce CO_2 emissions and lower the anode potential. Preliminary cyclic voltammetry experiments in $CaCl_2$-NaCl containing CO at 750^{o}C showed a reduction of approximately 0.3 V in the anode potential and cell voltage upon the introduction of H_2<g> at a Pt anode. Initial experiments with CH_4<g> were unsuccessful. Further work will be conducted over the coming months.

The complex nature of ionic liquid solutions: Aromatic solutes as templates of the ionic liquid solvent
José N. Canongia Lopes[1,2], K.Shimizu[1], M.F.Costa Gomes[3], A.A.H.Pádua[3] & L.P.N.Rebelo[2]
[1]IST/UTL, [2]ITQB2/UNL and [3]CNRS/UBP
The dipole and quadrupole moments of benzene and its 12 fluorinated derivatives were correlated to their solubilities in [C_2mim][Ntf_2]. The correlations took into account the molecular insights gained from *ab-initio* calculations of the isolated solute molecules and molecular dynamics simulations of all 13 solute plus ionic liquid binary mixtures. The charge distribution of the aromatic solute molecules promotes the segregation of the ionic liquid molecules which in turn defines the fluid behaviour. These calculations can be used to predict viscosities.

Electrical Conductivity of Low Melting Aqueous Molten Salts
Sanja Dožić, Slobodan Gadzuric, Milan Vranes & Borko Matijevic - University of Novom Sadu
Calcium nitrate tetrahydrate and its mixtures with organic and inorganic compounds have large enthalpies of fusion and are candidates for phase change materials for thermal energy storage. Some systems also exhibit a thermochromic effect and these have potential for use in the temperature control of solar heated structures. The properties of such systems fall between anhydrous melts and aqueous solutions. They are usually known as aqueous melts and in most cases there is insufficient water to surround each ion. The electrical conductivities of xCa$(NO_3)_2$.zH_2O - $(1-x)NH_4NO_3$ mixtures were measured over a range of temperatures and compositions. The electrical conductivities decreased with increasing temperature and also decreased with increasing x at all temperatures. These results were used in illustrate the differences in transport properties between aqueous solutions and aqueous melts.

Predicting the Properties of Ionic Liquids
Paul Nancarrow, Moira Lewis, Lizhe Liang, & Quan Gan - QUILL/Queen's University Belfast
In order for ionic liquids to be used successfully in industry many of their physical properties must be known for the design and operation of processes, equipment and systems. Such properties include: density, viscosity, thermal conductivity, diffusivity, surface tension, viscosity. A number of predictive tools have been identified to help in estimating some of the physical characteristics of ionic liquids. For example a model based on the assumption that the volumes of individual anions and cations are independent can be employed to predict the densities of ionic liquids. Using a database from 102 cations and 44 anions, the densities of approximately 22,000 ionic liquids can be estimated. The aim of this study is to develop a computational framework for ionic liquids which will enable ionic liquids to be designed for a specific purpose based on a selected set of properties.

The Preparation of Multiwalled Carbon Nanotubes from Graphite using a Molten Salt Electrochemical Technique
Carsten Schwandt - University of Cambridge
Graphite may be converted directly into nano-structured carbonaceous material by electrolysis of molten alkali metal chlorides in the presence of graphite electrodes. This approach typically gives a wide range of products & low yields and hence was generally regarded as being unsuitable for the production of carbon nanotubes. However, careful control of reaction conditions can give yields of several grams of carbon nanotubes per experiment. Constant current electrolysis of an EC4 graphite anode in molten LiCl produced a

mixture of nano particles, fibres and tubes. To get a high yield of nanotubes the temperature, current density, cathodic polarisation potential and reaction time must be carefully selected and controlled. The first step in the reaction is the intercalation of Li into the graphite followed by disintegration of the graphite microstructure and exfoliation.

Electrolytic Carburisation of Steel in Molten Salts
Nancy Julius Siambun & George Z.Chen - University of Nottingham
Carburisation, the addition of carbon to the surface of low carbon steels to increase hardness, is usually carried out in baths of molten barium cyanide. Typical reaction conditions are 870°C for 10 hours. In this study the carburisation was achieved using an electrolytic process in molten Na_2CO_3 - NaCl (1:4 molar ratio) under an atmosphere of CO_2. A mild steel rod was carburised by using it as the cathode and a SnO_2 rod as an inert anode. The effectiveness of the carburisation was evaluated by Vickers micro-hardness measurements. The hardness of the mild steel sample increased by approximately 49% following electro-carburisation at 800°C for 1.5 hours. The case hardened thickness was 0.6 mm. These results compare favourably to similar samples treated in a molten cyanide bath at ~880°C for 1.5 hours.

Rationalising Reaction Outcomes in Ionic Liquids Through Investigation of Substitution Processes
Honman Yau[1], Susan A.Barnes[2], Andrew G.Howe[1], Shon G.Jones[2], James M.Hook[3], Tristan G. A.Youngs[4], Anna K.Croft[2] & Jason B.Harper[1] - [1]University of New South Wales, [2]Bangor University and [3]Queen's University Belfast
Compared to molecular solvents, the understanding of the properties of ionic liquids is very limited. However, an understanding of the properties of a range of ionic liquids is important in order to explain the differences in reactions when carried out in ionic liquids rather than molecular solvents. The temperature dependent kinetics of substitution reactions with well-defined mechanisms have been studied in both molecular solvents and ionic liquids. The methanolysis of 3-chloro-3,7-dimethyloctane is known to proceed *via* a S_N1 mechanism. The enthalpies of activation were 97.3 $kJ.mol^{-1}$ in methanol and 43.2 $kJ.mol^{-1}$ in an ionic liquid. The corresponding entropy changes were -22 and -97 $J.K^{-1}.mol^{-1}$. Similar kinetic studies were carried out on substitution reactions with S_N2 and S_NAr mechanisms. Comparing activation parameters in molecular solvents with those in ionic liquids and by use of molecular dynamics simulations confirm that solvent reorganisation is an important factor in determining reaction products in ionic liquids.

John Slattery was unable to attend the meeting and to deliver his paper titled *Investigating Hiyama-type cross-coupling reactions in alkene-doped ionic liquids* following an accident in his laboratory. The MSDG wish John a speedy recovery and look forward to hearing his presentation at a future meeting.

Posters

Predicting the Heat Capacities of Ionic Liquids
Moira Lewis, P.Nancarrow & Q.Gan - QUILL/Queen's University Belfast
One of the main attractions of ionic liquids is the ability to select the physical properties by altering the anion/cation combination. This potentially provides a very high number of ionic liquids but it would be feasible to conduct experimental measurements only on a small fraction of them. Group contribution methods (GCMs) are widely used in industry to predict the physical properties of compounds but their use for ionic liquids has not been extensive. Two new GCMs were successfully employed in this study to predict the heat capacities of a wide range of ionic liquids. The predictions from the models were in good agreement with the experimental values.

Pyrolysis of Biomass in Molten Salts
Heidi Nygård & Espen Olsen - Norwegian University of Life Sciences
Pyrolysis is a thermochemical process in which organic material is heated in the absence of oxygen. The material decomposes into higher value products like liquid fuels, gases, charcoal and other chemicals. In molten salt pyrolysis biomass is fed into a molten salt bath. The advantages of using molten salts is that they have very high thermal stability, good heat transfer characteristics and a catalytic effect in cracking and liquefaction of large molecules found in biomass. Molten salts will retain some noxious contaminants which means contaminated biomass can be used as a feedstock.

An Improvement of the Alumina Membrane Ag/AgCl Reference Electrode
Han Wang & George Z.Chen - University of Nottingham
The recently developed alumina membrane Ag/AgCl reference electrode performed well in $CaCl_2$-based molten salts at temperatures above 700°C. However, at lower temperatures the iR-drop through the membrane was higher than ideal for electrochemical studies. The electrode design has now been modified to increase the membrane area of the alumina tube. This has resulted in improved performance at temperatures below 700°C as illustrated by a range of cyclic voltammetry measurements.

The effect of the ionic liquid anion in pre-treatment of pine wood chips
Agnieszka Brandt, Jason P.Hallett, David J.Leak, Richard J.Murphy & Tom Welton - Imperial College, London
The effect of the ionic liquid anion on the dissolution of pine wood (*Pinus radiata*) in ionic liquids was investigated. Using a protocol for assessing the change in size of wood blocks it was shown that the anion had a major impact on the ability to promote both swelling and dissolution of wood chips. Viscosity, temperature and water content were shown to be important parameters influencing the dissolution process. Measurement of the Kamlet-Taft solvent polarity of the ionic liquids revealed that the anion basicity, as described by the β parameter, correlates well with the ability to expand and dissolve pine wood.

Electrorefining of Silicon in Molten Salts
Shuihua Tang & Geir Martin Haarberg - Norwegian University of Science and Technology
99.9999% (4N) grade silicon is required for the fabrication of solar cells. Currently this is available mainly as a by-product from the manufacture of semiconductor grade silicon which means the cost is high. Some alternative methods for the production of 4N grade silicon have been investigated, these include directional solidification, slag refining, purification in a H_2/Ar or O_2/Ar plasma, electron beam melting and electrochemical approaches. Electrorefining of metallurgical grade silicon (MG-Si) in molten salts has been identified as one of the most promising methods for the production of solar grade silicon. In this study, a binary alloy of MG-Si and Cu was employed as the anode with a cathode of high purity silicon in an electrolysis cell at 850°C with a molten salt electrolyte. Preliminary results have shown this method to be effective but further work to improve the electrorefining process is needed.

Annual General Meeting 2009

The following appointments were made at the AGM.

Chairman	Derek Fray
Honorary Secretary	George Chen
Honorary Treasurer	Robert Watson
Newsletter Editor	Stuart Mucklejohn
Committee members	Andrew Doherty
	Trevor Griffiths
	Peter Licence
	Carsten Schwandt
European member	Rasmus Fehrmann
International member	Marcelle Gaune-Escard
Honorary Auditor	Tony Wilson

Annual subscriptions

The 2010 annual subscription to the MSDG for RSC members is £5.00.

MSDG Summer Meeting, July 2010

The MSDG Summer Meeting will be held at the University of Cambridge 06 to 08 July.

Forthcoming conferences

2010 EUCHEM Conference on molten salts & ionic liquids
14 - 19 March, Bamberg, Germany
See: http://www.dechema.de/euchem2010

Symposium on the physical chemistry of ionic liquids (part of the 239th ACS Meeting, Physical Division)
21 - 25 March 2010, San Francisco, USA
See: http://www.chemistry.bnl.gov/SciandTech/PRC/physchemil2010.html

Symposium in honour of Professor Don Sadoway
10 - 11 June 2010, MIT, Cambridge, USA
See: http://mit.edu/dsadoway/www/sadoway60.html

Discussion meeting on thermodynamics of alloys (TOFA 2010)
12 - 16 September 2010, Porto, Portugal
See: http://www.fe.up.pt/~tofa2010/

The science & technology of light sources - 12th international symposium (LS12) to be held in conjunction with White-LEDS & solid state lighting - 3rd international conference (White-LED3)
11 - 16 July 2010, Eindhoven, The Netherlands
See: http://www.ls-wled.org/index.php

Fray International Symposium

MSDG members are invited to submit papers to the Fray International Symposium. The organising committee is Florian Kongoli (Flogen Technologies, Inc.), Maurits Van Camp (UMICORE), R. Vasant Kumar (University of Cambridge), Hongmin Zhu(University of Science & Technology, Beijing), S. Komar Kawatra (Michigan Technological University), Mario Sanchez (Universidad de Concepción), Marcelle Gaune-Escard (Ecole Polytechnique, Universite de Marseille) & George Chen (University of Nottingham).

More details about the symposium can be found at www.flogen.com/FraySymposium.

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).

S.A.Mucklejohn, Newsletter Editor, 07 Jan 2010
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