Workshop on IONIC LIQUIDS: Properties of Ionic Liquids and their Application in Chemical Engineering.
IACT/IUPAC International Conference on Chemical Thermodynamics, Rostock, Germany, 27 July to 2 August 2002

A session on ionic liquids was held at ICCT 2002 that concluded in a panel discussion.

Report of the Panel Discussion:

Chair: Dr. John Dymond (University of Glasgow, UK)

Panel Members:
Professor Joan Brennecke (University of Notre Dame, Indiana, USA),
Professor Kenneth Seddon (The Queen's University of Belfast, Northern Ireland),
Professor Kenneth Marsh (University of Canterbury, Christchurch, New Zealand), and
Dr. Joe Magee (National Institute of Standards and Technology, Boulder, Colorado, USA)

There were 39 other people present at this session, which took place on Friday 2 August, 2002 during the 17th International Conference of Chemical Thermodynamics in Rostock, Germany.

After a brief introduction, the Chairman said that the main purpose of the session was to outline a strategy for future collaboration in the measurement of thermophysical properties for pure room-temperature ionic liquids and mixtures. This would involve the identification of i) key systems, ii) necessary properties and iii) participating groups. He thought that an initial general discussion might be helpful, and invited comments and questions. The following points arose:

- the possibility of round-robin measurements, as had been made with viscosity measurements on R134a
- how should liquid non-ideality be considered in gas solubility?
- the need to establish criteria for purity determination. It was recommended that physical chemists should collaborate with their organic chemistry and analytical chemistry colleagues
- the major components to be considered for analysis - water and halide (chloride) ion
- the need for a standard preparation protocol
- how to disseminate the conclusions from the panel discussion? All Conference attendees would receive a copy of the report by E-mail and Professor Heintz would send a copy to other interested groups. It was suggested that a report should be sent to Pure & Applied Chemistry or Chemistry International.
- should we continue to work with systems with $[PF_6]^-$ or $[BF_4]^-$ anions? Yes, there is a need for accurate data for systems with such small symmetrical ions
- there may be patent problems accessing some chemistry
- the need to be aware that $[PF_6]^-$ will give off HF if heated above 95°C
- the effects of water impurity on the property being measured should be investigated
- neutron diffraction studies should be made
- suggestions for cations and anions were made (see below)
- how large is the interest to develop a screening tool for these chemicals? We need an accurate study of a) properties of a given class, that is, cations/anions and b) trends in properties of a given class, with screening in terms of solubility or partitioning, to develop confidence in screening tools by comparison with results which already exist
- ready availability of the compounds is essential. A few compounds should be selected (see below)
- which properties should be measured (see below)

Anions:

The following ionic liquid anions were considered:

X^- , where X = Cl, Br, I ; $[BF_4]^-$; $[PF_6]^-$; $[CF_3SO_3]^-$; $[N(OTP)_2]^-$

$[RCO_2]^-$; $[N(CN)_2]^-$; $[C_6H_5CO_2]^-$; $[RPO_2]^-$; $[tartrate]^-$; $[lactate]^-$

$[RSO_3]^-$; $[NO_3]^-$; $[HSO_4]$- ; $[AlCl_4]$- (unstable)

The following recommendations were made:

a) useful for both fundamental understanding and practical/industrial applications:

$[N(OTP)_2]^-$ $(NO_3)^-$ Cl^-

Also $[CF_3SO_3]^-$ but there are patent problems here. Nitrate and chloride have the advantage of low toxicity, but the chloride is hydroscopic.

b) useful for fundamental understanding only:

$[PF_6]^-$ $[BF_4]^-$

$[BF_4]^-$ gives less of a problem than $[PF_6]^-$ with HF production, but is harder to purify.

Cations

Recommended cation types:

$[Rmim]^+$; $[Rpy]^+$; $[NR_4]^+$; $[pyrolidinium]^+$

About 10 members of each of the first two types can be considered. Even numbered carbon atom members of the group are less expensive.

Protonated species such as $[\sim NH]^+$ should never be used because of acid-base equilibria, the formation of HX and hence a finite vapour pressure.

The recommendation is to work with one cation type, and look at the properties of a series of compounds.

It was suggested that a few compounds could be prepared and circulated to groups making measurements of thermophysical properties. However, these are not stable substances and their purity will depend on the way they are handled. It was therefore preferable to make them in a local laboratory, standardise them before and after use, for example by melting point determinations, and establish the water and Cl^- ion concentrations before and after the measurements.

Pure component properties

The following properties were identified as being of importance for these systems:

Density (T)	Viscosity (T)	Isobaric heat capacity (T)
Speed of sound (T)	Thermal conductivity (T)	Refractive index (T)

Electrical conductivity
X-ray diffraction
Melting point/phase diagram
Lattice energy
Surface tension
Neutron diffraction
Glass transition temperature
Dielectric constant
Vapour pressure (T)
N.M.R. / I.R.
Enthalpies of fusion

The following groups present at this session are capable of making accurate measurements on viscosity, density and isobaric heat capacity :

Professor Andreas Heintz (Rostock)
Professor Kenneth Marsh (Christchurch) [also surface tension, and density to elevated pressures]
Dr. Michael Frenkel (NIST, Boulder)

Professor Joan Brennecke could make density measurements to elevated pressures.

Professor Glenn Hefter could make dielectric measurements. Professor Heintz will possibly be able to make electrical conductivity measurements in the future.

It was pointed out that refractive index values would be in the range 1.8 to 2.5

Mixture Properties

i) Ionic liquid + ionic liquid

ii) Ionic liquid + molecular compound
Molecular compounds: a) water b) alcohols, e.g. ethanol c) aliphatic alkanes e.g. heptane d) aromatic hydrocarbons e.g. toluene, e) chloroalkanes e.g. dichloromethane, and f) other compounds e.g. gases

Properties i) solubility (Prof. U. Domañska-Zalazna)
ii) activity coefficients at infinite dilution (Prof. Heintz)
iii) enthalpies of mixing (Professor Heintz)
iv) gas solubilities (Professor Brennecke, Dr. V. Mayer))

iii) Ternary systems
Partitioning e.g. octanol/water (bioaccumulation) (Prof. Heintz, possibly)

Kinetics to be studied at a later time.

As a result of circulation of the report of this panel discussion, it was anticipated that other groups would join in this measurement project.

Database

References were being collected and some evaluated data had already been entered on a database at NIST (Boulder, CO, USA), which would be made available publicly. It was essential that contributors characterised the uncertainties in their data.

THE WAY FORWARD:

i) Identify additional research groups for the measurement programme

ii) Take as standard systems : $[bmim]^+$ and $[emim]^+$ with Cl^-, $[PF6]^-$ and $[N(OTP)_2]^-$.

iii) Give a preparation protocol (on a web site) so groups can make their own compounds.

iv) Give a purity testing protocol (on a web site) with a note of properties to be measured, including Cl^- and water content, before and after the measurements.

v) Store the results in the NIST database for public availability.

vi) Interchange information between groups to compare results on given properties

vii) Contact theoretical groups so they can predict values for the properties considered, for comparison with experiment.

viii) Develop a fundamental understanding of the results.

Groups who wish to take part in this project are invited to complete the following form:

Name…………………………………………………………………………………

Affiliation……………………………………………………………………………….

Email…………………………………………………………………………………

Properties which we can measure………………………………………………………..

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Please return this completed form to John Dymond at johnd@chem.gla.ac.uk

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