



**Arrange Oral Session**

Shown below are accepted and unreviewed papers in this session (withdrawn and rejected papers are not shown). Papers must be reviewed and accepted before they can be scheduled, and you will not see some options (Duration, Order) until the paper has been accepted. After papers are ordered, click the Update button to save your changes.

See [step-by-step instructions](#) for arranging sessions.

minutes/paper

**Ionic Liquids: From Knowledge to Application: Thermophysical Properties** (Oral session #28032: Contains 8 papers: 8 **accepted**.)

Organizer: Joan F. Brennecke, Department of Chemical and Biomolecular Engineering, University of Notre Dame, 180 Fitzpatrick Hall, Notre Dame, IN 46556, [jfb@nd.edu](mailto:jfb@nd.edu); Robin D. Rogers, Department of Chemistry and Center for Green Manufacturing / School of Chemistry and Chemical Engineering, The University of Alabama, Tuscaloosa / The Queen's University of Belfast, Stranmillis Road, Belfast, Northern Ireland BT9 5AG United Kingdom, [rdrogers@bama.ua.edu](mailto:rdrogers@bama.ua.edu); Kenneth R. Seddon, QUILL Research Centre, Queen's University Belfast, David Keir Building, Stranmillis Road, Belfast BT9 5AG United Kingdom, [k.seddon@qub.ac.uk](mailto:k.seddon@qub.ac.uk)

Organizer, Presiding: Joseph W. Magee, Physical & Chemical Properties Division, National Institute of Standards & Technology, 325 Broadway, Boulder, CO 80305-3328, [joe.magee@nist.gov](mailto:joe.magee@nist.gov); Luis Paulo N. Rebelo, Molecular Thermodynamics Group, Instituto de Tecnologia Química e Biológica (ITQB-UNL), Avenida da República (EAN), Oeiras 2781-901 Portugal, [luis.rebelo@itqb.unl.pt](mailto:luis.rebelo@itqb.unl.pt)

| Start Time | Preferred Format | Special Duration (min.) | Final Paper Number   | Order                          | Accept                   | Move or Copy             | Event                                                                                                                                                                                                              |
|------------|------------------|-------------------------|----------------------|--------------------------------|--------------------------|--------------------------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
|            | ORAL !           | <input type="text"/>    | <input type="text"/> | <input type="text" value="1"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1201507) Vapourisation of ionic liquids: A temperature programmed desorption (TPD) study. P. Licence, R. G. Jones, K. R. J. Lovelock, A. Deyko, J. A. Corfield</a>                                    |
|            | ORAL             | <input type="text"/>    | <input type="text"/> | <input type="text" value="2"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1198495) Characterization of strong and super acids, using protic ionic liquids made with tertiary amine bases: The N-H chemical shift. J -P. Belieres, N. Byrne, C. A. Angell</a>                    |
|            |                  | <input type="text"/>    | <input type="text"/> | <input type="text" value="3"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1177146) Development of predictive models for the thermophysical properties of ionic liquids: A first step towards the CAMD of ionic liquids. J. A. P. Coutinho, R. Gardas</a>                        |
|            | ORAL !           | <input type="text"/>    | <input type="text"/> | <input type="text" value="4"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1193025) Chemical speciation in ionic liquids and their mixtures with polar solvents. G. Heffer, R. Buchner, J. Hunger, A. Stoppa</a>                                                                 |
|            |                  | <input type="text"/>    | <input type="text"/> | <input type="text" value="5"/> | <input type="checkbox"/> | <input type="checkbox"/> | Intermission.                                                                                                                                                                                                      |
|            |                  | <input type="text"/>    | <input type="text"/> | <input type="text" value="6"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1179218) Temperature and pressure dependencies of isobaric thermal expansivity and isobaric heat capacity of ionic liquids. J. Troncoso, P. Navia, Y. A. Sanmamed, D. Gonzalez-Salgado, L. Romani</a> |
|            | ORAL !           | <input type="text"/>    | <input type="text"/> | <input type="text" value="7"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1187492) Predicting thermophysical properties of ionic liquids. D. W. Rooney</a>                                                                                                                      |
|            | ORAL !           | <input type="text"/>    | <input type="text"/> | <input type="text" value="8"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1195805) Physicochemical properties and structures of ionic liquids. H. Tokuda</a>                                                                                                                    |
|            | ORAL !           | <input type="text"/>    | <input type="text"/> | <input type="text" value="9"/> | <input type="checkbox"/> | <input type="checkbox"/> | <a href="#">(1190268) On the nature of ionic liquids. K. N. Marsh</a>                                                                                                                                              |

Move selected papers to this session:

**Comments to Program Chair:**

**Key Speakers/Topics:**

**Session is Newsworthy Because:**

**Session is Industry Related Because:**

**Equipment Needed:**

**Estimated Seats Needed (Oral Sessions) Only numbers are accepted, not ranges, question marks, or other miscellanea.:**



Abstract Listing

Use your browser's Print button, or File-Print command sequence.

## 1177146: Development of predictive models for the thermophysical properties of ionic liquids: A first step towards the CAMD of ionic liquids

### Ionic Liquids: From Knowledge to Application

#### IEC 0 [1177146]: Development of predictive models for the thermophysical properties of ionic liquids: A first step towards the CAMD of ionic liquids

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#### ACCEPTED

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

**Inviting Chair:** *Joe Magee, [magee@boulder.nist.gov](mailto:magee@boulder.nist.gov)*

**Preferred Presentation Format:**

**Consider for Sci-Mix:**

**Conforms to Bylaw 6:** Y

**Last Modified:** *now()*

#### Abstract

The outstanding characteristics of Ionic liquids (ILs) and the easy manipulation of their properties by the interchange of thousands of cations and anions, make of the ILs "designer" solvents with a wide range of foreseeable applications.

The limited availability of thermophysical properties data and their questionable quality have hampered the development of correlations and predictive models and preventing the Computer Aided Molecular Design (CAMD) of ionic liquids of becoming a reality.

Having collected the available experimental thermophysical property data from the literature, we have carried a critical review of the data and the development of correlations or group contribution methods for thermophysical properties. It will be shown how the prediction of a number of thermophysical properties such as density, isobaric expansivity and isothermal compressibility, viscosity, surface tension, speed of sound, ionic conductivities and heat capacities, in a wide temperature range, can be achieved with the proposed models.

Finally it will be shown how the group contribution methods developed can be used for Computer Aided Molecular Design of Task Specific Ionic Liquids.

## 1179218: Temperature and pressure dependencies of isobaric thermal expansivity and isobaric heat capacity of ionic liquids

### Ionic Liquids: From Knowledge to Application

#### IEC 0 [1179218]: Temperature and pressure dependencies of isobaric thermal expansivity and isobaric heat capacity of ionic liquids

Jacobo Troncoso, [jacobotc@uvigo.es](mailto:jacobotc@uvigo.es), Paloma Navia, , Yolanda A Sanmamed, , Diego Gonzalez-Salgado, , and Luis Romani, , Departamento de Física Aplicada, Universidad de Vigo, As Lagoas s/n, Ourense 32004, Spain, [jacobotc@uvigo.es](mailto:jacobotc@uvigo.es)

#### ACCEPTED

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

**Inviting Chair:** *Joseph Magee, [joe.magee@nist.gov](mailto:joe.magee@nist.gov)*

**Preferred Presentation Format:**

**Consider for Sci-Mix:**

**Conforms to Bylaw 6:** Y

**Last Modified:** *now()*

#### Abstract

Isobaric thermal expansivity of Room Temperature Ionic Liquids (RTILs) often shows negative temperature dependence, fact very unusual for molecular solvents. From basic Thermodynamics it is easy to demonstrate that this may imply an anomalous, positive pressure dependence of isobaric heat capacity. It is the aim of this work to elucidate the causes of such behaviour. To this end, a microcalorimeter was used for determining isobaric heat capacity and isobaric thermal expansivity in the temperature and pressure ranges (278.15-343.15) K and (0.1 - 60) MPa for a set of RTILs. It was found out that the anomalous behaviour of both magnitudes is not an exception, but the rule for RTILs. The obtained results are explained through the use of well-known Equations of State and arguments based on the ionic nature of these compounds.

## 1187492: Predicting thermophysical properties of ionic liquids

### Ionic Liquids: From Knowledge to Application

#### IEC 0 [1187492]: Predicting thermophysical properties of ionic liquids

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**ACCEPTED**

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

**Inviting Chair:** Joe Magee , [magee@boulder.nist.gov](mailto:magee@boulder.nist.gov)

**Preferred Presentation Format:** OralOnly

**Consider for Sci-Mix:**

**Conforms to Bylaw 6:** Y

**Last Modified:** now()

**Abstract**

As ionic liquids begin to move from laboratory developments to industrial practice knowledge of their physical properties, both pure and mixed, becomes ever more important. However, due to the number of possible combinations of cation and anion an exhaustive study for the experimental determination of such properties is prohibitive, and thus predictive models are essential if ionic liquids are to realize their potential as "designer solvents".

Here we will describe our work on the prediction and/or measurement of a number of important thermophysical properties including density, viscosity and thermal conductivity over a wide temperature range. For example, densities and molar volumes have been predicted using a group contribution model as a function of temperature between 273 K and 423 K with an estimated repeatability and uncertainty of 0.36 % and 0.48 %, respectively. In thermal conductivity tests the behavior of ionic liquids was found to be more similar to organic liquids, such as methanol or toluene, than water, both in terms of absolute value and temperature dependence.

**1190268: On the nature of ionic liquids**

**Ionic Liquids: From Knowledge to Application**

**IEC 0 [1190268]: On the nature of ionic liquids**

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**ACCEPTED**

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

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**Preferred Presentation Format:** OralOnly

**Consider for Sci-Mix:** N

**Conforms to Bylaw 6:** Y

**Last Modified:** now()

**Abstract**

Until recently ionic liquids were believed to be molten salts with no measurable vapor pressure. Recent work indicates that many ionic liquids can be distilled at low pressure at 470 K with no significant decomposition. The mechanism for this transfer from the liquid to vapor remains unresolved. Hence it is appropriate to ask "what thermophysical properties should be used to classify materials as a salt as opposed to a high boiling organic compound". Such properties can include vapor pressure, electrical conductivity of the pure liquid, the electrical conductivity of the ionic liquid at low dilution in a polar solvent such as water or ethanol, and the zero frequency relative permittivity. In addition properties of mixtures of ionic liquids with organic compounds, such as vapor-liquid equilibria, liquid-liquid equilibria, excess enthalpies, and excess volumes can give a clue as to the nature of ionic liquids. Theoretical calculations based on ab-initio methods can also give a guide as to whether ionic liquids exist primarily as ions or as associated ion pairs in the pure liquid state and in mixtures with organic liquids.

The measurements and theoretical calculations of some of the above properties of selected ionic liquids and their mixtures will be reviewed and interpreted.

**1193025: Chemical speciation in ionic liquids and their mixtures with polar solvents**

**Ionic Liquids: From Knowledge to Application**

**IEC 0 [1193025]: Chemical speciation in ionic liquids and their mixtures with polar solvents**

**Glenn Hefter**, [g.hefter@murdoch.edu.au](mailto:g.hefter@murdoch.edu.au)<sup>1</sup>, Richard Buchner, [richard.buchner@chemie.uni-regensburg.de](mailto:richard.buchner@chemie.uni-regensburg.de)<sup>2</sup>, Johannes Hunger,<sup>2</sup> and Alexander Stoppa,<sup>2</sup> (1) Department of Chemistry, Murdoch University, Murdoch, WA 6150, Australia, Fax: +61-8-9310-1711, [g.hefter@murdoch.edu.au](mailto:g.hefter@murdoch.edu.au), (2) Institut für Physikalische und Theoretische Chemie, Universität Regensburg, D-93040 Regensburg, Germany

**ACCEPTED**

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

**Inviting Chair:** JW Magee , [joe.magee@nist.gov](mailto:joe.magee@nist.gov)

**Preferred Presentation Format:** OralOnly

**Consider for Sci-Mix:** N

**Conforms to Bylaw 6:** Y

**Last Modified:** now()

**Abstract**

Room temperature ionic liquids (RTILs) are undoubtedly not just simple mixtures of cations and anions, as indicated for example by their relatively low conductivities and high viscosities. Broadband dielectric relaxation spectroscopy (DRS) provides a very powerful tool for investigating the properties of RTILs. Apart from providing the only means to directly measure the dielectric constant, DRS also yields information on the nature and dynamics of any dipolar species present that would be difficult to obtain by any other method. As only limited information about the nature of the species present in RTILs

can be gained from studies of the pure ILs themselves, detailed investigations have been made into their mixtures with molecular solvents of varying polarity and chemical character. DRS results for a limited range of 1-alkyl-3-methyl imidazolium salts with a representative group of molecular solvents (water, DMSO, AN and DCM) have revealed some surprising features. Contrary to popular belief there is no evidence in the pure ILs for the existence of discrete ion pairs; such species appear to exist only at high dilution (typically  $x_{IL} < 0.1$ ) in molecular solvents. Larger, essentially non-dipolar, aggregates form at higher IL concentrations in molecular solvents although the exact nature of these species is unclear at present. At still higher  $x_{IL}$  there is evidence from DRS of microheterogeneous phase separation. However, the aggregates formed do not appear to be micelles (at least for short chain alkyl substituted ILs). The DR parameters for all the IL/co-solvent mixtures studied to date show no evidence for a sharp transition between electrolyte-solution-like and molten-salt-like behaviour.

#### 1195805: Physicochemical properties and structures of ionic liquids

##### Ionic Liquids: From Knowledge to Application

##### IEC 0 [1195805]: Physicochemical properties and structures of ionic liquids

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**ACCEPTED**

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** Y

**Inviting Chair:** Joseph Magee, magee@boulder.nist.gov

**Preferred Presentation Format:** OralOnly

**Consider for Sci-Mix:** N

**Conforms to Bylaw 6:** Y

**Last Modified:** now()

##### Abstract

To evaluate the ionic nature of the RTILs, the molar conductivity ratio, calculated from the molar conductivity measured by electrochemical impedance method and that estimated by PGSE-NMR ionic self-diffusion coefficients and the Nernst-Einstein relation, was introduced. The molar conductivity ratio well illustrates degree of formation of cation-anion aggregates in each ionic liquid under chemical equilibria, from the basis on experimental correlation of the conductivity ratio with anionic donor and cationic acceptor abilities estimated by solvatochromic UV-visible measurement. As a measure of electrostatic interaction of the RTILs, effective ionic concentration was introduced as a product of the conductivity ratio and molar concentration. Reduction of the effective ionic concentration for each RTIL well correlates with a decrease of reported normal boiling points and distillation rates. Such parameters become a key to select proper ionic structure for the lithium-ion cell electrolytes.

#### 1198495: Characterization of strong and super acids, using protic ionic liquids made with tertiary amine bases: The N-H chemical shift

##### Ionic Liquids: From Knowledge to Application

##### IEC 0 [1198495]: Characterization of strong and super acids, using protic ionic liquids made with tertiary amine bases: The N-H chemical shift

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**ACCEPTED**

**Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties*

**Invited:** N

**Comments to Organizer:** For Session 6. Thermophysical Properties - Joe Magee (NIST), Luis Rebelo (ITQB Lisbon)

**Preferred Presentation Format:** Oral

**Consider for Sci-Mix:**

**Conforms to Bylaw 6:** Y

**Last Modified:** now()

##### Abstract

In aqueous solutions it is common to record the proton chemical shift and observe it to move further downfield from standard references (e.g. TMS) as the acid strength increases. One can correlate downfield shift with pH. In protic ionic liquids it is also found that an "effective pH" exists. It is established by the transferred proton, and has proven useful in defining stable conditions for such proton activity-sensitive phenomena as the folding of proteins. In these protic media also, the chemical shift of protons of interest can be followed, but the key observed quantity (the chemical shift of the proton transferred in forming the salt) displaces in the opposite direction to that in aqueous solutions as the proton activity increases. When the Brønsted base involved in the formation of the protic ionic liquid is a nitrogen atom, we monitor the N-H proton chemical shift. We report this quantity for a variety of highly anhydrous protic ionic liquids. For a chosen base, the value of the N-H shift relates directly to the strength of the acid involved in the original PIL formation. In this study, we limit our base choices to two tertiary amines of comparable basicity, which together provide ambient temperature ionic liquids with all the common acids except the hydrogen halides. Some novel strong acids are identified using this approach. The possibility of correlating the N-H shift with the output of electrochemical devices designed to measure proton activity is considered, and the difficulties faced in the design of a suitable proton activity meter for ionic liquids are discussed.

#### 1201507: Vaporisation of ionic liquids: A temperature programmed desorption (TPD) study

##### Ionic Liquids: From Knowledge to Application

##### IEC 0 [1201507]: Vaporisation of ionic liquids: A temperature programmed desorption (TPD) study

Peter Licence, peter.licence@nottingham.ac.uk, Robert G. Jones, robert.g.jones@nottingham.ac.uk, Kevin R. J. Lovelock, pckl@nottingham.ac.uk, Aleksey Deyko, pcxad2@nottingham.ac.uk, and Jo A Corfield, School of Chemistry, The University of Nottingham, University Park, Nottingham, England, peter.licence@nottingham.ac.uk

**ACCEPTED****Topic Selection:** *Ionic Liquids: From Knowledge to Application: Thermophysical Properties***Invited:** Y**Inviting Chair:** Joe Magee, [magee@boulder.nist.gov](mailto:magee@boulder.nist.gov)**Preferred Presentation Format:** OralOnly**Consider for Sci-Mix:****Conforms to Bylaw 6:** Y**Last Modified:** now()**Abstract**

The volatility, or similarly lack of volatility, often associated with room temperature ionic liquids (RTILs) has, until quite recently been a hotly debated subject. Over the past 18 months a series of papers have been published discussing both the prediction and indeed the experimental determination of enthalpies of vaporisation ( $\Delta H_{\text{vap}}$ ) and related properties. We have used a range of ultra high vacuum systems to study both the liquids themselves (XPS, AES), and indeed thermally produced vapours thereof (LOS-MS, TPD). A selection of common RTILs have been studied to date and all were found to evaporate as ion pairs, with  $\Delta H_{\text{vap}}$  values that depend primarily on the electrostatic interactions within the liquid phase. This lecture will give an introduction to the techniques used in our laboratory and highlight the results of our most recent studies, we will present data on a range of RTILs including imidazolium, pyrrolidinium and pyridinium based liquids.

