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Essay

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Ionic Liquids—Progress on the Fundamental Issues

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Ionic liquids challenge conventional descriptions of fluids in a variety of ways. In the past, it has been common to oversimplify their behaviour and to ignore the complexity that was possible, given the burgeoning range of ionic liquids available. Here we discuss what is meant by the term 'ionic liquid' and some of the key fundamental issues in understanding their properties.

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Are there Generic Ionic Liquid Properties?

Ionic liquids have been attracting a greater than exponential growth of interest in the last decade. In 2005, more than 1400 papers were published in the field.^[1] describing an ever-growing range of applications and an ever-broadening range of fluids. At the same time, there has been a growing awareness of the range of properties that ionic liquids can possess. In the earlier days of ionic liquids research (around and before 2002), it was commonplace for authors and speakers to make a generic set of claims for ionic liquids as being non-volatile, non-flammable, intrinsically 'green', highly electrochemical stable, highly thermally stable, and comprising simple ionic species. In the last two or three years, partly as a result of increasingly intense investigation of physical properties and also as a result of the widening range of ionic liquid types available, it has become clear that almost none of these generic properties is ubiquitous and that ionic liquids exhibiting distinctly contrary properties are commonplace.^[2]

Some journal reviewers and editors in the field have thus begun to rein in the claims that authors are continuing to make for their compounds—but unfortunately far too many papers are still appearing with extravagant (verging on dishonest) claims. Some reviews (and, amazingly, a review appears every two to three days, one for every twenty original papers published^[1]!) have begun to emphasize the differences rather than the similarities in behaviour.

Have ionic liquids fallen off their pedestal? Hardly—but the field does need to realize and communicate just how richly textured the pedestal actually is and how that richness provides a wide range of interesting property combinations.

At this juncture, it is therefore appropriate to ask: What properties *are* generic and ubiquitous to ionic liquids? What properties do we expect to find *by definition* for an ionic liquid? If we accept the definition of an ionic liquid as being an ionic compound (a salt) which is liquid below 100° C, then in fact the only defining properties that one can expect to observe, a priori, are that, at some temperature below 100° C:

- (a) the substance is liquid (its glass transition temperature and/or melting point are below 100°C), and
- (b) it contains ions and therefore exhibits ionic conductivity.

The glass transition aspect of this definition is necessary to exclude the substances that are so viscous as to be glassy at our temperature of interest, so it simply adds some clarification to the word 'liquid'. The ionic conductivity is then the only property that we can *necessarily* expect to be present in these compounds. Given that the conductivity is strongly dependent



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Vapour Pressure and Thermal Stability?

Beyond this generic property, then, are others such as vapour pressure, which can exhibit a range of values depending on the structures involved: as Earle et al. have shown, the vapour pressures of even some very well-known ionic liquids are certainly not zero.^[3] Indeed, ionic liquids can be designed such they are distinctly distillable, and this is a useful feature in some cases.^[4] In a related vein, Scott and co-workers^[5] have shown that the use of scanning thermogravimetric analysis (TGA) to estimate the high temperature stability of ionic liquids can be misleading, as it leads to values of apparent decomposition temperatures which are much higher than those measured in isothermal studies. In fact, ionic liquids exhibit classical temperature-dependent decomposition reactions which are slow, but present, at temperatures as much as 100°C below the values of decomposition temperatures determined by scanning TGA.^[6] To properly characterize thermal stability and thereby justify the proposition that some ionic liquids can be useful as high temperature process solvents, much more of this type of work is needed, preferably coupled with mass spectrometry, or other structural analysis, of the decomposition products at each temperature. Nonetheless, the caveat emptor is clear: Most decomposition temperatures reported in the literature are significant over-estimates.

Biodegradability and Toxicity?

Scammells et al.^[7] pointed out in this journal that ionic liquids may not be as 'green' as many authors had claimed, because of several issues which, at the time, had been sorely neglected. They highlighted the dearth of data concerning the biodegradation, toxicity, and methods of recycling the ionic liquids that were being claimed as 'benign solvents'. These issues are now more routinely studied and discussed but, in fact, *all* research reports claiming their justification as the 'greening' of a reaction in this way should, at the very least, discuss and evaluate these issues. These issues are so important that they will be highlighted in a pending conference in Berlin: BATIL (Biodegradability and Toxicity of Ionic Liquids).^[8]

Electrochemical Stability?

Equally, it is beginning to be recognized that, in many cases, electrochemical stability is not all that it initially seems. In fact, some of the ionic liquids that were thought to be extremely stable to deeply negative potentials, an observation of some significance to the lithium battery field, are now being shown to be less stable than first thought. The {bis(trifluoromethyl)sulfonyl}amide, $[NTf_2]^-$, ion decomposes at potentials some 1.5 V less negative than previously thought,^[9] but forms a variety of insoluble compounds on metals such as lithium and magnesium that provide some measure of electrochemical inhibition. The role of impurities (such as water) in these breakdown reactions is also being recognized. These surface coatings probably explain why these ionic liquids are good electrolytes in contact with lithium metal, the lithium ion being easily transported through the film and hence a reversible Li/Li⁺ couple being nonetheless observable. They also prompt applications in corrosion protection of metals such as magnesium and its alloys, as described in two papers in this issue.^[10,11] But, equally, they are troublesome to current attempts by many groups to electroplate reactive metals, such as magnesium and titanium.

The related issue that these recent observations, both electrochemical and thermal, bring into stark focus is that even trace impurities may have strong catalytic effects on the observed bulk properties at these extremes of reaction energy. Hence careful attention to the level of such impurities is important in all discussions. The 'spiking' approach to determining their effect is particularly recommended.^[9]

Protic Ionic Liquids—True Ionic Liquids or Liquid Mixtures?

The family of protic liquids presents another set of fundamental issues. Protic ionic liquids are complex liquids in which a variety of proton transfer and association equilibria are likely to be established. These processes challenge our concept and definition of ionic liquids as 'liquids which are comprised entirely of ionic components'. In most ionic liquids, these components derive from a single compound, in other words a salt. The question of whether a liquid falls within this description, or not, is significant in that it serves to define whether we are dealing with the properties of a pure (liquid) compound or are instead dealing with a mixture (or solution) of ionic and molecular species. Equilibrium processes which can produce neutral species such as ion pairs are ubiquitous in ionic liquids and these make up part of the structure of the liquid. In the case of a protic ionic liquid formed from an acid, HA, and a base, B, there is clear scope for the proton transfer process to be incomplete, leaving an equilibrium fraction of the neutral acid and base as independent species present in the liquid. $HA + B = [BH]^+ + A^-$.

It is the potential independence of these species as additional components that makes this a more troublesome problem as compared to the 'ion-pair' equilibrium issue discussed above. This proton-transfer equilibrium bears many similarities to the neutralization equilibrium that can exist between HA and B in aqueous solution (where B can be water). In the latter context, the terms 'degree of dissociation' and 'degree of proton transfer' are used to describe the extent of this reaction. In preparing and using such protic ionic liquids, therefore, it is of importance to understand the position of this equilibrium in order to understand the concentration of the neutral species in the liquid. One then needs to ask: 'How far towards the right does the equilibrium have to lie, or how high does the degree of proton transfer have to be, in order for the substance to be properly termed an ionic liquid?' One approach to answering this question is to adopt criteria appropriate to the specification of any pure compound in chemical terms. A compound might not be considered pure unless the level of impurities is less than some specified value, for example 1%, that depends on the situation or application. At levels of impurity well above this, the properties of the compound (including the transport properties, melting point, etc.) will exhibit as those of a complex mixture rather than a pure compound. Impurities at such levels may also be of significance in chemical reactions involving such a compound, or where the compound was used as a solvent. Similarly, a compound that contained more than, for example, 1% of a solvent, or of water, would not be considered pure.

Thus, as a guideline in respect to protic ionic liquids, we propose that less than 1% of the neutral species should be present if the ionic liquid is to be considered a 'pure ionic liquid'. In other words the degree of proton transfer should be >99%. Fortunately, this is not a difficult goal to achieve in principle; many acid–base

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pairs are possible that should, on the basis of their aqueous pK_a values, easily proton-transfer to this extent. However, the aqueous pK_a data is only of fairly remote relevance to the ionic liquid state in which this proton-transfer takes place and there is, not surprisingly, growing evidence that the degree of proton-transfer from acid to base in ionic liquids is orders of magnitude lower than one would predict. Angell and co-workers^[12] have provided a very useful perspective on proton-transfer compounds in terms of the Walden plot and the aqueous pK_a data of the ions involved. The Walden plot compares the molar conductivity as a function of the fluidity (= inverse viscosity) of the liquid with an ideal behaviour derived from well-understood aqueous solutions. In some cases where the pK_a difference is insufficiently large, the liquid lies well below (by orders of magnitude) the ideal Walden plot line, meaning that the liquid contains substantial quantities of nonconductive HA and B, as well as [BH]⁺ and A⁻. Again, the degree of proton transfer in such cases is much lower than would be predicted from the aqueous pK_a data. The origins of this are not completely clear; much more work is needed to understand proton-transfer in this important class of ionic liquids, and to generate the much needed proton-transfer equilibrium constant data. Nonetheless at an empirical level, the Walden plot provides a convenient means of establishing, in qualitative terms, the likely degree of proton-transfer in a protic ionic liquid.

The question at issue here really is: Should such liquids be dubbed ionic liquids at all, poor or otherwise, or are they better thought of as *mixtures* of ionic liquids with neutral compounds? At the opposite extreme, should they be thought of as simple solutions of the salt in a neutral solvent mixture? Such questions are not designed to sideline what could be practically important liquids; rather they are intended to ensure that we approach our understanding of their behaviour in an appropriate light. We are, in other words, concerned with empiricism not theology!

Dielectric Constant and Polarity

After many years of discussion about the 'polarity' of ionic liquids and speculation about its connection to dielectric properties, the latter are finally attracting the attention of the dielectric spectroscopy community. The pattern in the measurements indicates 'static' dielectric constants between 10 and 15 in most of these liquids,^[13] somewhat lower than estimates on the basis of effective polarity would seem to indicate.^[14] However, these measurements are carried out at GHz frequencies and 'static' in this context is any timescale longer than about 1 ns. The bulk response of the liquid on a timescale of seconds mainly involves ion translations rather than dipole reorientations. A set of extended, broad-band, dielectric spectroscopy measurements are discussed in the paper in this issue by Schrödle et al.,[15] who show that the dielectric relaxation in the region above 20 GHz has an excess component of dielectric loss, which is explained in terms of translational oscillatory motions of the dipolar ions, and possibly fast rotatory motions in addition. Overall, the picture that emerges is that the dielectric response of an ionic liquid (and therefore its response to the presence of an ionic or dipolar solute) is complex-partly dipolar, partly ionic-and depends very much on the timescale of the response of interest. Again, further detailed analysis and modelling of such measurements is needed so that the responses of ionic liquids as solvents can be understood.

Computational Modelling Methods

Theoretical calculations and simulations are clearly an important approach to understanding some of these phenomena more deeply. Papers by Hunt^[16] and Izgorodina^[17] in this issue present a powerful insight into the molecular and interaction features of the archetypal ions that generate ionic liquids. Izgorodina discusses two issues of significance in applying ab initio techniques: (a) the poor performance of DFT in dealing with systems bearing the delocalized charge that is the hallmark of many ionic liquid ions, and (b) the fundamental problem of how to calculate a meaningful charge on each atom in a delocalized molecular ion. The latter issue is of major significance to molecular dynamics simulations of ionic liquids, since these charges are the basis of a large part of the intermolecular interactions in these systems. She investigates ways of characterizing the degree of charge delocalization in anions; a proton affinity scale is proposed as a way to quantify 'diffuseness' and she demonstrates that this correlates well with the trends in the ionic liquid families.

Thus, this Research Front in the *Australian Journal of Chemistry* collects together a variety of papers that constructively challenge, investigate, and extend our understanding of the field of ionic liquids. With over 4000 papers published in the past three years, the field is growing at a staggering rate. However, many of these papers are either highly derivative, or based on false, naïve assumptions, and the time for quiet contemplation is long overdue. The papers in this issue will hopefully contribute to that meditation on the fundamental issues.

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