On the concept of ionicity in ionic liquids

Douglas R. MacFarlane, Maria Forsyth, Ekaterina I. Izgorodina, Andrew P. Abbott, Gary Annat and Kevin Fraser

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Ionic liquids are liquids comprised totally of ions. However, not all of the ions present appear to be able to participate in conduction processes, to a degree that is dependent on the nature of the ionic liquid and its structure. There is much interest in quantifying and understanding this ‘degree of ionicity’ phenomenon. In this paper we present transport data for a range of ionic liquids and evaluate the data firstly in terms of the Walden plot as an approximate and readily accessible approach to estimating ionicity. An adjusted Walden plot that makes explicit allowance for differences in ion sizes is shown to be an improvement to this approach for the series of ionic liquids described. In some cases, where diffusion measurements are possible, it is feasible to directly quantify ionicity via the Nernst–Einstein equation, confirming the validity of the adjusted Walden plot approach. Some of the ionic liquids studied exhibit ionicity values very close to ideal; this is discussed in terms of a model of a highly associated liquid in which the ion correlations have similar impact on both the diffusive and conductive motions. Ionicity, as defined, is thus a useful measure of adherence to the Nernst–Einstein equation, but is not necessarily a measure of ion availability in the chemical sense.

Introduction

Ionic liquids are currently under widespread investigation for a very broad range of solvent and electrolyte applications as a result of the attractive combination of properties that some members of the family possess. For example, the bis(trifluoromethanesulfonyl) amide salts typically offer a very wide liquid range with very low vapour pressure (hence low flammability) and high ionic conductivity. Some level of ion conductivity is to be expected of all ionic liquids, but interestingly some exhibit much lower molar conductivity than others, even after differences in viscosity are allowed for; this is to be expected of concentrated ionic media in which ion pairs and other correlations can strongly influence conductivity. Ion pairs, if sufficiently long-lived, appear neutral in the electric field and thus cannot contribute to conductivity. Similarly, long-lived groups or aggregates of ions contribute less to conductivity than the independent ions would. Such conductivity effects are of extreme interest in most applications of ionic liquids as electrolytes in electrochemistry and electrochemical devices, including lithium batteries, double layer capacitors, and photo-electrochemical cells. Lack of conductivity, especially at low temperatures, is often one of the main disadvantages in the use of an ionic liquid and a number of research programs worldwide are dedicated to developing higher conductivity examples for these applications. An understanding of the factors that influence such ion correlation effects is also of importance as their impact extends beyond the electrolyte and electrochemistry to their solvent properties and vapour pressure. Thus the question of “how ionic is this ionic liquid?” becomes of quite general significance.

Angell and co-workers have described a qualitative approach to this question based on the Walden rule:

$$A\eta = k$$  

where $A$ is the molar conductivity and $\eta$ is the viscosity; $k$ is a temperature dependent constant. The Walden rule was originally based on observations of the properties of dilute aqueous solutions, but has since been found to be applicable in non-aqueous electrolyte solutions and molten salts. On a plot of log $A$ vs. log $\eta$ this rule predicts a straight line that passes through the origin; this has become known as a “Walden plot”. Data for a 0.01M KCl solution provide a useful calibration point that effectively allows estimation of the constant $k$ and hence allows the placement of a reference line on the Walden plot as shown in Fig. 1. Data from a wide range of electrolytes can then be placed on the Walden plot, including any ionic liquid for which viscosity and conductivity measurements are available. Except for one or two notable exceptions, most ionic liquids fall below the line, more or less so depending on their structure. Many protic ionic liquids fall well below the line, suggesting that full ionisation (proton transfer) is not complete in those cases. Some aprotic ionic liquids also fall well below this reference line indicating that their conductivity is as much as an order of magnitude lower than would be expected on the basis of the Walden rule, presumably as a result of ion association in its various forms.

On the other hand it could be considered remarkable that so many ionic liquids actually lie as close to (within 20% of) the line as they do, given that one would expect strong ion
correlations during conductive motions in response to an electric field, to an extent that would not be present in the dilute electrolyte represented by the 0.01M KCl solution. Indeed many decades of investigation have been devoted to understanding and developing equations to account for the various effects that become significant as one moves from dilute (usually aqueous salt) solution to concentrated salt solutions,23–26 including relaxation effects and the impact of ion association. One might predict that similar effects would be even more pronounced in the ionic liquid where a single ion cannot possibly move without affecting, or being affected by, its surrounding ion neighbours. Thus, one of our goals here is to understand more precisely what is indicated by such a high degree of concordance with the Walden rule.

The Walden plot represents a relatively qualitative approach to understanding these phenomena. In a variety of contexts a number of workers27,28 have used the Nernst–Einstein (NE) equation, which for a 1 : 1 salt can be written as:

\[
A = \frac{N_A e^2}{kT} (D^+ + D^-)
\]  

(2)
as a way of assessing the impact of ion correlations on conductivity in a more quantitative fashion. Here \( N_A \) is Avogadro's number, \( e \) is the electronic charge, \( k \) is Boltzmann's constant and \( D^+ \) and \( D^- \) are the diffusion coefficients of the cation and anion, respectively. From eqn (2) the molar conductivity can be calculated if the individual diffusion coefficients are known. Comparison of the calculated and measured molar conductivities, \( \Lambda_{\text{NE}} \) and \( \Lambda_M \), respectively, is then often interpreted in terms of a deviation, \( \Delta \):

\[
\Lambda_M = (1 - \Delta) \Lambda_{\text{NE}}
\]  

(3)
Such comparisons have been carried out for a range of molten salts29,30 and have, in many cases, been found to produce quite small values of \( \Delta \) (of the order of \( \pm 0.1 \)). In other words the deviation from the Nernst–Einstein equation in these molten salts can be as small as 10%. This indicates that the Nernst–Einstein equation can work moderately well in highly coloumbic systems such as molten salts. These represent a very useful point of reference for the more complex organic salts that make up the family of ionic liquids. Watanabe and co-workers31–34 have carried out similar investigations in a range of ionic liquids. In their work, the ratio \( \Lambda_M/\Lambda_{\text{NE}} \) was calculated and was discussed in terms of the degree of “ionicity” of the salt involved. The hypothesis involved was that the main cause of deviations from the Nernst–Einstein equation was ion aggregation and therefore \( \Lambda_M/\Lambda_{\text{NE}} \) was a measure of ionicity. They found that, in the ILs studied, ionicity was typically around 0.5–0.8 (corresponding to \( \Delta = 0.5 - 0.2 \)), again surprisingly high considering the correlations that must exist in ionic liquids. Here our goal is to understand the molecular and structural effects that control “ionicity” and therefore to examine the methods by which it can be qualitatively and quantitatively obtained. Thus we describe a set of measurements on a variety of ionic liquids ranging from those expected to exhibit high ionicity to those where ion pairing was suspected. An adjusted form of the Walden plot which takes into account the radius of the conductive species, as suggested by Bonhote et al.35,36 and Abbott,37 is shown to provide a more direct insight into ionicity where diffusion measurements are not practicable. In selected cases a full NMR diffusion analysis was possible and, in these cases, the ionicity is assessed via the Nernst–Einstein equation.

Experimental

Ionic liquids were obtained, or synthesised locally, and purified prior to measurements as described previously.4 Abbreviations used are explained in ref. 4 and for various non-standard anions are as follows: [Ace]– = acesulfamate, [Cyc]– = cyclamate, [Sac]– = saccharinate and [Dbsa]– = dodecylbenzenesulphonate. Density measurements were carried out using an Anton Paar DMA 5000 density meter. The density meter uses the ‘oscillating U-tube principle’ to determine the density of the liquid. Viscosity measurements were carried out using an Anton Paar AMVn viscosity meter which uses a falling ball technique.

Conductance measurements were performed using a locally designed dip cell probe consisting of two platinum wires sheathed in glass. The cell constant was determined with a solution of 0.01M KCl at 25 °C. Conductivities were obtained by measurement of the complex impedance spectra between 1 MHz and 0.01 Hz on a Solatron SI 1296 dielectric interface. The temperature was controlled at 10 °C intervals (±1 °C) using a Eurotherm 2204e temperature controller interfaced to the Solatron and a cartridge heater set in a brass block with a cavity for the cell. A K-type thermocouple was set in the block adjacent to the cell. The conductance was determined from the first real axis touchdown point in the Nyquist plot of the impedance data.

The diffusion data required can be obtained from a variety of measurements but most recently pulsed field gradient (PFG) NMR techniques have been applied and arguably provide the most direct means of obtaining the individual diffusion coefficients required. The details of such measurements are complex, as discussed recently.38 In the present case NMR multinuclear pulsed field gradient stimulated spin echo (PFGSTE) experiments were performed on a Bruker Avance 300 NMR spectrometer at either 20 °C or 80 °C (in the case of [P6,6,6,14][Sac] and [P4,4,4,4][Sac]). Diffusion experiments involved between 16 and 24 gradient steps, with diffusion time (\( \delta \)) between 10 and 80 ms, gradient ramp time (\( \Delta \)) = 3 ms and
a maximum gradient of 1400 G cm\(^{-1}\). Samples were loaded into Schott NMR glass tubes (5 mm outer diameter, 178 mm length). In the case of \([\text{P}_{6,6,6,14}]\text{NTf}_2\) temperature dependent diffusion coefficients were determined between 20 and 80 °C. For proton (\(^1\)H) diffusion experiments, a 300.14 MHz Larmor frequency was used with 7 \(\mu\)s for 90° and 14 \(\mu\)s for 180° pulse lengths.

All geometry optimizations were performed at the B3LYP/6-31+G(d) level of theory. For some ions that can exist in multiple conformations (such as \([\text{C}_3\text{mpyr}]^+,\) \([\text{C}_4\text{mpyr}]^+,\) \([\text{C}_2\text{minim}]^+\) and \([\text{NTf}_2]^−\)) a full conformational search was performed to establish the lowest-energy conformation. In the case of the \(\text{C}_6\text{mpyr}\) cation the conformation search was performed only on the terminal \(\text{C}_5–\text{C}_6\) bond, keeping the \([\text{C}_4\text{mpyr}]^+\) lowest-energy conformation for the rest of the cation. In the case of the \([\text{P}_{4,4,4,4}]^+\) and \([\text{P}_{6,6,6,14}]^+\) cations the alkyl chains were assumed to have a linear arrangement, as observed in the crystal structure of \([\text{P}_{10,10,10,10}]\text{Br}\).\(^{39}\)

Molecular volumes were computed using the HF/aug-cc-pVTZ electron density with tight criteria (an increased density of points for more accurate integration). Normally, within this approach the volumes are computed with an accuracy of 10%. Due to computational demands the \([\text{P}_{6,6,6,14}]^+\) cation volume was estimated only at the B3LYP/6-31+G(d) level of theory.

The effective ionic radii are calculated assuming that the ions studied have a spherical shape:

\[
V_{\text{theory}} = \frac{4}{3}\pi R_{\text{ion}}^3
\]

It should be noted that for most of the ions the effective radius defined this way is an underestimation of their true hydrodynamic radius.

### Results

The Walden plot is presented in Fig. 1 and typical conductivity and viscosity data are shown in Fig. 2. Note that in those cases where the sample freezes during the measurement at lower temperatures a distinct step in conductivity is often observed at the melting point.

The traditional Walden plot shows three distinct groups of ionic liquids. The first group, exemplified by \([\text{C}_2\text{mpyr}]\text{dca}\), lies quite close to the 0.01M KCl line labelled (A) in Fig. 1, suggesting that the ionic liquid is made up of almost independently mobile ions. The second group lies lower on the plot and is exemplified by \([\text{P}_{6,6,6,14}]\text{NTf}_2\). These ionic liquids exhibit distinct deviations from the 0.01M KCl line. Angell has quantified such deviations by measuring the vertical distance to the KCl line and denoting these as \(\Delta W\).

A \(\Delta W\) value of 1 indicates an ionic liquid that is exhibiting only 10% of the ionic conductivity that it would exhibit if it behaved according to the 0.01M KCl line; the line labelled (C) in Fig. 1 indicates this situation. A third group can be seen on this plot that lies well below the “10% line” as exemplified by \([\text{P}_{6,6,6,14}]\text{Cyc}\), which lies at around \(\Delta W = 1.4\), potentially indicating an ionicity around 4%. Such very low ionicity values have been described previously\(^9\) as indicating interesting intermediate cases between true ionic liquids and true molecular liquids, and as such may posses unique solvency properties.

Similar use of the Walden rule has been described previously in the context of molten salts.\(^{20}\) Remarkably similar values of \(k\) in eqn (1) have been observed for a pair of ions in the molten salt state compared with the same ions in aqueous solution, although some deviation from this is evident at much higher temperatures in these cases.\(^{37}\) This is equivalent to the behaviour observed in Fig. 1.

The Walden plot of Fig. 1 appears therefore to be useful as a qualitative tool for assessing ionicity in ionic liquids, requiring
where \( r^+ \) and \( r^- \) are the respective “effective” cation and anion sizes. Thus it is clear that, all other things being equal, ion size has an impact on the Walden plot and hence has an effect on what might be considered as ‘ideal’ or ‘associated’ behaviour. To treat this more explicitly we can therefore construct an adjusted Walden plot in which the molar conductivity is plotted vs. \( \log (\eta^{-1}(\frac{1}{r^+} + \frac{1}{r^-})) \) as suggested by eqn (6).

Such an adjusted plot is shown in Fig. 3. The adjustment is significant in terms of the conclusions drawn above, since now \( \Delta W \) is reduced in many cases. For example in the case of \([\text{P}_{6,6,6,14}]\text{NTf}_2\], \( \Delta W \) is reduced from 0.70 to 0.26. Similar adjustments to \( \Delta W \) values can be calculated for all of the ionic liquids, based on the ion size estimates, as tabulated in Table 1. Note that the effect of this adjustment is equivalent to moving the reference KCl(aq) line of Fig. 1 to create a new reference line for each ionic liquid, as shown by the line labelled (B) in Fig. 1.

These considerations produce a refinement of the Walden plot approach to ionicity and also serve to emphasise the very qualitative nature of the approach involved. In order to provide a more quantitative assessment of the validity of this approach a more direct measurement of ionicity is required for comparison. To this end we carried out direct diffusion coefficient measurements, where possible, that allow us to directly calculate ionicity using eqn (2) and (3) as defined above. Such data are shown in Fig. 4. In order to best compare the behaviour of such ionicity parameters for a variety of liquids, and over a range of temperatures, we have found it convenient to plot them in a fashion analogous to the Walden plot. Hence Fig. 4 shows a plot of \( \log A_M \) vs. \( \log A_{NE} \). An ideal line is drawn which corresponds to the Nernst–Einstein equation behaviour; this line indicates where \( \log A_M = \log A_{NE} \). The multiple points shown for some ionic liquids indicate that data for a range of temperatures have been plotted; generally, increasing temperature causes a shift diagonally to the right on this plot. All of the ILs studied fall below this ideal line, however, in some cases, such as \([\text{C}_3\text{mpyr}][\text{dca}]\), only by a surprisingly small amount. For comparison with the \( \Delta W \) values, a deviation \( \Delta I \) is measured and is tabulated also in Table 1. The correspondence between \( \Delta I \) and \( \Delta W \) is satisfactorily good, suggesting that the adjusted \( \Delta W \) can be used as a useful approximation to \( \Delta I \) when the latter is not readily obtainable.

**Discussion**

One of the remarkable features of Fig. 4 is just how close to the ideal Nernst–Einstein behaviour some ionic liquids lie (e.g. \([\text{C}_3\text{mpyr}][\text{dca}]\) and \([\text{C}_3\text{mpyr}][\text{NTf}_2]\)). These are, of course, some of the ionic liquids known for their high conductivity and low viscosity. It is challenging to inquire as to why such ionic liquids do not show more signs of ion correlations of the various types discussed above. Indeed theory and simulations of transport in ionic liquids have shown that small deviations should be expected from Nernst–Einstein behaviour. Detailed discussion of the origin of the deviations that do appear.

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**Table 1** Comparison of \( \Delta W \) (Walden plot) and \( \Delta I \) (Ionicity plot) for a range of ionic liquids

<table>
<thead>
<tr>
<th>IL</th>
<th>Temperature/K</th>
<th>( \Delta W ) (±0.1)</th>
<th>Radius cation/Å</th>
<th>Radius anion/Å</th>
<th>Adjusted ( \Delta W ) (±0.1)</th>
<th>( \Delta I ) (±0.1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>303</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.44</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>313</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.37</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>323</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.33</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>333</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.30</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>343</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.26</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{NTf}_2]</td>
<td>353</td>
<td>0.70</td>
<td>5.83</td>
<td>3.72</td>
<td>0.23</td>
<td>0.24</td>
</tr>
<tr>
<td>([\text{P}_{6,6,6,14}]\text{Sacc}]</td>
<td>353</td>
<td>0.91</td>
<td>5.83</td>
<td>3.55</td>
<td>0.31</td>
<td>0.63</td>
</tr>
<tr>
<td>([\text{P}_{4,4,4,4}]\text{Sacc}]</td>
<td>353</td>
<td>0.61</td>
<td>5.83</td>
<td>3.55</td>
<td>0.23</td>
<td>0.44</td>
</tr>
<tr>
<td>([\text{C}_3\text{mpyr}][\text{dca}]]</td>
<td>293</td>
<td>0.16</td>
<td>3.55</td>
<td>3.72</td>
<td>0.07</td>
<td>0.11</td>
</tr>
<tr>
<td>([\text{C}_3\text{mpyr}][\text{NTf}_2]]</td>
<td>293</td>
<td>0.14</td>
<td>3.76</td>
<td>3.72</td>
<td>0.06</td>
<td>0.12</td>
</tr>
<tr>
<td>([\text{C}_3\text{mpyr}][\text{NTf}_2]]</td>
<td>293</td>
<td>0.27</td>
<td>3.96</td>
<td>3.72</td>
<td>0.11</td>
<td>0.22</td>
</tr>
<tr>
<td>([\text{C}_3\text{mpyr}][\text{NTf}_2]]</td>
<td>293</td>
<td>0.13</td>
<td>3.39</td>
<td>3.72</td>
<td>0.06</td>
<td>0.20</td>
</tr>
<tr>
<td>([\text{C}_3\text{mpyr}][\text{NTf}_2]]</td>
<td>293</td>
<td>0.01</td>
<td>3.55</td>
<td>2.80</td>
<td>0.01</td>
<td>0.03</td>
</tr>
</tbody>
</table>
indicates that there are two main factors that contribute to $\Delta$. Firstly, the equation is strictly valid only in the limit of vanishingly small applied electric field.\textsuperscript{26,40} In the presence of a real field, the motion of an ion induces an internal field due to its oppositely charged ionic atmosphere; this internal field reduces the effect of the applied field. The deviation caused by this effect has been discussed in detail by Smedley,\textsuperscript{26} and more recently by Koishi and Tamaki.\textsuperscript{40} It tends, in simple molten salts such as the alkali halides, to produce a small contribution to $\Delta$ (i.e. $\sim 0.1$ which corresponds to about a 10% reduction in molar conductivity).\textsuperscript{26}

A second effect relates to the differing contribution ion–ion correlations make to the measured properties. The simplest type of correlation is the ion pair. Such correlations reduce the mobility and independence of the ions as they move and hence have an impact on both diffusion and conductivity; however, the reduced, or zero, net charge produced by such correlated motions means that they have a stronger impact on the conductivity.

This effect is apparent in the correlation functions on which these measureables are based. The diffusion coefficient can be calculated\textsuperscript{27,30,41} from the velocity auto-correlation function:

$$D_i = \frac{1}{3} \int_0^\infty (v_i(t)v_i(0)) dt$$

(7)

and the conductivity from a “current–current” correlation function, for example for the cation:

$$\Lambda^+ = \frac{2^2 F^2}{3RT} \int_0^\infty \langle \left( v_i^+(t) v_i^+(0) \right) - \left( v_i^-(t) v_i^-(0) \right) \rangle dt$$

(8)

and similarly for the anion. Eqn (7) calculates simply the velocity and position of each ion relative to its position at time $= 0$ and hence, from the Einstein relation, the diffusivity. On the other hand eqn (8) includes a second term which accounts for the effect of anion motions on each cation. Such correlations need not be long-lived, and lifetimes as short as $20 \times 10^{-14}$ s are sufficient to have an impact;\textsuperscript{26} notably such times are much too short to be detectable by dielectric spectroscopy which typically is sensitive to motions on a $10^{-11} - 10^{-9}$ s timescale. It is interesting to note that, though molecular dynamics simulations of simple molten salt systems have produced $\Delta$ values \textit{via} eqn (7) and (8) within 0.1–0.2 of the experimental values, recent simulations of ionic liquids\textsuperscript{42} seem to produce very low values of the calculated conductivity and thereby very large values of $\Delta$ (of the order of 0.99). This seems to suggest some transport mechanism in the ionic liquid that is too slow to be detected by the simulation timescale.

The picture that emerges from this discussion is of a highly associated liquid in which all motions are restricted by the interactions with the surrounding ions and in which longer range motions can involve pairs and aggregates of ions, some of which do not contribute to conductivity. In the cases of the liquids in Fig. 4 that lie close to the ideal line, the ions appear to be moving in an uncorrelated fashion 90% of the time as they move in an electric field. Thus in the most ideal cases such as [C$_3$mpyr][deca], even though motion of ions in these liquids is highly restricted because of the strong electrostatic interactions, ion pairing is not a significant factor; each ion is equally, but strongly, influenced by all of its neighbours on the timescale of the measurements. The success of the equation in these cases simply instructs us that these interactions have equivalent impact on the conductivity and diffusivity responses (\textit{i.e.} that specific correlations such as ion pairing that impacts on one more than the other are absent). Similar effects are seen in some high temperature molten salts where results for the alkali halides, for example, show $\Delta$ values as low as 0.04 for NaI at 1081 K. Models of conduction and transport, such as the hole models of Abbott \textit{et al.}\textsuperscript{37,41,43} are consistent with these observations as long as the model describes diffusion and conduction in the same terms.

On the other hand in the cases such as [P$_{6,6,6,14}$][Cyc] where either the ionicity plot or the Walden plot indicates large negative deviations from the ideal line, one needs to consider the possibility of much stronger correlations that are not present in the more ideal cases. Ion pairing is an obvious example of such a correlation, though large aggregates or networks of ions may also be significant. To be effective in this respect the ion pairs need only be long enough lived that their lack of contribution to the conduction process is important. This is not to say that the ion pair must have a lifetime longer than the characteristic relaxation timescale associated with conductivity, only that the time fraction that each ion spends involved in non-conductive states must be significant on that timescale. As discussed above the lifetime of each ion pair might be as short as $20 \times 10^{-14}$ s; however, the total time fraction that any given ion spends paired may nonetheless be large, for example 90%, which could produce $\Delta = 0.9$. Ion pairs of course can arise from specific interactions such as hydrogen bonds; the saccharinate cases may be examples of this. They may also arise from what we think of as “entrapment”, where a small ion such as Cl$^-$ can approach within the outer reaches of a large ion such as [P$_{6,6,6,14}$] and thereby suffer an unbalanced coulombic interaction with that particular ion.

Conclusions

We conclude that the concept of ionicity, as the effective fraction of ions available to participate in conduction, as discussed here, has value in understanding conductivity. The
adjusted Walden plot is a useful device in analysing such data, the \( \Delta W \) values from such a plot providing a good approximation to the deviations from ideality, \( \Delta I \), that can be calculated when a full diffusion analysis is available. However, the concept of ionicity does not necessarily describe the chemical availability of individual ions, which may depend more strongly on the associated nature of the ionic liquid. Such more chemical reflections of the state of ions will be described by much needed thermodynamic activity measurements in ionic liquids. Understanding such features of their behaviour is one of the remaining great challenges in the ionic liquids field.

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Notes and references