COMMUNICATION www.rsc.org/chemcomm | ChemComm

Liquids intermediate between "molecular" and "ionic" liquids: Liquid Ion Pairs?†

Kevin J. Fraser,[a] Ekaterina I. Izgorodina,[a] Maria Forsyth,[b] Janet L. Scott[a] and Douglas R. MacFarlane*[a]

Received (in Cambridge, UK) 2nd July 2007, Accepted 23rd July 2007
First published as an Advance Article on the web 31st August 2007
DOI: 10.1039/b710014k

Ionic liquids comprised of tetradecyltrihexyl- and tetrabutylphosphonium cations paired with chloride or sulfonyl amide anions exhibit properties that reflect strong ion association, including comparatively low viscosity as well as a degree of volatility, and hence exemplify an interesting intermediate state between true ionic and true molecular liquids.

Room temperature ionic liquids are currently attracting considerable attention as potentially benign solvents for many areas of chemistry, as well as electrochemical devices such as rechargeable lithium batteries, fuel cells, electrochemical capacitors, and photoelectrochemical solar cells.[1] This interest in ionic liquids can be attributed to the properties variously exhibited by some, though not all, members of the family, such as low volatility, nonflammability, electrochemical and thermal stability, and high ionic conductivity—all of which can be tailored through careful choice of cation and anion.[2,3]

Ionic liquids based on tetraalkylphosphonium cations have been demonstrated to exhibit greater thermal stability than their tetraalkylammonium based counterparts[4] and a range of phosphonium salts are commercially available in large quantities.[5] Many reports of the utility of ionic liquids prepared from phosphonium cations with anions such as $[PF_6]^-$, $[BF_4]^-$, $[NTf_2]^-$ have appeared.[6] The use of sweetener anions such as saccharinate $[Sacc]^-$, acesulfamate $[Ace]^-$ and cyclamate $[Cyc]^-$ to achieve ionic liquids has been reported by Davis *et al.*[7,8] and a communication by Pernak and co-workers disclosed a range of phosphonium ionic liquids with the acesulfamate anion.[9]

We describe here an expanded series of phosphonium salts of sweetener anions and compare these with more routinely used anions (as shown in Fig. 1) with a focus on their transport properties. Remarkably (and perhaps counter-intuitively) it appears that tetraalkylphosphonium halides exhibit lower ion conductivity than analogues with bulky, charge-diffuse anions such as saccharinate. Examination of the transport properties in terms of the Walden plot, as described by Angell *et al.*,[10] suggests that these liquids are strongly ion-paired or ion-associated. *Ab initio* calculations of the stability of the ion-pairs in each case supports this interpretation. Hence, they are perhaps best thought of as an interesting intermediate case between a true ionic liquid (*i.e.* a liquid salt of a high degree of ionicity[11]) and a true molecular liquid.

The compounds were synthesised and characterised as described in the supporting information. The $[Cl]^-$, dicyanamide $[dca]^-$, bis(trifluoromethylsulfonyl)imide $[NTf_2]^-$ and dodecylbenzenesulfonate $[dbsa]^-$ salts of the tetradecyltrihexyl phosphonium cation, $[P_{6,6,6,14}]^+$, were obtained from Cytec and purified/characterised as described in the supporting information†. The ionic liquid trioctylmethylammonium chloride $[N_{1,8,8,8}][Cl]$ (Sigma Aldrich) was also included for comparison as a hydrophobic ammonium ionic liquid.[12] Measurements of conductivity and fluidity ($\phi = \eta^{-1}$) were carried out using standard methods as described in the accompanying notes. Table 1 summarises some of the data obtained. $[P_{4,4,4,4}][Cyc]$ and $[P_{4,4,4,4}][Ace]$ were too viscous for measurement of η using the apparatus available (although this high viscosity supports our further findings).

The interdependence of ionic conductivity and viscosity is usefully considered by reference to the Walden plot of the data, as described by Angell *et al.*[10] On this plot an "ideal" line is constructed by using data for dilute aqueous KCl solutions as an exemplar of almost ideal behaviour and placing a unity gradient line through this data, as suggested by the Walden rule. Typically, data for ionic liquids fall below this ideal line because of the strong interaction between ions in the purely ionic medium, which renders

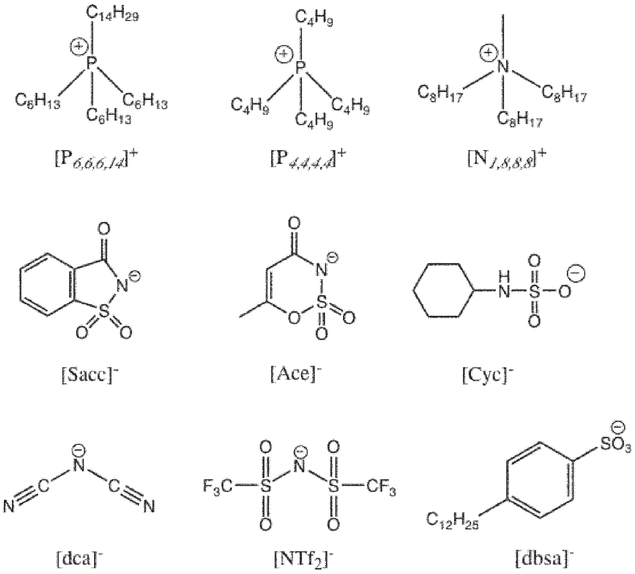

Fig. 1 Cation/anion combinations studied in this work.

---

[a] *School of Chemistry, Monash University, Clayton Vic 3800, Australia*
[b] *Department of Materials Engineering, Monash University, Clayton Vic 3800, Australia. E-mail: douglas.macfarlane@sci.monash.edu.au; Fax: +61 3 9905 4597; Tel: +61 3 9905 4540*

† Electronic supplementary information (ESI) available: full synthesis, ^1H NMR, ^{13}C NMR, discussion of thermal, physical and transport properties over temperature range 30–100 °C, and optimised geometries, electronic energies and zero point vibrational energies of ion pairs and the corresponding ions in the form of Gaussian archive entries. See DOI: 10.1039/b710014k

Table 1 Transport properties of phosphonium ILs at 40 °C

IL	Conductivity (S cm^{-1})	Viscosity (Pa. s)
[P$_{6,6,6,14}$][Cl]	9.5×10^{-6}	0.70
[P$_{6,6,6,14}$][Cyc]	8.9×10^{-6}	0.62
[P$_{6,6,6,14}$][dbsa]	6.7×10^{-6}	0.95
[P$_{6,6,6,14}$][Sacc]	3.0×10^{-5}	0.58
[P$_{6,6,6,14}$][NTf$_2$]	1.8×10^{-4}	0.15
[P$_{6,6,6,14}$][dca]	3.8×10^{-4}	0.12
[P$_{4,4,4,4}$][Sacc]	4.0×10^{-5}	1.58
[P$_{4,4,4,4}$][Ace]	1.5×10^{-4}	—
[P$_{4,4,4,4}$][Cyc]	8.7×10^{-5}	—
[N$_{1,8,8,8}$][Cl]	5.4×10^{-5}	0.57

the movement of most ions at least partially "correlated" with their immediate neighbours. The simplest example of such correlations is the ion pair, which is neutral and therefore does not contribute at all to the measured conductivity. Angell describes examples that lie more than an order of magnitude below the ideal line as "poor" ionic liquids, meaning that their ion conductivity is substantially less than would be expected on the basis of their viscosity. However, in the context of the application of these very interesting and useful liquids as solvents and electrochemical media, these cases might be more simply described as Liquid Ion Pairs (LIPs). Fig. 2 shows a Walden plot for the family of salts studied here, over the temperature range 30–100 °C. For comparison, ethylammonium nitrate (EAN) and α-picolinium triflate (αPic-Tf) from Angell[13] are also presented. The slope of the line with increasing temperature for each compound is 1 which indicates that the conductivity–fluidity relationship remains constant. In comparison to the ideal line it can be seen that all ionic liquids synthesised here lie below this line (for examples of materials that lie above the KCl line, see Bourlinos *et al.*[14]). Thus three of the eight ILs plotted ([P$_{6,6,6,14}$][Cl], [P$_{6,6,6,14}$][Cyc] and [P$_{6,6,6,14}$][dbsa]) could be described as Liquid Ion Pairs. [P$_{6,6,6,14}$][Sacc] and [N$_{1,8,8,8}$][Cl] lie on the borderline. The other salts, [P$_{6,6,6,14}$][dca], [P$_{6,6,6,14}$][NTf$_2$], and [P$_{4,4,4,4}$][Sacc] all lie well within an order of magnitude of the ideal KCl line and could be classified as true (or high ionicity) ionic liquids.

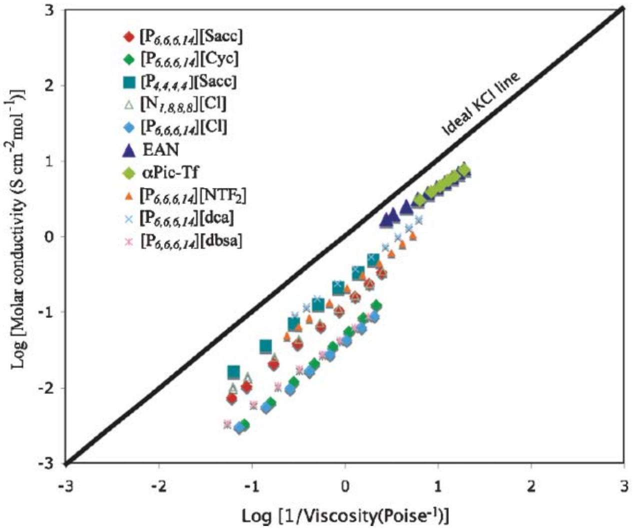

Fig. 2 Walden plot for phosphonium salts over temperature range 30–100 °C. Ethylammonium nitrate (EAN) and α-picolinium triflate (αPic-Tf) from ref. 10 for comparison.

As an example of these effects, [P$_{4,4,4,4}$][Sacc], although being almost three times more viscous (1.58 Pa.s at 40 °C) than [P$_{6,6,6,14}$][Sacc] (0.58 Pa s at 40 °C) nonetheless has similar conductivity, presumably because the degree of ion correlation and association is lower in the former case. Looking at this from a rather different point of view, one could consider [P$_{6,6,6,14}$][Sacc] to be surprisingly fluid given the size of the cation, but on consideration of its rather low conductivity, one realises that it is not behaving as a true ionic liquid and is better thought of as reflecting the properties of a liquid ion paired compound.

The deviations of the various ILs in Fig. 2 are summarised in Table 2 where ΔW is the vertical deviation from the ideal line. For the family of [P$_{6,6,6,14}$]$^+$ salts it can be seen that the deviation from the ideal line follows the trend; [Cl]$^-$ $\sim$ [Cyc]$^-$ $\sim$ [dbsa]$^-$ $>$ [Sacc]$^-$ $>$ [dca]$^-$ $\sim$ [NTf$_2$]$^-$.

To further investigate the role of ion pairs (and by implication larger ion aggregates) in the large ΔW observed for some of the salts, *ab initio* calculations of the corresponding ion pairs were carried out. Using molecular orbital theory calculations, the gas phase binding energy of each ion pair system was calculated and an anion displacement energy was obtained from this data. The anion displacement energies, ΔE_{disp}, are defined as binding energies relative to the ion pair with the lowest binding energy of the set (-321.6 kJ mol^{-1} for [P$_{4,4,4,4}$][NTf$_2$]); the displacement energy thus represents the energy of the gas phase anion exchange process: [P$_{4,4,4,4}$][NTf$_2$] + X$^-$ = [P$_{4,4,4,4}$]X + [NTf$_2$]$^-$. In the calculations a model cation [P$_{4,4,4,4}$]$^+$ was used instead of the [P$_{6,6,6,14}$]$^+$ cation due to the molecular size limitations of these high level calculations.

The calculated displacement energies are shown in Table 2, in which a negative ΔE_{disp} indicates a more tightly bound ion pair. From this it is seen that ion pairs [P$_{4,4,4,4}$][Cyc] and [P$_{4,4,4,4}$][Cl] are more strongly bound than [P$_{4,4,4,4}$][NTf$_2$] by almost 50 kJ mol^{-1}, thus indicating a tendency for very strong ion pairing in the former two ILs. It was found that the displacement energies (Table 2) tended to follow the trends in the Walden plot deviations.

Shown in Fig. 3 are the optimised structures for the calculated ion pairs. In the case of the [dbsa]$^-$ anion, the dodecyl chain was terminated at the hexyl position for the sake of calculational simplicity. In the case of the [Cl]$^-$ ion the strong binding appears to be the result of a single charged atom approaching quite closely to the positively charged centre of the cation. Note that the cation in this case has a distance to its extremities of approx. 6.3 Å; this distance might be considered to be a measure (in fact the upper bound) of the hydrodynamic size of the cation in the liquid state.

Table 2 Deviation of ILs from the ideal line in the Walden plot at 60 °C along with displacement energies (ΔE_{disp} in kJ mol^{-1}) calculated for the [P$_{4,4,4,4}$]$^+$ analogue

IL	ΔW ($\pm$0.1)	ΔE_{disp}
[P$_{6,6,6,14}$][Cl]	1.4	−46.0
[P$_{6,6,6,14}$][Cyc]	1.4	−48.5
[P$_{6,6,6,14}$][dbsa]	1.3	−44.7
[P$_{6,6,6,14}$][Sacc]	0.9	−32.4
[P$_{4,4,4,4}$][Sacc]	0.6	—
[N$_{1,8,8,8}$][Cl]	0.9	—
[P$_{6,6,6,14}$][dca]	0.6	−14.2
[P$_{6,6,6,14}$][NTf$_2$]	0.7	0.0

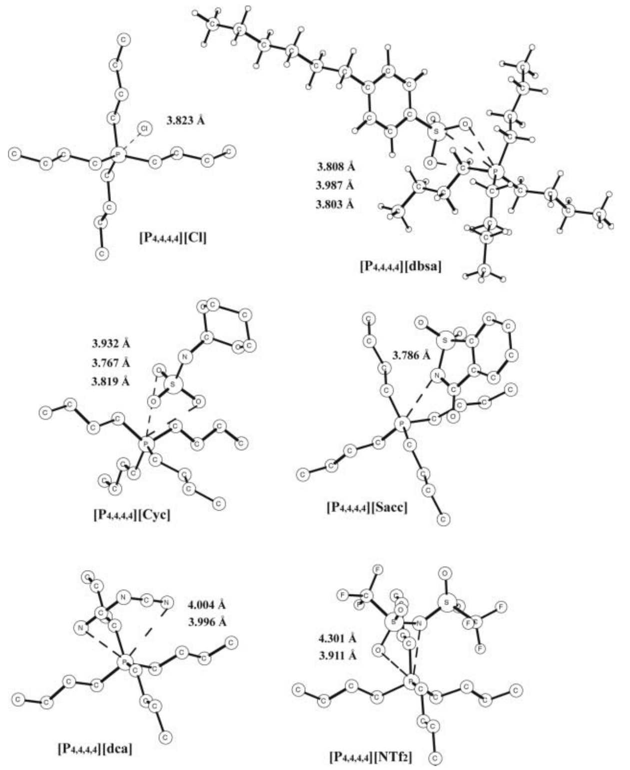

Fig. 3 B3LYP/6-31+G(d) optimised geometries and MP2/6-311+G(2df,p) binding energies of the gas phase $[P_{4,4,4,4}][X]$ ion pairs for X = $[Cyc]^-$, $[Cl]^-$, $[dbsa]^-$, $[Sacc]^-$, $[dca]^-$, $[NTf_2]^-$.

With the cyclamate anion there is equally close approach of all three binding oxygens, which are collectively good donor atoms despite the delocalisation of the charge. For all the other ions there is close approach (<4 Å) of at least one of the coordinating atoms, however the lower displacement energies indicates a weaker interaction.

Small spherical anions such as the halides can reside very close to the phosphonium centre. In turn, this would allow the alkyl chains of neighbouring phosphonium cations to align easily with respect to one another, thus effectively trapping the halide anion in a hydrophobic matrix. Fig. 4 shows an example of such a situation derived from a measured crystal structure for $[P_{10,10,10,10}][Br]$.[15] The Br^- ion in this case lies close to the phosphonium atom (4.8 Å) and well within the effective hydrodynamic radius of the cation ~13 Å. Structures such as this support the notion that bound ion-pairs dominate in these compounds, even in the ionic liquid state. With this in mind it is not surprising to see that $[P_{4,4,4,4}][Sacc]$ has a slightly higher degree of ionicity than $[P_{6,6,6,14}][Sacc]$ since the longer alkyl chains of the latter require a greater separation of anion from cation before the anion can move independently. Similarly, in $[N_{1,8,8,8}][Cl]$, the single methyl substituent provides sites near the nitrogen that are closer to the exterior of the cation and hence it exhibits a higher degree of ionicity than $[P_{6,6,6,14}][Cl]$.

The fact that some of these liquids lie in the liquid ion pair zone of the Walden plot does not necessarily mean that they are not of interest as solvents or media. Certainly their conductivity is lower than a true ionic liquid of comparable viscosity, however the high degree of ion pairing provides a range of other potentially useful and tunable properties. For example, if ion pairing is significant, it may be predicted that such compounds would exhibit higher vapour pressures. Indeed, these liquids are slightly volatile such that they can be removed by distillation; *e.g.* we have found that $[P_{6,6,6,14}][Cl]$ can be evaporated slowly at 0.1 Torr at 80 °C.

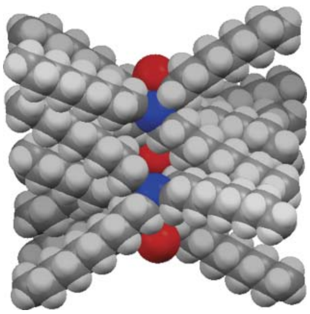

Fig. 4 Space filled crystal structure representation of $[P_{10,10,10,10}][Br]$ (crystal structure data from ref. 15). Phosphorus atoms are in blue and the bromide ions are in red. Some atoms are removed for clarity.

In conclusion, a Walden plot indicates that a number of phosphonium based ionic liquids appear to be of relatively low degree of ionicity due to strong ion pairing. The liquids can in some senses be thought of as liquid ion pairs. Lying between true molecular solvents and true ionic liquids they possess "intermediate", but nonetheless tunable properties. A slight degree of volatility is one consequence that is of value in some applications, as are the potentially adjustable solvency properties.

Funding is acknowledged in the form of a CRC smart print grant. Thanks also to Cytec for the samples of phosphonium salts used in this study. E.I.I. gratefully acknowledges general allocations of computing time from the Facility of the Australian Partnership for Advanced Computing.

Notes and references

1 K. Ohno, *Electrochemical Aspects of Ionic Liquids*, John Wiley and Sons, New Jersey, 2005.
2 P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.
3 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2083.
4 T. J. Wooster, K. M. Johanson, K. J. Fraser, D. R. MacFarlane and J. L. Scott, *Green Chem.*, 2006, **8**, 691–696.
5 C. J. Bradaric, A. Downard, C. Kennedy, A. J. Robertson and Y. Zhou, *Green Chem.*, 2003, **5**, 143–152.
6 T. Ramnial, D. D. Ino and J. A. C. Clyburne, *Chem. Commun.*, 2005, 325–327.
7 E. B. Carter, S. L. Culver, P. A. Fox, R. D. Goode, I. Ntai, M. D. Tickell, R. K. Traylor, N. W. Hoffman and J. H. Davis, Jr, *Chem. Commun.*, 2004, 630–631.
8 J. H. Davis, Jr, *US patent application* 2005194561 160 pp.
9 J. Pernak, F. Stefaniak and J. Weglewski, *Eur. J. Org. Chem.*, 2005, 650–652.
10 W. Xu, E. I. Cooper and C. A. Angell, *J. Phys. Chem. B*, 2003, **107**, 6170–6178.
11 H. Tokuda, S. Tsuzuki, M. A. B. H. Susan, K. Hayamizu and M. Watanabe, *J. Phys. Chem. B*, 2006, **110**, 19593–19600.
12 J.-P. Mikkola, P. Virtanen and R. Sjoeholm, *Green Chem.*, 2006, **8**, 250–255.
13 M. Yoshizawa, W. Xu and C. A. Angell, *J. Am. Chem. Soc.*, 2003, **125**, 15411–15419.
14 A. B. Bourlinos, K. Raman, R. Herrera, Q. Zhang, L. A. Archer and E. P. Giannelis, *J. Am. Chem. Soc.*, 2004, **126**, 15358–15359.
15 D. J. Abdallah, R. E. Bachman, J. Perlstein and R. G. Weiss, *J. Phys. Chem. B*, 1999, **103**, 9269–9278.