The Structure of Imidazolium-Based Ionic Liquids: Insights From Ion-Pair Interactions

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A large number of ab-initio (B3LYP/6–31+G(d,p)) computed ion-pair structures have been examined in order to determine if such calculations are capable of offering insight into the physical properties of the liquid state, particularly viscosity and melting point. Ion pairings based around the 1-butyl-3-methylimidazolium (C_4C_1im) cations and a range of anions (Cl, BF_4, and N(Tf)_2 where N(Tf)_2 is bis(trifluoromethylsulfonyl)imide) were chosen because of the range of viscosities exhibited by the corresponding ionic liquids. We have used these results to build up a ‘picture’ of the ionic liquid structure which is consistent with molecular dynamics simulations and experimental evidence. However, further work is required to established if such an analysis could be predictive. Nevertheless, we establish clear relationships relating ion-pair association energy, a derived ‘connectivity index’, and the diversity of structures with viscosity and melting point. Our calculations indicate that ions in C_4C_1imCl form a strong, highly connected and regular array thus rationalizing the high viscosity and melting point. In contrast the ion-pairs of C_4C_1imN(Tf)_2 form a weakly interacting, highly disordered, and low connectivity network consistent with the low viscosity and melting point. C_4C_1imBF_4 lies midway between these two extremes.

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In a statistical analysis of the melting points of pyridinium bromide ionic liquids the most important parameters were found to be coordination ability of the cation, electrostatic interactions, and conformational or rotational degrees of freedom. Thus we have examined ab-initio gas phase ion-pair calculations with these qualities in mind, extracting information on interaction strength, ion connectivity, and conformational diversity, and used these to develop relationships that offer insight into the physical properties (viscosity and melting point) of the liquid state. Ionic liquids based on the 1-butyl-3-methylimidazolium (C_4C_1im) cations and a range of anions (Cl, BF_4, N(Tf)_2) were chosen because they exhibit a range of viscosities and melting points.

The melting point gives an indication of the relative stability of the liquid versus the crystalline phase, and the viscosity an indication of the extent of ion–ion interactions, Table 1. Taking an average of the viscosities reported in Table 1, C_4C_1imCl has a very high viscosity and is essentially a solid at room temperature, C_4C_1imBF_4 (168 cP) is viscous, while C_4C_1imN(Tf)_2 (53 cP) is relatively fluid and the most viable ionic liquid for use in commercial applications. C_4C_1imCl and C_4C_1imBF_4 have no melting point but form an amorphous glass (the presence of a melting point for C_4C_1imCl is indicative of contamination by water), while C_4C_1imN(Tf)_2 has a distinct melting point. Perhaps a better relative evaluation can be obtained from (the averaged) glass transition temperatures which decrease in the order Cl (−69 °C) > BF_4 (−83 °C) > N(Tf)_2 (−91 °C).

Common rationalizations for the unusually low melting points of ionic liquids often refer to symmetry and ion size (Madelung constant), charge magnitude, and intercharge stabilization. This is, however, not the case for these particular ionic liquids, as Table 1 shows.

<table>
<thead>
<tr>
<th>Ionic Liquid</th>
<th>Viscosity at 298 K [cP]</th>
<th>Ref.</th>
<th>Melting Point (°C)</th>
<th>Ref.</th>
<th>Glass Transition Temperature (°C)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_4C_1imBF_4</td>
<td>92</td>
<td>[5]</td>
<td>−71</td>
<td>[9]</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

^A At 293 K.
Fig. 1. Stable conformers of (a) C$_4$C$_1$imCl, (b) C$_4$C$_1$imBF$_4$, and (c) C$_4$C$_1$imN(Tf)$_2$ (F atoms removed for simplicity). Lines indicate close contacts between atoms of the anion and cation.

Table 2. Dissociation energy [kJ mol$^{-1}$] and charge transferred [e] for ion-pairs with C$_4$C$_1$im

<table>
<thead>
<tr>
<th></th>
<th>Cl</th>
<th>BF$_4$</th>
<th>N(Tf)$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dissociation energy</td>
<td>375.55</td>
<td>344.96</td>
<td>315.26</td>
</tr>
<tr>
<td>Charge transfer</td>
<td>0.165</td>
<td>0.043</td>
<td>0.049</td>
</tr>
</tbody>
</table>

distance (Coulombic stabilization), as well as molecular interactions such as H-bonding, van der Waals forces, and π–π stacking. For example, crystalline phases are favoured by a high symmetry and a uniform (isotropic) charge distribution which allows for better packing. The presence of non-charged groups, asymmetric ions, or rotational and vibrational freedom can break up the lattice structure and increase inter-charge distances, thereby lowering the stability of the crystalline phase. These rationalizations are couched in general terms, however we are able to provide explicit conforming evidence in the form of energies and structures that allow a more specific ‘picture’ of the ionic liquid structure to emerge.

An estimate of the ionic strength of interaction can be obtained from ion-pair (Fig. 1) dissociation energies, which decrease C$_4$C$_1$imCl > C$_4$C$_1$imBF$_4$ > C$_4$C$_1$imN(Tf)$_2$ (Table 2). Numerous conformers exist for these ion pairings, however those shown in Fig. 1 represent the most stable we have identified to date. BSSE corrections (employing the counterpoise method)[15,16] are small, 1.17, 2.78, and 6.97 kJ mol$^{-1}$ respectively for the conformers shown in Fig. 1. In a liquid, more ions will be interacting, however, the total amount of stabilization is anticipated to be qualitatively the same across the series of anions.

Melting points and viscosity are dependent in part on local interactions between an ion and other molecules in the first solvation shell. An examination of ion-pair structures shows that the Cl anion forms a small number of very strong contacts, while the BF$_4$ and N(Tf)$_2$ anions form a larger number of weaker interactions, each approximately one quarter the strength of the Cl interaction. Strong interactions will enhance residence times for the first solvation shell, and contribute to ordering within the liquid. Multiple weak interactions may also enhance residence times through a chelating effect.

Interactions between the ions are dominated by Coulombic forces, and at close range will vary depending on the charge distribution within an anion. A measure of the covalent character of an interaction can be inferred from the amount of electron transfer as indicated by the natural charge determined from a natural bond orbital (NBO) analysis (see Computational Details for more information).[17] The charge transferred is more significant for the Cl based ion pair (Table 2). Interestingly, because less charge has been transferred the BF$_4$ and N(Tf)$_2$ anions are more ‘ionic’ than the Cl anion, however as these molecules are larger the charge is also more diffuse (consistent with the lower binding energies).

For imidazolium based cations nine sites of interaction are favoured by the anions, these include those shown in Fig. 2 and two sites above and below the C$_2$–H bond. Classical and ab-initio molecular dynamics simulations, as well as neutron diffraction experiments of imidazolium-based ionic liquids show that these sites are favoured by anions in the first solvation shell around a cation.[18–22] The relative stabilization of a particular anion site can be inferred from the relative stability of a single cation–anion pair, these vary from about 0 kJ mol$^{-1}$ for the front and top structures to +35 kJ mol$^{-1}$ for side structures and +60 kJ mol$^{-1}$ for back structures of C$_4$C$_1$imCl.[23] However, not all of these sites are occupied at one time, factors affecting occupancy include; size of the anion, charge on the anion contact points, stability of a site, and the proximity of sites. In the following we examine each of these points comparing and contrasting the anions Cl, BF$_4$, and N(Tf)$_2$.

Natural charges determined from B3LYP/6–31++G(d,p) optimized structures for the free anions are provided in Table 3. The fluorine atoms of BF$_4$ individually carry about two thirds the
charge of a single Cl anion. Perhaps more surprising is the extent of charge polarization on the N(Tf₂)₂ anion; key interaction sites are the oxygen and nitrogen atoms, which carry charges comparable to the isolated Cl anion, while the fluorine atoms carry only a minimal negative charge. The charges shown for N(Tf₂)₂ vary significantly from those predicted by approaches based on the electrostatic potential (ESP), and justify a short discussion of the different methods for predicting atomic charges. Because atomic charges are not observables, their generation can be a contentious issue. Methods based on the ESP (an observable) are usually employed when determining charges for use in classical simulations, while methods based on the electron density (an observable) are usually employed when examining bonding within a molecular species. The same molecular structure (density and ESP) can produce very different atomic charges depending on the method of analysis.

Methods based on the ESP estimate charges from a least-squares fit to the potential at specific points around a molecule. It is a well known problem that charges on interior atoms are not well defined because the fit is made to points outside the van der Waals radii, and thus the same external ESP can be accurately reproduced by two fits with widely different charges on the interior atoms. Predicted charges can also be highly conformationally dependent, and are dependent on the distribution of fit points around the molecule.[24,25] Thus while the ESP is accurately reproduced, the electronic distribution within the molecule is less well predicted. The NBO method describes bonding in terms of ‘natural orbitals’ which are adapted to the molecular environment, for example the NBO method accurately represents the atomic orbitals of a negatively charged atom, which can differ significantly from those of a neutral atom, not only near the core but also in the outer nodes where Pauli repulsion (due to interaction with other orbitals) is important.[26] While an optimal orbital description is produced the detailed ESP is less well predicted (the overall charge is accurate). Thus precedence cannot be placed on either method for a more or less accurate representation of atomic charges.

Coulombic repulsion makes it energetically unfavourable for sites of close proximity (around the cation) to be occupied simultaneously by two highly charged anions. For example, it is unlikely that two Cl anions will concomitantly occupy the two front sites, since this would place them only 1.73 Å apart. Examination of the crystal structures for C₄C₁imBF₄ shows that these sites are not occupied at the same time.[27,28] However, it can be seen from the C₄C₁imBF₄ ion-pair shown in Fig. 1b, that a larger anion with more contact points, each of which carries a smaller charge, can populate both sites simultaneously. Such an arrangement does not occur for the N(Tf₂)₂ anion because the oxygen and nitrogen atoms are too highly charged. Thus, it is possible for Coulomb repulsion between anions to limit the occupation of adjacent sites.

When a single large anion occupies adjacent sites the number of anions in the first solvation shell is reduced. However, the anion must be able to fit in the available space, and to conformationally and energetically make the required contacts. For example, the fluorine atoms of the BF₄ anion shown in Fig. 1b simultaneously occupies three sites, the two front sites and a top site above the C²⁻–H bond. Analysis of the many stable ion-pair conformers of BF₄ and N(Tf₂)₂ based ion pairs, shows that for anions of sufficient size additional interactions also occur with the hydrogen atoms of the alkyl chains.

The number of ways an anion can H-bond with the cation is important. The Cl anion is spherical and hence offers only one conformer in this respect. The BF₄ anion is tetrahedral, and can probably rotate in place with little cost in energy, consistent with the low energy of the H-bonds formed, the disorder found for BF₄ in crystal structures,[31] and the ‘spinning’ motion found for PF₆ in molecular dynamics studies.[32] Because the fluorine atoms are symmetrically arranged, rotated structures will appear identical. The N(Tf₂)₂ anion is less symmetrical, and an ‘in-place’ barrel like rotation is unlikely to be as energetically favourable because of the size of the anion, and its chelating ability. Moreover, rotations of this type are unlikely to produce conformers that appear identical. Rotation of one ‘arm’ of the anion relative to the other however, is expected to be favourable; the computed barrier to this rotation is low.[29,33] both cis and trans crystal structures occur[34] and interconversion is experimentally thermally accessible.[35,36] The key point here is that the loss of symmetry Cl > BF₄ > N(Tf₂)₂ plays an important role in determining the number of distinguishable H-bond conformers that can be formed.

We now consider the structural motifs of each anion in turn, highlighting the ability to form both ‘internal’ ion-pair cation–anion contacts, and then external ‘network’ forming cation–anion–cation contacts. There are nine possible sites for the Cl anion around the cation, however linear H-bonds at the rear of the ring are unlikely.[23] The remaining seven sites can all be occupied over time, however the top and front, or the two front sites, cannot be occupied at the same time (due to Coulomb repulsion), and thus at any given point in time the cation is likely to have only five sites occupied. These conclusions are consistent with molecular dynamics and neutron diffraction data which determine a first solvation shell coordination number between five and seven.[20,22] However, not only the ‘internal’ interactions of an ion-pair are important in the liquid, the number of ‘external’ connections each anion, makes with other cations will impact on the physical properties of the liquid. Crystal structures indicate that each Cl anion interacts with approximately four distinct cations.[23,27,28] Thus if each of the five interaction sites around the cation is filled by a Cl anion, and then each Cl anion interacts with another four cations, each cation is connected to 5 × 4 = 20 other cations. We define this number as the ‘connectivity index’ for the C₄C₁imCl ionic liquid.

Representative stable structures for the BF₄ ion pairs are shown in Fig. 1a (most stable configuration) and Fig. 3 (conformers a, b, and c, which lie 32.46, 33.91, and 45.10 kJ mol⁻¹ higher in energy respectively). A single BF₄ anion can occupy multiple cation sites, and the first solvation shell consists of approximately four BF₄ anions. However, over time a BF₄ anion may coordinate in a slightly different manner, for example, a ‘top’ coordinating anion (Fig. 1a), could be replaced by a ‘bottom’ coordinating anion, or the ‘bottom’ coordinating anion of Fig. 3c, could coordinate at the ‘top’ of the ring, lifting the time averaged coordination to approximately six BF₄ anions which
These show significant variation in binding motif due to structural flexibility, number of contact points, and size of the N(Tf)₂ anion. These features will lead to a highly disordered environment. Hence the weak interactions, configurational variation, and low connectivity allow us to rationalize (in part) the high viscosity and high ‘melting point’ of C₄C₁imCl.

At the other end of the scale, C₄C₁imN(Tf)₂, has a much lower association energy, more H-bonds are formed, but each contributes less to the overall stability of the ion-pair. Because this anion can span the full width of the imidazolium ring only two anions are required to ‘encapsulate’ a cation. However, the low energy structural changes that N(Tf)₂ can undertake lead to a highly disordered environment. Hence the weak interactions, configurational variation, and low connectivity allow us to rationalize (in part) the low melting point and low viscosity of C₄C₁imN(Tf)₂.

The viscosity and glass transition temperature of C₄C₁imBF₄ lie between those of the highly structured and ‘ionic’ liquid C₄C₁imCl and the more mobile ‘molecular’ ionic liquid C₄C₁imN(Tf)₂. The association energy of the ion-pair lies 30 kJ mol⁻¹ less than C₄C₁imCl and 30 kJ mol⁻¹ more than C₄C₁imN(Tf)₂. The BF₄ anions are large enough to occupy more than one cation site simultaneously, but not large enough to encapsulate the cation, and hence the connectivity index is slightly higher than for C₄C₁imN(Tf)₂. McLean et al. have also suggested that PF₆ (which is similar to BF₄ in this context) has a greater cross-linking ability compared to N(Tf)₂. The small size of the boron and fluorine atoms, and tetrahedral symmetry, place the fluorine atoms in an almost ideal position for interacting with multiple hydrogen atoms of the C₄C₁im cation. The tetrahedral symmetry also reduces the number of distinguishable conformations, and makes the formation of a regular pattern in H-bonding more likely (for example similar to, but not as regular or as strong as that of water). Thus while the BF₄ anion forms H-bond interactions of a similar strength to N(Tf)₂ the smaller size and symmetry of the ion ensure a more regular and better

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Fig. 3. Stable minima obtained for C₄C₁imBF₄ ion pairs at the B3LYP/6–31+G(dp) level, (a) BF₄ anion occupying the side-but and back-but sites of the cation, (b) BF₄ anion occupying the side-meth and back-meth sites, and (c) BF₄ anion occupying the two back sites.
connected network, leading to a higher viscosity and ‘melting point’.

Thus in conclusion, careful examination of relative energies and structural interactions (such as ion position, H-bonding and anion conformational variability) in gas-phase ion-pairs has highlighted how these quantities can be used to build up a picture of the local structure and interactions occurring in ionic liquids. C₄C₁imCl forms a highly connected liquid with relatively strong interactions, the high symmetry and charge density of the anion are important in forming a more regular network. In contrast, C₄C₁imN(Tf₂) forms a low connectivity network of weakly linked ions, and possibly small clusters, that are highly disordered due to the asymmetry, shielding, and conformational variety of the anion. C₄C₁imBF₄ lies midway between these two extremes, forming a weak but more regular network. Used judiciously and in concert with experimental data ab-initio calculations of gas-phase ion-pairs can be used to gain insight into the properties of ionic liquids.

Computational Methods

DFT calculations using Becke’s three-parameter exchange functional[40] in combination with the Lee, Yang, and Parr correlation functional[47] (B3LYP) have been carried out with a 6–31+G(d,p)[48–50] basis set as implemented in the Gaussian 03 suite of programs.[51] Structures have been fully optimized under no symmetry constraints, and the B3LYP structures confirmed by frequency analysis. Details of the optimization procedures are reported elsewhere.[23] Because these are interacting ion-pairs errors introduced by the inability of DFT to recover dispersion effects are expected to small except in the structures where a top coordination is indicated.[23] B3LYP has been shown to produce a reasonable correlation with MP2 data and experiment for systems containing hydrogen bonds.[52]

Population analysis was carried out using the Natural Bond Orbital (NBO) method (version 3) implemented in Gaussian 03.[56,53–56] From a purely theoretical standpoint no priority should be assigned to any population analysis method. However the natural bond orbital method is based on the electron density which is an observable, and is rigorous in that the natural orbitals are eigenvectors of a reduced one-particle density matrix, moreover they are orthonormal and represent a maximum occupancy criteria.[17] NBO orbitals are independent of the chosen basis to the extent that the density operator is basis set independent, and thus it is well known that natural orbitals do not exhibit a strong basis-set dependence (unlike the population analysis method of Mulliken).[57]

Acknowledgments

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References


[57] F. Jensen, Introduction to Computational Chemistry 1999, Ch. 9 (John Wiley: Chichester).