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Liquid structure of 1, 3-dimethylimidazolium salts

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Abstract

The structure of liquid 1, 3-dimethylimidazolium hexafluorophosphate is described in detail and compared with the structure of 1, 3-dimethylimidazolium chloride. In each case, the data were obtained from neutron diffraction experiments and analysed using an empirical potential structure refinement process. Overall, the structures are similar; however, significant differences arise from the variation in anion size.

1. Introduction

The field of ionic liquids [1] has attracted much interest recently for applications in, for example, clean synthesis [2] and electrochemistry [3], and as new materials [4]. This interest has increased because of the ability to tailor the physical properties of the ionic liquids by simply changing the anion or the alkyl chain length on the cation and their (effectively) zero vapour pressure [5]. Ionic liquids are distinguished from molten salts by virtue of their low melting points (typically <100–150 °C). This feature arises because of their composition comprising of a large asymmetric organic cation, which in many cases is based upon 1, 3-dialkylimidazolium cations (figure 1), normally coupled with large, weakly coordinating anions [6–9].

Little is known of the structure of any ionic liquid where one or both of the ions is highly *non-spherical*, yet it is this structure which governs many of the physical properties used in reactive chemistry, such as viscosity and density. The liquid structure of simple salts has been determined using a range of techniques, including neutron diffraction. For example CuBr [10] and NaCl–AlCl₃, and analogous mixtures [11, 12], have been studied extensively. For low-temperature ionic liquids, however, the only studies to date have been associated with binary ionic liquids comprised of either AlCl₃ with LiSCN [13] and [C₂mim]Cl [14] or HCl with [C₂mim]Cl [15, 16].

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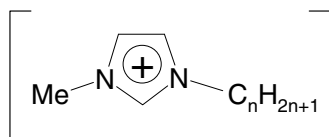


Figure 1. 1-alkyl-3-methylimidazolium $[C_n\text{mim}]^+$ structure, where $n = 1$; the structure represents the $[\text{dmim}]^+$ ion studied in this paper.

In a previous study in our laboratories, neutron diffraction data have been used to examine the structure of 1, 3-dimethylimidazolium chloride [17]. A close relationship between the crystal structure and the liquid structure was found in this system showing the importance of hydrogen bonding interactions particularly with respect to the imidazolium ring hydrogens. As part of an ongoing investigation into understanding the properties of ionic liquids from a molecular interaction perspective, Hanke *et al* [18] have also developed intermolecular potentials which have been used to simulate ionic liquids. The structures derived from these simulations and those from the experimentally determined neutron diffraction data are well matched [17].

In this paper we describe the liquid structure of 1, 3-dimethylimidazolium hexafluorophosphate salt, $[\text{dmim}][\text{PF}_6]$ (figure 1 where $n = 1$) and compare this structure with that previously determined for the chloride salt.

2. Experimental details

The hexafluorophosphate samples were prepared from the fully protiated, fully deuteriated (i.e. both the ring hydrogens and methyl hydrogens were isotopically exchanged), ring deuteriated (i.e. where only the ring hydrogens were isotopically exchanged) and side-chain deuteriated (i.e. where only the methyl hydrogens were isotopically exchanged) chloride salts [19] by metathesis with $[\text{NH}_4][\text{PF}_6]$. In each case, the standard literature procedure was followed [20]; however, for the preparation of the fully deuteriated and ring deuteriated salts, $[\text{NH}_4][\text{PF}_6]$ in D_2O was used to ensure that no proton exchange occurred and the imidazolium ring remained deuteriated. Each sample was a white crystalline solid and was analysed by ^1H and ^2H NMR, infrared and elemental analysis and showed $>97\%$ isotopic exchange. All samples were dried as liquids under high vacuum at 400 K, cooled and stored in a N_2 filled dry box prior to being loaded into the sample cells.

The samples were heated to 400 K in aluminium sample holders with 0.2 mm thick vanadium windows sealed using a PTFE-coated Viton 'o'-ring whilst in the diffraction vacuum chamber and left for 10 min to equilibrate before measurements were taken. The temperature was maintained to $\pm 0.1^\circ$ using a Eurotherm PID temperature controller. After normalization with respect to the cell, spectrometer and the vanadium window, good reproducibility was found between the sample cells. The neutron diffraction data were taken using the SANDALS diffractometer at the ISIS pulsed neutron source, Rutherford Appleton Laboratory, UK. This instrument has a wavelength range 0.05–4.5 Å and data are taken over the Q -range 0.05–50 Å $^{-1}$.

Data analysis was performed using the ATLAS package [21]. Differential scattering cross-sections for the four samples with different hydrogen isotope substitutions, as listed in figure 2, were extracted in order to highlight the ion–ion structure. The atomic density of the liquid was taken as 0.085 atoms Å $^{-3}$ [18].

To generate the partial radial distribution functions and spatial ion density distribution, the differential cross-sections were subjected to an empirical potential structure refinement

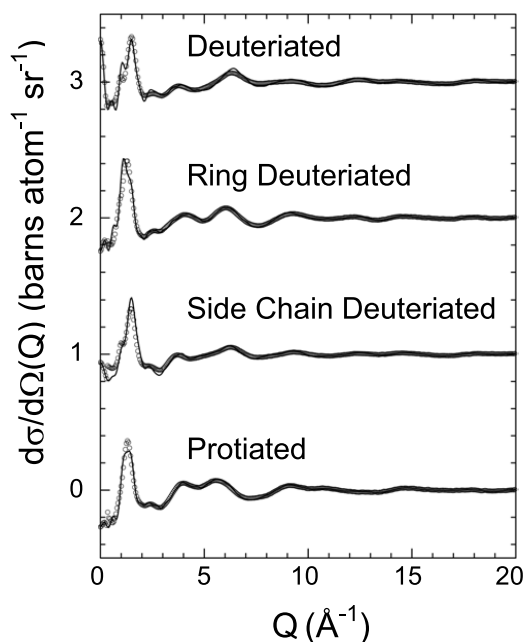


Figure 2. Experimental (circles) and EPSR fitted (solid curve) differential cross-sections as a function of Q for the fully protiated, fully deuteriated, ring deuteriated and side-chain deuteriated 1, 3-dimethylimidazolium hexafluorophosphate.

(EPSR) process, which attempted to generate configurations of molecules and ions, which are consistent with the diffraction data. The details of this method have recently been reported [22]. The full parameters of the reference potential used are given in table 1. EPSR gives a ‘best estimate’ of the pair correlation functions based on the diffraction data supplied, but also subject to the input constraints on molecular structure, molecular overlap and atomic charge distribution. There is the possibility of ambiguity in the derived structure. However, because the structure is dominated by the charges on the different molecules, and because this structure must also fit the measured data, it is likely that EPSR will capture the essential features of the ion–ion distribution functions presented in this paper.

3. Results and discussion

Figure 2 shows the experimental and EPSR modelled differential cross-sections as a function of Q , for liquid 1, 3-dimethylimidazolium hexafluorophosphate salts derived from the total structure factors for each sample. In each case, there is good agreement between the model and experimental data. Figure 3 shows the partial radial distribution functions for the anion around the imidazolium cation and the imidazolium cation around the imidazolium cation extracted from the EPSR model in both [dmim]Cl and [dmim][PF₆]. As reported for the chloride [17], charge ordering is found in the liquid [dmim][PF₆] and overall the radial distribution functions for the different anions are similar. However, in all the shells there is an expansion of the liquid network in the hexafluorophosphate salt relative to the chloride. For example, the first anion shell in the chloride is centred at ~ 4.3 Å compared with ~ 5.0 Å in the hexafluorophosphate. The increase in the cation–cation and second anion–cation distances are clearer than for the first shell, as expected. The expansion is due to the relative size of the two anions. The chloride

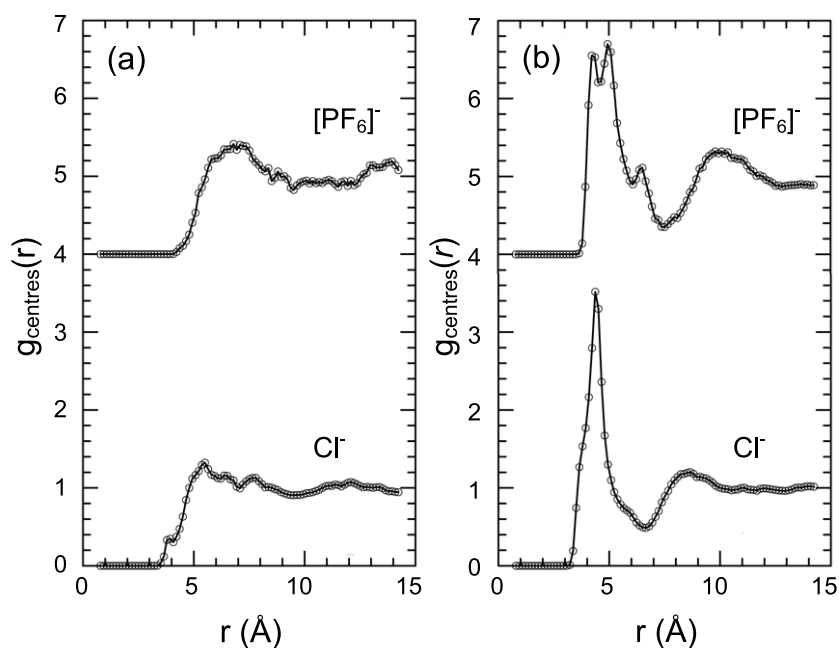


Figure 3. Comparison of the partial radial distribution functions for (a) the cation–cation distribution and (b) the cation–anion distribution for the 1, 3-dimethylimidazolium hexafluorophosphate and chloride salts derived from the EPSR model. Each radial distribution function is calculated from centre of the imidazolium ring and, in the case of $[\text{PF}_6]^-$, from the phosphorus atom.

Table 1. Lennard-Jones and Coulomb parameters used for the reference potential of the simulation of liquid 1, 3-dimethylimidazolium hexafluorophosphate. The charges were derived from Hanke *et al* [18]. The carbon and nitrogen atoms are defined as their position on the *molecular* skeleton with M referring to the methyl groups. The hydrogen atoms, $\text{H}(x)$, are defined as being bonded to carbon atom x . The Lennard-Jones parameters for interactions between unlike atoms were calculated by employing the usual Lorentz–Berthelot mixing rules.

Atom	σ (Å)	ε (kJ mol $^{-1}$)	q/e
H(2)	0.0	0.0	0.097
C(2)	3.9	0.79396	0.407
H(4,5)	0.0	0.0	0.094
C(4, 5)	3.9	0.79396	0.105
N(1, 3)	3.4	0.57341	−0.267
C(M)	3.9	0.79396	0.124
H(M)	0.0	0.0	0.064
P	2.2	7.177	0.740
F	2.66	0.59560	−0.290

is much smaller than the hexafluorophosphate and allows significantly tighter packing of the ions; hence the change observed. Integration of the first shell in the anion radial distribution up to 7.5 Å from the cation shows that the hexafluorophosphate–cation coordination number is approximately 6.8.

The probability distributions for $[\text{PF}_6]^-$ anion around the imidazolium cation and the imidazolium cation around the imidazolium cation extracted from the EPSR model are

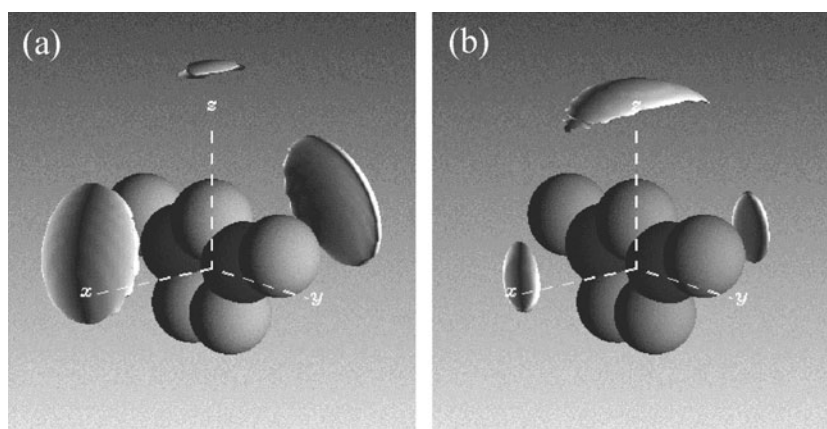


Figure 4. Probability distributions of (a) the hexafluorophosphate anion and (b) the chloride anion around a central imidazolium cation in [dmim][PF₆] and [dmim]Cl, respectively, derived from the EPSR model. In each case the distributions are of the probability of finding 2.5% of the ions out to a distance of 9 Å.

shown in figures 4 and 5. At high probabilities, shown in figure 4(a), the position of the hexafluorophosphate anion with respect to the cation is predominantly in positions facing the imidazolium ring, although there is some density axial to the hydrogen at the C(2) position on the ring (H(2)), whereas in the chloride salt, the main interaction is with the H(2) position. The comparison between the anion–cation interactions in the hexafluorophosphate and chloride salts is shown in figure 4. This difference largely reflects the relative hydrogen bonding ability of the two anions. The [PF₆][−] anion weakly hydrogen bonds and therefore its position is determined mainly by coulombic forces, i.e. towards the ring where the positive charge is concentrated, compared with the much stronger hydrogen bonding character of the chloride resulting in the initial dominant interaction being associated with most acidic hydrogen in the cation (H(2)). Using molecular dynamics simulations, Hanke *et al* also observed that the anion distribution in the chloride was much more defined than that found for the hexafluorophosphate. In both salts, however, the simulations indicated that the anion was still strongly associated with the ring hydrogens and little with the ring itself, unlike the distributions found in the present study. As the probability decreases, shown in figure 5(a), the hexafluorophosphate contact with all the ring hydrogens increases, i.e. with both the hydrogens at the C(4) and C(5) positions on the imidazolium ring (H(4, 5)) as well as with H(2). At very low probabilities, some anion density is found axial to the methyl groups. With the exception of the deviation at high probability, described above, similar distributions are found for both the chloride and hexafluorophosphate salts [17].

The cation–cation distribution, shown in figure 5(b), is significantly less evenly distributed in the case of the hexafluorophosphate salt compared with the chloride salt which was essentially spherical. As described above, the larger size of the [PF₆][−] anion prevents two imidazolium cations being in close proximity in the region where the anion is located. As a result, regions of low cation density face the ring, for example, and the cations and anions occupy almost mutually exclusive positions around a central imidazolium cation. Similar mutually exclusive distributions are found for the distribution of the anion and cation around a central [PF₆][−] ion, shown in figures 5(c) and (d), respectively. It is interesting to note that the anions reside along the P–F bond directors whereas the cations associate strongly with the

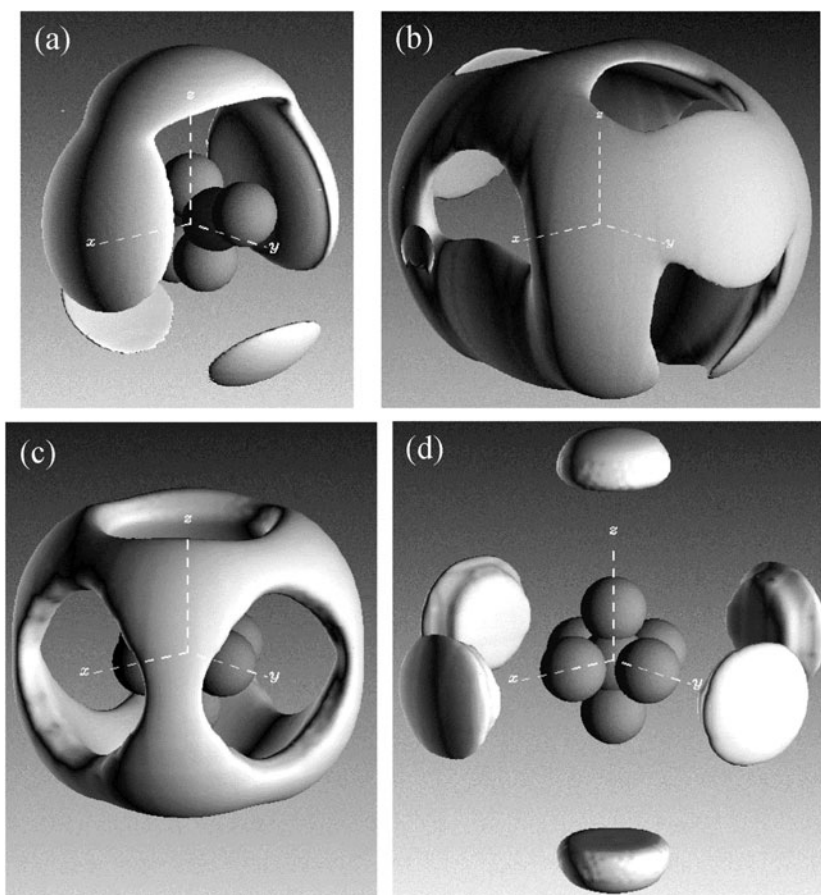


Figure 5. Probability distribution of (a) hexafluorophosphate anion around an imidazolium cation, (b) the imidazolium cation around an imidazolium cation, (c) the imidazolium cation around a hexafluorophosphate anion and (d) the hexafluorophosphate anion around a hexafluorophosphate anion derived from the EPSR model. In each case the distributions are of the probability of finding 20% of the ions out to a distance of 9 Å.

three fluorines on the faces of the octahedron in order to maximize the interaction with the sites of negative charge.

The partial radial distribution functions for the significant hydrogen–hydrogen contacts are shown in figure 6. Unsurprisingly, the closest cation–cation intermolecular contacts occur between the hydrogens on the cation. However, unlike in the chloride salt, where H(M)–H(M) and H(M)–H(2) contacts were observed, the only significant contacts in the $[\text{PF}_6]^-$ salt occur between methyl hydrogens (H(M)). The H(M)–H(M) contacts, in the $[\text{PF}_6]^-$ salt, are centred at 3.5 and 8.0 Å for the first and second cation shells, respectively, with there clearly being a second cation distance, unlike for the chloride salt where the imidazolium shells are less clearly defined.

As found for the dimethylimidazolium chloride salt, the solid-state crystal structure [23] and the liquid structure of $[\text{dmim}][\text{PF}_6]$ are very similar. Strikingly, the large ‘holes’ present in the cation–cation distribution described above are also present in the solid state. The short cation–cation contacts found in the solid state are also between methyl hydrogens and no

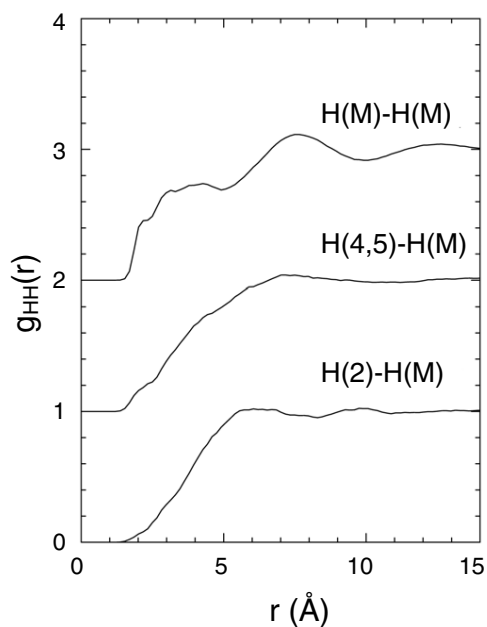


Figure 6. Partial radial distribution functions for the cation hydrogen–cation hydrogen distributions.

interaction between the H(2) and H(M) positions is observed. Unlike in the liquid structure, no $[\text{PF}_6]^-$ density is found associated with the H(2) position with the anion mainly interacting with the ring centres.

4. Conclusions

Overall the structures of 1, 3-dimethylimidazolium chloride and hexafluorophosphate are very similar despite the difference in hydrogen bonding ability. However, due to the size of the hexafluorophosphate anion compared with the chloride, the structure is expanded. Unlike for the chloride salt, the spatial distributions of the anions and cations in the hexafluorophosphate salt have an almost mutually exclusive arrangement. For both salts, the crystal and liquid structures correlate well.

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