Liquid Structure of 1-Butyl-3-methylimidazolium Hexafluorophosphate by Neutron Diffraction with H/D Isotopic Substitution Method

Mitsuhiro Kanakubo,*† Takuji Ikeda,* Takaumi Aizawa,* Hiroshi Nanjo,* Yasuo Kameda,** Yuko Amo,** and Takeshi Usuki**

*National Institute of Advanced Industrial Science and Technology (AIST),
4-2-1 Nigatake, Miyagino, Sendai 983-8551, Japan
**Department of Material and Biological Chemistry, Faculty of Science, Yamagata University,
1-4-12 Kojirakawa-machi, Yamagata 990-8560, Japan

The liquid structure of the ionic liquid 1-butyl-3-methylimidazolium hexafluorophosphate, [BMI]PF$_6$ was investigated by neutron diffraction with H/D substitution method, where the hydrogen atoms in the imidazolium ring were partially deuterated. The local structures around the ring hydrogen atoms in liquid are very similar to those estimated from the crystal structure.

(Received April 2, 2008; Accepted June 12, 2008; Published October 10, 2008)

Introduction

Room temperature ionic liquids (RT-ILs) have attracted much attention as green solvents in a wide range of applications such as reaction and separation chemistry, electrolyte devices, and material synthesis owing to a negligibly small vapor pressure, high thermal and chemical stability, sufficient electrochemical competence, and desirable solvent properties that can be adjusted by modifications of cation and anion structures. There have been a number of studies on the physical properties of RT-ILs; however, little is known of their liquid structures. Hardacre and coworkers have recently carried out neutron diffraction experiments for 1,3-dimethylimidazolium salts, [MMIM]X, of which the cation has $C_3$ symmetry, with chloride, hexafluorophosphate, and more bulky bis(trifluoromethylsulfonyl)amide. In their papers, the anion effect on the liquid structure was discussed carefully; however, there have been no reports that study the liquid structures of imidazolium salts with different alkyl chains in the cations.

Here, we investigate the liquid structure of 1-butyl-3-methylimidazolium hexafluorophosphate, [BMI]PF$_6$ (Fig. 1). This hydrophobic IL has been used and studied more extensively as a typical example because the asymmetric and intermediate alkyl substituents at the 1,3-positions in the imidazolium cation effectively decrease the melting point. In short-chain ILs electrostatic cation-anion interactions are very strong, leading to salts with high lattice energy and higher melting points, whereas in long-chain ILs hydrophobic alkyl chain-chain interactions govern the higher melting points. Recently, the crystal structure of [BMI]PF$_6$ demonstrates that the intermediate butyl chain-length structure can show unique features of both short- and long-chain analogs. In the present study, time-of-flight neutron diffraction measurements were carried out for H/D isotopically substituted [BMI]PF$_6$ samples, where the hydrogen atoms in the imidazolium ring were partially deuterated with the hydrogen atoms in the alkyl chains remaining natural. The local structures around the ring hydrogens were discussed in comparison with the crystal structure.

Experimental

Reagents and chemicals

First, the isotopically natural [BMI]PF$_6$ was synthesized and purified as described previously. Then, the hydrogen atoms in the imidazolium ring were partially deuterated with the hydrogens in the alkyl chains remaining natural. Three kinds of deuterated samples were synthesized: 2,4,5-deuterated (all the ring hydrogen atoms deuterated), 2-deuterated (4,5-protonated), and 4,5-deuterated (2-protonated) samples. All the ring hydrogen atoms in the imidazolium ring were deuterated as follows. The natural [BMI]PF$_6$ was mixed with an excess amount of CD-OD in the presence of K$_2$CO$_3$ at 50°C for 1 day. After evaporation of methanol, this procedure was repeated once again. Then, the sample was washed with D$_2$O five times or more to eliminate K$_2$CO$_3$. The 2-positioned hydrogen atom in the imidazolium ring, which is much more acidic than 4,5-hydrogens, was partially replaced by deuterium without K$_2$CO$_3$ in a similar manner. The 4,5-deuterated sample was prepared by

![Fig. 1 Structure of 1-butyl-3-methylimidazolium hexafluorophosphate with the numbers specified for the ring hydrogen atoms.](image-url)
mixing the 2,4,5-deuterated [BMIM]PF₆ with CH₃OH, which reversely caused the protonation at 2-hydrogen atom. All the samples were dried under vacuum at 70°C for 30 h. The isotopic compositions of the samples were determined by the signal integrals of ¹H NMR.

**Apparatus**

The neutron diffraction measurements were carried out at 25°C using the HIT-II spectrometer installed at the Neutron Science Laboratory (KENS). The sample cell was made from Ti-Zr null-alloy (8 mm inner diameter with 0.3 mm thick). The data acquisition time was approximately 12 h for each sample solution. The diffraction measurements were made for an empty cell, instrumental background, and vanadium rod (8 mm outer diameter), respectively. The scattering intensities observed for each sample were corrected for the instrumental background, absorption of both the sample and cell, and for multiple and incoherent scatterings. The effect of inelastic scattering due to residual protons was eliminated on the basis of the experimental results of null-H₂O. The data were analyzed as described previously.

### Results and Discussion

The five deuterated samples (I – V) with different H/D isotopic ratios of the ring hydrogen atoms in [BMIM]PF₆ were used for the neutron diffraction measurements as listed in Table 1. The samples IV and V are 1:1 mixtures of (I and II) and (I and III), respectively.

The first-order difference functions, $\Delta_t(Q)$, were derived from the numerical differences between the fully corrected scattering cross sections of the samples (I and II), (I and III), (I and IV), and (I and V), which are represented by $\Delta_{t,5.6}(Q)$, $\Delta_{t,6}(Q)$, $\Delta_{t,56}(Q)$, and $\Delta_{t,6}(Q)$, respectively. The $\Delta(Q)$, scaled to stoichiometric units, can be expressed by a linear combination of partial structure factors in terms of the hydrogen atoms:

$$\Delta(Q) = A[a_{aod}(Q) - 1] + B[a_{aod}(Q) - 1] + C[a_{aod}(Q) - 1] + D[a_{aod}(Q) - 1] + E[a_{aod}(Q) - 1] + F[a_{aod}(Q) - 1]$$  \(1\)

The weighting factors $A - F$ for $a_i$ in Eq. (1) were calculated from the compositions and the coherent scattering lengths in the usual manner. Then, the distribution function around the hydrogen atoms, $G_t(r)$, is derived from the Fourier transform of $\Delta(Q)$:

$$G_t(r) = 1 + (A + B + C + D + E + F)^{-1}(2\pi r)^{-1}\times \int_0^{Q_{max}} Q\Delta(Q)\sin(Qr)dQ$$  \(2\)

Subtracting the intramolecular $H_2\alpha$ contributions within [BMIM]$^+$ cation from the experimental $\Delta(Q)$, we obtain the inter-ionic difference function, $\Delta_{\text{inter}}(Q)$, and its Fourier-transformed distribution function, $G_{\text{inter}}(r)$. The $\Delta_{\text{inter}}(Q)$ and $G_{\text{inter}}(r)$ around 2- and 4.5-hydrogen atoms are given in Eq. (2). The first peaks in $G_{\text{inter}}(r)$ are quite different between the two hydrogen atoms. This peak appears at $r = \approx 2.6$ Å for acidic 2-hydrogen and at $\approx 3.2$ Å for 4.5-hydrogen. A very similar situation was observed for the crystal structure: the 2-hydrogen contacts more closely to the fluoride atoms (2.36 and 2.58 Å) than the 4.5-hydrogens (2.43 and 2.56 Å), whereas the absolute distances in crystal are slightly shorter than those in liquid. The local structures around the 2- and 4.5-hydrogen atoms will be revisited later in terms of the second-order difference functions.

The second-order difference functions between $\Delta_{5.6}(Q)$ and $\Delta_{5.6}(Q)$ and $\Delta_{5.6}(Q)$ and $\Delta_{5.6}(Q)$ can be related to the partial structure factors, $a_{2.5.6}(Q)$ and $a_{2.5.6}(Q)$, for the 2-H and 4.5-H autocorrelations, respectively.

$$\Delta_{5.6}(Q) - \Delta_{5.6}(Q) = (2\pi)^{-1}\int_0^{Q_{max}} \Delta_{5.6}(Q)\sin(Qr)dQ$$  \(3\)

$$\Delta_{5.6}(Q) - \Delta_{5.6}(Q) = (2\pi)^{-1}\int_0^{Q_{max}} \Delta_{5.6}(Q)\sin(Qr)dQ$$  \(4\)

Here $b_1$ and $b_0$ are the mean scattering lengths of hydrogen and deuterium atoms, respectively. The $a_{2.5.6}(Q)$ and $a_{2.5.6}(Q)$ thus obtained and the corresponding distribution functions, $g_{2.5.6}(r)$ and $g_{2.5.6}(r)$, are given in Fig. 3. On the assumption that the partial structure factor is divided into the short-range $H-H$ and long-range contributions, the least-squares refinements were carried out for the experimental $a_{2.5.6}(Q)$ and $a_{2.5.6}(Q)$.
Fig. 3 The partial structure factors $a_{ij}(Q)$ and the distribution functions $g_{ij}(r)$ for the 2- and 4,5-hydrogen autocorrelations in [BMIM]PF$_6$. The thin dots and solid lines represent the experimental data points and best-fitted results, respectively, in both figures (a) and (b). The residual functions $\delta(Q)$ are shown below in the upper figure (a), and the short- and long-range contributions are denoted respectively by the dashed and dotted lines in the lower figure (b).

![Image](https://example.com/image1.png)

![Image](https://example.com/image2.png)

**Fig. 4** The partial structure factors $a_{ij}(Q)$ and the distribution functions $g_{ij}(r)$ for the 2- and 4,5-hydrogen atoms in [BMIM]PF$_6$. The thin dots and solid lines represent the experimental data points and best-fitted results, respectively in both figures (a) and (b). The residual functions $\delta(Q)$ are shown below in the upper figure (a), and the short- and long-range contributions are denoted respectively by the dashed and dotted lines in the lower figure (b).

![Image](https://example.com/image3.png)

![Image](https://example.com/image4.png)

**Table 2** Results of the least-squares refinements for the partial structure factors $a_{i,j}=\text{H}l(\text{H},\text{H})$, and the coordination number, $n(\text{H},\text{H})$, in the short-range contribution were obtained together with the averaged distance, $r_0$, and the displacement, $b_0$, in the long-range contribution. The best-fitted results are given in Fig. 3, and the determined parameters are summarized in Table 2. The $r(\text{H},\text{H})$ for 2-hydrogen is shorter than that for 4,5-hydrogens, though $n(\text{H},\text{H}) =1$ for both hydrogens. In the case of the symmetric 1,3-dimethylimidazolium cation with Cl$^-$, the first peaks in $g_{ij}(r)$ appear at ~2.8 and 3.0 Å for 2- and 4,5-hydrogens, respectively.\(^{13}\) This is reasonable because the present PF$_6^-$ anion is larger than Cl$^-$ and the cation has a longer butyl chain. The closest distances between 2- and 4,5-hydrogen atoms in crystal\(^4\) are shown by the arrows in Fig. 3(b). The $r(\text{H},\text{H})$ for 4,5-hydrogens in liquid remains almost the same as the crystal distance, whereas $r(\text{H},\text{H})$ for 2-hydrogen in liquid seems to be shorter than that in crystal. We cannot immediately interpret this discrepancy only based on the present structural results around the hydrogen atoms in the imidazolium ring. Molecular simulation demonstrated that the longer alkyl side chains aggregate with each other, leading to nonpolar domains, in this series of imidazolium salts.\(^{14}\) Such aggregation could initiate asymmetric environment between the 2-H and 4,5-H autocorrelations in liquid as observed in this study. The recent *ab-initio* calculation by Bhargava and Balasubramanian\(^5\) gives broad peaks at similar distances ~3.6 Å for 2- and 4,5-hydrogen autocorrelations in [BMIM]PF$_6$.

The other second-order differences between $\Delta_{i,j}(Q)$ and $a_{i,j}(Q)$ and $\Delta_{i,j}(Q)$ and $a_{i,j}(Q)$ provide the partial structure factors, $a_{2,3H}(Q)$ and $a_{4,5H}(Q)$, around the 2- and 4,5-hydrogen atoms, respectively. The $g_{2,3H}(Q)$ and $g_{4,5H}(Q)$ and the corresponding distribution functions, $g_{2,3H}(r)$ and $g_{4,5H}(r)$, are shown in Fig. 4. These partial structure factors are expressed by the sum of interactions of the hydrogen atoms with other inter-ionic atoms, which could be mainly given by PF$_6^-$ anions in the solvation sphere. A glance at the first peaks in $g_{2,3H}(r)$ and $g_{4,5H}(r)$ in Fig. 4(b) indicates that the 2-hydrogen atom interacts with the fluoride in PF$_6^-$ more strongly than 4,5-hydrogens, probably due to the hydrogen bonding as in the crystal; however, it is not so strong in view of the broadening. In order to obtain more detailed information about the liquid
Table 3 Results of the least-squares refinements for the partial structure factors $a_{2H,6}(Q)$ and $a_{4H,5,6,5}(Q)$ around 2- and 4,5-hydrogen atoms in [BMIM][PF$_6$].

<table>
<thead>
<tr>
<th>Interaction</th>
<th>Parameter</th>
<th>$a_{2H,6}(Q)$</th>
<th>$a_{4H,5,6,5}(Q)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short-range</td>
<td>r(H–1F)/Å</td>
<td>2.56(1)</td>
<td>2.95(3)</td>
</tr>
<tr>
<td>(H–PF$_6^-$)</td>
<td>l(H–1F)/Å</td>
<td>0.22(1)</td>
<td>0.15(1)</td>
</tr>
<tr>
<td></td>
<td>l(H–2F)/Å</td>
<td>0.21(1)</td>
<td>0.14(1)</td>
</tr>
<tr>
<td></td>
<td>l(H–3F)/Å</td>
<td>0.25(1)</td>
<td>0.23(3)</td>
</tr>
<tr>
<td></td>
<td>l(H–4F)/Å</td>
<td>1.0(1)</td>
<td>0.4(1)</td>
</tr>
<tr>
<td></td>
<td>l(H–5F)/Å</td>
<td>0.39(1)</td>
<td>0.52(2)</td>
</tr>
<tr>
<td></td>
<td>l(H–6F)/Å</td>
<td>0.45(1)</td>
<td>0.52(2)</td>
</tr>
<tr>
<td></td>
<td>l(H–7P)/Å</td>
<td>0.31(1)</td>
<td>0.26(3)</td>
</tr>
<tr>
<td></td>
<td>α'/α</td>
<td>109(1)</td>
<td>110(1)</td>
</tr>
<tr>
<td></td>
<td>β'/β</td>
<td>47(1)</td>
<td>39(1)</td>
</tr>
<tr>
<td>Short-range</td>
<td>r(H–F')/Å</td>
<td>3.9(1)</td>
<td>4.18(9)</td>
</tr>
<tr>
<td>(H–F$^-$)</td>
<td>l(H–F')/Å</td>
<td>0.23(1)</td>
<td>0.38(4)</td>
</tr>
<tr>
<td></td>
<td>n(H–F')</td>
<td>1.44(2)</td>
<td>4.4(7)</td>
</tr>
<tr>
<td>Long-range</td>
<td>r(Å)</td>
<td>4.45(1)</td>
<td>4.4(1)</td>
</tr>
<tr>
<td></td>
<td>l(Å)</td>
<td>0.76(1)</td>
<td>0.55(6)</td>
</tr>
</tbody>
</table>

a. Estimated standard deviations are given in parentheses.
b. Angle between the H–1F vector and 1F–P bond.
c. Dihedral angle between the H–1F–P plane and 1F–P–2F plane in PF$_6^-$.

structures around the hydrogen atoms, we attempt to refine the experimental $a_{2H,6}(Q)$ and $a_{4H,5,6,5}(Q)$ by taking account of only the nearest-neighbor short-range interactions with PF$_6^-$ anions in a single state. The intramolecular structure of PF$_6^-$ was estimated from that in the crystal.16 The interatomic distance $r$(H–1F) between the hydrogen and nearest fluorine atoms and the coordination number $n$(H–PF$_6^-$) were determined by the least-squares refinements together with the angle α between the H–1F vector and 1F–P bond and the dihedral angle β between the H–1F–P plane and 1F–P–2F plane in PF$_6^-$ . This approach can reproduce the first peak in $g_{\alpha}(r)$ at 2.6 and 3.0 Å for 2- and 4,5-hydrogen atoms, respectively. However, there are still other peaks at longer distances, $r = 3.9$ and 4.2 Å for 2- and 4,5-hydrogens, respectively. This suggests that the PF$_6^-$ anions around the ring hydrogen atoms are not in a single state and/or the nearest-neighbor [BMIM]$^+$ cations make some contributions to $g_{2H,6}(r)$ and $g_{4H,5,6,5}(r)$. Assuming another short-range H–F$^-$ interaction arbitrarily, we re-analyzed $a_{2H,6}(Q)$ and $a_{4H,5,6,5}(Q)$ in Table 3. The results thus obtained show that both the 2- and 4,5-hydrogen atoms are oriented almost equivalently to three fluorine atoms in PF$_6^-$ . The H–F distances around 2- and 4,5-hydrogen atoms in crystal,4 as shown by the arrows in Fig. 4(b), overlap with the first peaks in $g_{2H,6}(r)$ and $g_{4H,5,6,5}(r)$ in liquid. This indicates that the local structures around the 2- and 4,5-hydrogen atoms remain practically the same in both liquid and crystal.

In this work, we have investigated the liquid structure of [BMIM][PF$_6$] by means of the neutron diffraction measurements with the H/D isotopic substitution technique. The partial deuteration of the hydrogen atoms in the imidazolium ring may be simple and practical. The local structures around the ring hydrogen atoms in liquid are not so far from those estimated from the crystal structure.

Acknowledgements

The authors thank Prof. Toshiharu Fukunaga and Dr. Keiich Itoh at Kyoto University for their assistance during the neutron diffraction experiments. M. K. would thank Dr. Bhargava and Prof. Balasubramanian at Jawaharlal Nehru Center for Advanced Scientific Research for their helpful discussions. This study was partially supported by Industrial Technology Research Grant Program in 2007 from New Energy and Industrial Technology Development Organization (NEDO) of Japan.

References

13. Unfortunately, $g_{\alpha}(r)$ for 2- and 4,5-hydrogen autocorrelations in [MMIM][PF$_6$] and [MMIM][TF$_2$N] are unavailable in Refs. 2 and 3.