Liquid Structure of Room Temperature Ionic Liquids Revealed by High-energy X-ray Diffraction and Molecular Dynamics Simulation

Room temperature ionic liquids (RTILs), which are solely composed of ions and have melting points below 100 °C, have environmentally friendly properties, such as that they are practically non-volatile and non-flammable. Thus, RTILs have attracted attention as the alternative to volatile organic solvents. In addition, they are expected to be superior materials for electrochemical devices with high-energy density due to their high conductivity and wide electrochemical window [1]. On the other hand, from the viewpoint of fundamental science, the understanding of structure and dynamics is still insufficient, although the studies on their physics and chemistry have been rapidly in progress. It is thus necessary to reveal the liquid structure at a molecular level.

X-ray diffraction is an essential tool to probe atomic arrangements in liquid and amorphous materials. However, it is not easy to reveal complicated structures in RTILs with enough real-space resolution using low energy X-rays from conventional X-ray sources. In fact, little has been published on the RTILs study by X-ray diffraction [2]. A high-energy X-ray diffraction experiment (HEXRD) covering a wide scattering vector and thus achieving high real-space resolution is one of the solutions to overcoming the problem [3]. Moreover, one can extract chemically valuable atom-atom correlations from the experimental correlation function with the aid of reliable molecular simulations [4]. It is also necessary to clarify in advance the flexibility of the ions [5]. We demonstrated the liquid structure of typical RTILs, 1-ethyl-3-methylimidazolium bis-(trifluoromethanesulfonyl) amide EMI^+TFSA^- and *N*-propyl-*N*-methylpyrrolidinium bis-(trifluoromethanesulfonyl) amide $P_{13}^+TFSA^-$ (Fig. 1) as revealed by a combination of HEXRD experiments and molecular dynamics (MD) simulations.

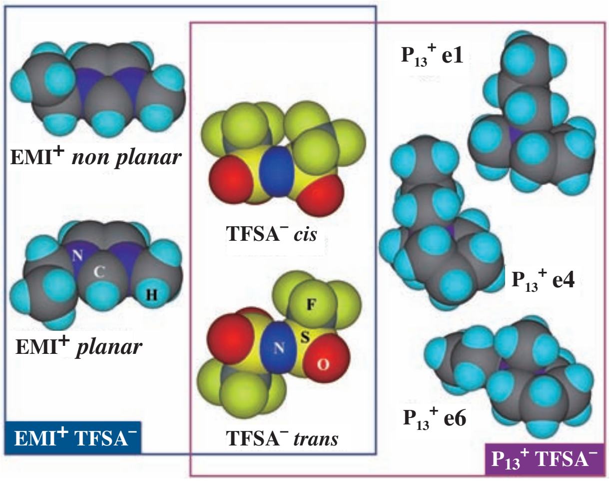

Fig. 1. Optimized geometries at the B3LYP/6-311G(d,p) level of theory for the isomers of ions composing RTILs examined in this study. All isomers exist in equilibrium in the respective ionic liquid as revealed by Raman spectroscopy, DFT calculations, and MD simulations. (Ref. [4] and Ref. [5])

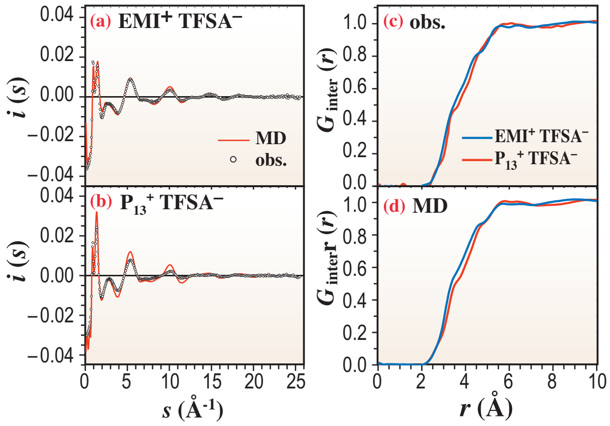

Fig. 2. X-ray structure factors **(a)** for EMI^+TFSA^- and **(b)** for $P_{13}^+TFSA^-$, and **(c)** X-ray weighted inter-molecular correlation functions obtained from HELAXS experiments (window function $W(s) = \exp(-Bs^2)$; B = 0.011 was used in Fourier transformation) and **(d)** derived from MD simulations with an *NTP* ensemble, $N = 256$ ion pairs, $T = 298$ K, and $P = 1$ atm.

The HEXRD experiments were carried out at **BL04B2**. Observed total X-ray interference functions $i^{\,\mathrm{HEXRD}}(s)$ for the respective ionic liquids are shown in Fig. 2. The total X-ray interference functions can be expressed as the sum of the intra-molecular $i^{\,\mathrm{HEXRD}}_{\mathrm{intra}}(s)$ and the inter-molecular X-ray interference functions $i^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(s)$; $i^{\,\mathrm{HEXRD}}(s) = i^{\,\mathrm{HEXRD}}_{\mathrm{intra}}(s) + i^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(s)$. $i^{\,\mathrm{HEXRD}}_{\mathrm{intra}}(s)$ can be estimated by knowing appropriate geometries and distributions of the conformational isomers of the ions (see Ref. [5]). By subtracting thus estimated $i^{\,\mathrm{HEXRD}}_{\mathrm{intra}}(s)$ from $i^{\,\mathrm{HEXRD}}(s)$, $i^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(s)$ was evaluated and Fourier transformed to yield the inter-molecular correlation function $G^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(r)$. As shown in Fig. 2, $G^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(r)$ for both ionic liquids shows bumps around 3.4 Å ascribable to the first neighbor atom-atom correlations (except proton) between cation and anion. It should be noted that $G^{\,\mathrm{HEXRD}}_{\mathrm{inter}}(r)$ for the EMI^+TFSA^- appears on the evidently shorter side relative to that for the $P_{13}^+TFSA^-$. This fact suggests that the inter-molecular interaction between EMI^+–$TFSA^-$ is stronger than that between P_{13}^+–$TFSA^-$. More favorable ion-ion interaction in the imidazolium ionic liquids relative to the pyrrolidinium ones has been proposed in terms of dynamics by Watanabe *et al.* [6]. HEXRD provides the direct structural evidence for this at a molecular level.

Total X-ray interference functions derived from the simulations $i^{\,\mathrm{MD}}(s)$ for both ionic liquids are also shown in Fig. 2. The interference functions are in good agreement with experimental ones, indicating that the liquid structure can be satisfactorily reproduced by simulations. X-ray weighted inter-molecular pair correlations derived from simulations $G^{\,\mathrm{MD}}_{\mathrm{inter}}(r)$ are shown in Fig. 2. It is clearly shown by $G^{\mathrm{MD}}_{\mathrm{inter}}(r)$ that peaks at *ca.* 3.5 Å define the closest atom–atom distance between the cation and anion.

Figure 3 displays the partial atom-atom pair correlation functions between the carbon in the cation and the oxygen $g_{\mathrm{C}n\text{-O}}(r)$ or the fluorine $g_{\mathrm{C}n\text{-O}}(r)$ in the anion. As clearly shown in Fig. 3, for both ionic liquids, the cations favor the oxygen rather than the fluorine as an interaction site on the anion. This fact suggests that the electrostatic force predominantly operates in the ion-ion interaction with the oxygen in TFSA$^-$, while van der Waals force contributes significantly to the inter-molecular interaction at the fluorine rather than the electrostatic one.

With EMI$^+$TFSA$^-$, the most intense peak appears in the $g(r)$ of C6–O, followed by the sharpest one with the lowest position in the $g(r)$ of C2–O. It should be emphasized that the *N*-methyl group in EMI$^+$TFSA$^-$ has a significant role in the inter-molecular interaction. On the other hand, the fluorine in TFSA$^-$ favors the C6 and the C9 carbons. With P$_{13}^+$, most intense peak is found in the correlation between the *N*-methyl carbon and the oxygen in TFSA$^-$. It should be noted that the inter-molecular atom-atom correlations of the *N*-methyl group and oxygen for both ionic liquids are similar to each other.

The spatial distribution function (SDF) shown in Fig. 4 is useful to reveal the ion–ion interactions from the other aspect. Significantly, the spatial distributions for EMI$^+$TFSA$^-$ are found to be more or less asymmetric compared with those for P$_{13}^+$TFSA$^-$. An asymmetric spatial distribution in the ion-ion interaction may increase the configuration entropy in the liquid state, which causes a lowering of the melting point. Actually, the melting point for EMI$^+$TFSA$^-$ (–20 °C) is lower than that for the other (10 °C), although the ion–ion interaction for EMI$^+$TFSA$^-$ is stronger in the liquid state. It is also clearly found in the SDFs that the liquid structure of the respective ionic liquid is different from each other. The structural differences may be related to the diverse dynamic properties of the ionic liquids such as larger diffusion coefficients for the imidazolium ionic liquids relative to the pyrrolidinium ionic liquids [6]. However, the liquid structure – dynamics relationship of the ionic liquids is not clear at the present stage. Thus, further investigation is now in progress.

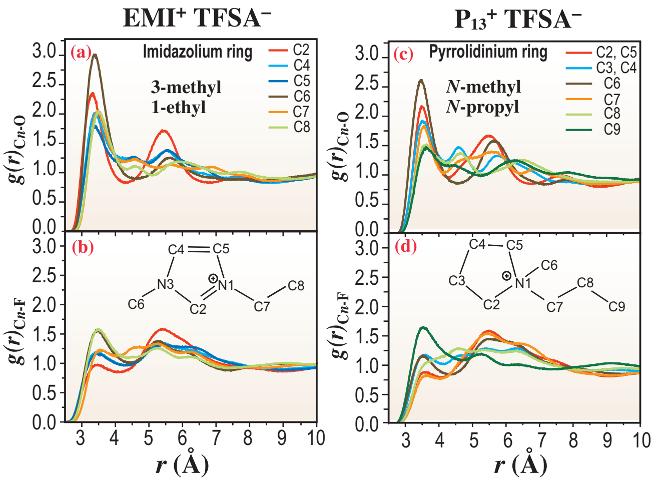

Fig. 3. Partial atom-atom pair correlation functions **(a)** of C*n* - O and **(b)** C*n* – F for EMI$^+$TFSA$^-$, and **(c)** and **(d)** for P$_{13}^+$TFSA$^-$. Panels **(c)** and **(d)** represent the same pair as panels **(a)** and **(b)**.

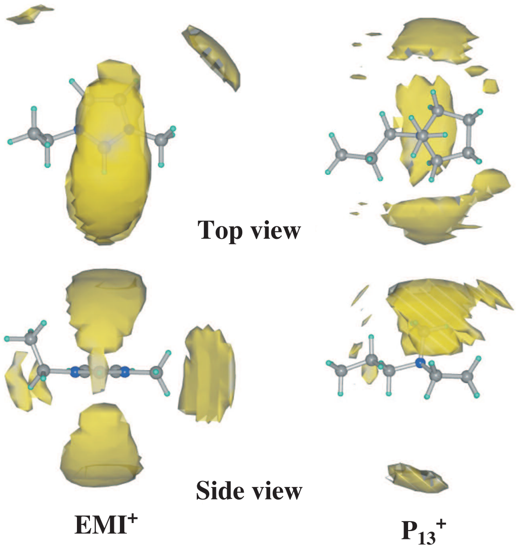

Fig. 4. Spatial distribution functions of the center of mass of TFSA$^-$ around C2 of EMI$^+$TFSA$^-$ (right) and around the nitrogen of P$_{13}^+$TFSA$^-$ (left). Yellow clouds around the cation correspond to the isoprobability surface for the center of mass of TFSA$^-$.

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