Effect of Methylation at the C2 Position of Imidazolium on the Structure of Ionic Liquids Revealed by Large Angle X-ray Scattering Experiments and MD Simulations

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Liquid structures of 1-butyl-3-methylimidazolium bis(trifluoromethanesulfonyl)amide [BMI$^+$][TFSA$^-$] and 1-butyl-2,3-dimethylimidazolium bis(trifluoromethanesulfonyl)amide [BDMI$^+$][TFSA$^-$] were studied by large-angle X-ray scattering (LAXS) experiments to elucidate methyl substitution effect at the C2 position of imidazolium cation on the long-range ordering of the ionic liquids. Radial distribution functions for both ionic liquids showed that the intermolecular correlations of ca. 5.5 and 10 Å are significantly different from each other, unlike that of ca. 15 Å. MD simulations were also performed. It turns out that the methyl substitution at the C2 position of imidazolium causes variation of the orientation of the nearest neighboring ion–ion interactions without significant changes in the long-range ordering, probably longer than 15 Å, of the ionic liquids.

Room-temperature ionic liquids (RTILs) are a new class of solvents and are a hot topic not only for the material sciences,[1] but also for the fundamental science of condensed matter.[2] Among them, imidazolium-based ionic liquids are the most popular, and their intermolecular cation–anion interactions have been studied.[3] Currently, it is considered that *hydrogen bonding* at the C2 hydrogen of the imidazolium ring plays an important role in cation–anion interactions.[4] Therefore, to obtain further insight, 1-alkyl-2,3-dimethylimidazolium-based ionic liquids have been also studied by various techniques such as NMR,[5] Raman/IR spectroscopy,[6] crystallography,[7] ab initio/DFT calculations,[8,9] and molecular simulations.[10]

Scattering experiments of neutron[11] and X-ray[12] with the aid of molecular simulations yield a radial distribution function (RDF) of liquids, which provides useful information, i.e., physicochemical properties of liquids such as thermodynamic and/or hydrodynamic quantities can be obtained from RDF according to statistical mechanics. However, there is no published work on 1-alkyl-2,3-dimethylimidazolium-based ionic liquids by such scattering techniques at the present stage. In this letter, we report the liquid structures of [BMI$^+$][TFSA$^-$] and [BDMI$^+$][TFSA$^-$] revealed by large-angle X-ray scattering (LAXS) experiments and MD simulations based on newly developed force fields. It is clearly shown that the orientation among the nearest neighbor cation–anion varies with the methyl substitution at the C2 hydrogen of the imidazolium ring; nevertheless, the long range ordering in the ionic liquids is similar.

[BMI$^+$][TFSA$^-$] and [BDMI$^+$][TFSA$^-$] specially made for spectroscopic grade (Nippon Synthetic Chemical Industry) were used without further purification. Water contents in both samples were checked by Karl Fischer analysis to be less than 100 ppm. LAXS measurements ($0.2 < s/\text{Å}^{-1} < 14.5$) were performed at 298 K. Details of LAXS measurements and data analyses to obtain an X-ray interference function $i(s)$ as a function of a scattering vector s, and a radial distribution function as the form of $D(r) - 4\pi r^2 \rho_0$ (RDF) has been described elsewhere.[12]

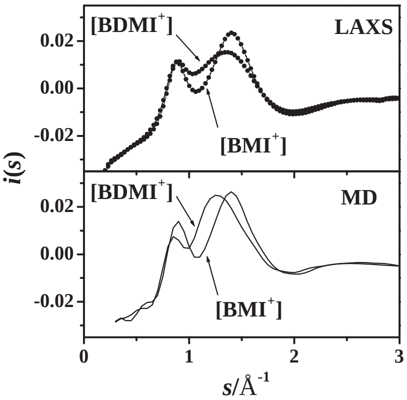

Figure 1. X-ray interference functions $i(s)$ for [BMI$^+$][TFSA$^-$] and [BDMI$^+$][TFSA$^-$] by LAXS experiments (upper panel) and by MD simulations (lower).

Figure 1 shows the $i(s)$ for both ionic liquids. The peak of $s < 1\,\text{Å}^{-1}$ mainly corresponds to the intermolecular atom–atom correlations of the composing ions. Although it was not shown in Figure 1, no significant difference among them appeared in $i(s)$ over the wide range ($s \geq 2\,\text{Å}^{-1}$), which implies that the molecular structures including the conformational isomerism in equilibrium of the composing ions hardly depend on the ionic liquids examined here, though the conformational behavior of BDMI$^+$ is not clear at the present stage, unlike BMI$^+$ and TFSA$^-$. It is plausible, if we take into consideration that the structural difference among the cations is solely at the C2 position; i.e., a hydrogen atom or a methyl group, whose X-ray scattering ability is relatively small. On the other hand, in the range of $s \leq 2\,\text{Å}^{-1}$, $i(s)$ yields information of the long-range ordering and the intermolecular correlations of the liquids. Intense peaks of 0.9 and 1.4 Å^{-1} appeared similarly for both ionic liquids. Interestingly, although the intensities of a peak at 0.9 Å^{-1} are similar to each other, a peak of 1.4 Å^{-1} and a valley at around 1.1 Å^{-1} for [BDMI$^+$][TFSA$^-$] are obviously lower and shallower than those for [BMI$^+$][TFSA$^-$], respectively, which suggests that the nearest neighbor cation–anion interaction and intermediate correlation are rather different from each other, while the long-range ordering of these ionic liquids is similar. This can be seen more clearly in RDF in the following discussion.

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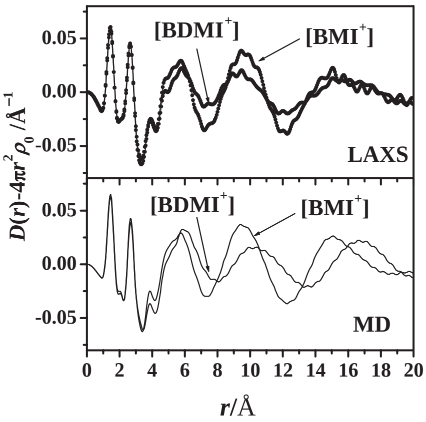

Figure 2. X-ray radial distribution functions $D(r) - 4\pi r^2\rho_0$ for [BMI$^+$][TFSA$^-$] and [BDMI$^+$][TFSA$^-$] by LAXS experiments (upper panel) and by MD simulations (lower).

Figure 2 shows RDFs for both ionic liquids. In these RDFs, peaks of $r < \approx 5$ Å can be reasonably assigned to the intramolecular atom–atom correlations within the composing ions. Broad peaks of ca. 5.5, 10, and 15 Å appeared for both ionic liquids, which can be ascribed to overlap of nonbonding intramolecular atom–atom correlations and the nearest neighbor intermolecular correlations between cation and anion, to the neighboring cation–cation and anion–anion correlations and to the further long-range ordering in the ionic liquids, respectively. RDF of $r > \approx 5$ Å for [BMI$^+$][TFSA$^-$] significantly differs from that for [BDMI$^+$][TFSA$^-$]; i.e., the oscillations in this region of RDF for [BDMI$^+$][TFSA$^-$] are considerably reduced relative to that for the other, though the peak positions are almost the same. In particular, the intensity of a broad peak ca. 5.5 Å for [BDMI$^+$][TFSA$^-$] is appreciably lower and higher in the shorter and the longer sides, respectively, than that of [BMI$^+$][TFSA$^-$]. As mentioned above, the broad peak of ca. 5.5 Å can be mainly ascribed to the nearest neighbor interactions among the ions oppositely charged. RDFs for both ionic liquids clearly show the dissimilar correlations among the first neighboring cation–anion, probably its orientation. This finding was supported by ab initio calculations by Tsuzuki et al.[8] As a final remark on the RDFs, the positions and heights of broad peaks of ca. 15 Å for both ionic liquids were similar to each other, which implies that the long-range ordering of the ionic liquids may be hardly affected by the methyl substitution at the C2 position. Though rather qualitatively, such similarity of the long-range ordering may be related with the hydrodynamic properties, if we take into account the fact that viscosity increases by the C2 methylation, while density decreases.

To obtain further insight into the C2 methylation effect on the liquid structures, we performed MD simulations, where the force fields proposed by Lopes, Pádua, and co-worker[13] and those newly developed were used for [BMI$^+$][TFSA$^-$] and [BDMI$^+$][TFSA$^-$], respectively.[14] Simulated density of 1.432(5) g cm^{-3} for [BDMI$^+$][TFSA$^-$] was in good agreement with an experimental value[15] (1.42 g cm^{-3}). MD-derived $i(s)$ and RDF appropriately agreed with the experimental ones, though the simulated peak position around 15 Å in RDF is rather different from the observed one.[14] As is clearly shown in a spatial distribution function SDF for [BDMI$^+$][TFSA$^-$] (Graphical Abstract), the orientation of the first neighboring TFSA$^-$ around BDMI$^+$ is rather different compared with that for [BMI$^+$]-[TFSA$^-$]. As shown by LAXS experiments and MD simulations, methyl substitution at the C2 position of the imidazolium ring causes variation of the orientation of the nearest neighboring ion–ion interactions without significant changes in the long-range ordering of the ionic liquids.

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