Hydrogen bond in imidazolium based protic and aprotic ionic liquids

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ABSTRACT

Liquid structure of bis-(trifluoromethanesulfonyl)amide TFSA$^-$ based protic and aprotic ionic liquids composed of imidazolium [h$_2$Im$^+$], N-methylimidazolium [C$_1$hIm$^+$] and N,N'-dimethylimidazolium [C$_1$mIm$^+$] were investigated by high-energy total scattering (HETS) experiments. The nearest neighboring cation–anon orientation variations by the N-methyl groups substitution to proton were suggested based on the peaks at around 6 and 9 Å in the differential radial distribution functions as the form of $r^2\{G^{X\text{-ray}}(r) - 1\}$ for these ionic liquids. It was supposed that the NH · · · O hydrogen bond causes the cation–anion orientation variations. To obtain further insight into the hydrogen bond in the PIL, MD simulations performed and agreed well with the experiments. According to spatial distribution functions (SDF) for the three ionic liquids, the O atom of TFSA$^-$ prefers the NH hydrogen of the imidazolium that has the most positive partial atomic charge in the cation, while the F atom locates right above and right below the imidazolium ring plane. In addition, the NH · · · O hydrogen bond has short bond lengths and linear bond angles, while the C$_2$H · ·O interaction is long and bent. The NH · · · O hydrogen bond in the PIL was discussed based on structural aspect accompanied by a thermodynamic viewpoint.

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1. Introduction

Protic ionic liquids (PIL) are one of the subclasses of ionic liquids [1, 2]. PIL [HB$^+$][A$^-$] can be simply prepared by mixing a Brønsted acid HA and a base B [3,4]. Nowadays, lots of PIL were reported that consists of various cation and anion [5,6] and have been well reviewed [7–10]. PIL has attracted much attention as new proton conductors for a new class of fuel cells [11–14], so that the proton conduction mechanisms in PIL have also been investigated by means of the pulse gradient spin echo NMR technique [15–17]. More recently, novel PIL applications were proposed such as the N doped carbon materials utilized PIL as a starting material [18,19].

Much effort has been made to quantify the cation–anion interactions in PIL as the Watanabe's Ionisity [20–23], and/or those estimated from the Walden plots [24–26]. Among them, the ΔpK$_a$ proposed by Angell et al. [26,27] can be a better measure for the cation–anion interactions in PIL and may be most used. ΔpK$_a$ is defined as the difference between the acid dissociation constants K$_a$ for HA and HB$^+$ in the aqueous solutions and well correlates with the Watanabe's Ionisity. Watanabe et al. found various physicochemical properties of PIL correlate with the ΔpK$_a$ [28,29]. Moreover, they pointed out possibility of the low-barrier

hydrogen bond in PIL [30]. All these solvent parameters are rather useful for understanding the macroscopic thermodynamic/transport properties of PIL.

From the structural viewpoint, the cation–anion interactions in PIL were well studied until now [31–34], particularly focusing on the hydrogen bond. Ludwig et al. studied the cation–anion interactions in PIL by means of far-IR and DFT calculations. They demonstrated that the PIL form three-dimensional hydrogen network structure on the basis of similarity of far-IR spectra for alkylammonium nitrate protic ionic liquids to that of water, and found that a nice linear relationship between the peak positions in far-IR spectra and the binding energy between cation and anion in the PIL [33,35–39]. They also reported such correlations can be found in imidazolium based ionic liquids [40,41].

On the other hand, the knowledge from X-ray/neutron liquid structural studies can yield a clear picture to reveal interactions among the solvents; i.e., the cation–anion interactions in PIL, especially the hydrogen bond at a molecular level. Hayes and Atkin et al. have reported liquid structure of alkylammonium and their analogues based PIL elucidated by small/large angle neutron scattering techniques [42–46]. They found that bi- or trifurcated hydrogen bonding results, leading to weaker, bent hydrogen bonds, decreasing cation–anion attractions and leading to a more fluid-like material, whilst attractions between ions increase and physical properties become more solid-like when the nanostructures have a relatively high proportion of hydrogen

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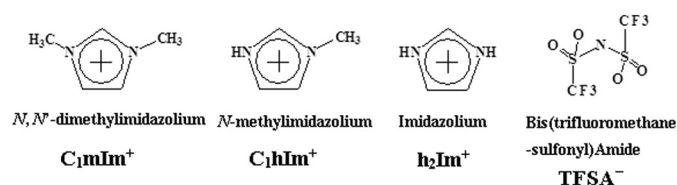E-mail address: yumescc@chem.sc.niigata-u.ac.jp (Y. Umebayashi).

Fig. 1. Structures and abbreviations for the cations and the anion of ionic liquids studied in this study.

bonds are linear (Fig. 1). However, liquid structural investigation is limited to the ammonium based PIL at the present stage [47–53], though numerous publications have been made on the imidazolium based PIL.

We have reported the acid–base property of PIL. Although the ΔpK_a is better as the solvent parameter for not only the inter-ionic interactions in PIL but also various static/dynamic macroscopic properties of PIL, the auto-protolysis constant K_s could be more suitable for representing the acid–base property as they are determined on the basis of directly measured pH in PIL [54–56]. Recently, we extended our work to the N-methylimidazolium [C_1hIm^+] based PIL combined with various conjugated anions from super to weak acids [56]. According to the pK_s, proton transfer from the acetic/formic acid to the base is unfavorable, i.e., these equimolar mixtures yield simple electrically neutral non-aqueous solvent mixtures, not PIL. Nevertheless, significant molar ionic conductivity was found in the N-methylimidazole and acetic acid equimolar mixture. We thus proposed such liquids can be called as the *pseudo*-protic ionic liquids [57]. On the other hand, the cation and the corresponding anion predominantly exist in [C_1hIm^+][$TFSA^-$] (TFSA: bis-(trifluoromethanesulfonyl)amide) and [C_1hIm^+][TFS^-] (TFS: trifluoromethanesulfonate), therefore these are essentially PIL. Raman spectroscopic speciation analysis and X-ray structural studies agree well with the pK_s conclusion [58].

In this paper, we investigated liquid structures of the $TFSA^-$ based protic and aprotic ionic liquids composed of imidazolium [h_2Im^+], N-methylimidazolium [C_1hIm^+] and N,N'-dimethylimidazolium [C_1mIm^+] by means of high-energy X-ray total scattering (HEXTS) experiments with the aid of MD simulations that well reproduced experimental X-ray structure factors. To the best of our knowledge, liquid structure of the imidazolium based PIL is reported for the first time as only the neutron diffraction of [C_1mIm^+][$TFSA^-$] have been published among ionic liquids examined here [59]. The closest cation–anion interactions, particularly the NH···O hydrogen bond was discussed by using spatial distribution functions (SDF) and pair correlation functions evaluated with the MD simulations.

2. Material and methods

2.1. Materials

For aprotic ionic liquid, [C_1mIm^+][Cl^-] was purchased from Tokyo Chemical Industry co. ltd., and was used without further purification. [C_1mIm^+][$TFSA^-$] was prepared by treating [C_1mIm^+][Cl^-] with HTFSA in an aqueous solution, then HCl and solvent water were repeatedly evaporated under reduced pressure to confirm neutral pH and a negligible $AgNO_3$ test. For preparation of protic ionic liquids, HTFSA and imidazole were sublimated under N_2 atmosphere to remove water and purify, and N-methylimidazole was stored with molecular sieve 4A to reduce water content under 100 ppm, then distilled under Ar atmosphere. Protic ionic liquids [h_2Im^+][$TFSA^-$] and [C_1hIm^+][$TFSA^-$] were prepared by mixing equivalent amount of HTFSA and imidazole/ N-methylimidazole. The sample preparation and treatment were performed in the glove box of Ar atmosphere with a water content kept less than 1 ppm. Finally, purity and water content of all of the sample ionic liquids were checked by elemental analysis and the Karl Fischer titration, respectively. Properties of all ionic liquids studied here are listed in Table 1.

2.2. High-energy X-ray Total Scattering

The HEXTS measurements were carried out using a two-axis diffractometer at the BL04B2 beam-line of SPring-8 at the Japan Synchrotron Radiation Research Institute (JASRI) [60,61]. The ionic liquid samples were set in a hermetically sealed capillary Pyrex glass tube of 3.5 mm diameter and 0.1 mm thickness. Monochrome 61.6 keV X-rays were obtained using a Si (220) monochromator. The observed X-ray intensity was corrected for absorption [62] and polarization. Incoherent scatterings [63–65] were subtracted to obtain coherent scatterings, $I_{coh}(Q)$. The X-ray structure factor $S^{X-ray}(Q)$ and X-ray radial distribution function $G^{X-ray}(r)$ per stoichiometric volume were respectively obtained according to

$$S^{X\text{-}ray}(Q) = \frac{I_{coh}(Q) - \sum n_i f_i(Q)^2}{\left(\sum n_i f_i(Q)\right)^2} + 1, \tag{1}$$

$$G^{X\text{-}ray}(r) - 1 = \frac{1}{2\pi^2 r \rho_0} \int_0^{Q\,max} Q\left\{S^{X-ray}(Q) - 1\right\} \sin(Qr) \exp\left(-BQ^2\right) dQ, \tag{2}$$

where n_i and $f_i(Q)$ denote the number and the atomic scattering factor of atom i [66], respectively, ρ_0 is the number density, and B is the damping factor. All data treatment was carried out using the program KURVLR [67].

2.3. Ab initio calculations

For the partial atomic charges of the cations, all of the ab initio calculations were carried out at the MP2/cc-pVTZ($-f$) level of theory, followed by partial charge evaluations at the MP2 density using the ChelpG methods [68]. Gaussian03 program suite was used [69]. Thus Evaluated atomic partial charges are listed in Table 2.

2.4. MD simulations

MD simulations of an *NTP* ensemble, i.e., 256 ion pairs in a cubic cell at temperatures corresponding respective experiment and

Table 1
Selected properties, melting point T_m, density ρ, ionic conductivity σ and viscosity h for [C_1mIm^+][$TFSA^-$], [C_1hIm^+][$TFSA^-$] and [h_2Im^+][$TFSA^-$].

	[C_1mIm^+][$TFSA^-$]	[C_1hIm^+][$TFSA^-$]	[h_2Im^+][$TFSA^-$]
T_m / °C	26[a]	49	73[b]
ρ / g cm^{-3}	1.557[c]	1.614[c]	1.552[f]
σ / mS cm^{-1}	11.0[a,d]	11.9[e]	24.0[b,g]
η / mPa s	31.0[a,d]	19.4[e]	–

[a]Ref. [22], b Ref. [13], [c] at 25 °C, [d] at 30 °C, [e] at 70 °C, [f] at 115 °C, [g] at 120 °C.