Research Article

Glass Transition Behavior of the Quaternary Ammonium-Type Ionic Liquid: *N,N*-Diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium Bromide- H_2O Mixtures

Yukihiro Yoshimura,¹ Naohiro Hatano,¹ Yusuke Imai,² Hiroshi Abe,² Osamu Shimada,³ and Tomonori Hanasaki³

¹ Department of Applied Chemistry, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan

² Department of Materials Science and Engineering, National Defense Academy, Yokosuka, Kanagawa 239-8686, Japan

³ Department of Applied Chemistry, Ritsumeikan University, Kusatsu, Shiga 525-8577, Japan

Correspondence should be addressed to Yukihiro Yoshimura, muki@nda.ac.jp

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By a simple differential thermal analysis (DTA) system, the concentration dependence of the glass transition temperatures (T_g s) for the quaternary ammonium-type ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bromide [DEME][Br] and H_2O mixtures, after quick precooling was measured as a function of water concentration x (mol% H_2O). We compared the results with the previous results of [DEME][I]- H_2O and [DEME][BF₄]- H_2O mixtures in which a double-glass transition behavior was observed. Remarkably, the [DEME][Br]- H_2O mixtures basically show one- T_g behavior and the T_g decreases monotonically with increasing H_2O content up to around $x = 91.5$. But it suddenly jumps to higher T_g value at a specific $x \approx 92$. At this very limited point, two T_g s (T_{g1} , T_{g2}) which we might consider as a transition state from the structure belonging to the T_{g1} group to another one due to the T_{g2} group were observed. These results clearly reflect the difference in the anionic effects among Br⁻, I⁻, and BF₄⁻. The end of the glass-formation region of [DEME][Br]- H_2O mixtures is around $x = 98.9$ and moves to more water-rich region as compared to those of [DEME][BF₄]- H_2O ($x = 96.0$) and [DEME][I]- H_2O ($x = 95.0$) mixtures.

1. Introduction

Room temperature ionic liquids (RTILs) are molten salts with melting temperature below (<373 K) and well known to have many attractive properties as solvents, for example, almost zero vapor pressure, wide electrochemical window, high recyclability, nonflammability, and so forth [1, 2], so that RTILs stimulate the interests of a wide range of applications [3, 4]. Many of the attractive features require a thorough knowledge of their thermophysical properties. Interactions in RTILs are characterized by the presence of Coulomb interactions among the constituent ions. Hydrogen-bonding, *van der Waals*, and π - π interactions also take place in RTILs and affect their nature and the liquid structures. Thus, the liquid structures of RTILs are determined by a balance be-

tween long-range electrostatic forces and local geometric factors. As a result, many RTILs can be easily supercooled and form the glassy state [5–7]. Changes in the cation and anion combinations allow the physical and chemical properties of ionic liquids to be effectively tuned, for example, for manipulating the solvent properties of RTILs in order to achieve different purposes [7–9].

Although thermodynamic properties including T_g have been so far investigated mainly on the imidazolium-based series of pure RTILs [10–12], we point out that investigations of glass transition behavior of the RTILs- H_2O mixtures are still scarce. In previous work, we reported the glass transition behavior of the quaternary ammonium-type ionic liquid, *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium tetrafluoroborate [DEME][BF₄]- H_2O [13]

and iodide [DEME][I]-H₂O [14] mixtures, after quick pre-cooling. Remarkably, double-glass transitions were observed in both mixtures. But concentrations of the two- T_g region are completely different from each other; the double-glass transitions for the [DEME][BF₄]-H₂O mixtures were observed in the RTIL-rich region of $x = 16.5 \sim 30.0$ (mol% H₂O), whereas the region moves to a water-rich side of $x = 77.5 \sim 85.0$ (mol% H₂O) for the [DEME][I]-H₂O mixtures. These clearly reflect the difference in the anionic effect between BF₄⁻ and I⁻ on the water structure. It is interesting to quote that the ionic radius of BF₄⁻ anion (229 pm [15, 16]) is slightly larger than that of I⁻ (216 pm [17]) anion. We suspect that the subtle difference in the ionic radii between BF₄⁻ and I⁻ anions together with the anionic nature plays an important role in determining the regions where double-glass transitions occur.

Then, what happens to the phase behavior of other quaternary ammonium-type ionic liquid, [DEME][Br]-H₂O mixtures, in which the anionic radius of Br⁻ (195 pm [18]) is smaller than that of I⁻ anion? Does the double-glass transition phenomenon occur or not? The aim of the present paper is to show the glass transition behavior of [DEME][Br]-H₂O mixtures and to compare the results with those of [DEME][BF₄]-H₂O [13] and [DEME][I]-H₂O [14] mixtures. Here we have measured the T_g variation of [DEME][Br]-H₂O mixtures as a function of H₂O concentration x (mol% H₂O). A limit of the glass-formation region is also determined.

2. Experiments

2.1. Material. As an RTIL in this study, we used *N,N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium bromide, [DEME][Br] which was synthesized in our laboratory. [DEME][Br] was synthesized following procedures reported in the literature [19]. The synthetic route of this material is shown in Scheme 1. The schematic chemical structures of [DEME][Br] are shown in Figure 1.

5.37 g (61.6 mmol) of *N,N*-diethylmethylamine and 8.03 g (57.8 mmol) of 1-bromo-2-methoxyethane were dissolved in about 7 mL of anhydrous acetone. The mixture was stirred overnight at $T = 373$ K in an autoclave. After cooling, the reaction mixture was poured into ice-cold diethyl ether. The precipitated crude product was filtered off and was repeatedly recrystallized from anhydrous acetone. The purified product, [DEME][Br] were a colorless crystal. The molecular structures of [DEME][Br] was identified by ¹H NMR spectra (JEOL JEM-ECS400). The spectral data (400 Hz, CDCl₃) of [DEME][Br] are as follows: δ 3.91 (t, 2H, $J = 4.3$ Hz, -CH₂-OCH₃), δ 3.87 (br s, 2H, -CH₂CH₂-OCH₃), 3.66 (m, 4H, -CH₂-CH₃), 3.37 (s, 3H, -OCH₃), 3.32 (s, 3H, -CH₃), 1.38 (t, 6H, $J = 7.2$ Hz, -CH₂-CH₃). No other peaks were observed except for the identified peaks from the objective compound mentioned above. This result suggests that organic impurities, for example, the starting materials, solvents, and byproducts, were fully removed. [DEME][Br] is a crystalline state at room temperature as described above. The melting temperature was reported to be 358.2 K in the available literature [19].

FIGURE 1: Schematic chemical structure of (a) [DEME]⁺ cation and (b) bromide anion.

We prepared the sample solutions of [DEME][Br]-H₂O mixtures at different concentrations, $x = 60.0 \sim 99.8 \pm 0.05$ (mol% H₂O). There was a limitation of the solubility of [DEME][Br] in water ($x < 60$). Special care was taken with the sample preparations in a dry box to avoid atmospheric H₂O and CO₂.

2.2. DTA Measurements. To detect the glass transition temperature, T_g , a simple differential thermal analysis (DTA) system designed for quick cooling experiments was used. As a reference material for the measurements, we used benzene (Wako Pure Chemical Co.). A sample cell (about 35 mm long and 2 mm i.d. glass tube with one side sealed) was filled with a mixture, and then a thermocouple junction was placed 25~30 mm from the mouth of the sample cell. As a precooling procedure, a vitrification was done by putting the whole sample solution directly into liquid nitrogen where the quenching rate was estimated to be about 500 K/min. After taking out the sample from the liquid nitrogen, the DTA traces were recorded. The detailed procedure is basically the same as the previously reported ones [13, 14]. T_g values were found to be reproducible in this study to within 0.5 K, and the accuracy of temperature reading is estimated to be 1 K from a determination of melting temperatures of several guaranteed grade reagents (absolute ethanol, acetone and chloroform).

2.3. Raman Spectral Measurements. Raman spectra were typically measured by a JASCO NRS-1000DT Raman spectrophotometer equipped with a single monochromator and a CCD detector at room temperature (298 K). The 533 nm from green laser (Showa Optronics Co., Ltd.) with a power of 100 mW was used as an excitation source.

3. Results and Discussion

3.1. Glass Transition Behavior of [DEME][Br]-H₂O Mixed Solutions. Schematic DTA thermograms of [DEME][Br]-H₂O mixed solutions at three typical concentrations ($x = 65.0, 92.0, 95.0$) are shown in Figure 2. At $x = 65.0$, the T_g was observed at 182 K. After the glass transition, we could not see the cold crystallization [20] with a large exothermal peak, which was observed in the case of [DEME][I]-H₂O mixed solutions [14]. Just at $x = 92.0$, we captured the intriguing result: the DTA trace gives a first glass transition followed by an exothermic crystallization-like peak at around

SCHEME 1: The synthetic route of [DEME][Br]. Reagents and conditions: anhydrous acetone, at 373 K, overnight, in autoclave.

FIGURE 2: Schematic DTA warm-up traces of 65.0, 92.0, and 95.0 mol% H₂O mixed solutions are shown.

161 K, then another set of an endothermic inflection at 172 K and an exothermic peak at 177 K in the DTA trace, respectively. To our knowledge, this is a typical DTA trace showing two glass transitions [21–23]. To ensure the second glass transition, we performed supplementary experiments using a requeenching method in the following way: just after recording the first T_g (T_{g1}) and the exothermic inflection as usual in the first run, we requeenched the sample to the liquid nitrogen at 77 K quickly and recorded a DTA trace repeatedly. If the exothermic peak just after the T_{g1} is due to the crystallization, we should have a clear downward C_p shift as the second T_g (T_{g2}) in the second run. The schematic DTA traces obtained in this way are shown in Figure 3. On the other hand, the DTA trace at $x = 95.0$ in Figure 2 shows one- T_g behavior, but interestingly the DTA trace keeps to show a cold crystallization peak. Taken together, glass transition behavior of the [DEME][Br]-H₂O mixed solutions basically shows one glass transition against the water content. But at only limited concentration region of $x = 91.5 \sim 92.5$, two glass transitions (T_{g1} , T_{g2}) were observed which we will describe in detail below.

Summarized results of T_g variations (●) as a function of x are shown in Figure 4. For comparisons, T_g data of [DEME][BF₄]-H₂O [13] and [DEME][I]-H₂O [14] are also shown. The T_g value monotonically decreases with increasing x up to ~ 91.5 mol%. But it suddenly jumps to higher T_g value at $x \geq 91.5$. At this very limited point ($x = 91.5 \sim 92.5$), two T_g s (□: T_{g1} , ○: T_{g2}) were observed. As to an explanation for the mechanism of a double-glass transition

FIGURE 3: The requeenching procedure for detecting the T_{g2} at $x = 92.0$ is shown.

phenomenon, the following was proposed [21–23]. When we lower a temperature of the sample, the homogeneous solution splits into two phases due to its thermodynamic instability where a metastable liquid-liquid immiscibility occurs. Based on the idea, we consider that the [DEME][Br]-H₂O mixed solution may separate into two phases from the original solution at $x = 91.5 \sim 92.5$. It is important to quote that the T_g of a glass-forming liquid has a correlation with its viscosity [24]. Thus, the two- T_g s behavior implies that the viscosities (and thus the structures) of two glassy phases are very different from each other. Looking into the results more closely, we may consider this as a transition state from the structure belonging to the T_{g1} group ($x < 91.5$) to another one due to the T_{g2} group ($x > 92.5$). At $x \geq 92.5$ some inclusions of H₂O ice crystals in the quenched samples were visually confirmed. However, the solutions keep showing the clear but small T_g value up to around 98.9 mol% meaning that the system still holds the glassy state. We find that the edge of a glass-forming composition range extends to more water-rich region as compared to those of the [DEME][I]-H₂O ($x = 95.0$) and/or [DEME][BF₄]-H₂O ($x = 96.0$) mixtures.

3.2. Comparison with the Glass Transition Behaviors of [DEME][I]-H₂O and [DEME][BF₄]-H₂O Mixed Solutions. Firstly, we compare the T_g behavior with the results of [DEME][I]-H₂O solutions. The double-glass transition phenomenon was observed in the [DEME][I]-H₂O mixtures, but there is a major difference in the region where the double glass transitions appeared. One is that the double- T_g s range is relatively wide ($x = 77.5$ to 85.0). Another one is that the T_{g2} value changes little with x in the double-glass transition

FIGURE 4: T_g variations as a function of x are shown. For comparison, T_g data of [DEME][I]-H₂O and [DEME][BF₄]-H₂O mixed solutions are also shown. $\square$: T_{g1} , $\circ$: T_{g2} , $\bullet$: T_g . (only one glass transition was observed except for the region $x = 91.5 \sim 92.5$).

region, though the T_{g1} value decreases with increasing x . This behavior is similar to that in the aqueous solutions of “normal salt” such as symmetrical tetraalkyl ammonium halide (R₄NX; R = Ethyl (Et), *n*-Propyl (*n*-Pr), and X = Cl⁻, Br⁻) [21–23].

On the other hand, the two- T_g s region moves to a very water-poor side in the case of [DEME][BF₄]-H₂O solution and the concentration range of the double glass transitions is much wider (13.5 mol%). These clearly reflect the difference in the anionic effects on the water structure. Previously, we explained that the differences in the results between the [DEME][BF₄] mixtures and the [DEME][I] mixtures come from the variation in the solvation abilities and also the relative positions of the respective anions (BF₄⁻ and I⁻) and [DEME]⁺ cation in the RTILs [14]. The interactions between water molecules and the anions are significantly different in the two RTILs. Considering the smaller ionic radius of the I⁻ anion rather than BF₄⁻ anion, the anion-water interaction in the [DEME][I] solution should be stronger than that in the [DEME][BF₄] solution. This was partly evidenced by

the existence of nearly free hydrogen-bonded Raman band (NFHB) of water molecules in the [DEME][BF₄]-H₂O system, which will be described in the next section. NFHB is assigned to the water molecules which exist as single molecules (not self-associated state) without forming the hydrogen-bonding network among themselves as in pure liquid H₂O [14]. Unfortunately nor the detailed liquid structure of [DEME][BF₄] or [DEME][I] has apparently not been reported as yet. It is interesting to point out that the double-glass transition behavior is systematically changing from [DEME][BF₄]-H₂O (two- T_g s behavior in water-poor region, $x = 16.5 \sim 30.0$), [DEME][I]-H₂O (two- T_g s behavior in water-rich region, $x = 77.5 \sim 85.0$), and finally to [DEME][Br]-H₂O (two T_g s at very limited concentrations, $x = 91.5 \sim 92.5$) with decreasing the anionic radii. Clearly the solvation abilities of the respective anions provide significant effect on the structures of the RTILs-H₂O mixtures which was reflected in the glass transition behavior.

3.3. Raman Spectra. To look further into states of the water structure in the mixtures, we measured Raman spectra. A vibrational spectroscopy is highly sensitive to the intermolecular interactions including hydrogen bonding among water molecules. Firstly, Figure 5(a) shows a comparison of the Raman spectra in the CH and OH stretching regions among [DEME][BF₄]-H₂O, [DEME][I]-H₂O, and [DEME][Br]-H₂O at $x = 65$ in the liquid state. The signals arising from the CH stretching modes of the [DEME] cation appear ranging from 2800 to 3100 cm⁻¹, though unfortunately the precise assignments of the respective peaks are not available at present. The overall CH frequency of the solutions shifts to a lower frequency side on going from [DEME][BF₄]-H₂O to [DEME][Br]-H₂O with slight changes in the spectral shapes. This indicates that the environment around the alkyl chains of [DEME] cation is perturbed with the change of anion.

On the contrary, peaks in the range from 3200 to 3800 cm⁻¹ belong to the OH stretching vibrational mode of water molecules. Figure 5(b) shows the enlarged spectra in this region. In viewing the results, the difference in the Raman spectra are very distinct. As pointed out in a previous paper [25], the spectrum of [DEME][BF₄]-H₂O typically displays a small peak at around 3565 cm⁻¹ with a shoulder of 3620 cm⁻¹. This peak is assigned to the nearly free hydrogen-bonded band (NFHB) of water molecules [26], as mentioned in the previous section. Here water molecules of the NFHB are probably very weakly interacting *via* H-bonding with the BF₄⁻ anions. There is no water molecules due from NFHB in the case where the anion is iodide. Instead, an intensity of the Raman peak centered at ~ 3440 cm⁻¹ is appreciable. This band is mainly due to the OH stretching vibrations of water molecules weakly hydrogen bonded to halide ions [27], suggesting that the interactions between water molecules and the anions are significantly different in the two RTILs, [DEME][BF₄] and [DEME][I] solutions; the anion-water interaction in the [DEME][I] solution is much stronger than that in the [DEME][BF₄] solution.

In viewing the results, the results of [DEME][Br]-H₂O show basically similar behavior to that of [DEME][I]-H₂O. The important result obtained from the comparison

FIGURE 5: Comparison of the Raman spectra among [DEME][BF₄]-H₂O, [DEME][I]-H₂O, and [DEME][Br]-H₂O at $x \approx 65$ in the liquid state. Peak intensities are normalized by the strongest peak of CH stretching vibrational mode of [DEME]⁺ cation. (a) The CH and OH stretching vibrational modes of the solutions and (b) the OH stretching vibrational region.

of the two spectra is that the OH stretching spectrum of the [DEME][Br]-H₂O solution lies as a whole in a lower-frequency region than that of the [DEME][I]-H₂O solution, although the shift is only a marginal one at room temperature. This shows that average strength of hydrogen bonds in [DEME][Br]-H₂O solution is slightly stronger than that in [DEME][I]-H₂O solution.

In summary, we have investigated the glass transition behavior of the quaternary ammonium-type ionic liquid, [DEME][Br]-H₂O mixtures by a simple DTA method. The T_g of [DEME][Br]-H₂O mixtures decreases with increasing x up to around $x = 91.5$ and basically show one- T_g behavior. But at a specific concentration of around $x = 92$ two T_g s were observed. Additionally, we have compared the anionic effect on the glass transition behavior of the series of [DEME][X]-H₂O ($X = \text{Br}^-$, I^- , BF_4^-) mixtures. Similar studies on other different RTILs with, for example, imidazolium-based cation-H₂O systems, will deepen our understanding of the property of mixed solutions. Actually, we reported the glass transition temperatures of 1-butyl-3-methylimidazolium tetrafluoroborate-H₂O mixed solutions as a function of H₂O concentration [28]. Interestingly, in contrary to the results of quaternary ammonium-type ionic liquids, the multiple glass transition behavior was not observed and the system shows only one T_g throughout the whole concentration range.

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