Pressure-induced Change in the Raman Spectra of Ionic Liquid [DEME][BF₄]-H₂O Mixtures

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Abstract. We have measured Raman spectral changes of N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate, [DEME][BF₄]-H₂O mixtures under high pressure. All the Raman spectra of mixtures of water concentrations below 50.0 mol% H₂O changed at around 1 GPa at room temperature. The spectrum at high pressure is completely different from that obtained by cooling the sample at a normal pressure.

1. Introduction

Room temperature ionic liquids (RTILs) are well known to be “room temperature molten salts”, which is consisted of a cation and an anion. RTILs are classified into the cationic series; imidazolium, pyridinium and aliphatic series. The essential physical property of RTILs is derived from a Coulomb interaction between the cation and the anion. RTILs have many characters, such as almost zero vapor pressure, wide electrical windows and the high solubility as solvents.

Recently, binary systems of RTILs have been investigated [1-4]. In particular, RTILs-H₂O systems show interesting physicochemical properties. Jeon et al. [1] investigated structural change of 1-buthyl-3-methylimidazolium tetrafluoroborate, [bmim][BF₄]-H₂O mixtures using attenuated total reflection infrared absorption and Raman spectroscopy. They found that hydrogen-bonded networks of H₂O are broken down with increasing [bmim][BF₄] concentration. Jiang et al. [2] performed molecular dynamics (MD) simulations of 1-octyl-3-methylimidazolium nitrate, [omim][NO₃]-H₂O mixtures. [omim][NO₃]-H₂O mixtures show a polar/nonpolar nano-phase separation (micro-heterogeneity) and a H₂O molecule individually exists in between the polar and the nonpolar regions below 80 mol% H₂O. Above 80 mol%, water tends to aggregate. Subsequently, based on the result of MD simulations of [bmim][BF₄]-H₂O mixtures, Schröder et al. [3] pointed out that H₂O molecules interact with [BF₄]⁻ anions and do not directly interact with [bmim]⁺ cations. In this situation, an interesting question is raised: what happen if RTILs-H₂O mixtures are compressed at room temperature. Reported high pressure researches of RTILs-H₂O systems are only the imidazolium based RTILs-H₂O mixtures [4]. In our previous study [5], we found that the crystal structure of the mixture at 12.0 mol% H₂O and 0.1 MPa is the same as that of pure [DEME][BF₄] and there are not lattice distortions. Here, we report pressure-induced phase transitions of the aliphatic series of RTIL, N,N-diethyl-N-methyl-N-(2-methoxyethyl) ammonium tetrafluoroborate, [DEME][BF₄]-H₂O mixtures.
2. Experiment

We used \(N,N\text{-diethyl-}N\text{-methyl-}N\text{-}(2\text{-methoxyethyl})\) ammonium tetrafluoroborate, \([\text{DEME}]\text{[BF}_4\text{]}\) (Kanto Chemical Co.) as RTIL in this study. This RTIL is hydrophilic [6,7] and the as-received \([\text{DEME}]\text{[BF}_4\text{]}\) contains a small amount of water, whose concentration is estimated to be 126 ppm. Water concentrations in the mixtures, \(x\) were 0, 8.80, 50.0 and 60.1 mol\% \(\text{H}_2\text{O}\). High pressure Raman spectra at room temperature were obtained by a JASCO NR-1800 spectrometer with a diamond anvil cell (DAC). In the DAC, few ruby chips and the sample were sealed by a stainless steel gasket and paired diamond anvils. In order to estimate the pressure, we applied the relationship between the pressure and the spectral shift of the \(R_1\) fluorescence line of the ruby chip [8]. The 514.5 nm line of argon ion laser excitation (~300 mW) was used.

3. Results and discussion

3.1. Pressure-induced Raman spectral changes of \([\text{DEME}]\text{[BF}_4\text{]}\)-H\(_2\)O mixed solutions

Raman spectra of \([\text{DEME}]\text{[BF}_4\text{]}\)-H\(_2\)O mixed solutions as a function of pressure are shown in Figure 1. The wavenumber region of 2700 – 3200 cm\(^{-1}\) is assigned to the CH stretching mode of cation. Even at room temperature, the spectra of pure \([\text{DEME}]\text{[BF}_4\text{]}\) and the mixtures of \(x = 8.80, 50.0\) mol\% \(\text{H}_2\text{O}\) changed at around 1 GPa. When the spectra changed, a peak at around 3000 cm\(^{-1}\) splits and a broad band at around 2850 cm\(^{-1}\) becomes sharp. As the applied pressure increased, the whole spectra shifted to a higher wavenumber region. Blueshifts of C-H bands imply the contraction of C-H covalent bonds [4]. Interestingly, at \(x = 60.1\), significant spectral change of the mixture did not occur up to 1.5 GPa. Figure 2 shows the \(v_1\) symmetric mode of \(\text{H}_2\text{O}\) corresponding to a nearly free hydrogen bond band (NFHB) of water [9] (\(x = 8.80\) and 50.0). The colored spectra in Figure 2 correspond to the state of mixtures where the structural change occurred. As the pressure increased, \(v_1\) symmetric modes of NFHB at around 3550 cm\(^{-1}\) apparently vanished upon compression. This is consistent with the results of [bmim][BF\(_4\)]-H\(_2\)O system as a function of pressure, reported by Chang et al. [4]. In the [bmim][BF\(_4\)]-H\(_2\)O system at 52 mol\% \(\text{H}_2\text{O}\), the mixture shows the bonded OH and the free OH bands

![Figure 1](image-url). The CH stretching Raman spectra of \([\text{DEME}]\text{[BF}_4\text{]}\)-H\(_2\)O mixed solutions as a function of pressure. Measured temperature is fixed at room temperature.
at ordinary temperature and a normal pressure. They reported that compression reduced the free OH band intensity in the IR spectra. Simultaneously, the bonded OH band intensity became stronger and the band width became sharper as the pressure increased. They concluded that the free OH switches into the bonded OH when high pressure is applied. Similar to the results of [bmim][BF₄]-H₂O mixtures, there is a possibility that the nearly free hydrogen bonds in [DEME][BF₄]-H₂O varied into the bonded OH with increasing the pressure. However, within the spectral resolution of the present data, it is not clear whether the bonded OH increased or not.

3.2. Pressure- vs. temperature-induced spectral changes

According to our previous study [5,10], we reported complicated phase transitions in [DEME][BF₄]-H₂O mixtures in the range from x = 0.0 ~ 12.0 mol% at a normal pressure: Typically, the crystal phase forms at x < 4.0 upon cooling, but the amorphous phase appears from 4 to 10 mol%. Above this concentration, two-phases of the amorphous and the crystal co-exist. Pure [DEME][BF₄] crystallized at around -30 ℃ and a normal pressure. In pure [DEME][BF₄], two different crystal structures were determined below crystallization temperature, Tc: One is orthorhombic space group Pbcm and the other is monoclinic space group P2₁. Importantly, we found that there are not lattice distortions in the [DEME][BF₄]-H₂O mixture at x = 12.0 in spite of the two-phase coexistence at low temperature. The crystal structure of the mixture was the same as pure [DEME][BF₄]. Thus, we expect that the structure at high pressure may also not depend on the H₂O concentration of the mixture.

For a comparison with the results of the pressure-induced structural change at room temperature, CH stretching Raman spectrum of the crystal at low temperature and normal pressure is displayed in Figure 3. It is to be noted that the spectra at high pressures are obviously different from that at low temperature. On the other hand, among the spectra of x = 0, 8.80 and 50.0, differences in spectral shapes were not observed. Thus, we can conclude that, at least, below x ≈ 50, H₂O molecules may not affect on the structures of the mixtures at high pressures, as well as the results at low temperature.

Discussions from the lower lattice mode due from the interaction between BF₄ and water, and/or e.g. C₄N stretching vibration of the [DEME] cation would be helpful for the interpretation of the present results. However, unfortunately detailed peak assignments of the mode for [DEME][BF₄] is not available. Thus, the present results are not able to explain the cause of the difference in the CH stretching bands. The band at around 3550 cm⁻¹ seems to fade away.

**Figure 2.** $v₁$ symmetric mode of H₂O corresponding to a nearly free hydrogen bond band (NFHB). Upon compression, the NFHB at around 3550 cm⁻¹ seems to fade away.

**Figure 3.** Raman CH stretching spectra at several concentrations where the pressure-induced structural change occurred are shown. For a comparison, the spectrum of pure [DEME][BF₄] at -80 ℃ at a normal pressure is shown at the bottom of the figure.
not available at moment. Nonetheless, we can give the plausible picture in view of the comparison of the Raman spectra. Raman spectra in the lattice vibrational region (500 ~ 1000 cm⁻¹) at high pressure was different from these at low temperature (data not shown.). Full width at half maximum (FWHM) of the peaks in the Raman spectrum corresponding to the phase where the pressure-induced structural change occurred is larger than that of the crystal at low temperatures. It is considered that lattice distortions of the phase at high pressures are remarkable and the phase contains more disordered structure than the temperature-induced crystal. We suppose that the RTIL may begin to interact with each other and organize themselves by enhanced molecular packing at high pressures. For a complete understanding of the structure under high pressure, high pressure X-ray experiments on the present system would be helpful.

4. Conclusion
We have demonstrated pressure-induced spectral change of [DEME][BF₄]-H₂O mixtures at various concentrations. We found that the structure at high pressure is totally different from that at low temperature and a normal pressure. Under high pressure, intermolecular interactions in the RTILs might be modified by a balance between the hydrogen bonding and the molecular packing.

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