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Local Structures of Water in 1-Butyl-3-methylimidazolium Tetrafluoroborate Probed by High-Pressure Infrared Spectroscopy

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We have investigated the aggregation behaviors of water molecules in 1-butyl-3-methylimidazolium tetrafluoroborate/water mixtures using high-pressure methods. Under ambient pressure, the IR spectra indicate that two types of O–H species: free O–H and bonded O–H, existing in ionic liquid/water mixtures. As samples were compressed, a continuous loss of the free O–H band intensity was observed. This observation may have arisen from changes in the local structures of water molecules, and the geometrical properties of the hydrogen-bond network are likely to be perturbed as the pressure is elevated. A complementary insight of the O–H spectral features is obtained by measuring the concentration-dependent variation in the mid-infrared spectra under high pressure. A sharp O–H stretching band was observed in a diluted mixture corresponding to the high order in an ice VII-like structure. Nevertheless, a very broad O–H feature was measured in a concentrated mixture, which may be attributed to the presence of more than one stable cluster.

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Introduction

Until recently, little was known about the fundamental physical chemistry of ionic liquids in general. At present, most interest in room-temperature ionic liquids is centered on the design of new non-volatile solvents.[1,2] While ionic liquids are composed of only ions, they also show very high ionic conductivity. The fact is that many ionic liquid are non-volatile and non-flammable which makes them a safer and more environmentally benign solvent for reactions and separations than are the traditional volatile organic solvents. Previous studies concerning the structure of ionic liquids have included the use of x-ray crystallography and vibrational spectroscopy under the condition of ambient pressure. Nevertheless, only little has been known about liquid structures of ionic liquids.[3-7] Although the results of crystal structures are highly informative concerning the relative geometry changes, crystallography does not provide any direct information on the local structure in the liquid state. An ionic liquid has a melting temperature around room temperature, and is built up by a bulky, asymmetric organic cation to prevent ions from packing easily. In recent years, ionic liquids based on the 1-alkyl-3-methylimidazolium cation have received much attention.[1-9] Various investigators have addressed the question of intermolecular interactions in systems containing 1-alkyl-3-methylimidazolium and a variety of anions. For instance, solvation of the lithium ion in room-temperature ionic liquids has been investigated *via* Raman spectroscopy and DFT calculations by Umebayashi and Ishiguro.[4] Although the literature contains many articles on the synthesis of ionic liquids and the application of ionic liquids as solvents, studies on their phase behavior in the presence of water are scarce. In our current investigation, we used various pressures as a window to look into the association of water molecules in 1-butyl-3-methylimidazolium tetrafluoroborate.

Molecular states of water dissolved in various solvents have been extensively studied using infrared spectroscopy.[10] In principle, information about the broad distribution of hydrogen bonds can be derived from the profiles of OH stretching bands (ν_1 and ν_3) in water.[10-12] In contrast, the bending mode of water, which can be found at *ca.* 1650 cm^{-1}, is seldom used to elucidate the molecular state of water, because it hardly changes its position upon hydrogen bonding.[12] The role of water in ionic liquids is complex, and depends on the supramolecular structures of ionic liquids. An interesting aspect of such ionic liquids is that the 1-alkyl-3-methylimidazolium cations possess an inherent amphiphilicity. Therefore, aggregation behaviors analogous to that exhibited by short-chain cationic surfactants may be displayed by these ionic liquids.[13-20] Based on the results of theoretical studies, at high ionic liquid concentrations ionic liquids seem to form clusters, as in the pure state, and water molecules interact with the clusters without interacting among themselves.[18-20] Nevertheless, direct experimental evidence at the molecular level is not easy to obtain to corroborate these simulation results.

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The redshift of the A–H stretching vibration is often used as evidence for A–H···B hydrogen bonding, where A and B are highly electronegative atoms, such as O and N. Recent studies have shown that if A is a carbon atom, which is attached to electronegative groups, the C–H groups may also form an energetically stable weak hydrogen bond.[21–25] Several studies have shown that C–H···O and C–H···X (X = F, Cl, Br) hydrogen bonds play an important role in the structure of ionic liquids, especially those derived from the 1-alkyl-3-methylimidazolium cation.[1,2,21,22] One of the intriguing aspects of weak hydrogen bonds is that the C–H covalent bond tends to shorten as a result of the formation of weak hydrogen bonds.[21–25] Associated with this contraction is a shift of the C–H stretching frequency to blue. Nevertheless, the mechanism is still under debate. Thus, we hope the present paper, describing the application of the high-pressure method to aqueous ionic liquids, will shed light on this controversy.

The use of pressure as a variable allows one to change, in a controlled way, the intermolecular interactions without encountering major perturbations produced by changes in the temperature and the chemical composition.[26–29] Changing the temperature of a chemical system at atmospheric pressure produces a simultaneous change in the thermal energy and the volume. To separate the thermal and volume effects, one must perform high-pressure experiments. For a pure solvent, it is well-known that the hydrogen-bond network is distorted by pressure. For a solution, on the other hand, it is still to be investigated how the hydration shell responds to pressure variations. The effects of high pressure on intermolecular interactions have been the subjects of extensive studies since Bridgman first examined the phase diagram of water.[30] The many ways in which the water molecules may link through hydrogen bonding give a remarkably rich phase diagram having more than 10 reported phases.[10,12] At room temperature, only three phases, *i.e.*, liquid water, ice VI, and ice VII, exist up to at least 38 GPa.[10,12] The high density of ices VI and VII is due to two interpenetrated, but unconnected, zeolite-like and diamond-type sublattices for ices VI and VII, respectively.[10] In the Results and Discussion section, we show that high pressure is a sensitive method to probe the molecular organization of water in 1-butyl-3-methylimidazolium tetrafluoroborate.

Experimental

Samples were prepared using 1-butyl-3-methylimidazolium tetrafluoroborate (>97%, Fluka), 1-butyl-3-methylimidazolium bromide (>97%, Fluka), D_2O (99.9%, Aldrich), and H_2O (for chromatography, Merck). A diamond anvil cell (DAC) of Merril–Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures of up to *ca.* 2 GPa. Two type-IIa diamonds were used for mid-infrared measurements. The sample was contained in a 0.3-mm-diameter hole in a 0.25-mm-thick inconel gasket mounted on the diamond anvil cell. To reduce the absorbance of the samples, CaF_2 crystals (prepared from a CaF_2 optical window) were placed into the holes and firmly compressed prior to inserting the samples. A droplet of a sample filled the empty space of the entire hole of the gasket in the DAC, which was subsequently sealed when the opposed anvils, were pushed toward one another. Infrared spectra of the samples were measured on a Perkin-Elmer Fourier-transform spectrophotometer (Model Spectrum RXI) equipped with a LITA (lithium tantalite) mid-infrared detector. The infrared beam was condensed through a 5X beam condenser onto the sample in the diamond anvil cell. Typically, we chose a resolution of 4 cm^{-1} (data point resolution of 2 cm^{-1}). For each spectrum, typically 1000 scans were compiled. To remove the absorption of the diamond anvils, the absorption spectra of DAC were measured first and subtracted from those of the samples. Pressure calibration followed the Wong's method.[31,32] We used the pressure shift of the uncoupled O–H stretching infrared band of HDO in D_2O systems for internal pressure measurements. The pressure-induced frequency shift of the uncoupled band is extremely large, and thus the frequency shift is very sensitive to pressure. The change in the frequency of the O–H band is plotted against the screw moving distances. The spectra of samples measured at ambient pressure were taken by filling samples in a cell having two CaF_2 windows without the spacers.

Results and Discussion

Figure 1 displays infrared spectra of 1-butyl-3-methylimidazolium tetrafluoroborate (curve a), 1-butyl-3-methylimidazolium tetrafluoroborate/H_2O (curve b), and 1-butyl-3-methylimidazolium tetrafluoroborate/D_2O (curve c) having a mole fraction of 1-butyl-3-methylimidazolium tetrafluoroborate equal to (b) 0.41, and (c) 0.25, obtained under ambient pressure in the region of the C–H and O–H stretching vibrations. To reduce the absorbance of the O–H stretching bands, we measured the infrared spectrum using D_2O, rather than H_2O, in Fig. 1c. The O–H bands in Fig. 1c arise from diluted HOD (impurity). As indicated in Fig. 1a, the infrared spectrum of pure 1-butyl-3-methylimidazolium tetrafluoroborate exhibits three discernible peaks, *i.e.*, 2876, 2940, 2964 cm^{-1}, respectively, in the 2800 – 3000 cm^{-1} region, corresponding to C–H stretching modes of the alkyl groups.[22,29] The 3122 and 3162 cm^{-1} bands can be attributed to coupled imidazolium C–H stretching vibrations and the stretching modes of OH due to the trace amount of water appear at *ca.* 3563 and 3637 cm^{-1} in Fig. 1a. According to Cammarata[11] and Lopez-Pastor,[16] the two narrow, well-separated bands observed at *ca.* 3563 and 3637 cm^{-1} can be assigned to the antisymmetric (ν_3) and symmetric (ν_1) stretch vibrations of the water monomer interacting with ionic liquids. As revealed in Fig. 1b, the O–H stretching modes underwent changes as H_2O was added, and the spectrum shows one band located at *ca.* 3618 cm^{-1} with a shoulder at 3577 cm^{-1} and a broad band centered at about 3454 cm^{-1}. The observation of the broad band at *ca.* 3454 cm^{-1} indicates the presence of water molecules interacting with each other. This result suggests that two different types of OH species are found in Fig. 1b. The 3618 and 3577 cm^{-1} bands can be assigned as free O–H or free-O–H interacting with ions, while the broad band at 3454 cm^{-1} (bonded O–H) should be attributed to the formation of O–H···O hydrogen bonds in water clusters. The O–H spectral features showed further evolution as the characteristic free O–H and bonded O–H bands were shifted to 3587 and 3439 cm^{-1}, respectively, in Fig. 1c. As H_2O or D_2O was added, *i.e.*, from curve a to curve c, the spectra in Fig. 1 show that more and more bonded O–H species were formed.

Figure 2 illustrates the band frequency of the dominant alkyl C–H stretching absorption *versus* the mole fraction of 1-butyl-3-methylimidazolium tetrafluoroborate and 1-butyl-3-methylimidazolium bromide, respectively. We can see that the dilution of ionic liquids with D_2O or H_2O leads to a shift of the alkyl C–H signal to higher frequencies. Previous studies have shown that the blue shifts of the C–H bands are closely related to changes in the liquid structure and the hydration states.[26–29] Looking into more details in Fig. 2, we observe no drastic changes in the concentration dependence of the alkyl C–H band

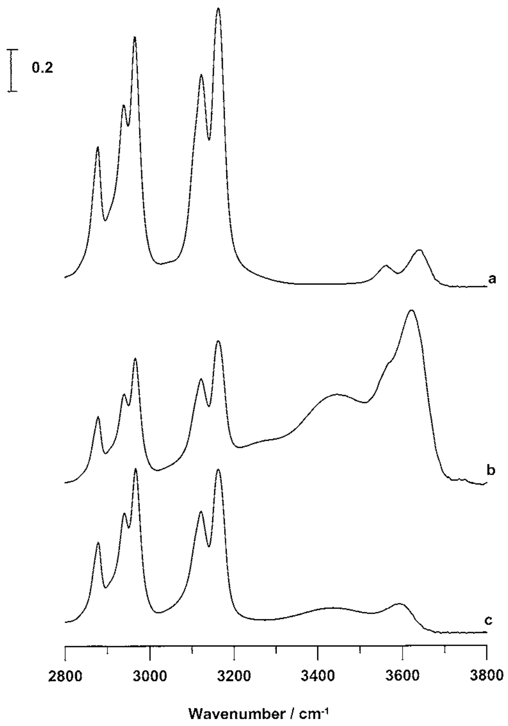

Fig. 1 IR spectra of (a) 1-butyl-3-methylimidazolium tetrafluoroborate, (b) 1-butyl-3-methylimidazolium tetrafluoroborate/H_2O, and (c) 1-butyl-3-methylimidazolium tetrafluoroborate/D_2O having mole fraction of 1-butyl-3-methylimidazolium tetrafluoroborate equal to (b) 0.41, and (c) 0.25 obtained under ambient pressure.

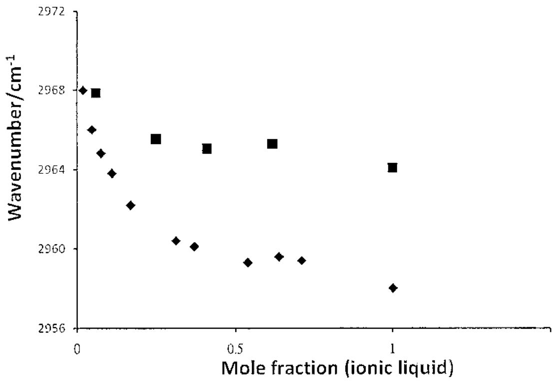

Fig. 2 Concentration dependence of the alkyl C–H stretching frequency *versus* the mole fraction of 1-butyl-3-methylimidazolium tetrafluoroborate (square) and 1-butyl-3-methylimidazolium bromide (diamond).

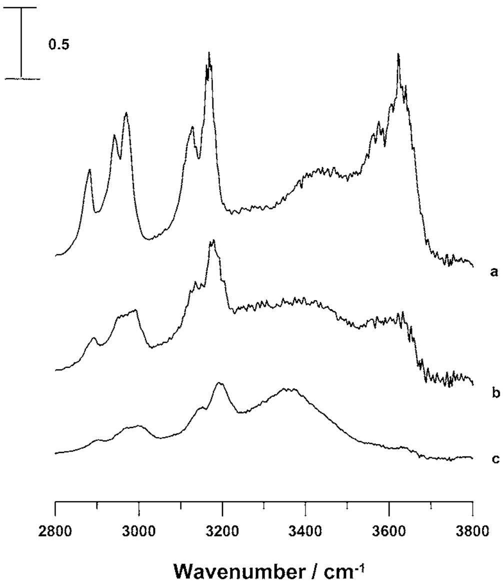

Fig. 3 Pressure dependence of the IR spectra in a 1-butyl-3-methylimidazolium tetrafluoroborate/water mixture with an ionic liquid mole fraction of 0.48 under the pressures of (a) ambient, (b) 0.9 GPa, and (c) 2.5 GPa.

frequency at high concentrations of ionic liquids; that is, $0.4 \leq$ mole fraction (ionic liquid) ≤ 1. This behavior may indicate a clustering of the ionic liquids and a slight perturbation due to the presence of H_2O or D_2O. We stress that the alkyl C–H stretching absorption exhibits increases in frequency upon dilution at low concentrations of ionic liquids. This observation suggests the formation of a certain water structure around cations of ionic liquids in a water-rich region, but the details remain not clear. We note that blue shifts of alkyl C–H vibrations strongly depend on the anion, as shown in Fig. 2. Anions, which interact directly with the hydrogen atoms of water molecules, were observed having a heavier effect on the spectroscopic characteristics of the O–H stretching bands, compared with cations that interact with the oxygen atoms of water molecules. For example, the O–H stretching mode arising from monomer-like water molecules can be observed in an aqueous solution containing hydrophobic perchlorate anions.[33]

Figure 3 displays the IR spectra of a 1-butyl-3-methylimidazolium tetrafluoroborate/H_2O mixture having its mole fraction of ionic liquid equal to 0.48, obtained under ambient pressure (curve a), and at 0.9 (curve b), and 2.5 GPa (curve c). By comparing Figs. 3a and 3b, the red shift of the bonded O–H band at *ca.* 3360 cm^{-1} is obvious as the pressure was elevated in Fig. 3b. This behavior is in accord with the general trend observed of a red shift with pressure for O–H and C=O stretching modes in a strongly hydrogen-bonded O–H···O and C=O···H system, respectively.[10] For instance, an increase in pressure shortens and strengthens the intermolecular hydrogen bond in ice VII, while intramolecular O–H bonds lengthen as the pressure is increased. Analyzing the pressure dependence of the dominant C–H stretches in Fig. 3 yielded blue frequency shifts that correspond to contraction of the C–H bond. At a pressure of 2.5 GPa (Fig. 3c), the spectral features showed further evolution through an observation of bandwidth narrowing for the peak at 3360 cm^{-1}. This observation indicates that a pressure-induced phase transition occurs in Fig. 3c. It is known that O–H···O hydrogen-bonded networks can be modified by varying the pressure, and the sharper structure of bonded O–H bands at *ca.* 3360 cm^{-1} revealed in Fig. 3c is in part due to the higher order and anisotropic environment in a solid structure.[26-29] As shown in Figs. 3a – 3c, compression leads to a continuous loss of the free O–H (at *ca.* 3620 cm^{-1}) band intensity. In other words, the energetically more favored O–H species is switched from free-OH to bonded O–H as high pressures are applied. The evolutions of the O–H spectral features observed in Fig. 3 may arise from changes in the local structures of water molecules and the geometrical properties of the hydrogen-bond network are likely perturbed as the pressure is elevated.

A complementary insight concerning the OH spectral features is obtained by measuring the concentration-dependent variation

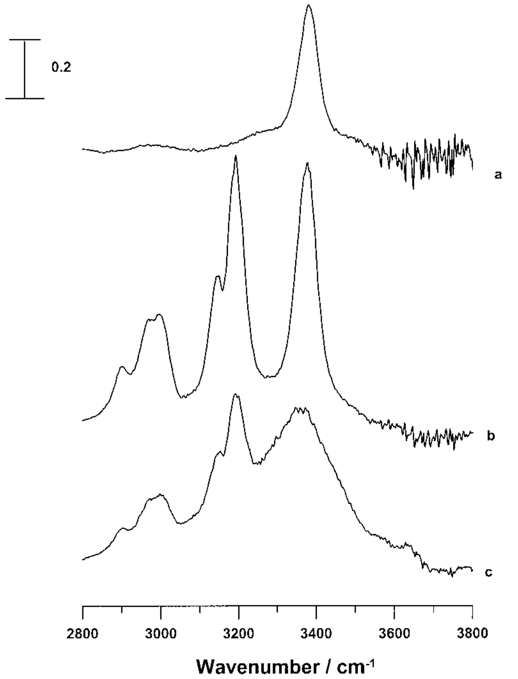

Fig. 4 IR spectra of (a) D_2O, (b) 1-butyl-3-methylimidazolium tetrafluoroborate/D_2O with a mole fraction (ionic liquid) = 0.08, and (c) 1-butyl-3-methylimidazolium tetrafluoroborate/H_2O with a mole fraction (ionic liquid) = 0.48, obtained at *ca.* 2.5 GPa.

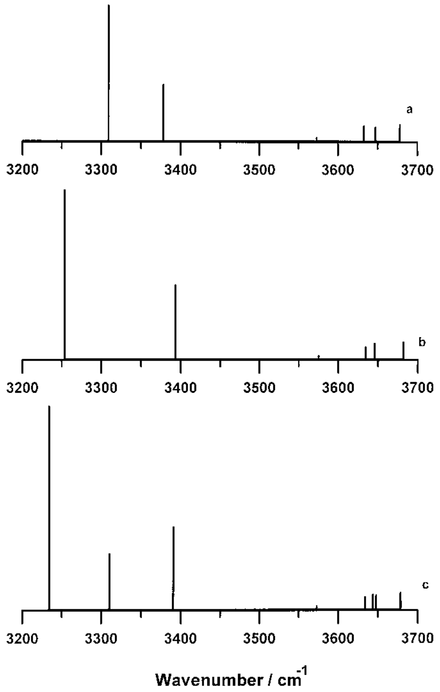

Fig. 5 DFT-calculated O–H stretching frequencies *versus* the absorption intensities of (a) and (b) 1-butyl-3-methylimidazolium cation-$(water)_3$, and (c) 1-butyl-3-methylimidazolium cation-$(water)_4$.

in the mid-infrared spectra under high pressure. Figure 4 illustrates the experimental IR spectra of D_2O (curve a) and mixtures with the mole fraction of 1-butyl-3-methylimidazolium tetrafluoroborate equal to 0.08 (curve b) and 0.48 (curve c) obtained at the pressure of *ca.* 2.5 GPa. Figure 4a indicates the IR spectra of the OH stretching mode of HOD (H_2O is negligible) in the state of ice VII. The frequency-shift of this OH stretching band was also used as an internal pressure gauge to calibrate pressures on the sample in the gasket, because the frequency-shift is very sensitive to pressure compared to those of the bending modes.[31,32] The O–H band of the liquid phase is broad, and the peak frequency decreases as the pressure is elevated. There are two discontinuities in the pressure dependence of the O–H frequencies as the result of liquid/ice VI and ice VI/ice VII transitions. By comparing Figs. 4a and 4b, we observed a similar sharp O–H feature in a diluted mixture in Fig. 4b corresponding to the high order environments in an ice VII-like structure. As shown in Fig. 4c, a further increase in the concentration of 1-butyl-3-methylimidazolium tetrafluoroborate does affect the bandwidths of the OH stretching bands, increasing *versus* the concentration. The OH spectral features revealed in Fig. 4, that is, their sensitivity to changes in concentration, may arise from changes in the water-cluster sizes and a perturbation in the geometrical properties of hydrogen-bond network.

To obtain a direct comparison of the effects of varying the composition, we performed density functional theory calculations using the Gaussian 03 program package,[34] and the predicted O–H absorption profiles are displayed in Fig. 5. The geometry optimization was calculated by using Becke3LYP level with 6-31 + G* and the optimized structures are displayed in Fig. 6. Harmonic vibrational frequencies were obtained from analytical second derivatives, and were scaled with a single factor (0.955). Compared to MP2/6-31 + G*, B3LYP/6-31 + G* offers the advantage of being less computationally demanding. As for the vibrational frequencies, the two methods provide similar values, with a typically difference of less than 3%, although the MP2/6-31 + G* computation requires much more disk space in handling larger clusters. Only two of the 1-butyl-3-methylimidazolium cation-$(water)_3$ complexes (Figs. 5a and 5b) and one of the 1-butyl-3-methylimidazolium cation-$(water)_4$ complexes (Fig. 5c) are reported in Fig. 5. Figure 5a displays two bonded O–H stretching vibrations located at 3309 and 3378 cm^{-1}, respectively, and four free O–H bands. Nevertheless, the bonded O–H bands are significantly shifted to 3254 and 3393 cm^{-1} in Fig. 5b. We note that the free O–H band frequencies are almost identical in Figs. 5a and 5b. Figure 5c reveals three bonded O–H absorption bands and five free O–H bands, while the bonded O–H bands are switched to 3234, 3310, 3390 cm^{-1}. As the clusters increase in size, the number of low-lying isomers increases exponentially, and the structural identification is complicated. It is instructive to note that the calculation in Figs. 5 and 6 may only provide qualitative support for the suggested interactions, since the calculations are based on gas-phase structures, and the anions are not included.

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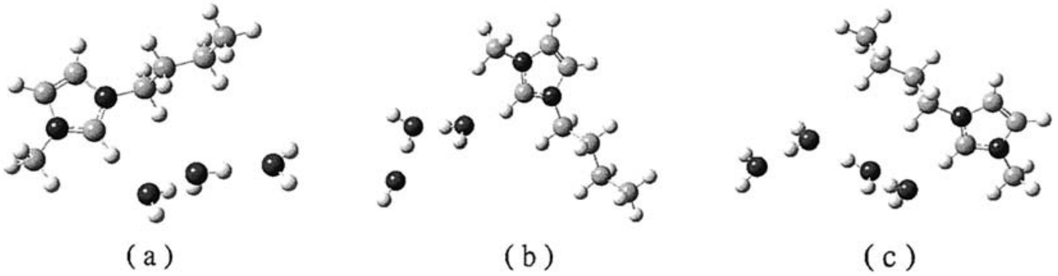

Fig. 6 Optimized structures of (a) and (b) 1-butyl-3-methylimidazolium cation-(water)$_3$, and (c) 1-butyl-3-methylimidazolium cation-(water)$_4$.

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