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Effects of water and methanol on the molecular organization of 1-butyl-3-methylimidazolium tetrafluoroborate as functions of pressure and concentration

Hai-Chou Chang,^{1,a)} Jyh-Chiang Jiang,² You-Chang Liou,¹ Chao-Hsin Hung,¹ Ting-Yun Lai,¹ and Sheng Hsien Lin^{3,4}

¹Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan

²Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan

³Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan

⁴Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan

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The structural organization in mixtures of 1-butyl-3-methylimidazolium tetrafluoroborate ($[\text{bmim}] \times [\text{BF}_4]$)/water or methanol was studied by infrared spectroscopy. No drastic change in the concentration dependence of the alkyl C–H band frequency was observed at high concentration of the ionic liquid. This behavior indicates a clustering of the ionic liquid in alkyl regions. Nevertheless, the presence of methanol significantly perturbs the ionic liquid–ionic liquid associations in the imidazolium region. On the basis of the responses to change in pressure and concentration, two different types of O–H species, i.e., free O–H and bonded O–H, were observed in the O–H stretching region. For $[\text{bmim}][\text{BF}_4]$ /water mixtures, the compression leads to loss of the free O–H band intensity. It is likely that free O–H is switched to bonded O–H as high pressures are applied. For $[\text{bmim}][\text{BF}_4]$ /methanol mixtures, the free O–H is still stable under high pressures.

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INTRODUCTION

Recently, room-temperature ionic liquids have received significant attention for their use in multidisciplinary chemistry areas.^{1–4} Ionic liquids are generally nonvolatile at room temperature. Their low vapor pressure decreases contamination from evaporation compared to other conventional non-ionic solvents. Due to this feature and to a number of other unique properties, ionic liquids have a high potential to be used as reaction media in green chemistry.^{1,2} Ionic liquids have a melting temperature around room temperature and are built up by a bulky, asymmetric organic cation to prevent ions from packing easily. This asymmetry opposes the strong charge ordering due to the ionic interactions that normally would cause the system to crystallize, and thus, a wide liquid range is obtained. In recent years, ionic liquids based on the 1-alkyl-3-methylimidazolium cation have received much attention.^{3–8} Combining organic cations with suitable anions allows one to tailor the thermodynamic properties of ionic liquids over a wide range of miscibility with other solvents.

Ionic liquids are generally miscible with water, being ionic compounds. However, they could be designed to be made hydrophobic by choice of anion species. The water miscibility of ionic liquids is also affected by the hydrophobicity of the alkyl substituents of the imidazolium cation. An interesting aspect of such ionic liquids is that the 1-alkyl-3-methylimidazolium cations possess an inherent

amphiphilicity.^{1–4} Long-chained imidazoliums (or pyrrolidiniums, pyridiniums, etc.) may act as surfactants. For example, the micellization of long-chained *N*-alkyl-*N*-methylpyrrolidinium bromides $[\text{C}_n\text{MPB} (n > 6)]$ in aqueous solution has been studied by Baker *et al.*⁹ The critical micelle concentration values for C_nMPB series are comparable to their respective alkyltrimethylammonium bromide counterparts. The role of water in ionic liquids is complex and depends on the supramolecular structures of ionic liquids.^{10–14} Researchers have demonstrated that small amounts of water in fluorinated ionic liquids, such as 1-butyl-3-methylimidazolium hexafluorophosphate ($[\text{bmim}] \times [\text{PF}_6]$) and tetrafluoroborate ($[\text{bmim}][\text{BF}_4]$), have a dramatic effect on the rate of diffusion.^{15–17} Measurements of the solvation responses and microscopic solvent properties have resulted in the accumulation of a sizable database on solvation dynamics in ionic liquids.^{18–21} Increasing attention has been devoted to conducting biocatalytic transformation in ionic liquids.^{22,23} The addition of water to $[\text{bmim}][\text{BF}_4]$ is very common in biocatalytic work and this is one of the motivations for the current work.^{22–24} Ionic liquids containing dissolved water may not be regarded as homogeneous solvents but have to be considered as nanostructured materials.^{25–28} Based on the theoretical results of Wang and Voth, 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.²⁵ Nevertheless, direct experimental evidence at the molecular level is not easy to obtain to corroborate these simulation results. Previous studies to the structure of ionic

^{a)}Author to whom correspondence should be addressed. Electronic mail: hcchang@mail.ndhu.edu.tw. Fax: +886-3-8633570. Tel.: +886-3-8633585.

liquids have included the use of x-ray crystallography and vibrational spectroscopy under the condition of ambient pressure.^{1–4} Nevertheless, only little has been known for liquid structures of ionic liquids. Although the results of crystal structures are highly informative on the relative geometry changes, crystallography does not provide direct information on the local structure in the liquid state. Over the last years the interest in pressure as an experimental variable has been growing in physicochemical studies.^{29–32} The study of pressure effects reveals the intermolecular interactions of the ionic liquid at a constant kinetic energy or temperature. In this study, we use variable pressure as a window into self-assembly behaviors in [bmim][BF₄]/water and [bmim] × [BF₄]/methanol, respectively.

Several studies have shown that C–H...O and C–H...X hydrogen bonds play an important role in the structure of ionic liquids, especially those derived from the 1-alkyl-3-methylimidazolium cation.^{3,29–32} It is assumed that the structure of these ionic liquids should be considered as networks of anions and cations, linked together by hydrogen bonds. Nevertheless, direct structural information of these materials in the liquid phase or in solution is difficult to obtain. One of the intriguing aspects of weak hydrogen bonds is that the C–H covalent bond tends to shorten as a result of formation of weak hydrogen bonds. Associated with this contraction is a shift of the C–H stretching frequency to the blue.^{33–35} Despite the rather large number of papers devoted to the phenomenon of blueshifting hydrogen bonds, the mechanism by which C–H bonds are strengthened by C–H...O or C–H...X interactions is still the subject of debate; two schools of thought have emerged to try to explain its physical basis. Hobza and Havlas³³ suggested the strengthened C–H bond originates from a new mechanism called antihydrogen bonding in which a secondary effect or structural reorganization of the proton donor framework occurs upon contraction of the C–H bond directly involved in weak hydrogen bonding. However, Gu *et al.*³⁴ and Masunov *et al.*³⁵ concluded that there are no fundamental differences between redshifting and blueshifting hydrogen bonding and explain the differences solely on the basis of a combination of electrostatic, polarization, charge transfer, dispersion, and steric repulsion forces between the proton donor and acceptor.

The effects of high pressure on intermolecular interactions have been the subjects of extensive studies since Bridgman first examine the phase diagram of water.^{36,37} The many ways in which the water molecules may link through hydrogen bonding give a remarkably rich phase diagram having more than ten reported phases.^{36,37} At room temperature, only three phases, i.e., liquid water, ice VI, and ice VII, exist up to at least 38 GPa. The high density of ices VI and VII is due to two interpenetrated, but unconnected, zeolitelike and diamond-type sublattices for ices VI and VII, respectively.^{36,37} The use of pressure allows one to change, in a controlled way, the intermolecular interactions without the major perturbations produced by changes in temperature and chemical composition. For the pure solvent, it is well known that the hydrogen-bond network is distorted by pressure. For the solution, on the other hand, it is still to be investigated how the hydration shell responds to pressure variation. In the

Results and Discussion section, we show that high pressure is a sensitive method to probe the molecular organization in [bmim][BF₄]/water or methanol.

EXPERIMENTAL SECTION

Samples were prepared using 1-butyl-3-methylimidazolium tetrafluoroborate (99.8% by HPLC, LOT 1225502, Fluka), D₂O (99.9%, Aldrich), H₂O (for chromatography, Merck), methanol (99.9%, Merck), and methanol-d₄ (99.8% D, Cambridge Isotope). A diamond anvil cell (DAC) of Merrill-Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to ca. 2 GPa. Two type-IIa diamonds were used for midinfrared 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, CaF₂ crystals (prepared from a CaF₂ optical window) were placed into the holes and compressed firmly 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 lithium tantalite midinfrared 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 follows the method of Moffatt and co-workers^{38,39} The pressure dependence of screw moving distances was measured. Spectra of samples measured at ambient pressure were taken by filling the samples in a cell having two CaF₂ windows but lacking the spacers.

RESULTS AND DISCUSSION

Figure 1 displays infrared spectra of [bmim] × [BF₄]/D₂O (curve a), [bmim][BF₄]/H₂O (curve b), and [bmim][BF₄]/methanol (curve c) having mole fraction of [bmim][BF₄] equal to (a) 0.059, (b) 0.41, and (c) 0.53 obtained under ambient pressure in the region of C–H and O–H stretching vibrations. The C–H stretching of [bmim][BF₄] overlaps with the O–H stretching bands of pure H₂O, so we measured the infrared spectrum in a solution of D₂O, rather than H₂O, in Fig. 1(a). As indicated in Fig. 1(a), the infrared spectrum exhibits three discernible peaks, i.e., 2878, 2943, 2967 cm⁻¹, respectively, in the 2800–3000 cm⁻¹ region corresponding to C–H stretching modes of the alkyl groups. 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 formation of HOD appear at ca. 3414 and 3557 cm⁻¹ in Fig. 1(a). The broad band at ca. 3414 cm⁻¹ could be attributed to hydrogen-bond network, i.e., bonded O–H. The weak shoulder at ca. 3557 cm⁻¹ indicates that at least two different types of HOD species were observed in Fig. 1(a) and the 3557 cm⁻¹ band can be assigned as free

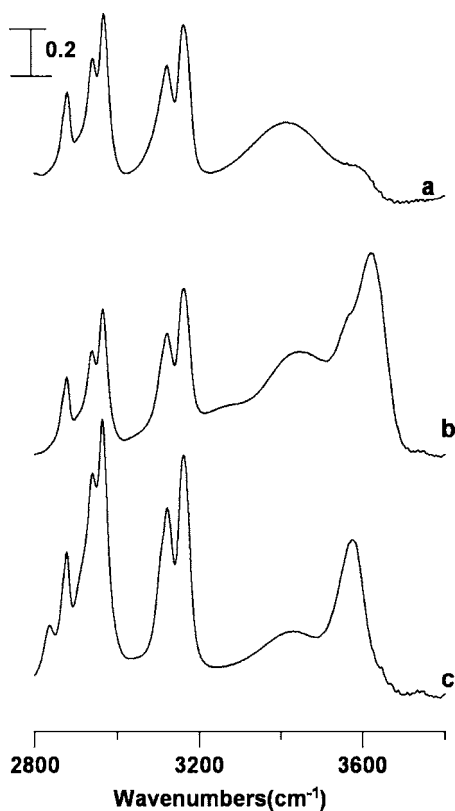


FIG. 1. IR spectra of [bmim][BF₄]/D₂O (curve a), [bmim][BF₄]/H₂O (curve b), and [bmim][BF₄]/methanol (curve c) having mole fraction of ionic liquid equal to 0.059, 0.41, and 0.53, respectively.

O–H or free O–H interacting with anions.^{8,40,41} As more [bmim][BF₄] was added, increasing the mole fraction from curve a to curve b, the relative absorption intensity of free O–H increases. As revealed in Fig. 1(b), the free O–H modes are located at ca. 3580 and 3617 cm⁻¹, respectively, and the bonded O–H absorption is located at ca. 3453 cm⁻¹. The IR absorption spectrum of [bmim][BF₄]/methanol is shown in Fig. 1(c) and we can observe the bonded O–H and free O–H at ca. 3440 and 3570 cm⁻¹, respectively.

To obtain a direct comparison of the effects of varying the composition, Fig. 2 shows the concentration dependence of alkyl [Fig. 2(a)] and imidazolium [Fig. 2(b)] C–H stretching vibrations at ambient pressure for [bmim][BF₄]/D₂O or methanol-d₄ mixtures. Looking into more detail in Fig. 2(a), we observe no drastic change in the concentration dependence of the alkyl C–H band frequency at high concentrations of ionic liquids, that is 0.3 < mole fraction (ionic liquid). This behavior may indicate a clustering of ionic liquids in nonpolar regions and a slight perturbation by the presence of D₂O or methanol-d₄ at high concentration. The aggregation of ionic liquids in solution and even in the gas phase is apparently a general trend.^{42,43} We stress that the alkyl C–H stretching absorption exhibits an increase in frequency upon dilution at low concentration of ionic liquids, that is 0.1 > mole fraction (ionic liquid), in Fig. 2(a).⁸ This observation suggests the formation of a certain water structure around alkyl C–H groups of ionic liquids in water-rich mixtures, but the details remain unclear. It is interesting to note that the imidazolium C–H band at ca. 3162 cm⁻¹ displays anomalous

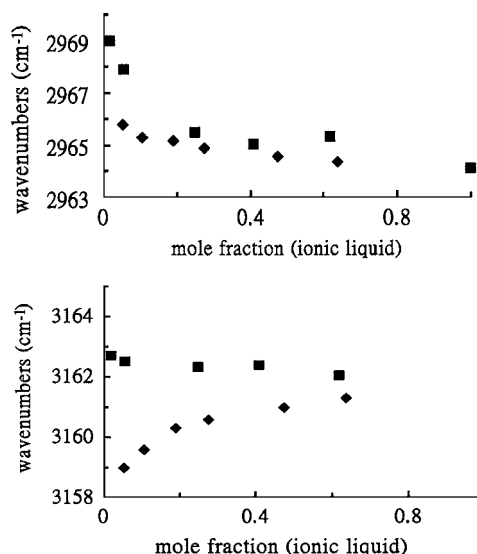


FIG. 2. Concentration dependence of the C–H stretching frequency of [bmim][BF₄]/D₂O (square) or methanol-d₄ (diamond) mixtures.

concentration-induced frequency shifts in Fig. 2(b). We noticed that no appreciable changes in band frequency of the imidazolium C–H occurred as the ionic liquid was diluted by D₂O,⁸ but a redshift in frequency was observed as the sample was diluted by methanol-d₄ in Fig. 2(b). This result is remarkably different from what is revealed for the alkyl groups in Fig. 2(a). As the BF₄⁻ anion should be strongly bound to the imidazolium cation for pure [bmim][BF₄], one can suggest that they are still attached even when the ionic liquid is diluted by D₂O. Nevertheless, methanol facilitates the dissociation of anion and cation. A possible explanation for this effect is the C–H···O interactions between imidazolium C–H groups and methanol molecules. In other words, methanol can be added to change the structural organization of [bmim][BF₄] by introducing methanol-imidazolium C–H interactions. Recent investigations have suggested that the structure of ionic liquids exhibits spatial heterogeneity that results from their polar/nonpolar phase separation.^{25–28} Ionic liquids tend to segregate into stable nonpolar regions by aggregation of the alkyl groups for C₄ and longer and polar regions by charge ordering of the anions and the imidazolium rings. Our results in Fig. 2(b) indicate that the presence of methanol significantly perturbs the ionic liquid–ionic liquid associations in the polar region.

Figure 3 displays IR spectra of a [bmim][BF₄]/D₂O mixture having its mole fraction of ionic liquid equal to 0.08 obtained under ambient pressure (curve a) and at 0.9 (curve b), 1.5 (curve c), 2.1 (curve d), 2.5 (curve e), and 3.0 GPa (curve f). As the mixture was compressed, i.e., increasing the pressure from ambient [Fig. 3(a)] to 0.9 GPa [Fig. 3(b)], alkyl and imidazolium C–H stretches showed blue frequency shifts, which correspond to contraction of the C–H bonds. Nevertheless, the redshift of the bonded O–H band at ca. 3328 cm⁻¹ is obvious as the pressure was elevated in Fig. 3(b). This behavior is in accord with the general trend observed of a redshift with pressure for O–H and C=O stretching modes in strongly hydrogen-bonded O–H···O and C=O···H systems, respectively.^{36,37} As shown in Fig. 3(b),

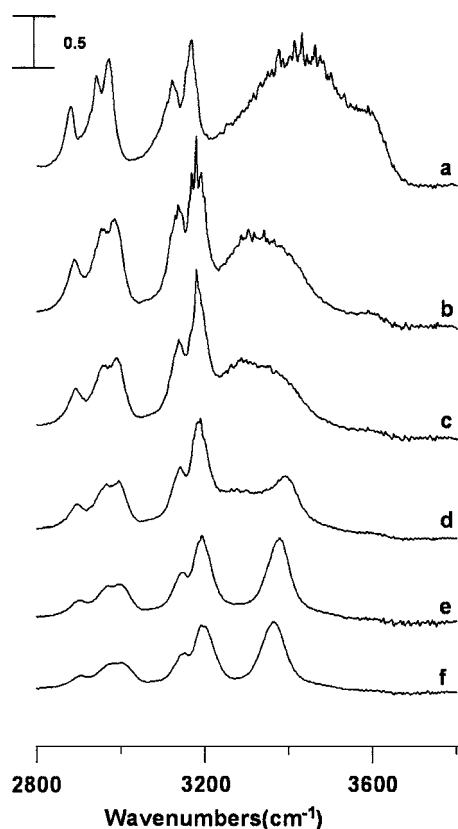


FIG. 3. Pressure dependence of the C–H and O–H modes in a [bmim] \times [BF₄]/D₂O mixture having its mole fraction of ionic liquid equal to 0.08 obtained under ambient pressure (curve a) and at 0.9 (curve b), 1.5 (curve c), 2.1 (curve d), 2.5 (curve e), and 3.0 GPa (curve f).

the compression leads to loss of the free O–H (at ca. 3580 cm⁻¹) band intensity. It is likely that free OH is switched to bonded O–H as high pressures are applied. The evolutions of the free O–H spectral features observed in Fig. 3 may arise from changes in the local structures of O–H groups and the geometrical properties of hydrogen-bond network are likely perturbed as the pressure is elevated. As pressure was further increased, the hydrogen-bond network transformed to tetragonal ice VI [Fig. 3(c)] and cubic ice VII [Figs. 3(d)–3(f)]. We observed a sharp O–H feature in Figs. 3(d)–3(f) corresponding to the high order environments in an ice VII-like structure. We note that infrared spectra for the tetragonal VI and cubic VII phases of ice were reported in Ref. 37.

Figure 4 displays IR spectra of a [bmim][BF₄]/H₂O mixture having its mole fraction of ionic liquid equal to 0.48 obtained under ambient pressure (curve a) and at 0.3 (curve b), 1.5 (curve c), 1.9 (curve d), and 2.3 GPa (curve e). As revealed in Fig. 4(a), the dominant O–H species is the free OH type. Comparing Figs. 4(a)–4(e), we note that the intensity ratio of the bonded OH and free O–H differs as the pressure is elevated. Similar observation is also observed for the water-rich mixture in Fig. 3. It appears that pressure somehow stabilizes the bonded-OH conformation. The bonded O–H band appears as a broad feature in Figs. 4(a)–4(c). The sharper structure of bonded O–H band at ca. 3360 cm⁻¹ revealed in Figs. 4(d) and 4(e) is in part due to the higher order and anisotropic environment in a solid struc-

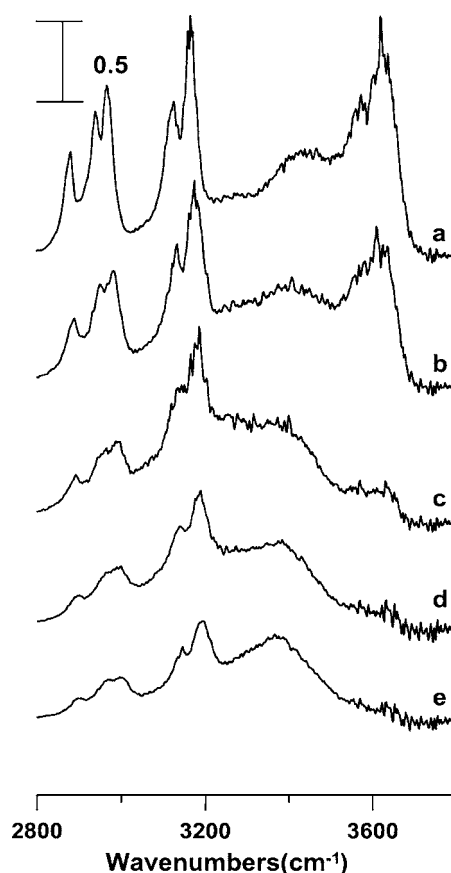


FIG. 4. Pressure dependence of the C–H and O–H modes in a [bmim] \times [BF₄]/H₂O mixture having its mole fraction of ionic liquid equal to 0.48 obtained under ambient pressure (curve a) and at 0.3 (curve b), 1.5 (curve c), 1.9 (curve d), and 2.3 GPa (curve e).

ture. By comparing Figs. 3(d)–3(f) and Figs. 4(d) and 4(e), an increase in the concentration of [bmim][BF₄] does affect the bandwidths of bonded O–H stretching bands under high pressure, increasing versus the concentration. The sensitivity to changes in concentration may arise from changes in water-cluster sizes and perturbation in geometrical properties of hydrogen-bond network. In other words, hydrogen-bond network of high pressure ice VII breaks down as the ionic liquid is further added.

Figure 5 displays IR spectra of a [bmim][BF₄]/methanol mixture having its mole fraction of ionic liquid equal to 0.62 obtained under ambient pressure (curve a) and at 0.9 (curve b), 1.5 (curve c), 1.9 (curve d), and 2.5 GPa (curve e). The bonded O–H band appears as a broad feature and the absorption band at 3575 cm⁻¹ is assigned to free O–H stretching vibration in Fig. 5(a). The prominent O–H species is the free O–H as shown in Fig. 5(a). As the sample was compressed [Figs. 5(b)–5(e)], we observed blueshifts in frequency for the C–H stretching modes in Fig. 5. Nevertheless, the free O–H stretching band did not change its position with pressure. It is interesting to note that the bonded O–H feature remains broad as the pressure was elevated. The broad feature of the bonded O–H represents inhomogeneous environment due to glasslike network and is correlated with the more disordered structure of methanol. The presence of 3575 cm⁻¹ band in Figs. 5(b)–5(e) indicates that the free O–H is still stable under high pressure. This observation is remarkably different

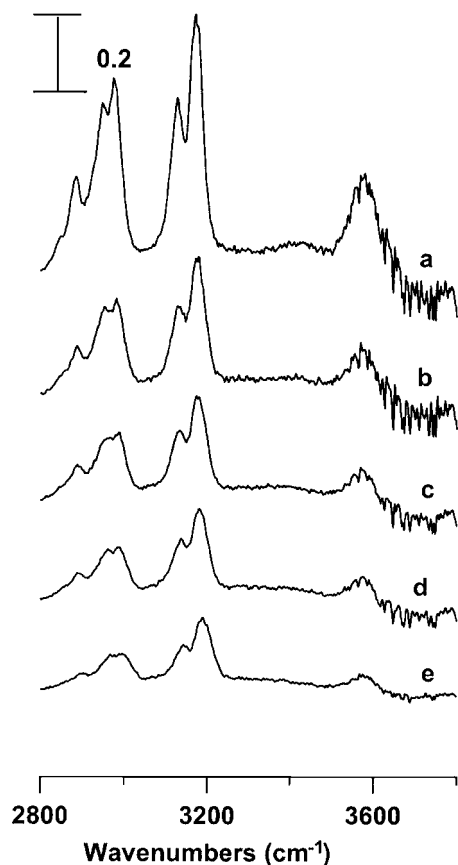


FIG. 5. IR spectra of a [bmim][BF₄]/methanol mixture having its mole fraction of ionic liquid equal to 0.62 obtained under ambient pressure (curve a) and at 0.9 (curve b), 1.5 (curve c), 1.9 (curve d), and 2.5 GPa (curve e).

from the results of ionic liquid/water mixtures, i.e., Figs. 3 and 4. Methanol is one of the simplest amphiphilelike molecules. The shortness of its alkyl chain means that methanol does not form conventional self-assembly behavior. Pure water forms three-dimensional hydrogen-bonding structures, but molecules in pure methanol associate with each other to form short chains with an average chain length of five or so molecules.⁴⁴ Both hydrogen-bond cooperative⁴⁵ and geometric effect may be attributed to the unique behavior of added methanol observed in Fig. 5.

We performed density functional theory (DFT) calculations using the GAUSSIAN program package;⁴⁶ Fig. 6 displays the DFT-calculated structures of ([bmim][BF₄])₂(water) complexes. We employed the B3LYP functional together with a standard 6-31+G* basis set. This combination of method and basis set (B3LYP/6-31+G*) has been successfully applied to protonated ammonia-water clusters⁴⁷ and neutral benzene-water clusters⁴⁸ before. We thus expect it to describe comparably well the interactions in ionic liquid-water clusters. Table I displays the predicted O–H and imidazolium C–H stretching frequencies of ([bmim] × [BF₄])₂(water) complexes and the scaling factor for the calculated frequencies is 0.955.^{29–32} Figure 6(a) displays bonded and free O–H stretching vibrations located at 3426 and 3649 cm⁻¹, respectively. As the clusters increase in size, the number of low-lying isomers increases exponentially and the structural identification is complicated. Thus, the broad O–H features observed in Figs. 3 and 4 may be attributed to

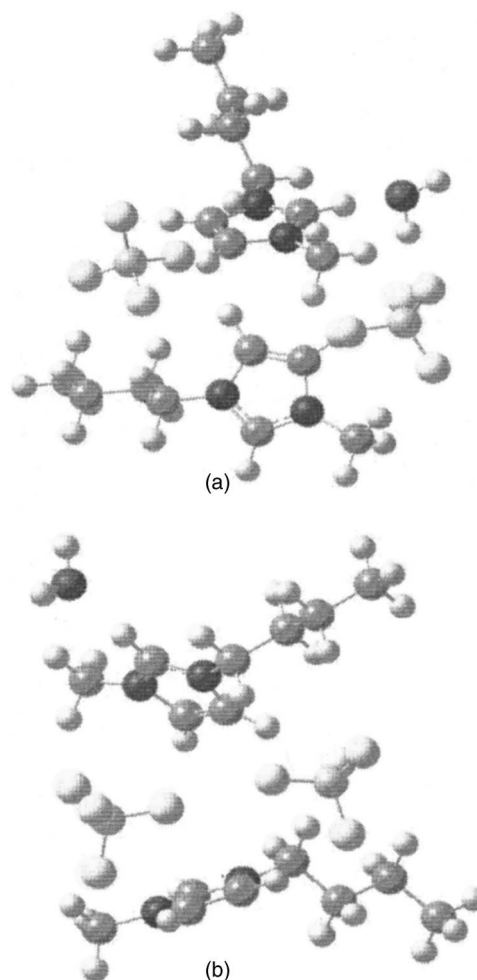


FIG. 6. DFT-calculated structures of ([bmim][BF₄])₂(water) complexes.

the presence of more than one stable isomeric form. Figure 6(b) exhibits two discernible O–H vibrations, i.e., 3567 and 3677 cm⁻¹, respectively, corresponding to coupled free-O–H stretching bands. This result agrees with the splitting of the free O–H bands revealed in Figs. 1(b) and 4(a). As revealed in Table I, there is strong correlation between the experimental results and the structures from the GAUSSIAN calculations. It is instructive to note that DFT calculations may only provide qualitative support for the suggested intermolecular interactions, because the calculations are based on gas phase structures. It is also known that hydrogen-bond cooperativity due to concerted charge transfer can greatly enhance the strength of the individual hydrogen bonds involved in the coupling. The calculations of larger clusters may be interesting, but structural identification is complicated by the presence of exponentially increased isomeric forms.

CONCLUSIONS

We demonstrate that the aggregation behaviors and hydrogen-bond network in [bmim][BF₄]/water or methanol mixtures can be studied using a combination of vibrational spectroscopy and high pressure techniques. The results indicate a slight perturbation of ionic liquid structures in nonpolar regions by the presence of water or methanol at high concentrations. The formation of a certain water structure

TABLE I. DFT-calculated O–H and imidazolium C–H stretching frequencies (cm^{-1}) and intensity (km/mol) of $([\text{bmim}][\text{BF}_4])_2$ (water) complexes.^{a,b}

Species ^a	Calc. frequencies (intensities) ^b	Assignment	
A	3075 (193)	C ² –H	
	3116 (147)	C ^{4,5} –H asym.	
	3136 (85)	C ^{4,5} –H asym.	
	3145 (106)	C ^{4,5} –H sym.	
	3159 (4)	C ² –H	
	3162 (6)	C ^{4,5} –H sym.	
	3426 (407)	O–H (bonded to BF_4^-)	
	3649 (99)	O–H (free)	
	B	3114 (207)	C ² –H
		3122 (69)	C ^{4,5} –H asym.
3127 (142)		C ^{4,5} –H asym.	
3140 (86)		C ^{4,5} –H sym.	
3156 (81)		C ² –H	
3162 (2)		C ^{4,5} –H sym.	
3567 (18)		O–H sym. (free)	
3677 (81)		O–H asym (free)	

^aStructures illustrated in Fig. 6.^bFrequencies scaled by 0.955.

around alkyl C–H groups was observed in water-rich mixtures. Nevertheless, methanol can be added to change the structural organization of the ionic liquid by introducing methanol-imidazolium C–H interactions. For $([\text{bmim}][\text{BF}_4])_2/\text{water}$ mixtures, the intensity ratio of the bonded O–H and free O–H differs as the pressure is elevated. In other words, free-O–H is switched to bonded O–H as high pressures are applied. However, the free O–H is still stable under high pressures for the methanol mixtures.

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