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Solvation and microscopic properties of ionic liquid/acetonitrile mixtures probed by high-pressure infrared spectroscopy

Yasuhiro Umebayashi,[1] Jyh-Chiang Jiang,[2] Kuan-Hung Lin,[3] Yu-Lun Shan,[3] Kenta Fujii,[4] Shiro Seki,[5] Shin-Ichi Ishiguro,[1] Sheng Hsien Lin,[6,7] and Hai-Chou Chang[3,a]
[1]*Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashi-ku, Fukuoko 812-8581, Japan*
[2]*Department of Chemical Engineering, National Taiwan University of Science and Technology, Taipei 106, Taiwan*
[3]*Department of Chemistry, National Dong Hwa University, Shoufeng, Hualien 974, Taiwan*
[4]*Department of Chemistry and Applied Chemistry, Faculty of Science and Engineering, Saga University, Honjo-machi, Saga 840-8502, Japan*
[5]*Materials Science Research Laboratory, Central Research Institute of Electric Power Industry, Komae, Tokyo 201-8511, Japan*
[6]*Department of Applied Chemistry, National Chiao Tung University, Hsinchu 30010, Taiwan*
[7]*Institute of Atomic and Molecular Sciences, Academia Sinica, P.O. Box 23-166, Taipei 106, Taiwan*

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The microscopic features of binary mixtures formed by an ionic liquid (EMI^+TFSA^- or EMI^+FSA^-) and a molecular liquid (acetonitrile or methanol) have been investigated by high-pressure infrared spectroscopy. On the basis of its responses to changes in pressure and concentration, the imidazolium C–H appears to exist at least in two different forms, i.e., isolated and associated structures. The weak band at approximately 3102 cm^{-1} should be assigned to the isolated structure. CD_3CN can be added to change the structural organization of ionic liquids. The compression of an EMI^+TFSA^-/CD_3CN mixture leads to the increase in the isolated C–H band intensity. Nevertheless, the loss in intensity of the isolated structures was observed for EMI^+FSA^-/CD_3CN mixtures as the pressure was elevated. In other words, the associated configuration is favored with increasing pressure by debiting the isolated form for EMI^+FSA^-/CD_3CN mixtures. The stronger $C-H\cdots F$ interactions in EMI^+FSA^- may be one of the reasons for the remarkable differences in the pressure-dependent results of EMI^+TFSA^- and EMI^+FSA^-. *© 2009 American Institute of Physics*. [doi:10.1063/1.3273206]

I. INTRODUCTION

Ionic liquids are salts with a melting temperature below the boiling point of water with negligible vapor pressure and high polarity. In recent years, ionic liquids have attracted considerable interest owing to their characteristics as environmentally friendly solvents.[1–4] Due to a number of unique properties, ionic liquids have been used as media for extractions, synthesis, gas storage fluids, and many other applications with industrial potential.[1,2] The importance of ionic liquids has consequently stimulated considerable in their solvation properties and a special issue (see Refs. 5 and 6) has been devoted to ionic liquids in 2007. Typically ionic liquids are built up by a bulky, asymmetric organic cation to prevent ions from packing easily. This asymmetry opposes the strong charge ordering and a wide liquid range is obtained. Some of the best-studied ionic liquids are those bearing imidazolium cations.[7–11] A number of studies have revealed that the structure of imidazolium-based ionic liquids is characterized by short- and long-range ordering that exists in both the solid and more remarkably, liquid states.[2,3] Perhaps more importantly, the thermodynamic properties and functions of ionic liquids can be controlled by judicious selection of the anion and cation components. Although ionic liquids have attracted much attention because of their useful characteristics, some fundamental questions still remain to be answered regarding the nature of the liquid state. Ionic liquids are composed of a cation and an anion and have an extremely high concentration of ions. Thus, the formation of associated species such as ion pairs and more highly associated ionic aggregates may be expected in neat ionic liquids.[12–14] The x-ray scattering paper by Triolo *et al.*[14] have demonstrated that structures having length scales ranging from 14 to 26 Å may exist in imidazolium ionic liquids having alkyl chains with 4–10 carbons. The size of structural heterogeneities is found to linearly scale with the alkyl chain length.

Studies on ionic liquid-based mixtures become more and more attractive in recent years.[15–17] The addition of water to ionic liquids is very common in biocatalytic work and the molecular state of water was investigated in some ionic liquids.[18] Water molecules seem to be separated from each other at low content, while self-association appears at higher concentration. The role of water in ionic liquids is complex and depends on the supramolecular structures of ionic liquids. At high ionic liquid concentrations ionic liquids seem to form clusters as in the pure state and water molecules

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[a] Author to whom correspondence should be addressed. Electronic mail: hcchang@mail.ndhu.edu.tw. FAX: +886-3-8633570. Tel.: +886-3-8633585.

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interact with the clusters without interacting among themselves. Compared to the intensive investigations on the ionic liquid/water mixtures, there have been a few reports on solvation behavior of ionic liquid in nonaqueous molecular liquids and our knowledge of the interaction between ionic liquids and organic solvents remain somewhat empirical. In the present study, our intent is to achieve further understanding of physicochemical properties in ionic liquid/CD_3CN or methanol-d_4 mixtures.

To understand the physical chemistry in ionic liquids, solvation dynamics are to be known. There is a strong literature existing related to dynamical properties in ionic liquids.[19–28] The early solvation dynamics measurement in ionic liquids based on the fluorescence behavior of C153 have indicated that the time-resolvable part of the dynamics is biphasic in nature.[24] Major questions regarding dynamic solvation by ionic liquids deal with whether the cation or anion solvates preferentially on different time scales, the role of the correlated motion of the ion pairs and their lifetime, and the importance of translational motion of the ion relative to dipolar relaxation. Several groups have used the femtosecond optical heterodyne-detected Raman-induced Kerr effect spectroscopy (OHD-RIKES) method to characterize the dynamics in ionic liquids.[6] Experimental techniques, such as IR spectroscopy, were often used to explore hydrogen-bonding structures of ionic liquid-based mixtures. Many of these researches are interested in the interactions between water and anions. For instance, the molecular states of water absorbed from air in ionic liquids have been studied by vibrational spectroscopy, which indicates that water molecules interact with the anions and exist in symmetric 1:2 type hydrogen-bonded complexes.[29,30] However, the interactions of water or organic solvent with cations have been limited studied. In this work, we demonstrate that cation-solvent interactions play a non-negligible role in ionic liquid mixtures.

A characteristic feature of hydrogen bonds is that when a hydrogen bond is formed, X–H (X=O, N, etc.) covalent bond elongates and consequently X–H stretching frequency redshifts. However, there are many recent investigations which report blueshifting of C–H stretching mode when C–H hydrogen bonds are formed.[31–33] As suggested by Hobza *et al.*,[31] the blueshifting $C-H\cdots O$ may be attributed to the electron density transfer from the proton acceptor to the remote part of the proton donor. Therefore, the blueshifting $C-H\cdots O$ interactions were labeled as antihydrogen bonds. However, Scheiner *et al.*[32] and Dannenberg *et al.*[33] have concluded from a set of theoretical calculations that antihydrogen bonds do not differ fundamentally from conventional hydrogen bonds. The origin of both the redshifted and blueshifted hydrogen bonds may be the same as shown by the Schlegel *et al.*[34] and the Hermansson.[35] Various studies have been made to elucidate the role of weak hydrogen bonds, such as $C-H\cdots O$ and $C-H\cdots X$, in the structure of ionic liquids.[15,36] For example, Mele *et al.* deduce a cation-water interaction from ROESY spectra.[36] The aromatic C–H groups, for example, are capable of forming C–H hydrogen bonds, particularly those C–H groups that are adjacent to more electronegative atoms as in imidazolium-based ionic liquids. The observation of the C–H stretching vibration is one of the keys to characterize the presence of such a weak hydrogen bond and can serve as a useful probe to reflect the interactions between ionic liquid and organic solvents or water.

The pressure-induced changes of the vibrational characteristics are of particular interest.[37–41] Studies have shown the potential significance that pressure has on controlling the strength of weak hydrogen bonds. They yield important information on the bonding properties, especially with regard to the interplay of covalent and hydrogen bonding. This is particularly useful because little is known about the relative importance of the hydrophilic versus hydrophobic part of molecules in the collapse and aggregation processes. For the pure chemicals in general, it is well known that the hydrogen-bond network is distorted by pressure. For solutions, on the other hand, how the solvation shell responds to pressure variation remains to be investigated. In this study, we combine pressure and vibrational spectroscopy as a window into solvation behaviors in ionic liquid mixtures.

II. EXPERIMENTAL

Samples were prepared using 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide (>97%, FLUKA), acetonitrile-d_3 (99.96% D, Cambridge Isotope), and methanol-d_4 (99.8% D, Cambridge Isotope). 1-Ethyl-3-methylimidazolium bis(fluorosulfonyl)amide of spectroscopic grade (Dai-ichi Kogyo Seiyaku Co., Ltd.) was used without further purification.[42] A diamond anvil cell (DAC) of Merril–Bassett design, having a diamond culet size of 0.6 mm, was used for generating pressures up to approximately 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, CaF_2 crystals (prepared from a CaF_2 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 PerkinElmer Fourier transform spectrophotometer (model Spectrum RXI) equipped with a lithium tantalite midinfrared detector. The infrared beam was condensed through a 5× 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 Wong's method.[43,44] Spectra of samples measured at ambient pressure were taken by filling the samples in a cell having two CaF_2 windows but lacking the spacers.

III. RESULTS AND DISCUSSION

Figure 1 displays infrared spectra of (a) pure 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($EMI^+(CF_3SO_2)_2N^-, EMI^+TFSA^-$), (b) pure 1-ethyl-3-

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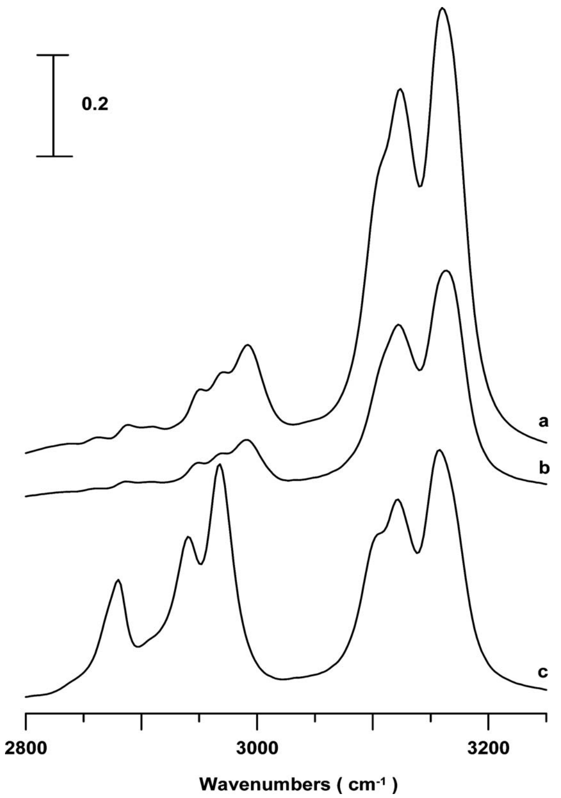


FIG. 1. IR spectra of pure (a) EMI^+TFSA^-, (b) EMI^+FSA^-, and (c) BMI^+TFSA^- obtained under ambient pressure.

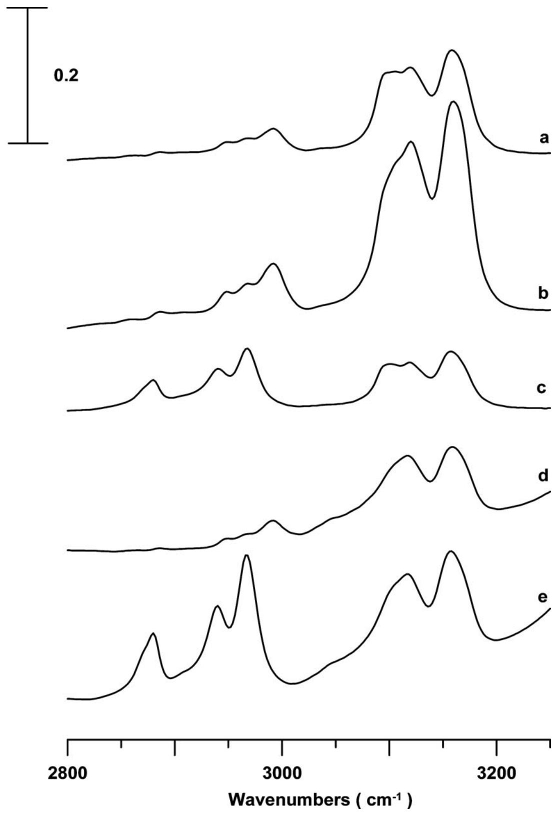


FIG. 2. IR spectra of (a) EMI^+TFSA^-/CD_3CN, (b) EMI^+FSA^-/CD_3CN, (c) BMI^+TFSA^-/CD_3CN, (d) EMI^+TFSA^-/CD_3OD, and (e) BMI^+TFSA^-/CD_3OD. The mole fractions of ionic liquids are (a) 0.07, (b) 0.09, (c) 0.08, (d) 0.04, and (e) 0.06.

methylimidazolium bis(fluorosulfonyl)amide ($EMI^+(FSO_2)_2N^-, EMI^+FSA^-$), and (c) pure 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide ($BMI^+(CF_3SO_2)_2N^-, BMI^+TFSA^-$) obtained under ambient pressure (see Table I for the molecular structures). The bis-(trifluoromethylsulfonyl)amide anion ($(CF_3SO_2)_2N^-$) is also called NTf_2^-, Tf_2N^-, and $TFSI^-$ in the literature. As indicated in Fig. 1(a), the infrared spectrum of pure EMI^+TFSA^- exhibits absorption bands at 2890, 2953, 2974, 2991, 3102, 3122, and 3162 cm^{-1} corresponding to C–H stretching modes.[37–39] The 2890, 2953, 2974, and 2991 cm^{-1} bands can be attributed to C–H stretching modes of the alkyl groups. The bands at 3122 and 3162 cm^{-1} correspond to coupled imidazolum C–H stretching vibrations. The appearance of a shoulder at approximately 3102 cm^{-1} indicates that the imidazolium C–H may exist at least in two different forms, i.e., isolated and associated structures. The nearly degenerated peaks (3102 and 3122 cm^{-1}) may be attributed to the perturbation of neighboring ions in the liquid state. The associated species may be ion pairs (or larger ion clusters) and the isolated species may mean the dissociation into free ion (or smaller ion clusters).[45–47] An indication of ion-pair formation in imidazolium-based ionic liquids was previous reported and a maximum of 30% of all ions form pairs at 273 K.[45] Some researchers even considered the neat ionic liquids as an hydrogen bonded polymeric supramolecule.[45] As the anion is replaced by FSA^- in Fig. 1(b), there are no significant changes in the shapes of the aliphatic C–H stretching bands. Nevertheless, the relative absorption intensity of the shoulder at approximately 3102 cm^{-1} slightly decreases in Fig. 1(b). We note that the spectral feature at approximately 3102 cm^{-1} is more pronounced for the $TFSA^-$ anion [Figs. 1(a) and 1(c)] than for the FSA^- anion [Fig. 1(b)].

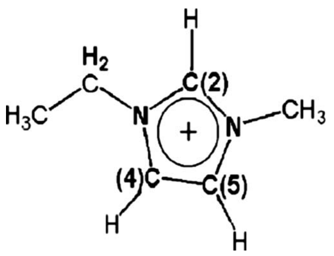
TABLE I. Calculated total interaction energies (kcal/mol).

Species[a–c]	$-\Delta E$[d]
EMI^+TFSA^-	72.58
a	78.13
b	79.29
c	78.49
d	79.74

[a] Structures illustrated in Fig. 6.

[b] $TFSA^-$: $[(CF_3SO_2)_2N^-]$, FSA^-: $[(FSO_2)_2N^-]$.

[c] EMI^+:



[d] Basis-set superposition error (BSSE) corrected.

In order to learn the insight of isolated and associated structures, further concentration-dependent studies on various amount of ionic liquid/CD_3CN and ionic liquid/CD_3OD provide direct evidences. Figure 2 presents infrared spectra of ionic liquid/CD_3CN mixtures (curves a–c) and ionic liquid/CD_3OD mixtures (curves d and e) obtained under am-

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bient pressure. As revealed, no appreciable changes in band frequencies and shapes of the alkyl C–H stretching bands occur due to the presence of CD_3CN in Fig. 2(a). Nevertheless, an increase in the imidazolium C–H intensity at approximately 3102 cm^{-1} was observed in Fig. 2(a). This observation is likely related to local structures of the imidazolium ring. Based on the concentration-dependent results, this spectral feature at approximately 3102 cm^{-1} should be assigned to the isolated (or dissociated) structure. A possible explanation is that the relative contribution of the isolated and associated components is different for the EMI^+TFSA^-/CD_3CN mixture. In other terms, CD_3CN can be added to change the structural organization of EMI^+TFSA^- [Fig. 2(a)] and BMI^+TFSA^- [Fig. 2(c)]. Although the local organization between the ionic species is preliminary governed by electrostatic interactions, the $C-H\cdots N$ interaction between the negative N atom in CD_3CN and the positive H atoms in the imidazolium C^2-H may be a compensatory mechanism to provide additional stability and enhances the dissociation as pointed out by Triolo *et al.*[48] It is instructive to note that the isolated feature at approximately 3102 cm^{-1} is more pronounced for the $TFSA^-$ anion [Figs. 2(a) and 2(c)] than for the FSA^- anion [Fig. 2(b)]. Indeed, evolution of the relative band intensities at 3102 and 3119 cm^{-1} is consistent with the signature of an isolated-associated structural equilibrium. As revealed in Figs. 2(d) and 2(e), weaker profiles at approximately 3102 cm^{-1} were observed for methanol-d_4 mixtures. These results in Figs. 2(d) and 2(e) suggest that the nature of local organization of imidazolium C–H in CD_3OD mixtures is different from that in CD_3CN mixtures.[49] The imidazolium C–H spectral features observed in Figs. 2(d) and 2(e) may be related to the geometrical properties of hydrogen-bond network in liquid methanol. Molecules in pure methanol tend to form chains with an average chain length of five or so molecules.[50] In the EMI^+TFSA^-/CD_3OD [Fig. 2(d)] and BMI^+TFSA^-/CD_3OD mixtures, CD_3OD molecules may prefer to aggregate with themselves by hydrogen bonding, and $TFSA^-$ interacts with the cations to form associated configurations.

Figure 3 displays infrared spectra of an EMI^+TFSA^-/CD_3CN mixture (mole fraction of EMI^+TFSA^-: 0.08) obtained under ambient pressure (curve a), 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g). Figure 3(a) reveals the imidazolium C–H absorption at 3102, 3124, and 3164 cm^{-1}. As the sample was compressed that is increasing the pressure from ambient [Fig. 3(a)] to 0.3 GPa [Fig. 3(b)], the imidazolium C–H bands were blueshifted to 3106, 3133, and 3174 cm^{-1}, respectively. The pressure-induced frequency shift of the imidazolium C–H band at approximately 3102 cm^{-1} (isolated structure) is relatively small, while the bands at approximately 3124 and 3164 cm^{-1} are more pressure-sensitive than the isolated feature. Changes in the relative band intensities of the imidazolium bands also occurred as the pressure was elevated in Fig. 3. As shown in Fig. 3, the compression leads to the increase in the isolated C–H (at approximately 3102 cm^{-1}) band intensity. It is likely that some associated species are switched to the isolated form (or some orderly oriented clusters) as high pressures are applied.

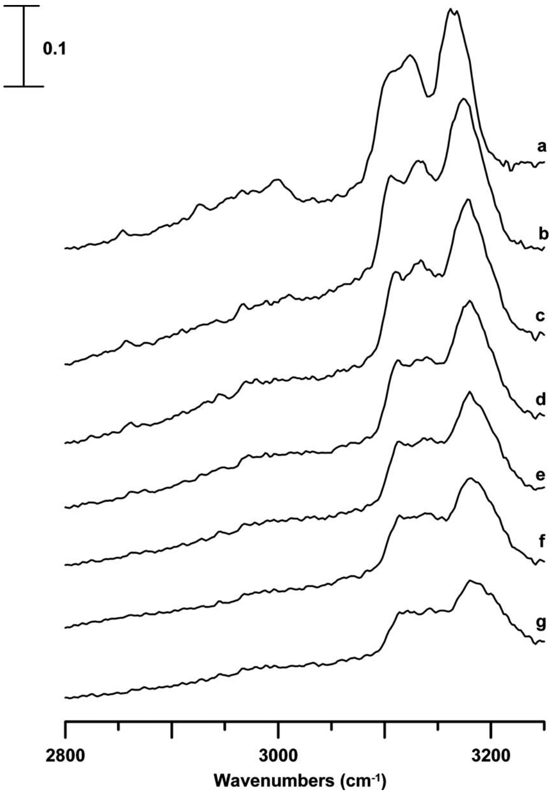

FIG. 3. IR spectra of a EMI^+TFSA^-/CD_3CN mixture (mole fraction of EMI^+TFSA^-: approximately 0.08) obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

Figure 4 illustrates infrared spectra of an EMI^+FSA^-/CD_3CN mixture (mole fraction of EMI^+FSA^-: 0.09) obtained under ambient pressure (curve a), 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.1 (curve f), and 2.5 GPa (curve g). The C–H stretching modes underwent dramatic changes in their spectral profiles as the pressure was elevated to 0.3 GPa in curve b. As revealed, Fig. 4(b) shows the loss in intensity of those nearly degenerated bands attributed to the isolated structures. In other words, the associated configuration is favored with increasing pressure by debiting the isolated form in Fig. 4(b). As the pressure was further elevated, the alkyl and imidazolium C–H bands were blueshifted in Figs. 4(b)–4(g). The monotonic blueshift in frequency for the characteristic C–H bands ($P > 0.3$ GPa) suggests that the associated configurations seems to be thermodynamically stable up to the pressure of 2.5 GPa. It is known that cohesion in ionic liquids is strong and mostly electrostatic, while previous studies indicate that the interaction energies of EMI^+TFSA^- and EMI^+FSA^- complexes are very similar. Therefore, some other factors such as weak hydrogen bonds may play the non-negligible role in the structures of EMI^+TFSA^- and EMI^+FSA^-. Average NBO charges of F atoms in $TFSA^-$ and FSA^- are equal to −0.36 and −0.51, respectively.[37] The stronger $C-H\cdots F$ interactions in EMI^+FSA^- may be one of the reasons for the remarkable differences in the concentration- and pressure-

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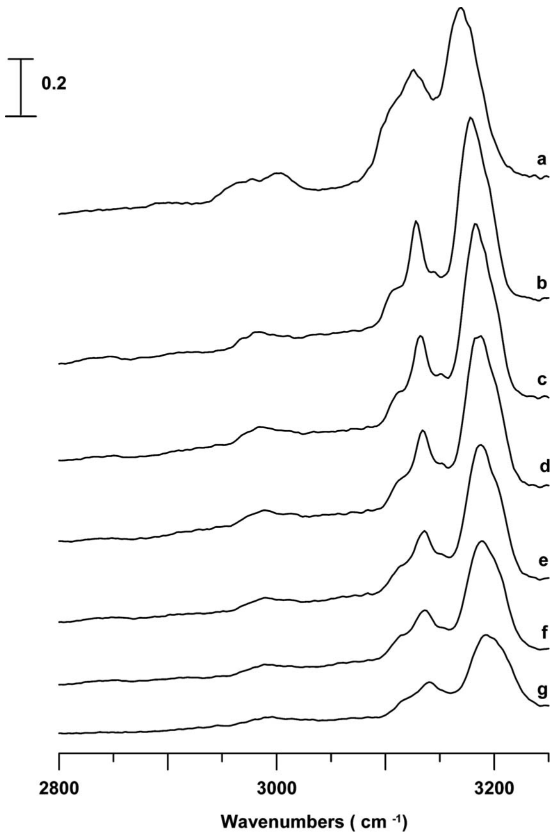

FIG. 4. IR spectra of a EMI$^+$FSA$^-$/CD$_3$CN mixture having mole fraction of EMI$^+$FSA$^-$ equal to 0.09 obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

dependent results of EMI$^+$TFSA$^-$ and EMI$^+$FSA$^-$.[37] It was known that a number of configurations are possible for EMI$^+$TFSA$^-$.[37,45,51] The imidazolium cation can be also hydrogen-bonded via C–H···N (Ref. 45) and C–H···O (Ref. 51) interactions.

To learn the alkyl chain-length dependence of the cations, the pressure study of BMI$^+$TFSA$^-$ seems to offer the direct approach. Figure 5 illustrates infrared spectra of an BMI$^+$TFSA$^-$/CD$_3$CN mixture (mole fraction of BMI$^+$TFSA$^-$:0.07) obtained under ambient pressure (curve a), 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.1 (curve f), and 2.5 GPa (curve g). For ionic liquids involving imidazolium cations, the relative distance between the two cations slightly increases as the alkyl chain lengthens. The increase in the alkyl chain length may weaken the attractive anion-cation interaction energies by a few percent. The observed IR absorption profiles in Fig. 5 clearly show that the relative intensities of the isolated/associated forms are similar to those found with the reference ionic liquid [EMI$^+$TFSA$^-$] (see Fig. 3). This observation leads us to suggest that the increase in the alkyl chain length may not significantly perturb the isolated-associated structural equilibrium in CD$_3$CN mixtures.

Figure 6 displays the predicted structures of EMI$^+$TFSA$^-$-acetonitrile [Figs. 6(a) and 6(b)] and EMI$^+$TFSA$^-$-methanol [Figs. 6(c) and 6(d)] clusters. Density functional theory calculations were performed at the B3LYP/6-31+G* level.[52] Energy results are shown in Table I. It was known that the TFSA$^-$ anion shows similar intensities of both the *trans* and *cis* conformers as revealed in OHD-RIKES spectra.[6] For the purpose of comparison with previous TFSA$^-$ calculations,[45] we only show the calculation results of the *trans* conformer in Fig. 6. As revealed in Table I, the interaction between EMI$^+$ and TFSA$^-$ is mostly electrostatic, i.e., −72.58 kcal/mol. By comparing

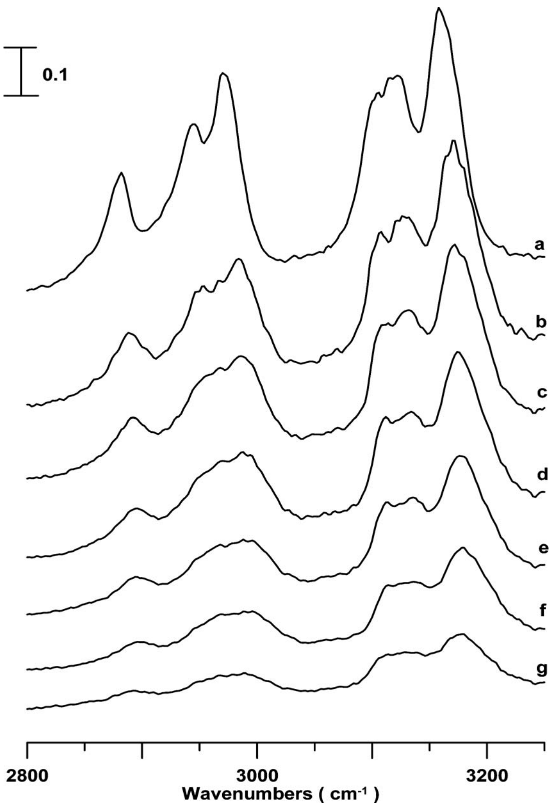

FIG. 5. IR spectra of a BMI$^+$TFSA$^-$/CD$_3$CN mixture having mole fraction of BMI$^+$TFSA$^-$ equal to 0.07 obtained under ambient pressure (curve a) and at 0.3 (curve b), 0.9 (curve c), 1.5 (curve d), 1.9 (curve e), 2.3 (curve f), and 2.5 GPa (curve g).

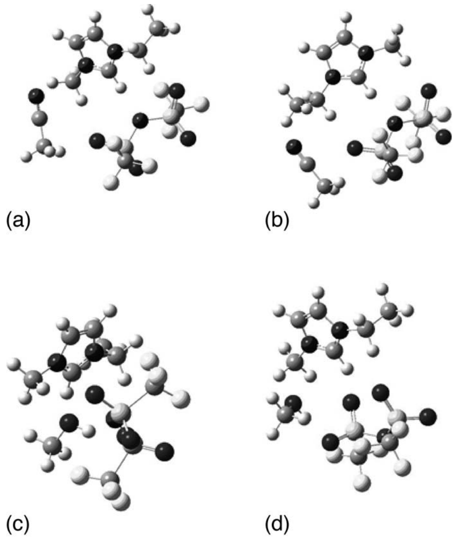

FIG. 6. Optimized structures of EMI$^+$TFSA$^-$-acetonitrile [(a) and (b)] and EMI$^+$TFSA$^-$-methanol [(c) and (d)].

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EMI^+TFSA^--acetonitrile [Figs. 6(a) and 6(b)] and EMI^+TFSA^--methanol [Figs. 6(c) and 6(d)], we observe similar total interaction energies (78 or 79 kcal/mol). The differences in total interaction energies represent the energy needed to separate the trimolecular complexes into a EMI^+TFSA^- and a single acetonitrile ($78-73=5$ kcal/mol) or a single methanol ($79-73=6$ kcal/mol). It appears that $C-H\cdots N$ and $C-H\cdots O$ interactions somehow provide complementary stabilization energies (approximately 5 or 6 kcal/mol) in the structures of EMI^+TFSA^--acetonitrile and EMI^+TFSA^--methanol clusters in Fig. 6 and Table I. Nevertheless, our experimental measurements (Figs. 2) reveal the remarkable differences of the local imidazolium C–H organization in acetonitirle-d_3 and methanol-d_4 mixtures, respectively. Thus, the interaction between EMI^+TFSA^- and acetonitrile/methanol may not be the solely factor to perturb the geometrical properties in ionic liquid mixtures. These observations support our arguments that the aggregation behaviors of the organic solvent (methanol) may play non-negligible roles. In $O-H\cdots O$ hydrogen bonding, methanol molecules can act as both proton donors and acceptors and aggregate with themselves. On the other hand, acetonitrile molecules weakly interact with themselves by the dipole-dipole interactions.

IV. CONCLUSION

Association structures between ionic liquids (EMI^+TFSA^-, EMI^+FSA^-) and conventional solvents (acetonitrile, methanol) have been investigated in this study. The infrared spectral features indicate that imidazolium C–H may exist in isolated and associated forms. Our results suggest that the nature of local organization of imidazolium C–H in methanol-d_4 mixtures is different from that in acetonitril-d_3 mixtures. In the EMI^+TFSA^-/CD_3OD [Fig. 2(d)] and BMI^+TFSA^-/CD_3OD mixtures, CD_3OD molecules may prefer to aggregate with themselves by hydrogen bonding, and $TFSA^-$ interacts with the cations to form associated configurations. As an EMI^+TFSA^-/CD_3CN mixture was compressed, the increase in the isolated C–H band intensity was observed and some associated species are switched to the isolated form. However, the associated configuration is favored with increasing pressure for EMI^+FSA^-/CD_3CN mixtures.

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