

# Hydrogen bonding mediated ion pairs of some aprotic ionic liquids and their structural transition in aqueous solution

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Ion pair speciation of ionic liquids (ILs) has an important effect on the physical and chemical properties of ILs and recognition of the structure of ion pairs in solution is essential. It has been reported that ion pairs of some ILs can be formed by hydrogen bonding interactions between cations and anions of them. Considering the fact that far-IR (FIR) spectroscopy is a powerful tool in indicating the intermolecular and intramolecular hydrogen bonding, in this work, this spectroscopic technique has been combined with molecular dynamic (MD) simulation and nuclear magnetic resonance hydrogen spectroscopy ( $^1\text{H}$  NMR) to investigate ion pairs of aprotic ILs [Bmim][NO<sub>3</sub>], [BuPy][NO<sub>3</sub>], [PyT<sub>14</sub>][NO<sub>3</sub>], [PP<sub>14</sub>][NO<sub>3</sub>] and [Bu-choline][NO<sub>3</sub>] in aqueous IL mixtures. The FIR spectra have been assigned with the aid of density functional theory (DFT) calculations, and the results are used to understand the effect of cationic nature on the structure of ion pairs. It is found that contact ion pairs formed in the neat aprotic ILs by hydrogen bonding interactions between cation and anion, were still maintained in aqueous solutions up to high water mole fraction (say 0.80 for [BuPy][NO<sub>3</sub>]). When water content was increased to a critical mole fraction of water (say 0.83 for [BuPy][NO<sub>3</sub>]), the contact ion pairs could be transformed into solvent-separated ion pairs due to the formation of the hydrogen bonding between ions and water. With the further dilution of the aqueous ILs solution, the solvent-separated ion pairs was finally turned into free cations and free anions (fully hydrated cations or anions). The concentrations of the ILs at which the contact ion pairs were transformed into solvent-separated ion pairs and solvent-separated ion pairs were transformed into free ions (fully hydrated ion) were dependent on the cationic structures. These information provides direct spectral evidence for ion pair structures of the aprotic ILs in aqueous solution. MD simulation and  $^1\text{H}$  NMR results support the conclusion drawn from FIR spectra investigations.

**ionic liquids, ion pair, hydrogen bonding, far infrared spectroscopy, solution**

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## 1 Introduction

Ionic liquids (ILs) are attracting increasing attention from scientific and industrial communities because of their potential applications in novel synthesis, CO<sub>2</sub> absorption, catalysis, separation, cellulose dissolution and electrochemistry [1–3].

One of the important features affecting the properties of ionic liquids is ion pair formation in which hydrogen bonding often imposes a high degree of directionality [4,5]. Thus, hydrogen bonding mediated ion pair of the ILs is different from that of inorganic salts. In addition, ion pairing in solution is the result of a subtle balance between ion-solvent and cation-anion interactions [6,7]. This is particularly true for ionic liquids where a mix of Coulomb forces, hydrogen bonds, and dispersion forces between the cation and anion leads to unique

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macroscopic properties of these Coulomb fluids. Thus, the study on hydrogen bonding mediated ion pair of ILs in condensate, gas phase and solutions is highly desired.

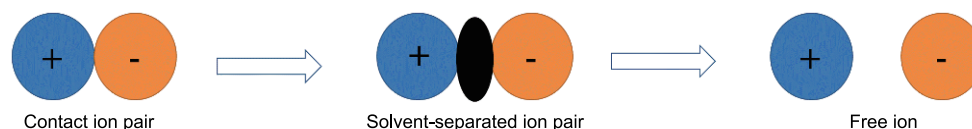
Recently, numerous theoretical studies on ion-pairs or ion aggregates (including *ab initio* calculations, classical molecular dynamics simulations and Car-Parrinello molecular dynamics simulations) have been reported in gas phase [8–11]. These studies revealed interaction energy, interaction site and charge distribution of ion pairs at molecular level and made a great progress in the recognition of ion pairs of ILs. In experimental aspects, ion pairs of some ILs in condense phase were studied by conductivity, NMR and X-ray technologies [12–17]. It was speculated that neat imidazolium ILs could be described as hydrogen-bonded polymeric supramolecules of the type  $[A_x B_{(x-n)}]^{n+} [A_{(x-n)} B_x]^{n-}$ , in which A is 1,3-dialkylimidazolium cation and B is anion. Ion pairs of some ILs in gas phase was also investigated through mass spectrometry [18–21], and supramolecules of the type  $[A_x B_{(x-n)}]^{n+} [A_{(x-n)} B_x]^{n-}$  in imidazolium-based ionic liquids were apparently maintained to a great extent in the gas phase. In solution phase, the investigations of ion pairs of ILs were conducted by conductivity, NMR, mass spectrometry, dielectric spectroscopy and IR spectroscopy [22–35]. It was deduced that not only contact ion pairs, but also triple ion, larger ionic and neutral aggregates were present in solution even when the ILs were dissolved in organic solvents with relatively high dielectric constants, such as acetonitrile and dimethyl sulfoxide. Although the above studies revealed some important aspects of ion pairs of ILs, only indirect information was given, and the search of direct experimental evidence for ion pair is still a great challenge.

Until recently, Ludwig *et al.* [36–41], for the first time, used far infrared spectroscopy (FIR) to directly characterize hydrogen bonding mediated contact ion pairs in neat ILs. The obtained experimental frequencies were assigned rationally with the introduction of density functional theory (DFT) calculations. For example, these authors selected the ILs with  $[C_2C_1im]^+$  cation and  $[N(CN)_2]^-$ ,  $[SCN]^-$ ,  $[NO_3]^-$ ,  $[CH_3COO]^-$  anions to study the effect of anion type on the hydrogen bonding interaction in ion pairs [40]. In order to eliminate frequency shift caused by the force, the anions considered have similar reduced mass. A shifting to the higher frequency was seen from the FIR bands in the order  $[N(CN)_2]^- < [SCN]^- < [NO_3]^- < [CH_3COO]^-$ , which indicates the increased hydrogen bonding interactions between the cation and anion in the ion pairs.

In order to investigate the effect of substituent group in cation on the hydrogen bonding interaction in ion pairs, the ILs with the same  $[NTf_2]^-$  anion but different cations including 1,2,3-trimethyl-imidazolium ( $[C_1C_1C_1im]^+$ ), 1,3-dimethyl-imidazolium ( $[C_1C_1im]^+$ ), 1,2-dimethylimidazolium ( $[C_1C_1'im]^+$ ) and 1-methyl-imidazolium ( $[C_1im]^+$ ) were selected [41]. It was found that the vibrational bands focused on the maximum absorption intensities of the FIR modes below  $150\text{ cm}^{-1}$  showed some differences. The frequencies were found to shift to higher wavenumbers in the order  $[C_1C_1C_1im]^+ < [C_1C_1im]^+ < [C_1C_1'im]^+ < [C_1im]^+$ , indicating the increased hydrogen bonding interaction strength in pairs. Considering the fact that FIR spectroscopy is a powerful tool to investigate the intermolecular and intramolecular hydrogen bonding, the above findings provide direct evidence for the hydrogen bonding mediated contact ion pairs in neat ILs.

Despite the progress in the studies on ion pairs in neat ILs by FIR spectroscopy, the structures of ion pairs of ILs in solutions are not well understood in this respect [42]. To the best of our knowledge, only one paper [43] has been published, up to now, to study ion speciation of a protic IL triethylammonium methylsulfonate ( $[TEA][MS]$ ) in water by FIR spectroscopy in combination with DFT calculations. It was reported that contact ion pairs were formed in water and four water molecules were needed to transform the contact ion pairs into solvent-separated ion pairs. However, only one protic IL was investigated in the work mentioned. For aprotic ILs, what is the structure of ion pairs in aqueous solutions in the whole concentration range? How the cationic and anionic nature of the ILs affects their structures with addition of water in succession? These issues have not been addressed.

In this work, a set of aprotic ILs including 1-butyl-3-methylimidazolium nitrate ( $[Bmim][NO_3]$ ), 1-butyl-4-methylpyridinium nitrate ( $[BuPy][NO_3]$ ), 1-butyl-1-methylpyrrolidinium nitrate ( $[Pyr_{14}][NO_3]$ ), 1-butyl-1-methylpiperidinium nitrate ( $[PP_{14}][NO_3]$ ), and *N*-butyl choline nitrate ( $[Bu-choline][NO_3]$ ) were chosen based on the difference of number of available sites for hydrogen bond in cation, and used to study ion speciation in aqueous solutions such as contact ion pairs, solvent-separated ion pairs, and free ion (full hydrated ion) (Scheme 1) as a function of cationic structure and IL concentration by FIR spectroscopy in combination with DFT calculation and molecular dynamic (MD) simulation. In addition, considering the fact that nuclear magnetic resonance hydrogen ( $^1H$  NMR) spectra can



**Scheme 1** The simplified 2D representation for the structures of contact ion pair, solvent-separated ion pair and free ion of ionic liquids. Black spot: solvent molecule (color online).

be affected significantly by solute-solute and solute-solvent interactions, this technology was also utilized to probe the structural transition of ion pairs in aqueous solutions and the interactions of cations with water. It was found that the conclusion obtained from FIR spectroscopy was supported by MD simulation and  $^1\text{H}$  NMR results.

## 2 Experimental

1-Butyl-3-methylimidazolium nitrate [Bmim][NO<sub>3</sub>] (99%), 1-butyl-4-methylpyridinium nitrate [BuPy][NO<sub>3</sub>] (98.5%), 1-butyl-1-methylpyrrolidinium nitrate [Py<sub>T14</sub>][NO<sub>3</sub>] (99%), 1-butyl-1-methylpiperidinium nitrate [PP<sub>14</sub>][NO<sub>3</sub>] (99%), and *N*-butyl choline nitrate [Bu-choline][NO<sub>3</sub>] (99%) were purchased from Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, China. The water content in the purchased ILs was stated to be less than 0.5 wt%. In order to reduce the water content in these ILs, all of them were dried under vacuum at 343 K for 2–3 d in the presence of P<sub>2</sub>O<sub>5</sub>. And then, the water contents in these dried ILs were determined by Karl Fischer titration. It was found that less than 0.07 wt% of water was remained.

FIR spectra measurements were carried out with a Perkin-Elmer Spectrum 400 FIR spectrometer (USA) consisting of a room temperature DTGS detector (Perkin-Elmer, USA) with preamplifier and polyethylene (PE) windows with 5 mm internal optical path. The wavenumber range was from 50 to 450 cm<sup>-1</sup> and the resolution of FIR spectrometer is 2 cm<sup>-1</sup>. A PE-94 temperature controller (Perkin-Elmer, USA) was used to keep the system temperature within ±1 K. In the measurements, a small droplet of IL was placed on the top of the PE windows, and each FIR spectrum was the result of 200 signal averaged scans.

The frequencies of the stable configurations of the ILs were calculated by using the internal stored 6-31+G\* basis set of Gaussian 09 D.01 program at the B3LYP/6-31+G\* level [44]. The binding energies were corrected for the basis set superposition error (BSSE) [45]. The vibrational frequencies for all clusters were corrected by the standard factor of 0.96. The interaction energy,  $\Delta E_{\text{int}}$ , was evaluated by the following equation:

$$\Delta E_{\text{int}} = E_{\text{ion-pair}} - (E_{\text{cation}} + E_{\text{anion}}) \quad (1)$$

where  $E_{\text{ion-pair}}$  is the single point energy of ion pair, and  $E_{\text{cation}}$  and  $E_{\text{anion}}$  are the single point energies of cation and anion in the geometry of the corresponding cation-anion pair, respectively. The value of  $E_{\text{anion}}$  is -280.457557 hartree. The calculated values of  $\Delta E_{\text{int}}$ ,  $E_{\text{ion-pair}}$ , and  $E_{\text{cation}}$  were shown in Table 1.

$^1\text{H}$  NMR spectra of the ILs in H<sub>2</sub>O were collected at 298 K on a Bruker Avance-400 NMR spectrometer (Germany) operating at 400.13 MHz. The internal standard tube with D<sub>2</sub>O and trimethylsilicon (TMS) was used. The chemical shifts

were given in ppm downfield from TMS.

All-atom force fields were used in our simulations. For [Bmim][NO<sub>3</sub>] [46] and [Bupy][NO<sub>3</sub>] [47], the reported parameters of AMBER force field were used, and the SPC model [48] was employed for water molecules. All simulations were performed with MDynaMix 5.2 package [49]. The double time-step algorithm [50] was adopted with long and short time steps of 2 and 0.5 fs, respectively. Ewald summation method [51] was used to treat the long-range electrostatic interaction, in which the long-range parts were cut off at 15 Å. All the simulations were carried out by using mixtures of IL and water with different mole fraction at 298 K, and the initial configuration was prepared by *PACKMOL* in a square box, typically larger than the “real” size to make the packing easier. The numbers of water molecules for each IL-H<sub>2</sub>O system were given in Table 2.

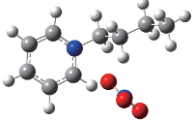
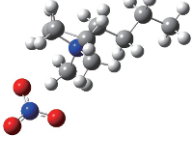
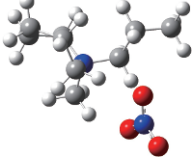
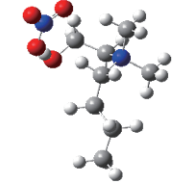
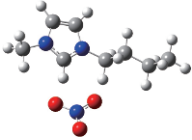
A starting simulation was carried out at 700 K in *NVE* ensemble. After a relaxation for a few MD steps to reduce the possible overlapping in the initial configuration, the Nose-Hoover *NPT* ensemble simulation [52] was performed. Descending from 700 K to the sampling temperature of 298 K, a series of *NPT* simulations were carried out under the standard atmospheric conditions. At the sampling temperature point, the system was equilibrated for at least 5 ns, and then the production phase was lasted for 4 ns. The conformations in trajectories were dumped with an interval of 20 fs for further analysis. The number and the radial distribution function of hydrogen bonding between cation and anion were obtained for all the systems.

## 3 Results and discussion

### 3.1 The assignments of FIR peaks in the neat aprotic ILs

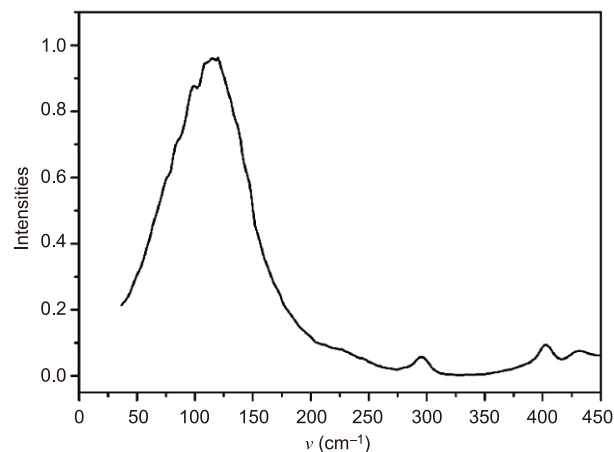
FIR spectrum of the neat [Bmim][NO<sub>3</sub>], [BuPy][NO<sub>3</sub>], [Py<sub>T14</sub>][NO<sub>3</sub>], [PP<sub>14</sub>][NO<sub>3</sub>] and [Bu-choline][NO<sub>3</sub>] was determined at 298 K, and the results were shown in Figure 1 and Figures S1–S4 in the Supporting Information online. To better identify and understand these peaks, density functional theory calculation was conducted, and chemical structures of the ILs were shown in Scheme 2. First of all, stable configuration was optimized for ion pairs of the ILs and their corresponding interaction energy between cation and anion was determined. These results were listed in Table 1. It can be seen that the interaction energy between cation and anion decreased in the sequence [Py<sub>T14</sub>][NO<sub>3</sub>] > [PP<sub>14</sub>][NO<sub>3</sub>] > [BuPy][NO<sub>3</sub>] > [Bmim][NO<sub>3</sub>] > [Bu-choline][NO<sub>3</sub>], indicating that the interaction strength between cation and anion increased in the order [Py<sub>T14</sub>][NO<sub>3</sub>] < [PP<sub>14</sub>][NO<sub>3</sub>] < [BuPy][NO<sub>3</sub>] < [Bmim][NO<sub>3</sub>] < [Bu-choline][NO<sub>3</sub>]. After that, vibrational frequencies were computed by determining the second derivatives of the energy of stable configuration of the ion pairs with res-

**Table 1** The optimized stable geometries for ion pairs of the ILs and the corresponding energies

IL	Optimized geometry	$E_{\text{ion-pair}}$ (hartree)	$E_{\text{cation}}$ (hartree)	$\Delta E_{\text{int}}$ (kJ mol <sup>-1</sup> )
[BuPy][NO <sub>3</sub> ]		-686.616199	-406.025743	-348.92
[Pyr <sub>14</sub> ][NO <sub>3</sub> ]		-690.230173	-409.642460	-341.72
[PP <sub>14</sub> ][NO <sub>3</sub> ]		-690.227403	-409.638616	-344.54
[Bu-choline][NO <sub>3</sub> ]		-727.361494	-446.765533	-363.38
[Bmim][NO <sub>3</sub> ]		-703.882485	-423.287870	-359.84

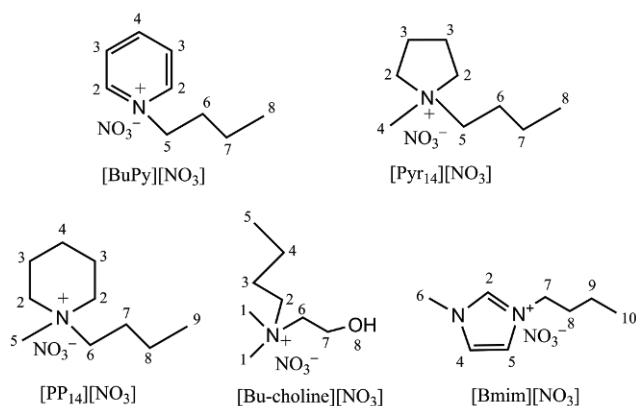
**Table 2** The molecule number of ILs and water for each simulated systems

System	IL	H <sub>2</sub> O
IL-H <sub>2</sub> O	128	0
	128	128
	128	256
	128	384
	128	512
	128	640
	128	768
	128	896
	128	1024
	128	1280

**Figure 1** FIR spectra of neat [BuPy][NO<sub>3</sub>] in the range of 50–450 cm<sup>-1</sup>.

pect to the Cartesian nuclear coordinates and then transforming to mass-weighted coordinates [44]. The experimental and calculated values of the vibrational frequencies in the 50–450 cm<sup>-1</sup> range as well as the corresponding vibrational assignments for these ILs were shown in Table 3 and Tables S1–S4 (Supporting Information online). It is clear that the experimental values of the vibrational peaks are in line with the cal-

culated values, and the peaks for hydrogen bonding, possibly formed by H2, H3 or H4 atom of [PP<sub>14</sub>]<sup>+</sup> and [BuPy]<sup>+</sup>, H2 or H3 atom of [Pyr<sub>14</sub>]<sup>+</sup>, H2, H4 or H5 atom of [Bmim]<sup>+</sup> and H atom in –OH group of [Bu-choline]<sup>+</sup> with O atom in [NO<sub>3</sub>]<sup>-</sup> anion, respectively, were identified in the neat ILs. Herein, it was found that the difference in the calculated values of hydrogen bonding peaks formed by different hydrogen



**Scheme 2** The chemical structures and H atom numbering of the ILs.

**Table 3** Wavenumber of neat [BuPy][NO<sub>3</sub>] at 298 K and the related assignments

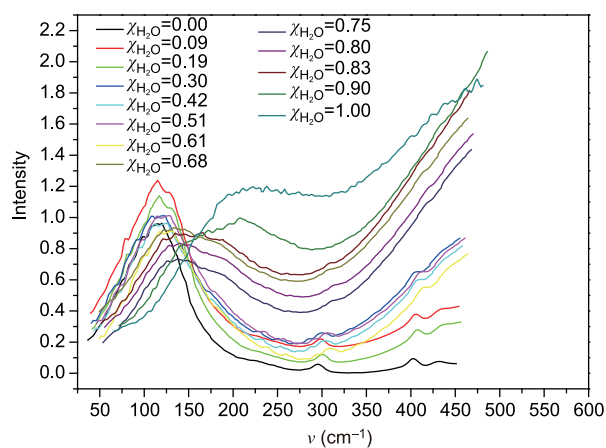
Experimental value (cm <sup>-1</sup> )	Calculated value (cm <sup>-1</sup> )	Assignment
112.3	136.7	stretching vibration of hydrogen bonding between H2, H3, H4 atoms and O atom in [NO <sub>3</sub> ] <sup>-</sup>
95.4	105.5	stretching vibration of cation
402.8	387.8/405.1	bending vibration of cation

atoms at the same cation is very small, and it is very difficult to distinguish them. Therefore, the hydrogen bonding peak observed in FIR was ascribed to that formed by these H atoms with O atom in [NO<sub>3</sub>]<sup>-</sup> anion. It is known that beside coulomb interactions, a strong and directional hydrogen bond between cation and anion provides strongly bound contact ion pairs in the neat ILs [42]. Therefore, the existence of hydrogen bonding peak in neat ILs indicates that contact ion pairs were formed in neat ILs, and the change of hydrogen bonding peak could be used as a probe to monitor the formation or breaking of ion pair structure of the ILs in solution, but cannot provide any structure information of ion clusters.

In addition, the vibrational frequencies of hydrogen bonding between cation and anion of the ILs increase in the sequence [Pyr<sub>14</sub>][NO<sub>3</sub>] (104.4 cm<sup>-1</sup>) < [BuPy][NO<sub>3</sub>] (112.3 cm<sup>-1</sup>) < [PP<sub>14</sub>][NO<sub>3</sub>] (113.5 cm<sup>-1</sup>) < [Bu-choline][NO<sub>3</sub>] (115.0 cm<sup>-1</sup>) < [Bmim][NO<sub>3</sub>] (119.9 cm<sup>-1</sup>). Based on the equation of the simple harmonic oscillator  $\nu = (1/2\pi) (\kappa/\mu)^{1/2}$ , the frequency (wavenumber) is determined by the square root of the ratio between the force constant  $\kappa$  and the reduced mass  $\mu$ . For the ILs investigated in this work, the mass of the cation is different, leading to the difference in reduced mass. Therefore, the order of vibrational frequencies of hydrogen bonding could not simply used to judge the order of the strength of hydrogen bonding interaction between cation and anion for different ILs.

### 3.2 The contact ion pairs and their structural change in aqueous solutions

It has been deduced from FIR spectra that contact ion pairs were formed in neat aprotic ILs, and their formation is dependent on hydrogen bonding between cation and anion. Considering the fact that ion pairing in aqueous solution is the result of a subtle balance between ion-water and cation-anion interactions [6,7], if the anion-cation interaction is sufficiently strong, contact ion pairs would be the dominant structure in the mixtures. On the other hand, when the ion-water interaction is much stronger, solvent-separated ion pairs prevail [42]. To verify whether the structure of ion pairs of the ILs in aqueous solution could undergo the transition from contact ion pairs to solvent-separated ion pairs and then to free ions as water was added into ILs in succession, FIR spectrum of the ILs was measured with the increase of mole fraction of water, and the results were shown in Figure 2 and Figures S1–S4. Taking [BuPy][NO<sub>3</sub>] as an example, the peak of hydrogen bonding between cation and [NO<sub>3</sub>]<sup>-</sup> is located at 112.3 cm<sup>-1</sup> in the neat IL. It can be seen from Figure 2 that when the mole fraction of water ( $\chi_{\text{H}_2\text{O}}$ ) was 0.19 and 0.61, the hydrogen bonding peak between cation and anion was shifted to 116.5 and 126.8 cm<sup>-1</sup>, respectively. This indicates that the hydrogen bonding peak between cation and anion showed a measurable blue-shift. It has been reported that when a X–H···Y group experiences a stronger H-bonding the X–H bond elongates (and hence red-shifts), while the H···Y bond shortens and hence blue-shifts [28]. Therefore, it can be deduced that addition of water reduced the hydrogen bonding interaction between cation and anion to a great extent, but the hydrogen bonding and the contact ion pairs were well present in the IL–H<sub>2</sub>O mixtures. As the mole fraction of water was increased to 0.80, the peak was shifted to 138.0 cm<sup>-1</sup> and became broad. Based on the result reported by Ludwig *et al.* [38], this peak was still assigned to hydrogen bonding between cation and



**Figure 2** FIR spectra of the IL in [BuPy][NO<sub>3</sub>]/H<sub>2</sub>O mixture in the range of 50–450 cm<sup>-1</sup> as a function of mole fraction of water ( $\chi_{\text{H}_2\text{O}}$ ) (color online).

anion, suggesting that contact ion pair of the IL was still present. Interestingly, when the mole fraction of water was up to 0.83, the hydrogen bonding peak disappeared, but a new peak occurred at  $150.7\text{ cm}^{-1}$ , which indicated that contact ion pair of the IL was broken and solvent-separated ion pair was formed [42]. In other words, about five water molecules were needed to disrupt one strongly bound contact ion pair of [BuPy][NO<sub>3</sub>], leading to the transition from contact ion pair to solvent-separated ion pair. Furthermore, as the mole fraction of water was increased to 0.9, only the peak at  $172.7\text{ cm}^{-1}$  was observed in FIR spectrum, which is assigned to the hydrogen bonding of H2, H3 or H4 atom in cation with O atom of H<sub>2</sub>O, as indicated from DFT calculations. At this stage, solvent-separated ion pairs would be transformed into free ion. At the same time, the hydrogen bonding peak formed by anion with water should be appeared at  $200\text{ cm}^{-1}$ , in principle, due to the breaking of ion pair [10,39]. However, because the hydrogen bonding peak formed among water molecules is also exhibited at about  $200\text{ cm}^{-1}$ , these two peaks overlap in FIR spectra and the hydrogen bonding peak formed by anion with water was not solely observed.

In addition, the transition from solvent-separated ion pair to free ion could not be determined definitely by us, because the change in the structure of ion pairs was only judged by the change of hydrogen bonding peak of ion pairs in FIR spectrum, and at this water content, hydrogen bonding peak was already vanished, resulting in the unavailability of the judgement through hydrogen bonding peak. Similar phenomenon was observed for the other ILs investigated in this work. The values of mole fraction of water and the number of water molecules needed for the disruption of contact ion pair were listed in Table 4. It is clearly indicated that the number of such water molecules decreased in the order [PP<sub>14</sub>][NO<sub>3</sub>]~[Bmim][NO<sub>3</sub>] > [Pyr<sub>14</sub>][NO<sub>3</sub>]~[BuPy][NO<sub>3</sub>] > [Bu-choline][NO<sub>3</sub>]. Indeed, this sequence is not in agreement with the order of the interaction strength between cation and anion of the ILs. This suggests that the breaking of ion pairs by water molecules is dependent not only on cation-anion interaction of the ILs, but also on the ion-water interaction.

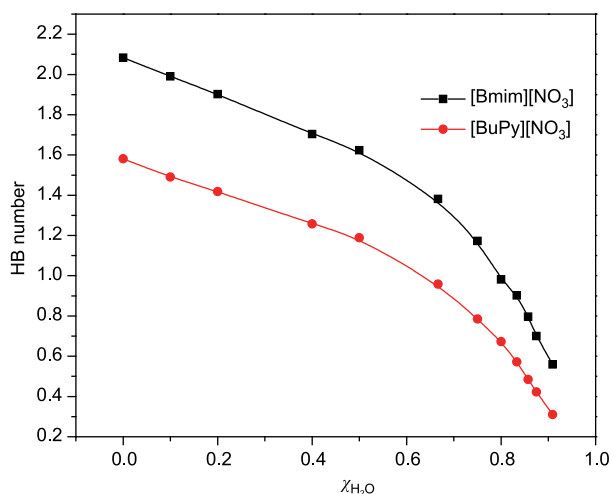
Molecular dynamics (MD) simulation is a powerful tool for studying the structure in ILs and IL solutions at molecular level [53]. From the above discussion, we understand that when water molecules were added in the neat ILs in succession, the hydrogen bonding between cation and anion was replaced gradually by the hydrogen bonding of cation-wa-

ter and anion-water. If so, the number of hydrogen bonding between cation and anion would decrease with the addition of water and the radial distribution function  $g(r)$ , which is a function that describes the spherically averaged local organization around any given atom, would be changed as well. Therefore, the change in the number of hydrogen bonding between cation and anion and the radial distribution function with water content was calculated from MD simulation in representative aqueous [BuPy][NO<sub>3</sub>] and [Bmim][NO<sub>3</sub>] solutions. Here, the number of hydrogen bond between cation and anion is defined as the average number of hydrogen bond formed per cation-anion ion pair in mixture system. The criterion for the formation of hydrogen bonding is described as [54]: the distance from a donor hydrogen to an acceptor is less than  $2.5\text{ \AA}$ , and the angle of acceptor-hydrogen-donor is larger than  $120^\circ$ . According to this definition, all the hydrogen bonding in the conformations that meet this criterion were statistically analyzed, and the average number of hydrogen bonding per ion pair of the ILs was calculated. Figure 3 describes the variety of average hydrogen bonding number between cation and anion with mole fraction of water. It was found that the average hydrogen bonding number was really decreased quickly with the increase of mole fraction of water. This supports our results from FIR spectroscopy.

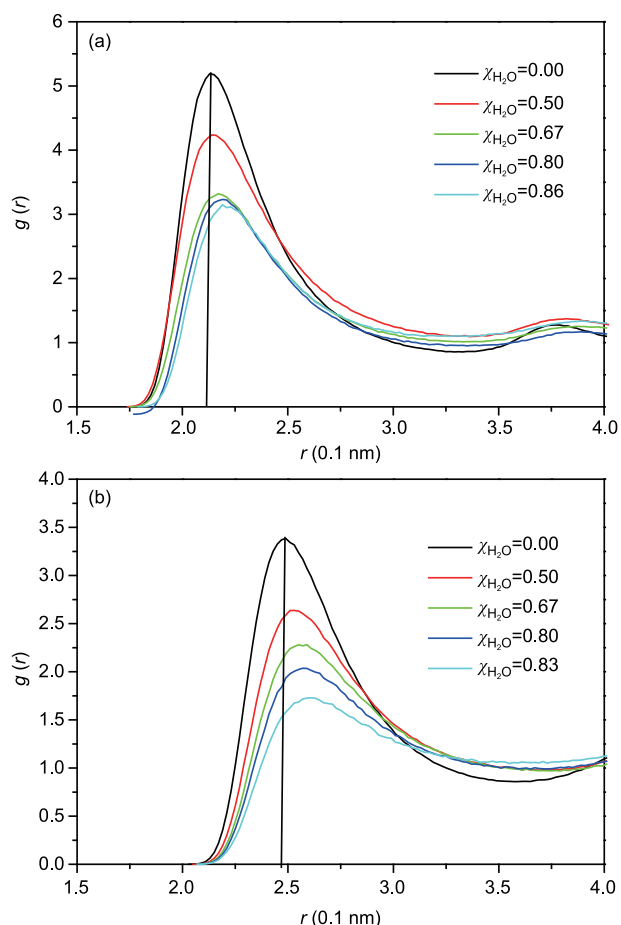
Figure 4 shows the radial distribution function of [NO<sub>3</sub>]<sup>-</sup> around H2 atom in [BuPy]<sup>+</sup> and [Bmim]<sup>+</sup> in neat ILs and ILs/water systems. It can be seen that the peak height for [NO<sub>3</sub>]<sup>-</sup> around H2 atom in [BuPy]<sup>+</sup> and [Bmim]<sup>+</sup> was much higher in neat ILs than in ILs/water systems. This indicates that the hydrogen bonding interaction of H2 atom in the cations with O atom in [NO<sub>3</sub>]<sup>-</sup> became weak with the addition of water. It is known that when the value of radial distribution function  $g(r)$  is small,  $g(r)$  can be used to describe bond length [55]. As shown in Figure 4, with the addition of water, the peak maximum for [NO<sub>3</sub>]<sup>-</sup> around H2 atom in [BuPy]<sup>+</sup> and [Bmim]<sup>+</sup> shifted to the right, which indicates that these hydrogen bondings were elongated and their strength became weaker. For example, the distance between H2 of the cation and O atom of [NO<sub>3</sub>]<sup>-</sup> was  $0.01\text{ nm}$  larger in [Bmim][NO<sub>3</sub>]-H<sub>2</sub>O mixture at  $\chi_{\text{H}_2\text{O}}=0.86$  than in the neat IL. Considering the fact that hydrogen bonding is a short-range and directional non-covalent force [54], this is an indicative that at this time, the hydrogen bonding of H2 atom of the cation with O atom of [NO<sub>3</sub>]<sup>-</sup> was broken and contact ion pair of the IL was transformed into solvent-separated ion

**Table 4** The mole fraction of water ( $\chi_{\text{H}_2\text{O}}$ ) and the number of water molecules ( $n$ ) needed for the transition of contact ion pair to solvent-separated ion pair

IL	[Bmim][NO <sub>3</sub> ]	[BuPy][NO <sub>3</sub> ]	[Pyr <sub>14</sub> ][NO <sub>3</sub> ]	[PP <sub>14</sub> ][NO <sub>3</sub> ]	[Bu-choline][NO <sub>3</sub> ]
$\chi_{\text{H}_2\text{O}}$	0.86	0.83	0.83	0.86	0.80
$n$	6	5	5	6	4



**Figure 3** The variation of average hydrogen bonding number between cation and anion of the ILs with mole fraction of water ( $\chi_{\text{H}_2\text{O}}$ ) at 298 K (color online).



**Figure 4** Radial distribution function of O atom of  $[\text{NO}_3]^-$  around H2 atom of the cations in neat ILs and ILs- $\text{H}_2\text{O}$  systems. (a)  $[\text{Bmim}][\text{NO}_3]$ ; (b)  $[\text{BuPy}][\text{NO}_3]$  (color online).

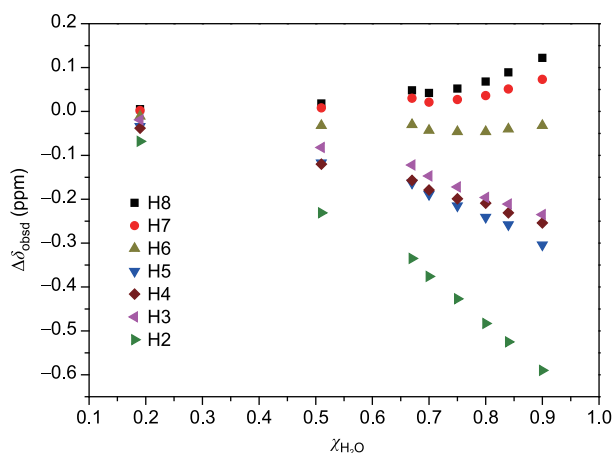
pair [56]. Similar situation was also found for the hydrogen bonding in  $[\text{BuPy}][\text{NO}_3]$  and in  $[\text{BuPy}][\text{NO}_3]\text{-H}_2\text{O}$  at

$\chi_{\text{H}_2\text{O}}=0.83$ . These MD results also support our results from FIR spectroscopy.

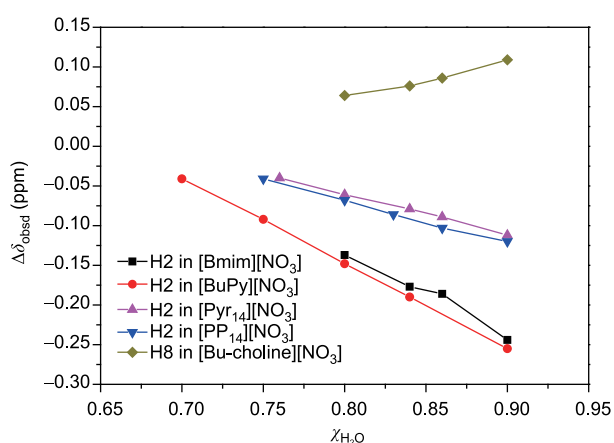
### 3.3 $^1\text{H}$ NMR clues for the structural transition of ion pairs in aqueous solutions

Here,  $^1\text{H}$  NMR technology was also used to investigate the transition of the contact ion pair to solvent-separated ion pair induced by the addition of water. The concentration dependences of the proton chemical shifts of the ILs were shown in Figure 5 and Figures S5–S8, and the proton numbering of the ILs could be found in Scheme 2. Since values of the experimental chemical shifts ( $\delta_{\text{obsd}}$ ) were greatly different for different protons, we plotted our data as  $\Delta\delta_{\text{obsd}}=\delta_{\text{obsd}}-\delta_{\text{obsd,m}}$ , where  $\delta_{\text{obsd,m}}$  is the observed chemical shift of a given IL at the lowest concentration under study. As an example, Figure 5 shows the variety of  $\Delta\delta_{\text{obsd}}$  for the protons of  $[\text{BuPy}][\text{NO}_3]$  with mole fraction of water in the IL- $\text{H}_2\text{O}$  mixture. Here, the lowest concentration of water is 0. It is clear that with increasing mole fraction of water, the protons H2, H3, H4, H5 and H6 shifted to upfield and the values of  $\Delta\delta_{\text{obsd}}$  were negative, while the protons H7 and H8 shifted to downfield and the values of  $\Delta\delta_{\text{obsd}}$  were positive. Hydrogen bonding is an important factor to influence the chemical shift of protons. It is generally accepted that formation of hydrogen bonding ( $\text{X-H}\cdots\text{Y}$ ) causes downfield chemical shift of H proton in  $\text{X-H}$  bond, whereas breaking of the hydrogen bonding results in the upfield shift in H proton of  $\text{X-H}$  bond [23]. Although the proton H2 can form hydrogen bonding with O atom in  $[\text{NO}_3]^-$  and  $\text{H}_2\text{O}$ , respectively, the strength of hydrogen bonding between H2 atom of the cation and O atom in  $[\text{NO}_3]^-$  is weaker than that between H2 atom and O atom in  $\text{H}_2\text{O}$  [57]. Therefore, the hydrogen bonding of H2 proton with O atom of  $[\text{NO}_3]^-$  was gradually destroyed by the addition of water, resulting in the upfield shift of H2 proton. Meanwhile, because of the breaking of the hydrogen bonding between cation and anion of  $[\text{BuPy}][\text{NO}_3]$ , the electron density of cation was increased and  $\pi$ - $\pi$  packing effect among the pyridine rings was reduced, thus leading to the upfield shift of the protons H3, H4, H5 and H6 [58]. However, in the case of protons H7 and H8, the downfield shift of the two protons could be ascribed to a partial changeover from gauche to trans conformations in the alkyl chain [59]. For the other aqueous ILs systems, similar results were obtained. These results support the idea that the formation of the hydrogen bonds of cation and anion with water molecules leads to the reduction of interactions between cation and anion, resulting in the transition of the ion pair structure from contact ion pair to solvent-separated ion pair.

In order to better understand the origin why the transition from contact ion pair to solvent-separated ion pair needs different number of water molecules for different ILs, we investigated the difference in the hydrogen bonding interaction of cations of the ILs with water. Figure 6 illustrates the change



**Figure 5** The variety of  $\Delta\delta_{\text{obsd}}$  of the protons for [BuPy][NO<sub>3</sub>] with mole fraction of water in the [BuPy][NO<sub>3</sub>]-H<sub>2</sub>O mixtures. In this system,  $\Delta\delta_{\text{obsd}}$  is defined as the difference between its chemical shifts in the mixtures and that in the neat ILs (color online).



**Figure 6** The change of  $\Delta\delta_{\text{obsd}}$  for protons of the cations in ILs-H<sub>2</sub>O systems as a function of  $\chi_{\text{H}_2\text{O}}$ , where  $\Delta\delta_{\text{obsd}}$  values were obtained with reference to the chemical shift of the protons at  $\chi_{\text{H}_2\text{O}}=0.67$  (color online).

of  $\Delta\delta_{\text{obsd}}$  for the protons of the cations in the ILs-H<sub>2</sub>O binaries as a function of water mole fraction. Based on the conclusion [58] that a more positive trend of  $\Delta\delta_{\text{obsd}}$  indicates a stronger hydrogen bonding interaction, it is clear that the strength of the hydrogen bonding interaction of the cations with water increases in the order [Bu-choline]<sup>+</sup>>[Pyr<sub>14</sub>]<sup>+</sup>>[PP<sub>14</sub>]<sup>+</sup>>[BuPy]<sup>+</sup>>[Bmim]<sup>+</sup>. This order is generally reverse to the order of mole fraction of water needed for the transition of contact ion pair to solvent-separated ion pair mentioned above. This suggests that contact ion pair would be easier to transform into solvent-separated ion pair when cation of the ILs has stronger hydrogen bonding interaction with water.

## 4 Conclusions

In summary, we investigated ion pairs and their structural

transition in aqueous ILs solutions by means of far infrared spectroscopy. It was found that although hydrogen bonding interaction between cation and anion of the aprotic ILs should be weaker than that of the protic ILs, hydrogen bonding mediated contact ion pairs present in neat aprotic ILs were still remained in aqueous solution up to high water mole fraction, and structurally transformed into solvent-separated ion pairs and free ions with the further addition of water, due to the formation of hydrogen bonding between ions (cation and anion) and water molecules. The values of mole fraction of water at which contact ion pair was transformed to solvent-separated ion pair were shown to decrease in the order [PP<sub>14</sub>][NO<sub>3</sub>]<sup>+</sup>≈[Bmim][NO<sub>3</sub>]<sup>+</sup>>[Pyr<sub>14</sub>][NO<sub>3</sub>]<sup>+</sup>≈[BuPy][NO<sub>3</sub>]<sup>+</sup>>[Bu-choline][NO<sub>3</sub>]<sup>+</sup>. These findings were supported by concentration dependence of the average hydrogen bond number between cation and anion of the ILs and the radial distribution function calculated from MD simulation. Furthermore, <sup>1</sup>H NMR spectroscopy was also used to investigate the transition of the contact ion pair to solvent-separated ion pair induced by the addition of water, and the results also support the conclusions drawn from the far infrared spectroscopy. In addition, it was noted from <sup>1</sup>H NMR spectroscopy that the strength of hydrogen bonding interaction of the cations with water increased in the sequence [Bu-choline]<sup>+</sup>>[Pyr<sub>14</sub>]<sup>+</sup>>[PP<sub>14</sub>]<sup>+</sup>>[BuPy]<sup>+</sup>>[Bmim]<sup>+</sup>, which is generally reverse to the order of mole fraction of water where contact ion pair was transformed into solvent-separated ion pair. This result confirms that the transition from contact ion pair to solvent-separated ion pair for the ILs in water is the result of a subtle balance between cation-anion interaction of the ILs and ion-water interaction.

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**Conflict of interest** The authors declare that they have no conflict of interest.

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