The Structural Organization in Aqueous Solutions of Ionic Liquids

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The ^{1}H NMR combined with the local composition (LC) model has been employed to investigate the structural organization of two aqueous solutions of ionic liquids (ILs), namely 1-ethyl-3-methylimidazolium tetrafluoroborate ($EmimBF_4$) and n*-butylammonium nitrate ($N4NO_3$). The correlation of chemical shifts using the LC model shows that the self-association of IL plays the leading role, and water prefers to interact with IL rather than self-association in IL-rich region. Instead the network of water molecules is established in water-rich region, because the self-association of water predominates. Furthermore, the difference between the local and the bulk composition presents the turnover at $x_{(IL)}$ (mole fraction of IL) close to 0.6 for $EmimBF_4$/water, which is in accordance with the change of excess function. Accordingly, it could be presumed that the excess properties for $N4NO_3$/water system should behave turnover at $x_{(IL)} \approx 0.55$ since the local and the bulk exhibit maximal difference at this composition.* © 2008 American Institute of Chemical Engineers *AIChE J*, 55: 198–205, 2009

Keywords: ionic liquids, local composition model, chemical shift, aqueous solutions, correlation

Introduction

Hydrophilic behavior is one of the most important properties for ionic liquids (ILs). Most of ILs present excellent mutual solubility with water at normal condition. Besides, even the so-called hydrophobic ILs can absorb certain amount of water from atmosphere when they are exposed in the air. Nowadays, the researches have shown that the presence of water not only could dramatically affect viscosity, density, conductivity,[1,2] volumes,[3] and other physical properties of neat IL, but also may change the chemical reaction process in which ILs serve as catalyst or solvent.[4] Consequently, the study on interaction between water and ionic liquids appears distinctly significant for chemistry and chemical engineering. Furthermore, the knowledge of mutual solubility between ILs and water is also of great importance in the evaluation of their environmental risk.[5] In fact, the behavior of ILs in aqueous solution has received considerable attentions. Various studies have been carried out using diversified approaches including experimental techniques, such as NMR,[6,7] FTIR,[8] far-IR,[9] electrochemistry method,[10] Raman spectroscopy,[11] as well as theoretical calculations such as molecular dynamic (MD) simulation[12,13] and quantum chemical calculation.[14,15]

Moreover, the influence of varied-amount water on the structural organization of ILs has been a central focus because of its potential application to chemistry and chemical engineering fields. Various kinds of theoretical methods[16–18] and experimental instruments[19–22] utilized in numerous literatures have shown clearly that nano-inhomogeneity can be generated not only in pure ILs but also in aqueous solutions of ILs. Therefore, the "wet" ILs may not be regarded as homogeneous solvents but have to be considered as "nanostructured" materials due to the impact of water.[22] Recently, NMR has been frequently utilized to study ILs/water mixtures because of its accuracy and sensitivity. For instance, the critical aggregation concentrations (CAC) and aggregation numbers of aqueous solutions of five ionic liquids (ILs) of the 1-*n*-alkyl-

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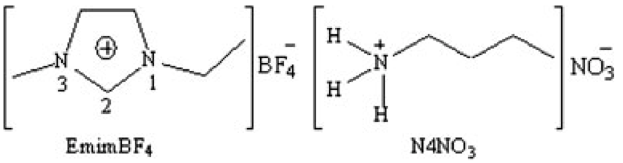

Figure 1. Sketch map of ionic liquids.

3-methylimidazolium bromide family, [C$_n$mim] Br (n = 4, 6, 8, 10, 12), have been investigated[23] by ^{1}H NMR measurements as a function of IL concentrations in D_2O, and it was deduced that the degree of hydration of the ILs in D_2O was reduced significantly by the stronger cation–anion association or the favorable aggregation of the ILs. Besides the butyl-methyl-imidazolium bis(trifluoromethylsulfonyl)-imide ([Bmim][TFSI]) IL has been probed[24] by self-diffusion coefficient of every species of aqueous solution determined by pulsed field gradient NMR. It has been put forward that water does not induce a significant increase of the ion pair dissociation but disturbs the RTIL cohesion and water is not homogenously mixed with RTIL but forms small aggregates whose size and connections increase with water. Nevertheless, other scholars[25] believed that water promotes significantly dissociation of ILs owing to the high dielectric constant of water and its ability to form strong hydrogen bonds with the anions of the ILs, which is inconsistent with other literatures.

On the other hand, various theoretical models have been another approach to study association behavior of aqueous systems.[26] Generally, the chemical association models[27] are frequently applied to describe association within aqueous systems. Although chemical association models give a direct understanding for the association behavior, the primary disadvantage is that a large number of adjustable parameters for the different aggregates are needed.[28] Simultaneously, the associated solutions can also be probed using the local composition (LC) theory, which accounts for all solution nonidealities in terms of nonspecific physical intermolecular forces; thus, fewer parameters are needed. In 2003, a simple semiempirical physical LC model was proposed by our group[29] to study the ^{1}H NMR chemical shifts of mixtures with satisfying results. Afterwards, the relation between thermodynamic and spectroscopic properties for mixtures has been established successfully with such LC model.[30–33] Virtually, some models have been used to analyze the special exhibition of solvents and ILs mixtures.[34,35] The studying of the structure of ILs and water mixtures by this LC model is our focus in this article.

Despite numerous computational and experimental studies on ILs/water mixtures till now, our knowledge of the interaction between water and ILs remains somewhat controversial. Furthermore, although NMR has been widely utilized in ILs field, ^{1}H NMR chemical shifts of ILs in aqueous solutions, especially within the whole concentration range, have seldom been mentioned in the former literatures. In the present work, our target is to achieve a more detailed description about the microscopic local structure of ILs/water mixtures focusing on ^{1}H NMR chemical shifts combined with the LC model. Ionic liquids involving 1-ethyl-3-methylimidazolium tetrafluoroborate (EmimBF$_4$) as well as n-butylammonium nitrate (N4NO$_3$), whose structures are shown in Figure 1, are chosen in this article as representative of imidazolium-based and ammonium-based ILs, respectively, on account of their relatively low-cost materials and easy preparation.

Experiments and Theory

Experiments

EmimBF$_4$ IL was prepared as reported[36] by N-methylimidazole, ethyl bromide as well as NaBF$_4$. N4NO$_3$ IL was prepared from n-butylamine and nitric acid according to the procedure reported previously by our laboratory.[37] All of the materials were analytical reagent and purchased from J&K Chemical. Aqueous solutions of ILs were prepared by using an analytical balance with a precision of ±0.0001 g in distilled water over the whole concentration range.

The internal reference method[38,39] was adopted to obtain the concentration-dependent chemical shifts of protons, including H_2O, C2—H (hydrogen atom in position two of the imidazolium ring of EmimBF$_4$ labeled in Figure 1) and N—H (—NH$_3$ of N4NO$_3$) for both of aqueous solutions. To avoid the influence of deuterated reagents, a 2-mm capillary tube, in which the deuterated chloroform (CHCl$_3$-d) was sealed, was placed at the center of a 5-mm sample tube filled with the chemical shift reference of tetramethylsilane (TMS) and the sample solutions. It is demanded that the inner capillary tube should be kept parallel with the exterior sample tube. The NMR spectra were obtained using a Bruker DMX 500 spectrometer operating at 500 MHz at different concentrations at 298.15 K and the experimental data for both ILs/water systems have been shown in Table 1.

Theory

In 1964, Wilson[40] proposed a local composition concept to describe the microscopic solution structure, which has been extensively used to correlate vapor-liquid equilibrium data of binary and multicomponent mixtures. On the basis of the Wilson's assumption, Deng et al.[29] assumed that the observed ^{1}H NMR chemical shifts at a certain composition in a binary system could be simply expressed as follows:

$$\delta_{1,\mathrm{cal}} = \delta_1^0 \phi_{11} + \delta_1^\infty \phi_{21} \tag{1}$$

where ϕ_{11} and ϕ_{21} are local volume fractions of molecules 1 and 2 around the central molecule 1, respectively. δ_1^0 and δ_1^∞

Table 1. Chemical Shift of the Various Protons (ppm) in Aqueous Solutions of EmimBF$_4$ and N4NO$_3$ ILs as a Function of Mole Fraction of IL $x_{\mathrm{(IL)}}$

EmimBF$_4$-Water			N4NO$_3$-Water		
$x_{\mathrm{(IL)}}$	C2—H	H_2O	$x_{\mathrm{(IL)}}$	N—H	H_2O
0.000	–	4.782	0.000	/	4.782
0.108	8.777	4.526	0.100	7.519	4.662
0.218	8.807	4.271	0.194	7.584	4.579
0.293	8.823	4.129	0.300	7.628	4.526
0.362	8.835	4.002	0.393	7.643	4.480
0.475	8.860	3.885	0.549	7.661	4.412
0.583	8.877	3.798	0.591	7.663	4.394
0.811	8.914	3.750	0.696	7.674	4.404
0.884	8.931	3.691	0.789	7.678	4.407
0.940	8.942	3.685	0.861	7.679	4.424
1.000	8.953	–	1.000	7.689	–

are pure substance and infinitely dilute chemical shifts of a certain proton of molecule 1, respectively. The latter is usually obtained by extrapolating the dilute chemical shift to zero concentration. Then, the local molar volume fractions can be defined as following:

$$\phi_{11} = \frac{x_1}{x_1 + \Lambda_{21}x_2} \tag{2}$$

$$\phi_{21} = \frac{\Lambda_{21}x_2}{x_1 + \Lambda_{21}x_2} \tag{3}$$

$$\Lambda_{21} = \frac{V_2}{V_1}\exp[-(g_{21} - g_{11})/RT] \tag{4}$$

where g_{21} and g_{11} are proportional to the 1-2 and 1-1 interaction energies, respectively, where V_1 and V_2 are the mole volumes of molecule 1 and 2, which are calculated by division of molecular weight and density. x_1 and x_2 denote bulk mole fractions of molecules 1 and 2, respectively. $(g_{21} - g_{11})$ is the mutual interaction energy parameter connected with the 1-2 and 1-1 pairs of molecules. According to Eqs. 1–4, the correlation of chemical shifts for ILs/water mixtures can be achieved using one set of energy parameter.

To obtain the interaction energy parameter by correlating ^{1}H NMR chemical shifts, the following objective function is used,

$$\text{O.F} = \left[\frac{1}{m-1}\sum_{k=1}^{m}(\delta_{1,\text{cal},k} - \delta_{1,\text{exp},k})^2\right]^{1/2} \tag{5}$$

where m denotes the size of the experimental data set. $\delta_{1,\text{cal},k}$ denotes kth calculated chemical shifts according to Eq. 1. $\delta_{1,\text{exp},k}$ denotes the kth experimental value, and $(g_{21} - g_{11})$ is the only optimized parameter.

Actually according to Wilson's definition of local composition (LC) model for a binary mixture, the ratios of the probability of finding the molecule 2 around the central molecule 1 can be defined in terms of bulk mole fractions x_2 and x_1 and interaction energies between 1-2 pair g_{21} and 1-1 pair g_{11} shown below,

$$\frac{x_{21}}{x_{11}} = \frac{x_2\exp(-g_{21}/RT)}{x_1\exp(-g_{11}/RT)} = \frac{x_2}{x_1}\exp[-(g_{21} - g_{11})] \tag{6}$$

where x_{11} and x_{21} denote the local mole fraction of molecule 1 and 2, respectively, around the central molecule 1. Apparently, the local mole fraction of every molecule in the vicinity of the central molecule 1 should be unity. Thus,

$$x_{11} + x_{21} = 1 \tag{7}$$

where the value of x_{11} as well as x_{21} can be calculated with Eqs. 5 and 6 at every composition after the correlation of chemical shifts has been carried out.

Results and Discussion

Correlation of ^{1}H NMR chemical shifts using the LC model

Unambiguously, such IL/water binary solution could not absolutely be homogeneous in the local area ascribed to discrepancy in interactions of molecule pairs IL–IL, IL–water, and water–water. Accordingly in the vicinity of any component, the number of IL or water in the local is believed to be not always the same as in the bulk, which is so-called the local composition. Actually, it has been experimentally demonstrated that the LC model proposed by our group can be successfully utilized to correlate the IR and Raman peak positions as well as ^{1}H NMR chemical shifts of varied binary mixtures[30–33] and even the prediction among different spectroscopic properties can be realized.[41] Thus, the good correlation of ILs/water system can also be well expected.

Taking EmimBF$_4$/water system for example, the concentration-dependent chemical shifts of H_2O and C2—H protons have been obtained by ^{1}H NMR experiments, respectively. First, EmimBF$_4$ IL is considered as the central molecule 1, then molecular 2 mentioned in equations above is assigned to water. Thus, according to Eqs.1–4 the chemical shifts of C2—H (acidic hydrogen attached to C2 defined in Figure 1) proton can be correlated with the only optimized parameter $(g_{21} - g_{11})$. At the same time, the corresponding local mole fraction x_{11} and x_{21}, which separately denote the distribution of IL and water around the IL, can be figured out with Eqs. 6 and 7. Similarly, when water is assigned to the central molecule 1, the concentration-dependent local mole fraction of water and IL around water molecules, namely x_{11} and x_{21}, can also be obtained. The calculation process for the correlation of N4NO$_3$/water system is similar to that of EmimBF$_4$/water. Furthermore, the comparison between calculation results and experimental data has been shown in Figures 2 and 3. The deviations of the correlation of chemical shifts including N—H proton of N4NO$_3$, C2—H of EmimBF$_4$ as well as water proton are listed in Table 2, where the root-mean square deviations are defined as,

$$\Delta\delta\% = \left[\frac{1}{m}\sum_{k=1}^{m}\left\{\frac{(\delta_{1,\text{cal},k} - \delta_{1,\text{exp},k})}{\delta_{1,\text{exp},k}}\right\}^2\right]^{1/2} \times 100\% \tag{8}$$

$$\Delta\delta = \left[\frac{1}{m}\sum_{k=1}^{m}(\delta_{1,\text{cal},k} - \delta_{1,\text{exp},k})^2\right]^{1/2} \tag{9}$$

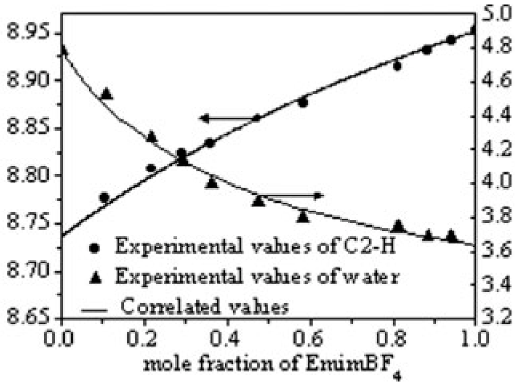

Figure 2. Comparison of experimental and correlated results with the LC model for EmimBF$_4$/water system.

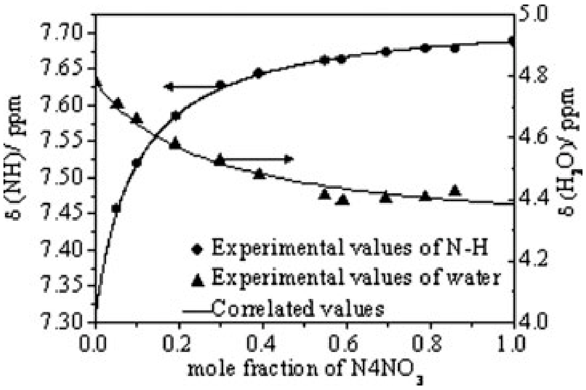

Figure 3. Comparison of experimental and correlated results with the LC model for N4NO$_3$/water system.

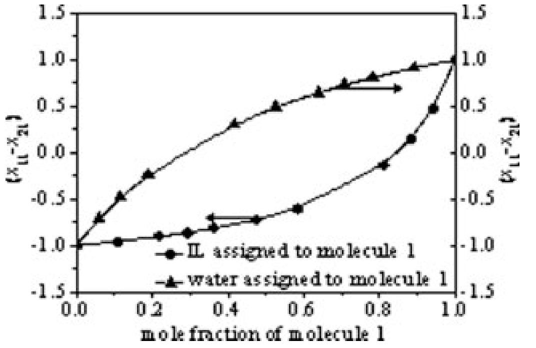

Figure 4. The difference between the local mole fraction for molecule 1 and 2 around the central molecule 1, namely (x_{11} − x_{21}), for EmimBF$_4$/water system.

The discussion about the local structure of ILs/water systems

Analogous to other macroscopical properties, the behavior of ^{1}H NMR chemical shifts of mixtures have been found to be nearly related to the concentration, which can be employed to probe into the microstructure within the mixed solutions. Accordingly, the investigation on the concentration-dependent chemical shifts of IL/water mixtures with the LC model should be expected to describe the reactions inside the aqueous solution of IL. To illustrate the local composition of mixtures more clearly, the concentration-dependent (x_{11} − x_{21}) and x_{11} has been shown graphically in Figures 4–7.

The description of EmimBF$_4$/water system

The local composition in the case of the EmimBF$_4$ IL regarded as the molecule 1. If the EmimBF$_4$ is taken as central molecule 1, then water is assigned to molecule 2. As illustrated in Figure 4, the (x_{11} − x_{21}), which is the difference between the local mole fraction of IL and water in the vicinity of IL, behaves the increasing with x_1 (the bulk mole fraction of EmimBF$_4$) over the whole concentration range and changes from −1 to 1. It is clear that when $x_1 < 0.8$, the value of (x_{11} − x_{21}) keeps negative, which indicates that there are a large number of water molecules but smaller amount of IL distributed around IL. However, the value of (x_{11} − x_{21}) exhibits positive within the IL-rich region $x_1 >$ 0.8, which suggests that there are more IL than water located around IL in the vicinity of EmimBF$_4$. Subsequently, it could be revealed that self-association among IL should preferably take place within the IL-rich region, maybe $x_{(\mathrm{IL})}$ = 0.8–1. In fact, the literature[42] have ever probed into hydrogen-bonding structures of 1-butyl-3-methylimidazolium halides/D$_2$O mixtures with high-pressure infrared spectroscopy and have detected a clustering of the alkyl groups at high IL concentration, which is interestingly in agreement with our observations.

Table 2. The Correlation Deviation of ^{1}H NMR Chemical Shifts for ILs/Water Systems

	EmimBF$_4$/Water		N4NO$_3$/Water	
	C2−H	H$_2$O	N−H	H$_2$O
Δδ	0.0049	0.0344	0.0024	0.0185
Δδ%	0.0549	0.8494	0.0308	0.4179

Δδ and Δδ% are the absolute and the relative root-mean square deviations of the correlation of the experimental ^{1}H NMR chemical shifts calculated according to Eqs. 8 and 9.

The local composition in the case of water regarded as the molecule 1. On the other hand, if water is regarded as the central molecule 1, then EmimBF$_4$ IL should be regard as the molecule 2. Likewise, the value of (x_{11} − x_{21}), which can be employed to depict the distributing circumstance around water, behaves increasing with bulk mole fraction of water x_1 and it has been also shown in Figure 4. It is worth to notice that when $x_1 < 0.3$, the value of (x_{11} − x_{21}) is smaller than zero, which indicates that the amount of water is less than IL distributed around water in the vicinity of the water. Consequently, it could be concluded that within the water-poor region, maybe $x_{(\mathrm{water})} < 0.3$, the interaction between IL and water predominates absolutely instead of the self-association of water molecules.

In summary, the component distributed mainly surrounding the IL is IL itself rather than water molecules when the concentration of IL is much more than water, namely $x_{(\mathrm{IL})} >$ 0.8. At the same time, the component located around the water is mainly IL rather than water molecules. In other words, most of IL is apt to self-associate with each other;

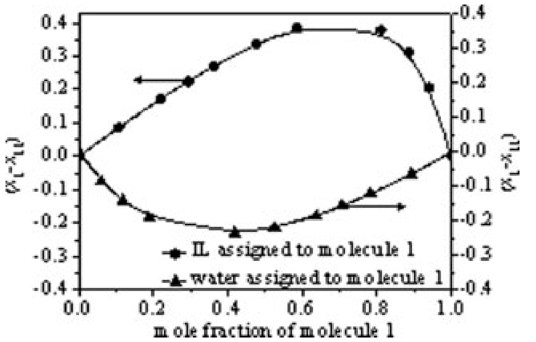

Figure 5. The difference between the bulk and the local mole fraction of molecule 1 around the central molecule 1, namely (x_1 − x_{11}), for EmimBF$_4$/water system.

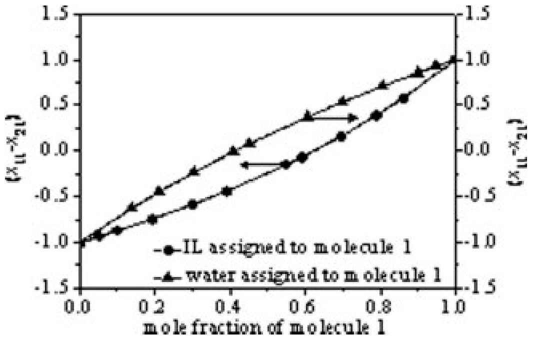

Figure 6. The difference between the local mole fraction for molecule 1 and 2 around the central molecule 1, namely ($x_{11} - x_{21}$), for N4NO$_3$/water system.

while it is favorable for water molecules to interact with IL instead of self-association within such IL-rich region.

Actually, many viewpoints concerning the interactions between ILs and water have been proposed. We can compare them with our results. ATR spectroscopy have been used to investigate the state of water in BmimBF$_4$[43] and it has been shown that water molecules absorbed from the air are present mostly in the "free" (not self-associated) state, bonded via H-bonding with BF$_4^-$ anion within water-poor range. In addition, MD simulations investigation on nanostructural organization in mixture of 1-octyl-3-methylimidazolium nitrate ionic liquid and water[18] have revealed that the anion-water H-bond interactions cause the water molecule to be attracted to the anion at lower concentrations of water. The analysis of both the local structure and the dynamics of the mixtures of two ionic liquids, namely 1,3-dimethylimidazolium chloride and1,3-dimethylimidazolium hexafluorophosphate, and water using MD simulation[19] illustrates the preference for water molecules to hydrogen-bond to the anions rather than to other water molecules at $x_{(\text{water})} < 0.5$, which is a consequence of the strong interaction with the anions. In fact many literatures have suggested that the interaction of anion-water plays the dominate role in determining IL solubility in water.[44,45] Therefore, our finding that water molecules prefer to interact with IL rather than self-associate within IL-rich region is in agreement with the former conclusions.

The difference between the local and bulk composition. Furthermore, the analysis of difference between the local and bulk mole fraction have also been carried out. The x_1 vs. ($x_1 - x_{11}$) have been illustrated in Figure 5, in which IL and water is considered as molecule 1 one by one. It is clear that the value of ($x_1 - x_{11}$) reaches the maximum at $x_1 \approx 0.6$ when IL is assigned to molecule 1. When water is regarded as molecule 1, the value of ($x_1 - x_{11}$) reaches the minimum at $x_1 \approx 0.4$. Such interesting phenomenon could tell us that the differences between the bulk and local composition are so conspicuous that we can speculate that the remarkable change on liquid structure should possibly take place at this concentration point, $x_{(\text{IL})} \approx 0.6$. Fortunately, some excess thermodynamic properties which can be applied to reflect the nonideality of the mixtures, as well as calculations have confirmed our hypothesis. Experimental data of densities and viscosities are have been presented for EmimBF$_4$/H$_2$O binary systems over the entire range of their compositions.[36] The molar excess volume V^E exhibit positive maximum at $x_{(\text{water})} \approx 0.5$ and viscosity derivation $\Delta\eta$ takes on negative maximum at $x_{(\text{water})} \approx 0.4$. Moreover, the mixture of 1-butyl-3-methylimidazolium tetrafluoroborate (BmimBF$_4$)/water has been investigated using MD simulation.[46] The results have shown that at $x_{(\text{IL})} = 0.6$, the solution behaves the highly poor stability. In addition, according to the report,[47] the excess volume as well as viscosity have been shown to be characteristic when $x_{(\text{IL})} = 0.5$–0.6. Evidently, our observation gained from EmimBF$_4$/water system is greatly coherent with above experimental results. Furthermore macroscopical physical properties, the direct measurement of the deviation from ideality of solutions, combined with our finding may offer us a clear insight that the solution structure of ILs/water mixtures behave characteristic change at $x_{(\text{IL})} = 0.5$–0.6.

The description of N4NO$_3$/water system

Apart from the aqueous solution of EmimBF$_4$ IL, the N4NO$_3$/water system have also been studied using the same process as that of EmimBF$_4$ and the local composition behavior has been shown in Figure 6.

The local composition in the case of N4NO3 IL regarded as the molecule 1. In the case of N4NO$_3$ IL regarded as the central molecule 1, the concentration-dependent x_{11} and x_{21} can be obtained through the correlation for chemical shifts of N—H proton. It can be detected obviously that the ($x_{11} - x_{21}$), which is the difference between the local mole fraction of IL and water around IL, behaves increasing with x_1 (the bulk mole fraction of IL) over the whole concentration range. It is interesting to focus on the point $x_1 \approx 0.6$. The value of ($x_{11} - x_{21}$) keeps positive when $x_1 > 0.6$, indicated that the there are fewer water but more IL distributed around IL. However, the value of ($x_{11} - x_{21}$) exhibits negative when $x_1 < 0.6$, suggested that there is more water than IL gathering around the central molecule IL in such region. Actually, the formation of a certain water structure around alkyl C—H groups of 1-butyl-3-methylimidazolium halides IL in the water-rich region has been noticed in the previous research.[42]

The local composition in the case of water regarded as the molecule 1. On the other hand, if water is regarded as central molecule 1, then N4NO3 should be regard as molecule

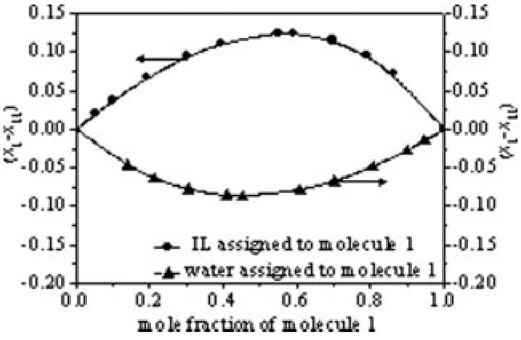

Figure 7. The difference between the bulk and the local mole fraction of molecule 1 around the central molecule 1, namely ($x_1 - x_{11}$), for N4NO$_3$/water system.

2. Likewise, the value of $(x_{11} - x_{21})$, which can be employed to describe the distributing circumstance around water, behaves increasing with bulk mole fraction of water (Figure 6). It is worth to notice that the value of $(x_{11} - x_{21})$ is smaller than zero when $x_{(\mathrm{water})} < 0.4$, which indicates that the amount of water assembled around water is less than that of IL. Consequently, it could be concluded that within the water-poor region water molecules mainly interact with IL rather than associate with each other, which is well consistent with the conclusion obtained from EmimBF$_4$/water. However, when $x_{(\mathrm{water})} > 0.4$, the $(x_{11} - x_{21})$ begins to be positive, demonstrated that the number of water molecules gathering around water is becoming more than that of IL. In other words, the association among water molecules starts to dominate in water-rich region and the network of water molecules is accordingly expected to come into being. In fact, many literatures have reported the state of water in IL aqueous solution. It has been put forward[18] that the turnover of the water–water correlation results from the competition between the water–water and water-anion interactions. With more than 50% mole fraction of water, the "active" water–water interactions has begin to dominate the water-anion interaction, causing a more complex water–water hydrogen bond network in addition to water hydrogen-bonded to nitrate anion. Also MD simulation[19] has revealed that a continuous water network appears at high water concentrations, because most of water molecules associate with each other rather than with ions of IL. Hereby, our result that the association among water molecules predominates in water-rich region is specifically in agreement with the former conclusions.

The difference between the local and bulk composition. Similarly, difference between the local and bulk mole fraction, namely $(x_1 - x_{11})$, for N4NO$_3$ aqueous solutions has been illustrated in Figure 7. It can be evidently detected that the maximum value of $(x_1 - x_{11})$ appears at $x_{(\mathrm{IL})} \approx 0.55$ in case of IL regarded as central molecule 1; and the minimum value of $(x_1 - x_{11})$ appears at $x_{(\mathrm{water})} \approx 0.45$ when water is taken as central molecule 1. Because the change of $(x_1 - x_{11})$ has been confirmed to be consistent with excess functions for EmimBF$_4$/water system, it could be hypothesized that remarkable changes on structure of solution would happen for N4NO$_3$/water mixture and excess function, such as excess volumes, could exhibit turnover around this concentration point $x_{(\mathrm{IL})} \approx 0.55$.

The difference between EmimBF$_4$/water and N4NO$_3$/water system

It is also very interesting to compare Figure 5 with Figure 7 in which the concentration-dependent $(x_1 - x_{11})$ for EmimBF$_4$ and N4NO$_3$ aqueous solution are shown respectively. In case of IL as central molecule 1, the maximum of $(x_1 - x_{11})$ is close to 0.4 for EmimBF$_4$/water, whereas the maximum of $(x_1 - x_{11})$ is about 0.12 for N4NO$_3$/water. In addition, in case of water as central molecule 1, the minimum of $(x_1 - x_{11})$ is close to -0.25 for EmimBF$_4$/water, whereas minimum of $(x_1 - x_{11})$ is about -0.12 for N4NO$_3$/water. Apparently, the absolute value of $(x_1 - x_{11})$ of EmimBF$_4$/water is always larger than that of N4NO$_3$/water system, which indicates that the difference between the bulk and the local for EmimBF$_4$/water is more prominent than that for N4NO$_3$/water. In other words, the nonideality of EmimBF$_4$/water system seems more notable than N4NO$_3$/water. This interesting distinction between these two aqueous systems may be due to the intrinsic order of ILs. It could be deduced that the organization of EmimBF$_4$ IL should be more difficult to be disturbed by water molecules in comparison to N4NO$_3$ due to the fact that the molecular weight of EmimBF$_4$ is larger than N4NO$_3$ and the structural order of EmimBF$_4$ IL may be greater than that of N4NO$_3$ IL. Consequently, N4NO$_3$/water system presents more homogeneous than EmimBF$_4$/water.

In summary, the changes on structure of EmimBF$_4$ and N4NO$_3$ aqueous solutions could be described as follows: initially the ions of IL interact with each other because of the strong electrostatic force in the pure IL. Then the addition of a small quantity of water begins to destroy the intrinsic organization of IL since water molecules can form strong interactions with anions of IL, although IL–IL association still dominates in this IL-rich region. Moreover, most of water molecules are apt to hydrogen-bond to IL (mainly to anions) rather than self-association with each other. As a result, with the amount of water keeps increasing until the mole fraction of water exceed that of ILs, namely water-rich range, water molecules begin to associate with each other to form network of water in addition to fewer water molecules hydrogen-bonded to anions of IL.

Conclusions

The correlation of ^{1}H NMR chemical shifts with the LC model for EmimBF$_4$ and N4NO$_3$ aqueous solutions reveals that IL mainly associates with each other and most of water prefer to be hydrogen-bonded to IL (basically anions) rather than self-associated in IL-rich region. Instead the association among water molecules themselves dominates the interaction between water-IL anions within water-rich region, causing the formation of network of water molecules. Nevertheless IL are chiefly hydrogen-bonded to water molecules leaving fewer ILs self-association with each other in such region. In one word, water should presumably not mix homogeneously with ILs in the local area. Furthermore, the difference between the bulk and the local have been shown to be in good agreement with the excess thermodynamic function for EmimBF$_4$/water system, which reinforces our viewpoint that the structure of this system could behave the most remarkable change around this composition. Accordingly, it is reasonable to predict that the excess properties of N4NO$_3$/water mixture, such as V^E and $\Delta\eta$, may possibly perform turnover at $x_{(\mathrm{IL})} \approx 0.55$.

Obviously, our results obtained from the LC model show good agreements with that from other techniques such as IR and MD and so on. On the one hand, the reliability of such traditional method that NMR spectroscopy coupled with the LC model has been further approved. On the other hand, the successful application on EmimBF$_4$/water and N4NO$_3$/water systems demonstrates the availability and convenience of this method which could be employed to offer us a detailed insight on the structure of other ILs/water mixtures.

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Notation

g = energy of interaction between a pair of molecules, J mol^{-1}
m = the number of ^1H NMR spectroscopic data
R = general gas constant, J mol^{-1} K^{-1}
T = absolute temperature, K
V = mole volume, cm^3 mol^{-1}

Greek letters

δ = chemical shift of ^1H NMR spectra
ϕ = local volume fraction
Λ = notations in Eq. 4

Subscripts

cal = calculated
exp = experimental
1, 2 = component 1 and 2

Superscripts

0 = pure substance
∞ = infinite dilute

Literature Cited

1. Kelkar MS, Maginn EJ. Effect of temperature and water content on the shear viscosity of the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl) imide as studied by atomistic simulations. *J Phys Chem B*. 2007;111:4867–4876.
2. Jacquemin J, Husson P, Padua AA, Majer V. Density and viscosity of several pure and water-saturated ionic liquids. *Green Chem*. 2006; 8:172–180.
3. Wang J, Wang H, Zhang S, Zhang H, Zhao Y. Conductivities, volumes, fluorescence, and aggregation behavior of ionic liquids [C_4mim][BF_4] and [$C_n$mim]Br (n = 4, 6, 8, 10, 12) in aqueous solutions. *J Phys Chem B*. 2007;111:6181–6188.
4. Gu Y, Ogawa C, Kobayashi S. Silica-supported sodium sulfonate with ionic liquid: a neutral catalyst system for Michael reactions of indoles in water. *Org Lett*. 2007;9:175–178.
5. Anthony JL, Maginn E, Brennecke JF. Solution thermodynamics of imidazolium-based ionic liquids and water. *J Phys Chem B*. 2001; 105:10942–10949.
6. Tejwant S, Arvind K. Aggregation behavior of ionic liquids in aqueous solutions: effect of alkyl chain length, cations, and anions. *J Phys Chem B*. 2007;111:7843–7851.
7. Mele A, Tran CD, Lacerda SH. The structure of a room-temperature ionic liquid with and without trace amounts of water: the role of C—H···O and C—H···F interactions in 1-*n*-butyl-3-methylimidazolium tetrafluoroborate. *Angew Chem Int Ed*. 2003;42:4364–4366.
8. Koddermann T, Wertz C, Heintz A, Ludwig R. The association of water in ionic liquids: a reliable measure of polarity. *Angew Chem Int Ed*. 2006;45:3697–3702.
9. Dominguez-Vidal A, Kaun N, Ayora-Canada MJ, Lendl B. Probing intermolecular interactions in water/ionic liquid mixtures by far-infrared spectroscopy. *J Phys Chem B* 2007;111:4446–4452.
10. Xu H, Pang Y, Li X, Ding H, Cheng Y, Shi G, Jin L. Study on electrochemical synthesis and electrochromism of poly(3-bromothiophene) in ionic liquid. *Acta Chim Sin*. 2006;64:2254–2258.
11. Miki H, Hayashi S, Kikura H, Hamaguchi HO. Raman spectra indicative of unusual water structure in crystals formed from a room-temperature ionic liquid. *J Raman Spectrosc*. 2006;37:1242–1243.
12. Sieffert N, Wipff G. The [BMI][Tf_2N] ionic liquid/water binary system: a molecular dynamics study of phase separation and of the liquid-liquid interface. *J Phys Chem B*. 2006;110:13076–13085.
13. Liu Z, Huang S, Wang W. A refined force field for molecular simulation of imidazolium-based ionic liquids. *J Phys Chem B*. 2004;108:12978–12989.
14. Zhang L, Li H, Wang Y, Hu X. Characterizing the structural properties of *N,N*-Dimethylformamide-based ionic liquid: density-functional study. *J Phys Chem B*. 2007;111:11016–11020.
15. Wang Y, Li H, Han S. A theoretical investigation of the interactions between water molecules and ionic liquids. *J Phys Chem B*. 2006;110:24646–24651.
16. Chiappe C. Nanostructural organization of ionic liquids: theoretical and experimental evidences of the presence of well defined local structures in ionic liquids. *Mon Chem*. 2007;138:1035–1043.
17. Jiang W, Wang Y, Voth GA. Molecular dynamics simulation of nanostructural organization in ionic liquid/water mixtures. *J Phys Chem B*. 2007;111:4812–4818.
18. Hanke CG, Lynden-Bell RM. A simulation study of water-dialkylimidazolium ionic liquid mixtures. *J Phys Chem B*. 2003;107:10873–10878.
19. Jeon Y, Sung J, Kim D, Seo C, Cheong H, Ouchi Y, Ozawa R, Hamaguchi H. Structural change of 1-butyl-3-methylimidazolium tetrafluoroborate + water mixtures studied by infrared vibrational spectroscopy. *J Phys Chem B*. 2008;112:923–928.
20. Saha S, Hamaguchi H. Effect of water on the molecular structure and arrangement of nitrile-functionalized ionic liquids. *J Phys Chem B*. 2006;110:2777–2781.
21. Bowers J, Butts P, Martin J, Vergara-Gutierrez C, Heenan K. Aggregation behavior of aqueous solutions of ionic liquids. *Langmuir*. 2004;20:2191–2198.
22. Schröder U, Wadhawan JD, Compton RG, Marken F, Suarez PA, Consorti CS, de Souza RF, Dupont G. Water-induced accelerated ion diffusion: voltammetric studies in 1-methyl-3-[2,6-(*S*)-dimethylocten-2-yl] imidazolium tetrafluoroborate, 1-butyl-3-methylimidazolium tetrafluoroborate and hexafluorophosphate ionic liquids. *New J Chem*. 2000;24:1009–1015.
23. Zhao Y, Gao S, Wang J, Tang J. Aggregation of ionic liquids [$C_n$mim] Br (n =4, 6, 8, 10, 12) in D_2O: a NMR study. *J Phys Chem B*. 2008;112:2031–2039.
24. Rollet AL, Porion P, Vaultier M, Billard I, Deschamps M, Bessada C, Jouvensal L. Anomalous diffusion of water in [BMIM][TFSI] room-temperature ionic liquid. *J Phys Chem B*. 2007;111:11888–11891.
25. Li W, Zhang Z, Han B, Hu S, Xie Y, Yang G. Effect of water and organic solvents on the ionic dissociation of ionic liquids. *J Phys Chem B*. 2007;111:6452–6456.
26. Jiang J, Liu H, Hu Y, Prausnitz JM. A molecular-thermodynamic model for polyelectrolyte solutions. *J Chem Phys*. 1998;108:780–784.
27. Karachewski AM, McNiel MM, Eckert CA. A study of hydrogen bonding in alcohol solutions using NMR spectroscopy. *Ind Eng Chem Res*. 1989;28:315–324.
28. Acree WE. *Thermodynamic properties of nonelectrolyte solutions*, Academic Press, Orlando, 1984.
29. Deng D, Li H, Yao J, Han S. Simple local composition model for ^1H NMR chemical shift of mixtures. *Chem Phys Lett*. 2003;376:125–129.
30. Xu Y, Li H, Wang C, Han S. Prediction of viscosity of alcohol + hydrocarbon systems by ^{1}HNMR and activity coefficients at infinite dilution. *Chem Eng Sci*. 2005;60:3621–3627.
31. Ma L, Li H, Wang C, Xu Y, Han S. Prediction of vapor-liquid equilibria data from C-H band shifts of Raman spectra and activity coefficients at infinite dilution in some aqueous systems. *Ind Eng Chem Res*. 2005;44:6883–6887.
32. Xu Y, Li H, Wang C, Han S. Prediction of vapor-liquid equilibria of alcohol-hydrocarbon systems by ^1H NMR and activity coefficients at infinite dilution. *Ind Eng Chem Res*. 2005;44:408–415.
33. Zhu X, Yao J, Li H, Han S. Prediction of vapor-liquid equilibrium data from C-H band shift of IR spectra in some binary systems. *Chin J Chem Eng*. 2007;15:97–101.
34. Shiflett MB, Yokozeki A. Solubility and diffusivity of hydrofluorocarbons in room-temperature ionic liquids. *AIChE J*. 2006;52:1205–1219.
35. Yokozeki A, Shiflett MB. Global phase behaviors of trifluoromethane in ionic liquid [bmim][PF6]. *AIChE J*. 2006;52:3952–3957.
36. Zhang S, Li X, Chen H, Wang J, Zhang J, Zhang M. Determination of physical properties for the binary system of 1-ethyl-3-methylimidazolium tetrafluoroborate + H_2O. *J Chem Eng Data*. 2004;49:760–764.
37. Weng J, Wang C, Li H, Wang Y. Novel quaternary ammonium ionic liquids and their use as dual solvent-catalysts in the hydrolytic reaction. *Green Chem*. 2006;8:96–99.

38. Zhang R, Li H, Lei Y, Han S. Different weak C—H···O contacts in *N*-methylacetamide-water system: molecular dynamics simulations and NMR experimental study. *J Phys Chem B*. 2004;108:12596–12601.
39. Zhang R, Li H, Lei Y, Han S. All-atom molecular dynamic simulations and relative NMR spectra study of weak C—H···O contacts in amide-water systems. *J Phys Chem B*. 2005;109:7482–7487.
40. Wilson GM. Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing. *J Am Chem Soc*. 1964;86:127–130.
41. Zhu X, Yao J, Li H, Han S. Prediction among different spectroscopic properties for aqueous systems. *J Chem Phys*. 2006;124:244501.
42. Chang HC, Jiang JC, Chang CY, Su JC, Hung CH, Liou YC, Lin SH. Structural organization in aqueous solutions of 1-butyl-3-methylimidazolium halides: a high-pressure infrared spectroscopic study on ionic liquids. *J Phys Chem B*. 2008;112:4351–4356.
43. Cammarata L, Kazarian SG, Salterb PA, Weltonb T. Molecular states of water in room temperature ionic liquids. *Phys Chem Chem Phys*. 2001;3:5192–5200.
44. Rivera-Ruberto S, Baldelli S. Influence of water on the surface of hydrophilic and hydrophobic room-temperature ionic liquids. *J Am Chem Soc*. 2004;126:11788–11789.
45. Almásy L, Turmine M, Perera A. Structure of aqueous solutions of ionic liquid 1-butyl-3-methylimidazolium tetrafluoroborate by small-angle neutron scattering. *J Phys Chem B*. 2008;112:2382–2387.
46. Wu X, Liu Z. Computer simulation study of the mixtures of room temperature ionic liquid [bmim][BF_4]and water. *Acta Phys Chim Sin*. 2005;21:1036–1041.
47. Seddon KR, Stark A, Torres MJ. Influence of chloride, water, and organic solvents on the physical properties of ionic liquids. *Pure Appl Chem*. 2000;72:2275–2287.

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