

Structural Heterogeneities in Solutions of Triethylamine Nitrate Ionic Liquid: ^1H NMR and LC Model Study

Xiao Zhu¹ · Huan Zhang¹ · Yingjie Xu²

Received: 5 June 2015 / Accepted: 3 December 2015 / Published online: 17 February 2016
© Springer Science+Business Media New York 2016

Abstract In order to uncover the micro-structural heterogeneities in solutions of ammonium based ionic liquids, triethylamine nitrate ($\text{N}_{222}\text{NO}_3$) has been synthesized using acid–base neutralization and the ^1H NMR spectra of two binary mixtures, namely $\text{N}_{222}\text{NO}_3$ /dimethyl sulfoxide (DMSO) and $\text{N}_{222}\text{NO}_3$ /acetone at different concentrations, have been measured at 298.15 K. The internal reference method was adopted to obtain the concentration-dependent chemical shifts of $-\text{CH}_3$ in $\text{N}_{222}\text{NO}_3$, which have been correlated using the ^1H NMR local composition (LC) model to obtain the local mole fractions. It has been revealed that within $\text{N}_{222}\text{NO}_3$ rich region, self-association of the ionic liquid was predominant instead of $\text{N}_{222}\text{NO}_3$ –solvent interactions. However, in the solvent rich region, $\text{N}_{222}\text{NO}_3$ mainly interacts with solvent molecules, indicating that the self-association network of $\text{N}_{222}\text{NO}_3$ has been greatly destroyed by solvents. In addition, the different influences of DMSO and acetone have been detected. DMSO molecules more effectively destroy the original network of the ionic liquid, due to its higher dielectric constant. Also, LC behavior in $\text{N}_{222}\text{NO}_3$ /DMSO systems is more significant than in $\text{N}_{222}\text{NO}_3$ /acetone, indicating that DMSO can induce more obvious heterogeneities in DMSO/ $\text{N}_{222}\text{NO}_3$ mixtures, which is consistent with physicochemical properties and cellulose solubility of solutions.

Keywords ^1H NMR chemical shifts · Ammonium-based ionic liquids · Binary solutions · LC model

✉ Xiao Zhu
xiaoxiao1982820@163.com

¹ School of Chemistry and Chemical Engineering, Qufu Normal University, Qufu 273165, People's Republic of China

² Department of Chemistry, Shaoxing University, Shaoxing 312000, People's Republic of China

1 Introduction

As typical protic ionic liquids (PILs), ammonium-based ILs are attracting more and more attention. On the one hand, they have general characteristics like other ILs such as low volatility, wide liquid range, good solubility with other solvents and are function adjustable according to different combinations of cations and anions. On the other hand, they also have many special properties, including low cost, high electrical conductivity, and ease of preparation through direct neutralization between corresponding acid and base, which can endow them excellent performance in many fields such as alkylation reactions [1], absorption of SO_2 [2] and CO_2 [3], extraction of soluble dyes [4], stability of proteins [5, 6], dissolution of cellulose [7], electrochemistry [8] and wastewater treatments [9]. Obviously, knowledge of interactions between ammonium based ILs and molecular solvents is essential for their applications in chemical and industrial processes. Some physicochemical properties of solutions containing ammonium based ILs, such as viscosity, density and conductivity, have been measured and the interactions between ILs and solvents have also been discussed [10, 11]. The molecular solvents could lead to great variations of physicochemical properties of ILs, which suggests; that the micro-structure of solutions can be changed since the properties depended on the structures. Recently it has been reported that nano-inhomogeneity structures can be generated in aqueous solutions of ILs [12, 13]. Also, a study [14] of the DMSO/trimethyl(butyl)ammonium bis((trifluoromethyl)sulfonyl)imide ($[\text{N}_{41111}] [\text{Tf}_2\text{N}]$) and DMSO/1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide ([bmim] $[\text{Tf}_2\text{N}]$) has shown that DMSO in mixtures with ILs can produce clusters, instead of homogeneous mixing. Moreover, the formation of localized, self-segregated, hydrogen-bonded nanostructures within the 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6])/tetraethylene glycol (TEG) binary mixtures has also been observed [15]. Accordingly, it has been emphasized that [16] considerable efforts should be made to investigate structural heterogeneities in mixtures of ILs with molecular solvents.

NMR has been frequently utilized to study the inhomogeneities in mixtures of ILs due to its accuracy and sensitivity [17, 18]. Undoubtedly the ^1H NMR chemical shifts can help us to determine the numbers and category of protons in pure substances. Furthermore, ^1H NMR chemical shifts also offer us much information about microscopic structure within solutions, since the chemical environments of protons can change due to the intermolecular interactions. More interestingly, ^1H NMR chemical shifts can be analyzed quantitatively by certain theoretical models. Deng [19] and co-workers have proposed a simple semi-empirical physical local composition (LC) model to correlate the ^1H NMR chemical shifts of binary mixtures with satisfying results. Subsequently, relations between the thermodynamic and spectroscopic properties of mixtures have been established successfully with this LC model [20–22]. In our previous work, IR, Raman and ^1H NMR measurements were made in solutions of ILs [23] and the local structure of aqueous solutions of 1-ethyl-3-methylimidazolium tetrafluoroborate (Emim BF_4) and *n*-butylammonium nitrate (N_4NO_3) [24] were studied using the LC model.

Because little is known about LC of ammonium-based ILs in solutions, the triethylamine nitrate ($\text{N}_{222}\text{NO}_3$) ionic liquid has been synthesized as described in the present paper and the ^1H NMR spectra of two binary mixtures, namely $\text{N}_{222}\text{NO}_3/\text{DMSO}$ and $\text{N}_{222}\text{NO}_3/\text{acetone}$ at different compositions, have been measured. DMSO is known for its special dissolving capacity and high polarity and is often used in company with ionic liquid to promote chemical reactions [25] and biological processes [26]. Acetone, as another

common organic solvent, has been regarded as an efficient solvent for ILs and several properties of the acetone–IL systems have been reported [27]. However, understanding of the micro-structures of $N_{222}NO_3$ /DMSO and $N_{222}NO_3$ /acetone solutions remains obscure and is the subject of the present paper.

2 Experiments and Theory

2.1 Experiments

2.1.1 Synthesis of $N_{222}NO_3$

$N_{222}NO_3$ was prepared from triethylamine and nitric acid according to the procedure reported previously [28] (see Scheme 1). Nitric acid (CAS No. 7697-37-2; 65–68 mass%), triethylamine (CAS No. 121-44-8; A.R.), and DMSO (CAS No.67-68-5; A.R.) were purchased from Aladdin Reagent Co. Ltd., (Shanghai, China) and acetone (CAS No. 67-64-1, A.R.) was purchased from Tianjin Damao Chemical Reagent Factory (Tianjin, China). The water content was below 200 ppm by Karl–Fischer titration (ZSD-1, ShangHai Anting Scientific Instrument Factory). The structure of $N_{222}NO_3$ was identified by its 1H NMR spectra. The chemical shifts δ (ppm) are as follows: 1H NMR (Bruker, 400 MHz, $CDCl_3$), δ (ppm): 9.49 (1H, ^+NH), 3.28 (6H, $-CH_2$), 1.34 (9H, $-CH_3$). All solutions of ILs were prepared by weight using an analytical balance with a precision of ± 0.0001 g.

2.1.2 Measurements of 1H NMR Chemical Shifts

The internal reference method [29] was adopted to obtain the concentration dependent chemical shifts of $-CH_3$ (whose chemical shifts change more obviously with concentrations) in $N_{222}NO_3$. 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 tetramethylsilane (TMS). It is necessary that the inner capillary tube should be kept parallel with the exterior sample tube. The 1H NMR spectra were obtained using a Bruker AV 400 spectrometer operating at 400 MHz at different concentrations at 298.15 K and all of the experimental data are included in Table 1 and Fig. 1.

2.1.3 Measurements of Viscosity and Electric Conductivity of Binary Solutions

The viscosities of the samples were measured with an Ubbelohde viscometer (inner diameter = 1.0 mm). Each sample was placed in an external water bath, which was controlled to 25 ± 0.1 °C for 30 min. Then the measurements of viscosity were performed. Each viscosity value was reported by averaging three consecutive runs. In order to

Scheme 1 Molecular structure and synthesis of $N_{222}NO_3$ ionic liquid

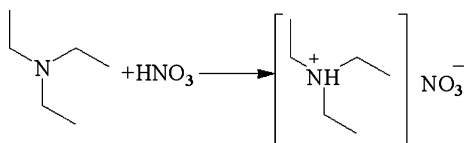


Table 1 Experimental ^1H NMR chemical shifts of $-\text{CH}_3$ of $\text{N}_{222}\text{NO}_3$ in $\text{N}_{222}\text{NO}_3/\text{DMSO}$ and $\text{N}_{222}\text{NO}_3/\text{acetone}$ systems at 25.0°C

$\text{N}_{222}\text{NO}_3$ (1)/DMSO (2)		$\text{N}_{222}\text{NO}_3$ (1)/acetone (2)	
x_1	$\delta(-\text{CH}_3)$	x_1	$\delta(-\text{CH}_3)$
0.0999	1.66	0.1000	2.13
0.1998	1.65	0.1998	1.98
0.3002	1.58	0.2999	1.85
0.3991	1.54	0.3993	1.78
0.4994	1.54	0.5023	1.69
0.5966	1.51	0.5842	1.63
0.6971	1.49	0.6992	1.57
1.0000	1.34	1.0000	1.34

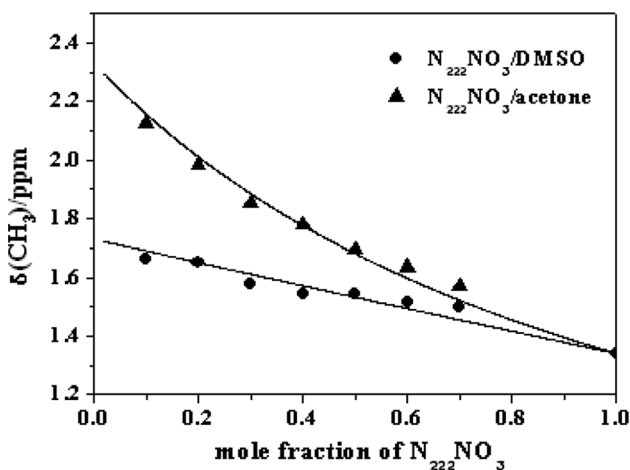


Fig. 1 Experimental and correlated ^1H NMR chemical shifts of $-\text{CH}_3$ of $\text{N}_{222}\text{NO}_3$ in $\text{N}_{222}\text{NO}_3/\text{DMSO}$ and $\text{N}_{222}\text{NO}_3/\text{acetone}$ systems at 25.0°C : (filled circle experimental values of $\text{N}_{222}\text{NO}_3/\text{DMSO}$; filled triangle experimental values of $\text{N}_{222}\text{NO}_3/\text{acetone}$; continuous line calculated values)

avoid moisture absorption, the ionic liquid was dried in a vacuum oven at 70°C for 24 h before use. And, experimental data are illustrated in Fig. 2.

The electric conductivities were measured with an electric conductivity meter produced by Shanghai Precision & Scientific Instrument Co., Ltd. (DDS-11D). The cell constant was determined by using $0.1\text{ mol}\cdot\text{L}^{-1}$ aqueous solution of KCl at 298.15 K. Each sample was placed in a water bath, which was controlled to $25 \pm 0.1^\circ\text{C}$ for 30 min before measurement. Each conductivity value of the samples was obtained by averaging three consecutive runs. The electric conductivity data of binary solutions are illustrated in Fig. 3.

2.1.4 The Solubility of Cellulose in Binary Solutions of $\text{N}_{222}\text{NO}_3$

Under the magnetic stirring and temperature control, sufficient microcrystalline cellulose (MCC) (the weight is m_1) was placed into a 100 mL three necked flask filled with $\text{N}_{222}\text{NO}_3$ solutions (the weight of $\text{N}_{222}\text{NO}_3$ is m_2). The temperature was kept at 60°C . After 24 h

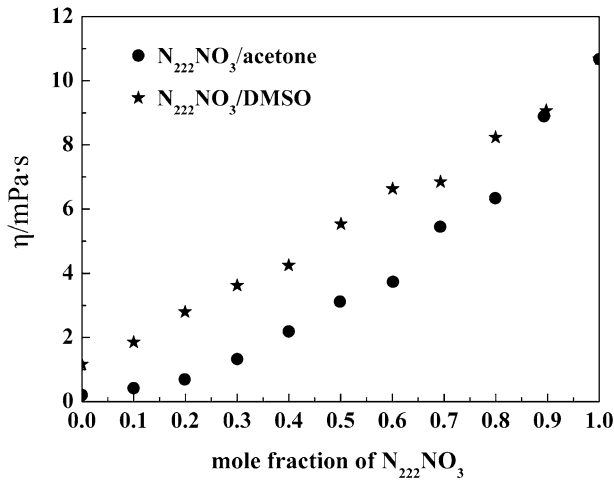


Fig. 2 Viscosity η versus mole fraction of $N_{222}NO_3$ for binary solutions at 25.0 °C

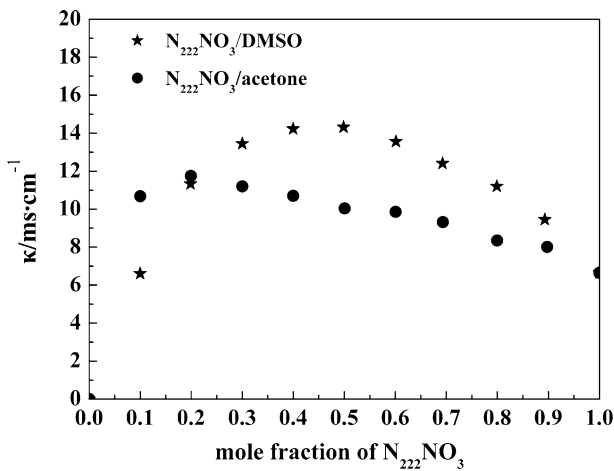


Fig. 3 Specific conductivity κ versus mole fraction of $N_{222}NO_3$ for binary solutions at 25.0 °C

Table 2 The solubility of MCC in the $N_{222}NO_3$ /DMSO and $N_{222}NO_3$ /acetone solutions

$N_{222}NO_3$ /DMSO			$N_{222}NO_3$ /acetone		
w (DMSO) ^a	m_2 (g) ^b	s (%)	w (acetone)	m_2 (g)	s (%)
0.0000	5.2321	0.1586	0.0000	5.2321	0.1586
0.1022	5.3421	0.1629	0.1022	5.3421	0.1479
0.3122	5.2078	0.1728	0.3112	5.2078	0.1444
0.5139	5.2801	0.1970	0.5009	5.0069	0.1318
0.7003	5.0171	0.3229	0.6927	5.0536	0.1009
0.9001	5.3760	0.625	0.9000	5.3570	0.0635

^a The mass fraction of DMSO in $N_{222}NO_3$ /DMSO solutions

^b The weight of $N_{222}NO_3$ in $N_{222}NO_3$ /DMSO solutions

dissolution, the mixtures were separated using high-speed centrifugation to obtain the precipitate (un-dissolved MCC, the weight is m_3). Then the solubility of MCC was calculated as follows and is shown in Table 2:

$$s = \frac{m_1 - m_3}{m_2}.$$

2.2 Theory and Calculations

In 1964, Wilson first [30] proposed the LC concept to describe the microscopic solution structure; this method has been extensively applied to correlate vapor–liquid equilibrium data of binary and multicomponent mixtures. Based on the Wilson's theory, Deng [19] assumed that the observed ^1H NMR chemical shifts at a certain composition in a binary system can be simply expressed as follows:

$$\delta_{1,\text{cal}} = \delta_1^0 \varphi_{11} + \delta_1^\infty \varphi_{21} \quad (1)$$

where φ_{11} and φ_{21} are local volume fractions of molecules 1 and 2 around the central molecule 1, respectively, and δ_1^0 and δ_1^∞ are the chemical shifts of a particular proton of the pure substance and infinitely dilute solution 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:

$$\varphi_{11} = \frac{x_1}{x_1 + A_{21}x_2} \quad (2)$$

$$\varphi_{21} = \frac{A_{21}x_2}{x_1 + A_{21}x_2} \quad (3)$$

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

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 molecules 1 and 2 which are calculated from the molecular weight and density (the measured densities of $\text{N}_{222}\text{NO}_3$, DMSO and acetone at 298.15 K are 1.055, 1.096 and 0.788 $\text{g}\cdot\text{cm}^{-3}$ respectively, using the pycnometer method). 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. The following objective function is used:

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

where m denotes the size of the experimental data set. $\delta_{1,\text{cal},k}$ denotes k th calculated chemical shift according to Eq. 1. $\delta_{1,\text{exp},k}$ denotes the k th experimental value, and $(g_{21} - g_{11})$ is the only optimized parameter. According to Eqs. 1–4, the correlation of chemical shifts of binary mixtures can be achieved using one set of energy parameters and the root-mean square deviations are defined as:

$$\Delta\delta\% = \left[\frac{1}{m} \sum_{k=1}^m \left\{ \frac{(\delta_{1,\text{cal},k} - \delta_{1,\text{exp},k})}{\delta_{1,\text{exp},k}} \right\}^2 \right]^{1/2} \times 100\% \quad (6)$$

$$\Delta\delta = \left[\frac{1}{m} \sum_{k=1}^m (\delta_{1,\text{cal},k} - \delta_{1,\text{exp},k})^2 \right]^{1/2} . \quad (7)$$

The $(g_{21} - g_{11})$ and correlated deviations of two systems are listed in Table 3. According to Wilson's definition of LC for a binary mixture, the ratio of the probability of finding the molecule 2 around the central molecule 1 can be defined in terms of bulk mole fractions and interaction energies between the 1–2 pair g_{21} and 1–1 pair g_{11} as shown below:

$$\frac{x_{21}}{x_{11}} = \frac{x_2 \exp(-g_{21}/RT)}{x_1 \exp(-g_{11}/RT)} = \frac{x_2}{x_1} \exp[-(g_{21} - g_{11})/RT] \quad (8)$$

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,

$$x_{11} + x_{21} = 1 \quad (9)$$

Subsequently, the value of x_{11} and x_{21} can be obtained at different compositions and then the concentration dependent $(x_{11} - x_{21})$ and $(x_1 - x_{11})$ can be calculated.

3 Results and Discussion

3.1 Correlation of ^1H NMR Chemical Shifts

Taking $\text{N}_{222}\text{NO}_3/\text{DMSO}$ for example, the $\text{N}_{222}\text{NO}_3$ could be regarded as the central substance 1 and then 2 is assigned to DMSO. Thus, according to Eqs. 1–4, the chemical shifts of $-\text{CH}_3$ of $\text{N}_{222}\text{NO}_3$ can be correlated with the only optimized parameter $(g_{21} - g_{11})$. Obviously, as is shown in Fig. 1, the $-\text{CH}_3$ chemical shifts of $\text{N}_{222}\text{NO}_3$ in solutions can be well correlated by this semi-empirical LC model, just as its excellent performance in the aqueous solutions of *n*-butylammonium nitrate (N_4NO_3) [23] and EmimBF₄ [24] ionic liquids.

3.2 Local Composition in the Solutions

According to the LC theory, it is easy to understand that the binary solutions of ILs should not be completely homogeneous in the local area. Therefore the number of IL or molecular solvent molecules in the local region should be not always be the same as in the bulk,

Table 3 The energy parameter $(g_{21} - g_{11})$ and the deviations of correlation of ^1H NMR chemical shifts

System	$(g_{21} - g_{11})$ ($\text{J}\cdot\text{mol}^{-1}$)	$\Delta\delta$ (ppm)	$\Delta\delta$ (%)
$\text{N}_{222}\text{NO}_3/\text{DMSO}$	-1877.3	0.0263	1.7
$\text{N}_{222}\text{NO}_3/\text{acetone}$	-249.5	0.0311	1.8

which is the so-called the LC behavior. In $N_{222}NO_3$ /DMSO systems, for example, since $N_{222}NO_3$ is considered as the substance 1, x_{11} denotes the local mole fractions of $N_{222}NO_3$ around the $N_{222}NO_3$, and x_{21} denotes the local mole fractions of DMSO around the $N_{222}NO_3$. With the help of the LC model, the local mole fractions x_{11} and x_{21} can be calculated using Eqs. 8–9 since the $(g_{21} - g_{11})$ can be obtained by the correlation of $\delta(-CH_3)$ of $N_{222}NO_3$. In order to illustrate the LC more clearly, the concentration-dependent $(x_{11} - x_{21})$ of the two systems is shown graphically in Fig. 4.

Clearly $(x_{11} - x_{21})$, which denotes the difference between the local mole fractions of $N_{222}NO_3$ and DMSO (or acetone) in the vicinity of $N_{222}NO_3$, behaves similarly in the two systems and decreases from 1 to -1 with x_2 (the bulk mole fraction of solvent) over the whole concentration range. Apparently, there are only $N_{222}NO_3$ in the pure ionic liquid (when $x_2 = 0$) and here $x_{11} = 1$ and $x_{21} = 0$. With x_2 increasing, $(x_{11} - x_{21})$ becomes smaller and the amount of solvent gathered around $N_{222}NO_3$ keeps increasing, indicating solvent molecules can gradually break into the self-associated organization of $N_{222}NO_3$ and destroy the network of $N_{222}NO_3$. Taking $N_{222}NO_3$ /DMSO for example, when $x(\text{DMSO}) < 0.3$, the value of $(x_{11} - x_{21})$ remains positive, indicated that there are more $N_{222}NO_3$ but fewer DMSO distributed around $N_{222}NO_3$. However, with the amount of DMSO increasing continuously ($0.3 < x(\text{DMSO}) < 1$), the negative value of $(x_{11} - x_{21})$ demonstrates predominance of the interactions between $N_{222}NO_3$ and DMSO instead of self-association of $N_{222}NO_3$. Within the $N_{222}NO_3$ -rich region, self-association among $N_{222}NO_3$ molecules should dominate, indicating that a small quantity of DMSO does not cause significant interference with the structure of $N_{222}NO_3$. When the amount of DMSO is further increased, much more DMSO can move into the local area of $N_{222}NO_3$ and the original network of $N_{222}NO_3$ can be gradually broken down due to the interactions between the DMSO and $N_{222}NO_3$. In the $N_{222}NO_3$ /acetone system, the local structure of solutions shows similar variations. Accordingly, $(x_{11} - x_{21})$ can offer us a picture of the change of micro-structure in binary solutions. Actually, it has been reported [14] that DMSO is not completely mixed with ionic liquid in DMSO/[N_{4111}][Tf_2N] mixtures. Venkatesu and co-workers [31, 32] have studied mixtures of trimethylammonium-based ILs with DMSO and detected that DMSO molecules can reduce hydrogen bonding between the cation and anion due to ion–dipole interactions between DMSO and ILs. However at higher IL

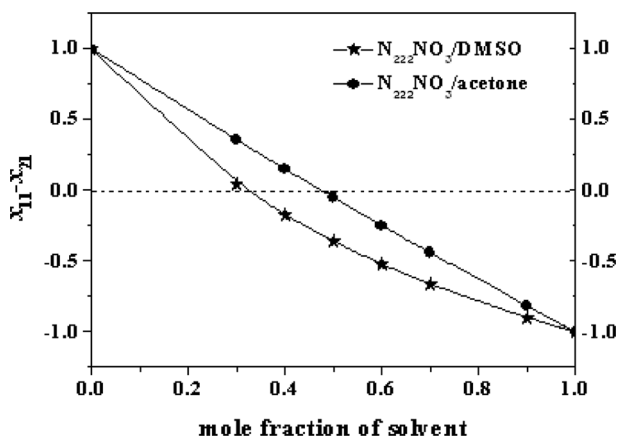


Fig. 4 Concentration-dependent $(x_{11} - x_{21})$ for binary solutions of $N_{222}NO_3$

concentrations, the interactions between DMSO and IL became weaker and extensive self-association in the IL has been detected, which is consistent with our results.

It is also interesting to focus on the differences of the two systems. As shown in Fig. 4, when $(x_{11} - x_{21}) = 0$, $x(\text{DMSO}) \approx 0.3$ and $x(\text{acetone}) \approx 0.5$. In other words, when $x(\text{DMSO})$ exceeds 0.3, there are more DMSO than $\text{N}_{222}\text{NO}_3$ molecules distributed around $\text{N}_{222}\text{NO}_3$. However in the case of $\text{N}_{222}\text{NO}_3/\text{acetone}$, the interactions between acetone and $\text{N}_{222}\text{NO}_3$ do not dominate before $x(\text{acetone})$ reaches 0.5. That is to say, DMSO molecules can break into the self-association structure of $\text{N}_{222}\text{NO}_3$ at lower concentrations than can acetone. In addition, the difference between the local and bulk composition $(x_1 - x_{11})$ has also been calculated and is shown in Fig. 5. Since x_1 and x_{11} denote the bulk and local concentrations of $\text{N}_{222}\text{NO}_3$, respectively, the absolute values of $(x_1 - x_{11})$ should represent the extent of LC in the binary solutions. It can be seen that the absolute values of $(x_1 - x_{11})$ change in the order: $\text{N}_{222}\text{NO}_3/\text{DMSO} > \text{N}_{222}\text{NO}_3/\text{acetone}$, indicating that the LC behavior should be more remarkable in $\text{N}_{222}\text{NO}_3/\text{DMSO}$ systems and be weaker in the $\text{N}_{222}\text{NO}_3/\text{acetone}$ system, which is consistent with the $(x_{11} - x_{21})$ analysis. So far as we know, the effect of the molecular solvents on the network of ILs mainly depends on the solvent dielectric constant [33]; other studies [34] have pointed out that molecular solvents with high dielectric constant have greater impact in disrupting the electrostatic attraction between the ions of the ILs. Accordingly it can be deduced that molecular solvents with higher dielectric constant, like DMSO, can give rise to more conspicuous LC behavior, the so-called structural heterogeneities, in solutions of $\text{N}_{222}\text{NO}_3$ ionic liquid.

In order to demonstrate our results, the physicochemical properties including viscosity and electric conductivity of $\text{N}_{222}\text{NO}_3/\text{DMSO}$ and $\text{N}_{222}\text{NO}_3/\text{acetone}$ have been measured. As shown in Fig. 2, the viscosity η of all solutions decreases greatly with increasing concentration of the molecular solvents. In addition, since the viscosity of acetone is smaller than that of DMSO, the viscosity of $\text{N}_{222}\text{NO}_3/\text{DMSO}$ is larger than that of $\text{N}_{222}\text{NO}_3/\text{acetone}$. However with increasing solvent concentration, the slope of the curve corresponding to the $\text{N}_{222}\text{NO}_3/\text{DMSO}$ system is more negative than that of $\text{N}_{222}\text{NO}_3/\text{acetone}$, especially within the range $0 < x(\text{N}_{222}\text{NO}_3) < 0.6$, indicating that DMSO more efficiently reduces the viscosity of $\text{N}_{222}\text{NO}_3$.

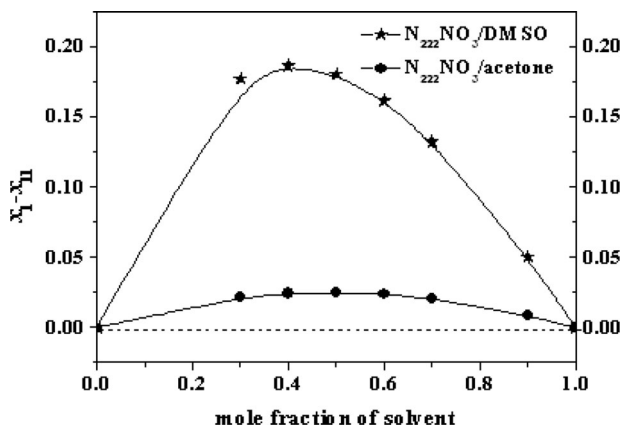


Fig. 5 Concentration-dependent $(x_1 - x_{11})$ for binary solutions of $\text{N}_{222}\text{NO}_3$

In the case of electric conductivity κ shown in Fig. 3, with mole fraction of $N_{222}NO_3$ increasing, κ sharply increases in the molecular solvent-rich region and then progressively became smaller in the $N_{222}NO_3$ -rich region. Also, the maximum value of κ of $N_{222}NO_3$ /DMSO is much larger than in the $N_{222}NO_3$ /acetone system, indicating DMSO molecules more effectively promote the dissociation of $N_{222}NO_3$.

In order to further elucidate this, the solubility of MCC in $N_{222}NO_3$ /DMSO and $N_{222}NO_3$ /acetone at different concentrations were measured. As show in Table 2, with increasing DMSO concentration, the solubility of MCC gradually increases in the $N_{222}NO_3$ /DMSO system. However the solubility of MCC decreases with increasing acetone concentration in the $N_{222}NO_3$ /acetone system. In other words, DMSO is an efficient co-solvent to enhance the ability of $N_{222}NO_3$ to dissolve the MCC. Actually, it has been detected [35] that the dissociation of cellulose in ionic liquids is mainly determined by the hydrogen bonding interactions of hydroxyl protons of cellulose with cations and anions. Therefore it can be deduced that DMSO should more readily break down the network of $N_{222}NO_3$ and promote the dissociation of ionic liquid. Accordingly, the experimental data of viscosity, electric conductivity and MCC solubility demonstrate that DMSO molecules easily interact with $N_{222}NO_3$ ionic liquid, which obviously is consistent with the LC analysis.

4 Conclusions

With the help of the LC model, the correlations of 1H NMR chemical shifts of two systems, $N_{222}NO_3$ /DMSO and $N_{222}NO_3$ /acetone, have been performed. The changes of local mole fractions have revealed that solvents do not mix homogeneously with $N_{222}NO_3$ in the local region. Furthermore, the micro-structure of systems change with the concentration of solutions. Specifically, $N_{222}NO_3$ mainly self-associates with itself in $N_{222}NO_3$ -rich region and a small quantity of solvent does not induce great variations of the original network of $N_{222}NO_3$. Nevertheless, in solvent rich region, $N_{222}NO_3$ chiefly interacts with molecular solvents leaving fewer $N_{222}NO_3$ molecular self-associated. In addition, compared to acetone, DMSO molecules appear more able to insert into the network of $N_{222}NO_3$. In other words, the ability of DMSO to break down the self-associated network of $N_{222}NO_3$ is greater than that of acetone, which is in accordance with the order of their dielectric constants. Consequently, the molecular solvents with higher dielectric constant should lead to more impact on the structure and properties of $N_{222}NO_3$ ionic liquid. Also, the experimental data of viscosity, electrical conductivity and MCC solubility show consistent results with the LC analysis.

Evidently it is interesting and practical to study the local heterogeneity of ILs in solutions which can dramatically affect the properties of ILs/solvent systems. This work offered us a clear insight about the LC behavior in $N_{222}NO_3$ solutions due to addition of solvents. More kinds of molecular solvents will be involved in further studies to verify this simple and convenient approach and final analysis results.

Acknowledgments This work was supported by the National Natural Science Foundation of China (Nos. 21206085 and 21406140).

References

1. Cui, P., Zhao, G.Y., Ren, H.L., Huang, J., Zhang, S.J.: Ionic liquid enhanced alkylation of iso-butane and 1-butene. *Catal. Today* **200**, 30–35 (2013)
2. Lin, H., Bai, P., Guo, X.H.: Ionic liquids for SO₂ capture: development and progress. *Asian J. Chem.* **26**, 2501–2506 (2014)
3. Tang, J.B., Tang, H.D., Sun, W.L., Radosz, M., Shen, Y.Q.: Low-pressure CO₂ sorption in ammonium-based poly(ionic liquid)s. *Polymer* **46**, 12460–12467 (2005)
4. Chen, X.C., Li, F.L., Asumana, C., Yu, G.R.: Extraction of soluble dyes from aqueous solutions with quaternary ammonium-based ionic liquids. *Sep. Purif. Technol.* **106**, 105–109 (2013)
5. Jha, I., Attri, P., Venkatesu, P.: Unexpected effects of the alteration of structure and stability of myoglobin and hemoglobin in ammonium-based ionic liquids. *Phys. Chem. Chem. Phys.* **16**, 5514–5526 (2014)
6. Vasantha, T., Attri, P., Venkatesu, P., Devi, R.S.R.: Ammonium based ionic liquids act as compatible solvents for glycine peptides. *J. Chem. Thermodyn.* **56**, 21–31 (2013)
7. Kohler, S., Liebert, T., Heinze, T.: Ammonium-based cellulose solvents suitable for homogeneous etherification. *Macromol. Biosci.* **9**, 836–841 (2009)
8. Vacek, J., Vrba, J., Zatloukalova, M., Kubala, M.: Electrochemical oxidation of proteins using ionic liquids as solubilizers, adsorption solvents and electrolytes. *Electrochim. Acta* **126**, 31–36 (2014)
9. Grabinska-Sota, E., Dmchowski, A.: Effect of the ammonium-based ionic liquid on the performance of wastewater treatment plant. *Przem. Chem.* **87**, 388–391 (2008)
10. Xu, Y.: Volumetric, viscosity, and electrical conductivity properties of aqueous solutions of two *n*-butylammonium-based protic ionic liquids at several temperatures. *J. Chem. Thermodyn.* **64**, 126–133 (2013)
11. Xu, Y., Yao, J., Wang, C., Li, H.: Density, viscosity, and refractive index properties for the binary mixtures of *n*-butylammonium acetate ionic liquid + alkanols at several temperatures. *J. Chem. Eng. Data* **57**, 298–308 (2012)
12. Jiang, W., Wang, Y., Voth, G.A.: Molecular dynamics simulation of nanostructural organization in ionic liquid/water mixtures. *J. Phys. Chem. B* **111**, 4812–4818 (2007)
13. Schröder, U., Wadhawan, J.D., Compton, R.G., Marken, F., Suarez, P.A., Consorti, C.S., de Souza, R.F., 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.* **24**, 1009–1015 (2000)
14. Ivanov, D.A., Petrov, N.K., Klimchuk, O., Billard, I.: The microheterogeneous structure of ionic liquid mixtures with organic solvent determined by a cyanine-dye fluorescent probe. *Chem. Phys. Lett.* **551**, 111–114 (2012)
15. Sarkar, A., Trivedi, S., Baker, G.A., Pandey, S.: Multiprobe spectroscopic evidence for “hyperpolarity” within 1-butyl-3-methylimidazolium hexafluorophosphate mixtures with tetraethylene glycol. *J. Phys. Chem. B* **112**, 14927–14936 (2008)
16. Russina, O., Triolo, A., Gontrani, L., Caminiti, R.: Mesoscopic structural heterogeneities in room-temperature ionic liquids. *J. Phys. Chem. Lett.* **3**, 27–33 (2012)
17. Xu, Y., Gao, Y., Zhang, L., Yao, Y., Wang, C., Li, H.: Microscopic structures of ionic liquids 1-ethyl-3-methylimidazolium tetrafluoroborate in water probed by the relative chemical shift. *Sci. China Chem.* **53**, 1561–1565 (2010)
18. Rollet, A.L., Porion, P., Vaultier, M., Billard, I., Deschamps, M., Bessada, C., Jouvansal, L.: Anomalous diffusion of water in [BMIM][TFSI] room-temperature ionic liquid. *J. Phys. Chem. B* **111**, 11888–11891 (2007)
19. Deng, D., Li, H., Yao, J., Han, S.: Simple local composition model for ¹H NMR chemical shift of mixtures. *Chem. Phys. Lett.* **376**, 125–129 (2003)
20. Xu, Y., Li, H., Wang, C., Han, S.: Prediction of viscosity of binary system by ¹H NMR and activity coefficient at infinite dilution. *Chem. Eng. Sci.* **60**, 3621–3627 (2005)
21. 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.* **44**, 6883–6887 (2005)
22. 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.* **15**, 97–101 (2007)
23. Zhu, X., Gao, Y., Zhang, L., Li, H.: Prediction among spectra data of ¹H NMR, Raman and IR in aqueous solutions of ionic liquid. *J. Mol. Liq.* **190**, 174–177 (2014)
24. Zhu, X., Wang, Y., Li, H.: The structural organization in aqueous solutions of ionic liquids. *AIChE J.* **55**, 198–205 (2009)

25. Lee, Y., Wu, K.: Conversion and kinetics study of fructose-to-5-hydroxymethylfurfural (HMF) using sulfonic and ionic liquid groups bi-functionalized mesoporous silica nanoparticles as recyclable solid catalysts in DMSO systems. *Phys. Chem. Chem. Phys.* **14**, 13914–13917 (2012)
26. Deng, S., Cheng, J., Guo, X., Jiang, L., Zhang, J.W.: Fiber spinning of polyacrylonitrile grafted soy protein in an ionic liquid/DMSO mixture solvent. *J. Polym. Environ.* **22**, 17–26 (2014)
27. Ruiz, E., Ferro, V.R., Palomar, J., Ortega, J., Rodriguez, J.J.: Interactions of ionic liquids and acetone: thermodynamic properties, quantum-chemical calculations, and NMR analysis. *J. Phys. Chem. B* **117**, 7388–7398 (2013)
28. Xu, Y., Chen, B., Qian, W., Li, H.: Properties of pure *n*-butylammonium nitrate ionic liquid and its binary mixtures of with alcohols at $T = (293.15 \text{ to } 313.15) \text{ K}$. *J. Chem. Thermodyn.* **58**, 449–459 (2013)
29. 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 system. *J. Phys. Chem. B* **109**, 7482–7487 (2005)
30. Wilson, G.M.: Vapor–liquid equilibrium. XI. A new expression for excess free energy of mixing. *J. Am. Chem. Soc.* **86**, 127–130 (1964)
31. Govinda, V., Reddy, P.M., Bahadur, I., Attri, P., Venkatesu, P., Venkateswarlu, P.: Effect of anion variation on the thermophysical properties of triethylammonium based protic ionic liquids with polar solvent. *Thermochim. Acta* **556**, 75–88 (2013)
32. Govinda, V., Reddy, P.M., Attri, P., Venkatesu, P., Venkateswarlu, P.: Influence of anion on thermophysical properties of ionic liquids with polar solvent. *J. Chem. Thermodyn.* **58**, 269–278 (2013)
33. 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* **111**, 6452–6456 (2007)
34. Lopes, J.N.C., Gomes, M.F.C., Husson, P., Padua, A.A.H., Rebelo, L.P.N., Sarraute, S., Tariq, M.: Polarity, viscosity, and ionic conductivity of liquid mixtures containing [C(4)C(1)im][Ntf(2)] and a molecular component. *J. Phys. Chem. B* **115**, 6088–6099 (2011)
35. Zhao, Y., Liu, X., Wang, J., Zhang, S.: Insight into the cosolvent effect of cellulose dissolution in imidazolium-based ionic liquid systems. *J. Phys. Chem. B* **117**, 9042–9049 (2013)