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## Temperature dependent dielectric relaxation of ionic liquid ([bmim][BF<sub>4</sub>])/alcohol binary mixtures

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A dielectric spectroscopy study on the binary mixtures of the ionic liquid (IL) 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF<sub>4</sub>]) and four kinds of alcohols as a function of temperature was carried out over a frequency range of 100 MHz to 20 GHz. A wide-band dielectric relaxation was found at about 1 GHz. The relaxation contains the contributions of the IL and alcohols respectively due to the reorientation of the polar cation bmim<sup>+</sup> and the cooperative dynamics of the alcohol molecules. The ion conduction ability of the IL in the four alcohols indicates that for IL/methanol and IL/ethanol systems, the interactions between solvents and the IL are stronger than those in IL/propanol (or isopropanol) systems, and the two components may not be uniformly mixed, which are also supported by the analysis of activation entropy. We also found that the isopropanol and propanol molecules have more influence on the rotation of the IL and cooperative motion of alcohols. From the temperature-dependent dielectric spectra, the thermodynamic parameters for the relaxation process such as activation energies, Gibbs free energy, enthalpy and entropy were obtained. It was found that the relaxation process observed in this work is driven by entropy.

## 1 Introduction

Room-temperature ionic liquids (ILs) have attracted wide spread attention from both academia and industry in the past few decades<sup>1–3</sup> due to their unique properties such as negligible vapor pressure, nonflammability, and wide electrochemical windows. Ionic liquids can be used as catalysts for many organic reactions.<sup>4–9</sup> Besides, ILs are also often used together with some organic solvents to design binary systems, thus the basic physical and chemistry properties of ILs and the interaction between ILs and organic solvents are of fundamental importance because they determine if the selected ILs can become irreplaceable solvents in some application systems.

In recent years, the properties and interaction of IL binary/ternary mixtures have been studied both from macroscopic<sup>10–14</sup> and microscopic<sup>15–24</sup> points of view *via* various methods. Han *et al.*<sup>25</sup> determined the solubility of ILs in scCO<sub>2</sub>/organic compounds using a flow apparatus, and they found that the solubility is related to the polarity of organic solvents, essentially to the interaction between ILs and the solvent molecules. By means of an automated laser light scattering technique, Rebelo *et al.*<sup>10</sup> showed that the phase equilibria between [C<sub>4</sub>mim][PF<sub>6</sub>] and (water + ethanol) mixtures can be fine-tuned by manipulating the water/ethanol ratio. Brennecke *et al.*<sup>11–13</sup> suggested that the liquid–liquid phase behavior of pyridinium ionic liquids with alcohols is

influenced by the characteristics of the IL. From the microscopic point of view, based on the measured and derived excess molar volume and isentropic compressibilities, Venkatesu *et al.*<sup>15</sup> described the interaction of an IL/*N,N*-dimethylformamide (DMF) system quantitatively. By analyzing the excess molar volume of IL/solvent systems, Wang *et al.*<sup>16</sup> found the ion–dipole interactions between a protic solvent and an imidazolium ring of the ionic liquid. Besides, by means of solvatochromic probes, Pandey *et al.*<sup>21</sup> presented the behavior of different solvatochromic probes dissolved in different compositions of ternary BMIMPF<sub>6</sub> + ethanol + water solutions. Their results showed that it is possible to significantly alter the physicochemical properties of BMIMPF<sub>6</sub> by simply adding appropriate amounts of ethanol and water due to the strong interaction between ethanol and the cation and/or anion. It is explicit that the methods used in above studies are powerful to get the properties and interaction information between ILs and solvents.

Alternatively, dielectric relaxation spectroscopy (DRS), which is sensitive to the polarization processes related to molecular-level dipoles (such as dipole orientation, fluctuations of ion pairs, charge transport, and cooperative motion between a variety of chemical bonds<sup>26–29</sup>), has been increasingly used to detect the interactions and dynamics of ILs and IL/solvent mixtures.<sup>29–31</sup> Besides, DRS is also capable of detecting long- and medium-range interactions between the solvated entities in IL mixtures, such as free ions and ion pairs.<sup>32,33</sup> Over the past decade, the studies on ILs using the DRS method mainly concentrated on pure ILs and IL/solvent mixtures. For example,

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the microstructure transformations of ion pairs of ILs in moderate and low polar solvents were studied by Weingartner *et al.*<sup>33,34</sup> using microwave and terahertz time domain spectroscopy. Buchner *et al.*<sup>35–37</sup> studied many IL mixture systems and various cosolvents using dielectric spectroscopy and found that at low ionic liquid concentrations, the mixtures behave like “normal” electrolyte solutions, while behave more like the typical cooperative dynamics for ILs at higher concentrations.<sup>37–39</sup> Recently, we also studied the micro-structure and interactions of an IL/ethanol (acetone) mixture and a hydrophilic or hydrophobic IL microemulsion.<sup>40,41,42–44</sup> We found that the percolation mode for these IL microemulsions could be identified from the relaxation parameters.

It is no doubt that the above research studies gave valuable results about the interactions between ILs and solvents, and ion association and solvation. Despite this, it can be found that the temperature-dependent dielectric behavior of IL/alcohol mixtures, which can detect the thermal effects of the system and contribute to a better understanding of the solubility and microstructure of ILs in solvents, has not been reported. Therefore, studies on the temperature-dependent dielectric behavior of mixtures that contain ILs are undoubtedly necessary.

To this end, we investigated the dielectric relaxation behaviors of a series of binary mixtures composed of [bmim][BF<sub>4</sub>] and four typical proton-type polar solvents: methanol, ethanol, propanol, and isopropanol with varying temperatures, respectively. In particular, we pay attention to the thermodynamic parameters of the observed relaxation. Moreover, we also expect to acquire information about the interaction between the IL and alcohols, as well as the rotation dynamics of the IL.

## 2 Experiments and methods

### 2.1 Materials

IL [bmim][BF<sub>4</sub>] (purity > 99.2%) used in this work was purchased from Shanghai Cheng Jie Chemical Co. Ltd China. The residual chloride in these products is less than 800 ppm, and the water content is less than 1000 ppm. Methanol, ethanol, propanol and isopropanol with analytical grade were purchased from Beijing Chemical Works, China. The IL/alcohol mixtures with 70% weight fractions of alcohol ( $c_{\text{IL}} \approx 1.166 \text{ mol L}^{-1}$ ) were prepared by dissolving the corresponding amount of alcohol into the IL, which were shaken and kept for 24 h prior to dielectric measurements.

### 2.2 Dielectric measurements

Dielectric measurements were carried out in the frequency range from 100 MHz to 20 GHz using an Agilent E8362B PNA series network analyzer (Agilent Technologies, America) equipped with an Agilent 85070E open-ended coaxial probe (Agilent Technologies, America). The permittivity  $\epsilon'$  and dielectric loss  $\epsilon''$  were automatically calculated as functions of frequency using the built-in software of this measuring system, which was calibrated in accordance with the procedures recommended by the manufacturers. The temperature was controlled using a circulation thermostat. The measurements

for the temperature dependence of these mixtures with 70% weight fractions of alcohol were performed at temperature points with an accuracy of 0.1 °C from 25 to 60 °C with an interval of 5 °C. The temperature was controlled using a circulation thermostat. The selection of 70% concentration for variable temperature measurements is because that in this mass fraction the dielectric loss peaks were obvious, which is beneficial for analysis according to our previous results.<sup>40</sup>

### 2.3 Analysis of dielectric data

The complex permittivity  $\epsilon^*$  of the IL/alcohol mixtures can be expressed as

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\frac{\kappa(\omega)}{\epsilon_0\omega} = \epsilon'(\omega) - j\epsilon''(\omega) - j\frac{\kappa_1}{\epsilon_0\omega} \quad (1)$$

where  $\omega (=2\pi f)$ ,  $f$  is the measurement frequency) is the angular frequency,  $\epsilon_0$  is the permittivity of vacuum,  $\kappa(\omega)$  is the conductivity, and  $\kappa_1$  is the low-frequency limit of conductivity (dc conductivity).  $\kappa(\omega)/\epsilon_0\omega$  is the total dielectric loss, which includes two parts, namely,  $\epsilon''(\omega)$  and dc conductivity contribution  $\epsilon_{\text{dc}}''$  which can be expressed as  $\epsilon_{\text{dc}}'' = \kappa_1/\epsilon_0\omega$ .<sup>45</sup> For the systems with higher conductivity like the samples in this work,  $\epsilon_{\text{dc}}''$  cannot be neglected. Thus  $\kappa_1$  can be calculated from the scaling dependence of the total dielectric loss with a slope of  $-1$  on  $\omega$ . Finally, all of the dielectric loss data were obtained from the conductivity spectra through the equation  $\epsilon''(\omega) = (\kappa(\omega) - \kappa_1)/\epsilon_0\omega$ .

To quantitatively analyze the complex dielectric permittivity, Havriliak–Negami functions were employed to fit the dielectric spectra:<sup>46</sup>

$$\epsilon^*(\omega) = \epsilon'(\omega) - j\epsilon''(\omega) = \epsilon_h + \sum_i \frac{\Delta\epsilon_i}{[1 + (j\omega\tau_i)^{\beta_i}]^{\alpha_i}} \quad (2)$$

where  $\epsilon_h$  is the high-frequency limit of permittivity,  $\Delta\epsilon_i$  is the relaxation intensity,  $\tau_i (=1/2\pi f_0)$  is the relaxation time,  $f_0$  is the characteristic frequency, and  $\beta$  ( $0 < \beta \leq 1$ ) and  $\alpha$  ( $0 < \alpha \leq 1$ ) are the parameters describing the shape of the curve.  $i$  is the number of the dielectric relaxation occurring in the system.

## 3 Results and discussion

### 3.1 Temperature dependent dielectric spectroscopy and relaxation mechanism

Fig. 1 shows the frequency dependence of the dielectric loss (after subtracting dc conductivity) for the binary mixtures of (a) [bmim][BF<sub>4</sub>]/methanol, (b) [bmim][BF<sub>4</sub>]/ethanol, (c) [bmim][BF<sub>4</sub>]/propanol, and (d) [bmim][BF<sub>4</sub>]/isopropanol at different temperatures. The insets of Fig. 1 are the corresponding three-dimensional representations. From these figures, one obvious dielectric relaxation with widespread distribution can be observed at about  $10^9$ – $10^{10}$  Hz. The relaxation intensity decreases and the relaxation frequency shifts to higher frequencies with the increase of the temperature as indicated by the arrows.

According to the literature, a major relaxation caused by cations of the ionic liquid will appear in a frequency range of 1–10 GHz,<sup>26,47,48</sup> and the relaxations ascribed to methanol,

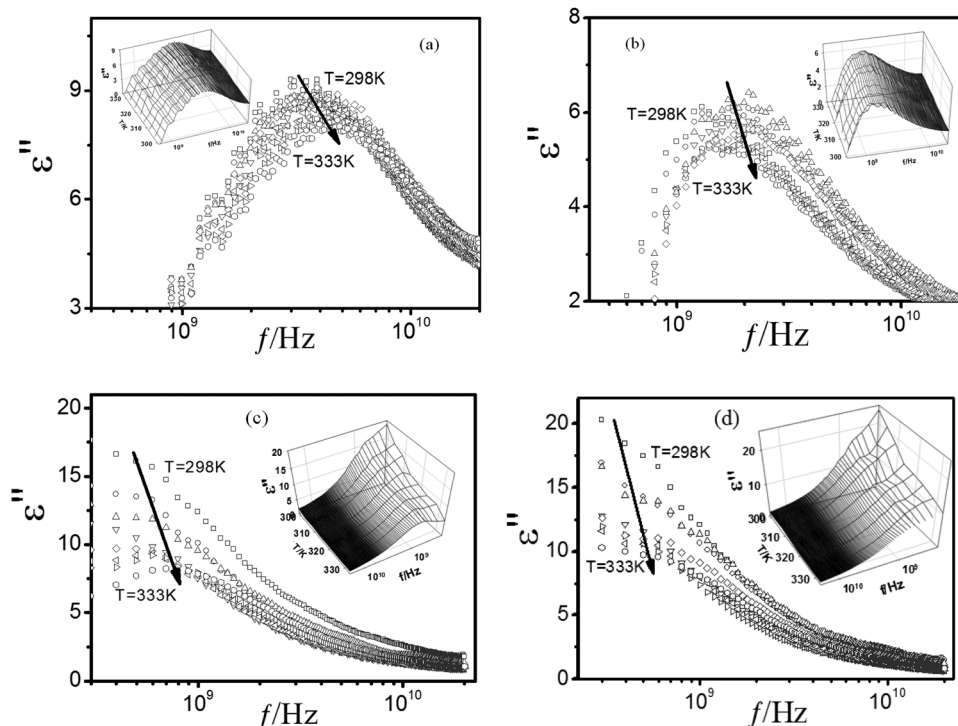


Fig. 1 Dielectric loss as a function of frequency for the binary mixtures of [bmim][BF<sub>4</sub>] with (a) methanol, (b) ethanol, (c) propanol, and (d) isopropanol. The insert shows the corresponding 3D plot as functions of frequency and temperature. The arrow indicates the relaxation frequency.

ethanol, propanol and isopropanol molecules are at about 4 GHz, 1 GHz, 500 MHz, and 400 MHz,<sup>49</sup> respectively. That is to say, the relaxation located about 10<sup>9</sup>–10<sup>10</sup> Hz is the superimpose result of the contributions of ILs and alcohols. The contribution of ILs can be ascribed to the reorientation of the dipolar cations bmim<sup>+</sup>, and the cooperative dynamics of the H-bond in alcohols also contributed to the relaxation, as illustrated in the insets of Fig. 2 and Fig. 4. The relaxation parameters were obtained by fitting Havriliak–Negami eqn (3) (where  $i = 1$ ,  $\beta = 1$  and  $0 < \alpha \leq 1$ ) to the dielectric spectra, and a typical fitting curve at 338 K for the [bmim][BF<sub>4</sub>]/methanol mixture is shown in Fig. 2. The low-frequency limit of conductivity  $\kappa_1$ , the relaxation time  $\tau$  and the molar conductivity  $A_{[\text{bmim}][\text{BF}_4]} (= \kappa_1 / c_{\text{IL}})$  of the four systems are listed in Table 1.

### 3.2 Interaction and rotation dynamics

To examine the dielectric spectra in detail, the relaxation time  $\tau$  and dc-conductivity  $\kappa_1$  are plotted against temperature, respectively, in Fig. 3(a) and (b). It can be seen from Fig. 3a that  $\tau$  declines with increasing temperature. This shows that the H-bond cooperative motion of alcohol is accelerated as the temperature rises. Such an orientation of dipole moments can keep up with the change of the electric field, as a result, the relaxation frequency shifts to a higher frequency, and accordingly the relaxation time decreases. The Stokes–Einstein–Debye equation<sup>50</sup> allows one to estimate the relationship between the relaxation time, the volume of the rotating unit and viscosity,

$$\tau = \frac{3V\eta}{k_{\text{B}}T} \quad (3)$$

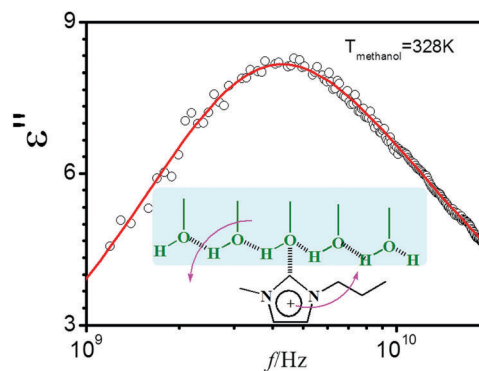


Fig. 2 Typical dielectric spectra extracted from Fig. 1 for [bmim][BF<sub>4</sub>]/methanol mixture ( $T_{\text{methanol}} = 328$  K). The solid line is the best-fit curve calculated from eqn (2). The inset represents the cooperative interaction of methanol and the cation of ionic liquid.

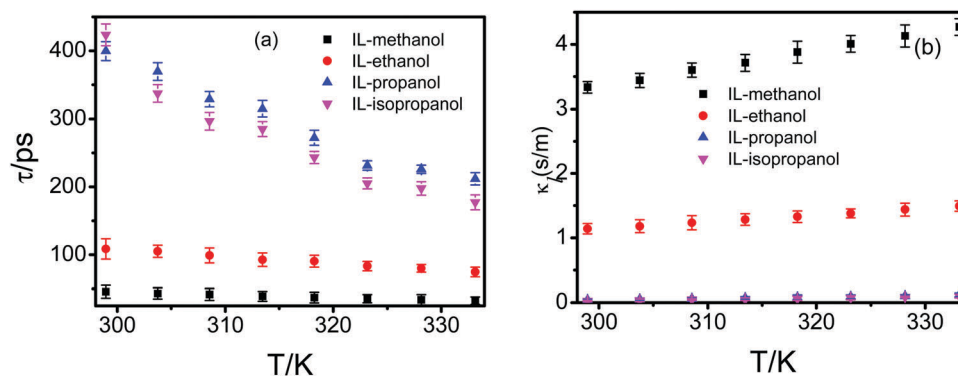
where  $\eta$  is the viscosity of the sample and  $V$  is the volume of the rotating unit as indicated in Fig. 4.  $k$  is the Boltzmann constant and  $T$  is temperature in K. From this equation, it is known that the relaxation time is proportional to the volume of the rotating groups and the viscosity of the system. The relaxation times of the four binary systems follow the order: methanol < ethanol < isopropanol  $\approx$  propanol. This is because increasing the carbon chain of alcohols will lead to an increase in the volume of the rotating units, accordingly, it will take longer to complete the reorientation, and  $\tau$  successively increases from methanol to propanol at the same concentration. The volumes of propanol and isopropanol are similar,<sup>51</sup> hence their relaxation times are

**Table 1** Relaxation time  $\tau$ , dc-conductivity  $\kappa_1$  and molar conductivity  $\Lambda_{[\text{bmim}][\text{BF}_4]}$  for the mixtures of IL and alcohol with varying temperatures at  $W_{\text{alcohol}} = 70\%$ 

T/K	$\tau/\text{ps}$	$\kappa_1$ (S m <sup>-1</sup> )		$\tau/\text{ps}$	$\kappa_1$ (S m <sup>-1</sup> )	
		Methanol	$\Lambda_{[\text{bmim}][\text{BF}_4]}$ ([S cm <sup>2</sup> mol <sup>-1</sup> ])		Ethanol	$\Lambda_{[\text{bmim}][\text{BF}_4]}$ ([S cm <sup>2</sup> mol <sup>-1</sup> ])
298	45.7 ± 9.5	3.33 ± 0.09	28.6 ± 0.8	108 ± 15	1.14 ± 0.08	9.83 ± 0.67
303	43.2 ± 8.2	3.44 ± 0.11	29.6 ± 0.9	105 ± 9	1.18 ± 0.10	10.2 ± 0.9
308	41.8 ± 8.7	3.60 ± 0.11	30.9 ± 0.9	99.0 ± 11.0	1.23 ± 0.11	10.6 ± 0.9
313	39.0 ± 7.3	3.71 ± 0.13	31.9 ± 1.1	92.6 ± 9.9	1.28 ± 0.09	11.1 ± 0.8
318	37.2 ± 7.9	3.88 ± 0.17	33.3 ± 1.5	90.5 ± 8.7	1.33 ± 0.09	11.4 ± 0.8
323	35.6 ± 6.1	4.01 ± 0.13	34.4 ± 1.1	83.3 ± 6.9	1.38 ± 0.07	11.9 ± 0.6
328	34.0 ± 7.6	4.13 ± 0.17	35.5 ± 1.5	79.9 ± 5.6	1.44 ± 0.10	12.4 ± 0.9
333	32.6 ± 5.4	4.27 ± 0.13	36.7 ± 1.1	74.6 ± 7.2	1.49 ± 0.08	12.9 ± 0.7

T/K	$\tau/\text{ps}$	$\kappa_1$ (S m <sup>-1</sup> )		$\tau/\text{ps}$	$\kappa_1$ (S m <sup>-1</sup> )	
		Propanol	$\Lambda_{[\text{bmim}][\text{BF}_4]}$ ([S cm <sup>2</sup> mol <sup>-1</sup> ])		Isopropanol	$\Lambda_{[\text{bmim}][\text{BF}_4]}$ ([S cm <sup>2</sup> mol <sup>-1</sup> ])
298	400 ± 14	0.04 ± 0.01	0.34 ± 0.09	424 ± 16	0.03 ± 0.01	0.22 ± 0.09
303	369 ± 13	0.05 ± 0.02	0.42 ± 0.17	337 ± 13	0.04 ± 0.01	0.30 ± 0.09
308	329 ± 11	0.06 ± 0.01	0.51 ± 0.09	297 ± 13	0.05 ± 0.01	0.41 ± 0.09
313	315 ± 12	0.07 ± 0.02	0.59 ± 0.17	285 ± 11	0.06 ± 0.02	0.46 ± 0.17
318	272 ± 11	0.08 ± 0.03	0.68 ± 0.25	243 ± 9	0.07 ± 0.03	0.55 ± 0.25
323	231 ± 7	0.09 ± 0.03	0.76 ± 0.25	205 ± 8	0.08 ± 0.03	0.66 ± 0.25
328	226 ± 6	0.10 ± 0.02	0.85 ± 0.17	198 ± 10	0.09 ± 0.01	0.76 ± 0.09
333	212 ± 9	0.12 ± 0.03	1.02 ± 0.25	177 ± 11	0.10 ± 0.03	0.87 ± 0.25

**Fig. 3** The dependences of relaxation time  $\tau$  (a) and dc-conductivity  $\kappa_1$  (b) for the mixtures of IL and alcohol on the temperature at  $W_{\text{alcohol}} = 70\%$ .

nearly equal at the same  $W_{\text{alcohol}}$ . In addition, the viscous drag of the mixture medium will also impede the reorientation of the dipole and increase the relaxation time as reported in the literature;<sup>52</sup> from methanol to propanol, the viscosity of the alcohols increases orderly, this is another reason that their relaxation times were extended in turn. For the mutual isomers propanol and isopropanol, their dipole moment and viscosity are closer to each other,<sup>51,52</sup> therefore, the relaxation times of propanol and isopropanol are nearly the same. Besides, for methanol and ethanol systems, the decrease in relaxation time is far less than those of isopropanol and propanol. This can be considered from the microstructure of the system. Because the methanol and ethanol molecules are relatively smaller and have less effect on the rotation of the IL and cooperative hydrogen bond, the energy required for the relaxation is smaller and the decrease in relaxation time with increasing temperature is less. While the isopropanol and propanol molecules are relatively larger and have obvious effect on the rotation of the IL and

cooperative hydrogen bond, so the energy required for the relaxation is much larger and the decrease in relaxation time with increasing temperature is evident.

Moreover, it is worth noting that the  $\kappa_1$  values (Fig. 3b) of the four systems gradually increased with increasing temperature. This shows that the thermal motion of the cation and anion of ILs is accelerated as the temperature rises.  $\kappa_1$  reflects the conduction ability of the solvated IL, therefore, the conductivity of the ionic liquid is affected by the interaction between the solvent molecules and the IL. The order of the ion conduction ability of IL in the four kinds of alcoholic solvents is methanol > ethanol > propanol  $\approx$  isopropanol. This may indicate that for IL/methanol and IL/ethanol systems, the interaction between solvents and IL are stronger and the two components are not uniformly mixed, *i.e.* the obstacles of these two solvents on ion movement are relatively smaller, thus the conductivity is greater. While for IL/propanol and IL/isopropanol systems, the interaction between solvents and IL may be weaker and the two

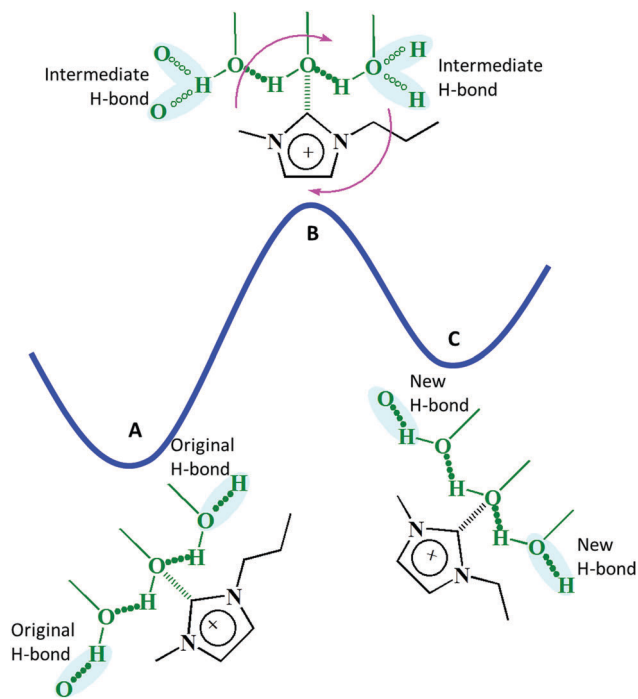


Fig. 4 Sketch of a potential energy barrier separating two states (A and C) of the solvated IL by taking methanol as a typical solvent molecule. State B is an intermediate state.

components may be uniformly mixed, so the ion conduction of the two mixed systems was greatly affected by the propanol and isopropanol solvents, accordingly, the conductivity of the two systems is smaller.

### 3.3 Thermodynamic analysis

The relaxation of IL/alcohol systems is essentially the transition between different dipole orientations: state A to state B crossing an intermediate state C, as sketched in Fig. 4. At a given time, the direction of rotation of the IL/alcohol system is in state A, while with the application of an external electric field, the solvated IL rotates in another direction denoted by C across an intermediate state B. Hence, different dipole orientations are separated by a potential energy barrier. Dielectric relaxation time ( $\tau$ ) and ionic conductivity ( $\kappa$ ) are all directly related to their

energy changes. Both these phenomena are thermally activated processes and, in most cases, follow the Arrhenius law as<sup>53</sup>

$$\ln \tau = \ln \tau_0 + \frac{E_a}{RT} \quad (4a)$$

$$\ln \kappa = \ln \kappa_0 - \frac{E_a'}{kT} \quad (4b)$$

where,  $\tau_0$  and  $\kappa_0$  are pre-exponential factors and  $E_a$  and  $E_a'$  are the activation energies, respectively, for dielectric relaxation and conductivity.  $R$  is a gas constant. The values of  $E_a$  and  $E_a'$  calculated by eqn (4a) and (4b) respectively from the plots of  $\ln \tau$  versus  $1/T$  and  $\ln \kappa$  versus  $1/T$  shown in Fig. 5(a) and (b) are summarized in Table 2.

As can be seen from Table 2, from methanol to isopropanol, both the values of  $E_a$  and  $E_a'$  increase successively. However, these values are smaller than those observed for the cooperative relaxation processes of strongly H-bonded liquids such as water, MeOH, EtOH, 1-PrOH and 1-BuOH, for which  $E_a = 15.9$ ,<sup>54</sup> 13.0,<sup>33</sup> 19.9,<sup>33</sup> 26.0<sup>33</sup> and 28.6 kJ mol<sup>-1</sup>,<sup>33</sup> respectively. This again suggests that the relaxation process is closely related to the orientation of the dipolar cation as well as the cooperative motions of the alcohol molecules as indicated in Fig. 2 and 4. For IL/methanol and IL/ethanol systems, the values of  $E_a$  and  $E_a'$  are much less than those of propanol and isopropanol, this is partially due to the smaller rotation volume for methanol and ethanol molecules. Besides, it may also indicate that the two alcohols are not uniformly mixed with ILs, therefore the reorientation of the cation of ILs and the cooperative dynamics of H-bonding became freer. As a result, the energy required to complete the relaxation process is smaller. While for IL/propanol and IL/isopropanol systems, the larger values of these activation energies probably reflect an unusually large energetic barrier to the rotation polarization of alcohol molecules. This also indicates that both propanol and isopropanol are uniformly mixed with ILs.

The temperature dependence of  $\tau$  follows an Eyring-type<sup>55</sup> behavior of an activated jump mechanism:<sup>56</sup>

$$\tau = \frac{h}{kT} \exp \left[ \frac{\Delta G}{RT} \right] \quad (5a)$$

where  $h$  denotes the Planck constant. Because the Gibbs free energy of activation  $\Delta G$  has a correlation with the activation

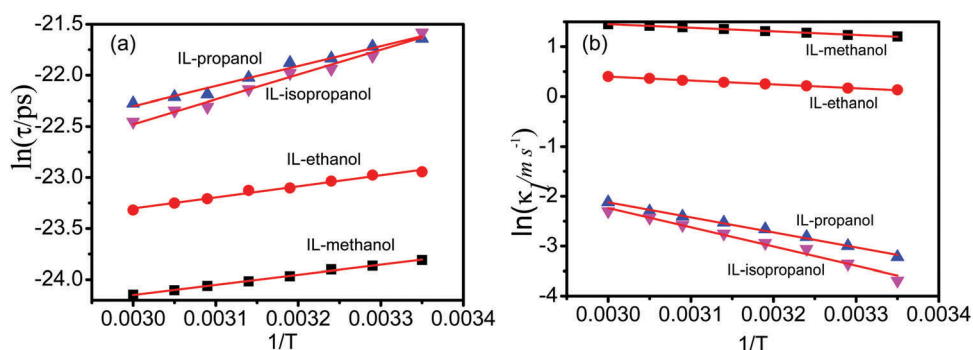


Fig. 5 Temperature dependences of  $\ln \tau$  (a) and  $\ln \kappa$  (b). The lines represent fits according to eqn (4a) and (4b).

**Table 2** Thermodynamic parameters,  $E_a'$  (in eV) and  $E_a$  (in  $\text{kJ mol}^{-1}$ ), calculated by Arrhenius law,  $\Delta G$ ,  $\Delta S$ ,  $\Delta H$  and  $\Delta H'$  calculated by the Eyring equation

	Methanol	Ethanol	Propanol	Isopropanol
$E_a'/\text{eV}$	0.063	0.068	0.26	0.335
$(E_a'/\text{kJ mol}^{-1})$	(6.068)	(6.55)	(25.3)	(32.3)
$E_a/\text{kJ mol}^{-1}$	8.26	9.12	16.36	20.30
$\Delta H/\text{kJ mol}^{-1}$	5.64	6.50	13.7	17.68
$\Delta S/\text{J mol}^{-1} \text{K}^{-1}$	-28.113	-26.45	-19.15	-5.86
$\Delta G/\text{kJ mol}^{-1}$	14.04	14.53	19.47	19.43
$\Delta H'/\text{kJ mol}^{-1}$	5.36	5.80	24.58	31.57

<sup>a</sup> Energy in  $\text{kJ mol}^{-1}$ , converted from eV.

enthalpy  $\Delta H$  and the corresponding activation entropy  $\Delta S$ :  $\Delta G = \Delta H - T\Delta S$ , eqn (5a) can be rewritten as:

$$\ln(\tau T) = \ln\left(\frac{h}{k}\right) - \frac{\Delta S}{R} + \frac{\Delta H}{RT} \quad (5b)$$

When we plot  $\ln(\tau T)$  against  $1/T$  according to eqn (5b), linear relationships between  $\ln(\tau T)$  and  $1/T$  for four systems are expected and the results are shown in Fig. 6(a). The values of  $\Delta S$  and  $\Delta H$  were obtained from the intercept and slope of these lines, along with  $\Delta G$ , and are also summarized in Table 2. Moreover, the temperature dependence of the molar conductivity yields Eyring's enthalpy of activation  $\Delta H'$ <sup>57</sup> required for charge transport:

$$\ln \Lambda + \frac{2}{3} \ln d_s = -\frac{\Delta H'}{RT} + B \quad (6)$$

where  $d_s$  is the density of the solvent and  $B$  is a constant. Likewise, we plot  $\ln \Lambda + \frac{2}{3} \ln d_s$  against  $1/T$  as shown in Fig. 6(b).  $\Delta H'$  values obtained from the slopes of these lines are also listed in Table 2.

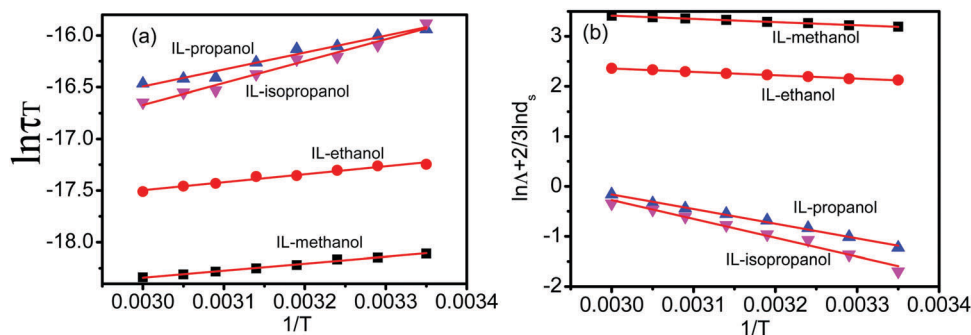
It is found from Table 2 that the activation entropy  $\Delta S$  values of the four systems are all negative, that is to say, the directional movement of relaxation species under an applied electric field makes the systems more orderly. In addition, from methanol to isopropanol, the absolute values of  $\Delta S$  decrease successively. Note that for IL/methanol and IL/ethanol systems, the absolute values of  $\Delta S$  are larger, showing that the systems are more disordered and confirmed that the IL and alcohols are not uniformly mixed as mentioned above, while for IL/propanol and IL/isopropanol systems, the  $\Delta S$  values are relatively smaller because of uniform mixing of the two components.

According to the principle of thermodynamics, the equilibrium state of a thermodynamic system is decided by the Gibbs free energy of activation  $\Delta G$ . In this work, from methanol to isopropanol, the values of  $\Delta G$  gradually increase, and the values for propanol and isopropanol are approximate, being consistent with the change in the microstructure of systems. For propanol and isopropanol, although their  $\Delta S$  values are different, their  $\Delta G$  values are nearly the same. This suggests that the entropy change of the mixed systems plays a dominant role in deciding the total energy, and the structure variation and corresponding relaxation behavior of the systems are driven mainly by entropy.

## 4 Conclusions

Dielectric spectra of four [bmim][BF<sub>4</sub>]/alcohol mixtures with varying temperatures were studied systematically over a frequency range from 100 MHz to 20 GHz. The present study involves the thermodynamics of the relaxation processes. The relaxation was interpreted well by the reorientation of the polar cation bmim<sup>+</sup> and cooperative dynamics of the H-bond of alcohol. Due to the interaction between IL and alcohol, the relaxation parameters were obtained by fitting an HN equation to the experimental dielectric data. The temperature-dependent dielectric spectra, in particular, the thermokinetic energies of the dielectric relaxation and ion conduction process, were discussed in detail. We found that isopropanol and propanol molecules have more influence on the rotation of IL and cooperative motion of alcohols. The ion conduction ability of the IL in different alcohols indicates that the interaction between IL and methanol (or ethanol) is stronger than that between IL and propanol (or isopropanol). It was also found that the systems would become more disordered with increasing chain length of alcohol molecules. This was supported by the analysis of activation entropy. Besides, we also found that the relaxation process was mainly driven by entropy.

This study provides some valuable guidance or inspiration for future research involving fundamental physical and chemical properties (internal energy, activation enthalpy and activation entropy) of ionic liquid mixing systems, in particular, in protic solvents. Moreover, it is worth noting that the hydrogen bond mediated association of the IL with other chemical species will also vary with the counter anion and thus affect the application of the IL, such as the catalytic efficiency reported by Chakraborti.<sup>4-9</sup>



**Fig. 6** Plots of  $\ln(\tau T)$  (a) and  $\ln \Lambda + \frac{2}{3} \ln d_s$  (b) against  $1/T$ . The lines represent fits according to eqn (5b) and (6).

Therefore, to analyse the credibility of an IL in chemical applications, more research about the anionic part of the IL is necessary.

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