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# Non-Ideal Mixing Behaviour of Hydrogen Bonding in Mixtures of Protic Ionic Liquids

Koichi Fumino,<sup>[a]</sup> Anne-Marie Bonsa,<sup>[a]</sup> Benjamin Golub,<sup>[a]</sup> Dietmar Paschek,<sup>[a, b]</sup> and Ralf Ludwig<sup>\*[a, b]</sup>

Ionic liquids (ILs) attract interest in science and technology as a result of their unique properties. Binary and ternary mixtures of ILs significantly increase the number of possible cation/anion combinations, resulting in targeted physical and chemical properties. In this work, we study the mixing behaviour of two protic ILs: triethyl ammonium methylsulfonate [Et<sub>3</sub>NH][CH<sub>3</sub>SO<sub>3</sub>] and triethylammonium triflate [Et<sub>3</sub>NH][CF<sub>3</sub>SO<sub>3</sub>]. We find a characteristic deviation from ideal mixing by means of low-frequency infrared spectroscopy. By using molecular dynamics simulations, we explain this behaviour as being the result of different strengths of anion/cation hydrogen bonding. This non-ideality of non-random H-bond mixing is also reflected in macroscopic properties such as the viscosity. Mixing suitable ILs may, thus, result in new ILs with targeted physical properties.

Since the beginning of this century, ionic liquids (ILs) have been receiving increasing interest from science and technology.<sup>[1–4]</sup> To expand the ability of designing ILs by selection of cations and anions, binary and ternary mixtures of these coulombic fluids came into the focus of research.<sup>[5,6]</sup> The subtle balance between Coulomb forces, hydrogen bonds and dispersion forces determines the interaction between the constituents of an IL and may result in targeted physical and chemical properties. The mixing behaviour of ILs has been reported for a number of thermodynamic and transport properties of mainly aprotic ILs.<sup>[5–11]</sup> Physical properties such as the density and viscosity have been found to show near-ideal mixing behaviour and, therefore, vary almost linearly with the composition. Also, molar enthalpies and entropies of mixing indicated only a small deviation from ideality.<sup>[8,9]</sup> Subtle deviations from ideal mixing behaviour for ILs were recently reported from spectroscopy studies. Quitevis and co-workers analysed optical Kerr effect (OKE) spectra for mixtures of ILs and found different behaviour for diverse mixtures.<sup>[11]</sup> The OKE spectra result from intermolecular vibrational modes and resemble Raman spectra.


For the 1:1 mixture of [C<sub>5</sub>C<sub>1</sub>mim][PF<sub>6</sub>]/[C<sub>5</sub>C<sub>1</sub>mim][CF<sub>3</sub>CO<sub>2</sub>], non-additivity was reported. The authors assumed new interactions between the mixed species, which are not present in the pure components. However, the phenomena of mixing could not be explained precisely in any of the given studies on the basis of interactions between the charged constituents. Thus, a molecular understanding of the structural and dynamical features of IL mixtures is still lacking. Recently, IL–IL mixtures received additional interest. Welton and co-workers reviewed the ideality and non-ideality of IL–IL mixtures with a focus on property changes and new opportunities for applications.<sup>[6,7]</sup> Despite instances of non-ideal behaviour, these are still regarded as simple mixtures of two compounds. In contrast, Rogers et al. argued that IL compositions do not retain their individual nature and supported the concept of double-salt ILs (DSILs).<sup>[5]</sup> DSILs are defined as ILs containing more than one cation or anion and presenting different physicochemical properties than that of the single ILs.

It is the purpose of this communication to understand the mixing behaviour of ILs at a molecular level. For a well-chosen binary mixture of protic ILs (PILs), we show that non-ideality can be explained by changing interaction strength between particular ions. In PILs, this interaction is considerably governed by hydrogen bonding. This goal could be achieved by using a combination of experimental and theoretical methods that provide detailed information for hydrogen-bonding characteristics upon mixing. Far-infrared (FIR) spectroscopy and molecular dynamics (MD) simulations allow molecular insight for the interaction characteristics in binary mixtures of PILs. At the end, we show that the non-ideal H-bond mixing behaviour in PIL–PIL mixtures is reflected in physical properties such as viscosity. Moreover, it can be used to accelerate or slow down anions for supporting or suppressing solvation and reaction.

Recently, we could show for pure PILs of [Et<sub>3</sub>NH][anion] type that the <sup>+</sup>N–H···A<sup>−</sup> interaction results in a distinct low vibrational band observed in FIR or THz spectra. This spectral feature could be related to hydrogen bonding and was observed in the frequency range from 100 to 180 cm<sup>−1</sup>, depending on the interaction strength of the anion. For [Et<sub>3</sub>NH][CH<sub>3</sub>SO<sub>3</sub>] (TEAMS) and [Et<sub>3</sub>NH][CF<sub>3</sub>SO<sub>3</sub>] (TEATF) PILs, these characteristic vibrational bands were observed at 149 and 129 cm<sup>−1</sup>, respectively.<sup>[12–15]</sup> Owing to the inductive effect of the fluorine atoms within the anion, the cation–anion interaction is significantly lowered indicated by a 20 cm<sup>−1</sup> shift to lower wavenumbers for TEATF.<sup>[13]</sup> The location and absorbance of this vibrational band is sensitive for the interaction strength between the PIL constituents. But, what happens if these two PILs are mixed?

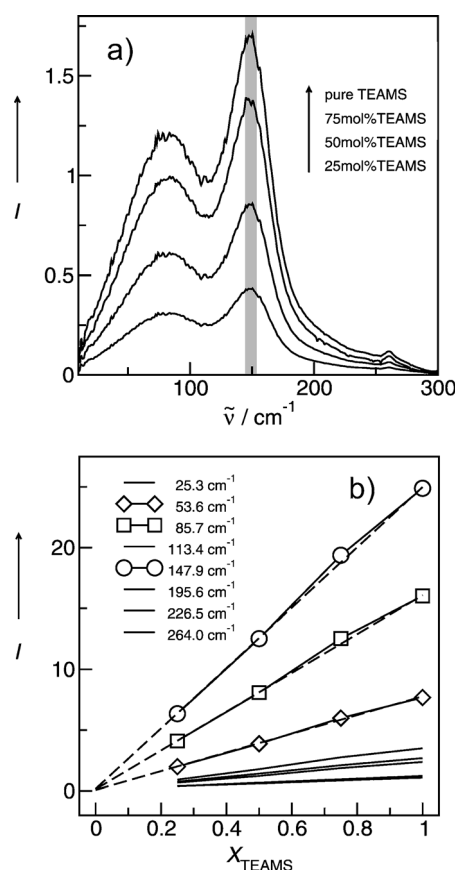
[a] Dr. K. Fumino, A.-M. Bonsa, B. Golub, Dr. D. Paschek, Prof. Dr. R. Ludwig  
Universität Rostock, Institut für Chemie  
Abteilung für Physikalische Chemie  
Dr.-Lorenz-Weg 1, 18059, Rostock (Germany)  
Tel.: (+49) 381-498-6517  
E-mail: ralf.ludwig@uni-rostock.de

[b] Dr. D. Paschek, Prof. Dr. R. Ludwig  
Leibniz-Institut für Katalyse  
an der Universität Rostock e.V.  
Albert-Einstein-Str. 29a, 18059 Rostock (Germany)

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Do both PILs retain their H-bond characteristics from the pure states? Is the H-bond mixing ideal? If not, can the non-ideal behaviour be detected experimentally? Can we draw some conclusion for the number and strength of H-bonding in these PIL mixtures? Is there a way to control the H-bond characteristics for assorted mixtures? And finally, is there any influence on macroscopic properties such as viscosity? All these issues are addressed in the present study.

Firstly, we would like to discuss the FIR spectra of pure TEAMS as well as its mixtures with a hydrophobic organic solvent: deuterated chloroform,  $\text{CDCl}_3$ . In Figures 1 a and 1 b, it is

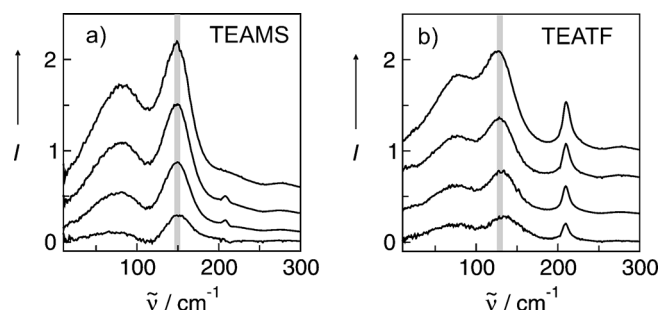


**Figure 1.** FIR spectra of TEAMS in mixtures with chloroform ( $\text{CDCl}_3$ ). a) The intensity of the targeting vibrational band at  $149\text{ cm}^{-1}$  decreases with increasing concentration of the solvent. b) The intensities of the deconvoluted vibrational bands decrease linearly and go through zero, indicating that the H-bond characteristics remain upon dilution in the hydrophobic environment.

shown that the absorbance of the distinct vibrational band at  $149\text{ cm}^{-1}$  decreases continuously with increasing solvent concentration. If we plot the intensities of the vibrational bands versus the composition, a straight line is obtained, starting with the pure PIL absorbance and ending at zero for zero PIL concentration. This is what we would expect from an ideal mixture of TEAMS with the organic solvent. A similar behaviour is also observed for TEATF in mixtures with chloroform (see SI1–2 in the Supporting Information). Apparently, the H-bond characteristics of the pure PILs are preserved when diluting

them with  $\text{CDCl}_3$ . This finding is in agreement with earlier results on ion speciation.<sup>[14–16]</sup> For both PILs, the apolar solvent molecule was not able to penetrate between the cation and anion, leaving the PIL bonding characteristics untouched. Obviously, the intensities of selected vibrational bands can be used as a probe for measuring molecular interactions in particular hydrogen bonding in solution.

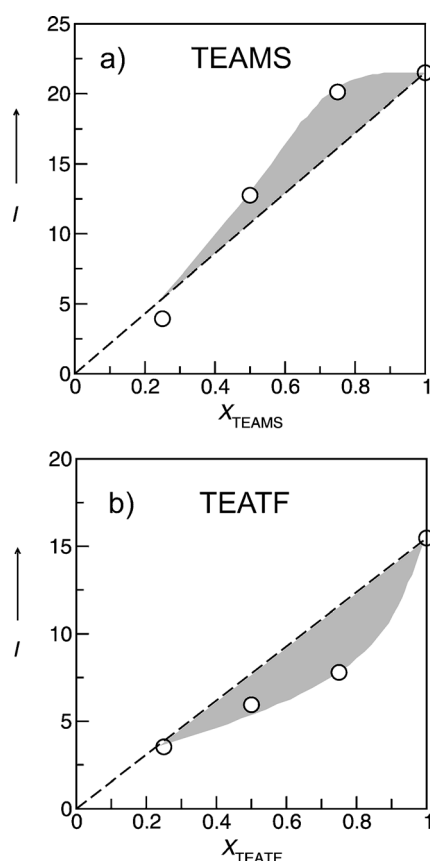
Secondly, we prepared molar mixtures of TEAMS and TEATF with  $x=0.75$ ,  $0.50$  and  $0.25$  mole fraction. Following the nomenclature suggested by Niedermeyer et al.,<sup>[6]</sup> we mixed two pure PILs, each describing one component including two constituents, resulting in two component mixtures  $[\text{Et}_3\text{NH}][\text{CH}_3\text{SO}_3]_x[\text{CF}_3\text{SO}_3]_{(1-x)}$  comprising three constituents. Then, we measured the FIR spectra between  $10$  and  $300\text{ cm}^{-1}$ . We obtained the mixture spectra for TEAMS and TEATF by subtracting the corresponding mole fraction of TEATF in the first and TEAMS in the latter case of the related spectra of the pure materials (see Figures 2 a and 2 b). As the background spectra, as



**Figure 2.** a) FIR spectra of the pure TEAMS and the difference spectra of the TEAMS/TEATF mixtures measured versus TEATF. b) FIR spectra of the pure TEATF and the difference spectra of the TEATF/TEAMS mixtures measured versus TEAMS. The vibrational bands at  $149$  and  $129\text{ cm}^{-1}$  indicate the  $^+\text{N}-\text{H}\cdots\text{A}^-$  cation–anion interaction. The intensities of these vibrational bands are used to study the mixing behaviour.

well as the sample spectra, are referred to the absorption of the pure PILs in the filled IR cell, the mole-fraction-weighted results had to be corrected for the different molar volumes of TEAMS and TEATF, respectively. The deconvoluted spectra are shown in SI3–5 in the Supporting Information.

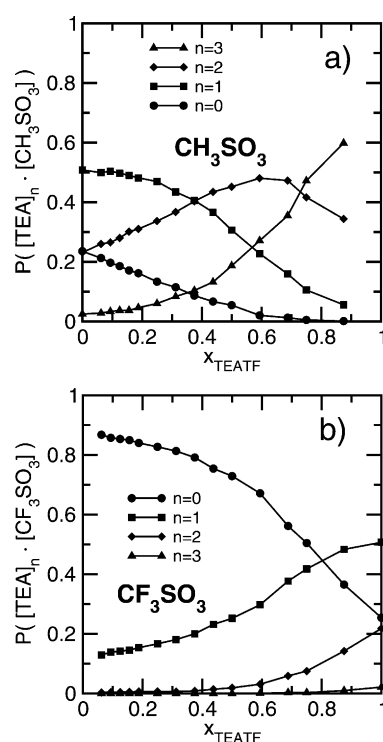
If we now plot the corrected absorbance of the distinct vibrational band  $^+\text{N}-\text{H}\cdots\text{A}^-$  against the mole fraction, we find characteristic deviations from linear, and thus ideal, mixing behaviour, as shown in Figures 3 a and 3 b. For TEATF, including the weaker interacting triflate anion, we observe lower intensities than expected for ideal random mixing (Figure 3 b). Apparently, the triflate anion forms fewer H-bonds with the triethylammonium cation in the mixtures compared to the situation in the pure PIL. It is plausible that the cations prefer to interact with the stronger H-bond acceptor anion in TEAMS and tend to replace the triflate for the methyl sulfonate anion. If this interpretation is correct, we should perhaps also observe an increased absorbance for TEAMS. Indeed, applying the same procedure results in higher intensities with increasing TEATF concentration (Figure 3 a). However, we would like to point out



**Figure 3.** Non-ideal mixing behaviour in the PIL mixtures of TEAMS and TEATF. For TEAMS, we observe enhanced intensity at  $149\text{ cm}^{-1}$ , whereas for TEATF the intensity at  $129\text{ cm}^{-1}$  is weakened compared to the expected ideal behaviour, as indicated by the dotted line.

that the observation of positive deviations for the methyl sulfonate ions is perhaps not as obvious as the negative ones for the triflate ion. For TEATF, a decreasing number or strength of H-bonds should result in negative absorbance. For the positive deviation of TEAMS, however, it is necessary to consider that the methylsulfonate anion can form one, two or even three H-bonds with surrounding ethylammonium cations at the same time through the three oxygen atoms of the  $\text{SO}_3$  group. This could explain the enhanced intensity, indicating increasing H-bond capacity. To support our experimental findings and for a more detailed interpretation, we performed MD simulations for the pure PILs and their mixtures (see SI7 in the Supporting Information).

From corresponding pair correlation functions, we could derive the distribution of the number of hydrogen bonds formed between the triflate and/or methylsulfonate anions and the ethyl ammonium cation in the mixtures. We would like to add that the probability of finding a N–H hydrogen-bond donor that is not involved in a hydrogen bond is very low, and well below 1%. In Figures 4a and 4b, it is shown whether the anions form zero, one, two or even three hydrogen bonds to the N–H bond of the cation. The hydrogen-bonding situation of the anion is similar in both pure ILs, that is, just over 50% of the anions form one hydrogen bond,

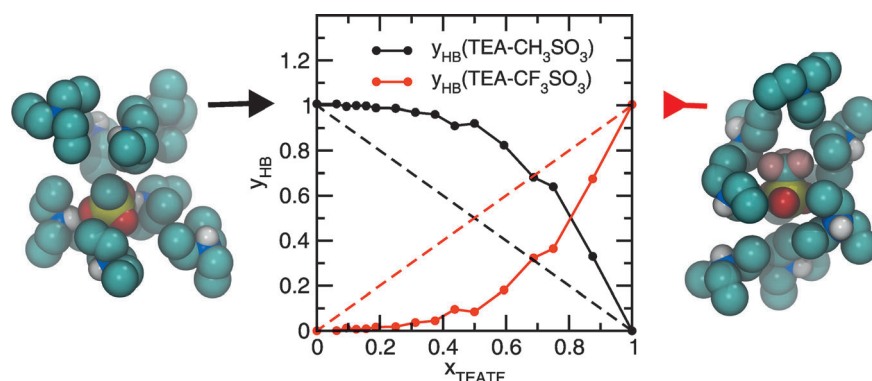


**Figure 4.** Probability of finding a certain number  $n$  of TEA cations attached to one type of anion through a hydrogen bond as a function of the mixture composition according to the MD simulations for a) methylsulfonate and b) triflate.

about 25% form two hydrogen bonds and 25% are not H-bonded at all.

In the mixture, the anions compete with each other; hence, the H-bond distribution changes systematically as a function of mixture composition. For the triflate anion, with increasing TEAMS concentration the doubly bound species ( $n=2$ ) disappear almost completely above a 1:1 mixture. Also, the fraction of single H-bonded species ( $n=1$ ) decreases significantly. Both are replaced by non-hydrogen-bonded triflate anions ( $n=0$ ), as shown in Figure 4b. The reverse situation is observed for TEAMS. Here, the number of non-H-bonded and single H-bonded methylsulfonate anions drastically decreases in favour of double and triple H-bonded species. As shown in Figure 4a, at a composition of  $x_{\text{TEATF}}=0.9$  (the highest TEATF concentration studied), the methylsulfonate anions bind mostly two and three triethylammonium cations, whereas methylsulfonate anions with  $n=0$  fully disappear and those with  $n=1$  contribute only 5% of the overall number of species at this concentration.

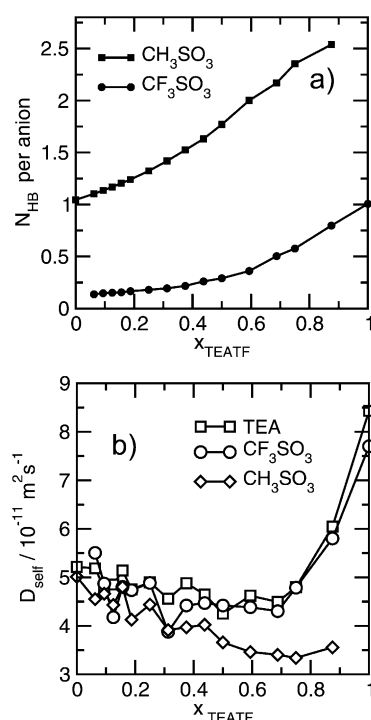
The H-bond characteristics of both PILs in the mixtures can be summarized by an increased H bonding for TEAMS and decreased H bonding for TEATF in the TEATF/TEAMS mixtures compared to an ideal random distribution. The positive and negative deviations for the fraction of hydrogen bonds of the TEA cation to each of the anion species in the TEATF/TEAMS mixtures are shown in Figure 5. For TEAMS, this fraction increases and for TEATF it decreases, indicating enhanced and weakened H bonding, respectively. This behaviour explains our



**Figure 5.** Fraction of hydrogen bonds of the TEA cation to one particular anion species according to MD data. The TEA cation prefers to interact with the methylsulfonate anion, as illustrated by the snapshots from the MD simulations: Two cations H-bonded to  $\text{CH}_3\text{SO}_3^-$  (left) and zero cations H-bonded to  $\text{CF}_3\text{SO}_3^-$ .

experimental findings of increased and decreased infrared intensities compared to those expected for ideal mixing.

In addition, the effect of unequal hydrogen-bond strength is also reflected in the transport properties, such as the MD-simulated self-diffusion coefficients of the TEA cation, the triflate anion and the methylsulfonate anion in the PIL mixtures. As shown in Figure 6a, the average number of multiple H-bonded methylsulfonate anions increases with increasing TEATF concentration. On average, this number ranges from one H bond in the pure TEAMS to an average of 2.5 H bonds at  $x_{\text{TEATF}} = 0.9$ .

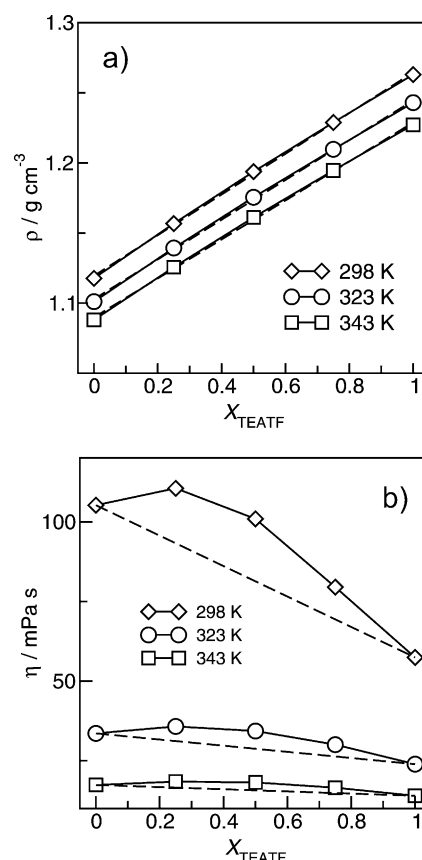


**Figure 6.** a) Average total number of hydrogen bonds for each of the anions to the neighbouring TEA cations as a function of composition in the TEA-triflate/TEA-methylsulfonate mixture at 400 K. b) Self-diffusion coefficients of the TEA cation, the triflate anion and the methylsulfonate anion in the TEA-triflate/TEA-methylsulfonate mixture at 400 K obtained from MD simulations.

The formation of those hydrogen-bonded methylsulfonate-TEA aggregates involving multiple TEA-cations results in a significantly reduced mobility, as illustrated in Figure 6b. Adding a small amount of TEAMS to TEATF leads to a significant drop in the diffusivity of both TEA and triflate ions. By further increasing the composition of TEAMS, the diffusivity goes through a shallow minimum, because at higher TEAMS concentrations the methylsulfonate anions compete with each other for TEA, which is reducing the

average size of the hydrogen-bonded aggregates, and is leading to a concerted increase of the self-diffusion coefficient of all ion species.

Now, is non-ideal H-bond mixing in the TEAMS/TEATF mixtures also reflected in physical properties, which are presently experimentally available to us? In Figure 7, the measured densities and viscosities of the pure PILs and their mixtures are shown as a function of temperature (see also SI6 in the Sup-



**Figure 7.** Measured densities (a) and viscosities (b) of the TEAMS/TEATF mixtures at three different temperatures. Whereas the densities show almost ideal mixing behaviour, the viscosities exhibit positive deviations from ideality, owing to enhanced H bonding of the MS anion.



porting Information). The densities show mainly linear behaviour with mixing. There is an almost straight line connecting the densities of the pure PILs. Obviously, the H-bond characteristic does not have any influence on the density of the mixtures in the Coulombic system. A completely different behaviour is found for the viscosities. For all PIL mixtures, the viscosity is larger than expected for ideal behaviour. However, this behaviour is in accord with our FIR spectra and can be understood from the H-bond statistics derived from our MD simulations. Starting with the pure TEAMS, we find an increase in viscosity, owing to enhanced hydrogen bonding. Here, the weak anion–cation interaction in TEATF is increasingly replaced by stronger multiple anion–cation interactions in TEAMS, leading to the formation of larger hydrogen-bonded aggregates with higher viscosity. This statement is not in contradiction to our earlier work with aprotic imidazolium-based ILs, where we claimed that hydrogen bonding can fluidise rather than toughen these Coulomb systems. In aprotic ILs with unique interaction sites, hydrogen bonds lead to the preformation of ion pairs, resulting in lower viscosities and enthalpies of vaporization.<sup>[18–21]</sup> Instead, in PILs and their mixtures, as discussed here, the formation of multiple H bonds lead to larger H-bonded complexes, which enhance the stiffness of the coulombic fluid.

Another important aspect of this non-ideal H-bond mixing behaviour is the nearly complete H-bond stripping of the triflate anion, which can be then regarded as a ‘quasi-free anion’. Such species will be available for supporting chemical reactions or improving conductivity. In this sense, our results support the DSIL concept by Rogers and co-workers.<sup>[5]</sup> The ions apparently change their identity in the mixture, resulting in a new liquid. We now have one pure liquid rather than two separate ILs. Our study also provides some hints for expanding the ability to design ILs by smart selection of cations and anions in binary or even ternary mixtures of ILs.

## Experimental Section

The water content of the two PILs, TEAMS and TEATF was below 100 ppm, as detected by using the Karl–Fischer titration method. The PIL mixtures were prepared under an argon atmosphere and put in an ultrasonic bath until they reached homogeneity.

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists of a multilayer mylar beam splitter and a room-temperature DLATGS detector with preamplifier. Polyethylene (PE) windows with an internal optical path of 0.1 mm were used. Further improvement could be achieved by using a high-pressure mercury lamp and a silica beam splitter. The accessible spectral region for this configuration now lies between 10 and 680 cm<sup>−1</sup> (0.3 and 20.3 THz). The spectra were deconvoluted simultaneously as well as separately into a number of Voigt profiles (convolution of Lorentzian and Gaussian functions) following the Levenberg–Marquardt procedure. The Voigt profile has four parameters: the intensity, the frequency, the half-width of the Lorentzian and the half-width of the Gaussian. The deconvolution procedure is described in detail in SI2–5 in the Supporting Information.

Temperature-dependent measurements of the density of the different mixtures were performed by using the oscillating tube densi-

tometer DSA 5000 m (Anton Paar/Austria) with internal viscosity correction. The density was determined in the range of 10–70 °C with intervals of 5 K (see SI6).

Temperature-dependent dynamic viscosities were measured with the Lovis 2000 ME (Anton Paar/Austria) microviscometer based on the rolling-ball principle. The viscosity was determined in the range of 10–70 °C with intervals of 5 K (see SI6).

We performed constant-pressure (NPT) MD simulations for 16 different mixtures of TEATF and TEAMS at a pressure of 1 bar and temperatures of 300 and 400 K. All simulated systems were composed of 256 ion pairs. A detailed description of the employed force-field parameters is provided in the Supporting Information. All simulations reported herein were performed with the GROMACS 4.5 simulation program.<sup>[17]</sup> Simulation runs of 100 ns length with time steps of 2 fs were analysed for *T* = 300 K (24 ns for *T* = 400 K). Based on computed radial pair distribution functions, hydrogen-bonded ion pairs were identified by a S=O⋯H–N cut-off distance of 0.24 nm. For MD simulations details see SI7 in the Supporting Information.

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**Keywords:** ionic liquids • IR spectroscopy • mixing behaviour • molecular dynamics • solvation chemistry

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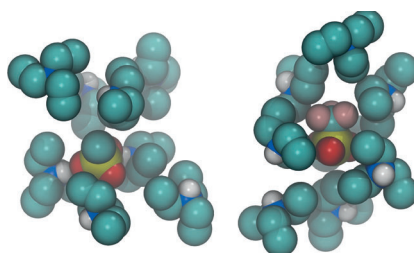
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## COMMUNICATIONS

**Go TEAMS:** Non-ideal mixing behaviour of hydrogen bonding in protic ionic-liquid mixtures can be detected by low-frequency spectroscopy. An understanding of this unique H-bond mixing in the coulombic fluid is provided by molecular dynamics simulations. The joint methods allow the analysis of macroscopic properties of non-ideal mixing at a molecular level. This knowledge may be used to design composite fluids with entities of individual character for solvation and reactivity.



TEAMS:  
2 H-bonds

TEATF:  
0 H-bonds

*K. Fumino, A.-M. Bansa, B. Golub,  
D. Paschek, R. Ludwig\**

■■ – ■■

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