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Raman and FTIR Spectroscopic Studies of 1-Ethyl-3-methylimidazolium Trifluoromethylsulfonate, its Mixtures with Water and the Solvation of Zinc Ions

Zhen Liu,^[a] Sherif Zein El Abedin,^[a, b] and Frank Endres^{*[a]}

In this paper we report on the interactions of the ionic liquid 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]-TfO) with water and the solvation of zinc ions in neat [EMIm]-TfO and [EMIm]TfO–water mixtures investigated by FTIR and Raman spectroscopy. The structures and physicochemical properties of the [EMIm]TfO–water mixtures are strongly dependent on the interaction between cations, anions, and water. The structure was changed from ionic-liquid-like to water-like solutions upon addition of water. In addition, zinc salts can precipitate in 0.2 M $\text{Zn}(\text{TfO})_2$ /[EMIm]TfO upon addition of 10% (v/v) water, presumably as a result of polarity change of the solution. The average coordination number of TfO^- per

zinc ion calculated from Raman spectra is 3.8 in neat [EMIm]-TfO, indicating that $[\text{Zn}(\text{TfO})_4]^{2-}$, and $[\text{Zn}(\text{TfO})_3]^-$ complexes are present in the solution. However, in the presence of water, water interacts preferentially with the zinc ions, leading to aqueous zinc species. The solvation of zinc ions in 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([Py_{1,4}]TfO) was also investigated. In [Py_{1,4}]TfO, there are, on average, 4.5 TfO^- anions coordinating each zinc ion, corresponding to the weak interaction between $[\text{Py}_{1,4}]^+$ cations and TfO^- anions. The species present in [Py_{1,4}]TfO are likely a mixture of $[\text{Zn}(\text{TfO})_4]^{2-}$ and $[\text{Zn}(\text{TfO})_5]^{3-}$.

1. Introduction

Ionic liquids have unique and interesting properties, such as negligible vapor pressure, high chemical and thermal stability, low flammability, wide electrochemical windows, and good ionic conductivities, and thus offer new opportunities for applications in electrochemical devices such as batteries, solar cells, supercapacitors, and fuel cells.^[1] Fundamental studies on zinc deposition from ionic liquids have been reported in recent years.^[2] Different kinds of ionic liquids have been employed as electrolytes for the deposition of zinc, including ZnCl_2 /1-ethyl-3-methylimidazolium chloride, urea and ethylene glycol/choline chloride based deep eutectic solvents, 1-ethyl-3-methylimidazolium dicyanamide ([EMIm]DCA), 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)amide ([Py_{1,4}]TFSA) and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([Py_{1,4}]TfO). The zinc species present in these ionic liquids are different and they play a certain role in electrodeposition mechanism and morphology of the deposits. However, the solvation of zinc ions in ionic liquids has been hardly reported, maybe a consequence of the difficulty to obtain structural data and identifying species in ionic liquid solutions. Understanding the rela-

tionship between zinc speciation, transport properties, ion conductivity and viscosity of the electrolyte is a critical component to improve the properties and performance of ionic liquids for specific applications.

Water is often present in ionic liquids. In some cases it is regarded as an impurity and can cause some problems, for example water leads to a reduced deposit quality in the deposition of aluminum. On the other hand water can reduce the viscosity of the solution and facilitate the deposition process. It was reported that the addition of water to ionic liquids can improve their conductivities and lead to a dendrite free morphology of zinc.^[2a–f] Therefore, mixtures of ionic liquids and water can also be potential electrolytes for rechargeable zinc-air batteries as such electrolytes would not, as with KOH, absorb environmental CO_2 . From a practical point of view, furthermore, rechargeable Zn-air batteries can absorb or even lose water under operational conditions. The investigation of the structure of an ionic liquid with water and the solvation of zinc ions in ionic liquid–water mixtures is of considerable interest for rechargeable Zn-air batteries.

The interaction between ionic liquids and water has been studied in recent years both experimentally and theoretically.^[3] Fourier transform infrared spectroscopy (FT-IR) and Raman spectroscopy are valuable methods to investigate intermolecular interactions between solute and solvent. Raman spectra as “molecular fingerprints”, allow researchers to investigate the structure and dynamics of molecules. The interaction of ionic liquids with water is rather complex, and strongly depends on the nature of the cation and the anion of the ionic liquid and water content, as well as on temperature.

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In this work, we have investigated the interaction of [EMIm]TfO with water and the solvation of Zn ions in [EMIm]-TfO and [EMIm]TfO–water mixtures by using Raman and FT-IR spectroscopy. Most metals form ionic complexes in ionic liquids, therefore the interaction between cation and anion of the ionic liquid may also have a strong effect on the metal solvation structure. Thus, a comparative study of the interaction of [EMIm]⁺ and [Py_{1,4}]⁺ cations with TfO[−] anions (chemical structures are shown in Figure 1) as well as zinc solvation in these two ionic liquids is also presented.

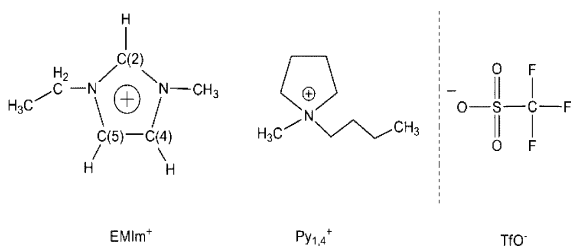


Figure 1. Chemical structures of 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ([EMIm]TfO) and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ([Py_{1,4}]TfO).

2. Results and Discussion

2.1. FTIR of [EMIm]TfO–Water Mixtures between 2800 and 3800 cm^{−1} (OH Stretching Vibrations)

Infrared spectroscopy is considered to be a powerful technique for exploring the molecular state of water in different solvents. The OH stretching vibrations are sensitive to the chemical environment and have been used widely to obtain structural information on interactions of electrolyte–water solutions. FTIR spectra of neat [EMIm]TfO and with different amounts of water from 5 to 80% (v/v) are shown in Figure 2. The mid infrared spectrum of liquid water (Figure 2 top, green curve) is composed of a broad band in the range from 2800 to 3800 cm^{−1}.

Many attempts were done to explain the OH stretching bands.^[4] In general, the OH stretching band around 3250 cm^{−1}

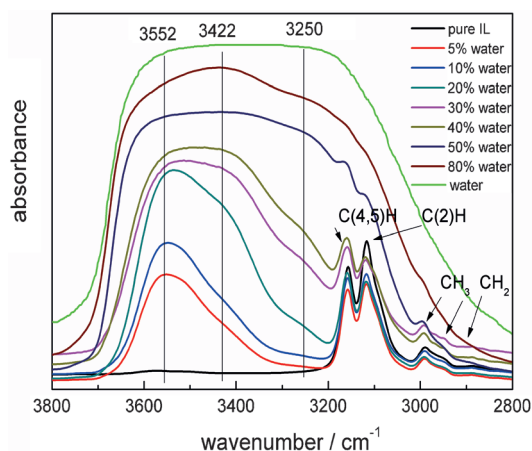


Figure 2. FT-IR spectra of [EMIm]TfO and of [EMIm]TfO–water mixtures between 2800 and 3800 cm^{−1}.

is assigned to an ice-like component with a tetrahedral structure and the band around 3420 cm^{−1} is assigned to an ice-like liquid component. The bands at 3550 and 3620 cm^{−1} are attributed to the OH asymmetric stretching vibrational modes of a liquid-like amorphous phase in which OH is hydrogen bonded, and of free OH group (monomer-like), respectively.

In Figure 2, a strong band centered at around 3552 cm^{−1} together with a small peak seen as a shoulder located at around 3422 cm^{−1} was observed for water concentrations from 5–20%, indicating that the water molecules are mainly H-bonded to the TfO[−] anions. Cammarata et al.^[3d] also reported that water molecules in the ionic liquid rich regime interact preferentially with anions through A...HOH...A (A: anion). The intensity of the peak at 3422 cm^{−1} increases with increasing water concentration. A new signal appears at around 3250 cm^{−1} if the water concentration is increased. The intensity of this signal increases as more water is added and becomes rather broad with a water content of 40–50%. In neat [EMIm]TfO (Figure 2 bottom, black curve), the vibration bands are found between 3200 and 2800 cm^{−1}, which are due to CH stretching vibration modes of imidazolium cations as will be further discussed below. Those signals become weaker with increasing water concentration and bulk behavior of water with little [EMIm]TfO signal is observed at a water concentration of 50%. The results indicated that large water aggregates are the dominant component at water contents of more than 50%, because the spectrum is close to the one of pure water.

2.2. Raman Spectroscopy of [EMIm]TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO with Different Amounts of Water between 2700 and 3300 cm^{−1} (CH Stretching Vibration)

Both the OH stretching vibration of water and the CH stretching vibration modes of imidazolium cations are found between 2700 and 3300 cm^{−1}. Unfortunately, they overlap in FTIR spectroscopy. Therefore Raman spectroscopy was used to investigate the structure change upon addition of water to [EMIm]-TfO. The CH stretching region of the Raman spectra of [EMIm]-TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO with different amounts of water are shown in Figure 3a and 3b, respectively. The peaks at low wavenumbers between 2800 and 3050 cm^{−1} are attributed to CH stretching vibrations of the methyl and ethyl groups of the imidazolium cations. Whereas the peaks at high wavenumbers between 3050 and 3200 cm^{−1} are assigned to the CH stretching vibration of C(2)H, C(4)H, and C(5)H of the imidazolium cation.^[5] The Raman spectra of 0.2 M Zn(TfO)₂/[EMIm]TfO/water (Figure 3b) is almost the same both in peak positions and in peak intensities as that in Figure 3a. There are only slight changes in the CH stretching vibration of C(2)H, C(4)H, and C(5)H of the imidazolium cation, which will be further discussed in the following section. At first glance, the intensities of the peaks are reduced with the addition of water. The intensity of the band at 2970 cm^{−1} as a function of water concentration is plotted in Figure 3c. Surprisingly, there is a sharp decrease in the intensity if the water concentration is increased from 40 to 50%. A similar behavior was observed by Jeon et al.^[3c] in 1-butyl-3-methylimidazolium tetrafluoroborate

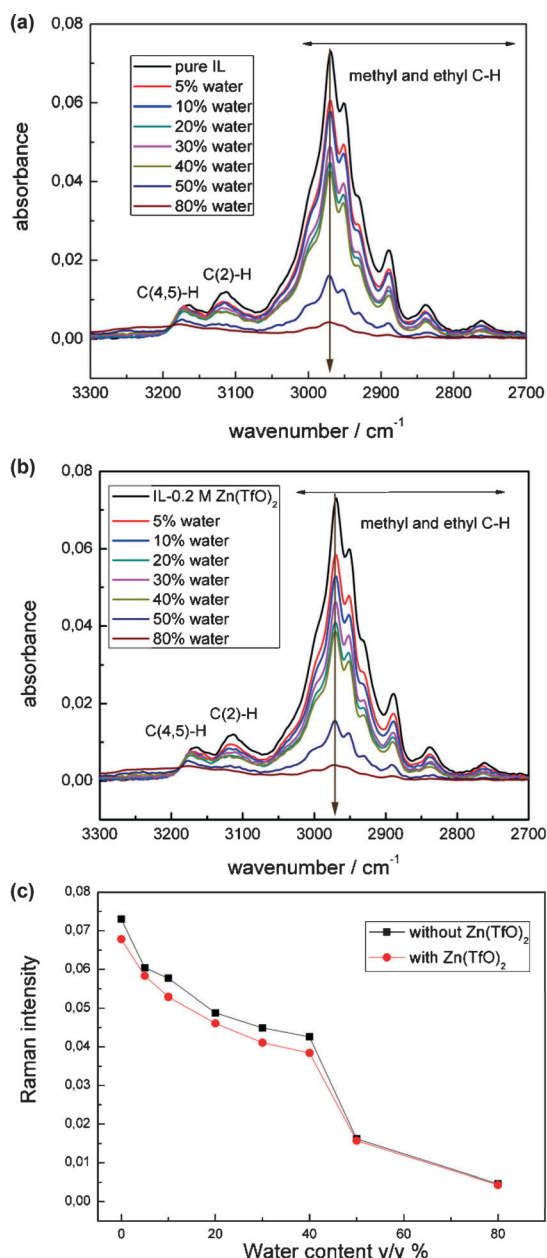


Figure 3. Raman spectra in the CH stretching regime of a) [EMIm]TfO and of b) 0.2 M Zn(TfO)₂/[EMIm]TfO with different amounts of water. c) Intensity of the 2970 cm⁻¹ band as a function of water content.

[BMIm]BF₄water mixtures at water concentrations of 32 ± 2 (≈ 55 v/v%) and 45 ± 2 mol L⁻¹ (≈ 80 v/v%) studied by attenuated total reflectance (ATR) IR and Raman spectroscopy. For better comparison to literature, the composition of the mixtures described by different quantities is listed in Table 1.

The observed sharp decrease in the peak intensity in the Raman spectra is a hint for a structural change. It was also reported that the structure of triethylammonium methylsulphonate can change to solvent-separated ion pairs upon addition of four water molecules (80 mol%). The study comprised Far-IR (FIR) measurements and DFT calculations.^[6] By studying molecular dynamics simulations, Niazi et al. revealed that several ionic liquid water mixtures (1-butyl-3-methylimidazolium chlo-

Table 1. The concentration of water in [EMIm]TfO–water mixtures described by volume concentration, mole fraction, molar concentration, and mass fraction, respectively.

Concentration	Definition	[EMIm]TfO(IL)–water(w) mixtures						
volume [%]	V_w/V_{IL+w}	5	10	20	30	40	50	80
mole [%]	n_w/n_{IL+w}	35	54	72	81	87	91	97
molar [mol L ⁻¹]	n_w/V_{IL+w}	2.8	5.5	11	17	22	28	44
mass [%]	m_w/m_{IL+w}	3.7	7.4	15	23	32	42	74

ride, 1-ethyl-3-methylimidazolium acetate, and 1,3-dimethylimidazolium dimethylphosphate) turned out to be aqueous solutions at water concentrations beyond 75 mol%.^[3a] Our experimental results indicated that 40% (v/v), which is equal to 22 mol L⁻¹ or 87 mol% of water (Table 1), is needed for such a structural transition. The intrinsic complexity of ionic liquids and their interaction with water molecules could influence the structural transition. If water is added, the interaction between the cations and anions get interrupted by association with water molecules. The anions can interact with water molecules first through H-bonding until they are surrounded by water molecules. Finally, water solvated ions of the former ionic liquid become the dominant species in bulk water. Raman and FT-IR results suggest that the structure transforms from ionic liquid-like to aqueous-like upon the addition of water to [EMIm]TfO.

2.3. FT-IR of Neat [EMIm]TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO between 2800 and 3200 cm⁻¹ (CH Stretching Vibrations)

The FTIR spectra of neat [EMIm]TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO in the range of 2800 to 3200 cm⁻¹ are shown in Figure 4. They have been deconvoluted into ten Gaussian bands, respectively. The bands in this range represent the CH stretching vibration modes of imidazolium cations.^[5] In neat [EMIm]TfO (Figure 4a), the peaks at low wavenumbers between 2800 and 3050 cm⁻¹ are attributed to CH modes of the methyl and ethyl groups of the imidazolium cations. The two bands at high wavenumbers (around 3117 and 3157 cm⁻¹) are attributed to the CH stretching modes of C(2)H and of C(4,5)H on the imidazolium ring, respectively. These assignments are consistent with that reported in literature.^[5] The two bands in the imidazolium ring have often been in the focus of research as they can be involved in hydrogen bonding through C(2)H...A or C(4,5)H...A. The imidazolium cation can undergo ion clusters and ion pairs. Their corresponding vibrational bands overlap and, therefore, they must be deconvoluted. Deconvoluted bands are found at 3088 (pink peak), 3117 (green peak), 3157 (blue peak), and 3190 cm⁻¹ (orange peak), respectively. The two bands at 3088 and 3157 cm⁻¹ can be attributed to the C(2)H and C(4,5)H stretching vibration in ion pairs, respectively whereas the peaks at 3117 and 3190 cm⁻¹ are assigned to C(2)H and C(4,5)H stretching vibration in larger hydrogen-bond networks, respectively.^[5a] These bands are sensitive to environment changes of the ionic liquid. For example, Köddermann et al.^[5a] revealed that the C(2)H and C(4,5)H vibra-

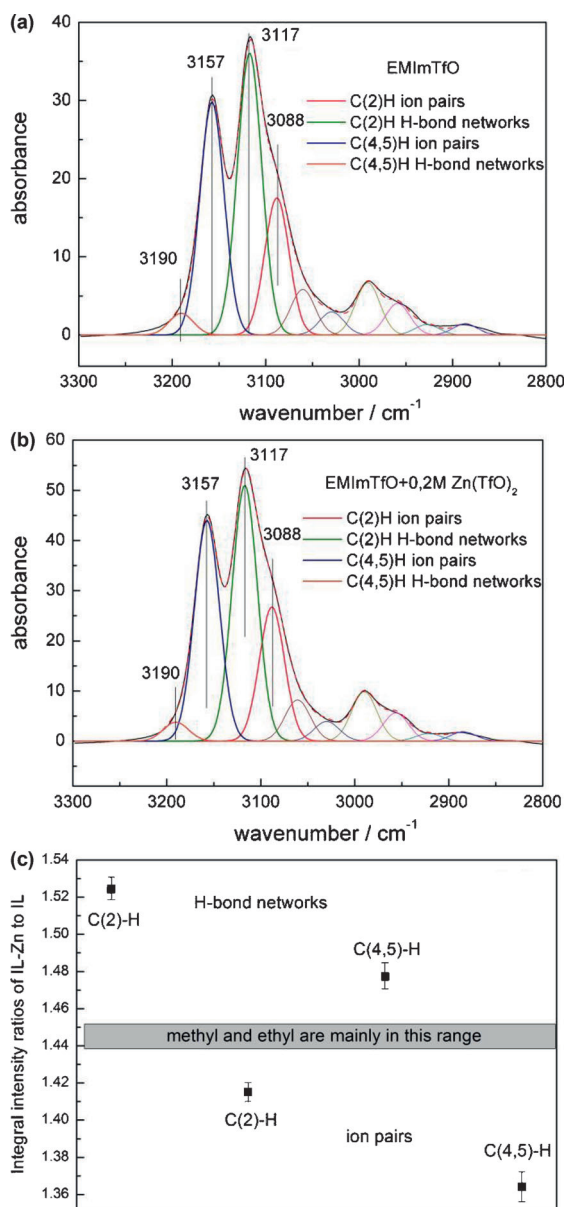


Figure 4. FT-IR spectra of a) [EMIm]TfO and of b) 0.2 M Zn(TfO)₂/[EMIm]TfO between 2800 and 3200 cm⁻¹, respectively. The spectra are deconvoluted into ten Gaussian bands. c) Integral intensity ratios of the deconvoluted peaks in IL-Zn to IL.

tional bands of hydrogen-bond networks decrease with increasing temperature, whereas those attributed to ion pairs continuously increase. Zheng et al.^[5b] reported that the number of ion clusters decrease and the number of ion pairs increase by addition of acetonitrile to the ionic liquid [BMIm][BF₄]. Upon addition of the zinc salt to the ionic liquid in our case, the intensities of these peaks change a bit as shown in Figure 4b. The relative ratios of the integral intensities of the deconvoluted peaks in 0.2 M Zn(TfO)₂/[EMIm]TfO to those in [EMIm]TfO are shown in Figure 4c. The ratios of the CH stretching vibrations of the methyl and ethyl groups are nearly constant and are located in the range of the gray bar shown in Figure 4c. However, the relative ratio of the C(2)H and C(4,5)H

vibrational modes of hydrogen-bond networks is increased (above the gray bar) whereas the relative ratio of the C(2)H and C(4,5)H vibrational modes of ion pairs is decreased (below the gray bar). This indicates that the hydrogen-bond network is favored and the contribution of ion pairs decreases upon addition of the zinc salts. This is consistent with the increase in the viscosity and the decrease in the conductivity on addition of metal salts to ionic liquid electrolytes. Upon addition of zinc salts to the ionic liquid, zinc ions are solvated by the anions leading to the formation of zinc-ion complexes. The TfO⁻ anions are less moveable compared with those in pure [EMIm]TfO, which leads to stronger hydrogen-bonding. The [EMIm]⁺ cations can also undergo a conformational change that favors hydrogen-bonding. It was reported that the ethyl group of the [EMIm] cation can rotate along the C–N bond, yielding non-planar and planar conformers.^[7]

2.4. Raman Spectroscopy of [EMIm]TfO–Water Mixtures between 300 and 1300 cm⁻¹ (Vibration Modes of TfO⁻ Anion)

The Raman spectra of [EMIm]TfO–water mixtures between 300 and 1300 cm⁻¹ are shown in Figure 5. The resulting vibrational bands of TfO⁻ anions are assigned as follows: the asymmetric stretching $\nu_{as}(\text{SO}_3)$, located at 1260 cm⁻¹ in neat [EMIm]TfO is gradually red shifted to 1252 cm⁻¹ with increasing water concentration. The symmetric stretching $\nu_s(\text{SO}_3)$, the asymmetric stretching $\nu_{as}(\text{CF}_3)$, and the symmetric stretching $\nu_s(\text{CF}_3)$ modes are located at 1034, 1173, and 1230 cm⁻¹, respectively.^[8] They do not shift upon increasing water concentration. The symmetric deformation $\delta_s(\text{CF}_3)$, the asymmetric deformation $\delta_{as}(\text{CF}_3)$, and the symmetric stretching $\nu_s(\text{C-S})$ modes are located at 757, 573, and 315 cm⁻¹, respectively, and are gradually blue shifted to 765, 577, and 319 cm⁻¹ with increasing water concentration. It was reported that the oxygen atoms of CF₃SO₃⁻ have larger negative charges than the fluorine atoms.^[9]

Therefore, the more negatively charged oxygen atoms associate preferably with water through hydrogen bonding. The increase in the strength of the hydrogen bond SO₃⋯H₂O resulted in a shortening of the hydrogen bonds SO₃⋯H₂O and a lengthening of the covalent bonds S–O. The weaker force constants for the S–O bonds lead to lower wavenumbers and thus red shifted vibrational bands. However, due to the Coulomb forces and hydrogen bonding, the deformation mode of CF₃ and stretching mode of C–S are blue shifted upon addition of water. These shifts clearly indicate the change of the coordination environment of the TfO⁻ anions upon addition of water. The interaction strength between cation and anion upon addition of water is discussed in the following section.

2.5. Cation–Anion Interaction of [EMIm]TfO–Water Mixtures between 30 and 300 cm⁻¹ Detected by Far-Infrared Spectroscopy

The FIR spectra of [EMIm]TfO–water mixtures in the range of 30–300 cm⁻¹ are shown in Figure 6. The vibrational bands centered at about 210 cm⁻¹ are due to the rocking modes of CF₃

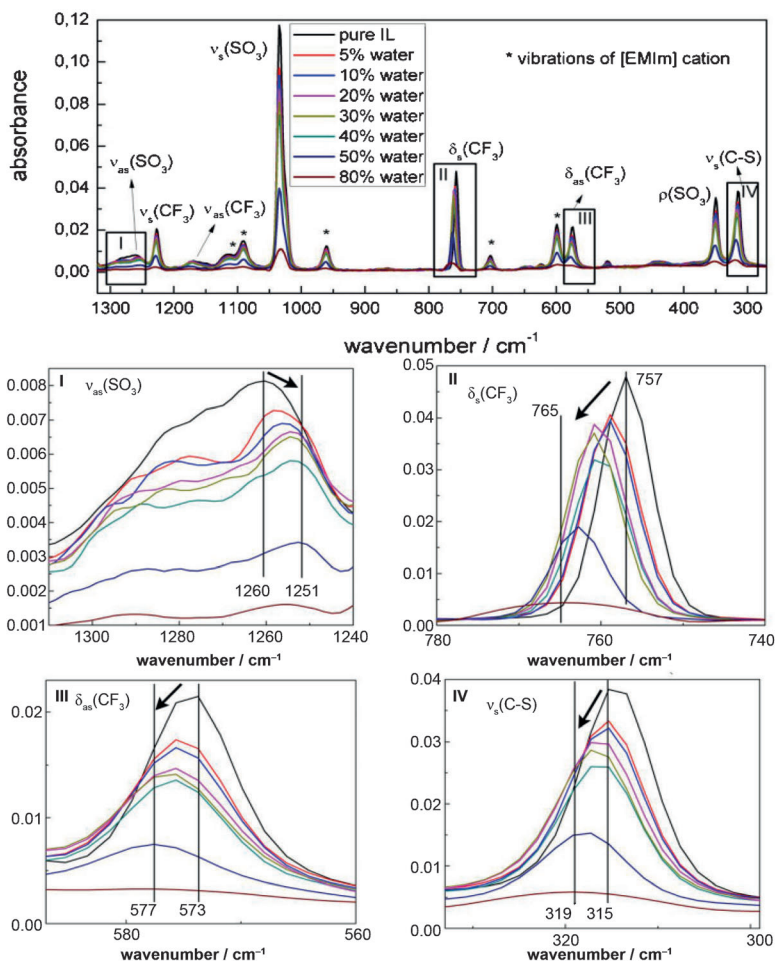


Figure 5. Raman spectra of [EMIm]TfO and of [EMIm]TfO–water mixtures between 270 and 1300 cm^{-1} .

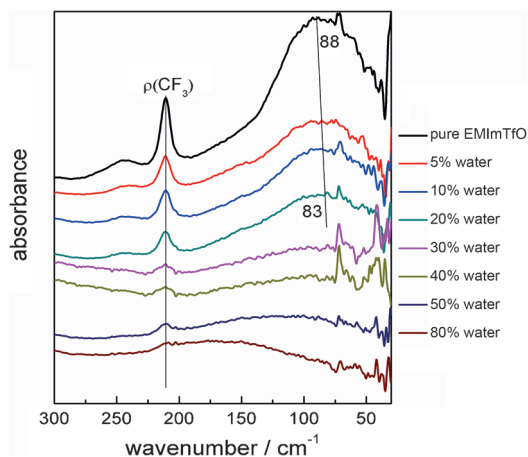


Figure 6. FIR spectra of [EMIm]TfO and of [EMIm]TfO–water mixtures between 30 and 300 cm^{-1} . The bands below 200 cm^{-1} indicate the cation–anion interaction.

(ρCF_3) and they do not shift upon increasing water concentration.

The research group of Ludwig has intensively investigated the cation–anion interaction of ionic liquids by FIR spectroscopy

in combination with DFT calculations.^[6,10] The low frequency vibrational signals below 200 cm^{-1} are assigned to bending and stretching modes of the $^+\text{C-H}\cdots\text{A}$ or $^+\text{N-H}\cdots\text{A}$ (A: anion) describing the cation–anion interaction. Therefore, the vibrational band centered at around 88 cm^{-1} in neat [EMIm]TfO is assigned to the interaction between [EMIm]⁺ cations and TfO[−] anions. The intensities of those vibrational bands are gradually reduced and a red shift of the frequencies is observed for water content from 5–20%, suggesting that the interactions between cations and anions, as a consequence of the association with water molecules, get weaker. The peak is no longer assignable at a water content of more than 30% as the anions are fully surrounded by water molecules.

2.6. The Solvation of Zn Ions in Neat [EMIm]TfO and in [EMIm]TfO–Water Mixtures

Some vibrational modes are known to be sensitive to the coordination environment in ionic liquid solutions such as bis(trifluoromethylsulfonyl)amide (TFSA)^[11] and trifluoromethylsulfonate (TfO[−]).^[8a,12] It was reported that the frequency of “free” TFSA anions located at about 742 cm^{-1} ($\delta_s(\text{CF}_3)$) in the Raman spectrum shifted to 748 cm^{-1} if it was coordinated with Li⁺.^[11b] In “free” TfO[−] anions, the comparable frequency was located at about 757 cm^{-1} ($\delta_s(\text{CF}_3)$) and shifted to 766 cm^{-1} if triflic acid was added to the solution.^[12] The Raman spectra of [EMIm]TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO between 740 and 780 cm^{-1} are presented in Figure 7a. The local environment of the TfO[−] anions in [EMIm]TfO and in 0.2 M Zn(TfO)₂/[EMIm]TfO electrolytes was investigated by monitoring the CF₃ symmetric deformation, $\delta_s(\text{CF}_3)$, of which the vibrational mode was located at 757 cm^{-1} . If zinc salt is added to the solution, a new signal appears between approximately 762 and 772 cm^{-1} , which is associated with Zn²⁺ coordinated TfO[−]. The spectrum can be deconvoluted into two peaks and the results are shown in Figure 8. The peak for Zn²⁺ coordinated TfO[−] is centered at 766 cm^{-1} . The average number of TfO[−] coordinated to each Zn²⁺ ion can be calculated according to the Raman peak areas, as described in the literature [Eq. (1)].^[11b]

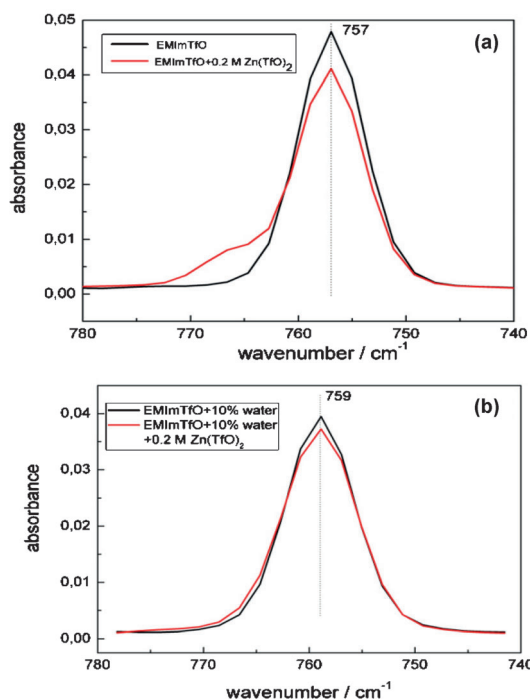


Figure 7. Raman spectra of [EMIm]TfO and of 0.2 M Zn(TfO)₂/[EMIm]TfO (a) between 740 and 780 cm⁻¹ and their mixtures with 5% water (b), respectively.

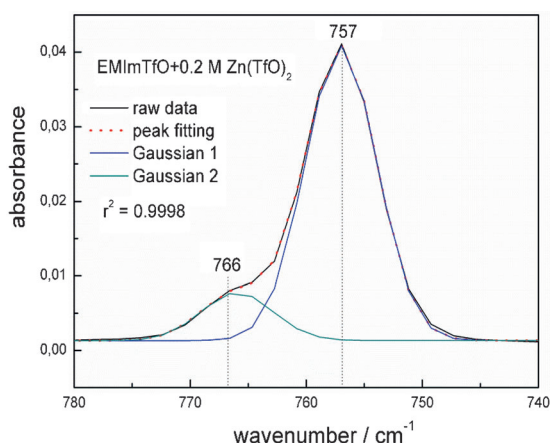


Figure 8. Raman spectra of 0.2 M Zn(TfO)₂/[EMIm]TfO between 740 and 780 cm⁻¹. The spectrum was deconvoluted into two bands. The band at 757 cm⁻¹ is attributed to free TfO⁻ anions and the band at 766 cm⁻¹ is assigned to coordinated TfO⁻ anions.

$$N = \frac{A_{\text{CO}}/(A_{\text{CO}} + A_{\text{free}})}{n_{\text{Zn}}/n_{\text{total TfO}^-}} \quad (1)$$

in which A_{CO} and A_{free} are the peak areas of the coordinated and of the free TfO⁻ at 766 and 757 cm⁻¹, respectively. n_{Zn} is the mole concentration of Zn(TfO)₂ (0.2 M) and $n_{\text{total TfO}^-}$ is the total mole concentration of TfO⁻, which is equal to n_{IL} (at room temperature $n_{\text{IL}} = 5.33 \text{ M} + 2 \times n_{\text{Zn}} (0.4 \text{ M})$).

The calculated average number of TfO⁻ coordinated to each Zn²⁺ ion is 3.8, which indicates that Zn²⁺ ions coordinates four

TfO⁻ ions. It is likely that [Zn(TfO)₄]²⁻ complexes, together with [Zn(TfO)₃]⁻ complexes, are presented in the solution. However, in the presence of water (taking 5% of water as an example, as shown in Figure 7b) only one peak at 759 cm⁻¹ was observed, the analysis of which shows the change of the coordination environment of Zn²⁺. In ionic liquid-water mixtures, Zn²⁺ ions are associated mainly with water forming aqueous complexes of the type [Zn(H₂O)_{*n*}]²⁺ with $n = 1-6$.^[13] The presence of smaller sized complexes [Zn(H₂O)_{*n*}]²⁺ is one of the factors that accounts for the increased conductivity and decreased viscosity of water containing ionic liquid electrolytes. Therefore, the electrochemical performance of ionic liquid-water mixtures, as electrolytes for the electrodeposition of zinc, was largely improved as shown in our previous report.^[2f]

2.7. Polarities of [EMIm]TfO–Water Mixtures

Upon addition of 10% water (corresponding to a roughly 1 ([EMIm]TfO) to 1 (H₂O) molar ratio) to 0.2 M Zn(TfO)₂/[EMIm]TfO solutions, a precipitate can be found on the bottom of the beaker. This process is slow and it can take one week or even more. We found a similar phenomenon upon dissolving copper triflate, tin triflate and nickel triflate in [EMIm]TfO followed by the addition of 10% water. Photos of the precipitates are shown in Figure 9. The zinc precipitate was isolated and

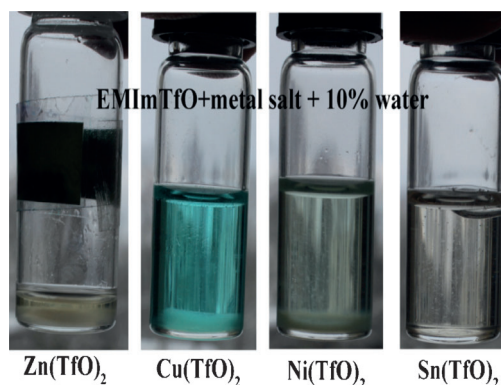


Figure 9. Photos of the solutions 0.2 M Zn(TfO)₂/[EMIm]TfO + 10% water, 0.2 M Cu(TfO)₂/[EMIm]TfO + 10% water, saturated Ni(TfO)₂/[EMIm]TfO + 10% water, and saturated Sn(TfO)₂/[EMIm]TfO + 10% water.

analyzed by XRD, XPS, and EDX. The XRD result gave no peaks, showing that the isolated precipitate is amorphous. Analysis of both the XPS and EDX confirmed that the obtained precipitate contains Zn, S, F, and O. The precipitate is hydrated Zn(TfO)₂. In neat [EMIm]TfO, the [EMIm]⁺ cations are hydrogen bonded to the TfO⁻ anions through C(2)H...A and/or C(4,5)H...A. The presence of water disturbs the hydrogen bond network of the ionic liquid, affecting the polarity of the solution. We did not observe this precipitation at water contents below or above 10%. Only in close proximity (10 v/v%, roughly a 1:1 molar ratio of the ionic liquid to water), the dissolved zinc salts are precipitated. Both the ionic liquid [EMIm]TfO and water are good solvents for Zn(TfO)₂. Without a detailed analysis of the

precipitate we can not speculate on its composition, but, with this composition the polarity of the ionic liquid-water mixture is disturbed, such that the zinc salt precipitates. Such polarizing/depolarizing effects in ionic liquid-water mixtures based on calculations were reported in the literature.^[3e,14] They all reveal that water molecules get depolarized by the ionic liquid in mixtures of 1-ethyl-3-methylimidazolium acetate-water,^[14a] mono-methylammonium nitrate-water^[14b], and 1-ethyl-3-methylimidazolium chloride-water.^[3e] The study of interactions between [EMIm]TfO, water, and dissolved salts is crucial, not only for a fundamental understanding of the structure and physico-chemical properties of the mixtures, but also for a practical use of the mixtures.

2.8. The Interaction of [EMIm]⁺ and [Py_{1,4}]⁺ Cations with TfO⁻ Anions in Comparison

The FIR spectra of [EMIm]TfO and of [Py_{1,4}]TfO between 30 and 300 cm⁻¹ are shown in Figure 10. The vibrational bands at about 210 cm⁻¹ are due to the rocking modes of CF₃ (ρCF₃)

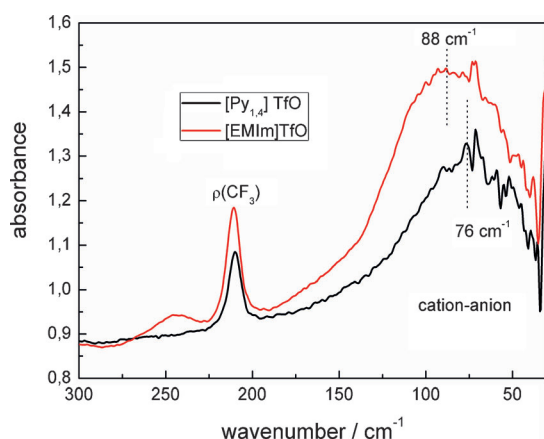


Figure 10. FIR spectra of [EMIm]TfO and of [Py_{1,4}]TfO between 30 and 300 cm⁻¹.

and are only shifted slightly, by approximately 1 cm⁻¹. The signals around 240–250 cm⁻¹, which only appeared in [EMIm]TfO, can be assigned to the out-of-plane bending mode of the CH₃-(N) methyl group in the imidazolium cation.^[10b] The low frequency vibrational bands below 200 cm⁻¹ are assigned to the cation-anion interaction. The peak is located at around 88 cm⁻¹ in [EMIm]TfO and red shifted to 76 cm⁻¹ in [Py_{1,4}]TfO. Analysis of the results suggest that [EMIm]⁺ has stronger hydrogen bonds to TfO⁻ anions than [Py_{1,4}]⁺ and the strength of the interaction between [Py_{1,4}]⁺ and TfO⁻ is weaker in comparison. The difference in the interaction between cations and anions should also result in a different solvation of zinc ions.

2.9. The Solvation of Zinc Ions in [Py_{1,4}]TfO

Raman spectra of [Py_{1,4}]TfO with different amounts of Zn(TfO)₂ between 740 and 780 cm⁻¹ are shown in Figure 11. The average number of TfO⁻ coordinated to each Zn²⁺ ion as calculated

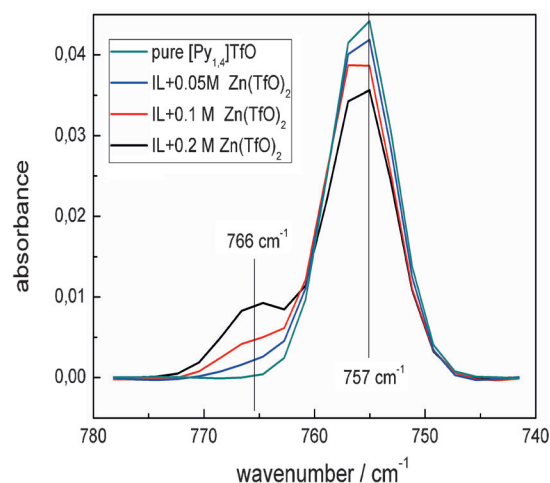


Figure 11. Raman spectra of [Py_{1,4}]TfO with different amounts of Zn(TfO)₂ between 740 and 780 cm⁻¹.

ed above is 4.5 in [Py_{1,4}]TfO. Analysis of the results suggest that in comparison with [EMIm]TfO more TfO⁻ anions are associated to Zn²⁺. The difference can be attributed to the different cation-anion interactions occurring in these two ionic liquids. The weaker hydrogen bond between [Py_{1,4}]⁺ and TfO⁻ seems to lead to an enhanced association of TfO⁻ anions with zinc ions. The species present in [EMIm]TfO are [Zn(TfO)₄]²⁻ and [Zn(TfO)₃]⁻, whereas a mixture of [Zn(TfO)₄]²⁻ and [Zn(TfO)₅]³⁻ are present in [Py_{1,4}]TfO. The difference of zinc species present in the two ionic liquids may also account for their different electrochemical performance and morphology of zinc deposits. The deposition of zinc from [Py_{1,4}]TfO needs larger overpotentials than that from [EMIm]TfO and nanocrystalline zinc is obtained from [Py_{1,4}]TfO whereas microstructured zinc is obtained from [EMIm]TfO,¹³ which also has to do with interfacial reactions.

3. Conclusions

The bulk coordination of [EMIm]TfO, [EMIm]TfO-water mixtures and the solvation of zinc ions were investigated by FT-IR and Raman spectroscopy. In neat [EMIm]TfO, imidazolium cations and TfO⁻ anions are hydrogen bonded through C(2)⋯H and/or C(4,5)⋯H. If water is added, the bulk interaction networks between cations and anions are interrupted by association with water molecules and the structure is changed from ionic liquid-like to aqueous-like, the more water is added.

The solvation of zinc ions in ionic liquid and in ionic liquid-water mixtures was investigated by Raman spectroscopy. The vibrational band at 757 cm⁻¹ is a probe for “free” TfO⁻ anions. Upon addition of zinc salts, a new band appears at 766 cm⁻¹ in the case of [EMIm]TfO, which is assigned to zinc coordinated TfO⁻. The average number of coordinated TfO⁻ per Zn²⁺ cation (*n*) is estimated to be 3.8, which indicates [Zn(TfO)₄]²⁻ and [Zn(TfO)₃]⁻. However, in the presence of water, only one peak is observed at 759 cm⁻¹, indicating that the zinc speciation is different, presumably Zn²⁺ ions are mainly associated

with water. In $[\text{Py}_{1,4}]\text{TfO}$, the average coordination number is 4.5. The species present in $[\text{Py}_{1,4}]\text{TfO}$ are likely to be a mixture of $[\text{Zn}(\text{TfO})_4]^{2-}$ and $[\text{Zn}(\text{TfO})_5]^{3-}$.

Experimental Section

Zinc trifluoromethylsulfonate, $\text{Zn}(\text{TfO})_2$ (99%) and the ionic liquids, 1-ethyl-3-methylimidazolium trifluoromethylsulfonate ($[\text{EMIm}]\text{TfO}$) and 1-butyl-1-methylpyrrolidinium trifluoromethylsulfonate ($[\text{Py}_{1,4}]\text{TfO}$) were purchased from IO-LI-TEC, Germany. The ionic liquids (chemical structures are shown in Figure 1) were dried under vacuum at $T=120^\circ\text{C}$ to water contents of below 3 ppm and stored in closed bottles in an argon filled glove box (OMNI-LAB from Vacuum Atmospheres) before use. From the synthesis process such liquids can contain several hundred ppm of trifluoromethylsulfonic acid. The concentration of $\text{Zn}(\text{TfO})_2$ in both ionic liquids is 0.2 mol L^{-1} . $[\text{EMIm}]\text{TfO}$ -water mixtures were prepared by adding different amounts of water to $[\text{EMIm}]\text{TfO}$ and stirred at room temperature for $t=24\text{ h}$ before measurements. The concentration of water in $[\text{EMIm}]\text{TfO}$ was varied from 5% to 80% (v/v). Unless otherwise stated, the concentration in this paper is assumed to volume concentration. The FT-IR measurements were performed on a Bruker VERTEX 70 FT-IR spectrometer. The instrument was equipped with an extension for measurements in the far IR region, which consists of a multilayer mylar beam splitter, a room temperature DLATGS detector with preamplifier and polyethylene (PE) windows for the internal optical path. The accessible spectral region for this configuration was between 30 and 680 cm^{-1} . The Raman measurements were carried out with a Raman module FRA 106 (Nd:YAG laser, 1064 nm) attached to a Bruker IFS 66v interferometer. The samples were sealed under an argon atmosphere in glass capillaries, and data were recorded at room temperature ($T\approx 22^\circ\text{C}$). The spectra were fitted by Gaussian response functions by using iterative methods controlled by the software PeakFit. The Gaussian profile had three parameters: intensity, frequency, and full width at half maximum (FWHM). The correlation (r^2) of each fitting was more than 0.999.

Acknowledgements

Financial support by the BMBF project AKUZIL is gratefully acknowledged.

Keywords: ionic liquids • IR spectroscopy • Raman spectroscopy • solvation • water

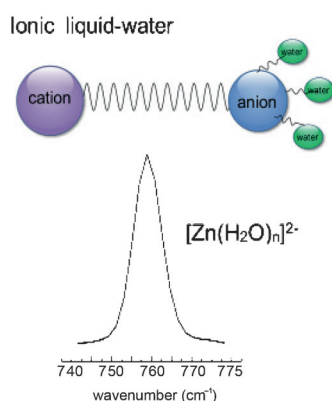
- [1] a) M. Armand, F. Endres, D. R. MacFarlane, H. Ohno, B. Scrosati, *Nat. Mater.* **2009**, *8*, 621–629; b) B. M. Quinn, Z. F. Ding, R. Moulton, A. J. Bard, *Langmuir* **2002**, *18*, 1734–1742; c) T. Sato, G. Masuda, K. Takagi, *Electrochim. Acta* **2004**, *49*, 3603–3611; d) D. Wei, A. Ivaska, *Anal. Chim. Acta* **2008**, *607*, 126–135; e) M. J. Earle, K. R. Seddon, *Pure Appl. Chem.* **2000**, *72*, 1391–1398; f) R. D. Rogers, K. R. Seddon, *Science* **2003**, *302*, 792–793; g) T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2083.
- [2] a) M. Xu, D. G. Ivey, W. Qu, Z. Xie, *J. Power Sources* **2014**, *252*, 327–332; b) T. J. Simons, P. C. Howlett, A. A. J. Torriero, D. R. MacFarlane, M. For-

- syth, *J. Phys. Chem. C* **2013**, *117*, 2662–2669; c) T. J. Simons, A. A. J. Torriero, P. C. Howlett, D. R. MacFarlane, M. Forsyth, *Electrochim. Commun.* **2012**, *18*, 119–122; d) T. J. Simons, P. M. Bayley, Z. Zhang, P. C. Howlett, D. R. MacFarlane, L. A. Madsen, M. Forsyth, *J. Phys. Chem. B* **2014**, *118*, 4895–4905; e) M. Xu, D. G. Ivey, Z. Xie, W. Qu, E. Dy, *Electrochim. Acta* **2013**, *97*, 289–295; f) Z. Liu, S. Zein El Abedin, F. Endres, *Electrochim. Acta* **2013**, *89*, 635–643; g) W. R. Pitner, C. L. Hussey, *J. Electrochem. Soc.* **1997**, *144*, 3095–3103; h) Y.-F. Lin, I.-W. Sun, *Electrochim. Acta* **1999**, *44*, 2771–2777; i) M.-J. Deng, P.-C. Lin, J.-K. Chang, J.-M. Chen, K.-T. Lu, *Electrochim. Acta* **2011**, *56*, 6071–6077.
- [3] a) A. A. Niazi, B. D. Rabideau, A. E. Ismail, *J. Phys. Chem. B* **2013**, *117*, 1378–1388; b) V. L. Martins, B. G. Nicolau, S. M. Urahata, M. C. C. Ribeiro, R. M. Torresi, *J. Phys. Chem. B* **2013**, *117*, 8782–8792; c) Y. Jeon, J. Sung, D. Kim, C. Seo, H. Cheong, Y. Ouchi, R. Ozawa, H. Hamaguchi, *J. Phys. Chem. B* **2008**, *112*, 923–928; d) L. Cammarata, S. G. Kazarian, P. A. Salter, T. Welton, *Phys. Chem. Chem. Phys.* **2001**, *3*, 5192–5200; e) C. Spickermann, J. Thar, S. B. C. Lehmann, S. Zahn, J. Hunger, R. Buchner, P. A. Hunt, T. Welton, B. Kirchner, *J. Chem. Phys.* **2008**, *129*, 104505.
- [4] a) J.-J. Max, C. Chapados, *J. Chem. Phys.* **2010**, *133*, 164509; b) S. Gopalakrishnan, D. Liu, H. C. Allen, M. Kuo, M. J. Shultz, *Chem. Rev.* **2006**, *106*, 1155–1175; c) J.-B. Brubach, A. Mermet, A. Filabozzi, A. Gerschel, P. Roy, *J. Chem. Phys.* **2005**, *122*, 184509; d) S. Y. Venyaminov, F. G. Prendergast, *Anal. Biochem.* **1997**, *248*, 234–245; e) W. B. Fischer, A. Fedorowicz, A. Koll, *Phys. Chem. Chem. Phys.* **2001**, *3*, 4228–4234.
- [5] a) T. Köddermann, C. Wertz, A. Heintz, R. Ludwig, *ChemPhysChem* **2006**, *7*, 1944–1949; b) Y.-Z. Zheng, N.-N. Wang, J.-J. Luo, Y. Zhou, Z.-W. Yu, *Phys. Chem. Chem. Phys.* **2013**, *15*, 18055–18064.
- [6] P. Stange, K. Fumino, R. Ludwig, *Angew. Chem. Int. Ed.* **2013**, *52*, 2990–2994; *Angew. Chem.* **2013**, *125*, 3064–3068.
- [7] Y. Umabayashi, T. Fujimori, T. Sukizaki, M. Asada, K. Fujii, R. Kanzaki, S.-I. Ishiguro, *J. Phys. Chem. A* **2005**, *109*, 8976–8982.
- [8] a) J.-M. Andanson, A. Baiker, *J. Phys. Chem. C* **2013**, *117*, 12210–12217; b) D. H. Johnston, D. F. Shriver, *Inorg. Chem.* **1993**, *32*, 1045–1047.
- [9] S. Tsuzuki, H. Tokuda, K. Hayamizu, M. Watanabe, *J. Phys. Chem. B* **2005**, *109*, 16474–16481.
- [10] a) K. Fumino, S. Reimann, R. Ludwig, *Phys. Chem. Chem. Phys.* **2014**, *16*, 21903–21929; b) K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2008**, *47*, 3830–3834; *Angew. Chem.* **2008**, *120*, 3890–3894; c) K. Fumino, K. Wittler, R. Ludwig, *J. Phys. Chem. B* **2012**, *116*, 9507–9511; d) A. Wulf, K. Fumino, R. Ludwig, *Angew. Chem. Int. Ed.* **2010**, *49*, 449–453; *Angew. Chem.* **2010**, *122*, 459–463; e) T. Köddermann, K. Fumino, R. Ludwig, J. N. Canongia Lopes, A. A. H. Pádua, *ChemPhysChem* **2009**, *10*, 1181–1186; f) K. Fumino, A. Wulf, R. Ludwig, *Phys. Chem. Chem. Phys.* **2009**, *11*, 8790–8794; g) K. Fumino, A. Wulf, R. Ludwig, *Angew. Chem. Int. Ed.* **2009**, *48*, 3184–3186; *Angew. Chem.* **2009**, *121*, 3230–3233.
- [11] a) Y. Umabayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanzaki, M. Takeuchi, S.-I. Ishiguro, *J. Phys. Chem. B* **2007**, *111*, 13028–13032; b) G. A. Giffin, A. Moretti, S. Jeong, S. Passerini, *J. Phys. Chem. C* **2014**, *118*, 9966–9973; c) J. Kiefer, J. Fries, A. Leipertz, *Appl. Spectrosc.* **2007**, *61*, 1306–1311.
- [12] C. M. Burba, N. M. Rocher, R. Frech, *J. Phys. Chem. B* **2009**, *113*, 11453–11458.
- [13] M. Hartmann, T. Clark, R. van Eldik, *J. Am. Chem. Soc.* **1997**, *119*, 7843–7850.
- [14] a) M. Brehm, H. Weber, A. S. Pensado, A. Stark, B. Kirchner, *Phys. Chem. Chem. Phys.* **2012**, *14*, 5030–5044; b) S. Zahn, K. Wendler, L. Delle Site, B. Kirchner, *Phys. Chem. Chem. Phys.* **2011**, *13*, 15083–15093.

Received: November 23, 2014

Published online on ■■■■, 2015

Solvation in changing phases: The structure of 1-ethyl-3-methylimidazolium trifluoromethylsulfonate changes from ionic-liquid-like to water-like solutions upon the addition of water. The solvation of zinc ions in ionic liquid and ionic liquid–water mixtures is also different due to the changing interactions between cations, anions, and water.



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Raman and FTIR Spectroscopic Studies of 1-Ethyl-3-methylimidazolium Trifluoromethylsulfonate, its Mixtures with Water and the Solvation of Zinc Ions