Ion Pairs

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Ion Speciation of Protic Ionic Liquids in Water: Transition from Contact to Solvent-Separated Ion Pairs**

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Ionic liquids (ILs) are receiving increasing amount of interest because of their potential applications, including novel synthesis, electrolyte devices, photochemical cells, separation, and catalysis.[1–4] One of the important features affecting the properties of ionic liquids is ion pair formation. Ion pairing in solution is the result of a subtle balance between ion–solvent interaction and cation–anion interaction.[5–9] This is in particular true for ionic liquids where a mix of Coulomb forces, hydrogen bonds, and dispersion forces between the cation and anion leads to unique macroscopic properties of these Coulomb fluids.[10–12] If the anion–cation interaction is sufficiently strong, contact ion pairs (CIPs) are the dominant structures in the mixtures. If the ion–solvent interaction is stronger, solvent-shared and solvent-separated ion pairs (SIPs) prevail.[5]

For aprotic ionic liquids, it is well known that the addition of hydrophobic organic solvents, such as chloroform or benzene, leads to the disruption of the Coulomb network.[3,13] In the highly diluted systems neutral aggregates and CIPs are formed. The electrical conductivity strongly decreases owing to these neutral configurations of ions.[13] Mixtures of the aprotic ionic liquid [$C_n$mim][BF_4] with water have also been reported.[14–16] The main focus was on low water concentrations. Strong anion–water interactions were observed, whereas the intermolecular anion–cation interaction essentially remained unperturbed.[14,15]

The situation for protic ionic liquids (PILs) can be completely different. A key feature in PILs is the possible proton transfer from the Brønsted acid to the Brønsted base, leading to the formation of proton acceptor and donor sites and possible hydrogen bonding.[17–24] The typical definition of distinguishing ion pairs from complexes does not hold here. CIPs in protic ionic liquids are held together by long-range, non-directional electrostatic forces as well as short-range, spatially directed donor–acceptor-type interactions.[5] Thus, CIPs can already exist in the neat protic ionic liquid. This is in particular true for PILs that include trialkylammonium as the cation. Beside Coulomb interactions, a strong and directional hydrogen bond between the NH of cation and the oxygen of the anion provides strongly bound CIPs for the pure Coulomb fluid.[23] Density functional theory (DFT) calculations showed that the interaction energy is between 300 and 500 kJ mol^{-1} depending on the specific nature of the cation and anion.[25–31] In recent studies we could demonstrate that the cation–anion interaction in these protic ionic liquids can be detected by far-infrared (FIR) spectroscopy.[32–37] Low vibrational modes between 100 and 180 cm^{-1} could be clearly assigned to the anion–cation interaction. Frequency shifts could be referred to the interaction strength of the anion and/or to inductive effects owing to the variation of the alkyl chain length at the cation.[23] For studying the transition from CIPs to SIPs, strongly polar solvents such as water are needed to overcome the strong cation–anion interaction. Compared to aprotic ILs such as [$C_n$mim][BF_4] the trialkylammonium containing PILs provide distinct low vibrational modes, which can be used as sensitive probes for the change of the anion–cation interaction upon dilution with water.[15,23]

The purpose of the present investigation is to determine how many water molecules are needed to disrupt these strongly bound CIPs and how the transition from CIPs to SIPs occurs. These points can be properly addressed by using well-chosen PILs and measuring difference spectra by FIR spectroscopy and also by calculating energies and frequencies for PIL/water aggregates by applying density functional theory (DFT) methods. For the PILs under investigation, the “magic number” of water molecules needed for the transition from CIPs to SIPs is four. The transition can be explained on mainly enthalpic grounds owing to the strong water affinity to the anion and substantial cooperative effects among the water molecules themselves. Overall, the experiments and calculations reported herein shed new light on the ion speciation of protic ionic liquids in water at molecular level.

FIR spectroscopy in combination with DFT calculations is an extremely powerful method for studying ion speciation of protic ionic liquids in aqueous solutions. The main focus is studying the transfer from CIPs to SIPs in these Coulomb fluids. This is demonstrated for aqueous solutions of the protic ionic liquid triethylammonium methylsulfonate [Et_3NH][CH_3SO_3] (TEAMS). The water concentrations were 50, 70, 80, and 90 mol%. The spectra of pure TEAMS and pure water are shown in the Supporting Information, S1. Both are used as background spectra for eliminating the contributions of the pure ionic and molecular liquids, respectively. As discussed in earlier studies, the vibrational band at 150 cm^{-1} in the PIL spectrum can be clearly assigned to the cation–anion

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interaction along the $^{+}N-H\cdots O^{-}$ bond.[23] The main feature in the water spectrum is the broad vibrational band at around 200 cm^{-1}, which is usually assigned to the intermolecular interaction within the extended hydrogen bonding network of water.[38–42] The difference spectra of the TEAMS–water mixtures measured versus the pure TEAMS and the pure water contributions are shown in Figure 1. These difference

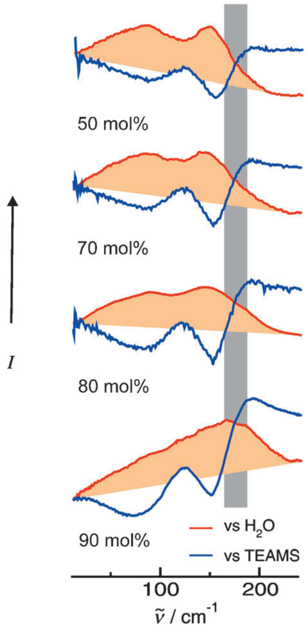

Figure 1. Far-infrared (FIR) difference spectra of the mixtures of triethylammonium methylsulfonate $[Et_3NH][CH_3SO_3]$ (TEAMS) with water. The spectra were obtained by subtracting the pure water (red line) and the pure TEAMS (blue line) contributions as background. The vibrational band at about 150 cm^{-1} in both difference spectra could be assigned to remaining or missing contributions from $^{+}N-H\cdots CH_3SO_3^{-}$ intermolecular interactions. With increasing water concentration, this vibrational mode disappears and a new maximum occurs at about 180 cm^{-1} above 80 mol% of water (indicated by the gray bar).

spectra could only be achieved by using a very small path length of 6 μm. The key idea of these measurements is discussed using the difference spectra of the 50 mol% PIL–water mixture as an example. If the pure water spectrum is subtracted from the mixture spectrum, positive contributions can stem from vibrational modes of the remaining internal TEAMS or new TEAMS–water interactions. Negative intensities can be attributed to missing pure water contributions. In contrast, if the pure TEAMS spectrum is subtracted from the mixture spectrum, positive contributions result from water–water or TEAMS–water interactions, whereas negative intensities can be referred to minor TEAMS concentration.

From both difference spectra of the 50 mol% mixture, it can be concluded that CIPs are fully present. This is indicated by nearly similar positive and negative vibrational signatures which are typical for pure TEAMS. Obviously the TEAMS/water vibrational modes occur in the same frequency range like those of pure water. If we now constantly increase the water concentration from 50 to 90 mol%, the difference spectra change characteristically. In the difference spectra where the pure water is subtracted, the typical vibrational mode describing the cation–anion interaction of the CIPs (150 cm^{-1}) disappears. At the same time, a new intensity maximum occurs at around 180 cm^{-1}. In the other difference spectra, the negative bands of the TEAMS are more pronounced. Obviously CIPs are significantly decreased in the mixtures with increasing water concentration. Simultaneously the TEAMS–water contributions increase in intensity. The intersection point for both difference spectra is found at the same frequency (around 180 cm^{-1}) and its intensity rises with increasing water concentration. These contributions cannot stem from anion/water interactions, which are present at about 200 cm^{-1}. Moreover, at these concentrations all proton acceptor sites of the anion are occupied. We propose that, owing to the transition from CIPs to SIPs in particular above 80 mol% water, cation–water interactions by $N-H\cdots O$(water) appear and contribute to the difference spectra. This interpretation of the difference spectra is supported by DFT calculations of an isolated contact ion pair and hydrated contact and solvent-separated ion pairs of TEAMS (Figure 2; see also the Supporting Information, S2).

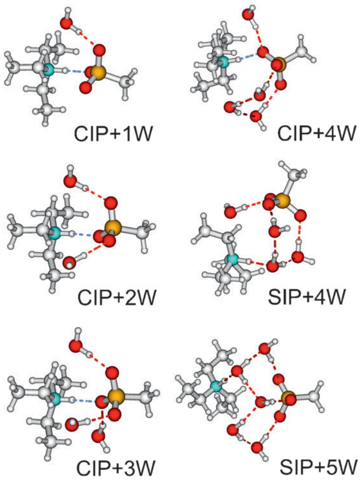

Figure 2. Density-functional-calculated clusters of TEAMS ion pairs and different numbers of water molecules representing 50, 66, 75, 80, and 83 mol% water concentration. Starting with the configurations including four water molecules (4W), the solvent-separated ion pairs (SIP) are enthalpically favored over the contact ion pairs (CIP). The intermolecular interaction between cation and anion ($^{+}N-H\cdots$anion, blue dotted line) is replaced by the intermolecular interaction between the cation and water ($^{+}N-H\cdots$water, red dotted line). In these SIP configurations (for example, SIP + 5W), one additional H-bond can be formed owing to the coordination ability of the water molecules.

The corresponding structural and energetic properties of these configurations are presented in Figure 3 and Figure 4. The 50 mol% PIL–water mixture can be represented by the calculated structure CIP + 1W. The water molecule interacts with the contact ion pair by one of the free proton acceptor sites of the methylsulfonate anion. This is well-known from mid-IR measurements of trace amounts of water in ILs. Usually single water molecules form two hydrogen bonds to the anions in 1:2 complexes.[43–46] In the structure CIP + 1W, the contact ion pair is still intact but the weakening interaction is expressed by the shortening of the intramolecular N–H bond and the lengthening of the intermolecular N–H···O(anion) bond (Figure 3). This behavior is also reflected in shifts to higher frequencies $\tilde{\nu}_{NH}$ for the intramolecular vibrational mode of the N–H bond of the cation and shifts to lower frequencies $\nu_{NH\cdots O(anion)}$ for the intermolecular cation–anion interaction, respectively.

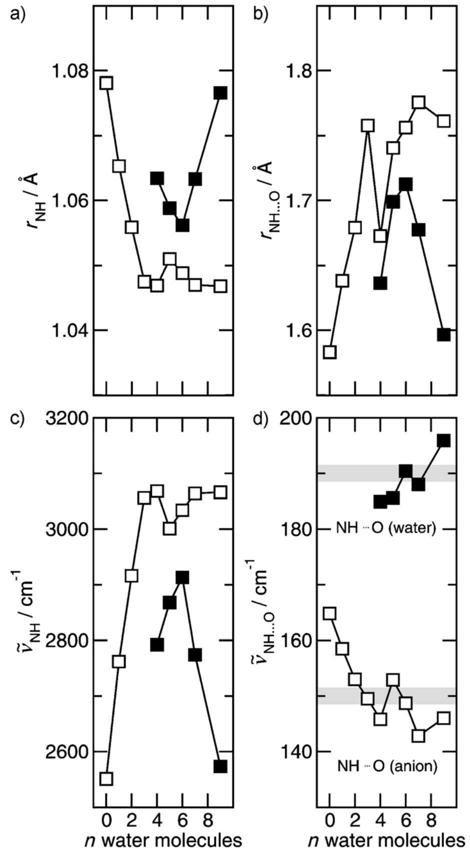

Figure 3. DFT calculated a) intramolecular bonds r_{NH}, b) intermolecular bonds $r_{N\text{-}H\cdots O(anion)}$ and $r_{N\text{-}H\cdots O(water)}$, c) intramolecular stretching frequencies ν_{NH}, and d) intermolecular frequencies $\nu_{NH\cdots O(anion)}$ and of $\nu_{NH\cdots O(water)}$ for clusters of TEAMS ion pairs and different numbers of water molecules representing water concentrations between 50 and 90 mol %. The properties for the SIPs are indicated by the filled symbols.

The addition of a second water molecule leads to a 66 mol % water–TEAMS mixture. This second water molecule also prefers to interact with the anion by the second available oxygen acceptor site. The contact ion pair is still stable but further weakened, as reflected in the structural and vibrational properties (Figure 3). The anion transfers more charge into the O–H antibonding orbitals of the two water molecules and less charge into the N–H antibonding orbital of the cation, leading to decreased interaction between anion and cation (Supporting Information, S3, S4).[47,48] If a third water molecule is added, it competes with the triethylammonium cation for one of the anion oxygen atoms as shown for the configuration CIP + 3W. The CIP is still present but is significantly more weakly bound, as indicated by its structural and vibrational signatures (Figure 3). Configurations including three water molecules with one shared water molecule in a solvent-separated ion pair are not stable in the DFT calculations. However, this situation changes upon adding a forth water molecule, representing a 80 mol % water–TEAMS mixture. Now the SIP is energetically favored over the contact ion pair configuration.

In Figure 4, the calculated total binding energies for all of the configurations are shown. For the configuration with four and more water molecules, the SIPs are more favorable in energy than the CIP structures. The reason is obvious: the SIP configurations provide better H-bond possibilities, and more of the OH proton donors of water can be involved in H-bonded structural motifs. This enthalpic preference of 20–30 kJ mol^{-1} is present for all of the configurations, including four or more water molecules (Figure 4). How do these structural and energetically arguments fit to the interpretation of the measured difference FIR spectra? The DFT calculated low vibrational modes support the idea of a transition from CIPs to SIPs. The calculated frequencies of anion–cation (N–H···O) interaction in the CIPs occur at about 150 cm^{-1}, which is in agreement with the measured spectra (Figure 3 d).[23] The water–anion interactions are represented by vibrational modes above 200 cm^{-1}; these vibrational modes replace the water/water contributions. However, they cannot further increase for water concentrations higher than 80 mol % because all of the proton-acceptor positions of the methylsulfonate anion are occupied. The frequencies describing the cation–water interaction by N–H···O(anion) can only show up for SIPs. They are calculated to lie between 180 and 190 cm^{-1}, which is just in the frequency range where the intensity of the difference spectra is dramatically increased for the 90 mol % mixture. That the vibrational modes of

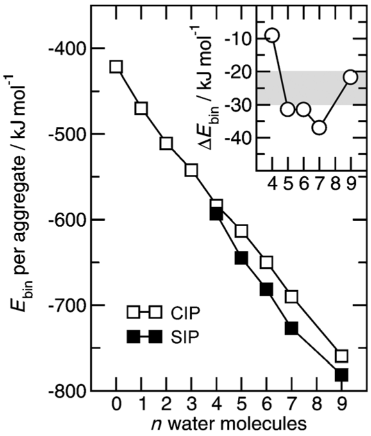

Figure 4. Total binding energies for clusters of TEAMS ion pairs and different numbers of water molecules representing water concentrations between 50 and 90 mol %. It is shown that the solvent-separated ion pairs (SIP) are energetically favored over the contact ion pair (CIP) configurations including four or more water molecules (filled symbols). The energies are lower by about 20–30 kJ mol^{-1} owing to the formation of one additional H-bond in the SIPs (see inset).

cation–water interactions occur at higher frequencies than those of the cation–anion interaction is due to smaller reduced masses rather than a result of stronger interaction.

In summary, we could show that FIR spectroscopy is a powerful method for studying intermolecular interaction in the condensed phase. As model systems, PIL–water mixtures were chosen for studying ion speciation. Vibrational bands representing the cation–anion interaction can be distinguished from those resulting from anion/water or cation–water interactions. Changing difference spectra in the far infrared region indicate the transition from CIPs to SIPs with increasing water concentration; a minimum of four water molecules are needed to initiate this process. The SIPs are enthalpically favored over the CIPs owing to increasing H-bond possibilities and cooperative effects. This interpretation is fully supported by calculated structures, energies, and frequencies of hydrated PIL ion pairs. Of course, the transition from contact to solvent-separated states strongly depends on the interaction power of the PIL anion. If the anion $CH_3SO_3^-$ is replaced by $CF_3SO_3^-$ the cation–anion interaction is weaker and the transition process may begin at lower water concentrations. Such studies are currently ongoing in our laboratories.

Experimental Section

The FTIR measurements were performed with a Bruker Vertex 70 FTIR spectrometer equipped with an extension for measurements in the FIR region that consists a multilayer mylar beam splitter, a room temperature DLATGS detector with preamplifier, and polyethylene (PE) windows for the 6 μm internal optical path. 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^{-1} (0.3 and 20.3 THz).

The frequencies of the configurations have been calculated at the DFT level B3LYP, using the internal stored 6-31+G* basis set of the Gaussian 09 program.[49] The binding energies have been corrected for the basis set superposition error (BSSE).[50] Different conformers were calculated for all of the structures, but only the best in energy have been considered.

Further details of the theoretical and experimental approaches are given in the Supporting Information.

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