DOI: 10.1002/anie.201411509

Controlling the Subtle Energy Balance in Protic Ionic Liquids: Dispersion Forces Compete with Hydrogen Bonds**

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Abstract: *The properties of ionic liquids are determined by the energy-balance between Coulomb-interaction, hydrogen-bonding, and dispersion forces. Out of a set of protic ionic liquids (PILs), including trialkylammonium cations and methylsulfonate and triflate anions we could detect the transfer from hydrogen-bonding to dispersion-dominated interaction between cation and anion in the PIL* $[(C_6H_{13})_3NH][CF_3SO_3]$. *The characteristic vibrational features for both ion-pair species can be detected and assigned in the far-infrared spectra. Our approach gives direct access to the relative strength of hydrogen-bonding and dispersion forces in a Coulomb-dominated system. Dispersion-corrected density functional theory (DFT) calculations support the experimental findings. The dispersion forces could be quantified to contribute about 2.3 kJ mol*$^{-1}$ *per additional methylene group in the alkyl chains of the ammonium cation.*

Investigating noncovalent interactions in liquids is still a challenge.[1–5] This is in particular true for ionic liquids, where a subtle energy balance between Coulomb interaction, hydrogen bonding, and dispersion forces results in unique properties.[4,5] Although the Coulomb interaction is the dominant intermolecular interaction, hydrogen-bonding and dispersion forces may become crucial for the structure and dynamics of ionic liquids.[6,7] We could show recently that local and directional hydrogen bonding in aprotic ionic liquids can result in more fluid rather than more viscous liquids.[7] For thermodynamic properties, such as enthalpies of vaporization, it was observed that they increase nearly linearly with the increasing alkyl-chain length of the imidazolium cation. A comparison with n-alkanes and n-alcohols showed that the linear increase in intermolecular interaction strength with each methylene group results from dispersion forces only.[8] There is no doubt that both, H-bonding and dispersion interactions are of importance for IL properties. However, the dissection and quantification of the different noncovalent interactions is still a difficult endeavor. Hydrogen bonding is somewhat easier to analyze, because H-bonds are both short-ranged and highly directional. The crucial role of dispersion forces in ILs is currently studied intensively.[9–14] Grimme and Kirchner could show that London dispersion interactions contribute significantly to the overall interaction energy in aprotic ionic liquids.[10] As benchmark they used accurate coupled-cluster methods. Izgorodina et al. showed that calculated energies are closely related to measured melting points if dispersion forces are taken into account.[14] However, there is no quantification of dispersion forces in ionic liquids reported from experiment. Thus it is the purpose of the present work to quantify those noncovalent interactions and to describe the competition between hydrogen bonding and dispersion-forces in a Coulomb-dominated fluid. In particular, it is shown that dispersion forces can outbalance hydrogen bonding with increasing temperature. The experimental results from far-infrared spectroscopy are supported by DFT calculations with and without taking explicitly dispersions forces into account.[10,15–17]

We measured the FIR spectra for triethylammonium methylsulfonate $[(C_2H_5)_3NH][CH_3SO_3]$ (TEAMS), triethylammonium triflate $[(C_2H_5)_3NH][CF_3SO_3]$ (TEATF), trihexylammonium methylsulfonate $[(C_6H_{13})_3NH][CH_3SO_3]$ (THAMS), and trihexylammonium triflate $[(C_6H_{13})_3NH][CF_3SO_3]$ (THATF), in the low-frequency range between 10 and 200 cm^{-1} as shown in Figure 1. The idea for choosing this set of PILs is simple: From TEAMS to TEATF, we weaken the H-bond interaction strength by replacing the stronger interacting anion with a weaker interacting anion. By changing from TEAMS to THAMS, and from TEATF and THATF, we increase the alkyl-chain lengths, resulting in a potentially enhanced dispersion interaction with the "alkane-side" of the ammonium cation. At low temperatures, all spectra show similar vibrational features. The origin of the vibrational band at about 70 cm^{-1} is not well described. Usually, it is attributed to cage rattling of interacting ions and bending modes of directional intermolecular interaction.[4,5] In contrast, the distinct vibrational bands at 129 cm^{-1} for TEATF and 149 cm^{-1} TEAMS could be assigned to local and directional hydrogen bonding along $^+$N–H $\cdot\cdot$A$^-$.[18–20] Owing to the inductive effect of the fluorine atoms within the anion the cation–anion interaction is weakened, indicated by a 20 cm^{-1} shift to lower wavenumbers for TEATF as outlined above.[18] The position and the absorbance of this vibrational band is

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[**] This work has been supported by the DFG Priority Programme SPP 1191 "Ionic Liquids" and by the DFG Collaborative Research Center SFB 652 "Strong correlations and collective effects in radiation fields: Coulomb systems, clusters and particles"

Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/anie.201411509.

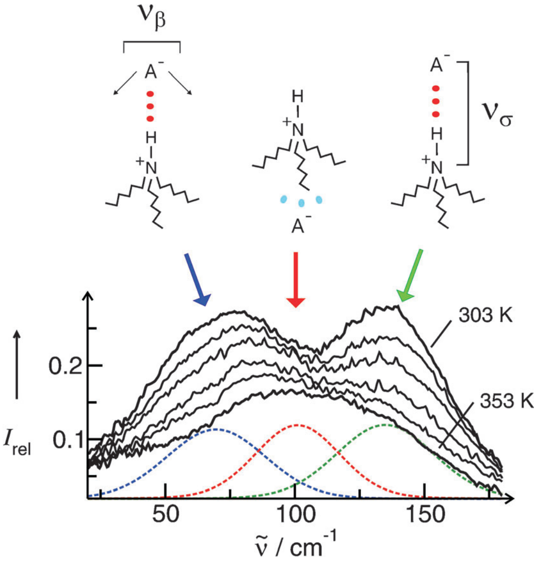

Figure 1. Far-infrared spectra of the pure protic ionic liquid [(C$_6$H$_{13}$)$_3$NH][CF$_3$SO$_3$] (THATF) recorded as a function of temperature in 10 K steps. At 303 K, the low-frequency spectrum is dominated by vibrational bands at 70 cm^{-1} and 130 cm^{-1} which could be assigned to the bending (ν_β) and stretching (ν_σ) modes of the hydrogen bond between cation and anion along the $^{+}$N–H···A^{-} bond. With increasing temperatures the intensities of these bands decrease in favor of a band at 100 cm^{-1} indicating ion pairs now dominated by dispersion forces with the hexyl groups of the trihexylammonium cation. As an example, the corresponding deconvoluted vibrational bands are shown for the spectrum measured at highest temperature (353 K). The deconvoluted spectra for all temperatures are given in Figure SI2.

sensitive for the interaction strength between the PIL constituents. In the far-infrared spectra of TEAMS, TEATF, and THAMS the spectral signatures do not change characteristically with temperature between 303 and 353 K (see Figure SI1 in the Supporting Information). Clearly, the hydrogen bonds along $^{+}$N–H···A^{-} are still intact. The situation changes for [(C$_6$H$_{13}$)$_3$NH][CF$_3$SO$_3$], as shown in Figure 1. With increasing temperature, the vibrational bands at 70 cm^{-1} and 130 cm^{-1} decrease whereas a new band at about 100 cm^{-1} increases in intensity. Clearly, the H-bonded ion pairs, indicated by the vibrational bands at 70 and 130 cm^{-1}, are replaced by another species with increasing temperature. Of course, in such a simple PIL only two states are possible: Either the polar site of the triflate anion (the SO$_3$-group) interacts with the N–H group by forming an H-bond, or it interacts with the alkyl groups by dispersion forces. Both states are depicted in Figure 1. All spectra could be deconvoluted into three distinct contributions at 70, 100, and 130 cm^{-1}. Supported by DFT calculated configurations, these vibrational bands could be assigned to the bending and stretching modes of the $^{+}$N–H···O$_3$S^{-} hydrogen bond which dominates at low temperatures, and a vibrational band that describes the interaction between the SO$_3$ group and the hexyl groups of the anion and cation.

The proper deconvolution of the temperature-dependent FIR spectra allows a quantitative description of the transition from the H-bonded to the dispersion-interacting species. We calculated the intensity ratios of the vibrational bands at 130 cm^{-1} and 100 cm^{-1}. Assuming that the intensities of the vibrational bands for both species (I_{130} and I_{100}) change in the same way with temperature, we could evaluate the equilibrium constants as a function of temperature. The van't Hoff analysis was obtained by plotting the logarithm of these ratios (filled black symbols in Figure 2) versus the inverse temperature. The slope of this plot yields the difference in average energy between the H-bonded and the dispersion-governed configurations. The resulting van't Hoff slope indicates that the H-bonded ion pairs are favored in energy over the dispersion-interaction dominated by about 34.3 kJ mol^{-1}. However, at higher temperatures, the dispersion interaction is able to compete with the H-bond strength, indicated by a nearly 1:1 ratio of both configurations. Additionally, we repeated the whole procedure for the ratios of the vibrational modes at 70 cm^{-1} and 100 cm^{-1}. The resulting intensity ratios I_{70}/I_{100} (filled red symbols in Figure 2) lead to nearly the same van't Hoff plot as before indicating that the vibrational bands at 70 cm^{-1} and 130 cm^{-1} are describing strongly correlated vibrational motion. In this case, the intensity of the vibrational mode at 70 cm^{-1} can be assigned to a large extent to the bending mode of the H-bond, as suggested by DFT calculations. This assignment has been made before and can be confirmed by this study.[4,5] In principle, we can now study the competition between hydrogen bonding and dispersion forces in a Coulomb-dominated system.

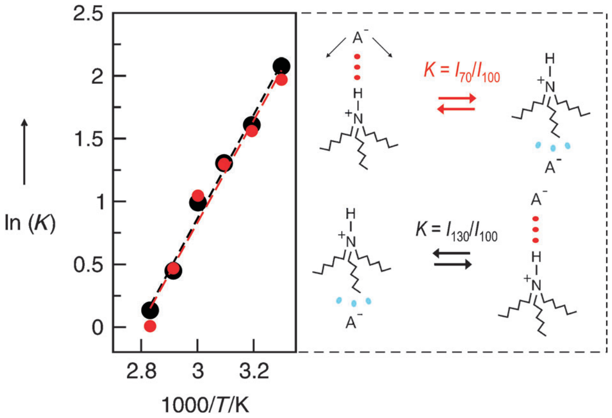

Figure 2. Van t'Hoff plots for the equilibrium constants K obtained from the intensity ratios I_{130}/I_{100} (black circles) and I_{70}/I_{100} (red circles) of the corresponding vibrational bands. The related equilibrium between the two ion-pair configurations is shown schematically.

We additionally show that the experimental findings strongly support the necessity of dispersion-corrected DFT methods (Grimme's DFT-D3) for properly describing intermolecular interactions, even in Coulomb-dominated fluids.[10,15,16,21] We have computed interaction energies for H-bonded and dispersion dominated ion-pair configurations of THATF (see Figure 1 and Figure 2). Because the alkyl groups result in different isomers, we have calculated energies for various species of each type (see Supporting Information).

The differences of the average energies for H-bonded and dispersion-dominated configurations result in 58 kJ mol^{-1} neglecting the dispersion correction or 34 kJ mol^{-1} taking dispersion correction into account. Without using the D3-correction, the dispersion interaction is strongly underestimated, and the H-bonded species dominate, in contrast to our experimental results. If dispersion-forces are considered, we obtained nearly quantitative agreement (34 kJ mol^{-1}) for the conversion energy between the two types of ion pairs, as shown in Figure 3 a. That we relate ΔH to ΔE is justified because the volume for both ion-pair configurations is similar.

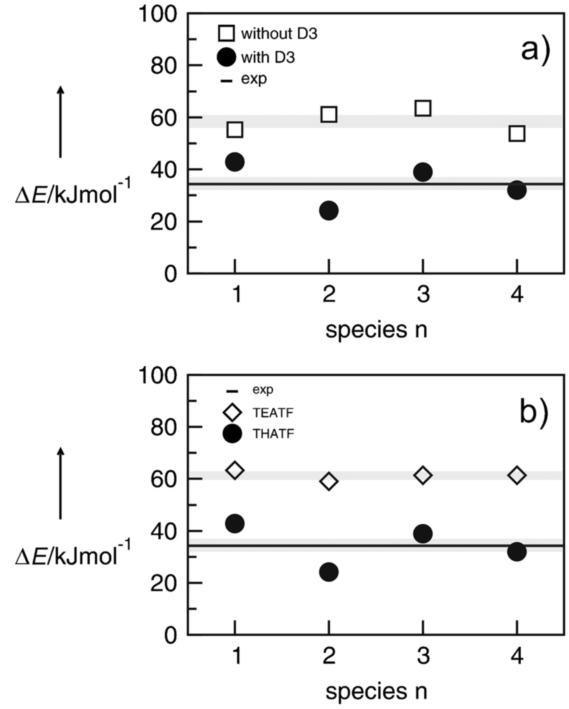

Figure 3. DFT-calculated energies of transformation from the H-bonded to the dispersion interacting ion pairs. a) ΔE for THATF species calculated with dispersion correction (filled circles) and without (open squares) dispersion correction. b) ΔE for THATF (filled circles) and TEATF (open diamonds) species, both calculated with D3 correction.[15] In both cases the experimental value is shown by the solid line.

The temperature-dependent FIR spectra clearly show that the transition from one species to the other takes place for THATF, but not for TEATF. Because the triflate anion is the same in both PILs, this effect can only result from a significant change in the dispersion interaction. We now calculated both types of ion pairs for THATF and TEATF by considering dispersion forces throughout. The result is shown in Figure 3 b: Whereas for THATF about 34 kJ mol^{-1} are required for the conversion, it needs approximately 61 kJ mol^{-1} in the case of TEATF. Assuming that the H-bond strength is similar for both PILs, the energy difference of about 27 kJ mol^{-1} can be referred to an increasing dispersion interaction arising from the longer alkyl-chain lengths in THATF than in TEATF. In total, this energy difference stems from an enhanced interaction with the twelve additional methylene groups, resulting in an increment of about 2.3 kJ mol^{-1} for each CH_2 group.

We could show that FIR spectroscopy is sufficiently sensitive to discriminate between different modes of non-covalent interaction in ionic liquids. Low-frequency vibrational bands for the protic ionic liquid $[(C_6H_{13})_3NH][CF_3SO_3]$ can be assigned to ion pairs which are dominantly interacting either by hydrogen bonds or by dispersion forces. The H-bonded species ($^{+}N{-}H\cdots O_3S^{-}$) are dominant at low temperatures, and are replaced by the dispersion-interacting species ($^{+}N(C_6H_{13})_3\cdots O_3S^{-}$) with increasing temperature. The transition between the two ion-pair species requires about 34 kJ mol^{-1}, as obtained from a van't Hoff analysis. A comparison with DFT-calculated configurations shows that dispersion-corrected methods are needed to explain these experimental results. For the first time we could study the competition between hydrogen bonding and dispersion forces in a Coulomb-dominated ionic liquid.

Received: November 28, 2014

Keywords: DFT calculations · dispersion forces · FIR spectroscopy · hydrogen bonding · ionic liquids

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