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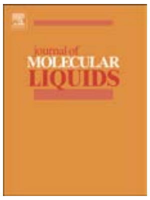

Review

Analyzing the interaction energies between cation and anion in ionic liquids: The subtle balance between Coulomb forces and hydrogen bonding[☆]

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ABSTRACT

Potential applications of ionic liquids depend on the properties of this class of liquid material. To a large extent the structure and properties of these Coulomb systems are determined by the intermolecular interactions among anions and cations. In particular the subtle balance between Coulomb forces, hydrogen bonds and dispersion forces is of great importance for the understanding of ionic liquids. All these issues are addressed by using a suitable combination of experimental and theoretical methods including specially synthesized imidazolium-based ionic liquids, far infrared spectroscopy (FIR) and density functional theory (DFT) calculations. The key statement is that although ionic liquids consist solely of anions and cations and Coulomb forces are the dominating interaction, a local and directional interaction such as hydrogen bonding has significant influence on the structure and properties of ionic liquids. In this review we mainly summarize the results we achieved within our project of the priority programme "Ionic Liquids" (SPP 1191), which has been funded by the German Science Foundation (DFG) between 2008 and 2012.

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Contents

1. Introduction

Knowledge of intermolecular forces is a requisite for understanding material properties. They determine whether matter sticks together, gases condense to liquids or liquids freeze to solids. To study these forces is in particular interesting for ionic liquids [1–4]. Although the structure and properties of these fluid materials are determined to a large extent by the Coulomb forces, hydrogen bonding and dispersion forces can play a crucial role for the understanding of their unique properties. The strong anion–cation interaction in these Coulomb fluids is reflected in the extremely low vapor pressures and high enthalpies of vaporization [5–12]. Among others these properties make them attractive for science and technology.

The measurement of the interaction between cation and anion in ionic liquids is still a challenge. In principle these interactions can be studied by experimental techniques which cover the frequency

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range of interest. Meanwhile there is a substantial number of spectra available covering the frequency range of interest between 1 and 300 cm^{-1}, corresponding to 0.03 and 9 THz. The palette of spectroscopic methods includes optical femtosecond Raman-induced Kerr-effect spectroscopy (RIKES) [13–36], terahertz time-domain spectroscopy (THz-TDS) [36–39], as well as conventional steady-state spectroscopic methods such as Raman spectroscopy [40–43], and far infrared spectroscopy (FIR) [43–51]. This experimental work has been accompanied by numerous theoretical studies including ab initio calculations on ion-pairs or ion-pair aggregates, classical molecular dynamics simulations as well as Car–Parrinello molecular dynamics simulations [52–75]. In most of the cases only a combination of experimental and theoretical methods provides a reasonable spectral assignment and reliable interpretation of the low frequency spectra.

In this review article we would like to summarize some of our recent results about the cation–anion interactions in aprotic and protic ionic liquids and their relevance for the properties of these unique liquid materials. In particular, we would like to emphasize that the interaction energies in aprotic and protic ionic liquids can be dissected into Coulomb forces, hydrogen bonding and dispersion forces. This is clearly shown by using a combination of experimental and theoretical methods. This review article is organized as follows: first we demonstrate by FIR that the vibrational bands in the low frequency range can be clearly assigned to anion–cation interactions in aprotic ionic liquids (APILs). Further on we show for the same family of APILs that the interaction strength between the ions can be controlled by a set of anions showing characteristically different interaction potential. We then illustrate that the interaction strength is significantly determined by hydrogen bonding within these Coulomb systems. This goal is achieved by a characteristic variation of the interaction sites at the imidazolium cations using the same anion throughout. We then switch to protic ionic liquids (PILs) because they show distinct anion–cation vibrational modes due to stronger hydrogen bonding and also provide access to interaction energies corrected for reduced masses. Finally we can relate the corrected frequency shifts to interaction energies between anions and cations. The benefit of this relation is demonstrated for the solid–liquid phase transition and temperature dependence. In this review we mainly summarize the results we achieved within our project of the priority programme “Ionic Liquids” (SPP 1191), which has been funded by the German Science Foundation (DFG) between 2008 and 2012 [45–50,65–90].

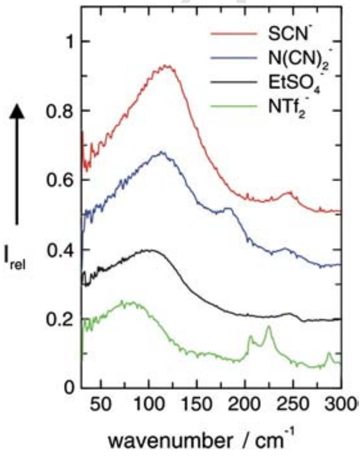

Fig. 1. Far-infrared (FIR) vibrational spectra of $[C_2mim][SCN]$, $[C_2mim][N(CN)_2]$, $[C_2mim][EtSO_4]$, and $[C_2mim][NTf_2]$ ionic liquids measured at 273 K.
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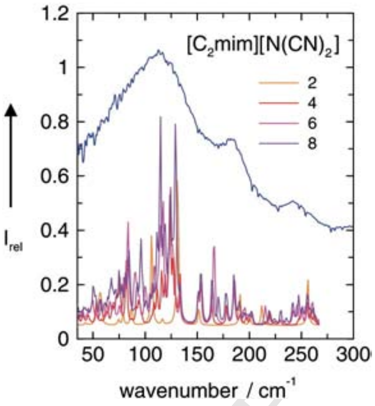

Fig. 2. FIR spectrum of $[C_2mim][N(CN)_2]$ at 273 K compared with ab initio calculated vibrational modes of corresponding IL clusters $[C_2mim][N(CN)_2]_x$ with $x = 2, 4, 6, 8$. It can be seen that the major vibrational bands are reflected by the calculated frequencies which are corrected for the harmonic approximation.
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2. The cation–anion interaction detected by far infrared spectroscopy

In the first study we could show that the cation–anion interaction in APILs can be detected by far infrared (FIR) spectroscopy. For that purpose we measured FIR spectra of these imidazolium-based ionic liquids $[C_2mim][SCN]$, $[C_2mim][N(CN)_2]$, $[C_2mim][EtSO_4]$ and $[C_2mim][NTf_2]$ [45,46]. The interpretation of the measured spectra was supported by ab initio calculated frequencies of ionic liquid clusters. The low frequency vibrational bands between 50 and 120 cm^{-1} could be assigned to the bending and stretching modes of the $^{+}C{-}H{\cdots}A^{-}$ cation–anion interaction in these ionic liquids. By varying the anion in the imidazolium-based ILs these bands shift in frequency and change intensity in a characteristic way corresponding to the strength of the calculated interaction energies. Thus we presented a direct probe for studying the strength of interaction energies between cations and anions in ionic liquids. The low frequency FTIR spectra for the neat ionic liquids $[C_2mim][SCN]$, $[C_2mim][N(CN)_2]$, $[C_2mim][EtSO_4]$, and $[C_2mim][NTf_2]$ for the range between 30 and 300 cm^{-1} are shown in Fig. 1. Overall it can be seen that the spectra show significant differences. Because we kept the imidazolium cation (C_2mim^{+}) fixed, the differences can only arise from weak intramolecular vibrations of various anions and/or specific cation–anion interactions. Beside wavenumbers also the vibrational intensities vary significantly with the used anions. Strong support for the interpretation of the low vibrational bands is coming from ab initio calculations of ionic liquid aggregates $([C_2mim][A])_x$ where x is the number of ion pairs contributing to the overall cluster and A^{-} represents the chosen anion, respectively. It is assumed that the largest clusters taken into account give the most liquid-like frequency spectra. In large clusters $C(2)-H$ as well as $C(4/5)-H$ are involved in hydrogen bonding with different strengths giving slightly different intermolecular frequencies and intensities. A detailed interpretation of the low frequency spectra is given for the ionic liquid $[C_2mim][N(CN)_2]$.

In Fig. 2 the measured spectrum is shown along with the ab initio calculated low frequencies of the IL clusters ($x = 2,4,6,8$). All vibrational modes could be assigned to weak intramolecular vibrational modes of the ions. However, the most interesting bands occur below 150 cm^{-1}. The calculated frequencies of differently sized IL clusters suggest that the main intensity at about 120 cm^{-1} can be clearly attributed to the stretching modes of the hydrogen bonds $^{+}C{-}H{\cdots}A^{-}$, where $C-H$ can be either $C(2)-H$ or $C(4/5)-H$ (see Fig. 2). The vibrational bands about 50–60 cm^{-1} are mainly derived from the corresponding bending modes of these hydrogen bonds. These modes are definitely weaker in intensity. The frequency range for the stretching mode of the hydrogen bond is a sensitive probe for the cation–anion interaction in a particular ionic liquid.

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