

The Influence of Hydrogen-Bond Defects on the Properties of Ionic Liquids**

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Ionic liquids (ILs) are salts with uncommonly low melting points that are formed by a combination of specific cations and anions; they display distinctive properties and can be used in a variety of applications.^[1,2] The working temperature range of an ionic liquid is set by the melting point and the boiling or decomposition point. In particular, the melting point (T_m) varies substantially between different ILs for reasons presently not fully understood, but which we explore herein.^[3–9] We show that the melting points of imidazolium ionic liquids can be decreased by about 100 K if an extended ionic and hydrogen-bond network is disrupted by localized interactions, which can also be hydrogen bonds.

Evidence for the presence of ion–ion interactions through hydrogen bonds was reported by Dymek et al., Avent et al., and Elaiwi et al. some time ago.^[10–12] It is reasonable to assume that the interesting features of the melting points must be related to the formation of structures in the solid and the liquid phases of the ILs. Extended hydrogen-bond networks in the liquid phase were reported with possible implications for both the structure and solvent properties of the ILs.^[13,14] Dupont et al. described pure imidazolium ILs as hydrogen-bonded polymeric supramolecules.^[15] Antonietti et al. suggested that these supramolecular solvent structures represent an interesting molecular basis of molecular recognition and self-organization processes.^[16] However, in all of these examples it is suggested that hydrogen bonds strengthen the structure of ILs leading to properties similar to those of molecular liquids.

This idea is also the basis of most of the structure–property relations discussed in the literature including quantitative structure–property relationships (QSPR) methods to correlate the melting points of ILs based on “molecular descriptors” derived from quantum chemical calculations.^[17–21] Such empirical correlations suffer from the fact that large experimental data sets are required and that the statistical methods used are rather complex. In addition, no interpretation of these fundamental physical properties at the molecular level is provided. Krossing et al. have developed a simple predictive framework to calculate the melting point of a given ionic liquid based on lattice and solvation free energies.^[22] They showed that ILs are liquid under standard ambient conditions because the liquid state is thermodynamically favorable, owing to the large size and conformational flexibility of the ions involved. This leads to small lattice enthalpies and large entropy changes that favor the liquid state. For such studies substituted imidazolium, pyrrolidinium, pyridinium, and ammonium cations have been used along with fluorometalate, triflate, and bis(trifluoromethylsulfonyl)imide anions. Unfortunately, Krossing’s results do not correlate with experimentally obtained melting points for protic ionic liquids (PILs) reported by Markusson et al.^[23] The reason for the large deviations of the predicted from the experimental melting points is probably related to the general trend of increasing T_m with the increasing size of the anions.

We do not intend to present another framework for predicting ionic liquid properties here. Instead we want to demonstrate that in addition to the large size and conformational flexibility of the ions, local defects such as directional hydrogen bonds can significantly decrease the melting points of ionic liquids. For eight imidazolium-based ionic liquids we show that these defects can increase their working temperature range by up to 100 K and thus expand the spectrum of potential applications. This was suggested previously by Fumino et al. based on spectroscopic measurements and DFT calculations on IL aggregates. They assumed that local and directional types of interactions present defects in the Coulomb system which may lower the melting points, viscosities, and enthalpies of vaporization.^[8,9] In contrast, based on quantum chemical calculations, Hunt claimed that an increase in the melting points and viscosities upon methylation at C(2) stem from reduced entropy.^[5,6] Noack et al. showed very recently that neither the “defect hypothesis” of Fumino et al. nor the “entropy hypothesis” of Hunt alone can explain the changes in the physicochemical properties.^[7] However, in all these studies the data base was not sufficiently large and other effects such as volume changes could not be excluded for the ILs under investigation.

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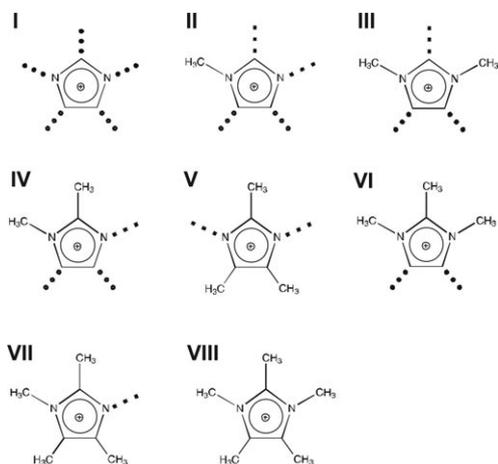
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To exclude effects from the different anions, we chose a set of eight ILs, all with the same bis(trifluoromethylsulfonyl)imide anion. Only the imidazolium cations are different: imidazolium (**I**), 1-monomethylimidazolium (**II**), 1,3-dimethylimidazolium (**III**), 1,2-dimethylimidazolium (**IV**), 2,4,5-trimethylimidazolium (**V**), 1,2,3-trimethylimidazolium (**VI**), 1,2,4,5-tetramethylimidazolium (**VII**), and 1,2,3,4,5-pentamethylimidazolium (**VIII**) (see Scheme 1).



Scheme 1. The imidazolium-based cations of the NTf_2 salts **I–VIII**. The different positions of the hydrogen bonds are indicated by bold dots and the remaining interaction sites are marked with dotted lines.

To minimize conformational flexibility of the cation only methyl groups and hydrogen atoms, but no extended alkyl chains, were taken into consideration as groups at the imidazolium ring. For a better understanding of our concept possible interaction sites of the imidazolium cations through C–H groups are marked with bold dots and dotted lines in the structures in Scheme 1. The bold dots indicate local and directional interactions through C(2)–H and/or N–H groups that are of importance for the structure and properties of ILs. It had been shown earlier by experiments and theory that interactions with C(4)–H and C(5)–H are significantly weaker than interactions with C(2)–H. These negligible interaction sites are indicated as dotted lines.

The given T_m values for **III**, **IV**, and **VIII** are taken from the literature including our own work.^[3,4,24–28] However, for the IL **II** a surprisingly low melting point of 9 °C had been reported.^[29] Thus, we recrystallized this IL purchased from IoLiTec GmbH and determined the melting point by DSC (differential scanning calorimetry) to be 52 °C. For IL **VI**, also purchased from IoLiTec GmbH, the T_m was measured to be 106 °C. ILs **I**, **V**, and **VII** were synthesized and the T_m values measured to be 69 °C (compared to 73 °C in the literature^[30]), 57 °C, and 40 °C, respectively. We plotted the melting points for ILs **I–VIII** (listed in Table 1) versus the ab initio computed volumes ($A^- + C^+$) of the anions and cations (Figure 1). In earlier work Krossing et al. and Markusson et al. showed that the calculated volumes are in good agreement with those obtained from crystal structure or density measurements.^[22,23]

Table 1: Melting points T_m of the ILs **I–VIII**.

IL	T_m [°C]	Ref.	T_m [°C] this work
I	73	[30]	69
II	9	[29]	52
III	22, 23, 26	[3, 4, 24–26]	–
IV	22	[29]	–
V	–		57
VI	–		106
VII	–		40
VIII	118	[27, 28]	118

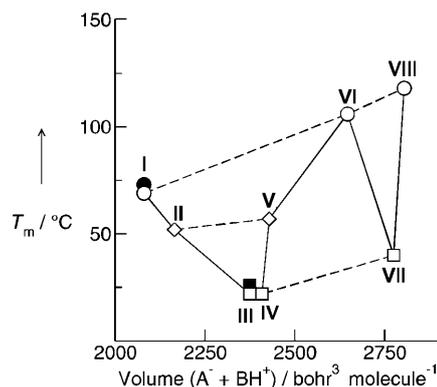


Figure 1. Plot of T_m versus volume ($A^- + C^+$) for the ionic liquids **I–VIII**, which include various imidazolium cations but always the same bis(trifluoromethylsulfonyl)imide anion (NTf_2^-). As indicated by the dotted lines, there is an increase in T_m with increasing volume for the ILs that have no specific interaction site (\square), with one interaction site (\circ), and with two interaction sites (\diamond). Overall it is shown that the presence of a single interaction site on the cation leads to a significant decrease in T_m , as found for ILs **III**, **IV**, and **VII**. The filled symbols indicate further T_m values from the literature.

As shown in Figure 1 there is no linear trend for T_m as a function of volume. The highest melting points are found for the species **I** and **VIII**, in which neither cation, imidazolium and 1,2,3,4,5-pentamethylimidazolium, have specific interaction sites. In principle, IL **I** has five interaction sites through C–H or N–H bonds as indicated by the black dotted lines in Scheme 1, but no single interaction site is preferred over others and thus the interactions are not specific. The melting point increases with increasing volume as indicated by the dashed line (Figure 1). It is observed that the T_m value of **VI** also lies on that line, although the 1,2,3-trimethylimidazolium cation can in principle interact with the anion through the C(4)–H and C(5)–H groups. However, in earlier studies these interactions were noted to be weak compared to those of the C(2)–H group, which is strongly acidic.^[31,32]

The largest decrease in T_m of about 100 K can be observed for the ILs **III**, **IV**, and **VII**. They are distinguished by single interaction sites such as C(2)–H in **III** and N–H in **IV** and **VII**. The local and directional interaction through hydrogen bonding leads to a preformation of ion pairs resulting in lower “lattice energies” relative to the energy of isolated ion pairs. In other words: the disruption of the hydrogen-bond network increases the quasi-molecular character of the pure

ILs. This is similar to Dupont's suggestion for the addition of other molecules and macromolecules to ILs. He stated that the disruption of the hydrogen-bond network can generate nanostructures with polar and nonpolar regimes.^[13,15]

Our hypothesis of preformed ion pairs is supported by ab initio calculations of the energies of IL aggregates. When we subtracted four times the energy of the isolated ion pairs from the tetramer energies for each IL, we obtained larger interaction contributions for the ILs with high T_m values and significantly smaller ones for the ILs with low T_m values; this can be explained by preformation of ion pairs. The simple result is that more strongly bound ion pairs give smaller "lattice energies" resulting in low T_m values. Again, all the ILs having one interaction site give T_m values that follow a straight line with increasing volume in the order **III**, **IV**, and **VII**. This line has about the same slope as the plot of the T_m values of **I**, **VI**, and **VIII** (see Figure 1). Here, it is interesting to note that the similar molecular volumes of **III** and **IV** result in similar melting points. Both cations also allow interactions through C(4)–H and C(5)–H, which apparently have no effect on the T_m , in agreement with the finding for **VI**.

Following the argument that single, local and directional interactions can lead to low melting points, the ILs **II** and **V** have T_m values between those of the other two groups (\diamond). These compounds have two interaction sites, C(2)–H and N–H for **II** and N–H and N–H for **V**. Local and directional interactions are possible, leading to T_m values lower than those of ILs **I**, **VI**, and **VIII**. However, more than one interaction site hinders the preformation of ion pairs and increases the "lattice energy" towards extended hydrogen-bond networks.^[13–16] As the interaction energy between "unsaturated" ion pairs increases, higher T_m values result than those for **III**, **IV**, and **VII**. This finding is also supported by ab initio calculations (see Table 2, Figure 2).

In Figure 2a the melting points are plotted versus interaction energies per ion pair defined as $E_{ip} = (E_4 - 4E_1)/4$. Four times the calculated energies of isolated ion pairs are subtracted from the corresponding tetramer energies. It is observed that the interaction energies increase almost linearly with increasing melting points. The larger scatter for the high-melting-point ILs (\circ) may result from not considering the different volumes of the species. A better representation of our concept is shown in Figure 2b, where these interaction energies are referred to the number of interaction sites at the

Table 2: Ab initio calculated total energies (in Hartrees) for tetramers (E_4) and monomers (E_1) of ion pairs of the ILs **I–VIII**. In addition, the energies per ion and per ion pair are given in kJ mol^{-1} .

IL	Tetramer E_4 [Hartree]	Monomer E_1 [Hartree]	Energy per ion [kJ mol^{-1}]	Energy per ion pair [kJ mol^{-1}]
I	–8141.850660	–2035.449504	–213.43	–34.55
II	–8297.077549	–2074.265686	–192.21	–9.72
III	–8452.315770	–2113.080019	–175.97	+2.83
IV	–8452.395913	–2113.097402	–185.08	–4.14
V	–8607.768535	–2151.934921	–191.37	–18.94
VI	–8607.612327	–2151.896047	–164.84	–18.47
VII	–8763.014030	–2190.751088	–180.69	–6.35
VIII	–8918.206619	–2229.540757	–155.73	–58.61

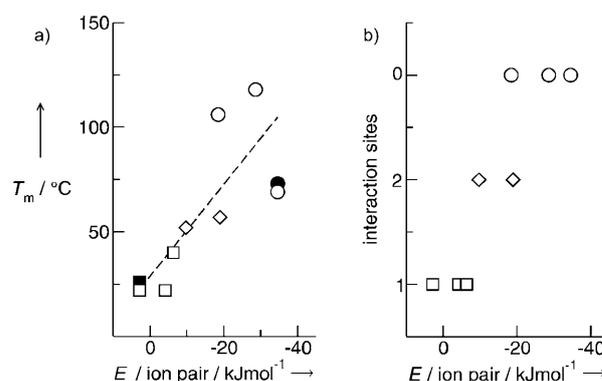


Figure 2. a) T_m values plotted versus calculated interaction energies per ion pair for tetramers of the ionic liquids **I–VIII**. b) The same interaction energies are given for the number of interaction sites in the corresponding imidazolium cations. Both plots show that T_m depends on the interaction energies between preformed ion pairs in the lattice. If most of the overall interaction energy is included in the cation–anion interaction of the preformed ion pair, which is best obtained with one interaction site, the melting point is low. The filled symbols indicate further T_m values from the literature.

given imidazolium cation. It can be seen clearly that the interaction energies range from +2 to -6 kJ mol^{-1} for cations with one interaction site, from -10 to -19 kJ mol^{-1} for species having two interaction sites, and from -18 to -34 kJ mol^{-1} for cations with no interaction sites. When the preformation of ion pairs is possible as in ILs **III**, **IV**, and **VII**, the lowest melting points are found (Figure 3).

Further evidence for this scenario can be derived from X-ray single-crystal structures. For the IL **VIII** the anion NTf_2^- is found in conformations in which the two SCF_3 groups are *trans* to one another.^[28] For the IL **III** the *cis* conformation is dominant.^[3] Holbrey et al. conjectured that this behavior is caused by structural constraints of extensive C–H \cdots O and N–H \cdots O cation–anion hydrogen bonding between neighboring molecules.^[3] The *cis* configuration, which is energetically

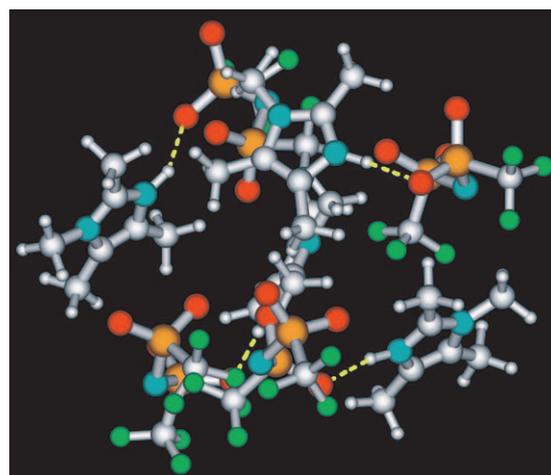


Figure 3. Calculated tetramer of the ionic liquid (1,2,4,5-MIm) NTf_2 (**VII**). The hydrogen bonds are indicated by the dotted lines. The single interaction site NH of each cation leads to a preformation of ion pairs in this IL.

disfavored in the gas-phase calculations, indicates local and directional interactions between cation and anion. The finding that both SO₂ groups point towards the cation supports our hypothesis of preformed ion pairs, which is also supported by the order of energies per ion pair in Figure 2. The structure of **II** (this work^[33]) is made up of two independent anions and cations, with both anions having the *trans* conformation. Nevertheless, the anions show strong (short) hydrogen bonds with two such contacts to only one cation (see Figure 4). This indicates the preformation of ion pairs, which lowers the melting point.^[4–9]

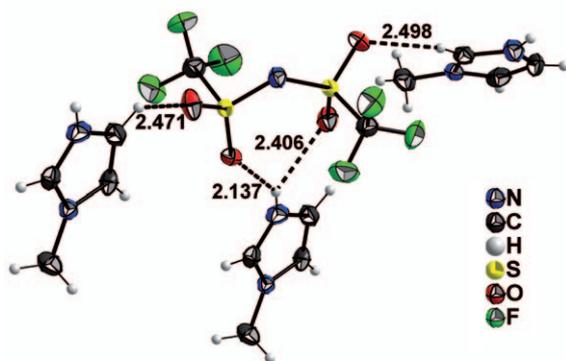


Figure 4. Environment of one of the two independent anions in the structure of **II** showing the preformation of hydrogen-bonded dimers.

Overall there is strong evidence that single, local and directional interactions such as hydrogen bonds lower the T_m significantly. For the given imidazolium-based ILs this change can be up to 100 K which greatly extends the working temperature range of the ionic liquids. Such phenomena have been observed before but have not been evaluated in detail. Already 14 years ago Bonhôte et al. synthesized ionic liquids made up of imidazolium cations and perfluorinated hydrophobic anions.^[4] They expected that suppressing the C(2)–H...A[–] hydrogen bond by alkyl substitution would lower the melting point. The opposite was observed: alkylation increased melting points as well as viscosities. Because Bonhôte et al. were mainly interested in synthesizing low-melting and highly conductive ILs for applications in solar cells, this phenomenon was not further considered. At that time it was also not clear to what extent symmetry and volume effects contribute to IL properties such as melting points. Although to a less extent, this has still been true for the recent studies of this phenomenon.^[5–9] Now it seems to be clear that hydrogen bonds can also have strong effects in Coulomb systems and that they can result in effects opposite to those expected for H-bonded molecular liquids.

Experimental Section

ILs **I**, **V**, **VII**, and **VIII** were synthesized by metathesis reactions of the corresponding imidazolium halides with Li(NTf₂). Experimental procedures are given in the Supporting Information. ILs **II** and **VI** were purchased from IoLiTec. For **I**, **II**, **V**, **VI**, **VII**, and **VIII** the

melting points were determined by DSC. Suitable single crystals for X-ray crystallography of **II** were obtained by drying liquid **II** in high vacuum (10^{–5} mbar) at ambient temperature.^[33,34]

The energies of monomeric and tetrameric ion pairs for all ionic liquids **I–VIII** were calculated at the Hartree–Fock level, using the internal stored 3-21G basis set of the Gaussian03 program.^[35] The binding energies per ion and per ion pair were corrected for the basis set superposition error (BSSE).^[36] The geometries of the monomers and tetramers can be obtained from the authors upon request.

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