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Ionic Liquids

Intermolecular Forces in an Ionic Liquid ([Mmim][Cl]) versus Those in a Typical Salt (NaCl)**

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Understanding chemical bonding and intermolecular forces is one of the major topics in chemistry.[1] In general, chemical compounds are divided into classes based on their properties. The class of ionic liquids (ILs) has been known since the beginning of the last century.[2–4] Owing to their tuneable properties and low vapor pressure, ILs have become a hot research area with a wide range of applications in recent years.[5–12] A promising route towards better understanding ionic liquids is to determine the dominating intermolecular forces and compare them to those in an example such as NaCl, which is solid at room temperature and, in other words, a compound representative of its class. One must be careful in probing for general properties of ILs, because the search for generality has led to many myths about ionic liquids. Often properties of ionic liquids are explained by the chemical nature of the particular substance and are not a general feature. As an example for imidazolium-based ionic liquids, we chose 1,3-dimethylimidazolium chloride ([Mmim][Cl]).

If one considers the theoretically predicted total interaction energies from ab initio calculations between a typical cation and an anion at the equilibrium distance in a typical IL, these energies range from -300 to $-400\,\mathrm{kJ\,mol^{-1}}$, in agreement with Ref. [13] (for details on the methods see the Supporting Information). Calculating the same energy for NaCl gives a value of $-545.0\,\mathrm{kJ\,mol^{-1}}$. This strongly points toward correlating these energies with melting points of the corresponding bulk system. It is obivous from Figure 1 that there is no correlation between the predicted energies and the melting points.[13] A simple model for estimating the melting points of ILs suggests that most likely the liquid behavior of ILs can be attributed to large, unsymmetrical ions with high conformational flexibility.[14,18,15] Recent studies reveal complex structures having microheterogenous polar and nonpolar domains[16,17] for imidazolium-based systems with extended side chains; this phenomenon is not observed when the side chains are shorter.

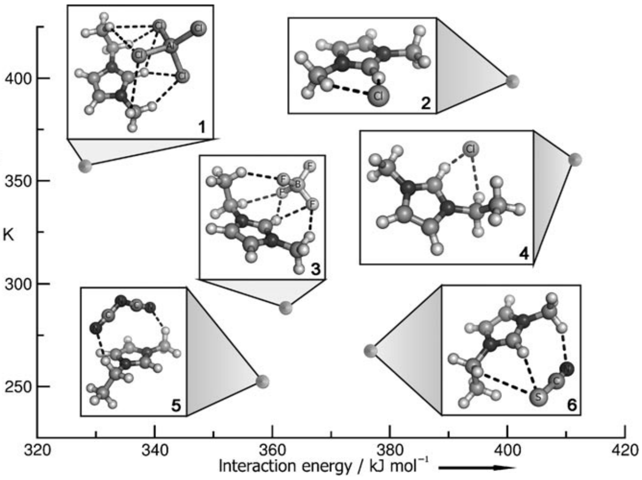

Figure 1. Melting points plotted against the interaction energies between one cation and one anion for several different ILs. A ball-and-stick model of each IL is also given in the figure. **1**: [Emim][AlCl$_4$], **2**: [Mmim][Cl], **3**: [Emim][BF$_4$], **4**: [Emim][Cl], **5**: [Emim][DCA], **6**: [Emim][SCN]. Emim = 1-ethyl-3-methylimidazolium ion, DCA = dicyanamide.

It has been inferred that other forces besides pure Coulombic interactions must play a role in ionic liquids.[13,19,20] Thus, we decompose the total interaction energy of one ion pair of [Mmim][Cl] and one ion pair of NaCl by the symmetry-adapted perturbation theory (SAPT) method into different contributions in analogy to a multipole expansion (Figures 2 and 3). Note that the equilibrium distance is set to zero in order to provide comparability.

For the NaCl pair (red diamonds in Figure 2) the dispersion term is negligible, whereas this contribution is comparable in magnitude to the induction term for the two conformers of the ionic liquid pair [Mmim][Cl] (blue and green diamonds in Figure 2). The main contribution to the total energy stems from the electrostatic interaction for all species, (circles in Figure 2) in agreement with Ref. [13].

For NaCl the total energy consists of only electrostatic, exchange, and induction contributions (see Figure 3; the curve with red squares almost exactly matches the curve with diamonds). In Figure 3 we can make another interesting observation concerning the minima: Whereas the NaCl pair features the minima for all curves exactly at the equilibrium distance (at zero, see black dotted vertical line), this is, surprisingly, not the case for the [Mmim][Cl] pairs (see black

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Supporting information for this article is available on the WWW under http://www.angewandte.org or from the author.

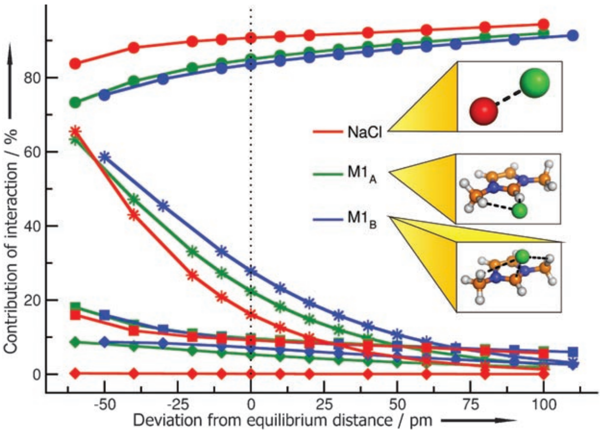

Figure 2. Contributions of different interactions to the total attractive (electrostatic + induction + dispersion) interaction energy. Circles: electrostatic, stars: exchange, squares: induction, diamonds: dispersion. The red curves indicate the NaCl ion pair, the blue and green curves represent the [Mmim][Cl] conformers. Further less stable conformers are given in the Supporting Information.

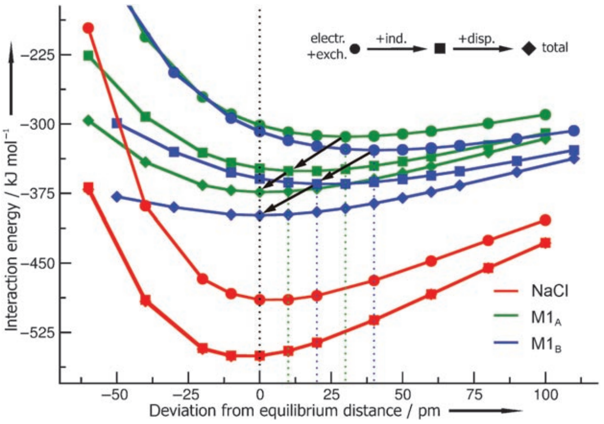

Figure 3. Plot of the interaction energy versus distance. Circles: electrostatic (elect.) and exchange (Pauli) terms; squares: electrostatic, exchange, and induction (ind.) term; diamonds: total energy including dispersion (disp.). The red curves indicate the NaCl ion pair, the blue and green curves are given for the two most stable conformers of [Mmim][Cl].

arrows in Figure 3). This means that the equilibrium distance (or the structure) is not exclusively determined by the most important attractive force, namely, the electrostatic interaction. This finding amply demonstrates that the ions of our example interact in the repulsive region of electrostatic potential only, if one considers that the hypothetical potential consists of electrostatic and exchange terms. This implies that our ionic liquid is not as ionic as one may naively imagine. Different contributions compensate each other partly, resulting in a very shallow potential energy curve. Consequently the system is highly flexible and liquidlike, and is also able to adjust easily to different situations, which might also explain the good solvating properties of ILs.

In 1914, Walden proposed that one should not think in terms of isolated ions.[2] The importance of ion-pair formation is also stressed by Schulz et al., who apply these effects for chirality transfer by means of ILs.[21] Again, there is no simple correlation between the degree of association and the melting point.[22] Thus we now turn to interaction energies between two ion pairs dissociating into separated ion pairs; again [Mmim][Cl] and NaCl serve as examples. If one compares the total energies at the equilibrium distance, one finds again that the [Mmim][Cl] dimer (SCS-MP2: 126.9 kJ mol^{-1}) is more weakly bound than the NaCl dimer (SCS-MP2: 212.9 kJ mol^{-1}). For reasons of computational feasibility, we now apply an alternative approach. We carry out single-point calculations with the Hartree–Fock (HF) method and the spin-component-scaled SCS-MP2 method at the same geometries. The difference between these energies provides us with a rough estimate of the dispersion forces, because HF does not describe dispersion interaction by definition while SCS-MP2 accounts for these interactions very well. (For details consult the Supporting Information.)

In Figure 4 the black curve with squares perfectly matches the black curve with diamonds, indicating that dispersion forces also play a negligible role for the interaction between NaCl ion pairs. This is not the case for our IL example. Here, almost 30% of the total energy (SCS-MP2) is missing in the HF curve at the equilibrium distance. The [Mmim][Cl] curves are much flatter and broader than those obtained for NaCl.

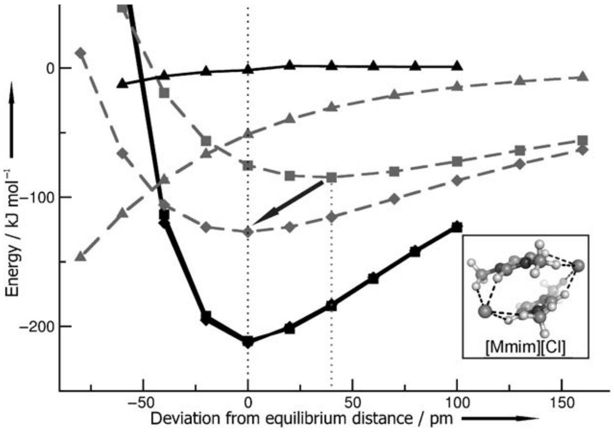

Figure 4. Interaction energies obtained from the HF (squares) and the SCS-MP2 (diamonds) approaches. The differences in energy between the two methods are represented by triangles. All gray curves indicate the IL dimer, while the black curves denote the NaCl dimer. Inset: Picture of the IL dimer. For comparability the equilibrium distance is set to zero.

For the location of the minima we again find the surprising effect that for our IL example the minimum of the HF curve is shifted by 40 pm towards the attractive region, whereas for the NaCl dimer the minimum distance is always the same, regardless of the applied method. Thus, not only are the cations and anions closer together than the electrostatic forces would allow, but that is also the case for the ion pairs. This effect might even have more severe consequences for the ion-pair interaction, because it means that not only are oppositely charged ions too close together but ions of the same charge are also too close to each other; this then results in a local violation of charge neutrality.

In conclusion, we have shown the importance of dispersion and induction interactions in an imidazolium-based IL; in contrast, in typcial salts like NaCl dispersion interactions apparently do not play a role. It is known that the repulsive region of a potential is linked to the melting point, while the attractive region is associated with the boiling point. A flat repulsive region corresponds better to a lower melting point than a steep curve would.[23] Such a flattening of the repulsive region is induced in ILs by dispersion and induction forces. Furthermore, our study of [Mmim][Cl] showed that the equilibrium distance is not exclusively determined by the most important attractive force, namely, the electrostatic interaction. It is, instead, shifted to smaller distances, implying that the ions interact in the repulsive potential region in terms of the electrostatic forces only. Since the individual contributions do not add up in an optimal fashion, we obtain a shallow potential curve for the IL in contrast to that of NaCl. Other, more complex imidazolium-based ionic liquids (with flexible side chains) will most likely show even more pronounced contributions of van der Waals and induction interactions and will thus exhibit even more flattened potential energy surfaces. In the condensed phase, where the complete potential energy surface plays a role, the increasing domains or nanostructures exhibiting microheterogeneity might have further consequences in depressing the melting point.[16,17]

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