Ionic Liquids

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Dispersion and Hydrogen Bonding Rule: Why the Vaporization Enthalpies of Aprotic Ionic Liquids Are Significantly Larger than those of Protic Ionic liquids

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Abstract: *It is well known that gas-phase experiments and computational methods point to the dominance of dispersion forces in the molecular association of hydrocarbons. Estimates or even quantification of these weak forces are complicated due to solvent effects in solution. The dissection of interaction energies and quantification of dispersion interactions is particularly challenging for polar systems such as ionic liquids (ILs) which are characterized by a subtle balance between Coulomb interactions, hydrogen bonding, and dispersion forces. Here, we have used vaporization enthalpies, far-infrared spectroscopy, and dispersion-corrected calculations to dissect the interaction energies between cations and anions in aprotic (AILs), and protic (PILs) ionic liquids. It was found that the higher total interaction energy in PILs results from the strong and directional hydrogen bonds between cation and anion, whereas the larger vaporization enthalpies of AILs clearly arise from increasing dispersion forces between ion pairs.*

Ionic liquids (ILs) are promising neoteric materials for science and technology.[1–3] ILs consist solely of ions and are characterized by unique physical properties. They are classified as aprotic (AILs) and protic (PILs) ionic liquids. PILs are a subset of ILs prepared through the stoichiometric neutralization reaction of certain Brønsted acids and Brønsted bases. A key feature of PILs is that they have an available proton on the cation allowing the formation of strong hydrogen bonds to the anion.[4] At first glance, the vaporization enthalpies of PILs are expected to be greater than those of AILs. This seems to be reasonable because besides strong Coulomb interactions characteristic for both subsets, hydrogen bonding should play a substantial role in protic ionic liquids. Admittedly, H-bonds can account for up to 50% of the overall interaction energies in these liquid Coulomb systems.[5–7] However, it is well-known that the interaction in ionic liquids is governed by a subtle energy balance between Coulomb forces, hydrogen bonds, and dispersion interactions.[8,9] All types of interaction have their special features: they can be strong and long-range, moderate and directional, or weak from short- to long-range. In molecular liquids such as alcohols the vaporization enthalpies are mainly stipulated by the hydrogen bonding network combined with increasing dispersion interactions due to increasing alkyl chain lengths.[10] It is easy to separate the two contributions to the vaporization enthalpies of alcohols through a comparison with alkanes, provided that the gas phase is dominated by monomeric species. If we increase the alkyl chain length in *n*-alcohols and *n*-alkanes we can attribute the differences to the H-bonds present in the *n*-alcohols and increasing dispersion forces with increasing alkyl chain length.[10–12] In ionic liquids the situation is more complicated. In the meantime, reliable vapor pressures and vaporization enthalpies of the subset of the low volatile AILs are available.[13–23] Most results indicate that ionic liquids evaporate as neutral ion pairs or ion pair aggregates. The experimental vaporization enthalpies of AILs range from 122 to 163 kJ mol^{-1}, thus substantial interaction energy must be overcome to get the ionic pair in the vapor. In contrast, vaporization enthalpies of PILs are practically absent in the literature, except for methylimidazolium nitrate[14] and ethylammonium nitrate.[24]

To clarify this situation and to work out the subtle balance of interaction energies in ionic liquids, we combined the results of experimental and theoretical studies on a well-chosen set of AILs and PILs. We studied the set of imidazolium-based AILs containing the 1-ethyl-3-methylimidazolium cation: 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide $[C_2mim][NTf_2]$ (**I**), 1-ethyl-3-methylimidazolium trifluoromethylsulfonate $[C_2mim][CF_3SO_3]$ (**II**), and 1-ethyl-3-methylimidazolium methylsulfonate $[C_2mim][CH_3SO_3]$ (**III**), as well as the set of ammonium-based PILs containing the triethylammonium cation: triethylammonium bis(trifluoromethylsulfonyl)imide $[(C_2H_5)_3NH][NTf_2]$ (**IV**), triethylammonium trifluoromethylsulfonate $[(C_2H_5)_3NH][CF_3SO_3]$ (**V**), and triethylammonium methylsulfonate $[(C_2H_5)_3NH][CH_3SO_3]$ (**VI**). The selection of anions is identical in the two series but the anions differ significantly in interaction strength. Additionally, the two cations have similar volumes.

For these sets of ionic liquids we measured the vaporization enthalpies, recorded the far-infrared spectra, and

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calculated the IL aggregates up to ten ion pairs. Measurements of vaporization enthalpies of extremely low volatile compounds like ILs remain a challenging task. At relatively low temperatures ILs exhibit no measurable vapor pressure, but at elevated temperatures (where the vapor pressure becomes detectable) many ILs undergo decomposition. In the last ten years we have worked systematically on the development of reliable experimental methods for the determination of vaporization enthalpies.[18–23] It has turned out that a method relying on the quartz-crystal microbalance (QCM)[18,19] is the most reliable for the series of thermally stable AILs. For the set of aprotic ILs (**I**–**III**) we used our primary data published in previous work,[20] but we have re-adjusted these results to the reference temperature $T = 298$ K (see Table 1). However, already preliminary studies of the PILs-set with the QCM method have shown irreproducible results with these ILs. In contrast, a differential fast scanning calorimetry (DFSC) method developed in our lab just recently[22] provided reliable results for the thermally instable PILs (**IV**–**VI**). The crucial advantage of the new DFSC method is the extremely high heating/cooling rates used with the nanosamples combined with high sensitivity.[22] We emphasize here that the DFSC method is suitable for the measurement of vaporization enthalpies even of PILs, which are known to be significantly less thermally stable than AILs.[24] We measured the vaporization enthalpies of PILs (**IV**–**VI**) by two independent methods: thermogravimetric analysis (TGA) and DFSC. Both methods are described in detail in the Supporting Information (SI 1). The resulting vaporization enthalpies are given in Table 1. For broader insight, we have considered the vaporization enthalpies of other AILs also of general type [C_2mim][anion], which we measured in previous work[20] but re-evaluated for the current study (see Table 1).

As expected, the vaporization enthalpies of the ILs listed in Table 1 increase with the increasing interaction potential of the anions in the order **I** to **III** and **IV** to **VI**. The surprising result is that in spite of the comparable size of the cations and the identical anions, the vaporization enthalpies for the AILs are between 28 and 34 kJ mol^{-1} higher than those of the PILs. This observation is in contrast to the typical behavior of molecular liquids, where the H-bonding network (as in alcohols) is always responsible for higher enthalpies of vaporization. Since the reason might be found in specific cation–anion interactions, we used the far-infrared spectra and quantum-chemical calculations to resolve this contradiction. We have shown recently that the vaporization enthalpies can be reasonably correlated with frequencies from vibrational modes in the far-infrared (FIR) spectra describing the cation–anion interaction.[25] This correlation worked perfectly for AILs as shown in Figure 1 (see also SI 2). The stronger unspecific cation–anion interaction logically results in a higher vaporization enthalpy. In the FIR spectra the contributions describing the H-bonds between cation and anion and the overall cation–anion interaction cannot be dissected properly because they are on the same order of magnitude. The situation is different for PILs, where the specific and linear H-bond N–H···O between cation and anion results in a distinct vibrational mode at a significantly higher frequency.[26] Thus, for the correlation with vaporization enthalpies we have to use the frequencies describing the unspecific cation–anion interaction rather than the directional interaction which is also present in the gas phase (Figure 2). We find comparable behavior for both types of ILs with changing anion interaction potential. The AIL (**I**–**III**) vaporization enthalpies ranging between 132 and 140 kJ mol^{-1} are related to frequencies in the range between 85 and 105 cm^{-1}, whereas the PIL values (**IV**–**VI**) between 105 and 107 kJ mol^{-1} are attributed the frequencies between 78 and 82 cm^{-1}. Although the corrections for the different reduced masses due to the different anions are not taken into account,

Table 1: Vaporization enthalpies $\Delta_l^g H_m^\circ$ (298 K) and frequence ν_σ for imidazolium-based ILs with the ethyl-substituted cation and ammonium-based PILs with the ethyl-substituted cation.

	T_{av}	$\Delta_l^g H_m^\circ$ (T_{av})[5]	$\Delta_l^g H_m^\circ$ (298 K)[a]	ν_σ
		AILs		
[C_2mim][CH_3SO_4]	442	135.2 ± 1.0	143.3	105.3
[C_2mim][SCN]	413	142.2 ± 1.0	148.7	116.3
[C_2mim][$(C_2H_5O)_2PO_2$]	393	136.6 ± 1.0	141.9	108.0
[C_2mim][$B(CN)_4$]	404	125.0 ± 2.2	130.9	84.2
[C_2mim][$C(CN)_3$]	423	126.0 ± 1.0	133.0[b]	97.5
[C_2mim][$C(CN)_3$]	298	138.8 ± 7.0[13]	138.8[b]	97.5
[C_2mim][FAP]	373	118.3 ± 1.0	122.5	72.4
[C_2mim][NO_3]	298	–	163.7[34]	118.9
[C_2mim][$N(CN)_2$]	298	–	156.4[34]	113.9
[C_2mim][NTf_2]	378	118.6 ± 1.0	*132.7*	84.8
[C_2mim][CF_3SO_3]	413	126.4 ± 1.0	*132.8*	89.5
[C_2mim][CH_3SO_3]	422	133.0 ± 1.0	*140.0*	105.1
		PILs		
[$NH(C_2H_5)_3$][NTf_2]	298	–	104.8 ± 0.9[c]	78.1[c]
[$NH(C_2H_5)_3$][CF_3SO_3]	298	–	104.9 ± 1.3[c]	80.5[c]
[$NH(C_2H_5)_3$][CH_3SO_3]	298	–	106.4 ± 1.3[c]	82.5[c]

[a] Adjusted to $T = 298$ K with the heat capacity difference $\Delta_l^g C_{p,m}^\circ = -56$ J K^{-1} mol^{-1} for all AILs. [b] The average value $\Delta_l^g H_m^\circ$ (298 K) = 135.9 kJ mol^{-1} was used for correlation. [c] Data from Table SI1.

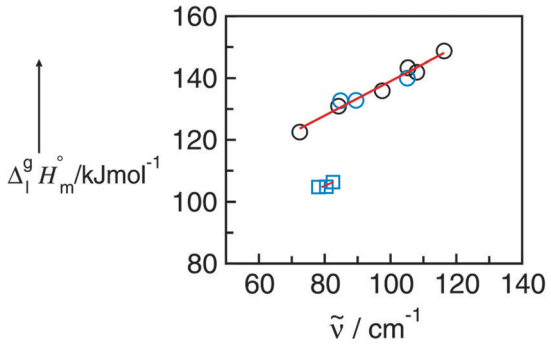

Figure 1. The experimental vaporization enthalpies, $\Delta_l^g H_m^\circ$, of AILs **I**–**III** (circles) and PILs **IV**–**VI** (squares) plotted versus the corresponding frequencies of maxima in the FIR spectra, which describe the unspecific cation–anion interaction. Linear relations could be achieved. We extended the data set for AILs containing the 1-ethyl-3-methylimidazolium cation (black circles) with the anions given in Table 1.

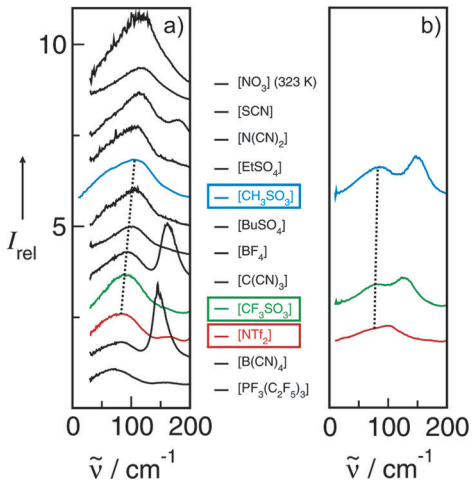

Figure 2. Far-infrared (FIR) spectra of a) AILs **I–III** and b) PILs **IV–VI** (spectra in red, blue, and green). Additionally, previously measured FIR spectra of AILs based on the 1-ethyl-3-methylimidazolium cation $[C_2mim]^+$ with the anions ethylsulfate $[EtSO_4]^-$, dicyanoamide $[N(CN)_2]^-$, tricyanomethide $[C(CN)_3]^-$, tetracyanoborate $[B(CN)_4]^-$, butylsulfate $[BuSO_4]^-$, nitrate $[NO_3]^-$, tetrafluoroborate $[BF_4]^-$, tris(pentafluoroethyl)trifluorophosphate $[C_2F_5)_3P_3]^-$ (FAP), and thiocyanate $[SCN]^-$ are shown.

we can conclude that higher vaporization enthalpies can be related to the higher frequencies that indicate stronger interaction between cation and anion. However, it is still not known why the vaporization enthalpies for AILs are between 28 and 34 kJ mol^{-1} higher than those for PILs.

To understand this behavior we calculated aggregates of the ILs for clusters of up to ten ion pairs ($n=10$) at the B3LYP-D3/6-31+G* level of theory considering Grimme's D3-dispersion correction (see SI 3–5).[27–30] We could show earlier that such a cluster size is sufficient to mimic liquid-phase properties.[31–33] Absolute accuracy in this case is not required because we compare the liquid- and gas-phase structures of AIL and PIL clusters of similar size. In Figure 3a we show the calculated total interaction energies for AIL **III** and PIL **VI**. We chose these ILs because they include the smallest anion (methylsulfonate) and thus reduce the computational efforts. The cooperative effects with increasing cluster size are nearly saturated at $n=8$. As expected, the total interaction energies for the PIL clusters are greater than those for the AIL clusters due to the enhanced cation–anion interaction via hydrogen bonding. The difference is approximately 20 kJ mol^{-1} per ion pair. It is also shown that the greatest energy difference can be observed for the simple ion pairs, suggesting that most of the difference in total interaction energies is included within the ion pairs. In the next step, we calculated the overall interaction energies relative to the energy of an isolated ion pair. We obtain the opposite sequence in energy, as shown in Figure 3b. Now, the AIL clusters are lower in energy by about 30 kJ mol^{-1}. Unfortunately, we were not able to calculate the frequencies and thus the thermal enthalpies for the largest clusters ($n>6$). For this reason we related the calculated energy differences for the various sized clusters to the measured vaporization enthalpies. And indeed, for larger cluster sizes the calculated values

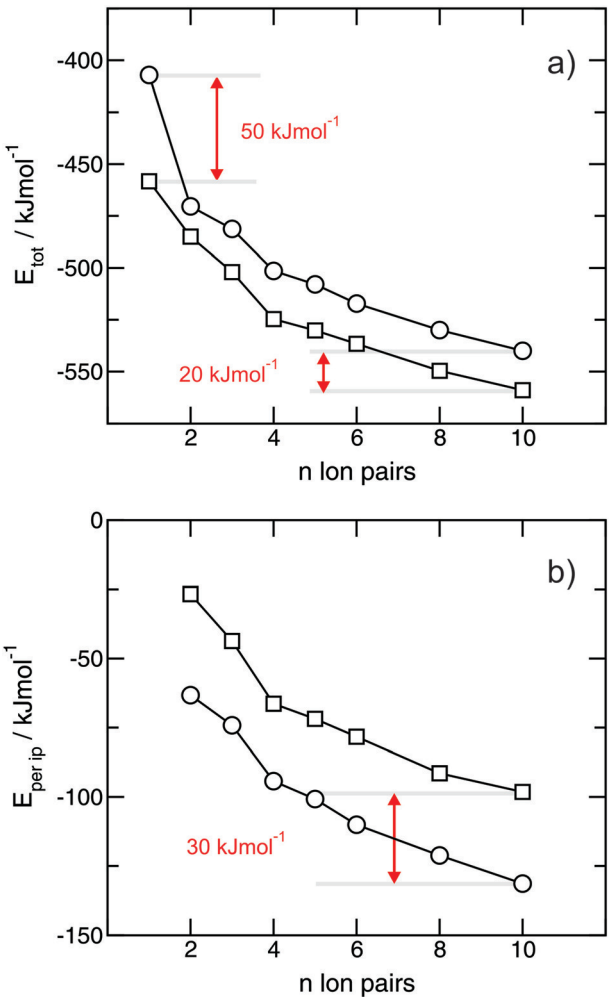

Figure 3. B3LYP-D3/6-31+G* calculated a) total energies and b) energies per ion pair in AIL **III** (circles) and PIL **VI** (squares) clusters containing $n=2$, 3, 4, 5, 6, 8, 10 ion pairs.

for the two ILs converge to the measured vaporization enthalpies, 106 kJ mol^{-1} for PIL **VI**, and about 140 kJ mol^{-1} for AIL **III**. We can calculate the difference in the vaporization enthalpies of AIL **III** and PIL **VI** to be about 30 kJ mol^{-1}, which is in good agreement with the measured data, as shown in Figure 4. If we calculate all clusters without considering dispersion forces, the vaporization enthalpies for both types of ILs are much lower than the experimental values, showing that dispersion forces need to be included for comparison with experiment. However, the energy gap between AIL and PIL clusters essentially remains, irrespective of the dispersion correction (see SI 6, Figure SI2).

But why are the vaporization enthalpies of AILs greater than those of PILs? The answer lies in the interaction strength within the ion pairs. The calculations of ion pairs and isolated cations for both types of ILs suggest that the PIL ion pair is favored not only by the strong and directional H-bond (N–H···O) but also by the dispersion forces between the ethyl groups within the $[(CH_3CH_2)_3NH]^+$ cation (see SI 7, Table SI2).[7–9] If the single cations, $[(CH_3CH_2)_3NH]^+$ and $[C_2mim]^+$, are calculated with and without D3-correction, the PIL cation becomes 18 kJ mol^{-1} more stable than the AIL

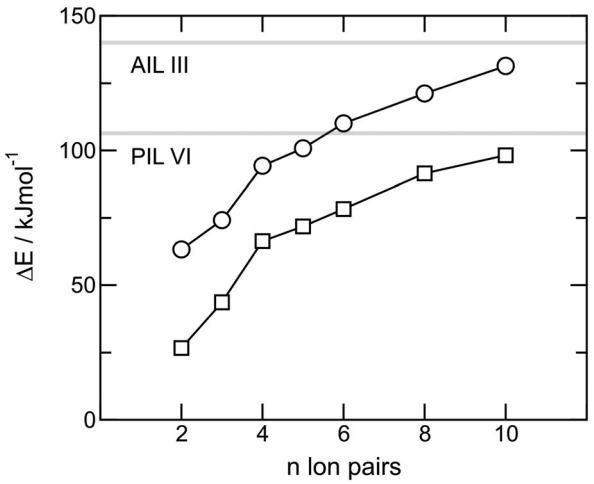

Figure 4. Estimated vaporization enthalpies of AIL $([C_2mim][CH_3SO_3])_n$ (circles) and PIL $([Et_3NH][CH_3SO_3])_n$ (squares) clusters containing $n = 2, 3, 4, 5, 6, 8, 10$ ion pairs calculated at 298 K. The calculations are based on the assumption that isolated ion pairs ([cation]-$[CH_3SO_3]$)$_1$ are present in the gas phase. The measured $\Delta_l^g H_m^\circ$ for the AIL and PIL are indicated as gray horizontal lines at 140 kJ mol^{-1} and 105.5 kJ mol^{-1}, respectively.

cation due to dispersion. Thus, for PILs substantial H-bond and dispersion energies are present in the gas-phase species and do not contribute to the vaporization enthalpies. The opposite is true for AILs. Substantial interaction energy between ion pairs has to be overcome, resulting in higher vaporization enthalpies.

In summary, we have presented combined experimental and computational methods for measuring accurate vaporization enthalpies and for clarifying the relevance of dispersion forces in ILs. With complementary methods, including fast scanning calorimetry and TGA, we have been able to measure consistent and reliable vaporization enthalpies for the thermally instable PILs (**IV**–**VI**). The surprisingly higher vaporization enthalpies for AILs are reflected in the stronger frequency shifts in the far-infrared spectra of these ILs. DFT calculations on larger clusters of these ILs with and without taking dispersion forces into account make it possible to dissect the different types of interaction energies. The fact that the vaporization enthalpies for PILs are lower than those for AILs results from hydrogen bonding within the PIL ion pair and dispersion forces between the ethyl groups within the ammonium cation. Thus substantial interaction energy is included in the gas-phase species, resulting in lower vaporization enthalpies for PILs.

Overall we provide evidence for and quantification of competing hydrogen bonds and dispersion forces in these interesting liquid materials. Our data analysis was based on the assumption that the IL vapor phase consists of ion pairs. This assumption has been essentially validated for the AILs,[18–23] as well as for the protic ionic liquid ethylammonium nitrate.[24] The nearly perfect agreement between the experimental and computed vaporization enthalpies for AILs and PILs suggests that this assumption is also justified for the ammonium-based protic ionic liquids studied in this work.

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