Ionic Liquids

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Do We Understand the Volatility of Ionic Liquids?**

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Ionic liquids (ILs) are organic salts with unusually low melting points, well below 100 °C. These substances have been suggested as potentially "green" replacements for traditional molecular solvents since they are nonvolatile, nonflammable, thermally stable, and recyclable. Additionally, they are opening the path to novel methods that are not possible using classical solvents. While remarkable progress has been made in recent years in the synthesis and application of ILs in catalytic and separation processes, as well as in electrochemistry, their physicochemical properties have not yet been studied systematically. This holds in particular for the thermodynamic properties of pure ionic liquids.[1–3] This is somehow surprising because a key property responsible for their increasing popularity is their essentially null volatility. This feature makes it easy to manipulate ionic liquids and facilitates their use in multiple reaction and extraction cycles, and it finally led to their recognition as environmentally friendly "green" solvents. Ironically, this characteristic has impaired many major developments toward the understanding of their macroscopic behavior through studies at the molecular level. The vapor pressure, enthalpy of vaporization, as well as the entropy of vaporization are among the fundamental properties required for developing and testing accurate molecular models. This is in particular true for the validation of new force fields used in molecular dynamics studies where the strength and nature of interactions between ions/molecules have to be adjusted (Figure 1).

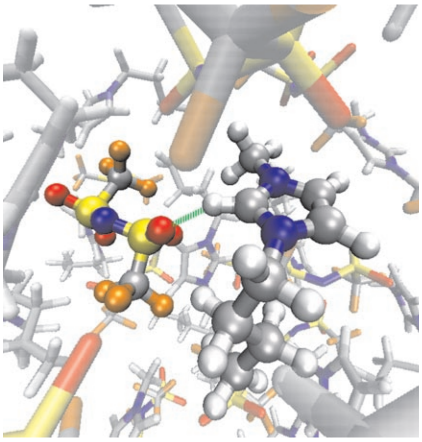

Figure 1. A snapshot of the ionic liquid [C_8MIM][NTf_2] from molecular dynamics simulations in the condensed phase. Recent experiments showed that the gas phase purely consists of ion pairs, as highlighted here.

Recent experiments have shed new light on the nature of the vapor, the heats of vaporization, and related vapor pressures and boiling points of ionic liquids. In practice, researchers are faced with two main problems: At room temperature the low vapor pressures of ILs are practically not measurable, whereas at high temperatures some of them may decompose through processes such as the transfer of an alkyl group or, in the case of protic ionic liquids, through deprotonation. For this reason, most of the exciting experiments highlighted herein are performed with 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [C_nMIM][NTf_2] ($n = 2$–8). This family of ionic liquids was chosen as a result of its thermal stability, which allowed measurements to be carried out up to 600 K.

In contrast to the common view that ionic liquids are nonvolatile substances, it was recently shown by Earle et al. that they can be distilled under reduced pressure.[4,5] The researchers could evaporate and recondense some ILs in the presumably stable regime below 500 K, and could even separate two ILs by distillation. Some time before, Swiderski et al. made use of the bimolecular rate constant of a Diels–Alder reaction to estimate Hildebrand's solubility parameter.[6] The reflected cohesive energy density of the liquid can be expressed in terms of the heat of evaporation $\Delta_{vap}H$. The obtained values of about 200 kJ mol^{-1} were much higher than those of common organic solvents but lower than estimates of up to 300 kJ mol^{-1} as sometimes reported.[7]

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Shortly thereafter, Rebelo et al. performed one-stage, reduced-pressure distillations at moderate temperatures of [C_nMIM][NTf_2] ionic liquids.[7] These liquid–vapor equilibria could be understood in light of predictions for boiling points (T_b) of ILs. The predictions are based on experimental surface tension and density data, which are used to estimate the critical points of several ILs and their corresponding normal boiling point temperatures. The estimated T_b values can be interpreted by considering that longer aliphatic chains in the 1-alkyl-3-methyimidazolium cation decrease the relative importance of the Coulomb forces, leading to smaller values of T_b. The surface tension decreases with increasing temperature and vanishes at the critical temperature T_c, as predicted by the well-accepted Eötvös rule, which is used to estimate critical temperatures and corresponding boiling temperatures. The Eötvös rule is founded in the corresponding states models. However, it is not quite sure whether such models can be easily transcribed to room-temperature ionic liquids (RTILs), although they are well fulfilled for alkali halides.

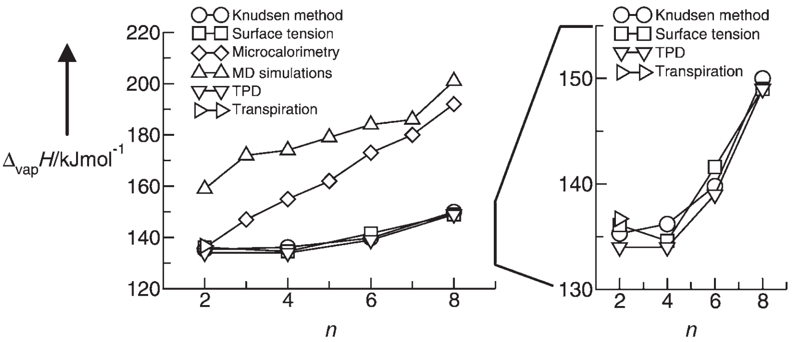

Figure 2. Molar enthalpies of vaporization of [C_nMIM][NTf_2] versus alkyl chain length as obtained by the Knudsen effusion method, surface tension measurements, microcalorimetric results, molecular dynamics (MD) simulations, the temperature-programmed desorption (TPD) method, and transpiration method.

Zaitsau et al. then measured vapor pressures for several homologues of [C_nMIM][NTf_2] using the Knudsen effusion method.[8] For temperatures near 450 and 550 K, they obtained vapor pressures between 10^{-8} and 10^{-7} bar. Extrapolation of the vapor pressure data to ambient pressure yields boiling temperatures of the order of 850–930 K, which is 200 K higher than the values predicted by Rebelo et al. on the basis of surface tensions.[7] Standard thermodynamic analysis of the vapor pressure curves provides molar enthalpies and entropies of vaporization at the average temperature (T_{av}) of the experiments. By means of heat capacity data, these may be extrapolated to 298 K.

Santos et al. used a vacuum-vaporization drop microcalorimetric method to measure the heat of vaporization of [C_nMIM][NTf_2] ionic liquids.[9] The total enthalpy change due to the heating of the liquid sample is measured by time integration of the heat flow entering the calorimeter. The enthalpy change corresponding to the vaporization of the sample can be easily separated from that due to the heating of the sample in the liquid phase from the initial (298.15 K) to the hot-zone temperature (577.8 K). The experimental data were compared with results from molecular dynamics simulations. The authors argue that although the simulation results overestimate the experimental values of about 5–15%, the predictive power of the model is very good since no data related to the energetics of these particular systems were introduced into the force field parametrization. Figure 2 shows the increase of the enthalpies of vaporization with the length of the alkyl side chain of the cation. This is the opposite statement given for the derived boiling points from surface tension measurements made by the same authors.[7] If Trouton's rule for ionic liquids is valid in the sense that the entropy of vaporization is definitely higher than 85 J mol^{-1} K^{-1} (the Trouton constant for non-associated liquids) but constant, then the heats of vaporization should increase with increasing boiling points.

Armstrong et al. presented the first detailed study of IL vapors using mass spectrometry.[10] They determined the nature of the vapor and the heats of vaporization of the liquids, and derived an electrostatic model relating the heats of vaporization to the molar volumes of the ILs. Ionic liquids were found to evaporate as ion pairs, with heats of vaporization which depend primarily on the coulombic interactions within the liquid-phase and the gas-phase ion pair.

Armstrong et al. measured the temperature-programmed desorption of eight ILs by sight mass spectrometry (LOSMOS) and observed an exponential increase of ion pairs leaving a thin liquid film of ILs.[10] By treating the process as a zero-order reaction, they could calculate an activation energy for desorption from a simple Arrhenius plot of the logarithmic counts (the LOS intensity) versus the inverse temperature. As evaporation occurs into the vacuum, the expanding gas does no work and the activation energy simply becomes the internal energy of vaporization. By addition of the term RT_{av} (T_{av} is the average desorption temperature), the authors obtained the heats of vaporization. By estimating the difference in heat capacity at constant pressure between the IL in the vapor and the liquid phase, these values could be converted into $\Delta_{vap}H_{298}$. The data are in excellent agreement with those obtained by Zaitsau et al. using the Knudsen effusion method but lower than the heats of vaporization measured by Santos et al. using the microcalorimetric method (Table 1).[8,9]

The finding that the gaseous phase of ionic liquids exists purely of ion pairs has been nicely supported by recent

Table 1: Estimated values of enthalpies of vaporization ($\Delta_{vap}H_{298}$ in kJ mol^{-1}) of [C_nMIM][NTf_2] (n = 2, 4, 6, 8) ILs obtained by various experimental and theoretical methods.

Ionic liquid	Knudsen[8]	Surface tension[8]	TPD[10]	Microcalorimetry[9]	MD simulations[9]	Transpiration[11]
[C_2MIM][NTf_2]	135.3	136.1	134	136	159 ± 10	136.7 ± 3.4
[C_4MIM][NTf_2]	136.2	134.6	134	155	174 ± 11	–
[C_6MIM][NTf_2]	139.8	141.6	139	173	184 ± 7	–
[C_8MIM][NTf_2]	150.0	149	149	192	201 ± 6	–

thermochemical measurements such as combustion and transpiration. Emel'yanenko et al. presented the first experimental determination of the gaseous enthalpy of formation based on experimental data of the enthalpy of vaporization and the enthalpy of combustion of an ionic liquid.[11] Quantum chemical calculations of the gaseous enthalpy of formation confirm the experimental value, indicating thermodynamic consistency of the procedure.

Overall, the new exciting findings comprise the volatility of some ionic liquids and the possibility to distil them, the proof that the gaseous phase exists purely of ion pairs combined with the determination of the gaseous enthalpy of formation, and finally the measurement of reliable enthalpies of vaporization showing that these values range between 120 and 200 kJ mol^{-1} rather than the tremendously high values as estimated in the past.

These facts open new possibilities for gas-phase processes involving ionic liquids, including their purification, high-temperature crystallization, and novel synthetic routes. It also has important theoretical implications: the nature of the gas phase has to be conclusively identified, and the vapor pressure and enthalpy of vaporization data should be rigorously determined as they are of inestimable value for the proper validation of molecular simulation protocols as well as the anchorage of parameters for equations of state.

However, there are still some weak points: There are potentially a million binary ionic liquids, whose physicochemical properties can be engineered to optimize temperature, substrate solubility, yield, and selectivity in chemical reactions. However, until now there have only been a few thermally stable ionic liquids that allow measurements to be carried out between 500 and 600 K and thus thermodynamic properties to be determined. The broad range of given enthalpies of vaporization still does not allow to parameterize reliable new force fields. For example, the measured values for [C_8MIM][NTf_2] range from 150 to 192 kJ mol^{-1} (see Figure 2). In other words, now that there are a variety of direct and indirect methods for determining thermodynamic properties, experimentalists should discuss which values are the most reliable and can be used for deriving IL force fields. There are further weak points: To adjust the values of enthalpy of vaporization to 298 K, one needs to evaluate the differences in heat capacity at constant pressure between the IL in the vapor and the liquid phases. Unfortunately these values are not known experimentally. In most of the cases, an estimated value of about 100 J mol^{-1} K^{-1} is used for all ionic liquids throughout.[11]

Vapor pressures, enthalpies of vaporization and boiling points are clearly physical chemical properties that depend on the cation–anion combination of a given ionic liquid. Up to now they have been checked experimentally for each new ionic liquid. Adjusting these properties should become an integral part of finding the best ionic liquid for a given application. From this respect, the combination of mass spectrometry with any other technique (Knudsen, thermogravimetric analysis) seems to be the most promising method to analyze vapors and to determine enthalpies of vaporization. However, we are still far from a situation where we can design ionic liquids on a basis of routinely measured properties including vapor pressures and enthalpy of vaporization as highlighted here.

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