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On the Critical Temperature, Normal Boiling Point, and Vapor Pressure of Ionic Liquids

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One-stage, reduced-pressure distillations at moderate temperature of 1-decyl- and 1-dodecyl-3-methylimidazolium bistriflilamide ($[Ntf_2]^-$) ionic liquids (ILs) have been performed. These liquid−vapor equilibria can be understood in light of predictions for normal boiling points 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 temperatures. In contrast to the situation found for relatively unstable ILs at high-temperature such as those containing $[BF_4]^-$ or $[PF_6]^-$ anions, $[Ntf_2]^-$-based ILs constitute a promising class in which reliable, accurate vapor pressure measurements can in principle be performed. This property is paramount for assisting in the development and testing of accurate molecular models.

1. Introduction

Ionic liquids (ILs) are a class of organic salts with unusually low melting temperatures that have attracted much attention from the scientific community in recent years. Besides being liquid at room temperature, ionic liquids exhibit interesting solvation and coordination properties that depend on the nature of the cation and/or anion. Another key factor responsible for their increasing popularity lies in their practically null volatility. This feature eases their manipulation and purification, facilitates their use in multiple reaction and extraction cycles, and has led to their recognition as environmentally friendly ("green") solvents.[1] Ironically, it is this same characteristic that has impaired many major developments toward the understanding of their macroscopic behavior via studies at a molecular level.

The vapor pressure (and its dependence on temperature) and, concomitantly, the enthalpy of sublimation or vaporization of a condensed phase are among those fundamental properties needed to contribute to the development and testing of accurate molecular models. To date, no such (reliable) data exist for ILs. For instance, the molecular modeling of ionic liquids faces a major challenge when it comes to the validation of new force-fields used in molecular dynamics studies: in the absence of experimental values of vapor pressure (or other energy-dependent phase transition data), it is difficult to justify the attribution of electrostatic interaction sites derived solely from quantum-mechanical studies of isolated molecules. Furthermore, in the case of "traditional" substances, the use of corresponding-states equations of state (EoS) has proven to be essential both for rationalizing experimental *p*,*V*, and *T* data of pure substances and their mixtures as well as for predictive purposes. Liquid−vapor critical parameters are obviously essential for the implementation of EoS correlations.

Even though the strength and nature of the intermolecular interactions are hard to quantify in the bulk of an ionic liquid, the same is not necessarily true with respect to its surface, where some surface tension results are becoming available.[2,3] This fact suggests two possible strategies: (i) validating new force-fields using nonisotropic molecular dynamics (MD) simulations capable of reproducing the surface tension data and/or ii) calculating relevant bulk-phase properties using surface tension data and comparing the outcome with traditional MD simulation results. The former is under implementation; the latter is explored in this paper. In addition, if estimations of normal boiling temperatures become available, one can identify those aprotic (in contrast to protic, relatively vaporizable ILs[4−6]), room-temperature ionic liquids in which higher chances of performing experimental vapor pressure measurements exist. This is done in the current work by comparing predicted normal boiling temperatures, T_b, with experimental decomposition ones, T_d, and, thus, identifying possible working-temperature windows.

To the best of our knowledge, there are neither experimentally available vapor pressures of ILs nor any kind of estimates regarding their critical point temperatures. Kabo and collaborators[7] attempted to determine the vapor pressure of [bmim][PF_6], but their results were inconclusive.

2. Critical Temperature from Surface Tension and Density Data of Pure Substances

The prediction of the critical temperature of a pure substance, based on the temperature dependence of its surface tension and liquid density, can be accomplished through the use of the Eötvos[8] or Guggenheim[9] empirical equations

$$\gamma V^{2/3} = A + BT; \quad T_c = -A/B \tag{1}$$

or

$$\gamma = \gamma^0 (1 - T/T_c)^{11/9} \tag{2}$$

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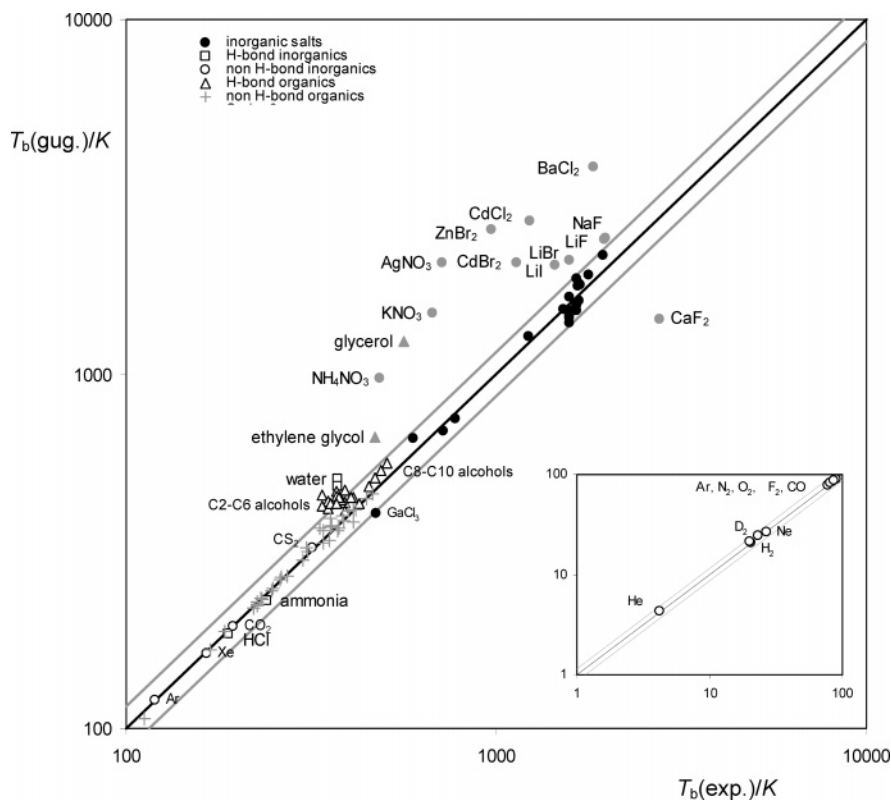‡ Instituto Superior Técnico.

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Figure 1. Comparison between experimental (*x* axis) and estimated (Guggenheim eq, *y* axis) normal boiling temperatures, T_b. The three lines represent +15, 0, and −15% inaccuracies. The insert shows the same comparison for substances with T_b up to 100 K. The gray circles and triangles correspond to compounds where the Eötvos and Guggenheim correlations yield inconsistent results. For the sake of clarity, some markers were left unlabeled; the corresponding names/values can be found in Table A, Supporting Information.

respectively, where γ is the surface tension, T_c is the critical temperature, and V is the orthobaric molar volume of the liquid. Both equations reflect the fact that γ becomes null at the critical point and are based on corresponding states correlations[10] that, following a suggestion by van der Waals more than a century ago,[11] link the dimensionless group $\gamma/(T_c^{1/3} p_c^{2/3})$ to $(1 - T/T_c)$. Since, for most substances, the normal boiling temperature, T_b, lies around 0.6 of T_c,[12] the prediction of T_c can also lead to an estimated value for T_b.

To test the adequacy of such equations in the prediction of critical/normal boiling temperatures, an extended set of 90 compounds with known T_c and/or T_b, $\gamma(T)$, and $V(T)$ was tested. The compounds ranged from quantum liquids (He, H$_2$, and Ne) with critical temperatures of a few units or tens of Kelvin to molten inorganic salts with normal boiling point temperatures above 1000 K. Inorganic and organic compounds with strong hydrogen bonding were also included. The results (including selected input data and their sources) are presented in Table A of the Supporting Information and depicted graphically in Figure 1. Since there are no available experimental critical data for molten inorganic salts, we chose to plot normal boiling point temperature values (estimated versus experimental) for all studied substances. The estimated T_b values were calculated by multiplying the predicted T_c values by the experimental ratio (T_b/T_c) (when both values were available) or the empirical value of 0.6 (for the molten inorganic salts).

Three main conclusions can be drawn from the results:

(i) The critical/normal boiling temperature of most substances can be predicted with an accuracy better than 10%. This is a very satisfactory result considering the fact that the predicted values of T_c span 3 orders of magnitude for markedly distinct substances. Moreover, in most cases, we used $\gamma(T)$ and $V(T)$ data in a temperature range much lower than T_c (cf. Table A,

Supporting Information) implying rather large extrapolations when using eqs 1 and 2.

(ii) The main exceptions to the first part of the previous statement are the cases of water, light alcohols, and a few inorganic molten salts. In the case of water and the alcohols, the inadequacy of the Eötvos and Guggenheim equations is a known fact (for instance the 11/9 exponent in the Guggenheim equations is modified to 0.8 in the case of strongly hydrogen bonded substances). As for some molten inorganic salts, it is more difficult to judge what is inadequate. First of all, it is important to stress that, in this class of compounds, the experimental values of the critical temperature are not known (as mentioned above, the comparisons are based on the experimental normal boiling temperatures versus the predicted critical temperatures multiplied by a factor of 0.6). Second, many of these compounds start to decompose as the temperature approaches its normal boiling point value (salts that include the nitrate anion are a good example). Third, the salts with greater deviations are those in which there are large charge densities (salts with lithium, fluorine, or divalent ions).

(iii) Whenever the two predicted T_c values (Eötvos and Guggenheim estimates) are far from the experimental one, they are also distant from each other. In other words, the use of both equations can be seen as a test of the internal consistency of the prediction method itself. This is illustrated by the behavior of the molten inorganic salts in Figure 1 (gray and black points): the gray points are shaded differently not because they lie outside the two 15% error lines but because for those points the two correlation methods give values more than 20% apart.

3. Normal Boiling-Point Temperatures of Ionic Liquids

As before, eqs 1 and 2 were used to estimate the normal boiling-point temperature of those ILs for which surface

TABLE 1: Estimated Critical Temperatures, T_c/K, and normal Boiling Temperatures, T_b/K, Using Both the Eötvos (Eot) and Guggenheim (Gug) Equations[a]

ionic liquid	T_c/K (Eot)	T_c/K (Gug)	T_b/K (Eot)	T_b/K (Gug)	$[T_b - (T_d)]$ range/K
series I[b]					
[C8mim][Cl]	931	969	559	581	580−(515)[18]
[C8mim][Br]	856	797	514	478	480−(n.a.)
[C4mim][BF4]	1240	1158	744	695	695−(630/710)[14a,15,16,18]
[C8mim][BF4]	1027	990	616	594	595−(630/710)*
[C12mim][BF4]	908	904	545	542	540−(630/710)*
[C4mim][PF6]	1051	1007	630	604	605−(620/710)[15,18]
[C8mim][PF6]	997	972	598	583	585−(650)[18]
[C12mim][PF6]	783	813	470	488	490−(620/710)*
series II[c]					
[C4mim][PF6]	1187	1102	712	661	660−(620/710)[15,18]
[C6mim][PF6]	1109	1050	665	630	630−(690)[18]
[C10mim][PF6]	906	896	544	538	540−(620/710)*
[C2mim][Ntf2]	1209	1100	725	660	660−(710/730)[17,18]
[C4mim][Ntf2]	1077	1012	646	607	605−(695/710)[14a,15,18]
[C6mim][Ntf2]	967	932	580	559	560−(695/710)*
[C10mim][Ntf2]	797	800	478	480	480−(695/710)*

[a] Approximate temperature ranges bounded by the boiling and the onset of thermal decomposition are defined as $[T_b - T_d]$. n.a., not-available. *, not-available but assuming that T_d is independent of the alkyl chain length. [b] Surface tension data needed for the calculations taken from ref 2. [c] Our results of surface tension[3] were used for the calculations.

tensions[2,3] as well as densities[13,14] are known (see Table B, Supporting Information). In all cases, differences in the estimated critical temperatures equated between the Eötvos and Guggenheim expressions are less than 9%, typically 5%, and are reported in Table 1. This table also shows predicted normal boiling temperatures ($T_b \sim 0.6T_c$).

Normal boiling temperatures of ionic systems are inherently high because strong, long-range Coulomb interactions prevent the particles' separation into the gas phase, even more so as the ion size decreases and charge density increases. However, ILs composed of structured, bulky cations and anions, present, in addition to Coulomb forces, not so strong short-range ones (van der Waals and hydrogen bonding). The estimated T_b values depicted in Figure 2 can be interpreted considering that longer aliphatic chains in the 1-alkyl-3-methylimidazolium cation decrease the relative importance of the Coulomb forces leading to smaller values of T_b.

Figure 2 plots the upper limit value within the estimated error bar of predicted T_b's against the alkyl chain length of the 1-alkyl-3-methylimidazolium-based ILs investigated. The plot shows a clear quasi-linear decrease in the normal boiling temperature as the alkyl chain length increases, and, perhaps, a tendency in the same direction as the counteranion becomes bulkier. If one compares the predicted T_b's with the corresponding experimentally available[14a,15−18] thermal decomposition temperatures, T_d's, windows of possible experimental working temperatures for vapor pressure measurements can be identified (see also Table 1 and note 19). [Ntf2]$^-$-based ILs clearly constitute a very promising case. A few comments are pertinent: (i) reliable, accurate, vapor pressure measurements can be performed at pressure values much lower than the atmospheric one, i.e., at temperatures below T_b, and, therefore, the range of working temperatures is broader than that suggested in Table 1; (ii) conversely, since the expected enthalpies of vaporization[20] are on the order of hundreds of kJ mol^{-1}, this temperature interval broadening is limited by the fact that vapor pressures will significantly drop as temperature does so (for instance, for a vaporization enthalpy of 300 kJ mol^{-1}, the vapor pressure drops 1 order of magnitude with each decrease of 15 K); (iii) on the other hand, degradation may start at temperatures below T_d. In any case, it seems clear that, at least for stable [Ntf2]$^-$-based ILs, and mainly for long alkyl chain lengths, it is worth exploring
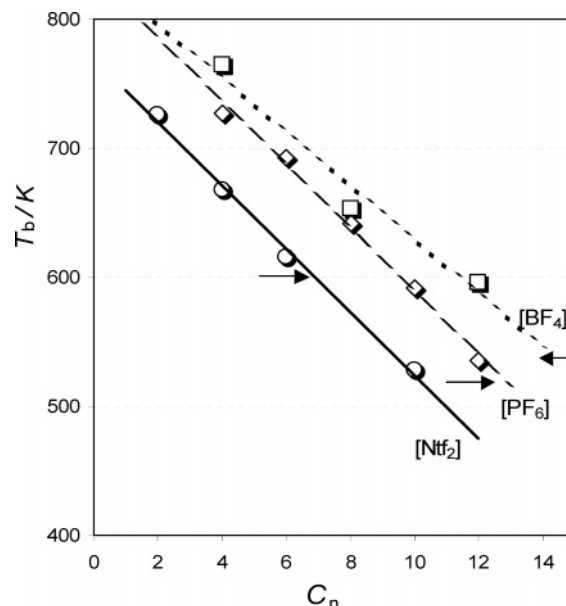

Figure 2. Effect of the alkyl chain on the estimated ($\pm$ 10% inaccuracy) normal boiling temperatures (Guggenheim equation) of the [BF4] (□), [PF6] (◇), and [Ntf2] (○) families of 1-alkyl-3-methylimidazolium − based ILs (see Table 1). Horizontal arrows stand for thermal decomposition temperatures.[19] We consider the most pessimistic scenario: (i) lowest T_d found in the literature (assuming an approximate independence on the length of the alkyl chain) minus 100 K, and (ii) upper limit of the estimated T_b's (T_b (Gug) + 10%) within their error bar range.

direct vapor pressure determinations between temperatures below T_b up to almost T_d.

Encouraged by these predictions, we decided to make a first attempt to distill samples of ILs. [C10mim][Ntf2] and [C12mim]-[Ntf2] seemed to constitute a good choice. The samples (aprox. 1 g) were initially degassed in 10 mL round-bottom flasks for 2 days at moderate temperature (70 °C) in a vacuum line (1 Pa). This procedure permitted the removal of both traces of water and any volatile impurities. The ILs were then heated to 450 K for several hours at reduced pressure, using a silicone oil bath and the same vacuum line. After the first initial 30 min, many small liquid droplets condensing on the upper, colder part of the flasks were clearly visible. The volume of the droplets

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increased with time, and after several hours already represented $\sim 5-10\%$ of the total initial mass of ILs used. Neither the residues nor the condensed droplets showed signs of thermal degradation as they appeared clearly transparent and colorless. The condensed droplets were analyzed by electro-spray mass spectrometry. The spectra only revealed the presence of the ILs and were similar to those of the residues and original samples. This simple experiment demonstrates the potential for distilling certain ILs at reduced pressure. We are currently designing a simple, moderately high-temperature apparatus for the accurate and precise determination of vapor pressures versus temperature in the $0-10$ mbar pressure range. We would also like to encourage other researchers to perform similar determinations. If one succeeds, enthalpies of vaporization (which are intimately related to lattice, cohesive, or configurational energies) can be obtained, providing the scientific community with one of the best tools for the validation of molecular simulations.

Supporting Information Available: Preparation, purification and characterization of [C$_{10}$mim][Ntf$_2$] and [C$_{12}$mim][Ntf$_2$]; ESI-MS spectra of the recondensed droplets of ILs (Figure S1); tabulated data of experimental and estimated T_c and T_b for 90 compounds (Table A); Surface tension and molar volume ranges of several 1-alkyl-3-methylimidazolium-based ILs (Table B). This material is available free of charge via the Internet at http://pubs.acs.org.

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