

Reviews

Volatility of Aprotic Ionic Liquids — A Review

José M. S. S. Esperança,[†] José N. Canongia Lopes,^{†,‡} Mohd Tariq,[†] Luís M. N. B. F. Santos,[§] Joseph W. Magee,^{||} and Luís Paulo N. Rebelo^{*,†}

Instituto de Tecnologia Química e Biológica, Universidade Nova de Lisboa, Av. da República, Apartado 127, 2780-901 Oeiras, Portugal, Centro de Química Estrutural, Instituto Superior Técnico, 1049-001 Lisboa, Portugal, Centro de Investigação em Química, Faculdade de Ciências, Universidade do Porto, 4169-007 Porto, Portugal, and Thermophysical Properties Division, National Institute of Standards and Technology, 325 Broadway, Boulder, Colorado 80305

Research on the volatility of aprotic ionic liquids is reviewed. This topic is limited to aprotic liquids since measurements have led to a generalization that this class of substances possesses extremely low vapor pressures. For research related to this topic, the period covered is 2003 to 2008. The review begins with a discussion of the earliest successful study of thermal vaporization of aprotic ionic liquids, the earliest indirect measurements of their vapor pressure, the first proof of conventional distillation of ionic liquids, and competition of vaporization with thermal decomposition seen at moderately high temperatures of (200 to 300) °C. The review then briefly discusses the nature of the vapor phase and proceeds to analyze the various approaches used to measure or predict the vapor–liquid equilibrium properties of ionic liquids, including their normal boiling point, vapor pressure, and enthalpy of vaporization. It is proposed that the most reliable thermodynamic data exist solely for the enthalpy of vaporization, and thus this property would be the best target for predictive approaches. Predictive approaches to calculate the enthalpy of vaporization are discussed in light of their ability to predict the experimentally observed trends with molar mass. The review concludes with a forward look at the following: expected effect of gas-phase ion clusters; anticipated trade-off between the energetic gain and the entropic penalty for cluster formation; and the possibility of a Trouton rule for the vaporization of ionic liquids.

Introduction

The field of ionic liquids research continues to witness an extraordinary period of rapid growth. Furthermore, an uncommonly broad range of topics has been covered by publications in this field. Research studies have run the gamut from the most fundamental topics¹ to the most applied² ones. Fundamental research has sought to better understand, often at a molecular level, the unusual and sometimes unexpected behavior of this class of compounds, while applied research has led to breakthrough applications that demonstrate the potential to improve well-established industrial processes or allow the design of novel or sustainable solutions to old problems. Ionic liquids can be subdivided into two classes, namely, protic—those that contain an acidic proton on the cationic species—and aprotic—those containing no acidic proton. The reason for this distinction is that protic ionic liquids are volatile by their nature because the acidic proton can be abstracted by the basic anion at ambient temperature. The acid–base equilibrium for the abstraction reaction allows the formation of neutral molecular species that readily evaporate. In fact, the first published vapor pressures³ on ionic liquid mixtures, by Wilkes and collaborators, brought into play the same type of chemical reaction equilibria. The present review focuses on volatility of aprotic ionic liquids.

From time to time, a specific topic within a field of research has matured to a point that a topical review is both useful and necessary. This need arises typically when an upsurge of new publications that contain useful data has made it impractical for researchers to collect and digest them on a large scale or to cite all or most of them as background information in their manuscripts. The volatility of ionic liquids may be considered to be such a topic. Reaching beyond the rather obvious utility, many underlying issues in this field are still controversial and thus under active debate. This review draws together both experimental and predictive approaches to explore such open questions. Until recently, ionic liquids were broadly regarded as nonvolatile salts. In addition to this, they were thought of as nonflammable and thermally and chemically stable salts. However, based on data published in the last several years, these assumptions have had to be progressively reconsidered. This review addresses the subject of ionic liquids' volatility with a chief aim to bring into perspective some of the more recent discoveries in this area.

The first successful study⁴ that dealt with the possibility of thermal vaporization of aprotic ionic liquids was published in March 2005. That work was immediately followed by that of Kabo and collaborators who reported the first indirect determinations of the vapor pressure of some ionic liquids⁵ and by the first irrefutable proof⁶ that vaporization did not occur by any mechanism other than the direct liquid-to-gas transfer of the

* Corresponding author. E-mail: luis.rebelo@itqb.unl.pt.

[†] Universidade Nova de Lisboa.

[‡] Instituto Superior Técnico.

[§] Universidade do Porto.

^{||} National Institute of Standards and Technology.

chemically intact cations and anions of the ionic liquid, which is directly analogous to the processes that occur in conventional distillations.

One of the most important aspects of these pioneering studies was the demonstration that, for selected families of ionic liquids, there were *windows of opportunity* for their distillation. Simultaneously, these studies clearly showed that, for many of them, the determination of relevant liquid–vapor equilibrium properties is either *extremely difficult* (thus, potentially inaccurate), such as for the vapor pressure, p_v , and the enthalpy of vaporization, $\Delta_{\text{vap}}H$, or is simply *forbidden territory*—as for the normal boiling temperature, T_b , and the critical temperature, T_c .⁷ This is due to the competition between vaporization and decomposition mechanisms as well as the non-negligible effect of the presence of trace impurities. These studies also demonstrated that the vapor pressure of ionic liquids can be very small ($\ll 1$ Pa) even at the relatively high temperatures of (200 to 300) °C, which for some ionic liquids was below the onset of decomposition. However, for many families of ionic liquids, the onset of decomposition starts at temperatures too low for significant vaporization to occur. In fact, the stage had been set by two earlier experimental studies^{8,9} of the thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate, [C₄mim][PF₆]. These studies were the first to present ideal gas thermodynamic properties calculated from spectral data and absolute entropy values of the condensed state calculated from heat capacity measured by adiabatic calorimetry. These authors also reported that vapor pressure p_v measurements by the Knudsen effusion approach was not possible due to slow decomposition reactions at a temperature of 220 °C, which was 200 °C below the reported thermal decomposition temperature. This technical failure was overcome to a degree by combining their thermodynamic properties of the gaseous and liquid states and the derived $\Delta_{\text{vap}}S(298.15 \text{ K})$ value with a value of $\Delta_{\text{vap}}H(298.15 \text{ K})$ calculated by molecular simulation^{10,11} to obtain the first estimate of the vapor pressure of [C₄mim][PF₆] to be 10^{-11} Pa at 25 °C. This estimate, though accurate only to an order of magnitude, made it abundantly clear why lab researchers had never before observed vaporization of [C₄mim][PF₆] under a typical lab vacuum (10^{-3} Pa) and ambient temperature. It was no surprise that there were experimental reports of *no vapor pressure* for [C₄mim][PF₆]. At the same time, this state of affairs did not deter theoretically oriented studies from trying to estimate the enthalpy of vaporization or the cohesive energy density of this and other ionic liquids. Apart from the already mentioned works of Maginn and collaborators,^{10,11} where values around $158 \text{ kJ}\cdot\text{mol}^{-1}$ were estimated by molecular dynamics simulations for the enthalpy of vaporization of [C₄mim][PF₆] at 298 K, Lee and Lee¹² reported internal energy of vaporization values (obtained using Hildebrands regular solution theory) for a series of ionic liquids in the (149 to 226) $\text{kJ}\cdot\text{mol}^{-1}$ range. Although these early results tended to overestimate the cohesive energies of ionic liquids, they represent the first attempts to quantify the energetics involved in the vaporization process.

A Case in Point

A recent topical publication (“Do we understand the volatility of ionic liquids?”), by Ludwig and Kragl,¹³ highlighted the recently discovered concept of ionic liquid volatility and its quantification. Although the title of their work embraces a question, the reader is left with the impression that for these salts the relations between the $\Delta_{\text{vap}}H$, p_v , and normal boiling temperature, T_b , have been worked out completely. However,

in consideration of all the research that has been reported to date, this is far from the case. In addition to issues related to the context in which the earliest distillations of ionic liquids were performed, two basic questions related to their volatility remain to be addressed. The first concerns the nature of the gaseous phase of ionic liquids. This issue includes those experiments that led to the conclusion that under normal distillation conditions at moderate temperatures and reduced pressures ionic liquids vaporize as neutral contact ionic pairs and that these are the ubiquitous species in the vapor phase. The second question concerns the measurement of liquid–vapor equilibrium thermodynamic data (namely, p_v or $\Delta_{\text{vap}}H$). This issue includes those problems arising from measurements under extremely difficult conditions (very low pressures and moderately high temperatures), the direct or indirect nature of the experimental methods, the apparent inconsistency between different sets of data, and the complex nature of ionic liquids that renders ineffective some of the assumptions and correlations that are usually taken for granted when dealing with molecular fluids.

Nature of the Vapor Phase

Published proof that aprotic ionic liquids could be vaporized⁶ led to a wealth of studies, both experimental and theoretical, which were designed to determine the nature of the vapor phase under reduced-pressure distillation conditions.^{14–21} Research on this very interesting subject is only tangentially related to this review, which is centered on liquid–vapor equilibrium (the vaporization or volatility of an ionic liquid) and not on the vapor phase per se. Nevertheless, the above-mentioned studies concluded that under moderate temperatures and low pressures the vapor phase of aprotic ionic liquids that vaporize without decomposing is most likely composed entirely of neutral contact ion-pairs.^{14–18} This finding is vital for both the calculation and comparison of $\Delta_{\text{vap}}H$ data obtained by use of either experimental or molecular simulation^{19,20,22,23} techniques that intrinsically depend on the nature of the vapor-phase species. In this context, it must be stressed that direct calorimetric results of enthalpy of vaporization data are intrinsically *per-mass* values; they do not depend on the vapor–liquid equilibrium model and contain no information that specifies the equilibrium. On the other hand, vapor pressure data, when indirectly obtained via Knudsen effusion experiments, are calculated with a defined hypothetical vapor–liquid equilibrium model in which the mass loss is related to the equilibrium vapor pressure. The analysis and real meaning of indirect results obtained for the vapor–liquid equilibrium in systems that also undergo other vapor-phase equilibria are a quite challenging task, which can be rationalized only in combination with other experimental results.

When the early studies on this subject^{4–6} were published, there was no evidence for the structure of the species that exist in the vapor phase of aprotic ionic liquids. Consequently, predicted values of $\Delta_{\text{vap}}H$ (ca. $300 \text{ kJ}\cdot\text{mol}^{-1}$ for a *generic* ionic liquid) were, in fact, justifiable at the time, in a scenario that assumed that the gas phase would be composed of dissociated ionic species. In addition, early simulation results for 1-alkyl-3-methylimidazolium-based ionic liquids had yielded similar energy differences between the liquid phase and the dissociated ions.²⁴

Presently, we know that under conditions of moderately high temperatures and low pressures the equilibrium gas phase of some commonly investigated aprotic ionic liquids is composed only of isolated neutral ion pairs. Furthermore, we know that within these working temperature and pressure ranges 1-alkyl-

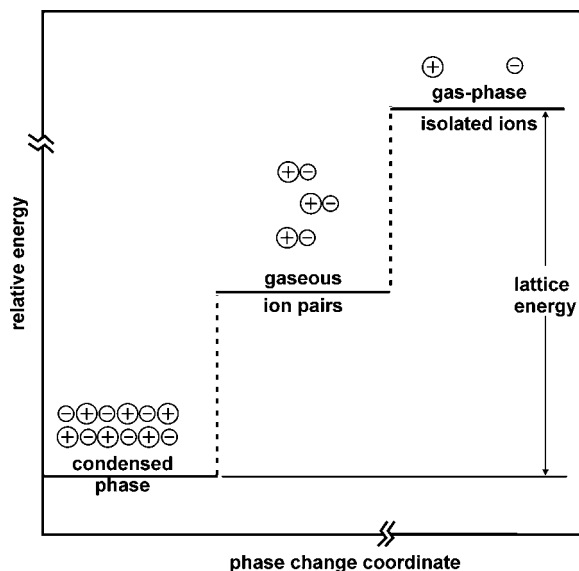


Figure 1. Schematic representation of the energy differences between the condensed phase and the gas phase composed of contact ion pairs and between the gas with ion pairs and gas phase with isolated ions. The lattice energy is shown schematically.

3-methylimidazolium-based ionic liquids, when combined with the bis(trifluoromethylsulfonyl)imide [NTf₂] anion, have $\Delta_{\text{vap}}H$ values in the range of (130 to 180) kJ·mol⁻¹. There are other ionic liquids, such as those based on the triazolium cation,²⁵ which present estimated (by simulation studies assuming contact ion-pairs in the gas phase) $\Delta_{\text{vap}}H$ values around 250 kJ·mol⁻¹.

The relations between the energies involved in the vaporization of an ionic liquid (in vapor–liquid equilibrium) and the structure of the gas are summarized in Figure 1. Molecular modeling calculations^{19,20} have yielded quantitative estimates of the energies involved in the formation of ionic liquid clusters of different sizes. Figure 1 shows the overall picture that points to differences of (300 to 500) kJ·mol⁻¹ between the internal energies of the isolated ionic species and the liquid, differences of (100 to 250) kJ·mol⁻¹ between the internal energies of ionic pairs and the liquid (related to enthalpies of vaporization), and differences of (250 to 400) kJ·mol⁻¹ between the internal energies of the isolated ionic species and the ionic pairs (energies of pair formation). Simulation results¹⁹ have also shown that at high temperatures (above those thus far used in vaporization experiments) ionic pairs present in the gas phase will dissociate into isolated ions and that at lower temperatures they will form larger ionic neutral aggregates, shown schematically in Figure 2.

In contrast to the aforementioned observations, the first matrix-isolated FTIR spectrum of a vaporized ionic liquid seems to indicate that the structures of the isolated species are different from both the liquid phase and from a 1:1 neutral contact ion pair.²¹ This result could reopen the debate on the nature of the gas phase of ionic liquids and highlights the need for further systematic studies on different classes of these compounds.

VLE Data

Correlations and Discussion. Figure 3 shows different approaches that have been used to estimate three properties related to vapor–liquid equilibria of ionic liquids: T_b , p_v , and $\Delta_{\text{vap}}H$. The different techniques are grouped into experimental, theoretical, and data correlation methods. Note that the first property, the normal boiling temperature, T_b , may be viewed

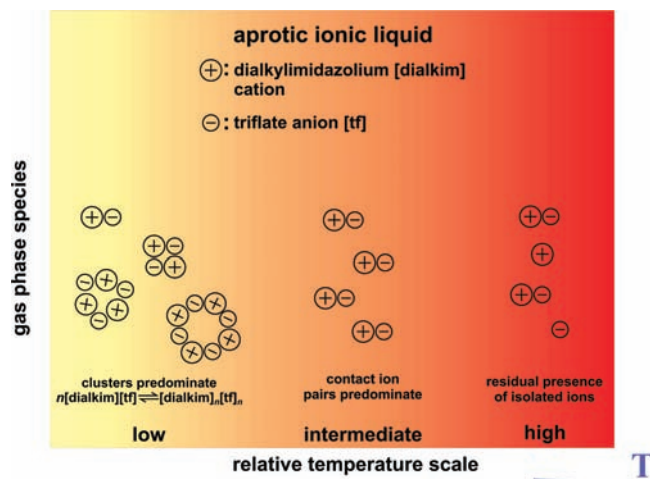


Figure 2. Scheme showing the distinct possibility of gaseous species ranging from clusters of n ion pairs, to contact ion pairs, to isolated single ions. The figure considers a typical aprotic ionic liquid family: a dialkylimidazolium triflate.¹⁹

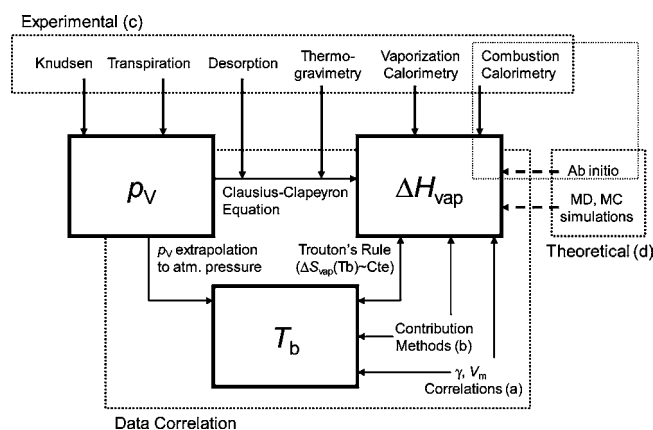


Figure 3. Schematic representation of four general approaches to obtain enthalpy of vaporization: (a) correlations; (b) group contributions; (c) experimental; and (d) theoretical.

as a hypothetical property—not experimentally accessible—due to thermal decomposition.

VLE properties of ionic liquids as a subject of research was launched with a correlation-oriented paper,⁴ in which the authors reported the estimation of hypothetical critical and normal boiling temperatures for different ionic liquids by use of density and surface tension experimental data (cf. Figure 3, label a). Recently, those ideas were taken even further, and values of molar enthalpies of vaporization at the normal boiling temperature were also calculated from density and surface tension data.²⁶ The authors of the latter publication referred to the use of the method described by Rebelo and collaborators in ref 4. However, despite its importance, the method described in that paper allows only for rough estimates of both the critical and normal boiling temperatures. The central problem with this approach is attributable to the use of the Eötvös and Guggenheim equations

$$\gamma V^{2/3} = A + BT \quad (1)$$

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

where γ is the surface tension; T_c is the critical temperature; and V is the orthobaric molar volume of the liquid. From these equations, the critical temperature, T_c , is estimated as the temperature for which the surface tension, γ , is inherently zero.

Therefore, these equations were used⁴ to perform very long extrapolations on the temperature axis to estimate critical temperatures. The authors used experimental density and surface tension data, which typically cover a limited temperature range of about 50 °C, and extrapolated them more than 1000 °C to very high temperatures. To reduce this long extrapolation, new surface tension data were measured²⁷ for the [C_nmim][NTf₂] family up to 200 °C. These newer results showed that the calculated critical temperatures vary monotonically from approximately (1200 ± 100) °C for [C₂mim][NTf₂] to (900 ± 100) °C for [C₁₄mim][NTf₂]. An empirical coefficient is used to calculate the normal boiling temperatures from the estimated critical temperatures. As stated in the original manuscript⁴ and again in other later publications, there are some substances that, due to strong hydrogen bonding, are not consistent with either the Guggenheim equation (i.e. the exponent changes from 11/9 to 8/10) or the ratio of the normal-boiling temperature to the critical temperature (i.e., the ratio changes from 0.6 to greater than 0.7).^{4,7} Other correlations have been used that are based on density and surface tension data, by use of the Stefan equation or the Fowkes approach^{28,29}

$$\gamma = \frac{\Delta_{\text{vap}}H Z_S}{V^{2/3} N_A^{1/3} Z} \quad (3)$$

$$\Delta_{\text{vap}}H = A(\gamma V^{2/3} N_A^{1/3}) + B \quad (4)$$

where Z_S and Z are the surface and bulk coordination numbers for the molecules in the liquid. This approach yields directly calculated values of $\Delta_{\text{vap}}H$ at room temperature and avoids the extremely long extrapolations of the previous method. However, this method involves fitting two empirical parameters, which means that the method is no longer purely predictive and relies on the hypothesis that the parameters obtained for a given ionic liquid family are transferable to other ionic liquids.

Group contribution methods for T_b or $\Delta_{\text{vap}}H$ have been suggested by different authors^{5,29–31} (Figure 3, label b). Paulechka et al.⁵ proposed a contribution method to estimate $\Delta_{\text{vap}}H$ from the atomic composition of a given molecule or ionic pair

$$\Delta_{\text{vap}}H_{298}/\text{kJ} \cdot \text{mol}^{-1} = 6.2n_C + 5.7n_O + 10.4n_N - 0.5n_F + 10.6n_S \quad (5)$$

where n_C , n_O , n_N , n_F , and n_S represent the number of carbon, oxygen, nitrogen, fluorine, or sulfur atoms in the ionic liquid.

Using another approach, Valderrama and Robles^{30,31} developed a contribution method to estimate the critical parameters and (indirectly) the normal boiling points of ionic liquids. Finally, Verevkin²⁹ developed an additive approach based on the empirical formula of an IL in which the enthalpy of vaporization is divided in two main contributions, one from the elemental constituents of the IL (independent of their position on the cation and anion) and the other from auxiliary contributions due to structural peculiarities of each IL.

From our perspective, the main problem with the application of these methods concerns the inadequacy of independent experimental data that are available to implement and validate them. For instance, in the case of Verevkin's method, where some, but not all, structural characteristics of ionic liquids are taken into account, the $\Delta_{\text{vap}}H$ of 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [C₄mim][NTf₂], and 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [C₃mmim][NTf₂], should be exactly the same. Unfortunately, structural differences between these two isomers are not taken

Table 1. Experimental Vapor Pressure Data, p_v , and Normal Boiling Temperature Calculation, T_b^a

| ionic liquid | method | T_i | T_i | $p_v(T_i)$ | $p_v(T_i)$ | T_b |
|---|-----------------------------|-------|-------|------------|------------|-------|
| | | K | K | mPa | mPa | K |
| [C ₂ mim][NTf ₂] | Knudsen ²⁸ | 442 | 484 | 6.2 | 109 | 907 |
| | transpiration ³⁸ | 499 | 538 | 157 | 1119 | 966 |
| [C ₄ mim][NTf ₂] | Knudsen ⁵ | 458 | 517 | 12.2 | 466 | 924 |
| | Knudsen ²⁸ | 438 | 517 | 3.6 | 515 | 933 |
| [C ₆ mim][NTf ₂] | Knudsen ²⁸ | 446 | 494 | 6.7 | 172 | 885 |
| [C ₈ mim][NTf ₂] | Knudsen ²⁸ | 455 | 498 | 7.8 | 154 | 857 |
| [C ₄ mim][dca] | transpiration ³⁸ | 449 | 480 | 192 | 2206 | 690 |

^a The experimental measurements were performed on the temperature range (T_i to T_i).

into account by the method in its present form, while experimentally determined $\Delta_{\text{vap}}H$ values³² show a difference of ca. 15 kJ·mol⁻¹. However, this method could undergo a refinement to account for this difference, with the caution that there are only limited high-accuracy data available. If one is less selective in choosing the best training data to be fitted, it would be possible to end up with a group contribution method that is fitted to nearly all experimental points but unfortunately has very limited predictive power.

Another important issue (especially in the context of Valderrama's work^{30,31}) is the fact that, for ionic liquids, T_b is a property that is inaccessible experimentally. This means we must select another thermodynamic property that is closely related to T_b to meaningfully compare with experimental data. Obviously, the cohesive energy of an ionic liquid would impact the value of its boiling point. However, it is not yet clear whether any Trouton-like correlation^{33,34}

$$\frac{\Delta_{\text{vap}}H_{T_b}}{T_b} = \Delta_{\text{vap}}S_{T_b} \approx 85 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1} \quad (6)$$

exists between $\Delta_{\text{vap}}H$ and T_b (see below).

After that first correlation-oriented paper (and contemporaneous with other correlation methods just described), some experimental results started to emerge in the literature. These results concerned either p_v or $\Delta_{\text{vap}}H$ measurements (cf. Figure 3, label c). In the case of ionic liquids, where the vapor pressure is typically near 1 Pa at temperatures just below the onset of decomposition, the pressure measurements were performed by effusion^{35–37} (Knudsen cell^{5,28})—see Appendix 1—or gas saturation (transpiration³⁸) methods. In the case of the Knudsen cell experiments, all measurements were performed with ionic liquids of the 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide family, [C_nmim][NTf₂], with $n = 2, 4, 6$, and 8. In the case of the transpiration method, the studied systems were [C₂mim][NTf₂] and 1-butyl-3-methylimidazolium dicyanamide, [C₄mim][dca] (see Tables 1 and 2). As a historical footnote, an early attempt^{8,9} to measure the vapor pressure of [C₄mim][PF₆] was not successful because vapor pressures were found to be below the detection limit (less than 10⁻² Pa) of the experimental setup.

In the case of the [C_nmim][NTf₂] family, the p_v data at a given temperature present a sawtooth-like trend along the series ($p_v(n=2) > p_v(n=6) > p_v(n=4) > p_v(n=8)$). This peculiar trend may be just a consequence of the difficulty of the p_v determinations; for instance, the values for [C₂mim][NTf₂] obtained using the Knudsen²⁸ and transpiration³⁸ methods are inconsistent with each other, but in spite of this they yielded very similar $\Delta_{\text{vap}}H$ values through the use of the Clausius–Clapeyron equation for each isolated data set

Table 2. Experimental and Calculated Thermodynamic Properties of Vaporization^a

| ionic liquid | method | T_{av} K | $\Delta_{vap}H(T_{av})$ kJ·mol ⁻¹ | $\Delta_{vap}H(298K)$ kJ·mol ⁻¹ | $\Delta_{vap}H(T_b)$ kJ·mol ⁻¹ | $\Delta_{vap}S(T_b)$ J·K ⁻¹ ·mol ⁻¹ |
|--|-----------------------------|---------------|---|---|--|--|
| [C ₂ mim][NTf ₂] | Knudsen ²⁸ | 463 | 119 | 135 | 74 | 82 |
| | transpiration ³⁸ | 519 | 115 | 137 | 70 | 73 |
| | desorption ¹⁴ | 430 | 121 | 134 | 70 | 75 |
| | calorimetry ⁴² | 578 | 110 | 136 | 72 | 77 |
| | gravimetry ³² | 496 | 121 | 141 | 77 | 82 |
| [C ₃ mim][NTf ₂] | calorimetry ⁴² | 578 | 121 | 147 | - | - |
| [C ₄ mim][NTf ₂] | Knudsen ⁵ | 487 | 120 | 138 | 75 | 82 |
| | Knudsen ²⁸ | 478 | 118 | 136 | 73 | 78 |
| | desorption ¹⁴ | 440 | 120 | 134 | 71 | 76 |
| | calorimetry ⁴² | 578 | 128 | 155 | 92 | 99 |
| | gravimetry ³² | 496 | 119 | 139 | 76 | 82 |
| [C ₅ mim][NTf ₂] | calorimetry ⁴² | 578 | 134 | 162 | - | - |
| [C ₆ mim][NTf ₂] | Knudsen ²⁸ | 462 | 123 | 140 | 81 | 92 |
| | desorption ¹⁴ | 445 | 124 | 139 | 80 | 91 |
| | calorimetry ⁴² | 578 | 145 | 173 | 114 | 129 |
| | gravimetry ³² | 503 | 124 | 145 | 86 | 98 |
| | calorimetry ⁴² | 578 | 151 | 180 | - | - |
| [C ₇ mim][NTf ₂] | Knudsen ²⁸ | 475 | 132 | 150 | 94 | 110 |
| [C ₈ mim][NTf ₂] | desorption ¹⁴ | 450 | 134 | 149 | 93 | 109 |
| | calorimetry ⁴² | 578 | 163 | 192 | 136 | 159 |
| | gravimetry ³² | 503 | 132 | 153 | 97 | 113 |
| | gravimetry ³² | 510 | 134 | 155 | - | - |
| | gravimetry ³² | 503 | 130 | 151 | - | - |
| [C ₁₀ mim][NTf ₂] | gravimetry ³² | 503 | 115 | 136 | - | - |
| [C ₃ mmim][NTf ₂] | gravimetry ³² | 503 | 115 | 136 | - | - |
| [C ₂ mim][beti] | gravimetry ³² | 503 | 115 | 136 | - | - |
| [C ₄ mim][beti] | gravimetry ³² | 503 | 114 | 135 | - | - |
| [C ₆ mim][beti] | gravimetry ³² | 503 | 118 | 139 | - | - |
| [C ₈ mim][beti] | gravimetry ³² | 499 | 125 | 145 | - | - |
| [C ₁₀ mim][beti] | gravimetry ³² | 510 | 127 | 148 | - | - |
| [C ₃ mmim][beti] | gravimetry ³² | 503 | 122 | 143 | - | - |
| [C ₄ mim][dca] | transpiration ³⁸ | 465 | 140 | 157 | 118 | 171 |
| [C ₂ mim][EtSO ₄] | desorption ¹⁴ | 500 | 144 | 164 | - | - |
| [C ₈ mim][BF ₄] | desorption ¹⁴ | 520 | 122 | 162 | - | - |
| [C ₈ mim][PF ₆] | desorption ¹⁴ | 530 | 146 | 169 | - | - |
| [C ₈ mim][OTf] | desorption ¹⁴ | 495 | 131 | 151 | - | - |

^a T_{av} is the average temperature of the experimental measurements; $\Delta_{vap}H(T)$ is the enthalpy of vaporization at temperature T ; and $\Delta_{vap}S(T)$ is the entropy of vaporization at temperature T .

$$\ln\left(\frac{p_2}{p_1}\right) = -\frac{\Delta_{vap}H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \quad (7)$$

The picture becomes even more puzzling if one includes the relative volatilities of several ionic liquids obtained from vacuum distillation of equimolar binary mixtures of ionic liquids. These vapor–liquid equilibrium experiments showed volatility maxima at $n = 4$ (where n is the number of carbons in the alkyl side chain) for both the [C_{*n*}mim][NTf₂] and *N*-alkyl-*N*-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [C_{*n*}mpyr][NTf₂], families of ionic liquids.³⁹

As stated above, T_b is not experimentally accessible but can be estimated by extrapolation of the corresponding p_v, T relationship²⁸ to atmospheric pressure. In the [C_{*n*}mim][NTf₂] family, the reported T_b values are 907 K, 933 K, 885 K, and 857 K for $n = 2, 4, 6,$ and $8,$ respectively. Assuming the vapor pressure measurements are sufficiently accurate, the trend shows a maximum in T_b at $n = 4$ and then an overall decrease with increasing n .

Besides the above-mentioned experimental difficulties and resulting inaccuracies, all these unusual trends can also be a consequence of the complex, nanosegregated nature of ionic liquids that can undergo noticeable structural changes in the liquid phase along a homologous series of cations or anions.^{40,41}

The $\Delta_{vap}H$ data that have been reported in the literature were obtained either directly or from Clausius–Clapeyron plots using p_v or other experimental data (cf. Figure 3). Armstrong et al.¹⁴ used a temperature programmed desorption method to estimate, through a Clausius–Clapeyron relationship, the values of $\Delta_{vap}H$

for eight different ionic liquids (four from the previously described [C_{*n*}mim][NTf₂] family, plus 1-ethyl-3-methylimidazolium ethylsulfate, [C₂mim][C₂H₅SO₄], and 1-octyl-3-methylimidazolium combined with the tetrafluoroborate, hexafluorophosphate, and triflate anions, [C₈mim][BF₄], [C₈mim][PF₆], and [C₈mim][CF₃SO₃]). Luo et al.³² used another indirect method (isothermal gravimetry) to determine the $\Delta_{vap}H$ of 12 ionic liquids ([C_{*n*}mim][NTf₂] and 1-alkyl-3-methylimidazolium bis(perfluoroethylsulfonyl)imide, [C_{*n*}mim][beti], families with $n = 2, 4, 6, 8,$ and $10,$ 1-propyl-2,3-dimethylimidazolium bis(trifluoromethylsulfonyl)imide, [C₃mmim][NTf₂], and 1-propyl-2,3-dimethylimidazolium bis(perfluoroethylsulfonyl)imide, [C₃mmim][beti]). Finally, Santos et al.⁴² used a direct method (vacuum-vaporization drop microcalorimetry—see Appendix 2) to determine the values of $\Delta_{vap}H$ for seven ionic liquids of the [C_{*n*}mim][NTf₂] family with n between 2 and 8.

It is worth noting that in the case of $\Delta_{vap}H$ values obtained using Clausius–Clapeyron plots most authors^{28,32,38} reported uncertainties in the values of $\Delta_{vap}H$ related to the uncertainty in the value of the p_v, T slope of those plots. Since there are only a few experimental points on all those curves (in most cases corresponding to four to seven distinct temperatures), the expanded uncertainties can be assumed to be higher than the reported uncertainties by a factor of 3. This factor was empirically determined by randomly omitting one datum point at a time in each curve and observing the impact on the recalculated slope.

The $\Delta_{vap}H$ of ionic liquids has also been estimated using theoretical calculations (Figure 3, label d). First, combustion

enthalpy measurements were combined with ab initio calculations in the gas phase (ionic pairs) to yield the corresponding $\Delta_{\text{vap}}H$ values; second, molecular dynamics (MD) simulations based on force fields commonly used for ionic liquids were performed to obtain the difference between the configurational energies of the gas and liquid phases and the corresponding $\Delta_{\text{vap}}H$ values; finally, the vapor pressures and vaporization enthalpies of a series of 1-*n*-alkyl-3-methylimidazolium-bis(trifluoromethanesulfonyl) amide ionic liquids have been predicted by using the COSMO-RS method combined with quantum chemical gas phase calculations.⁴³ Two different approaches were implemented. In approach “I”, the total Gibbs energy of vaporization was divided into three parts: the virtual Gibbs energies of vaporization of the cation, that of the anion, and the Gibbs energy of the ion pair formation in the gas phase. In approach “II”, it was assumed that both phases (vapor and liquid) consisted of ion pairs only. The vapor pressures obtained using approach “I” are 5 orders of magnitude lower than the experimental data, while those predicted by approach “II” showed improved results: they are lower just by 1 order of magnitude.^{5,28} On the other hand, the enthalpies of vaporization are reasonably well predicted by both approaches. The results are summarized in Table 3.^{19,20,38,42–49} At this point, a few issues are important to consider that are exclusive to the theoretical or simulation methods. First, all methods base their estimation of $\Delta_{\text{vap}}H$ on independent calculations for the gas and liquid phases. This means that the calculated $\Delta_{\text{vap}}H$ value will be the difference between two sometimes rather large quantities, with a rather large uncertainty. This is especially true for simulations in the gas phase that generally entail large statistical errors associated with the calculation of the thermodynamic properties such as the configurational energy. Second, most simulations were based on force fields that were validated taking into account only volumetric and structural properties of ionic liquids, which were the only ones that were available at the time of their development. This means, on one hand, that the simulations are acting in a truly predictive way with regard to the calculation of $\Delta_{\text{vap}}H$ and that in this context the observed (20 to 50) % deviations between the simulation and the existing experimental results are in fact quite reasonable, and on the other, that the force fields can be further improved by using VLE data as they become available. In fact, Ludwig et al.²² started to implement this last option by refining one of the available and most used force fields²⁴ using VLE data for the 1-alkyl-3-methylimidazolium bistriflamide family. Nevertheless, a general force field that is developed and validated taking into account the existing VLE data is a remote possibility at this stage. Third, even if they overestimate the $\Delta_{\text{vap}}H$ values, simulations can show the relative contributions to the cohesive energy of the condensed phase arising from the Coulombic and van der Waals interactions present in the liquid phase. Contrary to what would be expected, the latter forces are not negligible compared to the former and in some cases are even the predominant ones.

All results show (cf. Tables 1 to 3) that for a given ionic liquid family, $[C_n\text{mim}][\text{NTf}_2]$ or $[C_n\text{mim}][\text{beti}]$, the $\Delta_{\text{vap}}H$ values exhibit a general increase with *n*, with the disparities between results obtained by indirect^{14,28,32,38} and direct⁴² experimental methods essentially at the level of the shape and rate of that increase. The same applies to the comparison between experimental and theoretical methods. Simulations have shown that the increase of $\Delta_{\text{vap}}H$ with *n* is mainly related to the increase of the van der Waals interactions between the progressively longer alkyl side chains of the cations (the energy of the Coulombic

Table 3. Calculated Enthalpy of Vaporization Using Theoretical Methods^a

| ionic liquid | method | $\Delta_{\text{vap}}H$ | |
|---|---|---------------------------------|-------------|
| | | $\text{kJ}\cdot\text{mol}^{-1}$ | <i>T</i> /K |
| $[\text{C}_2\text{mim}][\text{EtSO}_4]$ | Molecular Dynamics ⁴⁵ | 178 | 298 |
| | Ab-initio + COSMO-RS ⁴³ | 164.6 | 298 |
| $[\text{C}_1\text{mim}][\text{NTf}_2]$ | Molecular Dynamics ²² | 132.1 | 298 |
| $[\text{C}_2\text{mim}][\text{NTf}_2]$ | Hildebrand Reg. Sol. Theory ¹² | 198.7 | 298 |
| | Molecular Dynamics ²⁰ | 146 | 293 |
| | Molecular Dynamics ²² | 130.6 | 298 |
| | Ab-initio + COSMO-RS ⁴³ | 119.5 ^b | 464.1 |
| | Ab-initio + COSMO-RS ⁴³ | 116.9 ^c | 464.1 |
| $[\text{C}_4\text{mim}][\text{NTf}_2]$ | Hildebrand Reg. Sol. Theory ¹² | 210.7 | 298 |
| | Molecular Dynamics ²⁰ | 151 | 293 |
| | Molecular Dynamics ²² | 135.1 | 298 |
| | Ab-initio + COSMO-RS ⁴³ | 120.1 ^b | 477.6 |
| | Ab-initio + COSMO-RS ⁴³ | 118.9 ^c | 477.6 |
| $[\text{C}_6\text{mim}][\text{NTf}_2]$ | Hildebrand Reg. Sol. Theory ¹² | 216.1 | 298 |
| | Molecular Dynamics ²⁰ | 157 | 293 |
| | Molecular Dynamics ²² | 143.8 | 298 |
| | Ab-initio + COSMO-RS ⁴³ | 125.2 ^b | 469.7 |
| | Ab-initio + COSMO-RS ⁴³ | 123.7 ^c | 469.7 |
| $[\text{C}_8\text{mim}][\text{NTf}_2]$ | Hildebrand Reg. Sol. Theory ¹² | 228.1 | 298 |
| | Molecular Dynamics ²⁰ | 162 | 293 |
| | Molecular Dynamics ²² | 153.6 | 298 |
| | Ab-initio + COSMO-RS ⁴³ | 128.4 ^b | 478.5 |
| | Ab-initio + COSMO-RS ⁴³ | 130.1 ^c | 478.5 |
| $[\text{C}_4\text{mim}][\text{PF}_6]$ | Hildebrand Reg. Sol. Theory ¹² | 186.8 | 298 |
| | Molecular Dynamics ⁴⁶ | 123.3 | 298 |
| | Molecular Dynamics ¹⁰ | 161 | 298 |
| $[\text{C}_6\text{mim}][\text{PF}_6]$ | Hildebrand Reg. Sol. Theory ¹² | 198.7 | 298 |
| $[\text{C}_8\text{mim}][\text{PF}_6]$ | Hildebrand Reg. Sol. Theory ¹² | 215.8 | 298 |
| $[\text{C}_4\text{mim}][\text{TfO}]$ | Hildebrand Reg. Sol. Theory ¹² | 151.5 | 298 |
| $[\text{C}_2\text{mim}][\text{NO}_3]$ | Ab-initio + Combustion ⁴⁷ | 163.7 | 298 |
| $[\text{C}_4\text{mim}][\text{NO}_3]$ | Molecular Dynamics ²⁵ | 159 | 298 |
| | Molecular Dynamics ⁴⁶ | 130.2 | 298 |
| | Ab-initio + Combustion ⁴⁴ | 162.4 | 298 |
| | Ab-initio + Combustion ³⁸ | 153.4 | 298 |
| $[\text{C}_4\text{mim}][\text{dca}]$ | Ab-initio + COSMO-RS ⁴³ | 159.3 | 298 |
| | Molecular Dynamics ⁴⁹ | 181 | 298 |
| $[\text{hmpy}][\text{NTf}_2]$ | Molecular Dynamics ⁴⁹ | 188 | 298 |
| $[\text{ompy}][\text{NTf}_2]$ | Molecular Dynamics ⁴⁹ | 177 | 298 |
| $[\text{hdmpy}][\text{NTf}_2]$ | Molecular Dynamics ⁴⁹ | 177 | 298 |
| $[\text{tmgu}][\text{HCO}_2]$ | Molecular Dynamics ⁴⁷ | 95.31 | 353 |
| $[\text{tmgu}][\text{lact}]$ | Molecular Dynamics ⁴⁷ | 118.70 | 298 |
| $[\text{tmgu}][\text{ClO}_4]$ | Molecular Dynamics ⁴⁷ | 184.19 | 318 |
| $[\text{tmgu}][\text{CF}_3\text{CO}_2]$ | Molecular Dynamics ⁴⁷ | 117.04 | 318 |
| $[\text{tmgu}][\text{Tf}]$ | Molecular Dynamics ⁴⁷ | 136.97 | 318 |
| $[\text{pmpgu}][\text{NO}_3]$ | Molecular Dynamics ⁴⁸ | 174.5 | 300 |
| $[\text{pmbgu}][\text{NO}_3]$ | Molecular Dynamics ⁴⁸ | 178.6 | 300 |
| $[\text{pmpgu}][\text{ClO}_4]$ | Molecular Dynamics ⁴⁸ | 189.2 | 300 |
| $[\text{pmbgu}][\text{ClO}_4]$ | Molecular Dynamics ⁴⁸ | 187.9 | 300 |
| $[\text{cycctmgu}][\text{NO}_3]$ | Molecular Dynamics ⁴⁸ | 200.8 | 300 |
| $[\text{cycctmgu}][\text{NO}_3]$ | Molecular Dynamics ⁴⁸ | 181.5 | 300 |
| $[\text{cycctmgu}][\text{ClO}_4]$ | Molecular Dynamics ⁴⁸ | 211.8 | 300 |
| $[\text{cycctmgu}][\text{ClO}_4]$ | Molecular Dynamics ⁴⁸ | 197.3 | 300 |
| $[\text{124tr}][\text{NO}_3]$ | Molecular Dynamics ²⁵ | 227 | 373 |
| $[\text{123tr}][\text{NO}_3]$ | Molecular Dynamics ²⁵ | 223 | 373 |
| $[\text{4am124tr}][\text{NO}_3]$ | Molecular Dynamics ²⁵ | 215 | 373 |
| $[\text{124tr}][\text{ClO}_4]$ | Molecular Dynamics ²⁵ | 238 | 373 |
| $[\text{123tr}][\text{ClO}_4]$ | Molecular Dynamics ²⁵ | 236 | 373 |
| $[\text{4am124tr}][\text{ClO}_4]$ | Molecular Dynamics ²⁵ | 227 | 373 |
| $[\text{1m4am124tr}][\text{ClO}_4]$ | Molecular Dynamics ²⁵ | 174 | 373 |

^a $\Delta_{\text{vap}}H$ is the enthalpy of vaporization at temperature *T*. ^b Calculated by the use of the Clausius–Clapeyron equation. ^c Calculated from COSMO-RS theory.

interactions remaining more or less constant throughout the entire homologous series) and that this fact can also be related to the complex, nanosegregated nature of ionic liquids.^{40–42}

It is important to stress that to obtain $\Delta_{\text{vap}}H$ values at a given temperature (e.g., 298 K or the hypothetical *T*_b) from experimental $\Delta_{\text{vap}}H$ values acquired at different temperatures, it is necessary to estimate the value of ΔC_p , the difference between the molar heat capacity at constant pressure of the gas and that

of the liquid—see Appendix 3. This quantity has been estimated^{5,42} to be about $(100 \pm 10) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for all members of the $[\text{C}_n\text{mim}][\text{NTf}_2]$ family and generally extrapolated to other ionic liquids. Such an approximation is not necessary in the case of the simulation methods, where the calculations can be performed at any desired temperature (generally 298 K).

However, this correction might suggest a more serious, fundamental flaw. At room temperature, large neutral ionic-pair aggregates are probably the predominant gas-phase species.¹⁹ Values of $\Delta_{\text{vap}}H$ are always calculated at a common reference of per mole of single cations plus one mole of single anions. At the crossover between the prevalence of ion pairs versus larger clusters, values of $\Delta_{\text{vap}}H$ ought to show a marked decrease. The vaporization of the liquid to form those clusters contains an additional, significant energetic gain,²⁰ which, in these low-temperature regimes, prevails over the inherent entropic penalty associated with cluster formation. For instance, $\Delta_{\text{vap}}H$ of $[\text{C}_2\text{mim}]_2[\text{NTf}_2]_2 = 184/2 = 92 \text{ kJ}\cdot\text{mol}^{-1}$ and that of $[\text{C}_2\text{mim}]_3[\text{NTf}_2]_3 = 219/3 = 73 \text{ kJ}\cdot\text{mol}^{-1}$, to be compared with $146 \text{ kJ}\cdot\text{mol}^{-1}$ for $[\text{C}_2\text{mim}][\text{NTf}_2]$. In short, the specific value of $\Delta_{\text{vap}}H$ might decrease with decreasing temperature, which is opposite that of compounds presenting a single species in the gas phase. Conversely, in the high-temperature regime, ca. (700 to 800) K, if the ionic liquids did not decompose, then one would see an increase in $\Delta_{\text{vap}}H$ and an upward bend in p_v, T with a temperature increase due to the increasing presence of high-entropy, isolated ions. Because of this, it is likely that T_b 's will be lower than predicted by a simple, linear treatment of p_v, T relations with the Clausius–Clapeyron equation. Thus, the underlying inaccuracy associated with this assumption can be quite large in terms of $\Delta_{\text{vap}}H$ values within a given ionic liquid family and can be even larger between unrelated ionic liquids.

In any case, the available experimental data (see Tables 1 and 2) show that within the $[\text{C}_n\text{mim}][\text{NTf}_2]$ family there is no direct proportionality between T_b and $\Delta_{\text{vap}}H$ —they show general decreasing and increasing trends with n , respectively—which suggests that no *Trouton-like* relation, ($\Delta_{\text{vap}}H/T_b = \text{universal constant}$) exists for this particular family of ionic liquids. If the Trouton rule does not apply, even within a given family of ionic liquids, a general Trouton-like rule for ionic liquids as an entire class of compounds is even less likely.

Specifically in the case of ionic liquids, the historically well-known and practical Trouton constant is estimated from the ratio of two hypothetical quantities. Several authors^{8,28} have made an attempt to calculate it, and therefore this issue is worth discussing. It is important to mention that in many studies the underlying reasoning behind the Trouton rule has not been used in the most correct way because the rule applies to normal (1 bar) pressure, not to the extremely low saturation pressures of the experiments. This apparent detail has nonetheless a huge effect on the entropy of the gas phase and thus on the rule itself, which is dictated by the value of $\Delta_{\text{vap}}S$ at the normal boiling point.

Interestingly, the estimates of Trouton constants based on the available T_b and $\Delta_{\text{vap}}H(T_b)$ data show that, for the smaller members of the $[\text{C}_n\text{mim}][\text{NTf}_2]$ family ($n = 2$ or 4), the constants (although not universal) will be in the range (70 to 90) $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. This range is not so different from those found for many nonassociated fluids and is smaller than the value for water ($109 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$). This paradox can be explained if one considers that, on the one hand, the vapor phase of ionic liquids is, even at those estimated high T_b 's, constituted largely by neutral ionic pairs and that, on the other hand, the liquid phase is composed to some extent of those same pairs. In other words,

although ionic liquids are composed exclusively of anions and cations, their interactions and structure are not conditioned exclusively by electrostatic interactions, but also by interactions between neutral ionic aggregates or residues. Another property where this fact is apparent is the dielectric constant of ionic liquids, which is smaller than that of water and closer to those of many dipolar organic fluids.¹ For the larger members of the $[\text{C}_n\text{mim}][\text{NTf}_2]$ family, the Trouton constants are equal to or greater than $100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, which again appears to contradict the fact that these ionic liquids have concomitantly larger nonpolar residues attached to the charged imidazolium ring. However, the higher degree of nanosegregation between polar and nonpolar domains found in these ionic liquids,^{40,41} as compared to that of the smaller members of the family, may explain the large entropy difference between the (highly structured) liquid phase and the gas. Therefore, thermodynamics dictates the existence of high values of the Trouton constant whenever the liquid phase is particularly structured or aggregated, and the gas phase is essentially constituted by neutral species. For example, results using the transpiration method, which yielded $\Delta_{\text{vap}}H$ values in agreement with the other methods for $[\text{C}_2\text{mim}][\text{NTf}_2]$, generate in the case of $[\text{C}_4\text{mim}][\text{dca}]$ a Trouton constant value of $171 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$.³⁸

Conclusions

At present, it may not be possible to measure the vapor pressures and/or the enthalpies of vaporization of any particular ionic liquid. Furthermore, the values for the (at times experimentally inaccessible) properties such as p_v or $\Delta_{\text{vap}}H$ are far from having been accurately established. Most methods present systematic errors related to the extreme experimental conditions of high temperatures that are not far from the decomposition temperatures of the ILs, extremely low pressures, limited number of experimentally feasible compounds, and difficult calibrations under these conditions. All of these factors can cause systematic errors within a given ionic liquid family. It must also be stressed at this point that although the amount of published VLE data is rapidly increasing it consists mainly of repetitions, extrapolations, or predictions based on a rather small set of independent experiments representing just two ionic liquid families plus four other ionic liquids; cf. Tables 1 and 2.

Nonetheless, those thermodynamic quantities, when they are accurately measured for a sufficiently comprehensive set of ionic liquids, will help researchers to refine force fields employed in molecular simulations as well as stringently test other theoretical models. These are absolutely essential tasks considering the enormous number of potentially available liquid salts. Hence, we defend the importance of further studies on this subject, culminating in a series of round-robin measurements using high-purity, single-batch ionic liquids of a model family that will allow us to compare vapor–liquid equilibrium data obtained by different methods and to discuss the possible causes of error or inconsistencies found in each case. Once this is accomplished it will be possible to give recommended values for the enthalpy of vaporization of aprotic ionic liquids.

Acknowledgment

Four of the authors (JMSSE, JNCL, JWM, and LPNR) thank our colleagues Martyn Earle, Manuela Gilea, Kenneth Seddon, and Jason Widegren, for the discussions regarding the topic of this review. M.T. is thankful to FC&T for the award of a postdoctoral grant (SFRH/BPD/34146/2006).

APPENDIX 1: Knudsen Effusion

The Knudsen effusion method is one of the most widely used methods for measuring the vapor pressures of crystalline or

liquid compounds for pressures less than 1 Pa. In a typical effusion experiment, the crystalline or liquid sample is placed at the bottom of a cylindrical cell kept at a constant temperature, and the vapor is allowed to effuse through a small orifice located at the top of the cell into an evacuated space. In an effusion experiment, a hypothetical liquid–gas equilibrium is considered as presented in eq A1.1. The gas phase is taken as an ideal gas, and the results obtained via Knudsen effusion experiments are attained in terms of the following defined hypothetical liquid–vapor equilibrium model, in which the mass loss is related to the equilibrium vapor pressure



In systems simultaneously forming parallel gas phase equilibria (e.g., dimerization in the gas phase), the analysis and real meaning of the results obtained for the liquid–gas equilibrium by Knudsen effusion is a rather challenging task that can be rationalized only in combination with other experimental results.

The measurements are typically made over a temperature interval, corresponding to a typical pressure range of (0.01 to 1) Pa.

The vapor pressure of the sample is calculated by eq A1.2

$$p = (m/A_0 w_0 t) \cdot (2\pi RT/M)^{1/2} \quad (\text{A1.2})$$

where m is the mass vaporized from the effusion cell; T is the temperature at which the vaporization occurred; t is the experimental time; M is the molar mass of the compound; R is the ideal gas constant ($R = 8.314\,472\ \text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$); A_0 is the area of the orifice; and w_0 is the transmission probability factor that could be calculated by means of eq A1.3 or eq A1.4

$$w_0 = \{1 + (3l/8r)\}^{-1} \quad (\text{A1.3})$$

$$w_0 = \{1 + (l/2r)\}^{-1} \quad (\text{A1.4})$$

where l and r are the thickness and the radius of the effusion orifice, respectively. Data concerning the thickness, radius, and the transmission probability factor calculated for each orifice are usually presented by the authors for each experimental setup. Experimental orifices are designed to get a transmission probability factor, w_0 , as near as possible to unity. For that reason, the ratio between the thickness and the radius of the orifice should be small (typically less than 0.01). To minimize the self cooling effects and the deviation of the equilibrium pressure inside the effusion cell due to the transient mass flow to the orifice, the radius of the effusion orifice should also be small when compared with the surface of the sample in the effusion cell.

The standard molar enthalpies of vaporization at the mean temperature, $\langle T \rangle$, are derived, using the integrated form of the Clausius–Clapeyron eq A1.5

$$\ln(p/\text{Pa}) = a - b \cdot (\text{K}/T) \quad (\text{A1.5})$$

where a is a constant and $b = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle)/R$. $\Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle)$ is the standard molar enthalpy of vaporization of the ionic liquid at the mean temperature, $\langle T \rangle$.

Appendix 2: The $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ Correction

The standard molar enthalpies of vaporization at $T = 298.15\ \text{K}$ are usually determined by eq A2.1

$$\Delta_1^{\text{g}}H_m^{\circ}(298.15\ \text{K}) = \Delta_1^{\text{g}}H_m^{\circ}(T) + \int_{298.15}^T C_p(l)dT - \int_{298.15}^T C_p(g)dT \quad (\text{A2.1})$$

where $C_p(l)$ and $C_p(g)$ stand for the liquid and gas heat capacities, respectively. Usually, the two heat capacity correction terms are condensed in a single term written as

$$\int_{298.15}^T \Delta_1^{\text{g}}C_p dT = -\left\{ \int_{298.15}^T C_p(l)dT - \int_{298.15}^T C_p(g)dT \right\} \quad (\text{A2.2})$$

which, in turn, can be simplified using the mean value of $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ in the respective temperature interval, between 298.15 K and $\langle T \rangle$. The temperature correction becomes

$$\Delta_1^{\text{g}}H_m^{\circ}(298.15\ \text{K}) = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle) + (298.15\ \text{K} - \langle T \rangle)\Delta_1^{\text{g}}C_{p,m}^{\circ} \quad (\text{A2.3})$$

at the equilibrium pressure at this temperature $p(\langle T \rangle)$.

Typically, to perform this $\Delta_1^{\text{g}}C_{p,m}^{\circ}$ calculation, the difference of the heat capacities at constant pressure between the gas and liquid phases was estimated by use of the expression derived from the energy equipartition principle and the difference between isochoric and isobaric heat capacities in the liquid and gas phases

$$\Delta_1^{\text{g}}C_p = C_{p,g} - C_{p,l} \approx (3R + R) - \left(6R + \frac{\alpha_p^2}{\kappa_T} V_m T \right) \quad (\text{A2.4})$$

$$\Delta_1^{\text{g}}C_p \approx -2R - \frac{\alpha_p^2}{\kappa_T} V_m T \quad (\text{A2.5})$$

The entropies of vaporization at equilibrium conditions, $\Delta_1^{\text{g}}S_m\{\langle T \rangle, p(\langle T \rangle)\}$, can be calculated by eq A2.6

$$\Delta_1^{\text{g}}S_m\{\langle T \rangle, p(\langle T \rangle)\} = \Delta_1^{\text{g}}H_m^{\circ}(\langle T \rangle)/\langle T \rangle \quad (\text{A2.6})$$

Using an identical approximation for the heat capacity correction, the standard ($p^{\circ} = 10^5\ \text{Pa}$) molar entropies of vaporization are calculated by

$$\Delta_1^{\text{g}}S_m^{\circ}(298.15\ \text{K}) = \Delta_1^{\text{g}}S_m\{\langle T \rangle, p(\langle T \rangle)\} + \Delta_1^{\text{g}}C_{p,m}^{\circ} \ln(298.15\ \text{K}/\langle T \rangle) - R \ln\{p^{\circ}/p(\langle T \rangle)\} \quad (\text{A2.7})$$

Appendix 3: Calorimetric Measurement of Enthalpies of Vaporization

Direct calorimetric measurements of enthalpies of vaporization are intrinsically specific (per mass) values; i.e., they do not depend on any vapor–liquid equilibrium model. In this case, the measured enthalpies are the balance between two well-defined energy states. Consequently, however, no information about the equilibrium can be derived.

According to the schematic thermodynamic diagram represented in Figure A2.1, the total enthalpy change measured for the process, $\Delta_{1,298.15}^{\text{g},T}H_m^{\circ}$, can be subdivided in two main terms

(i) the enthalpy change due to the heating of the sample in the liquid phase from $T = 298.15\ \text{K}$ to the hot-zone temperature T , $\Delta_{298.15}^T H_m^{\circ}(l)$, and

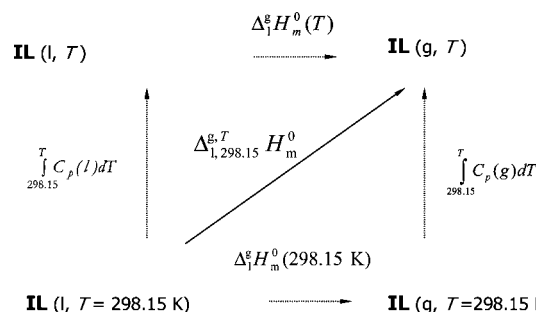


Figure A2.1. Hypothetical thermodynamic cycle for the vaporization of an ionic liquid.

(ii) the enthalpy change corresponding to the vaporization of the sample at the hot-zone temperature $T, \Delta_1^g H_m^o(T)$.

The first main term can be obtained, according to eq A3.1, from the integration of the experimental heat flow data, corresponding to the heat involved in the heating of the sample in the liquid phase from $T = 298.15$ K to the hot-zone temperature $T, \Delta_{298.15}^T H_m^o(l)$

$$\Delta_{298.15}^T H_m^o(l) = \int_{298.15}^T C_p(l) dT \quad (\text{A3.1})$$

The second term, the enthalpy change corresponding to the vaporization of the sample at the hot-zone temperature, can be derived from the difference between the total enthalpy change, $\Delta_{1,298.15}^{g,T} H_m^o$, and enthalpy change due to the heating of the sample in the liquid phase, $\Delta_{298.15}^T H_m^o(l)$, according to

$$\Delta_1^g H_m^o(T) = \Delta_{1,298.15}^{g,T} H_m^o - \Delta_{298.15}^T H_m^o(l) \quad (\text{A3.2})$$

The standard molar enthalpy of vaporization, at $T = 298.15$ K, $\Delta_1^g H_m^o(298.15 \text{ K})$, may be derived from the total enthalpy change measured for the process using eqs A3.3 or A3.4

$$\Delta_1^g H_m^o(298.15 \text{ K}) = \Delta_{1,298.15}^{g,T} H_m^o - \int_{298.15}^T C_p(g) dT \quad (\text{A3.3})$$

or

$$\Delta_1^g H_m^o(298.15 \text{ K}) = \Delta_1^g H_m^o(T) + \int_{298.15}^T C_p(l) dT - \int_{298.15}^T C_p(g) dT \quad (\text{A3.4})$$

Literature Cited

- Weingaertner, H. Understanding ionic liquids at the molecular level: Facts, problems, and controversies. *Angew. Chem., Int. Ed.* **2008**, *47*, 654–670.
- Plechkova, N. V.; Seddon, K. R. Applications of ionic liquids in the chemical industry. *Chem. Soc. Rev.* **2008**, *37*, 123–150.
- Oye, H. A.; Jagtoyen, M.; Oksefjell, T.; Wilkes, J. S. Vapour pressure and thermodynamics of the system 1-methyl-3-ethyl-imidazolium chloride - aluminium chloride. *Mater. Sci. Forum.* **1991**, *73–75*, 183–190.
- Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Filipe, E. On the critical temperature, normal boiling point, and vapor pressure of ionic liquids. *J. Phys. Chem. B* **2005**, *109*, 6040–6043.
- Paulechka, Y. U.; Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A. Vapor pressure and thermal stability of ionic liquid 1-butyl-3-methylimidazolium Bis(trifluoromethylsulfonyl)amide. *Thermochim. Acta* **2005**, *439*, 158–160.
- Earle, M. J.; Esperança, J. M. S. S.; Gilea, M. A.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Magee, J. W.; Seddon, K. R.; Widegren, J. A. The distillation and volatility of ionic liquids. *Nature* **2006**, *439*, 831–834.
- Rebelo, L. P. N.; Canongia Lopes, J. N.; Esperança, J. M. S. S.; Guedes, H. J. R.; Łachwa, J.; Najdanovic-Visak, V.; Visak, Z. P. Accounting for the unique, doubly dual nature of ionic liquids from a molecular thermodynamic, and modeling standpoint. *Acc. Chem. Res.* **2007**, *40*, 1114–1121.
- Paulechka, Y. U.; Kabo, G. J.; Blokhin, A. V.; Vydrov, O. A.; Magee, J. W.; Frenkel, M. Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the ideal gas state. *J. Chem. Eng. Data* **2003**, *48*, 457–462.
- Kabo, G. J.; Blokhin, A. V.; Paulechka, Y. U.; Kabo, A. G.; Shymanovich, M. P.; Magee, J. W. Thermodynamic properties of 1-butyl-3-methylimidazolium hexafluorophosphate in the condensed state. *J. Chem. Eng. Data* **2004**, *49*, 453–461.
- Morrow, T. I.; Maginn, E. J. Molecular dynamics study of the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate. *J. Phys. Chem. B* **2002**, *106*, 12807–12813.
- Shah, J. K.; Brennecke, J. F.; Maginn, E. G. Thermodynamic properties of the ionic liquid 1-n-butyl-3-methylimidazolium hexafluorophosphate from Monte Carlo simulations. *Green Chem.* **2002**, *4*, 112–118.
- Lee, S. H.; Lee, S. B. The Hildebrand solubility parameters, cohesive energy densities and internal energies of 1-alkyl-3-methylimidazolium-based room temperature ionic liquids. *Chem. Commun.* **2005**, *27*, 3469–3471.
- Ludwig, R.; Kragl, U. Do we understand the volatility of ionic liquids. *Angew. Chem., Int. Ed.* **2007**, *46*, 6582–6584.
- Armstrong, J. P.; Hurst, C.; Jones, R. G.; Licence, P.; Lovelock, K. R. J.; Satterley, C. J.; Villar-Garcia, I. J. Vaporisation of ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 982–990.
- Strasser, D.; Goulay, F.; Kelkar, M. S.; Maginn, E. J.; Leone, S. R. Photoelectron spectrum of isolated ion-pairs in ionic liquid vapor. *J. Phys. Chem. A* **2007**, *111*, 3191–3195.
- Leal, J. P.; Esperança, J. M. S. S.; Minas da Piedade, M. E.; Canongia Lopes, J. N.; Rebelo, L. P. N.; Seddon, K. R. The nature of ionic liquids in the gas phase. *J. Phys. Chem. A* **2007**, *111*, 6176–6182.
- Gross, J. H. Molecular ions of ionic liquids in the gas phase. *J. Am. Soc. Mass Spectrom.* **2008**, *19*, 1347–1352.
- Leal, J. P.; Minas da Piedade, M. E.; Canongia Lopes, J. N.; Tomaszowska, A. A.; Esperança, J. M. S. S.; Rebelo, L. P. N.; Seddon, K. R. Bridging the Gap between Ionic Liquids and Molten Salts: Group 1 Metal Salts of the Bistriflamide Anion in the Gas Phase. *J. Phys. Chem. B* **2009**, *113*, 3491–3498.
- Ballone, P.; Pinilla, C.; Kohanoff, J.; Del Pópolo, M. G. Neutral and charged 1-butyl-3-methylimidazolium triflate clusters: equilibrium concentration in the vapor phase and thermal properties of nanometric droplets. *J. Phys. Chem. B* **2007**, *111*, 4938–4950.
- Kelkar, M. S.; Maginn, E. Calculating the enthalpy of vaporization for ionic liquid clusters. *J. Phys. Chem. B* **2007**, *111*, 9424–9427.
- Akai, N.; Kawai, A.; Shibuya, K. First observation of the matrix-isolated FTIR spectrum of vaporized ionic liquid: an example of EmimTFSI, 1-ethyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imide. *Chem. Lett.* **2008**, *37*, 256–257.
- Köddermann, T.; Paschek, D.; Ludwig, R. Molecular dynamic simulations of ionic liquids: A reliable description of structure, thermodynamics and dynamics. *ChemPhysChem* **2007**, *8*, 2464–2470.
- Köddermann, T.; Paschek, D.; Ludwig, R. Ionic liquids: dissecting the enthalpies of vaporization. *ChemPhysChem* **2008**, *9*, 549–555.
- Canongia Lopes, J. N.; Deschamps, J.; Pádua, A. A. H. Modeling ionic liquids using a systematic all-atom force field. *J. Phys. Chem. B* **2004**, *108*, 2038–2047.
- Cadena, C.; Maginn, E. J. Molecular simulation study of some thermophysical and transport properties of triazolium-based ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 18026–18039.
- Tong, J.; Liu, Q. S.; Xu, W. G.; Fang, D. W.; Yang, J. Z. Estimation of physicochemical properties of ionic liquids 1-alkyl-3-methylimidazolium chloroaluminate. *J. Phys. Chem. B* **2008**, *112*, 4381–4386.
- Tariq, M.; Serro, A. P.; Mata, J. L.; Saramago, B.; Rebelo, L. P. N.; Canongia Lopes, J. N. manuscript in preparation.
- Zaitsau, D. H.; Kabo, G. J.; Strechan, A. A.; Paulechka, Y. U.; Tschersich, A.; Verevkin, S. P.; Heintz, A. Experimental vapor pressures of 1-alkyl-3-methylimidazolium bis(trifluoromethylsulfonyl) imides and a correlation scheme for estimation of vaporization enthalpies of ionic liquids. *J. Phys. Chem. A* **2006**, *110*, 7303–7306.
- Verevkin, S. P. Predicting enthalpy of vaporization of ionic liquids: a simple rule for a complex property. *Angew. Chem., Int. Ed.* **2008**, *47*, 5071–5074.
- Valderrama, J. O.; Robles, P. A. Critical properties, normal boiling point temperatures, and acentric factors of fifty ionic liquids. *Ind. Eng. Chem. Res.* **2007**, *46*, 1338–1344; *ibid.* 6063–6064.
- Valderrama, J. O.; Sanga, W. W.; Lazzús, J. A. Critical properties, normal boiling point temperature, and acentric factor of another 200 ionic liquids. *Ind. Eng. Chem. Res.* **2008**, *47*, 1318–1330.
- Luo, H.; Baker, G. A.; Dai, S. Isothermogravimetric determination of the enthalpies of vaporization of 1-alkyl-3-methylimidazolium ionic liquids. *J. Phys. Chem. B* **2008**, *112*, 10077–10081.
- Trouton, F. On molecular latent heat. *Philos. Mag.* **1884**, *18*, 54–57.
- Myrdal, P. B.; Krzyzaniak, J. F.; Yalkowsky, S. H. Modified Trouton's Rule for Predicting the Entropy of Boiling. *Ind. Eng. Chem. Res.* **1996**, *35*, 1788–1792.
- Knudsen, M. The laws of the molecular current and the internal friction current of gases by channels. *Ann. Phys.* **1909**, *28*, 75–130.
- Knudsen, M. The molecular current of gases through openings and the effusion. *Ann. Phys.* **1909**, *28*, 999–1016.
- Knudsen, M. Experimental determination of the pressure of saturated mercury steam at 0 degrees and at higher temperatures. *Ann. Phys.* **1909**, *28*, 179–193.
- Emel'yanenko, V. N.; Verevkin, S. P.; Heintz, A. The gaseous enthalpy of formation of the ionic liquid 1-butyl-3-methylimidazolium dicyanamide from combustion calorimetry, vapor pressure measurements, and ab initio calculations. *J. Am. Chem. Soc.* **2007**, *129*, 3930–3937.

- (39) Widegren, J. A.; Wang, Y.-M.; Henderson, W. A.; Magee, J. W. Relative volatilities of ionic liquids by vacuum distillation of mixtures. *J. Phys. Chem. B* **2007**, *111*, 8959–8964.
- (40) Canongia Lopes, J. N.; Pádua, A. A. H. Nanostructural organization in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 3330–3335.
- (41) Lopes, J. N. C.; Gomes, M. F. C.; Pádua, A. A. H. Nonpolar, polar, and associating solutes in ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 16816–16818.
- (42) Santos, L. M. N. B. F.; Canongia Lopes, J. N.; Coutinho, J. A. P.; Esperança, J. M. S. S.; Gomes, L. R.; Marrucho, I. M.; Rebelo, L. P. N. Ionic liquids: first direct determination of their cohesive energy. *J. Am. Chem. Soc.* **2007**, *129*, 284–285.
- (43) Diedenhofen, M.; Klamt, A.; Marsh, K.; Schafer, A. Prediction of the vapor pressure and vaporization enthalpy of 1-*n*-alkyl-3-methylimidazolium-bis-(trifluoromethanesulfonyl) amide ionic liquids. *Phys. Chem. Chem. Phys.* **2007**, *9*, 4653–4656.
- (44) Emel'yanenko, V. N.; Verevkin, S. P.; Heintz, A.; Schick, C. Ionic liquids. Combination of combustion calorimetry with high-level quantum chemical calculations for deriving vaporization enthalpies. *J. Phys. Chem. B* **2008**, *112*, 8095–8098.
- (45) Kelkar, M. S.; Shi, W.; Maginn, E. J. Determining the accuracy of classical force fields for ionic liquids: atomistic simulation of the thermodynamic and transport properties of 1-ethyl-3-methylimidazolium ethylsulfate ([emim][EtSO]) and its mixtures with water. *Ind. Eng. Chem. Res.* **2008**, *47*, 9115–9126.
- (46) Micaelo, N. M.; Baptista, A. M.; Soares, C. M. Parametrization of 1-butyl-3-methylimidazolium hexafluorophosphat/nitrate ionic liquid for the GROMOS force field. *J. Phys. Chem. B* **2006**, *110*, 14444–14451.
- (47) Liu, X.; Zhang, S.; Zhou, G.; Wu, G.; Yuan, X.; Yao, X. New force field for molecular simulation of guanidinium-based ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 12062–12071.
- (48) Klahn, M.; Seduraman, A.; Wu, P. A model for self-diffusion of guanidinium-based ionic liquids: a molecular simulation study. *J. Phys. Chem. B* **2008**, *112*, 13849–13861.
- (49) Cadena, C.; Zhao, Q.; Snurr, R. Q.; Maginn, E. J. Molecular modeling and experimental studies of the thermodynamic and transport properties of pyridinium-based ionic liquids. *J. Phys. Chem. B* **2006**, *110*, 2821–2832.

Received for review May 27, 2009. Accepted July 13, 2009. Part of this work was supported by FC&T, Portugal (PTDC/CTM/73850/2006, PTDC/QUI/66199/2006, and PTDC/EQU-FTT/65252/2006).

JE900458W