Ionic Liquids

DOI: 10.1002/anie.200800926

Predicting Enthalpy of Vaporization of Ionic Liquids: A Simple Rule for a Complex Property**

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Ionic liquids (ILs) have been suggested as replacement solvents in reactions and separations since they have negligible vapor pressure and thus would reduce the fugitive emissions that are common when organic solvents are used in these applications. This lack of volatility has been assumed to be common to all ionic liquids that do not undergo thermal decomposition, but recent experiments[1–3] have challenged this assumption. The first quantitative data on vapor pressures of 1-alkyl-3-methylimidazolium bis(trifloromethylsulfonyl)imide ILs [C_nMIM][NTf_2] (length of alkyl chain: $n = 2, 4, 6,$ or 8) were measured by well-established effusion techniques.[1] The temperature dependence of the vapor pressures allowed determination of their molar enthalpies of vaporization (see Table 1). Qualitatively, the possibility of distilling a number of pure ILs at 300 °C has been demonstrated by Earle et al.[2] Later, the relative volatilities of a variety of mixtures of common aprotic ionic liquids were studied in a glass sublimation apparatus at approximately 473 K by Widegren et al.[3] These findings have shown that not all thermally stable ILs have negligible vapor pressure, and therefore the vapor pressure of all new ILs should be checked experimentally.[4] For this reason, the scientific community has been faced with the continuously increasing challenge to measure or predict the vapor pressure and vaporization enthalpies of ILs. In practice researchers are confronted 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 by processes such as transfer of an alkyl group or, in the case of protic ionic liquids, through deprotonation.[5]

To date, only a few experimental studies on vapor pressures and vaporization enthalpies of ILs have become available,[1,6–9] (see Table 1), and rapid progress to address this paucity of data is hardly to be expected, due to the time-consuming nature of these experiments. Recently, a valuable procedure was developed to obtain vaporization enthalpies of ILs by using a combination of traditional combustion calorimetry with modern high-level ab initio calculations.[6] For this purpose, a thermodynamic relationship [Eq. (1)] was used to obtain the molar enthalpy of vaporization of 1-butyl-3-methylimidazolium dicyanamide [C_4MIM][$N(CN)_2$] (see Table 1).

$$\Delta_l^g H_m = \Delta_f H_m^\circ(g) - \Delta_f H_m^\circ(l) \qquad (1),$$

Herein, $\Delta_f H_m^\circ(l)$ is the molar enthalpy of formation in the liquid state obtained by high-precision combustion calorimetry, and $\Delta_f H_m^\circ(g)$ the gas-phase enthalpy of formation calculated by a suitable ab initio method (e.g., G3MP2). Note that quantum chemical calculations of the gas-phase enthalpy of formation of [C_4MIM][$N(CN)_2$] were performed under the assumption that the gaseous phase of ionic liquids exists entirely of isolated ion pairs. Furthermore, $\Delta_l^g H_m = (157.2 \pm 1.1)\ \text{kJ mol}^{-1}$ was independently obtained in this work, from the temperature dependence of the vapor pressure measured by the transpiration method. Excellent agreement between the values derived from Equation (1) and the experimental results have established the thermodynamic consistency of the experimental and theoretical approaches. Such a procedure[6] has opened a new avenue to obtaining thermodynamic properties of new ionic liquids. However, our new procedure will not be considered a panacea for the rapid accumulation of vaporization enthalpies for ILs. The restrictions are mainly due to the sophisticated and time-consuming combustion experiments, which must be performed on the highly pure (99.9 %) samples of ILs, and the time-consuming nature of ab initio calculations on "relatively" large molecules by composite methods such as G3, CBS, and W1 (the less time-consuming DFT methods are not precise enough[6] for the calculation of the gas-phase enthalpies of formation of ILs).

In spite of these restrictions, the combination of combustion calorimetry with high-level quantum chemical calculations is now in progress in our laboratory to derive the vaporization enthalpies for a new series of imidazolium-based ionic liquids [C_nMIM][NO_3] and [C_nMIM][$C(CN)_3$] and 1-butyl-1-methyl-pyrrolidinium dicyanamide [$Pyrr_{1,4}$][$N(CN)_2$]. In contrast to previous studies,[1,6] these new ionic liquids are not stable enough during transpiration experiments; hence, no experimental enthalpies of vaporization could be obtained independently for checking thermodynamic consistency according to Equation (1). Even though the enthalpy of vaporization of [$Pyrr_{1,4}$][$N(CN)_2$] has successfully been measured by a temperature-programmed desorption method[7] (see Table 1), the development of an empirical or semi-empirical method that yields a reasonable approximation of the enthalpies of vaporization $\Delta_l^g H_m$ for new ionic liquids is necessary. Classical methods such as QSAR[10] and group

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[**] This work has been supported by German Science Foundation (DFG) priority program SPP 1191, as well as by the Research Training Group "New Methods for Sustainability in Catalysis and Technique" (DFG).

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Table 1: Molar volume V_{m}, surface tension σ, and vaporization enthalpy $\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ of ILs at 298 K.[a]

1	2	3	4	5	6	7	8
		V_{m}[1,7] [cm^3 mol^{-1}]	σ[1,19] [mJ m^{-2}]	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}$ [kJ mol^{-1}]			Δ[b]
				exptl	calcd [Eq. (2)]	calcd [Eq. (3)]	
Calculation of the parameters							
[C$_2$MIM]	EtSO$_4$	201.8	42.50[19] 48.79[20]	**164.0 ± 4.0**[7]	136.3 156.1	163.8	0.2
[C$_2$MIM]	BF$_4$	148.1[17]	44.30[19] 54.4[21]	**149.0 ± 2.0**[7]	119.8 146.6	150.4	−1.4
[C$_2$MIM]	NTf$_2$	257.5	34.90	**135.3 ± 1.3**[1] 134.0 ± 2.0[7]	136.1	132.9	2.4
[C$_4$MIM]	NTf$_2$	291.8	31.76	**136.2 ± 1.7**[1] 134.0 ± 3.0[7]	134.6	137.9	−1.7
[C$_6$MIM]	NTf$_2$	328.0	30.94	**139.8 ± 0.8**[1] 139.0 ± 2.0[7]	141.6	142.9	−3.1
[C$_8$MIM]	NTf$_2$	366.3	30.63	**150.0 ± 0.8**[1] 149.0 ± 2.0[7]	149.0	147.9	2.1
[C$_8$MIM]	BF$_4$	258.0	31.39	**162.0 ± 3.0**[7]	122.0	160.4	1.6
[C$_8$MIM]	PF$_6$	277.8	35.24	**169.0 ± 4.0**[7]	144.3	168.9	0.1
[C$_8$MIM]	N(CN)$_2$	261.3		**162.0 ± 4.0**[8]		166.5	−4.5
[Pyrr$_{14}$]	PF$_3$(C$_2$F$_5$)$_3$			**152.0 ± 4.0**[8]		152.3	−0.3
[Pyrr$_{14}$]	N(CN)$_2$	219.3		**160.0 ± 2.0**[22] 159.7[22]		159.8	0.2
[C$_4$MIM]	N(CN)$_2$	194.1	44.4	**157.2 ± 1.1**[6] 153.4[6]	142.0	156.5	0.7
							± 1.5[c]
Proof of Equation (2)							
[C$_{10}$MIM]	NTf$_2$	402.9	29.66		155.5	152.9	
[C$_4$MIM]	BF$_4$	187.7	40.56		128.2	157.9	
[C$_{12}$MIM]	BF$_4$	350.2	27.29		130.7	155.4	
[C$_4$MIM]	PF$_6$	207.8	45.89		154.8	167.9	
[C$_6$MIM]	PF$_6$	241.5	37.45		139.8	163.9	
[C$_{10}$MIM]	PF$_6$	309.0	30.88		135.9	168.9	
[C$_{12}$MIM]	PF$_6$	346.6	23.49		112.0	178.9	
Validation of Equation (3)							
[C$_2$MIM]	NO$_3$			168.4[23]		164.7	**4.6**
[C$_4$MIM]	NO$_3$	174.1[18]		167.6[23]		169.7	**−0.8**
[C$_2$MIM]	C(CN)$_3$	181.1	47.90		147.5	156.5	
[C$_4$MIM]	C(CN)$_3$	224.8		155.6		161.5	**−5.9**

[a] Values in bold were taken for calculation of the parameters in Table 2. [b] Calculated as the difference between columns 5 and 7. [c] Average deviation.

additivity (GA)[11] methods that can make quantitative predictions of physical properties might satisfy this need.

The most promising, successful, and well-established empirical approach for prediction of the thermodynamic properties is the GA method.[12] Recently, Valderrama et al.[13] employed GA to predict critical properties and normal boiling temperatures of ILs. Unfortunately, properties of this type are essentially impossible to measure with current experimental methods. Consequently, the validity of these predictions is a subject of debate. The GA method also failed to predict vaporization enthalpies of ILs, firstly because the available data set of vaporization enthalpies[1,6,9] is too limited for quantitative parameterization of any specific IL groups. Secondly, a general transfer of the group contributions, which are well established for common organic compounds, to ionic "molten salts" seems inadequate. For example, the vaporization enthalpy of [C$_n$MIM][NTf$_2$] ($n = 2$, 4, 6, or 8) is expected to increase monotonically from [C$_2$MIM][NTf$_2$] to [C$_8$MIM][NTf$_2$], in accordance with the increasing number of CH$_2$ groups (a contribution to the vaporization enthalpy of 5.0 kJ mol^{-1} per CH$_2$ group is typical for the n-alkane family[12]). However, this is in disagreement with experimental observations (see Table 1). Indeed, the enthalpies of vaporization of the ethyl and the butyl derivatives should differ by about 10 kJ mol^{-1}, but they are hardly distinguishable within the boundaries of their experimental uncertainties. The enthalpy of vaporization of the hexyl derivate is expected to be 10 kJ mol^{-1} larger than that of [C$_4$MIM][NTf$_2$], but the experimental value is only slightly larger (see Table 1). Only for [C$_6$MIM][NTf$_2$] and [C$_8$MIM][NTf$_2$] does the assumed contribution of 5.0 kJ mol^{-1} per CH$_2$ group hold. The reason for such an anomaly (or nonadditivity) in the behavior of ILs is apparently due to interplay of van der Waals and Coulombic interactions. The increase in van der Waals interactions with increasing chain length, as is observed for pure n-alkanes and assumed for ILs, is virtually counteracted by electrostatic forces, and the energy required for transfer of the contact ionic pair to the gaseous state (in general: vaporization enthalpy) becomes unique for each of the [C$_n$MIM][NTf$_2$] species.

To sum up, classical predictive methods such as QSAR and GA are still limited in their application to ILs, because they need extended experimental data sets to derive correlations. Our new semi-empirical ab initio based procedure[6] is generally simple, but it involves time-consuming computational and experimental methods. Simple correlations based on empirical physicochemical properties provide an alternative. For example, Krossing et al.[14] recently developed a simple predictive framework for calculating the viscosity of an IL given knowledge of its molecular volume V_{m}. The applicability of this concept to the vaporization enthalpies of ILs is still to be established. Armstrong et al.[7] studied of IL vapors using mass spectrometry. Ionic liquids were found to evaporate as ion pairs, with enthalpies of vaporization which depend primarily on the Coulombic interactions within the liquid phase and the gas-phase ion pair. They determined the vaporization enthalpies of eight ionic liquids, and derived an electrostatic model relating the enthalpies of vaporization to the molar volumes of the ILs. However, in spite of very elaborate separation of the electrostatic and van der Waals interactions suggested in that work, this model is cannot make any general prediction of the vaporization enthalpy $\Delta_l^g H_m$ of ILs from knowledge of the molecular volume V_m. This conclusion is apparent from Figure 1 in the Supporting Information, in which only the homologous series of $[C_nMIM][NTf_2]$ shows the expected gradual increase with the increasing V_m. All other ILs which do not belong to this family are randomly distributed in this plot.

In contrast to the work by Armstrong et al.,[7] we used a somewhat more sophisticated volume based empirical correlation.[1] The experimental vaporization enthalpies of ionic liquids $[C_nMIM][NTf_2]$ ($n = 2$–8) were correlated with surface tension σ and molar volume (V_m) of the ionic liquids. The empirical relationship for the molar enthalpy of vaporization is given by Equation (2), where N_A is the Avogadro constant.

$$\Delta_l^g H_m(298\,K) = A(\sigma V_m^{2/3} N_A^{1/3}) + B \tag{2}$$

The empirical correlation parameters $A = 0.01121$ and $B = 2.4\,kJ\,mol^{-1}$ were calculated by a least-squares treatment.[1] With the help of Equation (2), the molar enthalpies of vaporization for the $[C_nMIM][NTf_2]$ family were calculated within an accuracy of 1–2 $kJ\,mol^{-1}$. Now we can extend the test of the predictive capacity of Equation (2) with help of new data published recently.[6–8] As can be seen from the data in Table 1 (column 5), Equation (2) provides results that are generally underestimated by 10–20 $kJ\,mol^{-1}$ for the vaporization enthalpies of ionic liquids other than the $[C_nMIM][NTf_2]$ family. Another aspect has become apparent due to new data on the surface tension of ionic liquids published recently.[19,20,21] The experimental values of σ derived by different methods and different authors vary significantly (see Table 1, column 3 for $[C_2MIM][EtSO_4]$ and $[C_2MIM][BF_4]$). It turns out that Equation (2) is extremely sensitive to the values of σ used in the calculations. The vaporization enthalpies can vary by as much 15–20 $kJ\,mol^{-1}$ due to using the σ values from two different sources (Table 1, column 6).

Thus, all previous attempts to make quantitative predictions of the vaporization enthalpies of ILs by means of simple correlations with their experimental surface tension and density data[1,6–7] have met with insufficient success. All these methods have significant drawbacks which limit their application in predicting the properties of unknown ILs. Furthermore, these methods need at least a minimal amount of experimental data from the ILs under study, which are not always readily available.

To overcome these difficulties, a simple straightforward additive approach based on the empirical formula of an IL has been developed. It seems to be reasonable to separate the bulk enthalpy of vaporization of an IL into two parts: a main contribution, which comes from the constituent elements (regardless of their position in the cation or anion), and an auxiliary contribution (correction) due to structural peculiarities of some ILs, as specified below. The general formula for the vaporization enthalpy calculations of ILs at 298 K is Equation (3).

$$\Delta_l^g H_m(\mathrm{IL}) = \sum n_i \Delta H_i + \sum n_j \Delta H_j \tag{3}$$

Herein, ΔH_i is the contribution of the ith element, n_i the number of elements of the ith type in the ionic liquid, ΔH_j the contribution of the jth structural correction, and n_j the number of structural corrections of the ith type in the ionic liquid. In the simple case of $[C_2MIM][EtSO_4]$ (empirical formula $C_{10}H_{16}N_2SO_4$) the calculation formula is Equation (4).

$$\Delta_l^g H_m([C_2MIM][EtSO_4]) = 10\,\Delta H_{(C)} + 2\,\Delta H_{(N)} + 4\,\Delta H_{(O)} + 1\,\Delta H_{(S)} \tag{4}$$

In the same manner, vaporization enthalpies could be calculated for half the ILs presented in the Table 1. However, at least one additional correction is required to obtain enthalpies of vaporization of the $[C_nMIM][NTf_2]$ family. The necessity of such a correction is already obvious from the data in Figure 1 of the Supporting Information. Indeed, the enthalpies of vaporization of the ILs with the $(CF_3SO_2)_2N^-$ anion are drastically lower than those of other ILs. From our earlier experience, even simple fluorine-containing organic compounds are substantially more volatile than their hydrocarbon analogues.[15] In this context, the CF_3 group is an extreme case; for example, the enthalpy of vaporization of trifluoromethylbenzene[16] of 37.7 $kJ\,mol^{-1}$ is 10 $kJ\,mol^{-1}$ lower than that of *tert*-butyl-benzene (47.7 $kJ\,mol^{-1}$).[16] Because each of IL in the $[C_nMIM][NTf_2]$ family contains two CF_3 groups, a structural correction $\Delta H_{(CF_3)}$ is suggested.

The second structural correction required for refinement of Equation (3) is the well-established[11] ring correction. A simple comparison of the enthalpy of vaporization of the cyclic amine pyrrolidine (37.5 $kJ\,mol^{-1}$) with that of its open-chain analogue diethylamine (31.5 $kJ\,mol^{-1}$) reveals the necessity for the ring correction $\Delta H_{(ring)}$ for ILs containing a pyrrolidine moiety.[16]

The additive parameters and structural corrections were derived by least-squares treatment of the data set of vaporization enthalpies for the twelve ILs collected in Table 1. These parameters are given in Table 2. Experimental and calculated values are compared in Table 1. The average deviation of experimental vaporization enthalpies and those calculated according Equation (3) does not exceed 1.5 $kJ\,mol^{-1}$. It is remarkable that using a very simple count of the constituent elements allows the vaporization enthalpies of 12 different ionic liquids to be predicted with an accuracy which compares well with the experimental uncertainties of ±(3–4) $kJ\,mol^{-1}$ for these compounds. The maximal deviation of 1–3 $kJ\,mol^{-1}$ was observed for $[C_nMIM][NTf_2]$, for

Table 2: Additivity parameters for calculation of vaporization enthalpies of ILs at 298 K.

Parameter	Value [$kJ\,mol^{-1}$]	Parameter	Value [$kJ\,mol^{-1}$]
$\Delta H_{(C)}$	2.5	$\Delta H_{(P)}$	4.1
$\Delta H_{(N)}$	26.3	$\Delta H_{(S)}$	−8.2
$\Delta H_{(O)}$	23.6	$\Delta H_{(CF_3)}$	−63.1
$\Delta H_{(B)}$	23.0	$\Delta H_{(ring)}$	27.1
$\Delta H_{(F)}$	13.7		

which the fine interplay of van der Waals and electrostatic interactions was totally neglected. Hence, even the simple additivity scheme applied in this work does not reveal any outliers in the data set of $\Delta_l^g H_m$(298 K) for imidazolium- and pyrrolidinium-based ILs with the most common anions NTf_2^-, BF_4^-, PF_6^-, $EtSO_4^-$, and $N(CN)_2^-$, and these experimental data (Table 1) could be recommended as a consistent basis set which can be further refined and developed to yield improved predictive models. The diversity of IL structures embraced in this study as well as the high accuracy of prediction of vaporization enthalpy according to Equation (3) ensures that the most significant contributions have been taken into account. However, from our experience, some further structural corrections could be required as new experimental data become available. For instance, it is probable that individual ring corrections should be applied for the pyridinium-based ILs. A special correction could be also necessary for ILs based on quaternary ammonium cations.

In spite of the remarkable predictive capability of Equation (3) for the twelve ILs shown in Table 1, further validation of the developed parameters (Table 2) is desirable. As was mentioned above, the new sets of ILs [C_nMIM][NO_3] and [C_nMIM][$C(CN)_3$] are currently under investigation in our laboratory. These ILs contain two anions NO_3^- and $C(CN)_3^-$ which have not been used for parameterization (Table 2). The enthalpies of vaporization for these new ionic liquids, derived according to Equation (1), are given in the Table 1 and they compare well to those predicted by Equation (3). The differences, which do not exceed 5 kJ mol^{-1}, are well within the experimental uncertainties of $\pm$(3–4) kJ mol^{-1} for the ILs involved in parameterization (Table 1). Thus, the parameters derived from the limited data set of 12 ionic liquids are valid over a broad range of ILs. Additionally, the selected experimental vaporization enthalpies of ILs (Table 1) have been proven to be internally consistent.

It is widely acknowledged that the number of possible combination of ions leading to the formation of ILs is huge. Since the vast majority of these ILs have yet to be synthesized, it is very important to develop methods to predict the physical properties of unknown ILs in order to facilitate the design of new materials and reduce the required experimental effort.[14] The simple approach suggested here is straightforward, quick, and easy. It is based on a common empirical formula and it does not require any experimental input or expensive computing resources. This method opens up a new way to obtain thermodynamic properties of ionic liquids which have not been available thus far and would provide valuable data for supporting ab initio procedures and molecular dynamic simulations techniques in order to understand thermodynamic properties of ionic liquids on a molecular basis.

Received: February 26, 2008
Revised: April 11, 2008

Keywords: ionic liquids · physical properties · predictive methods · vaporization enthalpies

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