

# Making Sense of Enthalpy of Vaporization Trends for Ionic Liquids: New Experimental and Simulation Data Show a Simple Linear Relationship and Help Reconcile Previous Data

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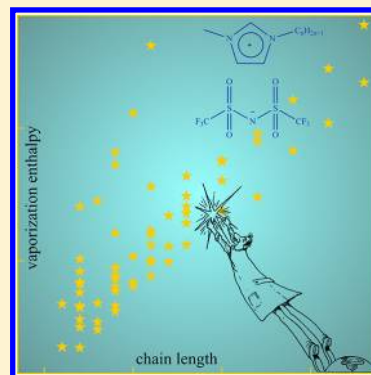
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## Supporting Information

**ABSTRACT:** Vaporization enthalpy of an ionic liquid (IL) is a key physical property for applications of ILs as thermofluids and also is useful in developing liquid state theories and validating intermolecular potential functions used in molecular modeling of these liquids. Compilation of the data for a homologous series of 1-alkyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imide ( $[\text{C}_n\text{mim}][\text{NTf}_2]$ ) ILs has revealed an embarrassing disarray of literature results. New experimental data, based on the concurring results from quartz crystal microbalance, thermogravimetric analyses, and molecular dynamics simulation have revealed a clear linear dependence of IL vaporization enthalpies on the chain length of the alkyl group on the cation. Ambiguity of the procedure for extrapolation of vaporization enthalpies to the reference temperature 298 K was found to be a major source of the discrepancies among previous data sets. Two simple methods for temperature adjustment of vaporization enthalpies have been suggested. Resulting vaporization enthalpies obey group additivity, although the values of the additivity parameters for ILs are different from those for molecular compounds.



## INTRODUCTION

Research on ionic liquids (ILs) and their industrial applications has expanded rapidly over the past decade. One of the most attractive features of ILs is their negligible vapor pressure at ambient temperatures. At elevated temperatures relevant for many applications of ILs, however, the vapor pressure is no longer negligible, even though it remains small (approximately at the level of a few Pa). Hence, for chemical processing with ILs, knowledge of the vapor pressure and vaporization enthalpies,  $\Delta_f^\circ H_m$ , is indispensable. Moreover, vapor pressures and enthalpies of vaporization also play a crucial role in the development of liquid state theories, and so there is additional

motivation to understand these properties for ILs. Experimental measurements of the vaporization enthalpies are extremely challenging because of two main problems. The vapor pressures of ILs at ambient temperature are so low as to be practically immeasurable, whereas at high temperatures where vapor pressures can be measured, possible thermal decomposition processes can distort the results. As a matter of fact, with the exception of the Knudsen method,<sup>1,2</sup> traditional experimental

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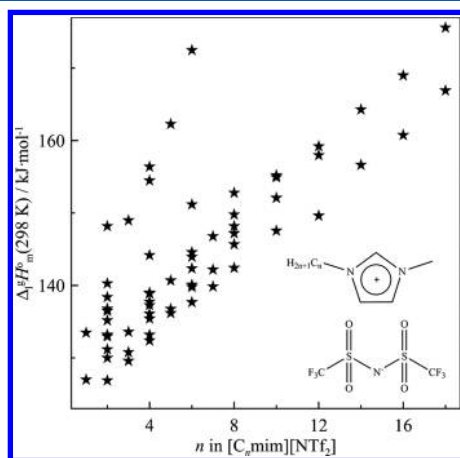
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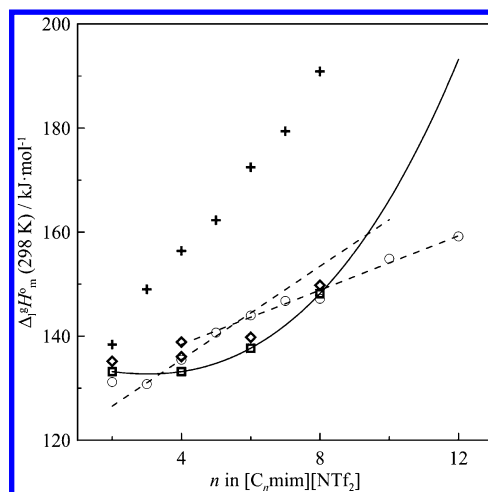
techniques for vapor pressure measurement have not been developed for extremely low volatility liquids such as ILs. This has stimulated the development of new direct experimental methods such as temperature programmed desorption and line of sight mass spectrometry (LOSMS),<sup>3,4</sup> thermogravimetry (TGA),<sup>5–7</sup> high-temperature UV spectroscopic technique (UV),<sup>8</sup> and quartz crystal microbalance (QCM).<sup>9,10</sup> As a rule, the vaporization studies of ILs have been conducted at temperatures between 360 and 600 K.<sup>3–10</sup>

A homologous series of the 1-alkyl-3-methylimidazolium bis(trifluoromethane-sulfonyl)imides or  $[C_n\text{mim}][\text{NTf}_2]$  is beyond any doubt the most frequently investigated class of IL for the study of vaporization enthalpies. There are at least two reasons for this extended interest. First, it is well-known that these ILs have remarkable thermal stability such that they can be distilled without decomposition at elevated temperatures of 473 to 573 K.<sup>11,12</sup> The second aspect is that the increasing length of the cation alkyl chain should lead to predictable monotonic structure–property relations such as those exhibited by molecular liquids such as alkanes. However, it is unclear whether ILs follow the same monotonic pattern or not, especially for the vaporization enthalpy. We have collected the available literature data on vaporization enthalpies of  $[C_n\text{mim}][\text{NTf}_2]$  in Table S1 (Supporting Information (SI)) and present these data graphically in Figure 1. It is apparent



**Figure 1.** Available literature data on the enthalpy of vaporization,  $\Delta^{\circ}H_m^o$  (298 K) chain length ( $n$ ) dependence for  $[C_n\text{mim}][\text{NTf}_2]$ .

that the available vaporization enthalpies of  $[C_n\text{mim}][\text{NTf}_2]$  are in total disarray. The vaporization enthalpy chain length dependence in Figure 1 resembles the “Milky Way” rather than any reasonable relationship. However, not without bias, some definite trends in the  $\Delta^{\circ}H_m^o$  values of  $[C_n\text{mim}][\text{NTf}_2]$  (see Figure 2) can be suggested and even justified. For example, a very unusual (for a homologous series) and noticeably nonlinear and even “bent up” dependence of  $\Delta^{\circ}H_m^o$  on alkyl chain length (in the imidazolium cation) was observed (see Figure 2) for ethyl-, butyl-, hexyl-, and octyl- derivatives determined by the Knudsen method<sup>2</sup> and by LOSMS.<sup>3</sup> By contrast, the direct calorimetrically measured values of vaporization enthalpies<sup>13</sup> for the same set of ILs demonstrated (see Figure 2) the expected linear dependence of the  $\Delta^{\circ}H_m^o$  on the chain length. What is curious about the calorimetry data, however, is the unusually high contribution each additional  $\text{CH}_2$  group makes to the vaporization enthalpy ( $8.9 \pm 0.6 \text{ kJ mol}^{-1}$ ).<sup>13</sup> For comparison, in alkanes, the incremental increase



**Figure 2.** Some possible trends in the vaporization enthalpy chain-length dependence. ( $\diamond$ ) Knudsen effusion method [2]; ( $\square$ ) LOSMS [3]; (+) calorimetry [13]; ( $\circ$ ) QCM-Knudsen [10].

in vaporization enthalpy per  $\text{CH}_2$  group is about half this ( $4.95 \pm 0.10 \text{ kJ mol}^{-1}$ ).<sup>14</sup>

Another and more sophisticated dependence of vaporization enthalpies was reported recently using the Knudsen effusion apparatus, combined with a QCM.<sup>10</sup> Two distinct slopes in the vaporization enthalpy versus alkyl chain length curve were clearly observed for the  $[C_n\text{mim}][\text{NTf}_2]$  ILs series, with the change in slope occurring at  $[C_6\text{mim}][\text{NTf}_2]$  (see Figure 2). This behavior was explained in terms of a structural percolation phenomenon in which the longer alkyl chains form aggregates in the liquid phase, thereby lowering the vaporization enthalpy for the longer alkyl chains.<sup>10</sup> Such an aggregation phenomenon has been reported in several simulation<sup>15,16</sup> and experimental studies,<sup>17</sup> but this was the first time such a phenomenon was used to explain<sup>10</sup> an anomaly in an enthalpy of vaporization trend.

Given all these conflicting results, the obvious questions are: What is the right trend within the “Milky Way” spread of the experimental results? Do vaporization enthalpies exhibit a typical linear increase in vaporization enthalpy with increasing chain length, albeit at a greater slope than alkanes? Or, do they show a “bent up” increase or an aggregate-driven decrease beyond a certain chain length?

We attempt to resolve this contradiction using a combination of precise experimental measurements and atomistic simulations to examine the vaporization enthalpies for the  $[C_n\text{mim}][\text{NTf}_2]$  family with odd and even chain length of the alkyl-imidazolium cation. Two recently developed methods<sup>7,9</sup> were used for the experimental investigation. The first method was a homemade set up for the Langmuir vaporization from the open liquid surface coupled with the QCM.<sup>9,18</sup> The combination of high-vacuum conditions with the extremely sensitive QCM allows measurements of mass loss rates for ILs at temperatures down to 363 K. In contrast to the conventional Knudsen method, the Langmuir vaporization is significantly more sensitive since the total open surface is exposed to the QCM under vacuum conditions. The second method used a commercially available TGA for the vaporization enthalpy measurements.<sup>7,19</sup> The TGA procedure has been carefully developed for very low volatility compounds. It has been shown that the vaporization enthalpies for the reference compounds

could be obtained with an accuracy better than  $\pm 2\text{--}3\text{ kJ}\cdot\text{mol}^{-1}$  in comparison to the reliable literature data.<sup>7</sup>

Atomistic molecular dynamics (MD) simulations were also carried out using force fields validated to capture the liquid phase properties of this class of ILs. Previous work from our group<sup>20</sup> and others<sup>21</sup> has shown that vaporization enthalpies can be reliably computed with MD. Since the aggregation phenomena used to explain the change in slope of the vaporization enthalpy occurring at  $[\text{C}_6\text{mim}][\text{NTf}_2]$  is observed in MD simulations, it will be of interest to see if this causes a change in slope for the simulation results.

The objectives of the present work were twofold: (a) to investigate structure–property relations within the  $[\text{C}_n\text{mim}][\text{NTf}_2]$  family using experimental and computational methods, and (b) to develop an approach for the temperature adjustments of IL vaporization enthalpies, required for the proper comparison of the experimental data. As to objective (a), we will show that the chain length dependence of the vaporization enthalpy of this family of ILs is (within the boundaries of experimental and simulation uncertainties) represented by a straight line. As to objective (b), it will be shown that most of the literature experimental data on vaporization enthalpies for the  $[\text{C}_n\text{mim}][\text{NTf}_2]$  series are of a good quality and the scattered “Milky Way” behavior depicted in Figure 1 is simply the consequence of oversimplified adjustment of the results from the elevated experimental temperatures to the reference temperature 298 K. Two simple and robust procedures will be suggested for the proper adjustment of the vaporization enthalpies to any required temperature.

## ■ EXPERIMENTAL SECTION

**General Procedures.** Samples of  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with even alkyl chain numbers were commercially available from IoLiTec, Sigma-Aldrich, and Merck. The samples with odd numbers were prepared and purified at the University of Freiburg (the procedure is given in the SI). Prior to the experiments, the ILs were subjected to vacuum evaporation at 333 K for more than 24 h. The highly pure sample of  $[\text{C}_1\text{mim}][\text{NTf}_2]$  was prepared and purified by Proionic GmbH. All ILs were fully characterized by IR, Raman, and NMR spectroscopy ( $^1\text{H}$  and  $^{19}\text{F}$  nuclei). Purity was additionally always controlled by  $^7\text{Li}$  NMR spectra, to ensure the absence of lithium halides. The ILs were dried at  $60\text{ }^\circ\text{C}/10^{-3}\text{ mbar}$  until water contents of  $<20\text{ ppm}$  were achieved (Karl Fischer-titration). Additional conditioning of an IL-sample was performed inside of the experimental set up in order to remove possible traces of solvents and moisture. The conditioning was repeated until a reproducible mass loss within two consecutive runs was recorded.

**QCM: Measurements of Vaporization Enthalpy.** Enthalpies of vaporization of the even and odd ILs have been measured using the QCM technique. The experimental procedure has been reported elsewhere.<sup>9</sup> In short, a sample of IL placed in an open cavity of a thermostatted metal block is exposed to a vacuum system (at  $10^{-5}\text{ Pa}$ ). The QCM is placed directly over the measuring cavity containing the IL. The change in the vibrational frequency of the crystal  $\Delta f$  is a measure of the amount of IL deposited on the cold QCM. The value of  $\Delta f$  was measured as a function of time at different temperatures. The change of the vibrational frequency  $\Delta f$  is directly related to the mass deposition  $\Delta m$  on the crystal surface according to equation<sup>9,18</sup>

$$\Delta f = -C \cdot f^2 \cdot \Delta m \cdot S_C^{-1} \quad (1)$$

where  $f$  is the fundamental frequency of the crystal (5 MHz in this case) with  $\Delta f \ll f$ ,  $S_C$  is the area of the crystal, and  $C$  is a constant.<sup>9,18</sup> Using the frequency change rate  $df/dt$  measured by the QCM the molar enthalpy of vaporization,  $\Delta_f^s H_m^\circ(T_0)$ , is obtained<sup>9</sup> by

$$\ln\left(\frac{df}{dt}\sqrt{T}\right) = A' - \frac{\Delta_f^s H_m^\circ(T_0) - \Delta_f^s C_{\text{pm}}^\circ T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_f^s C_{\text{pm}}^\circ}{R} \ln\left(\frac{T}{T_0}\right) \quad (2)$$

with a constant  $A'$ , which is essentially unknown including all empirical parameters which are specific for the apparatus and the substance under study.  $T_0$  appearing in eq 2 is an arbitrarily chosen reference temperature. In our study,  $T_0$  was set equal to 380 K, 542 K, or 298 K. The value  $\Delta_f^s C_{\text{pm}}^\circ = C_{\text{pm}}^\circ(\text{g}) - C_{\text{pm}}^\circ(\text{l})$  is the difference of the molar heat capacities of the gaseous  $C_{\text{pm}}^\circ(\text{g})$  and the liquid phase  $C_{\text{pm}}^\circ(\text{l})$ , respectively. The temperature-dependent vaporization enthalpy  $\Delta_f^s H_m^\circ(T)$  is given by

$$\Delta_f^s H_m^\circ(T) = \Delta_f^s H_m^\circ(T_0) + \Delta_f^s C_{\text{pm}}^\circ(T - T_0) \quad (3)$$

The frequency change rate  $df/dt$  was measured in a few consecutive series with increasing and decreasing temperature steps. The background noise can impact the QCM signal. As a rule, it depends on the vacuum conditions and possible deposits on the internal parts of the vacuum chamber. In order to reduce the impact of the background noise on the QCM, it was kept at a constant temperature of 30 K higher than the temperature of walls of the vacuum system. Preliminary experiments have revealed that the background noise was less than 0.5–1% of the frequency change rate at the lowest temperature of determination. After each run, the sample of IL was cooled down, and the effect of background noise was checked. The QCM method provides very reproducible temperature dependences of the frequency change rate  $df/dt$ . The experimental uncertainties assessed for the vaporization enthalpy from the  $df/dt$  temperature dependences were always better than  $\pm 1\text{ kJ}\cdot\text{mol}^{-1}$  (calculated as the twice standard deviation). In order to detect a possible decomposition of IL under the experimental conditions, the residual IL in the cavity and the IL-deposit on the QCM were analyzed by attenuated total reflectance-infrared (ATR-IR) spectroscopy. No changes in the spectra were detected with the ILs under study in this work.

**TGA: Measurements of Vaporization Enthalpy.** We used a carefully calibrated Perkin-Elmer Pyris 6 TGA in this work. About 50–70 mg of the IL sample was placed in a plain platinum crucible inside of the measuring head of the TGA. The sample was stepwise heated and a mass loss of 0.1–0.8 mg from the crucible was recorded at each isothermal step. Isothermal mass loss rate  $dm/dt$  was monitored in the temperature range 480–620 K at a nitrogen flow rate of  $140\text{ mL}\cdot\text{min}^{-1}$ . Isothermal mass loss rate  $dm/dt$  was measured in a few consecutive series with increasing and decreasing temperature steps. In order to confirm the absence of decomposition of IL in the experimental conditions, the residual IL in the crucible was analyzed by ATR-IR spectroscopy. No changes in the spectra before and after the experiment were detected for the ILs under study.



The relationship between the mass loss  $dm/dt$  and the vaporization enthalpy was derived according to eq 1 but by using the mass loss rate  $dm/dt$  measured by the TGA (instead of the frequency change  $df/dt$  by QCM). Combined experimental uncertainties of the determination of vaporization enthalpy with the TGA were assessed<sup>7</sup> to be at the level of  $\pm 3.0$   $\text{kJ}\cdot\text{mol}^{-1}$  (calculated as the twice standard deviation).

**Force Field and MD Methodology.** A force field for each cation and the  $[\text{NTf}_2]$  anion was developed using procedures described in detail elsewhere.<sup>22</sup> Briefly, a standard Class I force field was used, containing intramolecular bond stretching, angle bending, dihedral rotation and improper terms. Intermolecular pairwise Lennard-Jones and Coulombic terms were also used.<sup>23</sup> Atom types, Lennard-Jones parameters, and intramolecular terms were taken directly from the generalized Amber force field (GAFF).<sup>24</sup> Lennard-Jones terms for cross interactions were derived using Lorentz–Berthelot combining rules. Electronic structure calculations were carried out on an isolated cation and anion using the Gaussian 09 package<sup>25</sup> at the B3LYP/6-31g(d) level. The structure of the ions was optimized and partial atomic charges were determined using the restrained electrostatic potential (RESP) method.<sup>26</sup> The ion charges were constrained to be  $\pm 1$ , and then the resulting partial charges were uniformly scaled to achieve a net ion charge of  $\pm 0.8$ . This reduction of net charge has been shown to be an effective way to mimic charge transfer without using a polarizable force field, and is expected to give much more accurate enthalpies of vaporization.<sup>27–30</sup> The GAFF database does not do a particularly good job with alkyl chain dihedral angles, so the dihedral angle potential of the alkyl chains was parametrized by matching energy scans in which B3LYP/6-31g(d) geometry optimizations were performed, followed by single point energy calculations at the MP2/6-31g(d) level. Each calculation constrains a dihedral angle of interest to a specific value and lets all other degrees of freedom relax. MD simulations are then carried out with similar constraints, and the dihedral angle parameters were fit to match the ab initio energies.<sup>22</sup> MD simulations of the ILs  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with  $n = 1–12$  were carried out using the LAMMPS package.<sup>31</sup> The liquid phase consisted of 200 ion pairs simulated at constant pressure and temperature. Standard procedures were used to ensure the system was well equilibrated. The algorithm of Shinoda et al.<sup>32</sup> as implemented in LAMMPS was used, with thermostat and barostat time constants of 0.1 and 1.0 ps, respectively. The Lennard-Jones potential was truncated at 0.12 nm and tail corrections were used. Coulombic interactions were treated using the particle–particle–particle mesh approach. The liquid phase was simulated for 4 ns and an independent 40 ns simulation of a single ion pair in the vapor phase was also carried out. Previous simulations and experiments have shown that the ion pair is the dominant vapor phase species at low pressure.<sup>33–35</sup>

The enthalpy of vaporization was computed from the difference between the molar energies of the vapor and liquid phases

$$\Delta_f^{\text{g}}H_m^{\text{o}}(T) = \langle U^{\text{g}} \rangle(T) - \langle U^{\text{l}} \rangle(T) + RT \quad (4)$$

where  $\langle U^{\text{g}} \rangle$  and  $\langle U^{\text{l}} \rangle$  are the ensemble average internal energies of an ion pair in the gas and liquid phases, respectively. The difference in heat capacity at constant pressure between the liquid and gas phases  $\Delta_f^{\text{g}}C_{\text{pm}}^{\text{o}}$  was computed following a procedure given by Lagache et al.<sup>36</sup> The heat capacity can be split into ideal and residual components, with the residual heat

capacity obtained from the simulations via the following expression:

$$C_{\text{p}}^{\text{res}} = \frac{1}{k_{\text{B}}T^2} [\langle U^{\text{NB}}\hat{H} \rangle - \langle U^{\text{NB}} \rangle \langle \hat{H} \rangle + P(\langle V\hat{H} \rangle - \langle V \rangle \langle \hat{H} \rangle)] - R \quad (5)$$

where  $U^{\text{NB}}$  is the intermolecular “non-bond” energy, and  $\hat{H} = U + PV$  is the configurational enthalpy. The ideal contribution to the heat capacity can be obtained readily from electronic structure calculations, although since differences  $\Delta_f^{\text{g}}C_{\text{pm}}^{\text{o}}$  are required and the ideal contribution is unaffected by the condensed phase, the following expression was used:

$$\Delta_f^{\text{g}}C_{\text{p}} = C_{\text{p}}^{\text{res}}(\text{g}) - C_{\text{p}}^{\text{res}}(\text{l}) \quad (6)$$

to estimate the heat capacity difference by using MD and to compare it with the experimental value.

## RESULTS AND DISCUSSION

**Vaporization Enthalpies,  $\Delta_f^{\text{g}}H_m^{\text{o}}(T_{\text{av}})$ , of  $[\text{C}_n\text{mim}][\text{NTf}_2]$ : Experiment and Simulation.** Vaporization enthalpies,  $\Delta_f^{\text{g}}H_m^{\text{o}}(T_{\text{av}})$ , referred to average temperatures of the experimental temperature ranges obtained from temperature-dependent measurements of the frequency change  $df/dt$  by the QCM, and the mass loss rate  $dm/dt$  by TGA for the odd members of the homologous series  $[\text{C}_n\text{mim}][\text{NTf}_2]$  with the alkyl chain lengths  $n = 1, 3, 5$ , and  $7$  are given in Table 1 (the primary experimental data are listed in Table S1 in the SI). In order to get the full picture, we also collected in Table 1 our previous results for the even members of this family measured just recently by QCM<sup>18</sup> as well as by TGA.<sup>19</sup>

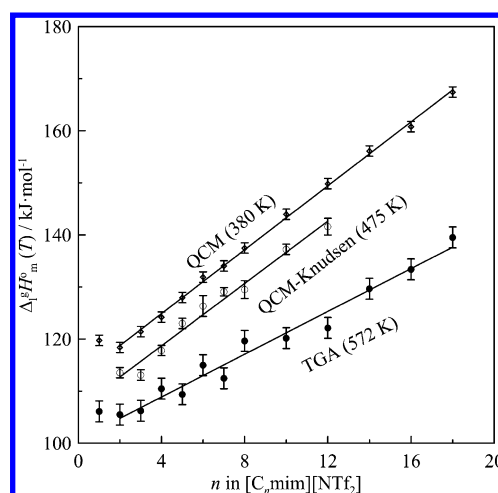
It is apparent from Table 1 that  $T_{\text{av}}$  values for ILs under study are significantly different depending on the chain length  $n$ , as well as on the method used: long-chained species were studied at significantly higher temperatures in comparison to shorter one, as well as the TGA studies were performed at temperatures of 30–150 K higher in comparison to the QCM. As a matter of fact, enthalpies of vaporization  $\Delta_f^{\text{g}}H_m^{\text{o}}(T_{\text{av}})$  derived from both methods (see column 3, Table 1) were not possible to compare because they referred to different  $T_{\text{av}}$  values. For the sake of comparison, enthalpies of vaporization  $\Delta_f^{\text{g}}H_m^{\text{o}}(T_{\text{av}})$  (column 3, Table 1) have to be adjusted to any arbitrary but reasonable common temperature, which ideally is close to the average temperatures  $T_{\text{av}}$  of the individual measurements. For the QCM studies, the suitable temperature was 380 K, while for the TGA results we chose 572 K for comparison (see Figure 3). For comparison as well as in order to keep consistency with our previous work, we *first* used in the current work the commonly acknowledged value<sup>37</sup>  $\Delta_f^{\text{g}}C_{\text{pm}}^{\text{o}} = -100$   $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  in eq 3. Comparison of the vaporization enthalpies at the selected temperatures 380 K for QCM and at 572 K for TGA should be least affected by an ambiguity of the  $\Delta_f^{\text{g}}C_{\text{pm}}^{\text{o}}$  value because of the deliberately short extrapolations from  $T_{\text{av}}$  of the individual measurements. It is apparent from Figure 3 that the vaporization enthalpies for the  $[\text{C}_n\text{mim}][\text{NTf}_2]$  family (omitting  $n = 1$ ) show an impeccable linear dependence on the number of C-atoms in the alkyl chain of the imidazolium cation,  $n$ , when measured by using the QCM. The scatter of the results obtained by the TGA is somewhat larger, but within the experimental uncertainties, the linear correlation (omitting  $n = 1$ ) is also apparent for the data from TGA. For comparison with our own vaporization enthalpies measured by TGA and QCM, we have added to

**Table 1.** Experimental Vaporization Enthalpies,  $\Delta_f H_m^\circ$ , of  $[C_n\text{mim}][\text{NTf}_2]$  at  $T_{\text{av}}$  and at 298 K

$T\text{-range/K}$	$T_{\text{av}}/\text{K}$	$\Delta_f H_m^\circ(T_{\text{av}})$ $\text{kJ}\cdot\text{mol}^{-1}$	$\Delta_f H_m^\circ(298\text{ K})^a$ $\text{kJ}\cdot\text{mol}^{-1}$	method
$[C_1\text{mim}][\text{NTf}_2]$				
345–400	381.6	$119.9 \pm 1.0$	$128.2 \pm 1.0$	QCM
543–623	590.0	$104.3 \pm 1.6$	$133.5 \pm 1.6$	TGA
$[C_2\text{mim}][\text{NTf}_2]$				
362–395	378	$118.6 \pm 1.0$	$126.9 \pm 1.0$	QCM
480–570	520.2	$110.5 \pm 1.5$	$132.7 \pm 1.5$	TGA
$[C_3\text{mim}][\text{NTf}_2]$				
362–395	380.3	$121.4 \pm 1.0$	$129.6 \pm 1.0$	QCM
480–570	546.2	$108.8 \pm 2.6$	$133.6 \pm 2.6$	TGA
$[C_4\text{mim}][\text{NTf}_2]$				
362–395	378	$124.4 \pm 1.0$	$132.4 \pm 1.0$	QCM
513–572	541.8	$113.5 \pm 1.5$	$137.8 \pm 1.5$	TGA
$[C_5\text{mim}][\text{NTf}_2]$				
362–404	381.7	$127.8 \pm 1.0$	$136.2 \pm 1.0$	QCM
523–603	560.8	$110.5 \pm 1.9$	$136.8 \pm 1.9$	TGA
$[C_6\text{mim}][\text{NTf}_2]$				
362–405	383	$131.6 \pm 1.0$	$140.1 \pm 1.0$	QCM
513–571	541.8	$118.0 \pm 1.8$	$142.3 \pm 1.8$	TGA
$[C_7\text{mim}][\text{NTf}_2]$				
364–406	385.3	$133.5 \pm 1.0$	$142.2 \pm 1.0$	QCM
503–603	553.7	$114.3 \pm 1.9$	$139.9 \pm 1.9$	TGA
$[C_8\text{mim}][\text{NTf}_2]$				
372–402	387	$136.8 \pm 1.0$	$145.7 \pm 1.0$	QCM
513–571	541.8	$122.6 \pm 1.0$	$147.0 \pm 1.0$	TGA
$[C_{10}\text{mim}][\text{NTf}_2]$				
380–410	394.6	$142.5 \pm 1.0$	$152.1 \pm 1.0$	QCM
493–552	522	$125.2 \pm 1.0$	$147.5 \pm 1.0$	TGA
$[C_{12}\text{mim}][\text{NTf}_2]$				
392–425	408.4	$147.0 \pm 1.0$	$158.0 \pm 1.0$	QCM
503–562	533.5	$126.0 \pm 1.1$	$149.5 \pm 1.1$	TGA
$[C_{14}\text{mim}][\text{NTf}_2]$				
400–432	416.2	$152.5 \pm 1.0$	$164.3 \pm 1.0$	QCM
513–571	541.8	$132.7 \pm 1.0$	$157.1 \pm 1.0$	TGA
$[C_{16}\text{mim}][\text{NTf}_2]$				
405–445	424.8	$156.3 \pm 1.0$	$169.0 \pm 1.0$	QCM
513–571	541.8	$136.4 \pm 1.4$	$160.8 \pm 1.4$	TGA
$[C_{18}\text{mim}][\text{NTf}_2]$				
410–452	430.3	$162.4 \pm 1.0$	$175.6 \pm 1.0$	QCM
546–621	582.5	$138.5 \pm 1.4$	$166.8 \pm 1.4$	TGA

<sup>a</sup>Enthalpies of vaporization for ILs were adjusted to 298 K with  $\Delta_f C_p = -100\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ ; uncertainties in the heat capacity differences were not taken into account.

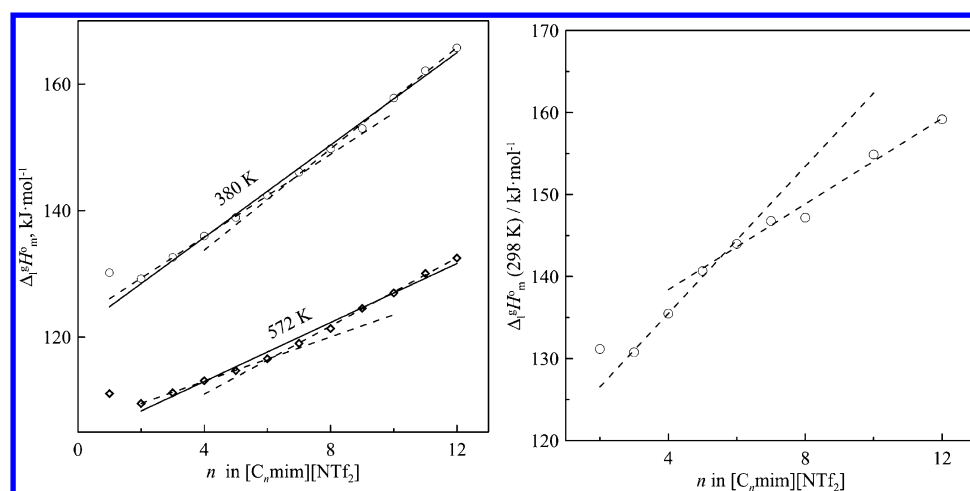
Figure 3 recent literature data from Rocha et al. measured by the combined Knudsen-QCM method.<sup>10</sup> We selected for comparison with their data the temperature 475 K, and in this case we again used the value  $\Delta_f C_p = -100\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  for interpolation of vaporization enthalpies from  $T_{\text{av}}$  to the selected  $T = 475\text{ K}$ . Experimental uncertainties of our measurements as well as of the literature data are presented in Figure 3 as the error bars. In our opinion, the experimental vaporization enthalpies from the combined Knudsen-QCM method<sup>10</sup> also fit very well (within the error bars) the linear dependence on the chain length  $n$ , similar to our own finding. This conclusion disagrees with the interpretation given in ref 10, where the authors consider their Knudsen-QCM results as an unusual evidence for “structural percolation phenomenon.” It is also clear from Figure 3 that, in order for one to observe a change in slope of the enthalpy of vaporization in Rocha et al.’s data,<sup>10</sup>

**Figure 3.** Dependence of the enthalpy of vaporization,  $\Delta_f H_m^\circ(T_{\text{av}})$  for 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides on the length of the cation alkyl chain ( $n$ ).

one must throw out the  $n = 2$  data point, despite the fact that Rocha et al. state in their paper that the enthalpy of vaporization “results for  $[C_2\text{mim}][\text{NTf}_2]$  and  $[C_4\text{mim}][\text{NTf}_2]$  from Santos et al.<sup>13</sup> are in reasonable agreement with the present set of results or most of the results found in the literature.” Thus we are unsure what the justification is to exclude the  $n = 2$  data from the fitting. We show that if one uses *all* of Rocha et al.’s data and consider the associated uncertainties, there is no change in slope. Or, if one chooses to take the  $n = 3$  point as an outlier (for example), there is also no break in slope. This is clearly seen in Figure 3 of the present work. In addition to pointing this out, we provide our own experimental data for even and odd  $[C_n\text{mim}][\text{NTf}_2]$  with  $n = 1$  to  $n = 18$  (see Table 1) and show that from  $n = 2$  to  $n = 18$  there is no change in slope. We do see an “outlier” at  $n = 1$ , but then also confirm both observations with simulations (see below), which shows why one should see an outlier at  $n = 1$  (due to Coulombic and van der Waals trends). From the data presented in Figure 3, we do not observe any discontinuities in the linear trend on enthalpy of vaporization with chain length (except for  $n = 1$ ) within the error bars for all three data sets. In our opinion, the “structural percolation phenomenon” or nanoscale aggregation of alkyl chains, which is thought to occur in ILs,<sup>10</sup> does not result in two distinct trends in the enthalpy of vaporization with chain length, as it has been claimed recently.<sup>10</sup> Rather, it seems that this is an artifact that was overinterpreted by the authors within the boundaries of their experimental uncertainties. Simulation results described below give further support for this conclusion.

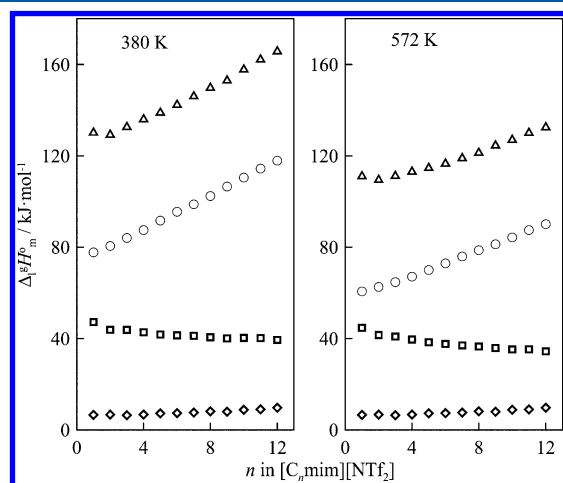
The enthalpies of vaporization  $\Delta_f H_m^\circ(T_{\text{av}})$  computed in the present work using MD simulations are shown in Figure 4 along with the experimental results from Rocha et al.<sup>10</sup>

The solid lines are linear fits to the  $n = 2$ –12 data. As can be observed, the MD results show a monotonic increase in the enthalpy of vaporization with no discontinuity, in agreement with the experimental results of the present QCM and TGA study, but in contrast to the experimental data of Rocha et al.<sup>10</sup> (right panel) where there is a change in slope claimed at about  $n = 6$ . We also tried to fit two different slopes through the simulation results for  $n = 2$ –6 and  $n = 7$ –12, and these fits are shown as dashed lines in the upper panel of Figure 4. It could be argued that there is a *slight* change in slope, with increment



**Figure 4.** Vaporization enthalpy of  $[C_n\text{mim}][\text{NTf}_2]$  at 380 and 572 K from MD simulations (this work, left) compared with the experimental data of Rocha et al.<sup>10</sup> (right) where a discontinuity in the trend is observed at around  $n = 6$ .

of vaporization enthalpy per  $\text{CH}_2$  actually increasing slightly for the longer alkyl chains. However, this change is minuscule compared to the uncertainties in the calculations, and thus within the statistical uncertainties of the simulations. It can be concluded that the MD simulations show that the enthalpy of vaporization exhibits a simple linear dependence with chain length for  $n = 2$ –12. Following previous procedures,<sup>38,39</sup> the internal energies for the liquid and the vapor phases were divided into the contributions from Coulomb, van der Waals, and intramolecular terms. The differences for all three contributions or the driving forces for the vaporization enthalpy obtained from the MD simulations are shown in Figure 5 for the ILs  $[C_n\text{mim}][\text{NTf}_2]$ .



**Figure 5.** Effect of alkyl chain length on the total enthalpy of vaporization and the various components at 380 K and 572 K. The symbols have the following meaning: triangles (total enthalpy); circles (van der Waals contribution); squares (Coulombic contribution); diamonds (intramolecular contribution).

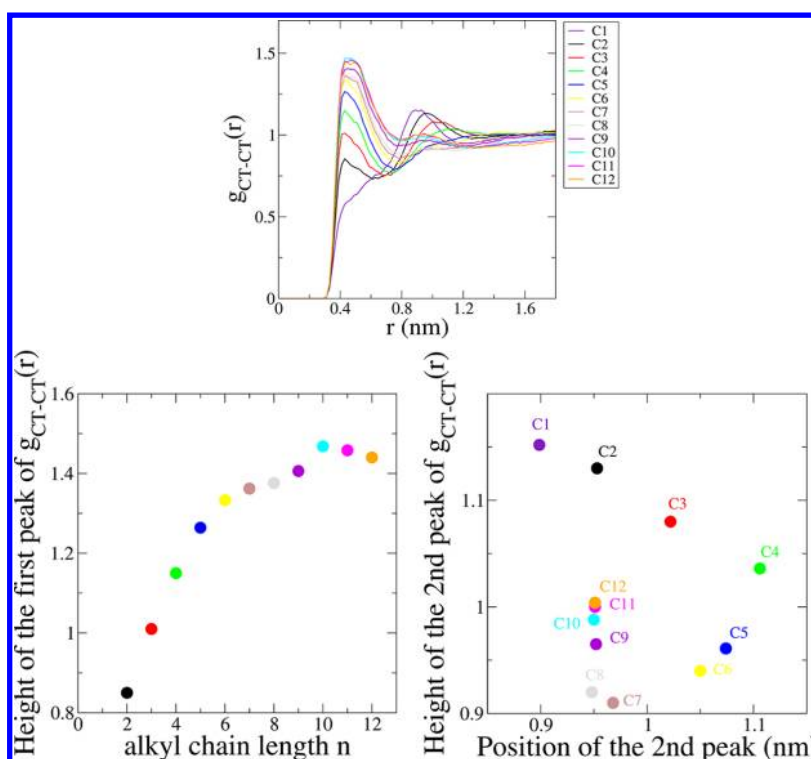
The Coulomb energy monotonically decreases from  $[C_2\text{mim}][\text{NTf}_2]$  to  $[C_{12}\text{mim}][\text{NTf}_2]$  by  $4 \text{ kJ}\cdot\text{mol}^{-1}$  for 380 K ( $7 \text{ kJ}\cdot\text{mol}^{-1}$  at 572 K) for all ILs, and shows a slightly larger drop per  $\text{CH}_2$  in going from  $[C_1\text{mim}][\text{NTf}_2]$  to  $[C_2\text{mim}][\text{NTf}_2]$ . This latter feature is similar to the calculations by Köddermann et al.,<sup>39</sup> where the Coulomb energy drops by  $4.5 \text{ kJ}\cdot\text{mol}^{-1}$  (at 298 K) from  $[C_1\text{mim}][\text{NTf}_2]$  to  $[C_2\text{mim}][\text{NTf}_2]$ ,

and is consistent with the physical argument presented above. In contrast to the present study, however, the results of Köddermann et al.<sup>39</sup> suggest that the Coulombic energy contribution remains unchanged as the length of the alkyl chains increase beyond  $n = 2$ . Consistent with the findings of Köddermann et al.,<sup>39</sup> however, we also find that the increase in enthalpy of vaporization for  $[C_n\text{mim}][\text{NTf}_2]$  with increasing chain length arises completely from van der Waals interactions, which are the dominant driving force of the vaporization process.

Rocha et al.<sup>10</sup> attributed the change in slope of the vaporization enthalpy with chain length to a structural percolation phenomenon associated with the aggregation of cation alkyl tails for  $n > 6$ . The percolation phenomena was first observed by MD simulations<sup>15,16</sup> and further quantified by Rocha et al.<sup>10</sup> Color-coded simulation snapshots were used to provide qualitative evidence that the alkyl tails of the cations tend to aggregate as  $n > 6$ . To quantify this behavior, Rocha et al.<sup>10</sup> computed the height of the first and second peaks on the terminal alkyl carbon–carbon radial distribution function (RDF), identified as the CT–CT RDF, for  $n = 2$ –10. They observed a growth in the height of the primary CT–CT peak for  $n = 2$ –6, and then a plateau of the peak height for  $n > 6$ . They also observed that the distance of the second peak shifts from about 0.95 to 0.85 nm as the chain length increases above  $n = 6$ . These features provide clear evidence for nanoscale ordering in the MD simulations, which was then used to explain the change in slope of the experimental vaporization enthalpy curve. Unfortunately, the authors did not report the enthalpies of vaporization from the MD simulations where this aggregation behavior was observed.

To examine this further, we carried out the same analysis that Rocha et al.<sup>10</sup> did to see whether our MD simulations exhibited a similar aggregation behavior. The results are shown in Figure 6.

Similar to what Rocha et al.<sup>10</sup> observed, our MD simulations show clear evidence of nanoscale ordering of the alkyl tails. The lower left panel of Figure 6 shows that the primary peak height plateaus at around  $n = 6$ –7. The lower right panel of Figure 6 shows that the location of the second peak changes significantly for  $n < 6$  and decreases by about 0.1 nm in going from  $n = 4$  to  $n = 8$ . The exact values of the peak heights and positions obtained in the present work differ from those of Rocha et al.<sup>10</sup>



**Figure 6.** (Top): Terminal alkyl carbon RDF (CT–CT) for  $[C_n\text{mim}][\text{NTf}_2]$ ,  $n = 1-12$ . (lower left): Height of the first peak of the CT–CT RDF as a function of chain length. (Lower right): Height of the second peak of the CT–CT RDF as a function of position of the second peak.

because a different force field was used. In particular, Rocha et al.'s force field results in a more structured liquid than that obtained in our simulations, which is likely because they used integer charges on their cations and anions, while scaled charges of  $\pm 0.8$  were used in the present study. Nevertheless, the similarity between the two simulations is striking. Both sets of simulations show clear evidence of nanoscale ordering, but despite this, *the present MD simulations do not show deviations from the monotonic change in vaporization enthalpy with chain length.* This suggests that, at least to the extent that the MD simulations are capturing the energetics of these ILs, the presence of nanoscale ordering does not necessarily result in the kind of slope change in the vaporization enthalpy curve reported by Rocha et al.<sup>10</sup>

A comparison of the absolute  $\Delta_f^{\circ}H_m(T)$  values from the MD simulations and experiments is given in Table 2 and Figure 7. At 380 K, there is a consistent offset with the MD simulations predicting vaporization enthalpies about 10% higher than the experimental QCM data. At 572 K, the MD results are in better agreement with the experimental TGA data, although the relatively large uncertainties of the TGA experiment make it harder to be certain of this. What is clear is that the MD simulations and two different sets of experiments have essentially the same slope, and no discontinuities are observed. The similarity of slopes for short and long chains supports the assumption made in the MD simulations that the vapor phase consists of single ion pairs. However, in recent work,<sup>40</sup> we have observed that at high temperature and pressure, clusters could be formed, and, in fact, van der Waals interactions go down with increasing chain length. The present experiments are at sufficiently low pressure, however, that we do not expect to observe any significant amount of clustering in the vapor phase.

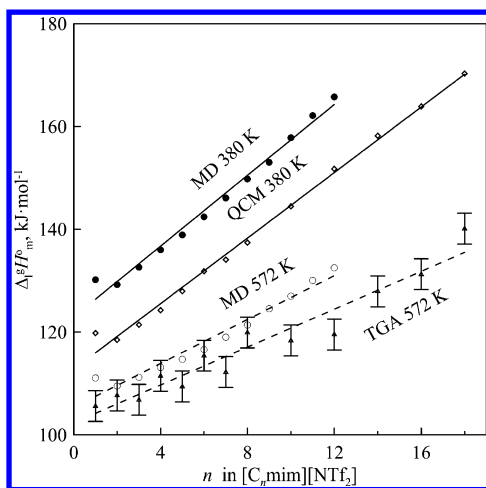
**How Does One Adjust  $\Delta_f^{\circ}H_m(T)$  Values to the Reference Temperature 298 K Properly?** In order to

**Table 2. Experimental and MD Calculated Enthalpies of Vaporization,  $\Delta_f^{\circ}H_m$ , of  $[C_n\text{mim}][\text{NTf}_2]$**

$n$ in $[C_n\text{mim}][\text{NTf}_2]$	$\Delta_f^{\circ}H_m$ (QCM)	$\Delta_f^{\circ}H_m$ (MD)	$\Delta$ (QCM-MD)	$\Delta_f^{\circ}H_m$ (TGA)	$\Delta_f^{\circ}H_m$ (MD)	$\Delta$ (TGA-MD)
	380 K			572 K		
1	119.8	130.2	−10.4	105.6	111.1	−5.5
2	118.5	129.3	−10.8	107.7	109.5	−1.8
3	121.4	132.6	−11.2	106.8	111.2	−4.4
4	124.3	136.0	−11.7	111.5	113.1	−1.7
5	128.0	138.9	−11.0	109.4	114.7	−5.3
6	131.9	142.4	−10.6	115.4	116.6	−1.2
7	134.1	146.1	−12.0	112.2	119.0	−6.8
8	137.4	149.8	−12.4	119.9	121.4	−1.5
9		153.0			124.6	
10	144.5	157.8	−13.4	118.4	127.0	−8.6
11		162.2			130.1	
12	151.8	165.8	−14.0	119.5	132.5	−13.0

reveal reliable structure–property relationships for the  $[C_n\text{mim}][\text{NTf}_2]$  family, the experimental values  $\Delta_f^{\circ}H_m(T_{\text{av}})$  (column 3, Table 1) were adjusted using eq 3 to 380 K (for QCM) and 572 K (for TGA), which were reasonably close to the  $T_{\text{av}}$  of the individual experiments. That is why the values of vaporization enthalpies were hardly affected by uncertainty in the  $\Delta_f^{\circ}C_{\text{pm}}$  value used for extrapolation. Such a procedure has allowed a proper interpretation of the chain-length trends at the selected temperatures. However, it is very common to adjust the vaporization enthalpies also to the reference temperature 298 K, because the  $\Delta_f^{\circ}H_m(298\text{ K})$  data are required for validation of the high-level first principle calculations<sup>41</sup> as well as for development of the reliable force fields for MD





**Figure 7.** The experimental and calculated enthalpies of vaporization for  $[C_n\text{mim}][\text{NTf}_2]$  at 380 and 572 K.

simulations.<sup>40</sup> Extrapolation to  $T = 298$  K is usually done by using eq 3, but it is essential to realize that over large differences (over 100 K) between  $T_{\text{av}}$  and the reference temperature, the value of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  used in the extrapolation is crucial. Small differences in  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  will result in large differences in  $\Delta_f^{\circ}H_m^{\circ}(298 \text{ K})$ . However, ambiguity of the  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values required for the extrapolation of experimental vaporization enthalpies to the reference temperature 298 K has been discussed recently.<sup>7,9,19</sup> As a matter of fact, in the recent literature, the value  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (regardless of the structure of the IL) has been systematically used for the temperature adjustments according to eq 3. This  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  value is based on the calorimetric liquid heat capacity measurements for a single IL  $[C_4\text{mim}][\text{PF}_6]$  and statistical thermodynamic calculations.<sup>41</sup> A similar value of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -105.4 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  was also derived, according to a procedure developed by Chickos and Acree<sup>42</sup> using the experimental isobaric molar heat capacity of  $[C_4\text{mim}][\text{N}(\text{CN})_2]$ .<sup>43</sup> However, it should be mentioned that the estimation procedure by Chickos and Acree<sup>43</sup> was parametrized only for molecular liquids and not for ILs. Thus, the current  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  value broadly applied for temperature adjustments for ILs is a rough estimate used regardless of the structure of an IL.

Formally,  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  is the difference of molar heat capacities of the liquid and the gaseous samples:  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = C_{\text{pm}}^{\circ}(\text{g}) - C_{\text{pm}}^{\circ}(\text{l})$ . As a rule, for ILs, the values of  $C_{\text{pm}}^{\circ}(\text{l})$  can be reliably measured by calorimetry or even be assessed by simple additivity rules.<sup>44</sup> In contrast, the experimental determination of the heat capacity of a gaseous IL is not possible. Therefore the heat capacity  $C_{\text{pm}}^{\circ}(\text{g})$  is usually derived using the frequencies calculated by quantum chemistry, which are then used to estimate  $C_{\text{pm}}^{\circ}(\text{g})$  using well-known statistical thermodynamics procedures.<sup>45</sup> However, it has turned out that use of this procedure in the case of the  $[C_n\text{mim}][\text{NTf}_2]$  family seems to be incorrect, e.g., for  $[C_2\text{mim}][\text{NTf}_2]$ , we estimated the value  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}(298 \text{ K}) = -137.7 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , where we used the experimental  $C_{\text{pm}}^{\circ}(\text{l})$ ,<sup>44</sup> and  $C_{\text{pm}}^{\circ}(\text{g})$  was calculated in this work by using density functional theory (DFT) calculations. However, this  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  estimate contradicts recent experimental results, which showed that enthalpy of vaporization data for  $[C_2\text{mim}][\text{NTf}_2]$  obtained using different experimental methods agree only for the heat capacity difference not higher than  $-50 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  (see details in ref 9).

How to resolve this contradiction? As a matter of fact, in the literature, there are no other data or even ideas of how to obtain  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values for ILs. As a consequence, by using the value of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ , the  $\Delta_f^{\circ}H_m^{\circ}(298 \text{ K})$  data are generously overestimated, and this fact has heavily aggravated comparison of vaporization enthalpies measured by different methods.<sup>5–19</sup> This fact also has thwarted further development of these methods. The common use of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  as a constant for all ILs regardless on the structure is obviously an oversimplification since  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  will differ for ILs with different cations and anions, as well as it should also vary as a function of alkyl chain length  $n$ . A significant amount of the discrepancies among the literature vaporization enthalpies for the  $[C_n\text{mim}][\text{NTf}_2]$  series at 298 K as measured by different methods is most likely due to the long temperature range (80–270 K) over which extrapolation of the measured  $\Delta_f^{\circ}H_m^{\circ}$  at  $T_{\text{av}}$  to the reference temperature is performed. As a consequence, accurate  $\Delta_f^{\circ}H_m^{\circ}(298 \text{ K})$  data will not be available until reliable values of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  or  $C_{\text{pm}}^{\circ}(\text{g})$  for ILs have been obtained.<sup>19</sup>

In this work we provide a simple and elegant procedure for properly assessing the correct  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values to use for the  $[C_n\text{mim}][\text{NTf}_2]$  series. This procedure is based on the experimental measurements of vaporization enthalpies  $\Delta_f^{\circ}H_m^{\circ}(T_{\text{av}})$  with two different methods at two different  $T_{\text{av}}$ . In the current work, we deliberately measured for each IL under study the enthalpies of vaporization  $\Delta_f^{\circ}H_m^{\circ}(T_{\text{av}})$  (column 3, Table 1) using QCM and TGA at two significantly different average temperatures  $T_{\text{av}}$ . Hence, we need only to rewrite eq 3 as follows:

$$\Delta_f^{\circ}C_{\text{pm}}^{\circ} = \frac{(\Delta_f^{\circ}H_m^{\circ}(T_{\text{av}})_{\text{QCM}} - \Delta_f^{\circ}H_m^{\circ}(T_{\text{av}})_{\text{TGA}})}{[(T_{\text{av}})_{\text{QCM}} - (T_{\text{av}})_{\text{TGA}}]} \quad (7)$$

in order to obtain the experimental differences between heat capacities  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  indirectly. These values for the  $[C_n\text{mim}][\text{NTf}_2]$  series calculated with eq 7 are given in Table 3.

It is apparent from Table 3 (column 3) that  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values estimated from eq 7 are definitely chain length dependent. They are also quite different from the “acknowledged” constant value  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$  used by most of the community.<sup>37</sup> For the calculation according to eq 7, we have deliberately used only our own  $\Delta_f^{\circ}H_m^{\circ}(T_{\text{av}})$  data; however, the  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values derived according to eq 7 using all available data collected for  $[C_n\text{mim}][\text{NTf}_2]$  in Table S1 (SI) are indistinguishable within the boundaries of their uncertainties (see Table S1, column 4 and 5). The latter fact serves as good evidence that the simple  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  procedure designed in the current study is correct, because the assessed resulting  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values are independent of the experimental method. It is quite surprising that the level of absolute  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values for the initial representatives of the  $[C_n\text{mim}][\text{NTf}_2]$  family were significantly lower than the “expected” value of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ . For the sake of comparison, we have also calculated  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  for the similarly shaped linear alkanols  $C_n\text{H}_{2n+1}\text{OH}$  with  $n = 1–14$  (see Table S3 column 4). Once again, we were very surprised that the absolute values of  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  as well as the general trends with increasing chain length are very close for ILs and the polar molecular compounds like linear alkanols (see Table S3 column 4).

Being simultaneously surprised and confused with the general level of the heat capacity difference  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  for ILs, it became apparent that at least one additional approach is required to assess this difference independently from the



**Table 3.** Heat Capacity Differences between Liquid and Gas Phases for  $[C_n\text{mim}][\text{NTf}_2]$  and Heat Capacities for Liquid  $[C_n\text{mim}][\text{NTf}_2]$  in  $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ 

$[C_n\text{mim}][\text{NTf}_2]$	$C_{\text{pm}}^{\circ}(\text{l})$ (298 K) <sup>a</sup>	$\Delta_f^{\circ}C_{\text{pm}}^{\circ}(T_{\text{av}})^b$	$\Delta_f^{\circ}C_{\text{pm}}^{\circ}(298\text{ K})^c$	$C_{\text{pm}}^{\circ}(\text{g})$ (298 K) <sup>d</sup>	$\Delta_f^{\circ}C_{\text{pm}}^{\circ}(298\text{ K})^e$
1	2	3	4	5	6
$[C_1\text{mim}][\text{NTf}_2]$	473.9	$-73 \pm 9$		348.1	-125.8
$[C_2\text{mim}][\text{NTf}_2]$	506.3	$-56 \pm 13$	-85	368.6	-137.7
$[C_3\text{mim}][\text{NTf}_2]$	536.4	$-76 \pm 17$	-73	389.2	-147.2
$[C_4\text{mim}][\text{NTf}_2]$	565.4	$-67 \pm 11$	-88	409.6	-155.8
$[C_5\text{mim}][\text{NTf}_2]$	598.9	$-96 \pm 12$	-89	429.8	-169.1
$[C_6\text{mim}][\text{NTf}_2]$	631.4	$-86 \pm 13$	-95	450.2	-181.2
$[C_7\text{mim}][\text{NTf}_2]$	661.4	$-114 \pm 13$	-113	470.6	-190.8
$[C_8\text{mim}][\text{NTf}_2]$	692.6	$-92 \pm 9$	-124	491.2	-201.4
$[C_{10}\text{mim}][\text{NTf}_2]$	755.2	$-136 \pm 11$		511.6	-243.6
$[C_{12}\text{mim}][\text{NTf}_2]$	817.6	$-167 \pm 12$		532.0	-285.6
$[C_{14}\text{mim}][\text{NTf}_2]$	885.9	$-161 \pm 11$		552.4	-333.5
$[C_{16}\text{mim}][\text{NTf}_2]$	942.6	$-170 \pm 15$		572.8	-369.8
$[C_{18}\text{mim}][\text{NTf}_2]$	1005.1	$-157 \pm 11$		593.2	-411.9

<sup>a</sup>The evaluated experimental data<sup>44</sup> were approximated with the linear regression:  $C_{\text{pm}}^{\circ}(\text{l}, 298\text{ K}) = 31.7n + 440.5$  (with  $r^2 = 0.999$ ) and the missing  $C_{\text{pm}}^{\circ}(\text{l}, 298\text{ K})$  were estimated by interpolation and extrapolation. <sup>b</sup>Calculated using eq 7 from QCM and TGA data measured in this work (uncertainty is estimated according to the following equation  $\Delta\Delta_f^{\circ}C_{\text{pm}}^{\circ} = [(\Delta_f^{\circ}H_m^{\circ}(\text{TGA}))^2 + (\Delta_f^{\circ}H_m^{\circ}(\text{QCM}))^2]^{1/2}/[(T_{\text{av}}(\text{TGA}) - (T_{\text{av}}(\text{QCM}))]$ ). <sup>c</sup>Estimated from  $C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ}$  difference (see text). <sup>d</sup>Calculated in ref 45 using DFT at the B3LYP/6-311+G(d,p) level. Values of  $C_{\text{pm}}^{\circ}(\text{g}, 298\text{ K})$  were estimated in ref 45 with B3LYP/6-311+G(d,p), and these values were approximated in this work with the linear regression:  $C_{\text{pm}}^{\circ}(\text{g}, 298\text{ K}) = 20.4n + 327.8$  (with  $r^2 = 0.9999$ ) and the missing  $C_{\text{pm}}^{\circ}(\text{g}, 298\text{ K})$  for  $n = 10-18$  were estimated by interpolation and extrapolation. <sup>e</sup>Difference (column 5 - column 2).

experimental procedure designed above. For this purpose, we decided to use the basics of statistical thermodynamics where the heat capacities of liquid and gaseous phases can be assessed as a sum of translational, rotational, and vibrational contributions. The isobaric and the isochoric heat capacities of both phases are usually expressed with the following equations:

$$C_{\text{pm}}^{\circ}(\text{l}) = C_{\text{vm}}^{\circ}(\text{transl}, \text{l}) + C_{\text{vm}}^{\circ}(\text{rot}, \text{l}) + C_{\text{vm}}^{\circ}(\text{vib}, \text{l}) + C_{\text{vm}}^{\circ}(\text{conf}, \text{l}) + (C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{l}} \quad (8)$$

$$C_{\text{pm}}^{\circ}(\text{g}) = C_{\text{vm}}^{\circ}(\text{transl}, \text{g}) + C_{\text{vm}}^{\circ}(\text{rot}, \text{g}) + C_{\text{vm}}^{\circ}(\text{vib}, \text{g}) + C_{\text{vm}}^{\circ}(\text{conf}, \text{g}) + (C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{g}} \quad (9)$$

where the contribution  $C_{\text{vm}}^{\circ}(\text{conf})$  is responsible for the equilibrium mixture of conformers. Assuming the equality of the vibrational contributions into the heat capacity of the liquid and the gaseous phase, as well as the similarity for mixtures of

conformers at equilibrium in these phases, the heat capacity difference was expressed as follows:

$$\Delta_f^{\circ}C_{\text{pm}}^{\circ} = C_{\text{vm}}^{\circ}(\text{transl}, \text{g}) + C_{\text{vm}}^{\circ}(\text{rot}, \text{g}) + (C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{g}} - C_{\text{vm}}^{\circ}(\text{transl}, \text{l}) - C_{\text{vm}}^{\circ}(\text{rot}, \text{l}) - (C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{l}} \quad (10)$$

From common rules of statistical thermodynamics, a sum of contributions for the free rotation and the free translational motion of a molecule into the ideal gas heat capacity can be assigned to be equal to  $3R$ . From the oscillation theory,<sup>46</sup> the free rotation or linear motion of a molecule in the condensed state is converted into the low frequency vibrations. The contribution of vibrations at low frequencies into the heat capacity is equal to  $R$  for each degree of freedom: all together,  $6R$  for the sum of rotational and translational contributions. Assuming that for the ideal gas the relation  $(C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{g}} = R$  is valid, we can simplify eq 10 to

$$\Delta_f^{\circ}C_{\text{pm}}^{\circ} = -2R - (C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{l}} \quad (11)$$

It is obvious from eq 11 that the contribution  $(C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{l}}$  is the main part of the heat capacity difference  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$ . It has turned out that this contribution can be easily estimated from the volumetric properties according to following equation:<sup>47</sup>

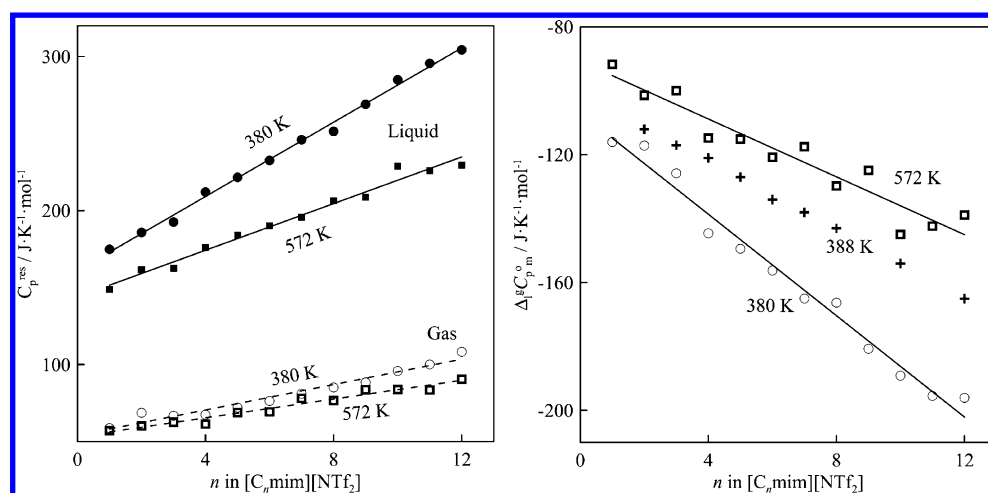
$$(C_{\text{pm}}^{\circ} - C_{\text{vm}}^{\circ})_{\text{l}} = \frac{\alpha_p^2}{\kappa_T} V_m T \quad (12)$$

where  $\alpha_p$  is the thermal expansion coefficient,  $\text{K}^{-1}$ ;  $\kappa_T$  is the isothermal compressibility,  $\text{Pa}^{-1}$ . The molar volume  $V_m$  as well as the thermal expansion coefficient  $\alpha_p$  are usually determined from the temperature dependence of the density of liquid. The compressibilities  $\kappa_T$  can be calculated from the pressure dependence of density in the isothermal conditions. Compressibilities are more often derived from the speed of sound  $W(T, P)$  measurements as follows:

$$\kappa_T = \frac{1}{\rho} \left( \frac{1}{W^2} + \frac{T\alpha_p^2 M}{C_{\text{pm}}^{\circ}} \right) \quad (13)$$

where  $\rho$  is the density of an IL ( $\text{kg}\cdot\text{m}^{-3}$ ) and  $M$  is the molar mass ( $\text{kg}\cdot\text{mol}^{-1}$ ). We collected the volumetric properties and the speed of sound data for the  $[C_n\text{mim}][\text{NTf}_2]$  series from the ILthermo database<sup>48</sup> (see Table S5, SI). The resulting heat capacity differences  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  derived from the volumetric properties are given in Table 3, column 4. Comparison of the  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  values derived from the QCM and TGA experiments (Table 3 column 3) with those from the volumetric properties (Table 3 column 4) have shown that these results are hardly distinguishable for the homologous series of  $[C_n\text{mim}][\text{NTf}_2]$  ILs. Thus two independent procedures have ascertained the level of the  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  differences for the ILs under study, and both procedures could be recommended for the practical estimations required for temperature adjustment of experimental vaporization enthalpies. Importantly, both procedures suggest that  $\Delta_f^{\circ}C_{\text{pm}}^{\circ}$  is dependent on the chain length of the cation.

In order to gain more insight in this problem, it is useful to analyze separately the heat capacities  $C_{\text{pm}}^{\circ}(\text{g})$  and  $C_{\text{pm}}^{\circ}(\text{l})$  for the  $[C_n\text{mim}][\text{NTf}_2]$  series. The experimental values for  $C_{\text{pm}}^{\circ}(\text{l}, 298\text{ K})$  have been critically evaluated just recently.<sup>44</sup> We report the recommended values in Table 3, column 2. It turns out that the evaluated experimental data<sup>44</sup> (for  $n = 2, 4, 6, 8$ , and  $14$ ) fit very well to the linear chain length dependence. They were



**Figure 8.** Residual heat capacities of the liquid and gas phase obtained from MD simulations (left) and computed  $\Delta_f^o C_{p,m}^o$  (right) as a function of cation alkyl chain length.

approximated with a linear regression (see Table 3, footnote a), and the missing  $C_{p,m}^o(l, 298\text{ K})$  for the  $[C_n\text{mim}][\text{NTf}_2]$  were estimated by interpolation and extrapolation (see Table 3, column 2). As has been already pointed out, available experimental methods are unable to measure  $C_{p,m}^o(g, 298\text{ K})$  for ILs. Therefore we have calculated these values for the  $[C_n\text{mim}][\text{NTf}_2]$  family using DFT at the B3LYP/6-311+G-(d,p) level (see Table 3, column 5). The differences between the gaseous heat capacities (from DFT) and the liquid heat capacities (from experiment) are given in Table 3 (column 6). These differences follow the already expected increasing trend with the increasing chain length, but the absolute values are about twice as large as those obtained from our experimental findings from TGA and QCM methods (Table 3, column 3). In order to better understand this discrepancy, we also calculated the  $\Delta_f^o C_{p,m}^o$  values for the ILs  $[C_n\text{mim}][\text{NTf}_2]$  using MD simulation. The results are given in Figure 8 and in Table S4. It is interesting that the results of the MD simulations are in a good agreement with those obtained from the DFT calculations (Table 3, column 6), but disagree with the experimental values (Table 3, column 3). The  $\Delta_f^o C_{p,m}^o$  values from experiment and MD are deliberately referred to the similar temperatures, but, to our surprise, the MD absolute values for  $\Delta_f^o C_{p,m}^o$  are about twice as large as the experimental values.

A search of the literature has revealed that Ködermann et al.<sup>39</sup> also reported the overall linear decrease of  $\Delta_f^o H_m^o(T_{av})$  for  $[C_2\text{mim}][\text{NTf}_2]$  from 132 kJ·mol<sup>-1</sup> to 111 kJ·mol<sup>-1</sup> over the temperature range of 273–473 K. From their MD simulations, a value of  $\Delta_f^o C_{p,m}^o = -108\text{ J·K}^{-1}\cdot\text{mol}^{-1}$  can be obtained, which is in agreement with our MD values (see Figure 8).

We are reticent now to give any reasonable explanation for the significant difference between experimental and theoretical  $\Delta_f^o C_{p,m}^o$  values. For the DFT calculations, the disagreement could be attributed to the simple rigid rotor-harmonic oscillator approximation used in the first principles calculations of the  $C_{p,m}^o(g, 298\text{ K})$ . Unfortunately, the size of the ILs under study in the current work is too large to make calculations without this approximation. However, it should be mentioned that there is no rigid rotor approximation in MD. Thus the currently observed disagreement of the absolute experimental and theoretical  $\Delta_f^o C_{p,m}^o$  values merits further extended investigation. In spite of this fact, the general trends regarding  $\Delta_f^o C_{p,m}^o$  from the experiment and MD simulations are very similar, and they

allow one to make recommendations on how to adjust vaporization enthalpies to the reference temperature properly. Clearly, the use of a constant value for  $\Delta_f^o C_{p,m}^o$  is not recommended, as all the procedures show that there is a strong dependence on chain length.

Taking into account that the experimental data on  $C_{p,m}^o(l, 298\text{ K})$  for the  $[C_n\text{mim}][\text{NTf}_2]$  are quite reliable, it seems to be reasonable to develop an empirical correlation between the experimental  $C_{p,m}^o(l, 298\text{ K})$  and the experimental  $\Delta_f^o C_{p,m}^o$ . It turns out that a simple linear correlation:

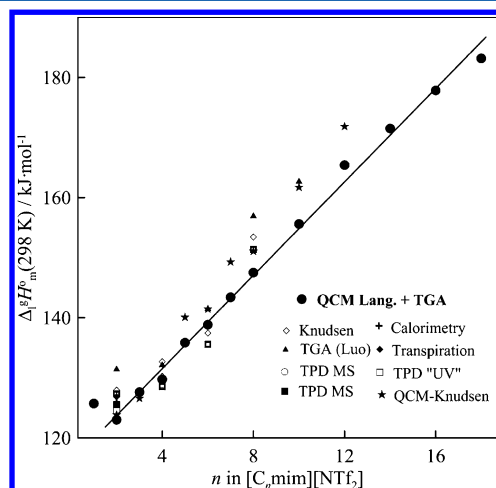
$$\Delta_f^o C_{p,m}^o = C_{p,m}^o(l, 298\text{ K})(-0.26 \pm 0.05) + (68.7 \pm 37.0) \quad (14)$$

with  $r^2 = 0.950$

can be derived using our own QCM and TGA data (except for  $n = 1, 12$ , and 18) and the literature  $C_{p,m}^o(l, 298\text{ K})$  data, which are given in Table 3 (column 2), which will be very useful for quick appraisal of  $\Delta_f^o C_{p,m}^o$  for the  $[C_n\text{mim}][\text{NTf}_2]$  series with any chain length. The correlation according to eq 14 is adjusted now for the  $[C_n\text{mim}][\text{NTf}_2]$  series, but we would recommend applying this simple correlation for other ILs instead of using the conventional constant  $\Delta_f^o C_{p,m}^o = -100\text{ J·K}^{-1}\cdot\text{mol}^{-1}$ . We are conscious that the coefficients in eq 14 could vary depending on the particular class of IL under study (e.g., pyridinium, pyrrolidinium, or ammonium based ILs), but we expect that the fluctuations of these coefficients should be not too large. At the current state of our knowledge, eq 14 seems to be of a crucial importance because it helps to avoid ambiguity of the  $\Delta_f^o C_{p,m}^o$  values commonly used nowadays in the literature, taking into account at least the chain-length dependence. Equation 14 is easy to apply because the  $C_{p,m}^o(l, 298\text{ K})$  of ILs are easily measured using the commercially available DSC (differential scanning calorimeters), which are commonly found in modern IL laboratories. Moreover, the  $C_{p,m}^o(l, 298\text{ K})$  values required for eq 14 could be also predicted with a reasonable accuracy<sup>49</sup> as a function  $C_{p,m}^o(l, 298\text{ K}) = f(V_m)$  of the molar volume  $V_m$ . This simple empirical correlation was shown to be reliable within 3% (or  $\pm 16\text{ J·K}^{-1}\cdot\text{mol}^{-1}$ ).<sup>49</sup> The molar volume  $V_m$  values are usually obtained from the densities of ILs, which are routinely determined as a part of a physical-chemical attestation of new ILs. Thus, use of eq 14 for temperature adjustment of vapor pressure measurements opens a new way for comparison and validation of experimental results measured by different

techniques and could significantly contribute to the development and refinement of experimental methods dealing with ILs.

In order to demonstrate the advantage of using eq 14 and  $\Delta_f^\circ C_{pm}$  values derived in this work, we have adjusted experimental results for the  $[C_n\text{mim}][\text{NTf}_2]$  series measured by all available methods from  $T_{av}$  to the reference temperature 298 K. The resulting plot is given in Figure 9. In contrast to the



**Figure 9.** The experimental  $\Delta_f^\circ H_m(298\text{ K})$  adjusted with  $\Delta_f^\circ C_{pm}$  from Table 3, column 3.

“Milky Way” discussed at the beginning of this paper and presented in Figure 1, it is now quite obvious that there is a simple linear dependence of the vaporization enthalpy on the chain length. Certainly, some scatter of the  $\Delta_f^\circ H_m(298\text{ K})$  data still remains, but in our opinion this scatter is rather the evidence of the challenging task to measure the vapor pressure and the vaporization enthalpy of extremely heavy, low volatility ILs. The outlying values of  $\Delta_f^\circ H_m(298\text{ K})$  obtained from TGA<sup>5</sup> and a high-temperature spectroscopic technique<sup>8</sup> could be an indicator that these methods still require further development. We also deliberately omitted from Figure 9 the calorimetric data measured by drop microcalorimetry<sup>13</sup> for  $[C_n\text{mim}][\text{NTf}_2]$ , due to a systematic error discussed elsewhere.<sup>7</sup> It is very disheartening that the data for  $C_{10}$  and  $C_{12}$  measured<sup>10</sup> with the very good QCM-Knudsen method are significantly out of the linear correlation apparent on Figure 9. However, a careful analysis of the primary experimental data of this work has revealed that both ILs were measured in a very narrow (about 15 K, see Table S1) temperature range. From our experiences, a larger range of about 30–50 K is necessary to provide a reliable slope and  $\Delta_f^\circ H_m(T_{av})$ . Thus, the proper adjustment of vaporization enthalpies to 298 K using simple empirical rules developed in the current study has converted the mess of experimental points available in the literature (see Figure 1) into the logical structure–property dependence presented in Figure 9. In this context, it is also important to point out that enthalpies of vaporization for the  $[C_n\text{mim}][\text{NTf}_2]$  family with odd and even chain length of the alkyl-imidazolium cation fit the same straight line, and it is obvious that  $\Delta_f^\circ H_m(298\text{ K})$  of ILs follows the same pattern as the molecular liquids, where the odd and even effect was observed for such thermodynamic properties as melting point, fusion, or sublimation enthalpy but not for vaporization enthalpy.<sup>50</sup>

**Is there any Difference Between ILs and Molecular Liquids?  $\text{CH}_2$ -Increment.** Group-additivity procedures for

prediction of thermodynamic properties of molecular liquids are well established.<sup>50,51</sup> In our recent studies we have tried to establish whether the thermodynamic properties such as enthalpy of vaporization and enthalpies of formation of ILs obey the group additivity rules.<sup>51</sup> This knowledge could simplify reliable predictions for ILs, provided that a general transfer of the group contributions established for the molecular compounds to the ILs is valid. A most simple manifestation of additive rules is the correlation of any property, e.g., the enthalpy of vaporization, with the number of C-atoms. This correlation in the series of homologues is additionally a valuable test to check the internal consistency of the experimental results. Using the QCM and TGA results obtained in our work, the dependence of vaporization enthalpy on the number of C-atoms,  $n$ , in the alkyl chain of the imidazolium cation follows the equation

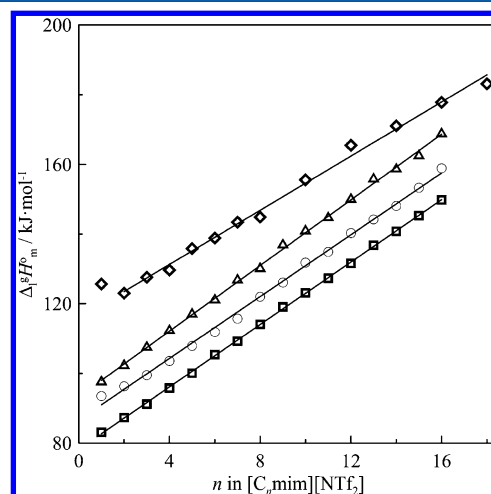
$$\Delta_f^\circ H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 115.7 + 3.89n$$

from experiment (with  $r^2 = 0.995$ ) (15)

$$\Delta_f^\circ H_m(298\text{ K})/\text{kJ}\cdot\text{mol}^{-1} = 124.8 + 3.65n$$

from MD (with  $r^2 = 0.997$ ) (MD) (16)

from which the enthalpy of vaporization  $\Delta_f^\circ H_m(298\text{ K})$  of other representatives in this series with different  $n$  can be calculated. For comparison, we present the  $\Delta_f^\circ H_m(298\text{ K})$  chain length dependence for some molecular homologous series together with the results for the ILs  $[C_n\text{mim}][\text{NTf}_2]$  in Figure 10. It is



**Figure 10.** The enthalpies of vaporization for 1-alkyl-3-methylimidazolium bis(trifluoromethanesulfonyl)imides, alkyl benzenes, alkyl nitriles, and alcohols at 298 K. ( $\diamond$ )  $[C_n\text{mim}][\text{NTf}_2]$  (joined treatment of the QCM and TGA results from this work); ( $\Delta$ )  $n$ -alcohols (for comparison with ILs, the data were shifted by  $60\text{ kJ}\cdot\text{mol}^{-1}$ ); ( $\circ$ )  $n$ -alkyl nitriles (for comparison with ILs, the data were shifted by  $60\text{ kJ}\cdot\text{mol}^{-1}$ ); ( $\square$ )  $n$ -alkyl benzenes (for comparison with ILs, the data were shifted by  $45\text{ kJ}\cdot\text{mol}^{-1}$ ).

apparent from this figure that the intercepts for the different families are totally different, and we have even scaled them in order to fit them on the same plot. However, all the slopes presented in Figure 10 seem to be similar, and they generally represent the contribution of the  $\text{CH}_2$ -group to the vaporization enthalpy  $\Delta_f^\circ H_m(298\text{ K})$ . We calculated and collected the appropriate numbers in Table 4 for comparison.

**Table 4.** The Values of the CH<sub>2</sub> Group Increment into the Enthalpy of Vaporization for the Different Classes of Molecular and Ionic Compounds

compound	CH <sub>2</sub> increment, kJ·mol <sup>-1</sup>	refs
[C <sub>n</sub> mim][NTf <sub>2</sub> ]	3.89 ± 0.20 3.65	this work (exp) this work (MD)
C <sub>n</sub> H <sub>2n+1</sub> CN	4.44 ± 0.12	52
C <sub>n</sub> H <sub>2n+1</sub> OH	4.71 ± 0.08	53
C <sub>n</sub> H <sub>2n+1</sub> C <sub>6</sub> H <sub>5</sub>	4.48 ± 0.04	54
C <sub>n</sub> H <sub>2n+2</sub>	4.95	14
CH <sub>2</sub> =CH-C <sub>n</sub> H <sub>2n+1</sub>	4.97	14
HS-C <sub>n</sub> H <sub>2n+1</sub>	4.76	14
Cl-C <sub>n</sub> H <sub>2n+1</sub>	4.85	14
Br-C <sub>n</sub> H <sub>2n+1</sub>	4.80	14
C <sub>n</sub> H <sub>2n+1</sub> CO <sub>2</sub> -CH <sub>3</sub>	5.03	14

According to the data given in Table 4, most of the homologous series exhibit CH<sub>2</sub> group contribution to the vaporization enthalpy very close around 5.0 kJ·mol<sup>-1</sup>. However, a somewhat lower contribution of 4.5 kJ·mol<sup>-1</sup> is also observed for *n*-alkylbenzenes and for *n*-alkyl-nitriles. This seems to be a consequence of high dipole–dipole interactions in these molecular liquids. Probably, the intensive Coulomb forces specific for ILs also have a consequence in decreasing the CH<sub>2</sub> group contribution to 3.9 kJ·mol<sup>-1</sup> for the ILs under study (3.7 kJ mol<sup>-1</sup> for the MD simulations). It is important to note that, in spite of the obviously small difference of about 1 kJ·mol<sup>-1</sup> between CH<sub>2</sub> contributions in *n*-alkanes and in ILs, this CH<sub>2</sub> contribution was determined very precisely (±0.2 kJ·mol<sup>-1</sup>), and this value will significantly contribute to the reliable predictions especially for the long chained imidazolium, ammonium, pyridinium, pyrrolidinium, or phosphonium-based ILs. The specific value for the CH<sub>2</sub> contribution in ILs is the clear evidence that the additivity rules are generally valid for ILs, but the additive contributions become unique in comparison to the well-established group-contributions developed for the molecular liquids.

Having established the CH<sub>2</sub> contribution to Δ<sup>‡</sup>H<sub>m</sub><sup>o</sup>(298 K) in ILs from experiment, it is also interesting to compare how different MD procedures are able to obtain this value. Köddermann et al.,<sup>39</sup> using a different force field, developed in their group having integer partial charges on the ions calculated at 298 K an increase of about 4.7 kJ·mol<sup>-1</sup> per CH<sub>2</sub> group in the [C<sub>n</sub>mim][NTf<sub>2</sub>], which exactly coincides with the increase in the enthalpy of vaporization for *n*-alkanols but is in disagreement with our MD results. The MD simulations of the present study find that the increment is 3.7 kJ·mol<sup>-1</sup>, which is in quite good agreement with our current experiments.

Finally, it is interesting to note that the enthalpy of vaporization of the first representative of the series [C<sub>1</sub>mim][NTf<sub>2</sub>] deviates slightly from the linear correlation. However, starting with [C<sub>2</sub>mim][NTf<sub>2</sub>], the Δ<sup>‡</sup>H<sub>m</sub><sup>o</sup> correlation holds for all other values of *n* (see Figure 10). This outlier could be understood by the competition of the corresponding Coulomb and van der Waals interactions in the comparably small [C<sub>1</sub>mim][NTf<sub>2</sub>]. According to the MD simulations, the Coulomb energy for [C<sub>1</sub>mim][NTf<sub>2</sub>] is slightly higher than that for other ILs in the series (by about 4.5 kJ·mol<sup>-1</sup>), and it is this contribution that results in the larger enthalpy of vaporization than would be expected. This effect can be also attributed to the symmetry of the cation and a specific structuring of the bulk liquid due to this symmetry as well as due to the delicate

balance of Coulomb and van der Waals interactions, which impacts the enthalpy of vaporization for [C<sub>1</sub>mim][NTf<sub>2</sub>]. This finding is also in agreement with the MD-simulation studies of the [C<sub>n</sub>mim][NTf<sub>2</sub>] series by Köddermann et al.<sup>39</sup> and also in this work. It is important to note for further development of the additivity rules<sup>51</sup> for ILs that the aforementioned competition of the Coulomb and van der Waals interactions in [C<sub>1</sub>mim][NTf<sub>2</sub>] seems to be completed for [C<sub>2</sub>mim][NTf<sub>2</sub>], and this compound could be already considered as the “regular” representative of the family with the constant CH<sub>2</sub>-contribution.

## CONCLUSIONS

Our new experimental results based on the concurring results from QCM and TGA methods have revealed, in contrast with the available literature data, the definite linear dependence of the vaporization enthalpies on the chain length. Ambiguity of the Δ<sup>‡</sup>C<sub>pm</sub> values required for temperature adjustments of vaporization enthalpies was resolved, and a simple method based on the experimental liquid heat capacities has been suggested. We have shown that enthalpies of vaporization generally obey group additivity; however, the values of the additivity parameters for ILs are different from those for molecular compounds. The results of MD simulations generally agree with the experiments and, although evidence is found in the simulations to support the formation of nonpolar domains of aggregation for cations having longer alkyl chain lengths, this aggregation does not appear to change the slope of the enthalpy of vaporization versus chain length.

## ASSOCIATED CONTENT

### Supporting Information

Experimental details and data evaluation procedure. This material is available free of charge via the Internet at <http://pubs.acs.org>

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### Notes

The authors declare no competing financial interest.

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