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Imidazolium Based Ionic Liquids: Impact of the Cation Symmetry and Alkyl Chain Length on the Enthalpy of Vaporization

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Abstract. The vaporization thermodynamics of symmetric imidazolium based ionic liquids of the general formula $[C_nC_nIm][Br]$ with the chains length $n = 4, 5, 6,$ and 8 were investigated using a combination of DSC, TGA and QCM methods with quantum chemical calculations. Comparison of vaporization enthalpies for the symmetric ($[C_nC_nIm][Br]$) and asymmetric imidazolium based ILs ($[C_nmim][Br]$) revealed a general trend with the lower vaporization enthalpies of the symmetric species indicating a significant decrease of the Coulombic interactions affecting energetics of vaporisation.

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1. Introduction

Ionic liquids (IL) as neoteric solvents exhibit unique properties which make them suitable for replacement of common media for diverse chemical reactions as well as for materials production. Application of ILs instead of common solvents have been demonstrated to be especially effective for the synthesis of nanoparticles. For example, by fabrication of highly efficient thermoelectric materials based on Sb_2Te_3 nanoparticles, the alkyimidazolium bromide IL served a threefold purpose: it acted as the solvent and nanoparticle stabilizer as well as the heat-transfer medium.^[1] In addition, transition-metal-nanoparticles (Fe or Ag) can be stabilized by the ionic charge, high polarity, high dielectric constant and supramolecular network.^[2] The lack of volatility of ILs at ambient temperature and good thermal stability at elevated temperatures has been also considered as a prerequisite for successful practical applications of ILs. Moreover, the possibility of distilling a number of pure aprotic ILs has been demonstrated by Earle *et al.*^[3] and this feature of ILs could be useful for separation of nanoparticles from IL-solvent. In this context, an understanding of volatility, thermal stability and vaporization thermodynamics at the molecular level, leading to reliable prediction of ILs thermochemical properties, seem to be both of practical and theoretical interest.

The thermodynamics of vaporization of alkyimidazolium ionic liquids containing bromine-anion are in the focus of the current study. These ILs have been successfully used for the synthesis of thermoelectric materials based on Sb_2Te_3 nanoparticles.^[1] The structure-property relationships and standard molar vaporization enthalpies $\Delta_{\text{v}}^{\text{g}}H_m^{\circ}$ (298 K) chain length dependence of ILs with the Br^- anion and the asymmetric 1-alkyl-3-methyl-imidazolium cation $[\text{C}_n\text{mim}]^+$ were reported recently.^[4,5] Aiming at the evaluation of the impact of the cation symmetry on the vaporization thermodynamics, in this work, ILs containing the symmetric 1,3-alkylated imidazolium cation $[\text{C}_n\text{C}_n\text{Im}]^+$ (with the chain length $n = 4, 5, 6,$ and 8) have been studied. Rocha *et al.*^[6] observed that the IL family with the symmetric cation $[\text{C}_n\text{C}_n\text{im}][\text{NTf}_2]$ have the linear trend in the $\Delta_{\text{v}}^{\text{g}}H_m^{\circ}$ (298 K) - alkyl-chain length (n) dependence shifted in comparison to those linear trend observed for the asymmetric series $[\text{C}_n\text{mim}][\text{NTf}_2]$. This difference could be an evidence for unusual interplay between van der Waals and Coulomb interactions in such type of symmetric ILs. In the current work we intend to evaluate the impact of the cation symmetry on the vaporization enthalpy in ILs with the bromine anion.

2. Experimental Section

2.1 Materials and Chemicals

1-Alkyl-imidazoles (1-butylimidazole, 1-C₄Im, 1-pentylimidazole, 1-C₅Im, 1-octylimidazole, 1-C₈Im) and alkyl bromides (C_nBr with $n = 4, 5,$ and 8) were commercially available with purity \geq

99%. No impurities (greater than 0.1 mass per cent) could be detected in the samples for the DSC experiments using a gas chromatograph equipped with a flame ionization detector. All precursors were freshly distilled before use. Samples of the ionic liquids *1,3-dibutyl-imidazolium bromide* [C₄C₄Im][Br], *1,3-dihexyl-imidazolium bromide* [C₆C₆Im][Br], and *1,3-dioctyl-imidazolium bromide* [C₈C₈Im][Br] were freshly prepared and characterized as follows.

1,3-Dibutyl-imidazolium bromide [C₄C₄Im][Br]. A mixture of 1-butylimidazole (10 g, 80.6 mmol) and 1-bromobutane (22.08 g, 16.1 mmol) in 70 mL of acetonitrile was heated to reflux for four days. After evaporation of the solvent a yellowish liquid was obtained. For purification, activated carbon was added and the mixture was stirred overnight at room temperature. After filtration over an Al₂O₃/celite column, the solvent was removed in vacuum. The product was dried in vacuo at 50 °C for 24h and was obtained as a colorless highly viscous liquid (20.09 g, 77.2 mmol, 95.45%) at room temperature. ¹H-NMR (200 MHz, DMSO-d₆): δ 10.39 (s, C¹H, 1H), 7.50 (s, C²H, 2H), 4.28 (t, ³J_{HH} = 7.3 Hz, C³H₂, 4H), 1.79-1.93 (m, ³J_{HH} = 10.4 Hz, C⁴H₂, 4H), 1.23-1.34 (m, ³J_{HH} = 7.5 Hz, C⁵H₂, 4H), 0.86 (s, C⁶H₃, 6H). ¹³C NMR (50 MHz, DMSO-d₆): 136.0 (C¹), 122.4 (C²), 48.5 (C³), 31.3 (C⁴), 18.7 (C⁵), 13.3 (C⁶). MS (FAB): m/z = 181.2 (100 %, C₁₁H₂₁N₂⁺), 441.2 (87 %, C₂₂H₄₂N₄²⁺ - Br⁻). Elemental analysis calcd (%) for C₁₁H₂₁BrN₂: C 50.58, H 8.10, N 10.72; found: C 50.03, H 9.67, N 10.68.

1,3-Dihexyl-imidazolium bromide[C₆C₆Im][Br]. 1,3-Dihexyl-imidazolium bromide was synthesized from 1-hexylimidazole (10 g, 65.7 mmol) and (21.70 g, 13.1 mmol) 1-bromohexane in 50 mL of acetonitrile with the same procedure as described for C₄C₄ImBr. The product was obtained as a colorless highly viscous liquid (12.40 g, 39.2 mmol, 59.48 %). Product was liquid at room temperature. ¹H-NMR (200 MHz, DMSO-d₆): δ 10.27 (s, C¹H, 1H), 7.46 (s, C²H, 2H), 4.27 (t, ³J_{HH} = 7.4 Hz, C³H₂, 4H), 2.02 – 1.58 (m, C⁴H₂, 4H), 1.22 (m, ³J_{HH} = 7.5 Hz, C⁵⁻⁷H₂, 12H), 0.77 (s, C⁸H₃, 6H). ¹³C NMR (50 MHz, DMSO-d₆): 136.0 (C¹), 122.5 (C²), 48.8 (C³), 30.5 (C⁴), 29.2 (C⁵), 25.1 (C⁶), 21.9 (C⁷), 13.8 (C⁸). MS (FAB⁺): m/z = 237.2 (100 %, C₁₅H₂₉N₂⁺), 553.3 (67 %, C₃₀H₅₈N₄²⁺ - Br⁻). Elemental analysis calcd (%) for C₁₅H₂₉BrN₂: C 56.78, H 9.21, N 8.83; found: C 56.47, H 11.71, N 8.85.

1,3-Dioctyl-imidazolium bromide[C₈C₈Im][Br]. A mixture of 1-octylimidazole (10 g, 55.5 mmol) and 1-bromooctane (21.44 g, 11.1 mmol) in 50 mL of acetonitrile was heated to reflux for four days. After evaporation of the solvent a yellowish liquid was obtained.

For purification, activated carbon was added and the mixture was stirred overnight at room temperature. After filtration over an Al₂O₃/celite column, the solvent was removed in vacuum. The product was dried in vacuo at 50 °C for 24h and was obtained as a colorless highly viscous liquid (19.45 g, 52.3 mmol, 94 %) at room temperature. ¹H NMR (200 MHz, DMSO-d₆): δ 9.33 (s, C¹H, 1H), 7.83 (s, C²H, 2H), 4.17 (t, ³J_{HH} = 7.1 Hz, C³H₂, 4H), 1.90 – 1.65 (m, C⁴H₂, 4H), 1.42 – 0.98 (m, C⁵⁻⁹H₂, 20H), 0.84 (s, C¹⁰H₃, 6H). ¹³C NMR (50 MHz, DMSO-d₆): δ 136.00 (C¹), 122.4 (C²), 48.8 (C³), 31.1 (C⁴), 29.3 (C⁵), 28.5 (C⁶), 28.3 (C⁷), 25.4 (C⁸), 22.0 (C⁹), 13.9 (C¹⁰). MS (FAB⁺): m/z = 293.3 (100 %, C₁₉H₃₇N₂⁺), 665.5 (70 %, C₃₈H₇₄N₄²⁺ - Br⁻), Elemental analysis calcd (%) for C₁₉H₃₇BrN₂: C 61.11, H 9.99, N 7.50; found: C 60.73, H 11.76, N 7.93.

IL samples prior thermochemical experiments were kept at 333 K in vacuum for more than 24 hours in order to remove possible traces of solvents and moisture prior to thermochemical experiments.

2.2 Enthalpies of ILs Synthesis Reactions from DSC

Enthalpies of reaction were measured using the calibrated computer controlled Mettler-Toledo 822 DSC. Experimental details are described elsewhere.^[4] 10-15 mg of the precursor was placed in a 40 μL aluminum pan. In order to prevent the start of reaction outside the DSC, the pan was filled with the definite amount of the first precursor 1-alkyl-bromide, then with the layer of the solvent [C₄mim][NTf₂], and finally with the second precursor 1-alkyl-imidazole. We used some excess of 1-alkyl-imidazole (see Table 1) in order to reach complete conversion of the alkyl bromide at the end of reaction. The DSC pan was weighed with the resolution of ±0.000005 g and air buoyancy corrections were taken into account. The pan was hermetically sealed with a cover. The pan was weighed before and after each experiment to detect any mass loss during the measurements. Measurements were performed in the range of 293 K to 458 K with scanning rates of 50 K·min⁻¹. The heat released during the IL synthesis reaction was related to the molar amount of a stoichiometrically deficient reactant in the starting formulation. Experimental results of the DSC study are collected in Table 1.

2.3 Vaporization Enthalpies of ILs from TGA Measurements

We used a Perkin Elmer Pyris 6 TGA to measure enthalpies of vaporization $\Delta_1^g H_m^\circ$ from the temperature dependence of the mass loss rates measurements. The detailed experimental procedure has been elaborated in our lab and was reported previously.^[7] 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 step-wise 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 from 401 to 490 K at a nitrogen flow rate of $140 \text{ ml}\cdot\text{min}^{-1}$. The relationship between the mass loss dm/dt and the vaporization enthalpy was derived according to the Clausius-Clapeyron equation but by using the mass loss rate dm/dt measured instead of the absolute pressure (see details in the ESI). A possible decomposition of the IL in the TGA experimental conditions was controlled by ATR-IR spectroscopy of samples taken from the initial and the residual IL in the crucible. For the ILs under study the spectra of initial sample and cover condensate shows incredible difference. Experimental results of the TGA studies are collected in Table 2.

2.4 Vaporization Enthalpies of ILs from QCM Measurements

The experimental setup was constructed in our lab and developed for measuring of compounds with the extremely low vapour pressures at possibly low temperatures.^[8] An IL sample is placed in an open cavity inside of the thermostatted block and exposed to vacuum (10^{-5} Pa) with the whole open surface of the loaded compound (Langmuir evaporation). The QCM is placed directly over the measuring cavity containing the sample. During the vaporization into vacuum, a certain amount of sample is deposited on the quartz crystal. The change of the vibrational frequency Δf was directly related to the mass deposition Δm on the crystal. The vaporisation enthalpies were derived from the temperature dependences of the experimentally measured change in the vibrational frequency of the quartz crystal. The temperature dependence of the measured frequency rate (df/dt) was used to estimate the vaporization enthalpy according to the Clausius-Clapeyron equation (see details in ESI). In order to confirm the absence of decomposition of IL under the experimental conditions, the residual IL in the crucible and the IL-deposit on the QCM were analysed by ATR-IR spectroscopy. No changes in the spectra have been detected. Primary experimental results of the QCM studies are provided in Table S1 in the Supporting Information.

2.5 Quantum-Chemical Calculations

The gas-phase enthalpies of the ILs synthesis reactions were calculated using the Gaussian 09 program package.^[9] Conformations of the molecular and ionic species were optimized on the B3LYP/6-311G** level of the theory. Details on the procedure were reported elsewhere.^[10] Calculated values of the enthalpies of reaction are based on the electronic energy calculations obtained using standard procedures of statistical thermodynamics.^[11]

3. Results and Discussion

From our experience, the reliable evaluation of thermochemical data as well as a discussion of the structure-property relations can be performed, when consistent experimental values are independently measured by using several and different techniques. However, studying the vaporization thermodynamics of ILs remains a challenging task due to at least two main problems. At ambient temperatures the extremely low vapor pressures of ILs (comparable to those of iron) are practically not measurable, whereas at high temperatures some of ILs may decompose during vaporization. The decomposition products usually possess significantly higher vapor pressures in comparison to an IL. As a rule, the degree of decomposition is not clear thus the absolute vapor pressure measurement of an IL is often failed. Imidazolium based ionic liquids, containing the Br⁻ anion are known to be thermally labile.^[4] That is why it is reasonable to apply a number of complementary techniques like DSC, TGA, and QCM in order to get reliable thermodynamic data for the vaporization process of the desired bromide-containing ILs [C_nC_nIm][Br]. In our previous study,^[4] an indirect way to derive vaporization enthalpies of alkyl-imidazolium bromide via the DSC-measured enthalpies of ILs synthesis reactions, $\Delta_r H_m^\circ$, (according to eq. 1) have been established. This indirect method was used in this work to obtain enthalpies of vaporization, $\Delta_1^g H_m^\circ$ (298 K), of [C_nC_nIm][Br] for comparison with those derived from the conventional direct methods: TGA and QCM.

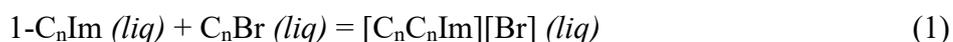
Table 1. Experimental results for measurements of reaction enthalpies, $\Delta_r H_m^\circ$ (liq), by using DSC.

Reaction	Molar ratio	Solvent % wt.	T_{\max} . K	$\Delta_r H_m^\circ$ (liq) ^a kJ mol ⁻¹
n-Butyl-Im+n-Butyl-Br	0.40	75	445±5	-101.3±1.8
n-Pentyl-Im+n-Pentyl-Br	0.44	70	438±5	-102.4±2.3
n-Octyl-Im+n-Octyl-Br	0.30	75	456±5	-100.2±2.3

^a Uncertainties are twice the standard deviations of the mean value from 5-6 individual DSC experiments.

3.1 DSC: Enthalpies for ILs Synthesis Reactions

Enthalpies of the ILs synthesis reactions, $\Delta_r H_m^\circ$ (liq.), were derived according to eq. 1



in a series of three consequent DSC runs under optimized conditions elaborated elsewhere.^[4] A sharp reaction peak with well-defined baseline was achieved in these conditions providing reproducible results. The area of the DSC peak occurring during the chemical reaction was a

measure of the reaction enthalpy. Enthalpies of reaction, $\Delta_r H_m^\circ$, derived by integration of the DSC peak are referred to the temperature of the peak maximum, T_{\max} (see Table 1). The necessary adjustment of the reaction enthalpy to the reference temperature does not exceed 0.3-0.4 kJ·mol⁻¹ and this correction is well negligible within the boundaries of the DSC experimental uncertainties of 1-3 kJ·mol⁻¹. In this work the experimental DSC values of $\Delta_r H_m^\circ$ measured at T_{\max} (see Table 1) have been assumed to be equal to those at the reference temperature 298 K.

As can be seen from Table 1 all IL synthesis reactions were strong exothermic and they hardly exhibit any chain-length dependence (at least within the boundaries of experimental uncertainties). The same trend was also observed for the asymmetric ILs [C_nmim][Br].^[4] The reaction enthalpies $\Delta_r H_m^\circ$ (liq) as derived from DSC measurements (see Table 1) can be used now in combination with the results from quantum-chemical (QC) calculations as follows.

3.2 Vaporization Enthalpy from Combination of DSC and QC Reaction Enthalpies

The thermochemical properties of our interest are generally interrelated by the common textbook equation:

$$\Delta_1^g H_m^\circ = \Delta_f H_m^\circ (\text{gas}) - \Delta_f H_m^\circ (\text{liq}) \quad (2)$$

where $\Delta_1^g H_m^\circ$ is the standard molar enthalpy of vaporization, $\Delta_f H_m^\circ$ (gas) is the standard molar gaseous enthalpy of formation of an IL, and $\Delta_f H_m^\circ$ (liq) is the standard molar enthalpy of formation in the liquid state. The latter value is usually derived from a high-precision combustion calorimetry,^[10] or by using DSC to measure enthalpy of reaction, $\Delta_r H_m^\circ$ (liq), of an ionic liquid synthesis from the precursors.^[4] The enthalpy of vaporization of an IL is usually determined by any of the following suitable methods: Knudsen effusion,^[12] transpiration,^[10] QCM,^[8] or TGA^[7] which are well in our lab. Finally, the experimental value of $\Delta_f H_m^\circ$ (g) is calculated as the sum of the experimental $\Delta_f H_m^\circ$ (liq) value and $\Delta_1^g H_m^\circ$ value. The theoretical $\Delta_f H_m^\circ$ (g) value can be calculated using one of the suitable high-level quantum-chemical methods (e.g. G3(MP2), CBS-QB3, etc.)^[4,5] For the purpose of this work, the Eq. 2 can be rewritten as follows:

$$\Delta_1^g H_m^\circ ([\text{C}_n\text{C}_n\text{Im}][\text{Br}]) = \Delta_r H_m^\circ (\text{gas}) - \Delta_r H_m^\circ (\text{liq}) + \Delta_1^g H_m^\circ (1-\text{C}_n\text{Im}) + \Delta_1^g H_m^\circ (\text{C}_n\text{Br}) \quad (3)$$

where $\Delta_r H_m^\circ$ (liq) is the enthalpy ascribed to the reaction (1) and measured in this work by the DSC, values of vaporization enthalpies of precursors $\Delta_1^g H_m^\circ (1-\text{C}_n\text{Im})$ and $\Delta_1^g H_m^\circ (\text{C}_n\text{Br})$ are

available from our previous work^[13] or from the literature (see Table S1). The $\Delta_r H_m^\circ$ (gas) value is referred to the following gas-phase reaction:



It is important to underline that the value $\Delta_r H_m^\circ$ (gas) is derived using suitable quantum chemical methods *directly* from the calculated H_{298} bypassing the conventional calculation of the enthalpies of formation with help of atomization or isodesmic procedures. This $\Delta_r H_m^\circ$ (gas) value is not affected by the choice of atomization or bond separation procedure required for the latter conventional ways.^[4,5] In our previous studies we have successfully used very time consuming CBS-QB3 method for calculations of $[\text{C}_n\text{mim}][\text{Br}]$ family.^[4,5] Unfortunately, the $[\text{C}_n\text{C}_n\text{Im}][\text{Br}]$ species are too large to complete calculations with this method in reasonable time. As a compromise, the $\Delta_r H_m^\circ$ (gas) values for the $[\text{C}_n\text{C}_n\text{Im}][\text{Br}]$ series were additionally calculated using B3LYP/6-311G** method (see Table 2, column 3). A comparison of reaction enthalpy values, $\Delta_r H_m^\circ$ (gas) for $[\text{C}_n\text{mim}][\text{Br}]$ family calculated by the CBS-QB3 and B3LYP/6-311G** (see Table 2) showed that the constant difference ($-31.4 \text{ kJ}\cdot\text{mol}^{-1}$) results from these methods. We used this shift of $-31.4 \text{ kJ}\cdot\text{mol}^{-1}$ for correction of $\Delta_r H_m^\circ$ (gas)-values obtained by B3LYP/6-311G** method for the $[\text{C}_n\text{C}_n\text{Im}][\text{Br}]$ series (see Table 2, column 4). Enthalpies of vaporisation of the symmetric ionic liquids $[\text{C}_n\text{C}_n\text{Im}][\text{Br}]$ (see Table 2, column 5) have been estimated according to Eq. 3 with help of the theoretical $\Delta_r H_m^\circ$ (gas)-values and $\Delta_r H_m^\circ$ (liq)-values measured by the DSC. These vaporization enthalpies derived in the indirect way can be now compared with those derived directly from the TGA and QCM methods.

Table 2. Vaporization enthalpies of ILs at 298 K, derived from combination of DSC measurement and quantum chemical calculations (in $\text{kJ}\cdot\text{mol}^{-1}$).

IL	$\Delta_r H_m^\circ$ (liq) _{exp}	$\Delta_r H_m^\circ$ (g) _{QC}	$\Delta_r H_m^\circ$ (g) _{theor}	$\Delta_1^g H_m^\circ$
$[\text{C}_4\text{C}_4\text{Im}][\text{Br}]$	-105.4 ± 1.8	-19.6^a	-51.0 ± 5.0^b	152.1 ± 5.3
$[\text{C}_5\text{C}_5\text{Im}][\text{Br}]$	-102.4 ± 2.3	-19.8^a	-51.2 ± 5.0^b	161.4 ± 5.6
$[\text{C}_8\text{C}_8\text{Im}][\text{Br}]$	-100.2 ± 2.3	-20.5^a	-51.9 ± 5.0^b	185.3 ± 5.6

^a Calculated with B3LYP/6-311G**

^b Theoretical values were corrected by $-31.4 \text{ kJ}\cdot\text{mol}^{-1}$ (see explanation in text).

^c Uncertainty of vaporization is expressed as standard uncertainty combined from uncertainty of the experiment and uncertainty of the QC method. The latter uncertainty was assessed to be $\pm 5.0 \text{ kJ}\cdot\text{mol}^{-1}$.

3.3 Vaporization Enthalpy from TGA

TGA studies, which have been established as the express method for the determination of vaporization enthalpies of extremely low volatile molecular and ionic liquids, have been performed using a commercially available device.^[7] However, even in spite of the very high sensitivity of the microbalance of the TGA, the reliably measurable mass uptake of the sample can be achieved only at elevated temperatures of 400 to 450 K. Unfortunately, not all ILs can stand such temperatures without partial decomposition. Nevertheless, TGA is a valuable method to assess the temperature range where an IL remains stable, providing important experimental conditions for another suitable methods, e.g. for the QCM. Enthalpies of vaporization of the $[C_nC_nIm][Br]$ series derived at the average temperature T_{av} of the temperature interval of the TGA studies are as follows (see Table 3, column 4): $\Delta_1^g H_m^\circ(T_{av}= 423.9 \text{ K}) = 84.9 \pm 0.6 \text{ kJ}\cdot\text{mol}^{-1}$ for $[C_4C_4Im][Br]$, $\Delta_1^g H_m^\circ(T_{av}= 456.4 \text{ K}) = 152.9 \pm 0.8 \text{ kJ}\cdot\text{mol}^{-1}$ for $[C_6C_6Im][Br]$, and $\Delta_1^g H_m^\circ(T_{av}= 470.9 \text{ K}) = 139.5 \pm 0.3 \text{ kJ}\cdot\text{mol}^{-1}$ for $[C_8C_8Im][Br]$. These experimental results are not logical. Even having in mind somewhat different temperatures T_{av} for each of IL under study it is hardly possible to expect such an unusual sequence of $\Delta_1^g H_m^\circ$ for the homologous species, which differ by four CH_2 -fragments of the alkyl chain systematically. Thus, the vaporization enthalpy is expected to more or less steadily grow from $[C_4C_4Im][Br]$ to $[C_8C_8Im][Br]$. The disagreement with such a simple logic can be an indicator that $[C_nC_nIm][Br]$ may undergo decomposition reactions under the TGA experimental conditions. This conclusion was partly supported by the QCM method where the experimental conditions are significantly milder.

Table 3. Standard molar enthalpies of vaporization, $\Delta_1^g H_m^\circ$, of ILs derived from TGA.

IL	T -range	T_{av}	$\Delta_1^g H_m^\circ(T_{av})$	$-\Delta_1^g C_{p,m}^\circ$ ^a	$\Delta_1^g H_m^\circ(298 \text{ K})$ ^b
	K	K	$\text{kJ}\cdot\text{mol}^{-1}$	$\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$	$\text{kJ}\cdot\text{mol}^{-1}$
$[C_4C_4im][Br]$	401 - 451	423.9	(84.9±0.6)	125	-
$[C_6C_6im][Br]$	441 - 471	456.4	152.9±0.8	152	177.0±4.9
$[C_8C_8im][Br]$	450 - 490	470.9	(139.5±0.3)	179	(170.5±6.2)

^a From Table S2

^b Calculated from the TGA data at T_{av} (column 4) with $\Delta_1^g C_{p,m}^\circ$ (from column 5). Uncertainty of vaporization is expressed as standard uncertainty combined from uncertainty of the experiment and uncertainty of temperature adjustment. The latter uncertainty was assessed to be 20% of the contribution to vaporization enthalpy due to adjustment. Results in brackets were affected by decomposition.

3.4 Vaporization Enthalpy from QCM

Due to the very high sensitivity of the QCM it has been possible to reduce the average temperature of the vaporization studies by approximately 100 K in comparison to other conventional techniques such as transpiration^[10] or Knudsen effusion method.^[12] The QCM method has opened a new way to obtain reliable values of vaporization enthalpies of thermally unstable ionic liquids. Results from the QCM study are collected in Table 4. As it can be seen from this table for the [C₆C₆Im][Br] it was possible to begin the reliable measurements even at 393 K.

Table 4. Standard molar enthalpies of vaporization, $\Delta_1^g H_m^\circ$, of ILs derived from QCM.

IL	T -range	T_{av}	$\Delta_1^g H_m^\circ (T_{av})$	$-\Delta_1^g C_{p,m}^\circ$ ^a	$\Delta_1^g H_m^\circ (298\text{ K})$ ^b
	K	K	kJ·mol ⁻¹	J·K ⁻¹ ·mol ⁻¹	kJ·mol ⁻¹
[C ₄ C ₄ Im][Br]	403 - 448	425.3	151.0 ± 1.1	125	166.9±3.4
[C ₆ C ₆ Im][Br]	393-441	417.5	159.8 ± 2.2	152	177.9±4.2
[C ₈ C ₈ Im][Br]	413 - 461	436.6	156.6 ± 1.0	179	181.4±5.1

^a From Table S2

^b Calculated from the QCM data at T_{av} (column 4) with $\Delta_1^g C_{p,m}^\circ$ (from column 5). Uncertainty of vaporization is expressed as standard uncertainty combined from uncertainty of the experiment and uncertainty of temperature adjustment. The latter uncertainty was assessed to be 20% of the contribution to vaporization enthalpy due to adjustment.

Enthalpies of vaporization of the ILs from [C_nC_nIm][Br] series derived at the average temperature T_{av} of the temperature interval of the QCM studies are as follows (see Table 4, column 4): $\Delta_1^g H_m^\circ (T_{av}=425.3\text{ K}) = 151.0 \pm 1.1\text{ kJ}\cdot\text{mol}^{-1}$ for [C₄C₄Im][Br], $\Delta_1^g H_m^\circ (T_{av}=417.5\text{ K}) = 159.6 \pm 2.2\text{ kJ}\cdot\text{mol}^{-1}$ for [C₆C₆Im][Br], and $\Delta_1^g H_m^\circ (T_{av}=436.6\text{ K}) = 156.6 \pm 1.0\text{ kJ}\cdot\text{mol}^{-1}$ for [C₈C₈Im][Br]. These experimental results seem to be of the similar size, but the proper comparison is not possible because these values are referenced to the different temperatures T_{av} , thus they have to be adjusted to any common temperature (e.g. reference temperature 298 K)

3.5 Comparison of Vaporization Enthalpy from DSC, TGA and QCM

Experimental results from TGA and QCM studies (see Tables 3 and 4) are referenced to different temperatures T_{av} for each IL under study. In order to compare these results with the results of DSC studies, values of $\Delta_1^g H_m^\circ (T_{av})$ have to be adjusted to the reference temperature $T = 298\text{ K}$ with help of suitable values of $\Delta_1^g C_{p,m}^\circ$ (see Table S2). The experimental values $\Delta_1^g H_m^\circ (298\text{ K})$ from all three methods are given for comparison in Table 5.

Table 5. Enthalpies of vaporization, $\Delta_1^g H_m^\circ$, of $[C_n C_n \text{Im}][\text{Br}]$ family at 298 K (in $\text{kJ}\cdot\text{mol}^{-1}$).

IL	Method ^a	$\Delta_1^g H_m^\circ$ ^b
$[C_4 C_4 \text{Im}][\text{Br}]$	DSC	152.1±5.3
	QCM	166.9±3.4
	average	162.6±2.9
$[C_5 C_5 \text{Im}][\text{Br}]$	DSC	161.4±5.6
$[C_6 C_6 \text{Im}][\text{Br}]$	TGA	177.0±4.9
	QCM	177.9±4.2
		177.5±3.2
$[C_8 C_8 \text{Im}][\text{Br}]$	DSC	185.3±5.6
	QCM	181.4±5.1
	average	183.2±3.8

^a Methods: DSC = differential scanning calorimetry; TGA = thermogravimetric analysis; QCM = quartz-crystal microbalance. ^b Uncertainties of vaporisation enthalpies are expressed in this table as standard deviations. ^c Average values were calculated using the uncertainty of the experiment as a weighing factor. Recommended values are given in bold.

As can be seen from Table 5, the results as-obtained with different methods agree very well except for $[C_4 C_4 \text{Im}][\text{Br}]$, where the agreement can be considered as acceptable taking into account the combined experimental uncertainties. The average value $\Delta_1^g H_m^\circ$ (298 K) for each IL under study was calculated using the uncertainty of the experiment as a weighing factor (see Table 5). These values can now be used for the structure-property correlations.

3.6 Chain Length Dependence of Vaporization Enthalpy for $[C_n C_n \text{Im}][\text{Br}]$ and $[C_n \text{mim}][\text{Br}]$ - Series

Relating the thermochemical property of an IL with its molecular structure is always interesting. Structure-property relationships within a homologous series is the most prominent example of the simple correlations. For example, for the asymmetric imidazolium based ILs of general formula $[C_n \text{mim}][\text{Halogen}]$ a linear correlations between vaporization enthalpy $\Delta_1^g H_m^\circ$ (298 K) and the alkyl chain length were observed for the chlorine and bromine anions. Do we also expect the linear dependence of $\Delta_1^g H_m^\circ$ (298 K) on the chain length for the symmetric ILs $[C_4 C_4 \text{Im}][\text{Br}]$ studied in this work? The plot of $\Delta_1^g H_m^\circ$ (298 K) against the total number of C-atoms in alkyl chains (N_C) of the asymmetric $[C_n \text{mim}][\text{Br}]$ and the symmetric $[C_n C_n \text{Im}][\text{Br}]$ ILs is presented in Figure 1.

As can be seen in Fig. 1 both families of the asymmetric and the symmetric imidazolium based bromides exhibit linear dependence with the chain length, but each series demonstrate obviously the own line! Surprisingly, the symmetric ILs from $[C_nC_n\text{im}][\text{Br}]$ series have significantly lower vaporization enthalpies in comparison to the asymmetric one with the appropriate number N_C . For example vaporization enthalpy $\Delta_1^g H_m^\circ(298\text{ K}) = 161.4\text{ kJ}\cdot\text{mol}^{-1}$ (see Table 5) of $[\text{C}_5\text{C}_5\text{Im}][\text{Br}]$ is of $12.6\text{ kJ}\cdot\text{mol}^{-1}$ lower in comparison to $\Delta_1^g H_m^\circ(298\text{ K}) = 174.0\text{ kJ}\cdot\text{mol}^{-1}$ (see Table S2) for $[\text{C}_9\text{mim}][\text{Br}]$. However the same (but less profound) trend can be also observed by comparison families of the asymmetric^[14] and the symmetric^[6] imidazolium based ionic liquids with the $[\text{NTf}_2]$ -anion (see Fig. 1), where the experimental data are available from the recent literature. For example vaporization enthalpy $\Delta_1^g H_m^\circ(298\text{ K}) = 145.0\text{ kJ}\cdot\text{mol}^{-1}$ (see Table 5) of $[\text{C}_5\text{C}_5\text{Im}][\text{NTf}_2]$ is of $5.7\text{ kJ}\cdot\text{mol}^{-1}$ lower in comparison to $\Delta_1^g H_m^\circ(298\text{ K}) = 150.7\text{ kJ}\cdot\text{mol}^{-1}$ (see Table S2) for $[\text{C}_9\text{mim}][\text{NTf}_2]$.

The vaporization behaviour of an IL in a homologous series is obviously affected by the interplay of the van der Waals and Coulombic interactions. The increase of the van der Waals interactions with the growing chain length of the imidazolium cation is for a certain extend counterbalanced by electrostatic forces. The lower vaporization enthalpies $\Delta_1^g H_m^\circ(298\text{ K})$ of the symmetric ILs of the general type $[C_nC_n\text{Im}][\text{Anion}]$ compared to those for the asymmetric ILs $[C_n\text{mim}][\text{Anion}]$ are most probably indicating a significant decrease of the Coulombic interactions in the symmetric species and as the consequence somewhat less energy required for the transfer of the contact ionic pair to the gaseous state.

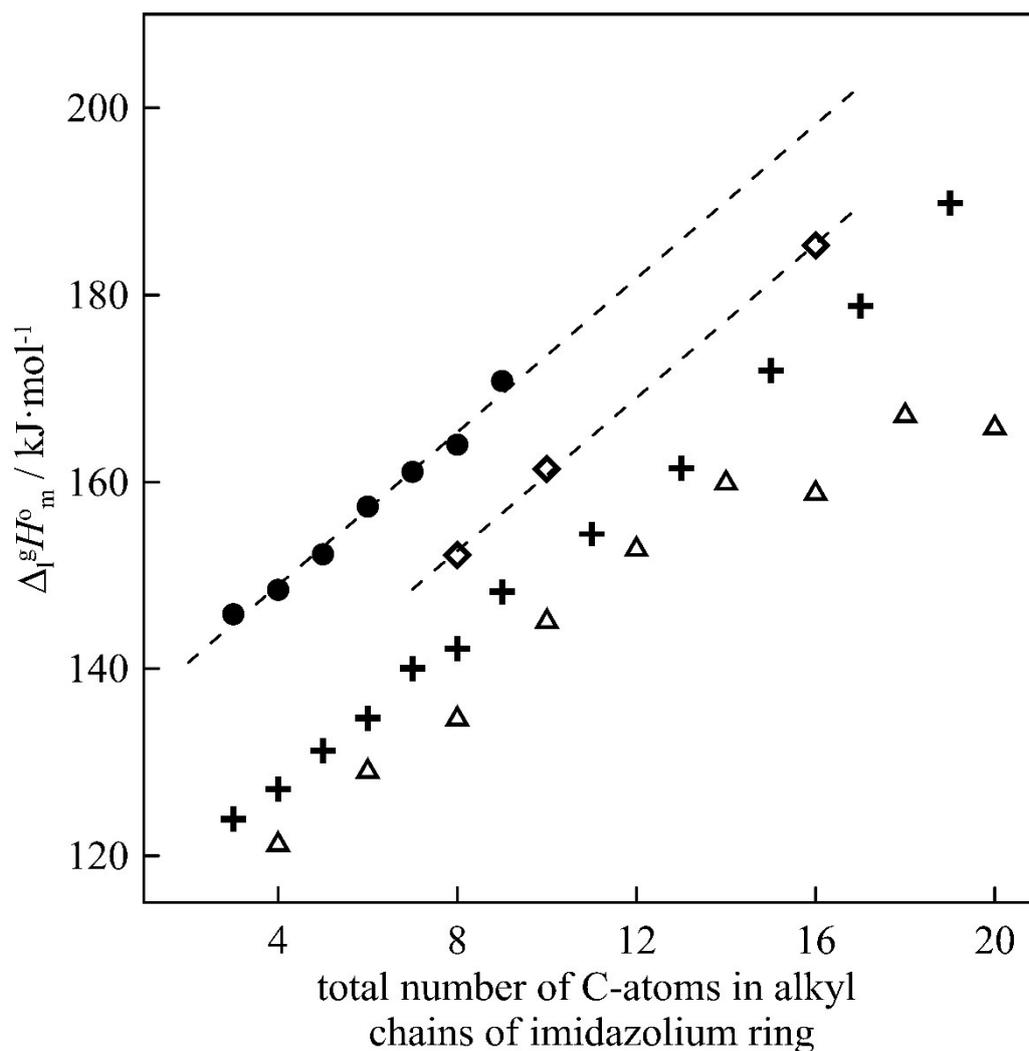


Figure 1. Dependence of the enthalpy of vaporization, $\Delta_1^g H_m^\circ$ (298 K) for imidazolium based on the total number of C-atoms in the cation alkyl chains (N_C): \diamond - $[\text{C}_n\text{C}_n\text{im}][\text{Br}]$; \bullet - $[\text{C}_n\text{mim}][\text{Br}]$; $+$, $[\text{C}_n\text{mim}][\text{NTf}_2]$; Δ - $[\text{C}_n\text{C}_n\text{im}][\text{NTf}_2]$

Conclusions

Complimentary experimental and computational methods have been applied to derive reliable vaporization enthalpies of the symmetric $[\text{C}_n\text{C}_n\text{Im}][\text{Br}]$ ionic liquids. These values are key properties required for temperature management and optimization of the IL synthesis as well as for using ILs for material synthesis in ILs. Comparison of vaporization enthalpies for the symmetric and asymmetric imidazolium based ILs has revealed a general trend that the lower vaporization enthalpies of the symmetric species is indicating a significant decrease of the Coulombic interactions affecting energetics of vaporisation.

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