

Supporting Information

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Happily coupled: an elegant access to vaporization enthalpies of ionic liquids by indirect thermochemical experiments and “in-silico” calculations.

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1. Materials and chemicals

Samples of 1-methylimidazole (MeIm) and butyl bromide were commercially available with purity $\geq 99\%$ but they were additionally distilled under reduced pressure prior to use and stored under dry nitrogen. The degree of purity was determined using a gas chromatograph (GC) equipped with a flame ionization detector. No impurities (greater than 0.05 mass per cent) could be detected in the samples used for the DSC measurements.

The commercial sample of 1-butyl-3-methylimidazolium chloride [C₄mim][Cl] from Io-li-tec was used in the TGA studies. The 1-ethyl-3-methyl-imidazolium bis-(trifluoromethanesulfonyl)-imides [C₄mim][NTf₂], used as a solvent in the DSC studies, was also available from Io-li-tec. Prior to experiments, the ILs were subjected to vacuum evaporation at 333 K for > 24 hours to remove possible traces of solvents and moisture. The water content (<100 ppm) was determined by Karl Fischer titration. An additional conditioning of the sample was performed during the TGA mass loss rate determinations. The reproducibility of the 2-3 consecutive serieses of temperature dependent mass loss measurements was a good indicator for absence of volatile impurities inside the sample. Handling with the IL samples occurred in a glove box.

2. Differential Scanning Calorimetry – Measurements of Reaction Enthalpy.

The enthalpy of reaction (1) was measured using the computer controlled Mettler-Toledo 822 heat flux DSC. The heat flow scale of the DSC was calibrated with indium (99.999% pure) and zinc (99.999% pure) as standard materials. The area of the DSC peak occurring during the chemical reaction was a measure of the reaction enthalpy. The heat released during the IL synthesis reaction (1) was related to the molar amount of a stoichiometrically deficient reactant in the starting formulation. The experimental procedure has been elaborated in our

lab and it was reported elsewhere ³. The optimal conditions suggested for the DSC studies of the IL synthesis reactions were as follows: ratio of precursors (1-Me-imidazole):(Bu-Cl) = 0.3:1.0 mol/mol; dilution with the solvent [C₄mim][NTf₂] 70wt. %; temperature scanning with 50 K/min in the range 298-523 K. In these conditions a sharp reaction peak with well defined baseline was achieved providing reproducible results.

3. Enthalpies of Vaporization from QCM Method.

Vaporization enthalpy of [C₄mim][Cl] has been measured using the QCM technique. The experimental setup and the measuring procedure have been reported recently ⁶. In short, a sample of IL in the open stainless steel crucible is placed in a vacuum chamber (at 10⁻⁵ Pa). In contrast to the Knudsen-technique the sample is exposed with its total open surface to the vacuum. The QCM is placed directly over the measuring cavity containing the IL. The change in the vibrational frequency of the crystal Δf (which is a measure of an amount of IL deposited on the cold QCM) was measured as function of time at different temperatures of the sample. Results obtained from the temperature dependent measurements of df/dt by QCM for [C₄mim][Cl] are given in Table S2. Enthalpy of vaporization $\Delta_{\text{l}}^{\text{g}}H_{\text{m}}^{\circ}(T_{\text{av}})$ obtained at the average temperature T_{av} has been adjusted to the reference temperature $T = 298$ K using the previously acknowledged for ILs value $\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\circ} = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the sake of comparison with our earlier work.

4. TGA – Measurements of Vaporization Enthalpy.

We used a Perkin Elmer Pyris 6 TGA in this work. Mass calibration was performed with help of a standard weight of 100 μg . The uncertainty of temperature calibration was less than 0.5 K. The detailed experimental procedure has been elaborated in our lab and it was reported elsewhere ²². In the TGA experiments about 70 mg of the IL sample was placed in a plane platinum crucible with vertical walls, diameter of 10 mm and height 3 mm and it was stepwise heated inside of the measuring head of the TGA. A mass loss from the crucible was recorded at each isothermal step. Prior to the measurement of the vaporization enthalpy, a careful conditioning of the sample inside the TGA have been performed. A heating ramp of $10 \text{ K}\cdot\text{min}^{-1}$ was used, followed by a 4 h static hold period at 423 K, allowing for the slow removal of volatile impurities and traces of water prior to stepwise isothermal runs. The conditioning was repeated until a reproducible mass loss within two consequent runs was recorded.

The optimal conditions for reliable TGA determinations of vaporization enthalpies of ILs were carefully elaborated in our previous work²²: the mass loss was within 0.1-0.8 mg at each temperature step; the minimal duration of the isothermal steps at elevated temperatures at least 10 min; the temperature range of the TGA study - at least 60 K. Isothermal mass loss was monitored in the temperature range 403-462 K at a nitrogen flow rate of 140 ml·min⁻¹. In order to trace any possible effect of impurities on the measured mass loss rate dm/dt a typical experiment was performed in a few consequent series with increasing and decreasing temperature steps. Every step consisted of 7 to 11 points of mass loss rate determination at each temperature. Several runs have been performed to assess the reproducibility of the results. In order to confirm the absence of decomposition of the 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. Experimental results from temperature dependent measurements of dm/dt by using the TGA for [C₄mim][Cl] are given in Table S3.

The relationship between the mass loss $r = dm/dt$ and the vaporization enthalpy was derived according to the Clausius-Clapeyron equation but by using the mass loss rate dm/dt measured by the TGA (instead of the absolute pressure)²²:

$$\ln\left(\frac{dm}{dt}\sqrt{T}\right) = A' - \frac{\Delta_1^g H_m^\circ(T_0) - \Delta_1^g C_{p,m}^\circ T_0}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) + \frac{\Delta_1^g C_{p,m}^\circ}{R} \ln\left(\frac{T}{T_0}\right) \quad (2)$$

with a constant A' which is essentially unknown and which includes parameters specific for our setup but is independent from the substance studied. T_0 appearing in Eq. (2) is an arbitrarily chosen reference temperature (which here has been chosen to be 298 K) and $\Delta_1^g C_{p,m}^\circ = C_{p,m}^\circ(g) - C_{p,m}^\circ(l)$ is the difference of the molar heat capacities of the gaseous $C_{p,m}^\circ(g)$ and the liquid phase $C_{p,m}^\circ(l)$ respectively. Enthalpy of vaporization $\Delta_1^g H_m^\circ(T_{av})$ obtained at the average temperature T_{av} has been adjusted to the reference temperature $T = 298$ K using the previously acknowledged for ILs value $\Delta_1^g C_{p,m}^\circ = -100 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for the sake of comparison with our earlier work.

5. Quantum Chemical Calculations. Calculation of the Gas Phase Enthalpy of Reaction and Formation.

Standard first-principles molecular orbital calculations were performed using the Gaussian 03 Rev.04 program package¹. Conformation analysis of the IL was performed using B3LYP/6-31+G(d,p) with help of the procedure developed in our previous work². Optimized structure,

and energy of the most stable conformer of the ionic pair was further obtained using the CBS-QB3 composite method. CBS-QB3 theory uses geometries from B3LYP/6-311G(2d,d,p) calculation, scaled zero-point energies from B3LYP/6-311G(2d,d,p) calculation followed by a series of single-point energy calculations at the MP2/6-311G(3df,2df,2p), MP4(SDQ)/6-311G(d(f),p) and CCSD(T)/6-311G[†] levels of theory.³ Calculated values of the enthalpy of reaction are based on the electronic energy calculations obtained using standard procedures of statistical thermodynamics.⁴

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6. Force Field and Molecular Dynamics Methodology

Briefly, the molar enthalpy of vaporization was computed as

$$\Delta_l^g H_m^o(T,P) = \langle h_{vap}(T,P) \rangle - \langle h_{liq}(T,P) \rangle \quad (1)$$

where $\langle h_{vap}(T,P) \rangle$ and $\langle h_{liq}(T,P) \rangle$ are the molar average enthalpies of an ideal gas and the condensed phase, respectively, at T and P. The individual components are computed as

$$\langle h_{vap}(T,P) \rangle = \langle u_{vap}(T) \rangle + RT \quad (2)$$

$$\langle h_{liq}(T,P) \rangle = \langle u_{liq}(T,P) \rangle + Pv \quad (3)$$

where u is the internal energy, R is the gas constant, P and v are the pressure and molar volumes of the liquid phase, respectively. The gas phase was assumed to be ideal. The magnitude of the Pv term was negligible in Eq. (3) and was neglected.

The CMJJ force field described elsewhere¹ was used to model [C4mim][Cl]. For computing the liquid phase internal energy, simulations were conducted in the isothermal-isobaric ensemble at the temperature and pressure of interest on 216 ion pairs for 500 ps using the Nosé-Hoover thermostat and barostat². Then, simulations were performed on the resulting equilibrated structure in the canonical ensemble for 1 ns using the Nosé-Hoover temperature thermostat³, and the internal energy was accumulated. For the ideal gas phase, one ion pair was simulated in the NVT ensemble in a large, non-periodic box to prevent edge effects. For all simulations, a timestep of 1 fs was used, and for all thermostats, a thermostat time constant of 0.1 ps was used, while for the barostat, a time constant of 0.5 ps was used. The Lennard-Jones and Coulombic interactions were truncated at 11 Å, with long range corrections being applied for the Lennard-Jones interactions. The Particle-Particle-Particle-Mesh⁴ algorithm

was used for the Coulombic interactions in the liquid phase. For the vapor phase, a large cutoff (50 Å) was used for both the Lennard-Jones and Coulombic interactions. All simulations were conducted using LAMMPS⁵.

Charges on the cation and anion scaled to $+0.9e$ and $-0.9e$ were found to predict more accurate $\Delta_f^s H_m^o$, as compared to $+1e$ and $-1e$. This was observed to be true for various ionic liquids. The choice of fractional charges on the ions can be justified by the charge transfer taking place between them, and has been observed by others.⁶⁻⁸

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Table S1. Experimental DSC results for the reaction: 1-Me-imidazole (*liq*) + C₄H₉Cl (*liq*) = [C₄mim][Cl] (*liq*)

Temperature range, °C	Heating rate, K min ⁻¹	Peak temperature, °C	BuCl, mg	1-MIM, mg	Molar ratio n_{BuCl}/n_{1-MIM}	Mass of the solvent, mg	Degree of conversion	Measured heat effect, mJ	Measured enthalpy of reaction, kJ mol ⁻¹	Enthalpy of reaction, kJ mol ⁻¹
25-350	50	230±8	19.03	3.56	0.22	14.57	0.9879	736.41	76.8	77.4
25-350	50		17.94	3.13	0.19	14.15	0.9913	560.08	78.5	79.2
25-350	50		17.85	3.02	0.19	14.18	0.9929	565.14	78.6	79.2
25-350	50		12.36	2.10	0.42	9.62	0.9963	847.05	78.4	78.7
										78.6±0.8 ^a

^a Uncertainties are twice the standard deviations of the mean value.

Table S2. Results of the temperature dependence of frequency shift velocity df/dt of the QCM for [C₄mim][Cl] and vaporization enthalpies $\Delta_l^g H_m^o(T)$

Run	T / K	$df \cdot dt^{-1} / \text{Hz} \cdot \text{s}^{-1}$	T^{-1} / K^{-1}	$R \cdot \ln(df \cdot dt^{-1} \cdot T^{1/2})$	$\frac{\Delta_l^g H_m^o(T)}{\text{kJ} \cdot \text{mol}^{-1}}$
[C ₄ mim][Cl]					
$\ln\left(\frac{df}{dt} \sqrt{T}\right) = -\frac{154.4}{R} - \frac{145239}{R} \left(\frac{1}{T} - \frac{1}{T_0}\right) - \frac{100}{R} \ln\left(\frac{T}{T_0}\right)$					
$\Delta_l^g H_m^o(298.15) = 153.5 \pm 1.5 \text{ kJ} \cdot \text{mol}^{-1}$					
1	442.94	0.08260	0.002258	44.18	139.0
	437.93	0.05315	0.002283	39.33	139.6
	432.89	0.03490	0.002310	34.63	140.1
	427.85	0.02232	0.002337	29.69	140.6
	422.82	0.01354	0.002365	24.31	141.1
2	460.56	0.3532	0.002171	60.32	137.3
	455.51	0.2270	0.002195	55.50	137.8
	450.48	0.1484	0.002220	50.81	138.3
	445.44	0.09858	0.002245	46.24	138.8
	440.41	0.06511	0.002271	41.61	139.3
	435.39	0.04276	0.002297	36.92	139.8
3	430.36	0.02777	0.002324	32.12	140.3
	442.94	0.08255	0.002258	44.2	139.1
	437.91	0.05332	0.002284	39.4	139.6
	432.89	0.03490	0.002310	34.6	140.1
	427.86	0.02219	0.002337	29.6	140.6

Table S3. TGA measurement for [C4mim][Cl]

pass	T / K	$10^{11} r / \text{kg} \cdot \text{s}^{-1}$	T^{-1} / K^{-1}	$R \cdot \ln(r \cdot T^{1/2})$
1	402.68	0.29	0.00248	-14.65
	422.14	2.38	0.00237	-32.33
	432.02	6.36	0.00231	-40.61
	441.98	13.78	0.00226	-47.13
	451.96	29.13	0.00221	-53.45
	461.97	58.82	0.00216	-59.38
2	402.67	0.29	0.00248	-14.70
	412.36	0.97	0.00243	-24.76
	422.12	2.45	0.00237	-32.57
	432.00	6.17	0.00231	-40.36
	441.96	13.40	0.00226	-46.90
	451.94	28.67	0.00221	-53.31
3	402.68	0.29	0.00248	-14.76
	412.38	0.92	0.00242	-24.33
	422.15	2.34	0.00237	-32.20
	432.04	5.04	0.00231	-38.68
	441.99	12.20	0.00226	-46.12
	451.96	26.85	0.00221	-52.77
	461.96	54.17	0.00216	-58.70

$$\Delta_f^s H_m^\circ ([\text{C}_4\text{mim}][\text{Cl}], 431.25 \text{ K}) = 138.0 \pm 1.7 \text{ kJ mol}^{-1}$$

$$\Delta_f^s H_m^\circ ([\text{C}_4\text{mim}][\text{Cl}], 298.15 \text{ K}) = 151.3 \pm 1.7 \text{ kJ mol}^{-1}$$

Table S4. Internal energies and enthalpy of vaporization calculated from MD at 343, 353, 363, 373, and 383 K for [C4mim][Cl]. Subscripts denote uncertainty in the final digit.

Temperature (K)	u_{liq} $\text{kJ} \cdot \text{mol}^{-1}$	u_{vap} $\text{kJ} \cdot \text{mol}^{-1}$	$\Delta_f^s H_m^\circ$ $\text{kJ} \cdot \text{mol}^{-1}$
343	-93.93 ₄	50.6 ₂	147.4 ₂
353	-87.74 ₄	57.3 ₄	148.1 ₄
363	-80.17 ₄	63.8 ₃	147.0 ₃
373	-72.76 ₄	70.6 ₄	146.5 ₄
383	-63.60 ₄	76.2 ₄	143.0 ₄

7. Temperature dependence of enthalpies of reaction

Strictly speaking, the enthalpy of reaction, $\Delta_r H_m^\circ$, obtained by integration of the DSC-peak is referenced to the temperature of the peak maximum, T_{max} . But, a small correction of the order of 0.3-0.4 $\text{kJ} \cdot \text{mol}^{-1}$ (see below) was required in practice to match the two quantities. This correction is definitely within the boundaries of the DSC experimental uncertainties of 1-2 $\text{kJ} \cdot \text{mol}^{-1}$ and the measured $\Delta_r H_m^\circ$ could be simply referred to the reference temperature. As a matter of fact, the ionic liquid [C4mim][Cl] is not liquid at room temperature. It is a solid with a melting point of $341.8 \pm 0.2 \text{ K}$ and the molar fusion enthalpy $\Delta_{\text{fus}} H_m^\circ = 21.7 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ at

T_{fus} . When adjusted to to 298 K $\Delta_{\text{fus}}H_m^0 = 18.6 \pm 0.5 \text{ kJ} \cdot \text{mol}^{-1}$ (see details in SI) and hence, the enthalpy of formation in the solid state is given by:

$$\Delta_f H_m^0 ([\text{C}_4\text{mim}][\text{Cl}], \text{ s}, 298 \text{ K}) = (-196.1) - (18.6) = (-214.7 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$$

It should be emphasized that this enthalpy of formation of the solid ($[\text{C}_4\text{mim}][\text{Cl}], \text{ s}$) has been obtained indirectly in several steps but by using only experimental data.

As a matter of fact, the enthalpy of reaction, $\Delta_r H_m^\circ$, obtained by integration of the DSC-peak is referred to the temperature between the on-set and end-set of the peak. In most cases we measured the symmetrical types of reaction peaks and we could assign the $\Delta_r H_m$ to the temperature of the peak maximum, T_{max} . To calculate the enthalpy of reaction, $\Delta_r H_m^\circ$ at $T = 298.15 \text{ K}$ for the reactions of methyl imidazole (Me-Im) with alkyl-halides (RX), the difference, $\Delta_r C_{p,m}$, between heat capacity of an ionic liquid $C_p^l(\text{IL})$ and precursors $C_p^l(\text{Me-Im})$ and $C_p^l(\text{RX})$ is required:

$$\Delta_r H_m (298.15 \text{ K}) / \text{J} \cdot \text{mol}^{-1} = \Delta_r H_m (T_{\text{max}}) - \Delta_r C_{p,m} (T_{\text{max}} - 298.15) \quad (1)$$

The values for C_p^l and calculations of $\Delta_r C_{p,m}$ are collected in Table S5. It is apparent from this table that the values of $\Delta_r C_{p,m}$ for all three reactions are slightly negative. Using the results for $\Delta_r C_{p,m}$ for synthesis of $[\text{C}_4\text{mim}][\text{Br}]$ and $[\text{C}_4\text{mim}][\text{I}]$ the average value $\Delta_r C_{p,m} = -(1.4 \pm 3.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ was estimated. The data for $[\text{C}_4\text{mim}][\text{Cl}]$ are in agreement with estimate within the boundaries of experimental uncertainties, however we excluded this data from calculation of the average $\Delta_r C_{p,m}$ because the heat capacity of $[\text{C}_4\text{mim}][\text{Cl}]$ reported in the reference ³ has an uncertainty of 25% according to the recent evaluation by Paulechka et al. ⁴. Application of the average value $\Delta_r C_{p,m} = -(1.4 \pm 3.3) \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}$ estimated in this work for adjustment of the measured enthalpies to the reference temperature should provide very small correction at the level of 0.3-0.4 $\text{kJ} \cdot \text{mol}^{-1}$ and this correction is well within the boundaries of the DSC experimental uncertainties of 1-3 $\text{kJ} \cdot \text{mol}^{-1}$. For this reason we ascribed in this work the enthalpies of reactions measured by DSC to the reference temperature without any temperature correction.

Table S5. Heat capacities, C_p^l , of precursors and changes of reaction heat capacities, $\Delta_r C_{p,m}$, for the reactions of synthesis of imidazolium halides from 1MIM and alkylhalides.

C_p^l in J·K ⁻¹ ·mol ⁻¹		
BuCl	MeIm	[C ₄ mim][Cl]
158.9±0.6 [1]	147.3±0.6 [2]	299±7.5 [3,4]
$\Delta_r C_{p,m} = -7\pm8$		
BuBr	MeIm	[C ₄ mim][Br]
162.3±0.6 [1]	147.3±0.6 [2]	308.7±1.0 [5]
$\Delta_r C_{p,m} = -0.9\pm1.3$		
BuI	MeIm	[C ₄ mim][I]
164.5±4.9 [1]	147.3±0.6 [2]	310.0±5.1 [6]
$\Delta_r C_{p,m} = -1.8\pm5.1$		

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