Thermochemistry of imidazolium-based ionic liquids: experiment and first-principles calculations†

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In this work the molar enthalpy of formation of the ionic liquid 1-ethyl-3-methylimidazolium dicyanoamide in the gaseous phase [C_2MIM][N(CN)$_2$] was measured by means of combustion calorimetry and enthalpy of vaporization using transpiration. Available, but scarce, primary experimental results on enthalpies of formation of imidazolium based ionic liquids with the cation [C_nMIM] (where n = 2 and 4) and anions [N(CN)$_2$], [NO_3] and [NTf_2] were collected and checked for consistency using a group additivity procedure. First-principles calculations of the enthalpies of formation in the gaseous phase for the ionic liquids with the common cation [C_nMIM] (where n = 2 and 4) and with the anions [N(CN)$_2$], [NO_3], [NTf_2], [Cl], [BF_4] and [PF_6] have been performed using the G3MP2 theory. It has been established that the gaseous phase enthalpies of formation of these ionic liquids obey the group additivity rules.

1. Introduction

Imidazolium based dicyanoamides [C_nMIM][N(CN)$_2$] are low melting, water-miscible, ionic liquids (ILs) of relatively low viscosity which have a considerable potential as a reaction medium.[1] The dicyanoamide anion is a ligand having Lewis basic properties in contrast to many of the anions, such as [PF_6], [BF_4], [TFSA], [CF_3SO_3], typically present in ionic liquids, which are characterized as being very weak Lewis bases.[2] Thus, dicyanoamide ILs possess the potential to provide ionic liquids which have powerful Lewis base donor solvent properties and therefore are expected to have solvating properties for a range of metal ions or carbohydrates.[3]

There are only a few experimental studies of thermochemical properties of ILs in the recent literature[4–7] and rapid progress to address this paucity of data is hardly to be expected, due to the time-consuming nature of these experiments. In our recent work, we have developed a valuable procedure to obtain vaporization enthalpies of ILs using a combination of the traditional combustion calorimetry with the modern high-level *ab initio* calculations.[7] For that purpose, the following thermodynamic relationship has been used to obtain the molar enthalpy of vaporization of an ionic liquid:

$$\Delta_f^g H_m = \Delta_f H_m^o(g) - \Delta_f H_m^o(l)$$

where $\Delta_f H_m^o(l)$ is the molar enthalpy of formation in the liquid state obtained by high precision combustion calorimetry, and $\Delta_f H_m^o(g)$ the gaseous enthalpy of formation calculated by one of the suitable *ab initio* methods (*e.g.* G3MP2). It should be noted that quantum chemical calculations of the gaseous enthalpy of formation of the ionic liquids have been performed under assumption that the gaseous phase of ionic liquids exists entirely of isolated ion pairs.

This work continues our study of the thermodynamic properties of pure ionic liquids.[4–7] We have used a combination of traditional experimental techniques—combustion calorimetry and transpiration method—with modern, high-level first-principles calculations in order to obtain the molar enthalpy of formation and molar enthalpy of vaporization of [C_2MIM][N(CN)$_2$]. Moreover, a set of thermochemical properties of ILs of the general formula [C_nMIM][Anion] has been collected and analyzed in terms of group additivity rules.[8,9]

2. Experimental procedure and methods of *first-principles* calculations

2.1 Materials

The sample of 1-ethyl-3-methyl-imidazolium dicyanoamide [C_2MIM][N(CN)$_2$], $C_8H_{11}N_5$ (CAS 370865-89-7) was of commercial origin (Sigma-Aldrich, 00796) with a purity of $\geq$ 99.0% (HPLC). It contains <200 ppm of halide according to specifications stated by the suppliers. Such amount of halide impurity does not impact vapor pressure measurements and combustion experiments. Prior to experiments, all IL-samples were subjected to vacuum evaporation (while being stirred) at 333 K for more than 24 hours to remove possible traces of solvents and moisture. The water concentration of 1940 ppm in this sample of [C_2MIM][N(CN)$_2$] was determined by Karl Fischer titration before starting experiments and appropriate

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corrections have been made for combustion results. Samples of the ILs were kept and handled under a nitrogen stream in a special glass device furnished with a septum for sample extraction using a syringe.

2.2 Thermochemical measurements: combustion calorimetry

An isoperibol bomb calorimeter was used for measuring the energy of combustion of $[C_2MIM][N(CN)_2]$. The construction of the calorimeter and the detailed experimental procedure have been described previously.[5,10] A careful encapsulation of the IL-sample is required due to its hygroscopic nature. In the present study, we used commercially available polyethylene bulbs (Fa. NeoLab, Heidelberg, Germany) as 1 cm^3 sample containers. The molten sample was transferred from the stock bottle into the polyethylene bulb with a syringe and sealed according to a procedure described earlier.[5] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none of these substances were detected. The energy equivalent of the calorimeter ε_{calor} was determined with a standard reference sample of benzoic acid (sample SRM 39i, NIST). The calorimeter was specially calibrated for a temperature increase of 1.7 K, which was specific for combustion experiments with the IL enclosed in a polyethylene bulb (at least half of the temperature increase is due to the combustion energy of polyethylene). Correction for nitric acid formation was based on titration with 0.1 mol dm^{-3} NaOH (aq). The atomic weights used were those recommended by the IUPAC Commission.[11] The sample masses were reduced to vacuum, taking into consideration the density value ρ (293 K) = 1.08 g cm^{-3} for the liquid $[C_2MIM][N(CN)_2]$.[12] For converting the energy of the actual combustion process to that of the isothermal process, and reducing to standard states, the conventional procedure[13] was applied. Results for combustion experiments with $[C_2MIM][N(CN)_2]$ are summarized in Table 1 and in the supporting materials (Tables S1 and S2, ESI†). The total uncertainty of $\Delta_f H^o_m(l)$ was calculated according to the guidelines presented by Olofsson.[14] The uncertainty assigned to $\Delta_f H^o_m(l)$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H_2O and CO_2.

2.3 Thermochemical measurements: transpiration method

The enthalpy of vaporization, $\Delta^g_l H_m$, and the vapor pressure of $[C_2MIM][N(CN)_2]$ were determined using the method of transference in a saturated stream of inert gas and by applying the Clausius–Clapeyron equation. The method is especially applicable at low pressures. It has been described in detail before[15,16] and has proven that it gives results in good agreement with other established techniques. A sample of approximately 0.5 g was mixed with glass beads and placed in a thermostatted U-tube of length 10 cm and diameter 0.5 cm. A preheated nitrogen stream was passed through the U-tube at constant temperature (±0.1 K). The flow rate of the nitrogen stream was measured using a soap bubble flow meter (±0.2–0.3%) and optimized in order to reach the saturation equilibrium of the transporting gas at each temperature under study. The material transported was condensed in a cold trap. The amount of condensed product in the trap was determined by weighing (±0.0001 g).

The saturated vapor pressure p_i^{sat} at each temperature T_i was calculated from the amount of product collected within a definite period of time. Assuming the validity of Dalton's law of partial pressures applied to the nitrogen stream saturated with the substance of interest i, values of p_i^{sat} were calculated according to the ideal gas law. Experimental vapor pressures of $[C_2MIM][N(CN)_2]$ have been measured by using the transpiration method in the temperature range (453–472) K. The following equation was fitted to the experimental p, T data using a and b as adjustable parameters:

$$R \ln p_i^{sat} = a + \frac{b}{T} + \Delta^g_l C_p \ln\left(\frac{T}{T_0}\right), \qquad (1)$$

where T_0 is an arbitrarily chosen reference temperature (in this case T_0 = 298.15 K), and $\Delta^g_l C_p$ represents the difference in molar heat capacities of the gaseous and liquid phases. The expression for the enthalpy of vaporization at temperature T has been derived from eqn (1) by incorporating the Clausius–Clapeyron equation to give:

$$\Delta^g_l H_m(T) = -b + \Delta^g_l C_p T \qquad (2)$$

Values of $\Delta^g_l C_p$ have been calculated according to a procedure developed by Chickos and Acree[17] using the experimental isobaric molar heat capacity of $[C_2MIM][N(CN)_2]$[18] C^l_p = 375.7 J K^{-1} mol^{-1} (at 298.15 K). The value of $\Delta^g_l C_p$ = −108.3 J K^{-1} mol^{-1} of $[C_2MIM][N(CN)_2]$ estimated in this work is in excellent agreement with those determined for $[C_4MIM][PF_6]$, $\Delta^g_l C_p$ = −105.4 J K^{-1} mol^{-1}, from calorimetric data and statistical thermodynamic calculations.[19] In order to be consistent with our previous work,[4] in this paper the value $\Delta^g_l C_p$ = −100.0 J K^{-1} mol^{-1} was used for $[C_2MIM][N(CN)_2]$. Experimental results and parameters a and b are listed in Table 2.

2.4 *First-principles* calculations

Standard quantum-chemical calculations were performed by NIST staff members on the NIH Biowulf cluster[20] using the Gaussian 03 Rev.04 program package.[21] The parallel nature of the Biowulf cluster allowed for the simultaneous study of a

Table 1 Thermochemical data at T = 298 K (p^o = 0.1 MPa) for $[C_nMIM][N(CN)_2]$, kJ mol^{-1}

ILs	$\Delta_c H^o_m(l)$	$\Delta_f H^o_m(l)$	$\Delta^g_l H_m$	$\Delta_f H^o_m(g)$ exp	$\Delta_f H^o_m(g)$ G3MP2	$\Delta_f H^o_m(g)$ CBS-Q3B
$[C_2MIM][N(CN)_2]$	−4955.4 ± 3.0	235.3 ± 3.1	156.4 ± 3.3	391.7 ± 4.5	401.3 ± 5.0	392.5 ± 5.0
$[C_4MIM][N(CN)_2]$[a]	−6273.9 ± 2.4	195.0 ± 2.7	157.2 ± 1.1	352.2 ± 2.9	359.7 ± 5.0	344.1 ± 5.0

[a] Experimental results from ref. 5.

Table 2 Results from measurements of the vapor pressure p of $[C_2MIM][N(CN)_2]$ using the transpiration method

T^a/K	m^b/mg	$V_{(N2)}{}^c$/dm^3	Gas-flow/dm^3 h^{-1}	p^d/Pa	$(p_{exp} - p_{calc})$/Pa	$\Delta_l^g H_m$/kJ mol^{-1}
$[C_2MIM][N(CN)_2]$; $\Delta_l^g H_m$ (298.15 K) = (156.4 ± 3.3) kJ mol^{-1}						
$\ln(p/\mathrm{Pa}) = \frac{444.6}{R} - \frac{186210.7}{R(T,K)} - \frac{100}{R}\ln\left(\frac{T,K}{298.15}\right)$						
453.2	10.8	400.444	9.15	0.37	0.00	140.9
460.2	20.1	418.902	9.15	0.67	0.01	140.2
466.2	19.5	264.674	9.15	1.02	−0.03	139.6
472.2	15.0	122.803	9.15	1.70	0.03	139.0

[a] Temperature of saturation. [b] Mass of transferred sample, condensed at T = 299 K. [c] Volume of nitrogen, used to transfer mass m of sample. [d] Vapor pressure at temperature T, calculated from m and the residual vapor pressure at the cooling temperature T = 299 K.

range of structures and conformations. Rotational conformers of the $[C_2MIM]$ cation were studied at the level HF/6-31G* at 0 K. Molecular structures and relative energies of all conformations for the cation formed by rotation of the alkyl group around the N–C bond by 360° have been studied with 10° steps starting from the co-planar conformation. It was found that the cation has two stable conformations. Energies and frequencies of normal modes were calculated for all the stable conformers using the B3LYP/6-31+G(d,p) basis set. Corresponding calculations have been performed for the molecular ionic pair $[C_2MIM][N(CN)_2]$ at the HF/3-21G*, HF/6-31G(d,p) level and fully optimized at the B3LYP/6-31+G(d,p) level. Starting from 20 to 30 initial geometries, the energy of formation of ion pairs from separated ions was calculated using the supermolecule method at the B3LYP level. The optimized structure of the $[C_2MIM][N(CN)_2]$ ion pair is presented in Fig. 1.

Optimized structures and energies of the ion pair were also obtained using the G3MP2 and CBS-QB3 methods. The G3 theory is a procedure for calculating energies of molecules containing atoms of the first and second row of the periodic table based on *ab initio* molecular orbital theory. A modification of G3 theory that uses reduced orders of Møller–Plesset perturbation theory is the G3MP2 theory.[22] This method saves considerable computational time compared to the G3 theory with limited loss in accuracy, but is much more accurate than G2(MP2) theory. G3(MP2) theory uses geometries from the second-order perturbation theory and scaled zero-point energies from the Hartree–Fock theory followed by a series of single-point energy calculations at the MP2(Full)/6-31G(d), QCISD(T)/6-31G(d) and MP2/GTMP2Large levels of theory (for details see ref. 22). 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)/6-31G(d(f),p) and CCSD(T)/6-31G† levels of theory.[23] Calculated values of the enthalpy and Gibbs enthalpy of ions and ion pairs are based on the electronic energy calculations obtained by the G3MP2 method using standard procedures of statistical thermodynamics.[24]

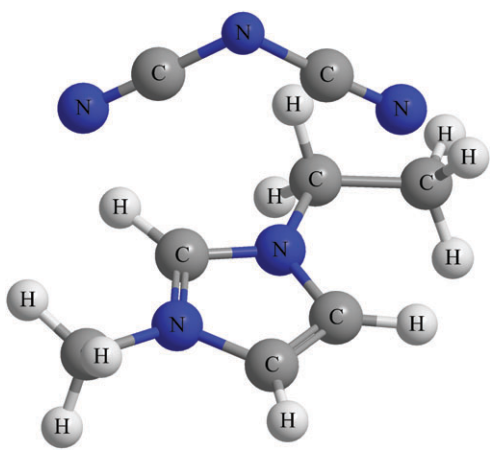


Fig. 1 Optimized with MP2full/6-31G(d) structure of the $[C_2MIM][N(CN)_2]$.

3. Results and discussion

3.1 Combustion calorimetry

Results of combustion experiments on $[C_2MIM][N(CN)_2]$ are summarized in the ESI.† The value of the standard energy of combustion $\Delta_c u^\circ$ = −(27960.6 ± 7.8) J g^{-1} has been used to derive the standard molar enthalpy of combustion $\Delta_c H_m^o$ = −(4955.4 ± 3.0) kJ mol^{-1} and the standard molar enthalpy of formation in the liquid state $\Delta_f H_m^o(l)$ = (235.3 ± 3.1) kJ mol−1 based on the reaction:

$$C_8H_{11}N_5 + 10.75O_2 = 8CO_2 + 5.5H_2O + 2.5N_2 \quad (3)$$

$\Delta_f H_m^o(l)$ of the $[C_2MIM][N(CN)_2]$ has been obtained from the enthalpic balance according to eqn (4):

$$\Delta_f H_m^o(l, [C_2MIM][N(CN)_2]) = 8\Delta_f H_m^o(g, CO_2) + 5.5\Delta_f H_m^o(l, H_2O) - \Delta_c H_m^o \quad (4)$$

where molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$ were taken from the literature, as assigned by CODATA.[25]

3.2 Transpiration method: enthalpy of vaporization $\Delta_l^g H_m$ of $[C_2MIM][N(CN)_2]$

The thermal stability of ILs is an important factor in any kind of measurements of the vapor pressure. According to studies of the thermal stability of the homologous series $[C_nMIM][N(CN)_2]$ with the help of thermogravimetry (TGA),[12] the ILs start to decompose upon heating at 270 °C for ($[C_1MIM][N(CN)_2]$, at 240 °C for $[C_2MIM][N(CN)_2]$, at

220 °C for $[C_4MIM][N(CN)_2]$, and at 230 °C for $[C_6MIM][N(CN)_2]$. In any case the temperature range (180–199 °C) used in this investigation of $[C_2MIM][N(CN)_2]$ with the transpiration method was substantially below the possible decomposition temperature. The IL inside the saturation tube became slightly yellow in color. In most experiments the condensate in the cold trap was colorless. In cases when the condensate was slightly colored the experimental vapor pressures did not deviate significantly from the smoothing line. A similar appearance of color was observed in our previous study[4] of vapor pressure of $[C_nMIM][NTf_2]$ using the Knudsen effusion method. IR spectra of $[C_2MIM][NTf_2]$ taken from the effusion cell before and after all the experiments, and those from condensate were identical. We conclude from these results that the yellowing of the ILs during investigation did not result from appreciable decomposition. Additionally, in order to confirm the stability of the ionic liquid in the experimental conditions of the vapor pressure measurements, the samples of $[C_2MIM][N(CN)_2]$ collected in the cold trap (at the highest temperatures used in studies) were analyzed using the GC-MS technique. No traces of a possible decomposition were found.

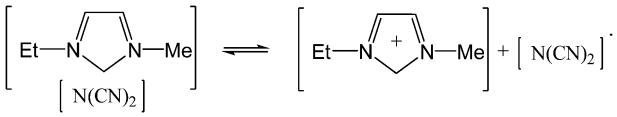
The value of the enthalpy of vaporization of $[C_2MIM][N(CN)_2]$ $\Delta_l^g H_m$ (298 K) = 156.4 ± 3.3 kJ mol^{-1} was obtained by using eqn (2). This result is close to the enthalpy of vaporization of $[C_4MIM][N(CN)_2]$ $\Delta_l^g H_m$ (298 K) = 157.2 ± 1.1 kJ mol^{-1} derived in our previous work[5] (also using the transpiration method). Our new result is consistent with the enthalpy of vaporization of $[C_8MIM][N(CN)_2]$ $\Delta_l^g H_m$ (298 K) = 162 ± 4 kJ mol^{-1} recently obtained from ultra-high vacuum mass spectrometry.[26]

3.3 Determination of the gaseous enthalpies of formation of $[C_2MIM][N(CN)_2]$

The enthalpy of formation, $\Delta_f H_m^o(l)$ = (235.3 ± 3.1) kJ mol^{-1}, of $[C_2MIM][N(CN)_2]$, derived from the combustion experiments together with the vaporization enthalpy $\Delta_l^g H_m$ = (156.4 ± 3.3) kJ mol^{-1}, derived from the vapor pressure measurements are referred to the reference temperature T = 298.15 K. Using the equation $\Delta_f H_m^o(g) = \Delta_f H_m^o(l) + \Delta_l^g H_m$ we calculated the value of the standard molar enthalpy of formation $\Delta_f H_m^o(g)$ = (391.7 ± 4.5) kJ mol^{-1}. This value has been used to check the validity of first-principle methods as follows.

3.4 Quantum chemical calculations for $[C_2MIM][N(CN)_2]$

In recent papers[5–7] we have shown that the aprotic ILs such as $[C_4MIM][N(CN)_2]$, $[Pyrr_{1,4}][N(CN)_2]$, and $[C_nMIM][NO_3]$ exist in the gaseous phase as contact ion pairs and not as separated ions. Calculations for the free cation $[C_2MIM]^+$, the free anion $[N(CN)_2]^-$, and the ion pair $[C_2MIM]^+[N(CN)_2]^-$ have been performed (Table S4 in ESI†). Results of the electronic energy at 0 K, the molecular structures in the lowest energetic state and all vibrational frequencies of each species have been obtained (Table S5 in ESI†). These data are available in the ESI.† On the basis of these quantum mechanical results, the molar Gibbs energy, the molar enthalpy, and the molar entropy have been calculated at 298.15 K and at 423.15 K using standard procedures of statistical thermodynamics. The purpose of this procedure was to obtain values of the molar standard Gibbs energy of reaction $\Delta_r G^0$, the standard molar entropy of reaction $\Delta_r S^0$, and the molar reaction enthalpy $\Delta_r H^0$ for the process of dissociation of the ion pair $[C_2MIM][N(CN)_2]$ into ions in the gaseous phase according to



(5)

The chemical equilibrium constant K_p in the ideal gas state has been calculated at 298 K (Table S6, ESI†) using the G3MP2 method as described in detail previously.[5] We have obtained $K_p = 3.4 \times 10^{-56}$ for $[C_2MIM][N(CN)_2]$ and this value is in agreement with $K_p = 1.4 \times 10^{-54}$ for $[C_4MIM][N(CN)_2]$ derived in our previous work.[5] Such extremely low values allow us to conclude with high reliability that the degree of dissociation of the ion pair is zero for both the ionic liquids under study, *i.e.* these ionic ILs exist exclusively as ion pairs in the gaseous phase.

We have calculated the enthalpies of formation, $\Delta_f H_m^o(g)$, of $[C_2MIM][N(CN)_2]$ using G3MP2 and CBS-QB3 methods with the help of the atomization reaction as well as with the following three reactions:

$$[C_2MIM][N(CN)_2] + 20C_2H_6 = 2HCN + 3NH_3 + 2C_2H_4 + 14C_3H_8 \quad (6)$$

$$[C_2MIM][N(CN)_2] + 9C_2H_6 = 2HCN + 1H\text{-Imidazole} + 7C_3H_8 + NH_3 \quad (7)$$

$$[C_2MIM][N(CN)_2] + 16C_2H_6 = 2HCN + (CH_3)_3N + NH_2\text{–}(CH_2)_2\text{–}NH_2 + 11C_3H_8 \quad (8)$$

Using standard enthalpies of the reactions in eqn (6)–(8) calculated by G3MP2 or CBS-QB3 and experimental

Table 3 Calculated standard molar enthalpy of formation $\Delta_f H_m^o(g)$ for $[C_2MIM][N(CN)_2]$ and $[C_4MIM][N(CN)_2]$ in the gaseous phase at 298 K (in kJ mol^{-1})

	G3MP2				CBS-QB3			
ILs	Atomiz.	Eqn (6)	Eqn (7)	Eqn (8)	Atomiz.	Eqn (6)	Eqn (7)	Eqn (8)
$[C_2MIM][N(CN)_2]$	401.7	403.1	402.4	397.9	400.7	383.4	398.3	387.5
			Average	*401.3*[a]			*Average*	*392.5*[a]
$[C_4MIM][N(CN)_2]$	360.1	361.6	360.8	356.4	354.2	334.4	349.3	338.5
			Average	*359.7*[b]			*Average*	*344.1*[b]

[a] Experimental value $\Delta_f H_m^o(g)$ = 391.7 ± 4.5 kJ mol^{-1}. [b] Experimental value $\Delta_f H_m^o(g)$ = 352.2 ± 2.9 kJ mol^{-1}.

enthalpies of formation $\Delta_f H^o_m(g)$ for species involved in the reactions (6)–(8) as recommended by Pedley *et al.*[27] (see Table S5 in ESI†), the enthalpy of formation of $[C_2MIM][N(CN)_2]$ has been calculated (see Tables 1 and 3). In addition to our previous work,[5] calculation with the CBS-QB3 method has been performed for $[C_2MIM][N(CN)_2]$. As shown in Table 3 the averaged values for $\Delta_f H^o_m(g)$ calculated by G3MP2 $[C_nMIM][N(CN)_2]$ using the atomization procedure and reactions in eqn (6)–(8) are in agreement with the experimental values within the combined uncertainties. The averaged results from the CBS-QB3 method are in even better agreement with the experimental values. However, it is worth mentioning that the CBS-QB3 method is substantially more time-consuming in comparison to G3MP2 and with calculations of $[C_nMIM][N(CN)_2]$ we are already at the limit of our computational capacities. Other ILs with longer alkyl chains would be too time consuming to be calculated using the CBS-QB3 method with our current computational resources. Nevertheless, the remarkable ability of the composite G3MP2 method to calculate gaseous enthalpies of formation of ionic liquids close to the experimental results is encouraging for further IL studies.

3.5 Application of group-additivity rules for ILs

Group-additivity (GA) methods are well recognized approaches to prove consistency of the experimental data on thermochemical properties of molecular compounds.[8,9] One of the best indicators of possible experimental errors is a large deviation between experimental values and those calculated by GA—especially if other, closely related compounds show no such discrepancy. The most successful GA method for estimating the thermodynamic properties was suggested by Benson.[8] This method serves as a valuable tool for many scientists and engineers whose work involves thermodynamic characterization of elementary and overall reaction processes.

Are GA methods able to predict thermochemical properties of ILs properly? Getting a definitive answer to this question is difficult. First of all, there are only about 30 available data points of vaporization enthalpies,[4–7] and even fewer for enthalpies of formation.[5–7] This information is too limited for a quantitative parameterization of any groups specific for ILs. A further question arises—is it generally possible to transfer group contributions established for common organic compounds to ionic liquids? To answer these questions, we collected the thermochemical data available from the literature in Table 4. In our previous work we deliberately investigated imidazolium based ionic liquids $[C_nMIM][Anion]$ with $n = 2$ and 4 in order to get insight into possible group additivity rules for ionic liquids. Due to scarcity of the available data, only simple structural patterns could be considered before starting the development of any kind of GA method. As a first step in this direction let us compare differences in enthalpies (vaporization or formation) of structurally parent molecules:

$$CH_3–[CH_2]_2–CH_3 \text{ and } CH_3–[CH_2]_4–CH_3$$

$$CH_3–[CH_2]_2–OH \text{ and } CH_3–[CH_2]_4–OH$$

$$[C_2MIM][Anion] \text{ and } [C_4MIM][Anion]$$

Table 4 Compilation of the enthalpies of vaporization, enthalpies of formation in the liquid, $\Delta_f H^o_m(l)$, and in the gaseous phase $\Delta_f H^o_m(g)$ for some alkanes, alcohols, and imidazolium based ILs at 298 K (in kJ mol^{-1})

Fragment	$\Delta^g_l H_m$	$\Delta_f H^o_m(l)$	$\Delta_f H^o_m(g)$
$CH_3–[CH_2]_2–CH_3$[27]	22.4 ± 0.1	−146.6 ± 0.7	−125.6 ± 0.7
$CH_3–[CH_2]_4–CH_3$[27]	31.7 ± 0.1	−198.7 ± 0.8	−167.1 ± 0.8
Δ[a]	**9.3**	**−52.1**	**−41.5**
$CH_3–[CH_2]_2–OH$[27]	52.3 ± 0.1	−302.6 ± 0.5	−255.1 ± 0.5
$CH_3–[CH_2]_4–OH$[27]	61.7 ± 0.1	−351.6 ± 0.4	−294.7 ± 0.5
Δ[a]	**9.4**	**−49.0**	**−39.6**
$[C_2MIM][N(CN)_2]$	157.0 ± 2.1	235.3 ± 3.1	392.3 ± 3.7
$[C_4MIM][N(CN)_2]$[5]	157.2 ± 1.1	195.0 ± 2.7	352.2 ± 2.9
Δ[a]	**0.2**	**−40.0**	**−40.1**
$[C_2MIM][NTf_2]$[4]	135.3 ± 1.3	—	—
$[C_4MIM][NTf_2]$[4]	136.2 ± 1.7	—	—
Δ[a]	**0.9**	—	—
$[C_2MIM][NO_3]$[7]	163.7 ± 5.3	−216.9 ± 2.0	−53.2 ± 4.9
$[C_4MIM][NO_3]$[7]	162.4 ± 5.7	−261.4 ± 2.9	−99.0 ± 4.9
Δ[a]	**−1.3**	**−44.5**	**−45.8**

[a] Difference between C_4 and C_2 derivatives

These differences could serve as simple indicators of whether or not molecules obey additivity rules.

3.5.1 Vaporization enthalpy, $\Delta^g_l H_m$. It is well established that enthalpies of vaporization in most homologous series C_nH_{2n+1}–R (alkanes,[28] 1-substitued-alkanes,[28] alcohols,[15] esters,[29] aldehydes,[30] *etc.*) linearly correlate with the chain length N_c. Experimental data on vaporization enthalpies of two *n*-alkanes and *n*-alcohols are presented in column 2 of Table 4. It is also evident from this column that the differences between $CH_3–[CH_2]_4–R$ and $CH_3–[CH_2]_2–R$ are identical (9.3 kJ mol^{-1}) within the boundaries of the experimental uncertainties in alkanes and alcohols. We should expect a similar tendency for ILs. Surprisingly, this is not the case for ionic liquids! The corresponding differences between $[C_4MIM][Anion]$ and $[C_2MIM][Anion]$ (Table 4, column 2) are almost zero (within the boundaries of the experimental uncertainties) and no additivity for this property seems to exist for ILs. However, let us additionally consider some imidazolium based ILs with longer alkyl chains.[4,31–33] For ILs of the general formula $[C_nMIM][NTf_2]$ with $n = 2$, 4, 6, 8, and 10 the vaporization enthalpy is expected to increase monotonically from $[C_2MIM][NTf_2]$ to $[C_{10}MIM][NTf_2]$ in accordance with the increase of the number of CH_2 groups (the contribution to vaporization enthalpy of 5 kJ mol^{-1} per each CH_2 group is typical for the derivatives of the *n*-alkane family[28] or the alkylbenzenes).[34] However, this is in disagreement with experimental observations as shown in Fig. 2. Indeed, the enthalpies of vaporization of the ethyl to the hexyl derivatives are hardly distinguishable within the boundaries of their experimental uncertainties. Only for $[C_nMIM][NTf_2]$ with $n \geq 6$ is the assumed contribution of 5.0 kJ mol^{-1} per CH_2 group approximately observed. The reason for such an anomaly (or non-additivity) in the behavior of ILs is apparently due to interplay of the van der Waals and coulombic interactions. We can conclude that group additivity rules for enthalpies of vaporization of the series of $[C_nMIM][Anion]$ ionic liquids seem to be valid for the ILs with alkyl chain length starting from $N_c \geq 6$.

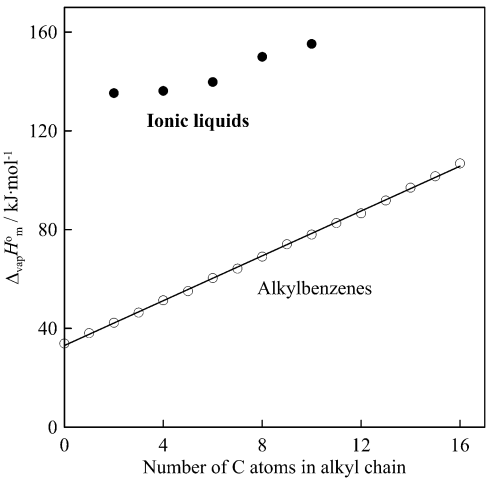


Fig. 2 Correlation between enthalpy of vaporization (in kJ mol^{-1}) and the alkyl chain length (N_c) in alkylbenzenes (data from ref. 34) and ionic liquids [C_nMIM][NTf_2] (data from ref. 30).

3.5.2 Enthalpy of formation in the liquid state, $\Delta_f H^o_m$(l). Experimental data on enthalpies of formation, $\Delta_f H^o_m$(l), of two *n*-alkanes and *n*-alcohols are presented in column 3 of Table 4. The difference between CH_3–$[CH_2]_4$–R and CH_3–$[CH_2]_2$–R are *ca.* −50 kJ mol^{-1} for both homologous series. The corresponding difference for the [C_4MIM][Anion] and [C_2MIM][Anion] (Table 4, column 3) is only –(40 to 45) kJ mol^{-1} which is distinctly lower than 2 × (CH_2) = 2 × (−25.5) = −51.0 kJ mol^{-1} expected[9] from the molecular compounds. However, due to the relatively high combined experimental uncertainties of about ±(3–4) kJ mol^{-1}, more experimental information is still required to establish additivity rules for $\Delta_f H^o_m$(l) of ILs.

3.5.3 Enthalpy of formation in the gaseous state, $\Delta_f H^o_m$(g). Experimental data on enthalpies of formation, $\Delta_f H^o_m$(g), of two *n*-alkanes and *n*-alcohols are presented in column 4 of Table 4. The differences between CH_3–$[CH_2]_4$–R and CH_3–$[CH_2]_2$–R as well as for [C_4MIM][Anion] and [C_2MIM][Anion] (Table 4, column 4) seem to be remarkably consistent. On average, the contribution of −(40 to 45) kJ mol^{-1} for two CH_2 groups is common to molecular species and ionic liquid molecules. Such a similarity supposes that gaseous enthalpies of formation, $\Delta_f H^o_m$(g), of ILs follow the group additivity rules established for molecular compounds. Being encouraged by this fact, we have used the G3MP2 method to calculate $\Delta_f H^o_m$(g) for the [C_4MIM][Anion] with the common anions [NTf_2], [NO_3], [BF_4], [PF_6], and [Cl]. Results are collected in Table 5. Analysis of differences between [C_4MIM][Anion] and [C_2MIM][Anion] (see column 4, Table 5) reveals that the contribution from two CH_2 groups in ionic liquids seems to be somewhat more negative (an average of about −48 kJ mol^{-1}) in comparison to 2 × (CH_2) = 2 × (−20.9) = −41.8 kJ mol^{-1} expected[9] for normal molecular compounds. However, this difference for ionic liquids could be considered as acceptable, taking into account the uncertainties assigned[21] for the G3MP2 method of ±5.0 kJ mol^{-1}. We conclude that group additivity rules for the gaseous enthalpies of formation of the series of [C_nMIM][Anion] ionic liquids are valid for the ILs with both short and long alkyl chain lengths on the cation. However, more experimental information is required for detecting similarities or disparities of additivity parameters of molecular and ionic compounds.

Table 5 Standard molar enthalpy of formation $\Delta_f H^o_m$(g) for [C_nMIM][Anion] in the gaseous phase at 298 K (in kJ mol^{-1}) calculated by G3MP2 (using atomization procedure)

Anion	[C_2MIM]	[C_4MIM]	Δ^a
[$N(CN)_2$]	401.7	360.1	−41.6
[NTf_2]	−1773.7	−1828.3	−54.6
[NO_3]	−46.6	−93.0	−46.4
[Cl]	10.2	−37.5	−47.7
[PF_6]	−1909.2	−1957.9	−48.7
[BF_4]	−1692.2	−1740.1	−47.9

[a] Difference between columns 3 and 2.

4. Conclusions

The combination of experimental methods (combustion calorimetry, vapor pressure measurements) with high-level first-principles calculations produces reliable sets of molar enthalpies of vaporization and enthalpies of formation for the series of the ILs: [C_nMIM][Anion]. Simple additive rules have been tested for these thermochemical properties. We have shown that enthalpies of formation generally obey group additivity; however the values of the additivity parameters for ionic liquids seem to be somewhat different from those for molecular compounds.

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