



Imidazolium based ionic liquids. 1-Ethanol-3-methyl-imidazolium dicyanoamide: Thermochemical measurement and first-principles calculations

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ARTICLE INFO

Article history:

Received 22 November 2010
Received in revised form 27 January 2011
Accepted 9 February 2011
Available online 21 February 2011

Keywords:

Ionic liquids
Combustion calorimetry
Enthalpy of formation
Enthalpy of vaporization
First-principles calculations

ABSTRACT

The standard molar enthalpy of formation $\Delta_f H_m^\circ(l)$ of the ionic liquid 1-ethanol-3-methylimidazolium dicyanoamide has been determined at 298.15 K by means of combustion calorimetry. First-principles calculations of the enthalpy of formation in the gaseous phase have been performed for the ionic species using the composite G3(MP2) method. The combination of combustion calorimetry with the high-level quantum-chemical calculations allows to estimate the molar enthalpy of vaporization of the ionic liquid under study. It has been established, that the liquid phase enthalpy of formation of this ionic liquid presumably obeys the group additivity rules.

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1. Introduction

Ionic liquids (ILs) are currently attracting considerable attention as potentially benign solvents for many areas. Most frequently the imidazolium based ILs $[C_n\text{mim}][\text{anion}]$ with the variation of alkyl chain $n = 1-16$ have been studied [1]. Imidazolium based ILs with functional groups (OH, OR, SO_3H , CN) introduced into the alkyl chain has been investigated less intensively. The hydroxyl- and ether-derivatized ILs were found capable of dissolving a large variety of substances such as triglycerides, sugars, cellulose, and amino acids. Here we present the first experimental and theoretical study of the enthalpy of combustion and enthalpies of formation, $\Delta_f H_m^\circ$, in the liquid as well as in the gaseous state of the ionic liquid 1-ethanol-3-methylimidazolium dicyanoamide (see Fig. 1). We also report the enthalpy of vaporization, $\Delta_1^g H_m^\circ$, of this ionic liquid derived according to the general equation:

$$\Delta_1^g H_m^\circ = \Delta_f H_m^\circ(g) - \Delta_f H_m^\circ(l) \quad (1)$$

where the standard molar enthalpy of formation of the IL in the liquid phase $\Delta_f H_m^\circ(l)$, was obtained from the calorimetrically measured energy of combustion, and the molar enthalpy of formation, $\Delta_f H_m^\circ(g)$, was obtained by the high-level first-principles calculations.

2. Experimental procedure and methods of ab initio calculations

2.1. Materials

The sample of 1-ethanol-3-methylimidazolium dicyanoamide $[\text{C}_2\text{OHmim}][\text{DCA}]$, $\text{C}_8\text{H}_{11}\text{ON}_5$, was of commercial origin (Solvionic, France, Im 2011c) with purity >98%. It contained ≤ 250 ppm of halide and ≤ 1000 ppm water according to specifications stated by the suppliers. Prior to experiments the IL samples were subjected to vacuum treatment at 333 K and 10^{-2} mbar for more than 24 h to reduce possible traces of solvents and moisture. The water concentration 400 ppm was determined by Karl Fischer titration immediately before the combustion experiments were started and an appropriate correction was applied to the results.

2.2. Thermochemical measurements. Combustion calorimetry

An isoperibol bomb calorimeter was used for the measuring of the energy of combustion of $[\text{C}_2\text{OHmim}][\text{DCA}]$. Five successful experiments were carried out for this compound (see Tables 1 and 2). The detailed procedure has been described previously [2–4]. The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on the titration with 0.1 mol dm^{-3} NaOH (aq). For converting the energy of the actual bomb process to that of the isothermal

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Table 1
Results for typical combustion experiments at $T = 298.15\text{ K}$ ($p^\circ = 0.1\text{ MPa}$) of the $[\text{C}_2\text{OHmim}][\text{DCA}]^{\text{a}}$

m (substance)/g ^b	0.576614	0.485179	0.456418	0.508695	0.424503
m' (cotton)/g ^b	0.000801	0.00088	0.001055	0.000915	0.001087
m'' (ampule)/g ^b	0.258694	0.268576	0.305839	0.267091	0.269234
$\Delta T_c/\text{K}^{\text{c}}$	1.7806	1.65843	1.72671	1.69305	1.55906
$(\varepsilon_{\text{calor}})(-\Delta T_c)/\text{J}$	-26381.4	-24571.4	-25582.9	-25084.2	-23099.1
$(\varepsilon_{\text{cont}})(-\Delta T_c)/\text{J}$	-28.98	-26.78	-28.08	-27.41	-24.95
$\Delta U_{\text{decomp}} \text{HNO}_3/\text{J}$	92.87	84.21	82.42	85.71	76.15
$\Delta U_{\text{corr}}/\text{J}^{\text{d}}$	10.84	9.72	9.94	10.03	8.9
$-m' \Delta_c u'/\text{J}$	13.57	14.91	17.88	15.5	18.42
$-m'' \Delta_c u''/\text{J}$	11992.46	12450.57	14177.99	12381.72	12481.07
$\Delta_c u^\circ (\text{liq})/(\text{J g}^{-1})^{\text{e}}$	-24801.1	-24812.9	-24807.9	-24805.9	-24827.9
$-\Delta_c u^\circ (\text{liq})/(\text{J g}^{-1})$			24811.1 ± 4.6		

^a For the definition of the symbols see Ref. [5]; $T_{\text{h}} = 298.15\text{ K}$; $V(\text{bomb}) = 0.320\text{ dm}^3$; $p^\circ(\text{gas}) = 3.04\text{ MPa}$; $m^\circ(\text{H}_2\text{O}) = 1.00\text{ g}$.

^b Masses obtained from apparent masses.

^c $\Delta T_c = T^{\text{f}} - T^{\text{i}} + \Delta T_{\text{corr}}$; $(\varepsilon_{\text{cont}}) \times (-\Delta T_c) = (\varepsilon_{\text{cont}}^{\text{i}}) \times (T^{\text{i}} - 298.15\text{ K}) + (\varepsilon_{\text{cont}}^{\text{f}}) \times (298.15\text{ K} - T^{\text{f}} + \Delta T_{\text{corr}})$.

^d ΔU_{corr} , the correction to standard states, is the sum of items 81–85, 87–90, 93, and 94 in Ref. [5].

^e $\varepsilon = 14816.0 \pm 0.8\text{ J K}^{-1}$.

Table 2
Formula, density ρ ($T = 293\text{ K}$), molar heat capacity c_p ($T = 298.15\text{ K}$), and expansion coefficients $(dV/dT)_p$ of the materials used in the present study.

Compounds	Formula	ρ^{b} (g cm^{-3})	c_p ($\text{J K}^{-1} \text{ g}^{-1}$)	$10^{-6} \cdot (dV/dT)_p^{\text{c}}$ ($\text{dm}^3 \text{ K}^{-1}$)
$[\text{C}_2\text{OHmim}][\text{DCA}]$	$\text{C}_8\text{H}_{11}\text{O}_1\text{N}_5$	1.12	1.20	1.0
Polyethen ^d	$\text{CH}_{1.93}$	0.92	2.53 ^a	0.1
Cotton ^e	$\text{CH}_{1.774}\text{O}_{0.887}$	1.50	1.67 ^a	0.1

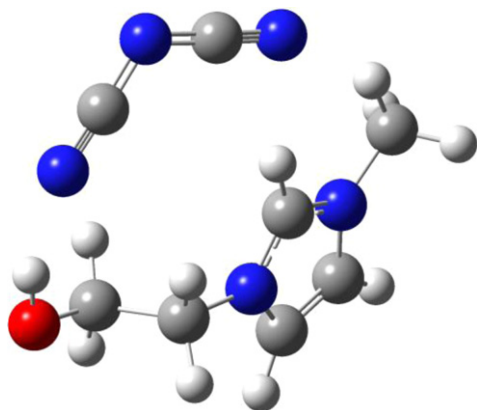
^a From d.s.c. measurements.

^b Measured with a pycnometer.

^c Estimated.

^d From 10 combustion experiments, $\Delta_c u^\circ = -(46357.7 \pm 3.5)\text{ J g}^{-1}$.

^e From 10 combustion experiments, $\Delta_c u^\circ = -(16945.2 \pm 4.2)\text{ J g}^{-1}$.

**Fig. 1.** The most stable conformation of $[\text{C}_2\text{OHmim}][\text{DCA}]$.

process, and reducing to standard states, the conventional procedure was applied [5]. Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with the necessary auxiliary quantities, are given in Table 2. To derive $\Delta_f H_m^\circ(\text{l})$ from $\Delta_c H_m^\circ$, molar enthalpies of formation of $\text{H}_2\text{O}(\text{l})$ and $\text{CO}_2(\text{g})$ were taken, as assigned by CODATA [6]. Table 3 contains the derived standard molar enthalpy of combustion, and standard molar enthalpy of formation of the $[\text{C}_2\text{OHmim}][\text{DCA}]$. The total uncertainty was calculated according to the guidelines presented by Olofsson [7]. The

Table 3
Thermochemical data at $T = 298.15\text{ K}$ ($p^\circ = 0.1\text{ MPa}$) for $[\text{C}_2\text{OHmim}][\text{DCA}]$ in (kJ mol^{-1}).

$\Delta_c H_m^\circ(\text{l})$	$\Delta_f H_m^\circ(\text{l})$	$\Delta_f H_m^\circ(\text{g})$ G3(MP2)	$\Delta_f^\ddagger H_m^\circ$ ^a
-4793.0 ± 2.1	72.9 ± 2.3	235.6	162.7

^a The differences between the $\Delta_f H_m^\circ(\text{g})$ derived using G3(MP2) method and the $\Delta_f H_m^\circ(\text{l})$ from the combustion experiments.

uncertainty assigned to $\Delta_f H_m^\circ$ 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. First-principles calculations

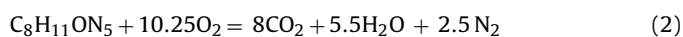
Standard ab initio calculations were performed using the Gaussian 03 Rev.04 program package [8]. Optimized structures and energies of ionic pair were also obtained using the G3(MP2) method. The G3 theory exhibits a reliable procedure for calculating energies of molecules containing atoms of the first 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 G3(MP2) theory [9]. This method saves considerable computational time compared to the G3 theory with limited loss in accuracy. G3(MP2) theory uses geometries from second-order perturbation theory and scaled zero-point energies from 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. Values of the energies and enthalpies of ions and ion pairs are based on the electronic energy calculations obtained by the G3(MP2) method using standard procedures of statistical thermodynamics [10].

3. Results and discussion

3.1. Combustion calorimetry

Results of combustion experiments with $[\text{C}_2\text{OHmim}][\text{DCA}]$ are summarized in Tables 1–3. The value of the standard specific energy of combustion $\Delta_c u^\circ = -(24811.1 \pm 4.6)\text{ J g}^{-1}$ has been used to derive the standard molar enthalpy of combustion $\Delta_c H_m^\circ = -(4793.0 \pm 2.1)\text{ kJ mol}^{-1}$ and the standard molar enthalpy of formation in

the liquid state $\Delta_f H_m^\circ(l) = (72.9 \pm 2.3) \text{ kJ mol}^{-1}$ based on the reaction:



$\Delta_f H_m^\circ(l)$ of the $[\text{C}_2\text{OHmim}][\text{DCA}]$ has been obtained from the enthalpic balance according to Eq. (3):

$$\begin{aligned} \Delta_f H_m^\circ(l, [\text{C}_2\text{OHmim}][\text{DCA}]) \\ = 8 \Delta_f H_m^\circ(g, \text{CO}_2) + 5.5 \Delta_f H_m^\circ(l, \text{H}_2\text{O}) - \Delta_c H_m^\circ \end{aligned} \quad (3)$$

Results are given in Table 3.

3.2. Quantum chemical calculations for $\Delta_f H_m^\circ(g)$ of $[\text{C}_2\text{OHmim}][\text{DCA}]$

In our recent work [2–4] we have shown, that one of the aprotic ionic liquids $[\text{C}_4\text{MIM}][\text{DCA}]$ exist in the gaseous phase as contact ion pairs and not as a gas of separated ions. We have calculated the enthalpy of formation of $[\text{C}_2\text{OHmim}][\text{DCA}]$ using G3(MP2) and applying atomization procedure.

Energies and frequencies of normal modes for cation and anion of $[\text{C}_2\text{OHmim}][\text{DCA}]$ were preliminary evaluated on RB3LYP/6-31+G(d,p) level of theory. After that according to the distribution of the partial charges on the atoms (Mulliken charges) in cation and anion the 20 different initial conformations for the $[\text{C}_2\text{OHmim}][\text{DCA}]$ were generated. The geometry of which were optimized on RB3LYP/6-31+G(d,p) theory level.

Five most stable conformers were chosen from the previous set. The total energies and enthalpies at 298.15 K for them were calculated by G3(MP2) method. We have obtained the G3(MP2) total energy at 0 K, $E_0 = -659.408942$ Hartree, and enthalpy at 298.15 K, $H_{298} = -659.392926$ Hartree for the most stable conformer. From these values the enthalpy of formation $\Delta_f H_m^\circ(g) = 235.6 \text{ kJ mol}^{-1}$ at 298.15 K was calculated (see Table 3).

3.3. Are the group contribution methods applicable to $[\text{C}_2\text{OHmim}][\text{DCA}]$?

Group-additivity (GA) methods are well recognized to provide a reasonable consistency test of experimental data on thermochemical properties of molecular compounds [11–14]. One of the indicators to detect possible experimental errors is a large deviation between experimental and calculated by GA values – especially if other, closely related compounds show no such discrepancy. The most successful GA method for estimating thermodynamic properties has been suggested by Benson [11]. Unfortunately, the available data of enthalpies of formation [2–4] are too limited for a quantitative parameterization of any specific for ionic liquids groups. Due to scarcity of the available data, we decided to check validity of the group-additivity rules using the comparison of our new experimental value of $\Delta_f H_m^\circ(l)$ for $[\text{C}_2\text{OHmim}][\text{DCA}]$ measured by combustion calorimetry with the $\Delta_f H_m^\circ(l)$ of a structurally parent ionic liquid 1-ethyl-3-methylimidazolium dicyanamide $[\text{C}_2\text{MIM}][\text{DCA}]$, where experimental data on $\Delta_f H_m^\circ(l, [\text{C}_2\text{MIM}][\text{DCA}], 298.15 \text{ K}) = 235.3 \pm 3.1 \text{ kJ mol}^{-1}$ was measured in our lab recently [14]. Provided that the Benson's group additivity values [11,12] derived for molecular compounds are transferable to ionic liquids, it is easy to calculate enthalpy of formation of $[\text{C}_2\text{OHmim}][\text{DCA}]$ using the enthalpy of formation of $[\text{C}_2\text{MIM}][\text{DCA}]$ as a starting molecule and group-additivity values given in Ref. [12]. Indeed, the enthalpy of formation of $[\text{C}_2\text{OHmim}][\text{DCA}]$ could be obtained from enthalpy of formation of $[\text{C}_2\text{MIM}][\text{DCA}]$ by the subtraction of contribution for the methyl group and adding the contributions for hydroxyl group

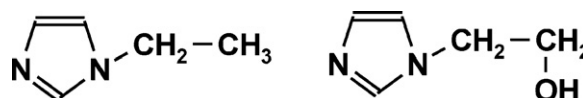


Fig. 2. Structures of 1-ethyl-imidazole and 1-ethanol-imidazole.

and methylene group connected to OH as follows:

$$\begin{aligned} \Delta_f H_m^\circ(l, [\text{C}_2\text{OHmim}][\text{DCA}]) \\ = \Delta_f H_m^\circ(l, [\text{C}_2\text{MIM}][\text{DCA}]) - \text{C}-(\text{C})(\text{H})_3 - \text{C}-(\text{C})(\text{O})(\text{H})_2 + \text{O}(\text{C})(\text{H}) \\ = 235.3 - (-48.5) + (-38.1) + (-190.4) = 55.3 \text{ kJ mol}^{-1} \end{aligned}$$

As can be seen, the disagreement between this estimate with the experimental value $\Delta_f H_m^\circ(l, [\text{C}_2\text{OHmim}][\text{DCA}]) = 72.9 \pm 2.3 \text{ kJ mol}^{-1}$ is about 17 kJ mol^{-1} . However, these excessive 17 kJ mol^{-1} could be ascribed to the non-bonded interactions between hydroxyl and the imidazole-ring. The latter interaction is not taken into account in the frame of group-additivity procedure [11,12]. It is interesting to validate this non-bonded interaction with a comparison of enthalpies of formation of two molecules (see Fig. 2): 1-ethyl-imidazole ($\Delta_f H_m^\circ(g) = 110.8 \pm 4.3 \text{ kJ mol}^{-1}$) [15] and 1-ethanol-imidazole ($\Delta_f H_m^\circ(g) = -52.5 \text{ kJ mol}^{-1}$ was calculated using G3(MP2) and atomization procedure in this work). Using the procedure similar to those described above for ionic liquids (with the increments from [12]) we have obtained the following result:

$$\begin{aligned} \Delta_f H_m^\circ(g, 1\text{-ethanol-imidazole}) \\ = \Delta_f H_m^\circ(g, 1\text{-ethyl-imidazole}) - \text{C}-(\text{C})(\text{H})_3 - \text{C}-(\text{C})(\text{O})(\text{H})_2 \\ + \text{O}(\text{C})(\text{H}) = 110.8 - (-41.5) + (-33.9) + (-158.6) \\ = -39.9 \text{ kJ mol}^{-1} \end{aligned}$$

And again the difference between this estimate and the enthalpy of formation predicted by G3(MP2) for 1-ethanol-imidazole ($-52.5 \text{ kJ mol}^{-1}$) is about 13 kJ mol^{-1} and this value is in acceptable agreement with the value for the non-bonded interactions between hydroxyl and the imidazole-ring in the ionic liquid. This fact can be considered as the evidence, that enthalpies of formation of ionic liquids do obey the simple additivity rules and that group-additivity values developed for the molecular compounds [11,12] could be generally used for predicting thermochemical properties of the ionic species. However, in our recent work we have shown that the additivity parameters for ionic liquids could be somewhat different from those for molecular compounds [14].

3.4. Enthalpy of vaporization $\Delta_v H_m^\circ$ of $[\text{C}_2\text{OHmim}][\text{DCA}]$

In this work we tried to perform the transpiration experiments on $[\text{C}_2\text{OHmim}][\text{DCA}]$ in the temperature range 423–443 K at a flow rate of $8 \text{ dm}^3 \text{ h}^{-1}$. Such a flow rate is close to the upper limit of our apparatus $12 \text{ dm}^3 \text{ h}^{-1}$, where the saturation of the transporting gas with the IL in the saturation tube is still ensured. However, no condensate was detected in the cold trap. Observation of the sample in the saturation tube revealed an intense brown coloration of the IL. Clearly, neither the vapor pressure nor the enthalpy of vaporization of this IL can be determined using the transpiration method. Thus, another indirect method has been applied for this purpose. In our recent papers [2–4] we have developed an alternative procedure to estimate vaporization enthalpies of ILs in such cases using a combination of the traditional combustion calorimetry with the high-level quantum chemical calculations according to Eq. (1). In order to obtain the molar enthalpy of vaporization of $[\text{C}_2\text{OHmim}][\text{DCA}]$ at 298.15 K we

have used the molar enthalpy of formation of [C₂OHmim][DCA] in the liquid state, $\Delta_f H_m^\circ(l) = 72.9 \pm 2.3 \text{ kJ mol}^{-1}$ obtained by precision combustion calorimetry (see Table 3), and the gaseous enthalpy of formation, $\Delta_f H_m^\circ(g)$, of [C₂OHmim][DCA] calculated by first-principles methods. We already demonstrated that good agreement between $\Delta_f^\circ H_m$ values derived from Eq. (1) with the experimental results is obtained in case of other systems [2–4,14]. Therefore, we have also applied this method in the present work to derive the vaporization enthalpy of [C₂OHmim][DCA]. Using the averaged value of $\Delta_f H_m^\circ(g) = 235.6 \text{ kJ mol}^{-1}$ calculated by the G3(MP2) and applying Eq. (1) the enthalpy of vaporization $\Delta_f^\circ H_m$ ([C₂OHmim][DCA]) = 162.7 kJ mol⁻¹ at 298.15 K has been obtained. Our result is consonant with the enthalpy of vaporization of the structurally parent imidazolium based ionic liquid $\Delta_f^\circ H_m$ ([C₄MIM][DCA]) = 157.2 ± 1.1 kJ mol⁻¹ measured by the transpiration method in our lab recently [4].

4. Conclusions

Combination of the experimental methods (combustion calorimetry, vapor pressure measurements) with the high-level first-principles calculations has turned out to be an alternative and reliable method to obtain the molar enthalpies of formation and enthalpy of vaporization of [C₂OHmim][DCA]. Simple group-additivity rules have been tested for the enthalpy of formation in the liquid phase, but it seems to be that the group-additivity parameters derived for molecular compounds could be generally applied for ionic liquids. Our new results can be used as reference values for molecular modeling studies and validation for their quality.

Acknowledgment

This work has been supported by the German Science Foundation (DFG) in the frame of the priority program SPP 1191 “Ionic Liquids”.

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