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S Supporting Information

ABSTRACT: Thermochemical studies of the ionic liquids 1-ethyl-3-methylimidazolium tricyanomethanide [C₂MIM][C(CN)₃] and 1-butyl-3-methylimidazolium tricyanomethanide $[C_4MIM][C(CN)_3]$ have been performed in this work. Vaporization enthalpies have been obtained using a recently developed quartz crystal microbalance (QCM) technique. The molar enthalpies of formation of these ionic liquids in the liquid state were measured by means of combustion calorimetry. A combination of the results obtained from QCM and combustion calorimetry lead to values of gaseous molar enthalpies of formation of $[C_nMIM][C(CN)_3]$. First-principles calculations of the enthalpies of formation in the gaseous phase for the ionic liquids $[C_nMIM][C(CN)_3]$ have been performed using the CBS-QB3 and G3MP2 theory and have been compared



with the experimental data. Furthermore, experimental results of 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 $[C(CN)_3]$ available in the literature have been collected and checked for consistency using a group additivity procedure. It has been found that the enthalpies of formation of these ionic liquids roughly obey group additivity rules.

1. INTRODUCTION

The almost negligible vapor pressure of ionic liquids (ILs) at ambient temperatures is one of the most remarkable features of these neoteric solvents. It is of importance for many practical applications, where ILs are used as a valuable alternative for common volatile solvents.¹ The structure of ionic liquids directly impacts their properties. ILs are well-known as the "designer solvents" with easily tunable properties. Experimental and theoretical study of the relationship between structure and properties of ionic liquids may provide an important basis for designing new ionic liquids with desired properties. Ionic liquids with the tricyanomethanide anion $[C(CN)_3]$ are low melting, thermally stable ($T_{dec} \approx 300$ °C) compounds which have a considerable potential as a reaction medium.² The tricyanomethanide ionic liquids have electric conductivities, thermal stabilities, and electrochemical properties similar to the dicyanoamide ILs, but they are less hygroscopic.² Studies of vaporization enthalpies and vapor pressures of ILs are scarce³ because of obvious problems with measuring the extremely low vapor pressures and their temperature dependencies. We have contributed to the solution of this problem by using an improved version of the Knudsen method⁴ and the transpiration method⁵ as well as by combination of quantum-chemical calculations with the combustion calorimetry.^{4–8} Just recently a new method for the determination of vaporization enthalpies of extremely low volatile ionic liquids has been developed using the quartz crystal microbalance (QCM) tecnique.⁹ Due to the very high sensitivity of the quartz sensor,

it has become possible to measure vaporization enthalpies at T < 400 K. In this work, we have measured the enthalpies of vaporization enthalpies for 1-butyl-3-methylimidazolium tricyanomethanide $[C_2MIM][C(CN)_3]$ and 1-ethyl-3-methylimidazolium tricyanomethanide $[C_4MIM][C(CN)_3]$ using the QCM method. The combination of vaporization enthalpies obtained with the results from combustion calorimetry has allowed us to determine gaseous molar enthalpies of formation $\Delta_{f}H^{\circ}_{m}(g)$ of $[C_{n}MIM][C(CN)_{3}]$. Additionally, first-principles calculations for these compounds have been performed to test the consistency of the experimental data with calculated ones. Moreover, a set of thermochemical properties of ILs of the general formula [C_nMIM] [Anion] have been collected and analyzed in terms of group additivity rules.^{10,11}

2. EXPERIMENTAL PROCEDURE AND METHODS OF FIRST-PRINCIPLES CALCULATIONS

2.1. Materials. 1-Ethyl-3-methylimidazolium tricyanomethanide $[C_2MIM][C(CN)_3]$, $C_{10}H_{11}N_5$ (CAS 666823-18-3), was synthesized. The purity of the sample for the thermochemical studies was \geq 99.0% (NMR). The sample of 1-butyl-3-methylimidazolium tricyanomethanide [C₄MIM][C(CN)₃], C₁₂H₁₅N₅ (CAS 878027-73-7), was of commercial origin (Merck, 4.90330)

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with a purity of \geq 98.0% (HPLC). It contains <0.1% of halides according to specifications stated by the suppliers. Such an amount of halide impurity does not affect vapor pressure measurements and combustion experiments. Prior to experiments, all IL samples were subjected to vacuum at 333 K for more than 24 h to remove possible traces of solvents and moisture. The water concentration of 712 ppm in $[C_2MIM][C(CN)_3]$ and of 660 ppm in $[C_4MIM][C(CN)_3]$ was determined by Karl Fischer titration before starting the experiments, and appropriate corrections have been made for combustion results. We used a Mettler DL35 Karl Fischer Titrator with Hydranal Composite 2, Hydranal Methanol Dry, and Hydranal Eichstandard 5.0 (Riedel-de Haen). Samples of the ILs were kept and handled under a nitrogen stream in a special glass device furnished with a septum for the sample extraction using a syringe.

2.2. Synthesis of $[C_2MIM][C(CN)_3]$. 1-Ethyl-3-methylimidazolium tricyanomethanide $[C_2MIM][C(CN)_3]$ was not commercially available, and it was synthesized according to the procedure developed by Brand et al.² The first synthetic step includes the formation of the nearly insoluble silver salts in water (Ag[$C(CN)_3$]) from AgNO₃ and Na[$C(CN)_3$]. Reaction of Ag[$C(CN)_3$] with $[C_2MIM][Br]$ results in the formation of a water-soluble $[C_2MIM]$ - $[C(CN)_3]$ which can be separated from the AgBr precipitate by filtration. A specific drying procedure involving stepwise adding and removing dried methanol, tetrahydrofuran, and dichloromethane followed by removing traces of water or solvent molecules in high vacuum is necessary to obtain pure ionic liquids.

2.3. Determination of the Vaporization Enthalpy Using the Quartz Crystal Microbalance Technique. Enthalpies of vaporization of of $[C_nMIM][C(CN)_3]$ have been measured using the QCM technique. The experimental setup and the measuring procedure have been reported recently.9 In short, a sample of IL filled into an open stainless steel (316Ti) crucible is placed in a vacuum chamber (at 10^{-5} Pa). In contrast to the Knudsen technique, the total surface of the sample in the crucible is exposed to vacuum. The QCM is positioned directly over the crucible with the IL. The change of the vibrational frequency of the crystal Δf (is a measure of an amount of IL deposited on the cold QCM) was registered at constant temperatures. The quartz crystal is part of a commercially available sensor (BSH-150 by Inficon). The distance between the surfaces of the quartz crystal and IL was kept constant at ca. 25 mm. The temperature of the QCM and its holder is kept at (30.0 ± 0.1) °C by using a Julabo F12-MC thermostat. The change of the resonance frequency Δf was measured by a commercial device Q-pod from Inficon. The value of Δf is directly related to the mass deposition on the crystal according to the Sauerbrey equation¹²

$$\Delta f = -C \cdot f^2 \cdot \Delta m \cdot S_{\rm C}^{-1} \tag{1}$$

where *f* is the fundamental frequency of the crystal (6 MHz in this case); Δm is the mass increase (in g); S_C is the area of the crystal (in cm²); and *C* is a constant (2.26 × 10⁻⁶ cm² · g⁻¹ · Hz⁻¹).¹² The measured frequency loss rate *d*f/*d*t is related to the molar enthalpy of vaporization by eq 2⁹

$$\ln\left(\frac{\mathrm{d}f}{\mathrm{d}t}\sqrt{T}\right) = A' - \frac{\Delta_{\mathrm{l}}^{\mathrm{g}}H_{\mathrm{m}}^{\mathrm{o}}(T_{0}) - \Delta_{\mathrm{l}}^{\mathrm{g}}C_{\mathrm{pm}}^{\mathrm{o}}T_{0}}{R} \left(\frac{1}{T} - \frac{1}{T_{0}}\right) + \frac{\Delta_{\mathrm{l}}^{\mathrm{g}}C_{\mathrm{pm}}^{\mathrm{o}}}{R}\ln\left(\frac{T}{T_{0}}\right)$$

$$(2)$$

Table 1. Enthalpies of Vaporization of $[C_nMIM][C(CN)_3]$ (in kJ·mol⁻¹)

ILs	T-range, K	T _{av} , K	$\Delta^{ m g}_{ m I} H^{ m o}_{ m m}$ at $T_{ m av}$	$\Delta^{ m g}_{ m I} H^{ m o}_{ m m}$ at 298.15 K a	
$[C_2MIM][C(CN)_3]$	400-448	423.2	126.0 ± 1.0	138.8 ± 5.0	
$[C_4MIM][C(CN)_3]$	405-453	428.3	129.8 ± 1.4	143.2 ± 5.0	
⁴ Experimental enthalpies of vaporization for ILs are obtained at 298 K					
with $\Delta_{\rm l}^{\rm g} C_{\rm p,m}^{\rm o} = -100$	[∙K ^{−1} ∙mol [−]	-1			

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

$$\Delta_l^g H_m^{\circ}(T) = \Delta_l^g H_m^{\circ}(T_0) + \Delta_l^g C_{pm}^{\circ} \cdot (T - T_0)$$
(3)

To detect and avoid any possible effect of the impurities on the measured frequency loss rate df/dt, a typical experiment has been performed in several series with increasing and decreasing temperature steps. Every step consisted of 7 to 11 constant temperature points of mass loss rate determination. The study was finished when the enthalpy of vaporization obtained in sequential runs agreed within the assessed uncertainty of determination of $\pm 1 \text{ kJ} \cdot \text{mol}^{-1}$. To confirm the absence of decomposition of IL under the experimental conditions, the residual IL in the crucible and the IL deposit on QCM were analyzed by ATR-IR. Experimental results are given in Table 1, and the primary experimental data are listed in Tables S1 and S2 (see Supporting Information).

Due to the very high sensitivity of the quartz crystal microbalance, it is possible to study vaporization processes already at 400 K, reducing the temperature of measuring vaporization enthalpies by approximately 100 K in comparison to other conventional techniques. Test measurements with $[C_2mim][NTf_2]$ gave results very close to the available experimental values indicating thermodynamic consistency of the procedure.⁹ In the current work, we have obtained vaporization enthalpies of $[C_mMIM][C(CN)_3]$ using the QCM method.

Our primary experimental results obtained by the QCM measurements on $[C_nMIM][C(CN)_3]$ are given in Tables S1 and S2 (Supporting Information). We measured vaporization enthalpies for [C₂MIM][C(CN)₃] in the range 400-448 K and for $[C_4MIM][C(CN)_3]$ in the range 405–453 K. To apply eqs 2 and 3 for the data treatment, values of $\Delta_l^g C_{pm}^o$ are required. We have already discussed recently⁹ that the value of $\Delta_{\rm f}^{\rm g} C_{\rm pm}^{\rm o} = -$ 100 $J \cdot K^{-1} \cdot mol^{-1}$ commonly used for all ILs regardless of their structure is apparently a doubtful choice due to the lack of experimental data and questionable quantum-chemical estimations of $C_{pm}^{o}(g)$. To assess the impact of the $\Delta_{f}^{g}C_{p}$ on $\Delta_{f}^{g}H_{m}^{o}(T)$, we have calculated enthalpies of vaporization using arbitrary fixed $\Delta_{\rm I}^{\rm g}C_{\rm p}$ values of -40, -100, and -200 J·K⁻¹·mol⁻¹ which cover the range of $\Delta_{I}^{g}C_{pm}^{o}$ values expected (see Tables S1 and S2 in Supporting Information). It turned out that changes of the $\Delta_1^g H^{\circ}_m$ -(T) values were about 2.5 kJ·mol⁻¹ within the range of these $\Delta_{I}^{g}C_{pm}^{o}$ values. This increases the uncertainties of the vaporization enthalpy derived by all experimental methods due to ill-defined $\Delta_{\rm l}^{\rm g} C_{\rm p}$ values.

ILs	$\Delta_{\rm c} {H^{\rm o}}_{\rm m}({\rm l})$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({\rm l})$	$\Delta^{g}_{I}H^{\circ}_{m}$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({\rm g}) \exp$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({\rm g})$ CBS-QB3	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({ m g})~{ m G3MP2}$
$[C_2 MIM][C(CN)_3]$	-5849.4 ± 2.2	342.2 ± 2.5	138.8 ± 5.0	481.0 ± 5.6	473.3 ± 5.0	486.0 ± 5.0
	-/143.1 ± 2.1	2/9.2 ± 2.0	143.2 ± 3.0	422.4 ± 3.0	429.7 ± 3.0	439.8 ± 3.0

Table 2. Thermochemical Data at T = 298.15 K ($p^{\circ} = 0.1$ MPa) for $[C_nMIM][N(CN)_3]$, kJ·mol⁻¹

Figure 1. Optimized with G3MP2 structures of $[C_2MIM][C(CN)_3]$ and $[C_4MIM][C(CN)_3]$.

From adjusting eq 2 to the QCM data with $T_0 = 298$ K and $\Delta_{\rm I}^{\rm g} C_{\rm pm}^{\rm o} = -100 \, {\rm J} \cdot {\rm K}^{-1} \cdot {\rm mol}^{-1}$, enthalpies of vaporization at the reference temperature 298 K have also been obtained (see Table 1). For $[C_2 \text{mim}][C(CN)_3]$, the values of $\Delta_l^g H_m^o(298 \text{ K})$ of 131.3, 138.8, and 151.3 kJ·mol⁻¹, as well as for $[C_4 \text{mim}]$ - $[C(CN)_3]$, the values of $\Delta_1^g H_m^o(298 \text{ K})$ of 135.4, 143.2, and 156.2 kJ·mol⁻¹, have been obtained using $\Delta_{\rm f}^{\rm g}C_{\rm pm}^{\rm o}$ of -40, -100, and -200 J·K⁻¹·mol⁻¹, respectively (Table S3 in Supporting Information). Obviously the uncertainty of $\Delta_{I}^{g}C_{pm}^{o}$ affects distinctly the values of $\Delta_l^{g} H^{\circ}_{m}$ at 298 K. As a result, no reliable standard data for $\Delta_l^g H_m^o(298 \text{ K})$ can be obtained. For the sake of comparison with our earlier work, we calculated $\Delta_{I}^{g}H_{m}^{o}(298 \text{ K})$ using the previously acknowledged⁵ for ILs value $\Delta_I^g C_{pm}^o = -$ 100 $J \cdot K^{-1} \cdot mol^{-1}$. Values of $\Delta_l^g H_m^o(298 \text{ K})$ are given in Table 1 together with the data referred to the average temperatures $\Delta_{\rm I}^{\rm g} H^{\circ}{}_{\rm m}(T_{\rm av})$. To account for the uncertainty of the vaporization enthalpy due to use of the ill-defined for ILs $\Delta_{l}^{g}C_{pm}^{o}$ values, we suggest to assign an uncertainty of 5.0 kJ·mol⁻¹ for $\Delta_{\rm f}^{\rm g}H_{\rm m}^{\rm o}(298 \text{ K})$.

2.4. Thermochemical Measurements: Combustion Calorimetry. An isoperibol bomb calorimeter was used for measuring the energy of combustion of $[C_nMIM][C(CN)_3]$. At least six successful experiments were carried out for each compound (see Table S4 and S5 in Supporting Information). The detailed procedure has been described previously.⁵ The combustion products were analyzed for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter ε_{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 \cdot dm⁻³ NaOH (aq). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure was applied.¹³ Values of the standard specific energies of combustion $\Delta_c u^{\circ}$, together with the necessary auxiliary quantities, are given in Table S6 (Supporting Information). To derive the molar enthalpy of formation in the liquid state $\Delta_{\rm f} H^{\circ}{}_{\rm m}(l)$ from the molar standard enthalpy of combustion $\Delta_c H^{\circ}_{m}$, molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$ were taken from the literature, as assigned by CODATA.¹⁴ Table 2 contains the derived standard molar enthalpy of combustion and standard molar enthalpy of formation of the $[C_nMIM][C(CN)_3]$. The total uncertainty was calculated

according to the guidelines presented by Olofsson.¹⁵ The uncertainty assigned to $\Delta_{f}H^{\circ}_{m}(l)$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and of the enthalpies of formation of the reaction products H₂O and CO₂.

Results of combustion experiments on $[C_nMIM][C(CN)_3]$ are summarized in the Supporting Information. The standard energies of combustion $\Delta_{c}u^{\circ} = -(29\,065.6 \pm 4.4) \text{ J} \cdot \text{g}^{-1}$ for $[C_2\text{MIM}][C(\text{CN})_3]$ and $\Delta_{c}u^{\circ} = -(31149.5 \pm 3.3) \text{ J} \cdot \text{g}^{-1}$ for $[C_4MIM][C(CN)_3]$ have been measured and used to derive standard molar enthalpies of combustion and standard molar enthalpies of formation in the liquid state, $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$, based on the chemical reactions

$$C_{10}H_{11}N_5 + 12.75O_2 = 10CO_2 + 5.5H_2O + 2.5N_2$$
(4)

$$C_{12}H_{15}N_5 + 15.75O_2 = 12CO_2 + 7.5H_2O + 2.5N_2$$
(5)

Since the molar enthalpies of formation of $H_2O(l)$ and $CO_2(g)$ are known,¹⁴ values for $\Delta_{f}H^{\circ}_{m}(l)$ of $[C_{n}MIM][C(CN)_{3}]$ have been obtained from the enthalpic balance according to eqs 3 and 5 (see Table 2)

2.5. First-Principles Calculations. Standard ab initio calculations were performed using the Gaussian 03 Rev.04 program package.¹⁶ Rotational conformers of the $[C_nMIM]$ 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 coplanar conformation. 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 $[C_nMIM][C(CN)_3]$ 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 the separated ions was calculated using the supermolecule method at the B3LYP level. The optimized structures of the $[C_nMIM][C(CN)_3]$ ion pairs are presented in Figure 1.



Figure 2. Most stable conformer of $[C_2MIM][C(CN)_3]$ calculated using G3MP2 and CBS-QB3. The difference in the enthalpies is 3.4 kJ·mol⁻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. Its modification, the G3MP2 theory, reduces orders of Møller-Plesset perturbation theory.¹⁷ This method saves considerable computational time compared to the G3 theory with limited loss in accuracy. G3MP2 uses geometries from 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 the theory (for details see ref 17). The CBS-QB3 theory uses geometries from B3LYP/6-311G(2d,d,p) calculation and 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.¹⁸ Calculated values of the enthalpy of formation in the gaseous phases are based on the electronic energy calculations using standard procedures¹⁹ of statistical thermodynamics for calculating temperature-dependent contributions to the enthalpy based on all frequencies and moments of inertia.

3. DISCUSSION

3.1. Enthalpies of Formation of $[C_nMIM][C(CN)_3]$ in the Gaseous State. The enthalpies of formation, $\Delta_f H^{\circ}_m(1)$, of $[C_nMIM][C(CN)_3]$, derived from the combustion experiments (Table 2, column 3) together with the vaporization enthalpies, derived from the QCM method (Table 2, column 4), are referred to the reference temperature T = 298.15 K. Using the equation $\Delta_f H^{\circ}_m(g) = \Delta_f H^{\circ}_m(1) + \Delta_f^g H^{\circ}_m$, we calculated the experimental values of the standard molar enthalpies of formation $\Delta_f H^{\circ}_m(g)$ for (Table 2, column 5). These values have been used to check the validity of first-principle methods as follows.

3.2. Quantum Chemical Calculations for $[C_nMIM][N(CN)_3]$. In recent papers, ^{5–7} we have shown that 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. We have calculated the enthalpies of formation, $\Delta_f H^{\circ}_m(g, 298 \text{ K})$, of $[C_nMIM][C(CN)_3]$ using G3MP2 and CBS-QB3 methods with the help of the following reactions

$$[C_2MIM][C(CN)_3] + 34CH_4 = 22C_2H_6 + 5NH_3 \quad (6)$$

$$[C_4MIM][C(CN)_3] + 36CH_4 = 24C_2H_6 + 5NH_3$$
(7)

Using enthalpies of the chemical reactions (according to eqs 6 and 7) calculated by G3MP2 or CBS-QB3 and experimental enthalpies of formation $\Delta_{f}H^{\circ}_{m}(g, 298 \text{ K})$ for CH₄, C₂H₆, and M_3 as recommended by Pedley et al.²⁰ (see Table S7 and S8 in Supporting Information), the enthalpies of formation of [C_nMIM]- $[C(CN)_3]$ have been calculated (see Table 2). Figure 1 shows the structures of the ILs optimized using G3MP2. In contrast to our previous experiences⁵⁻⁸ with the composite methods G3MP2 and CBS-QB3, the optimized conformations of ionic liquids $[C_nMIM][C(CN)_3]$ obtained from both methods have turned out to be slightly different (see Figure 2). The difference in the enthalpies between the most stable conformer of $[C_2MIM]$ $[C(CN)_3]$ calculated using G3MP2 and CBS-QB3 is 3.4 kJ·mol⁻¹. The difference in the enthalpies between the most stable conformer of [C₄MIM][C(CN)₃] calculated using G3MP2 and CBS-QB3 is 8.8 kJ·mol⁻¹. As a consequence, values of $\Delta_{\rm f} H^{\circ}_{\rm m}(g,$ 298 K) derived for $[C_2MIM][C(CN)_3]$ and $[C_4MIM]$ -[C(CN)₃] by using G3MP2 and CBS-QB3 are noticeably different. The results from the CBS-QB3 method are in agreement with the experimental values. The result obtained by the G3MP2 method is in good agreement with the experimental value for $[C_2MIM]$ - $[C(CN)_3]$ and is overestimated for $[C_4MIM][C(CN)_3]$. The result from the CBS-QB3 method is in good agreement with the experimental value for [C₄MIM][C(CN)₃] and is underestimated for $[C_4MIM][C(CN)_3]$. Both theoretical methods, G3MP2 and CBS-QB3, are supposed to be not reliable enough to predict the experimental results for ILs containing the tricyanometanide anion. These composite methods should be applied with precautions when calculating gaseous enthalpies of formation of ionic liquids containing the $[C(CN)_3]$ anion.

3.3. Application of Group-Additivity Rules for ILs. Groupadditivity (GA) methods are well-acknowledged approaches for testing the consistency of the experimental data of thermochemical properties of molecular compounds.^{8–11} The most successful GA method for estimating thermodynamic properties was suggested by Benson.¹⁰ This method serves as a valuable tool in

Table 3. Compilation of the Enthalpies of Vaporization, $\Delta_{\rm f}^{\rm g} H^{\circ}_{\rm m}$ and Enthalpies of Formation in the Liquid, $\Delta_{\rm f} H^{\circ}_{\rm m}(l)$, and in the Gaseous Phase, $\Delta_{\rm f} H^{\circ}_{\rm m}(g)$, for Some Alkanes, Alkanols, And Imidazolium-Based ILs at 298.15 K (in kJ·mol⁻¹)

fragment	$\Delta_l^g H_m^o$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({\rm l})$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({\rm g})$		
$CH_3-[CH_2]_2-CH_3$	22.4 ± 0.1	-146.6 ± 0.7	-125.6 ± 0.7		
$CH_3-[CH_2]_4-CH_3$	31.7 ± 0.1	-198.7 ± 0.8	-167.1 ± 0.8		
Δ^a	$\textbf{9.3}\pm\textbf{0.2}$	-52.1 ± 1.1	-41.5 ± 1.1		
$CH_3-[CH_2]_2-OH$	52.3 ± 0.1	-302.6 ± 0.5	-255.1 ± 0.5		
$CH_3-[CH_2]_4-OH$	61.7 ± 0.1	-351.6 ± 0.4	-294.7 ± 0.5		
Δ^a	$\textbf{9.4} \pm \textbf{0.2}$	-49.0 ± 0.6	-39.6 ± 0.7		
$[C_2MIM][N(CN)_2]^5$	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	$\textbf{0.2}\pm\textbf{2.4}$	-40.0 ± 4.1	-40.1 ± 4.7		
$[C_2MIM][NO_3]^7$	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 ± 7.8	-44.5 ± 3.5	-45.8 ± 6.9		
$[C_2MIM][C(CN)_3]$	138.8 ± 5.0	342.2 ± 2.5	481.0 ± 5.6		
$[C_4MIM][C(CN)_3]$	143.2 ± 5.0	279.2 ± 2.6	422.4 ± 5.6		
Δ^a	$\textbf{4.4} \pm \textbf{7.0}$	-63.5 ± 3.6	-58.6 ± 7.9		
^a Difference between C ₄ and C ₂ derivatives.					

chemical engineering. In our recent study, we have shown the general capability to apply a group contribution method to ionic liquids.⁸ We have extended now these studies using the new data obtained in the current work. In Table 3 the thermochemical data on imidazolium-based ionic liquids $[C_nMIM]$ [Anion] with n = 2 and 4 are collected. Due to the 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, differences in enthalpies (vaporization or formation) of structurally parent molecules have to be considered

$$\begin{array}{l} {\rm CH}_{3}-{\rm [CH}_{2}{\rm]}_{2}-{\rm CH}_{3} \mbox{ and } {\rm CH}_{3}-{\rm [CH}_{2}{\rm]}_{4}-{\rm CH}_{3} \mbox{ } \\ {\rm CH}_{3}-{\rm [CH}_{2}{\rm]}_{2}-{\rm OH} \mbox{ and } {\rm CH}_{3}-{\rm [CH}_{2}{\rm]}_{4}-{\rm OH} \mbox{ } \\ {\rm [C}_{2}{
m MIM}][{
m Anion}] \mbox{ and } {\rm [C}_{4}{
m MIM}][{
m Anion}] \end{array}$$

These differences could serve as a simple indication whether the molecules obey additivity rules or not.

Experimental data on vaporization enthalpies of two *n*-alkanes and *n*-alcohols are presented in column 2 of Table 3. It is 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) and are within the boundaries of the experimental uncertainties for 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 3, column 2) are close to zero (within the boundaries of the experimental uncertainties), and no additivity rules for this property seem to exist for ILs. However, our new results from QCM for $[C_nMIM]$ [C(CN)₃] with the difference between C₄ and C₂ derivatives of $\Delta = (4.4 \pm 7.0)$ kJ·mol⁻¹ demonstrate distinctly the trend which is similar with those for molecular liquids where Δ is typically between 4 and 5 kJ·mol⁻¹.

Experimental data on enthalpies of formation, $\Delta_{f}H^{\circ}_{m}(l)$, of two *n*-alkanes and *n*-alcohols are presented in column 3 of Table 3. The difference between $CH_{3}-[CH_{2}]_{4}-R$ and $CH_{3}-[CH_{2}]_{2}-R$ is ca. $-50 \text{ kJ} \cdot \text{mol}^{-1}$ for both homologous series. The corresponding difference for the [C₄MIM][Anion] and [C₂MIM]-[Anion] (Table 3, column 3) is only -(40-45) kJ·mol⁻¹, which is distinctly lower than $2(CH_2) = 2(-25.5) = -51.0$ kJ·mol⁻¹ expected⁹ from the molecular compounds. Our new results obtained from combustion calorimetry for [C_nMIM][C(CN)₃] with the difference between C₄ and C₂ derivatives of $\Delta = -(63.5 \pm$ 3.6) kJ·mol⁻¹ do not correspond to our expectation for similarity in comparison with the data available for molecular and ionic compounds collected in Table 3.

Experimental data on enthalpies of formation, $\Delta_f H^{\circ}_m(g)$, of two *n*-alkanes and *n*-alcohols are presented in column 4 of Table 3. 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 3, column 4) seem to be remarkably consistent. On average, the contribution of -(40 - 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, $\Delta_f H^{\circ}_m(g)$, of ILs follow the group additivity rules established for molecular compounds. However, our new $\Delta_f H^{\circ}_m(g)$ results for $[C_nMIM][C(CN)_3]$ with the difference between C_4 and C_2 derivatives of $\Delta = -(58.6 \pm 7.6)$ kJ·mol⁻¹ are somewhat higher in comparison with the data available for molecular and ionic compounds collected in Table 3.

We conclude that application of group additivity rules for the enthalpies of vaporization and enthalpies of formation of the series of $[C_nMIM]$ [Anion] ionic liquids is still questionable. Apparently, more experimental information is required for detecting similarities or disparities of additivity parameters of molecular and ionic compounds.

ASSOCIATED CONTENT

Supporting Information. Primary experimental results from OCM techniques; results for combustion experiments; auxiliary quantities for combustion calorimetry; CBS-QB3 and G3MP2 energies and enthalpies of compounds under study; and spectra of $[C_nMIM][C(CN)_3]$ used in QCM investigations. This material is available free of charge via the Internet at http://pubs. acs.org.

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