Ionic Liquids: Differential Scanning Calorimetry as a New Indirect Method for Determination of Vaporization Enthalpies

Sergey P. Verevkin,*^{,†} Vladimir N. Emel'yanenko, Dzmitry H. Zaitsau, and Ricardas V. Ralys

Department of Physical Chemistry, University of Rostock, Dr-Lorenz-Weg. 1, 18059 Rostock, Germany

Christoph Schick[†]

Department of Physics, University of Rostock, Wissmarsche Str. 43-45, 18057 Rostock, Germany

Supporting Information

ABSTRACT: Differential scanning calorimetry (DSC) has been used to measure enthalpies of synthesis reactions of the 1-alkyl-3-methylimidazolium bromide [C, mim][Br] ionic liquids from 1-methylimidazole and *n*-alkyl bromides (with n = 4, 5, 6, 7, and 8). The optimal experimental conditions have been elaborated. Enthalpies of formation of these ionic liquids in the liquid state have been determined using the DSC results according to the Hess Law. The ideal-gas enthalpies of formation of $[C_n \min][Br]$ were calculated using the methods of quantum chemistry. They were used together with the DSC results to derive indirectly the enthalpies of vaporization of the ionic liquids under study. In order to validate the indirect determination, the experimental vaporization enthalpy of [C₄mim][Br] was measured by using a quartz crystal microbalance (QCM). The combination of reaction enthalpy measurements by DSC with modern high-level first-principles calculations opens valuable indirect thermochemical options to obtain values of vaporization enthalpies of ionic liquids.



1. INTRODUCTION

Ionic liquids (ILs) exhibit unique physical-chemical properties such as negligibly low vapor pressure at ambient temperatures and thermal stability at elevated temperatures. ILs might be useful as environmentally benign solvents that could replace volatile organic compounds. ILs have also widespread potential for practical applications such as heat transfer and storage medium in solar thermal energy systems as well as for many other areas such as fuel cells and rechargeable batteries. By varying the length of the alkane chains of the cationic core and the type or size of the anion, the solvent properties of ILs can be tailored to meet the requirements of specific applications to create an almost infinite set of "designer solvents". Systematic studies of thermodynamic properties within ionic liquid homological series (e.g., imidazolium-, pyridinium-, ammonium-, or pyrrolidinium-based ILs) are of interest, because they are required for the validation and development of the molecular modeling¹ and first-principles methods² toward this new class of solvents.

Currently, the most widely used starting materials for imidazolium-based ionic liquids are imidazolium halides (mostly bromides and chlorides). The latter are commonly synthesized by a quaternization reaction of a substituted imidazole with alkyl halides. In most cases the IL synthesis reactions are highly exothermic and the kinetics was shown to be fast.³ The heat management for the reactor design and operation is a crucial point leading to high quality of the resulting product and preventing of a thermal runaway. Thus, a systematic accumulation of reaction enthalpy data of ILs synthesis is apparently required and calorimetry is a suitable experimental tool for this purpose.

Differential scanning calorimetry (DSC) is widely used for studies of heat capacities, enthalpies of phase transitions (fusion, mesomorphic, vaporization), and chemical reactions, etc.⁴ This technique offers important advantages, such as the small quantity of sample necessary for the experiment (a few milligrams), handiness of manipulation, rapidity of measurement, versatility, and precision of temperature control. DSC is also very useful in the study of physical-chemical processes, such as the determination of the kinetics and thermodynamics of polymerization,⁵ due to the fact that these types of reactions are exothermic and so they can be easily followed isothermally and dynamically by DSC. This study reports an elaboration and development of a DSC procedure for reliable measurements of reaction enthalpies of ILs synthesis.

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Figure 1. A cycle of the thermochemical measurements and calculation leading to the vaporization enthalpies of ILs.

In this work, the enthalpies of reaction of 1-methylimidazole with the linear butyl-, pentyl-, hexyl-, heptyl-, and octyl bromides:

were determined in the liquid phase with a commercially available DSC. Using these results, the molar enthalpies of formation, $\Delta_f H^o{}_m(liq)$, of the $[C_n mim][Br]$ family were derived according to the Hess law. Experimental values of $\Delta_f H^o{}_m(liq)$ together with the gaseous enthalpies of formation $\Delta_f H^o{}_m(g)$ of these ILs calculated by first-principles composite CBS-QB3 method were used to derive enthalpies of vaporization of $[C_n mim][Br]$ indirectly. In order to validate this indirect procedure, the enthalpy of vaporization of $[C_4 mim][Br]$ was also measured using a quartz crystal microbalance (QCM). A cycle of the thermochemical measurements and calculation leading to the vaporization enthalpies of ILs is presented in Figure 1.

2. EXPERIMENTAL SECTION

2.1. Materials and Chemicals. Samples of 1-methylimidazole (MeIm) and *n*-alkyl bromides (R-Br) were of commercial origin, and they were 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 %) could be detected in the samples used for the measurements. The purity of the reactants (especially water traces) was decisive for the quality of the measurements by any method, but it was of crucial importance for the DSC method because of the very tiny amounts of samples used. The filling station for the DSC pans was in a glovebox under protecting nitrogen atmosphere.

2.2. Differential Scanning Calorimetry: Measurements of Reaction Enthalpy. The general principles for the heat-flux DSC measuring the enthalpies of chemical reactions are well documented.^{4,6} In short, in order to obtain a reaction heat effect in a dynamic temperature scan mode, the temperature difference between a sample pan and an empty reference pan was measured and converted into a heat flux value. The peak

corresponding to this exothermic heat effect was then integrated over the time range of the effect and a total enthalpy of reaction was determined from the area of the DSC peak. The heat released during the IL synthesis reaction 1 was related to the molar amount of a stoichiometrically deficient reactant in the starting formulation.

In the present work, the enthalpy of reaction was measured using a Mettler-Toledo 822 heat flux DSC with a MultiSTAR FRS5 sensor and a mechanical refrigerating system. Before measurements on the ILs, two standard materials, indium (99.999% pure) and zinc (99.999% pure), were used to calibrate the temperature and heat flow scales of the DSC.

ILs are most commonly synthesized by a quaternization reaction of a substituted amine (or phosphine, N-heterocycles, etc.) with alkyl halides, alkyl sulfates, alkylmethanesulfonates, etc. As a rule, such N-alkylation reactions are highly exothermal and very fast even at room temperature. For example, the reaction of MeIm with trifluoromethanesulfonate⁷ at room temperature is extremely fast, and also the reaction of MeIm with diethyl sulfate is fast,⁸ but the reaction of MeIm with butyl chloride is very slow.⁹ As a consequence, two different procedures have to be developed to prepare samples for DSC studies, depending on the reaction rate at room temperature. The first one was applied for the slow reactions, and the second procedure requiring additional precautions in order to preclude any reaction before equilibration of the DSC measuring cell.

2.2.1. Slow Reactions. Since the reaction rates at room temperature were considered as negligible, the reactants can be mixed without any precautions. Typically, 6-15 mg of starting materials was placed in a standard 40 μ L aluminum DSC pan which was weighed with an electronic balance with the resolution of ± 0.00005 g. Air buoyancy corrections were made, using known densities of materials. Charging of the pan with the starting materials was convenient to perform with one-way syringes. The pan was hermetically sealed with a cover to eliminate any evaporation of the reagents. The pan was weighed before and after each experiment to detect any mass loss during the measurements. Experiments with an occasional mass loss were rejected. Measurements were performed in the

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range 273–500 K with scanning rates between 10 and 50 $\text{K}\cdot\text{min}^{-1}$.

2.2.2. Fast Reactions. Due to the fact that for fast reactions part of the heat could be released already by charging of the pan at room temperature, the reactants have to be thoroughly separated inside the pan before the onset of the measurement. Any separation membrane or any other mechanical facility is hardly possible to install inside of the tiny (40 μ L) aluminum pan. In preliminary experiments, a separation of reactants in the pan with a wax baffle has heavily aggravated the acquisition of the reaction peak because of an additional contribution from fusion of the wax. This idea was rejected. Instead, silicone oil has turned out to be a very practical thing for the reactants' separation. Indeed, the silicone oil is nonvolatile, chemically inert, and thermally stable, and, as a rule, it has negligible miscibility with chemicals common for the ionic liquids synthesis. Moreover, different types of commercially available silicone oils have broad variations of densities. Hence, it is easy to find a specific silicone oil with the density just between the values of the two starting reactants. Thus, the thorough separation of the reactants in the pan was achieved according to the "sandwich" layers having the denser compound on the bottom of the pan, the silicone oil layer in between, and the second reactant as the upper layer. In the course of the experiment, heating of the pan inside the DSC led to an intensive mixing of the ingredients due to thermal convection. In such a way, a controlled reaction start and a measurement of the total heat release was achieved even for very fast reactions. Preliminary test runs with the pan filled only with a portion of one of the reactants together with the silicone oil have confirmed the absence of any detectable mixing effects, providing easy acquisition of the reaction peak without the necessity of taking into account additional heat effects. Thus, the reaction enthalpy $(\Delta_r H^{\circ}_m)$ was determined by integration of the experimentally obtained heat flux signal, assuming heat effects due to mixing was negligible.

For some reactions which could slowly start already at room temperature, it was practical to dilute the reactants with the final product (ionic liquid) in order to slow down the reaction rate and to avoid an uncontrolled conversion within the baseline stabilization period in the DSC.

2.2.3. Molar Ratio of Reagents. Syntheses of ILs are usually performed in an excess of the highly volatile alkylating reagent in order to reach high degrees of conversion and to easily purify the prepared IL by gentle heating in vacuum. However, sometimes reactions have to be performed at the excess of MeIm to provide homogeneity of the reaction mixture at the end of the experiment.¹⁰ For our DSC studies of the energetics of the IL synthesis reactions, an excess of the volatile component seems to be impractical. Indeed, in the course of the temperature scan it elevates the total pressure in the pan and the pan usually explodes on heating. In contrast, at the excess of the substituted amine (MeIm in this case), the pressure inside of the pan remains moderate and it keeps tight during the experiment. From a chemical point of view, the molar reaction enthalpy should be independent of the excess of reactants, provided that complete conversion of the stoichiometrically deficient reactant was achieved. We tested the experimental conditions using as an example the molar ratios MeIm:C₄H₉Br at the three levels 0.3:1, 0.9:1, and 1.3:1. We have not found any differences in the measured reaction enthalpies within the boundaries of the experimental uncertainties of ± 0.5 kJ·mol⁻¹, proving the completeness of the IL synthesis reaction in the

DSC experiment independent of the molar ratio of the reactants.

2.2.4. Solvent or Solventless? Commonly, the quaternization reactions are carried out in batch reactors. Organic solvents (e.g., toluene, ethanol) have often been used in order to improve the heat removal, to increase safety of the process, and to obtain high quality ILs. Also, many ILs or their intermediates can often be quite viscous. By using a solvent, the product can be kept in a relatively low viscosity liquid solution that can be more easily processed.¹¹ However, the solvent use leads to increased reaction times due to the dilution and requires quantitative removal in an additional process step.

For our DSC studies, use of the solvent has been of crucial importance since the highly volatile alkyl halides were used as alkylating agents (see reaction 1). DSC experiments at neat conditions were hardly possible due to the risk of possible pan explosion. Common solvents mentioned above are as a rule also too volatile. Another apparent problem is the miscibility of the reactants; e.g., for the synthesis of the ionic liquid 1-butyl-3methylimidazolium chloride from (MeIm) and 1-chlorobutane already for a MeIm conversion of 8%, the neat synthesis lead to two phases either rich in IL or 1-chlorobutane, whereby MeIm is soluble in both phases. Only an addition of 20 vol % of ethanol led to a single-phase synthesis.¹² Such a complex phase behavior during the DSC study could impact the acquisition of the reaction peak. To overcome these two problems, a very low volatile solvent, which is miscible with the reactants and the resulting ionic liquid, is required. It has turned out that the most suitable solvent for the imidazolium-based ILs studied in this work was another ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfono)imide $([C_2mim][NTf_2])$ (99.9%, Iolitec). This solvent was ideal to the decrease the total pressure in the reacting system. It was miscible with the precursors and the resulting ILs. In addition, the [C₂mim]-[NTf₂] as the solvent was very advantageous for a high conversion and selectivity of the MeIm alkylation with alkyl halides. We tested the influence of the amount of $[C_2mim]$ -[NTf₂] (between 10 and 70 wt %) on the reproducibility of the measured enthalpy of reaction and selected to keep dilution of the reacting mixture on the level of >50-70 wt % where the measured reaction enthalpies were most reproducible.

2.2.5. Temperature Range: Reactions in Isothermal or in Scanning Mode? There are at least four main prerequisites for reliable and reproducible measurements of reaction enthalpies by DSC: (1) high selectivity of the chemical reaction; (2) completeness of the chemical reaction; (3) well-defined and sharp reaction peak; and (4) stable baseline with well-defined on-set and end-set of the reaction peak.

Fortunately, the two first requirements, selectivity and high conversion degree, could be generally fulfilled for IL synthesis reactions¹³ provided that the reaction is performed at a suitable temperature (or temperature range). Our preliminary experiments (MeIm + C_4H_9Br) were carried out under isothermal conditions at temperatures commonly recommended for synthesis of imidazolium-based ILs. However, the main problem with isothermal measurements results from the ill-defined behavior of the signal following the initial approach to steady state of the instrument with the sample. In isothermal conditions, we also obtained very broad reaction peaks with an ambiguous conversion of reactants and unclear end set. Thus, our further experiments were performed under nonisothermal conditions with dynamic temperature ramps which provide the most reproducible DSC curves. We have studied different

temperature profiles with scanning rates from 5 to 50 K·min⁻¹. It has turned out that the most reproducible results could be obtained at scanning rates above 30 K·min⁻¹. At increasing scanning rates, thermal lag increases too and may result in serious smearing of the curves. Thus, in this work the reaction enthalpy measurements were performed at 50 K·min⁻¹ heating rate in the temperature range from room temperature up to 523 K.

In general, the selection of the upper temperature of the DSC investigation depends crucially on the thermal stability of the ILs under study. For the reactions of the imidazolium-based halides (reaction 1), we have deliberately set the end temperature to 523 K in order to obtain complete conversion. But it should be mentioned that this end-set temperature was well below the decomposition temperatures (around 560 K) of $[C_n mim][Br]$.¹⁴ It is quite obvious that, in studies of ILs where decomposition is expected, the upper limit of the DSC study should be adjusted to lower values which have to be at least 20–30 K below the expected decomposition temperature.

In general, the selection of the lowest start temperature of the DSC investigations depends on the reaction rate. As a rule, after the beginning of the experiment the calorimeter needs certain time to reach steady-state conditions at the start temperature and to stay in this state at least for 2 min. It is important that the onset of the reaction peak is outside of this equilibration period. If the reaction under study is too fast, the lowest temperature of the DSC runs could be also selected below room temperature. In this case, the mixing of the reactants during room temperature handling of the sample pan had to be prevented; see section 2.2.2.

2.2.6. Proof of Completeness of the IL Synthesis Reaction. In each experiment, we have optimized the temperature range and the scanning rate in order to achieve the maximal possible conversion of the precursor which was in stoichiometric deficiency. In order to check the completeness of the reaction, the aluminum pan with the sample was taken from the DSC and cooled down to room temperature. After weighing of the pan, its top cover was punctured and the pan was heated at 373-393 K in a special vacuum oven for several hours until a constant mass was reached. In such conditions, the IL and the silicone oil could not be evaporated from the pan. Thus, the mass loss from the pan was ascribed to the loss of the MeIm which was usually taken in excess. Having the record of masses before and after the experiment, the degree of conversion was calculated. As a rule, the level of conversion in all experiments was about 99% (with the estimated uncertainty of 0.5%). Small corrections for the incomplete conversion have been taken into account for each reaction under study.

2.2.7. Summary of the Experimental Conditions. According the results of the screening of the experimental parameters that has been performed in this work, the following optimal conditions for DSC studies of the IL synthesis reactions of starting with precursors MeIm and alkyl bromides could be recommended: (1) ratio of precursors (MeIm)(R-Br) = 0.3 mol:1.0 mol; (2) dilution with a suitable low-volatile solvent—about 70 wt %; (3) temperature range 373–523 K; and (4) heating rate 50 K·min⁻¹.

In these conditions, a sharp reaction peak with well-defined onset, end set and, baseline could be achieved providing the completeness of the chemical reaction and an easy to draw baseline for peak integration. These optimal conditions have been also tested for pyridinium-, pyrrolidinium-, and piperidinium-based ionic liquids synthesis reactions with alkyl halides (chlorine, bromine, and iodine) successfully. **2.3. QCM: Measurements of Vaporization Enthalpy.** Enthalpies of vaporization of $[C_4mim][Br]$ was measured using the QCM technique.¹⁵ A sample of the IL was placed in an open cavity of a thermostated metal block and it was exposed to a vacuum system at 10^{-5} Pa. The quartz crystal microbalance was placed directly over the measuring cavity containing the IL. The change in the vibrational frequency of the crystal Δf was a measure of the amount of IL deposited on the cold QCM. The value of Δf was measured as function of time at different temperatures, *T*. The change of the vibrational frequency Δf was directly related to the mass deposition Δm on the crystal surface. Using the frequency change rate df/dt measured by the QCM, the molar enthalpy of vaporization, $\Delta_f^{e}H_m(T_0)$, was obtained¹⁵ by

$$\ln\left(\frac{\mathrm{d}f}{\mathrm{d}t}\sqrt{T}\right) = A' - \frac{\Delta_{\mathrm{l}}^{\mathrm{g}}H^{\circ}{}_{\mathrm{m}}(T_{0}) - \Delta_{\mathrm{l}}^{\mathrm{g}}C^{\circ}_{\mathrm{pm}}T_{0}}{R}\left(\frac{1}{T} - \frac{1}{T_{0}}\right) + \frac{\Delta_{\mathrm{l}}^{\mathrm{g}}C^{\circ}_{\mathrm{pm}}}{R}\ln\left(\frac{T}{T_{0}}\right)$$
(2)

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 (we used 298 K in this work). The value $\Delta_l^g C_{pm}^o = C_{pm}^o(g) - C_{pm}^o(l)$ is the difference of the molar heat capacities of the gaseous $C_{pm}^o(g)$ and the liquid phase $C_{pm}^o(l)$, respectively. The frequency change rate df/dt was measured in a few consequent series with increasing and decreasing temperature steps. In order to detect a possible decomposition of IL under the experimental conditions, the residual IL in the cavity and the IL deposit on the QCM were analyzed by ATR-IR spectroscopy. No changes in the spectra have been detected with ILs under study in this work. The primary experimental data are listed in Table S1 (Supporting Information).

2.4. Computations. Standard ab initio molecular orbital calculations were performed using the Gaussian 03 Revision 04 program package.¹⁶ Conformations of molecular and ionic species were optimized on the B3LYP/6-31+G(d,p) level of the theory. After that, the lowest energy conformations were calculated on the CBS-QB3 level. The 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 the theory.¹⁷ The calculated values of enthalpy and Gibbs energy of ions and ion pairs are based on the electronic energy calculations obtained by the CBS-QB3 method using standard procedures of statistical thermodynamics.¹⁸ The CBS-QB3 calculations were carried out using Linux cluster (AMD Opteron processor) in the University of Rostock (Germany). During calculations, eight processors with 2.5 GB RAM for each processor were used. The calculating procedure took from 1 day to 1 week depending on the size of molecule.

3. RESULTS AND DISCUSSION

Ionic liquids are often considered as the new class of environmentally friendly solvents due to their molecularly "tunable" properties and lack of volatility. New applications are being developed at a rapid pace. However, the lack of kinetic and thermodynamic data of their synthesis with emphasis on reaction engineering and process intensification is acknowledged in the literature.¹¹ Only a few experimental kinetic and thermochemical studies of the imidazolium halide synthesis reaction 1 were published until December 2011.^{7,9,11,12,19–24} Schleicher and Scurto¹¹ performed extended studies on kinetics and solvent effects in the synthesis of $[C_6 mim][Br]$ in 10 different solvents: acetone, acetonitrile, 2-butanone, chlorobenzene, dichloromethane, dimethyl sulfoxide, ethyl formate, ethyl lactate, methanol, and cyclopentanone. The first thermochemical study of the reaction 1 was published by Waterkamp et al.¹⁹ Formation of [C₄mim][Br] by reaction of MeIm and 1-bromobutane was performed with a reaction enthalpy of $-96.0 \text{ kJ} \cdot \text{mol}^{-1}$ at 338-358 K and 1-2 bar, but unfortunately, no experimental details are available in this work.¹⁹ They also estimated the adiabatic temperature for a runaway reaction for this system and suggested a way to intensify the synthesis of $[C_4 \text{mim}][Br]$ by using a continuously operating microreactor system. Further and very promising developments of heat pipe controlled syntheses of ionic liquids in microchannel reactors were reported by Löve et al.^{7,20,21} In this work, we have focused our experimental efforts on the precise quantitative determination of the heat effects, as presented in eq 1, for ILs synthesis reactions.

3.1. DSC Results for ILs Synthesis Reactions. The reaction enthalpies according to eq 1 were determined in a series of 3–5 DSC runs applying the optimized conditions described in section 2.2.7. The experimental results are collected in Table 1.

Table 1. Experimental Results for Measurements of Reaction Enthalpies, $\Delta_r H_m$ (liq), Using DSC

system (1) + (2)	molar ratio	solvent (wt %)	T_{\max} (K)	$\Delta_{\rm r} H_{ m m}({ m liq})^a \ ({ m kJ}\cdot{ m mol}^{-1})$
MeIm + BuBr	0.40	70	448 ± 5	-89.0 ± 0.8
MeIm + PenBr	0.44	70	433 ± 5	-91.6 ± 1.8
MeIm + HexBr	0.32	70	433 ± 2	-89.4 ± 2.2
MeIm + HepBr	0.36	75	433 ± 2	-87.5 ± 1.8
MeIm + OctBr	0.30	75	458 ± 5	-89.2 ± 2.2
^{<i>a</i>} Uncertainties	are twice th	e standard d	leviations of (the mean value.

As a matter of fact, the enthalpy of reaction, $\Delta_r H_{m'}$ obtained by integration of the DSC peak is referred to the temperature between the onset and end-set of the peak. In most cases we measured symmetric 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 $\Delta_r H_m$ at T = 298 K for the reactions of MeIm with alkyl bromides, the difference, $\Delta_r C_{pm'}$ between heat capacities of the ionic liquid $C_p^1(IL)$ and the precursors $C_p^1(MeIm)$ and $C_p^1(R-Br)$ is required:

$$\Delta_{\rm r} H_{\rm m}(298 \text{ K})/\text{J} \cdot \text{mol}^{-1} = \Delta_{\rm r} H_{\rm m}(T_{\rm max})$$
$$- \Delta_{\rm r} C_{\rm p,m}(T_{\rm max} - 298 \text{ K}) \qquad (3)$$

For example, with the values $C_p^1 = 162.1 \pm 0.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for 1-butyl bromide,²⁵ $C_p^1 = 147.2 \pm 0.6 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for MeIm,²⁶ and $C_p^1 = 308.7 \pm 1.0 \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for $[C_4\text{mim}][\text{Br}]$,²³ the value $\Delta_r C_{p,m} = -(0.6 \pm 1.3) \text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ was estimated. Similar results were also obtained for other alkyl bromides: all $\Delta_r C_{p,m}$ values were negative and of the order of 1 $\text{J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$. Application of these $\Delta_r C_{p,m}$ values for adjustment of the measured reaction enthalpies to the reference temperature 298 K provided very small corrections not larger than 0.3-0.4 kJ·mol⁻¹ and these corrections are well within the boundaries of the DSC experimental uncertainties of 1-2 kJ·mol⁻¹ (see Table 1). For this reason, it was reasonable to ascribe in this work the enthalpies of reactions measured by DSC to the reference temperature without any temperature correction.

It is apparent from Table 1 that the enthalpies of the ILs synthesis reactions were independent of the chain length of the alkyl bromide (within the boundaries of the experimental uncertainties). Our result for the $[C_4 mim][Br]$ is in good agreement with the value $\Delta_r H_m(298 \text{ K}) = -(87.7 \pm 1.6) \text{ kJ} \cdot \text{mol}^{-1}$ determined in an isoperibol calorimeter.²² It should be mentioned that the study of reaction 1 in the isoperibol calorimeter is generally more complex in comparison to the DSC applied in this work. In ref 22 the $\Delta_{\rm r} H_{\rm m}$ was determined in a series of five experiments at 334 K and then adjusted the value to the reference temperature 298 K. The reaction was performed at the 1.50-1.65 excess of MeIm to provide homogeneity of the reaction mixture at the end of the experiment. However, the degree of 1-bromobutane conversion at 334 K was only about 95%. In order to obtain enthalpy of reaction according to eq 1, the authors²² were also challenged to take into account the following: the enthalpy of mixing of 1-bromobutane with MeIm; the enthalpy of dissolution of $[C_4 \text{mim}][Br]$ in IL + MeIm solution; the incomplete conversion of 1-bromobutane; and the enthalpy of fusion of $[C_4 mim][Br]$. The most important steps 1 and 2 were taken into account with a series of calorimetric measurements on model mixtures.²² The enthalpy of fusion of $[C_4 mim][Br]$ was also obtained from adiabatic calorimetry. 23 In spite of the complexity of the isoperibol calorimetric study, their result for the quaternization reaction according to eq 1 was in agreement with our DSC result (see Table 1) within the combined experimental errors. In contrast, reaction enthalpy for the $[C_4 mim][Br]$ synthesis reaction measured by Waterkamp et al.¹⁹ was about 10 kJ·mol⁻¹ less negative in comparison with those from this work, but absence of experimental details in ref 19 did not allow to explain the difference. Summarizing, values of $\Delta_r H_m$ listed in Table 1 are consistent and precise and they are important for technical as well as for theoretical purposes.

3.2. Molar Enthalpies of Formation of ILs from DSC Measurements. Differential scanning calorimetry (in comparison to the isoperibol reaction calorimetry) is a simple and reliable experimental technique which allows examining thermal properties of different substances, among them are thermal effects of different phase transitions. Obviously the idea to apply the DSC for the investigation of thermochemistry of ILs appears to be very attractive. The $\Delta_r H_m$ values (see Table 1) are practically important for the heat management, assessment of thermal runaways and the quality of the products. However, at the same time the $\Delta_r H_m$ results are also of theoretical importance to derive molar enthalpies of formation of ILs, $\Delta_{f}H^{\circ}_{m}$ from DSC measurements. Enthalpies of formation of ionic liquids in combination with the high-level ab initio calculations have opened a new way to obtain enthalpies of vaporization of ILs.² Traditionally, the combustion calorimetry is used as the well-established method to provide enthalpies of formation.^{2,27–29} However, this method is sophisticated and needs extended experience to obtain reliable results. Also, the method has several shortcomings and restrictions. The most crucial prerequisite for the combustion calorimetry is the quality and amount of sample required for the study. In order to complete the experiment successfully, about 10-20 g of the

Table 2. Thermodynamic Data for IL Synthesis Reaction: Total Enthalpies H_{298} and Reaction Enthalpies, $\Delta_r H^{\circ}_{m}(g)$, and Enthalpies of Formation, $\Delta_f H^{\circ}_{m}(g)$, Calculated Using the CBS-QB3 Composite Method and Properties Derived from This Calculation: Enthalpies of Formation, and Enthalpies of Formation, $\Delta_f H^{\circ}_{m}(liq)$, and Enthalpies of Vaporization, $\Delta_I^{\circ} H^{\circ}_{m}$, of $[C_n mim][Br]$ (in kJ·mol⁻¹)

ILs	H_{298} (hartrees)	$\Delta_{\rm r} {H^{\circ}}_{\rm m}({ m g})$	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({ m g})$	$\Delta_r H^{\circ}_m(liq)$ (DSC)	$\Delta_{\rm f} {H^{\circ}}_{\rm m}({ m liq})$, eq 4	$\Delta^{g}_{l}H_{m}$, eq 6	$\Delta^g_{ m l} H_{ m m}$, eq 9
$[C_1 mim][Br]$	-2.877.746896	-15.9	68.0	$(-81.0)^{a}$	$(-69.7)^{a}$	$(137.7)^{a}$	$(143.3)^{a}$
$[C_2 mim][Br]$	-2.916.976825	-24.5	33.6	$(-87.0)^{a}$	$(-106.4)^{a}$	$(140.0)^{a}$	$(145.8)^a$
[C ₃ mim][Br]	-2.956.202413	-27.5	10.6	$(-89.0)^{a}$	$(-140.1)^{a}$	$(150.7)^{a}$	$(148.4)^a$
[C ₄ mim][Br]	-2.995.427190	-28.5	-10.5	-89.0	-162.1	151.6	152.2
[C ₅ mim][Br]	-3.034.652454	-30.3	-32.5	-91.6	-191.1	158.6	157.4
[C ₆ mim][Br]	-3.073.876527	-29.4	-51.5	-89.4	-212.9	161.4	161.1
[C ₇ mim][Br]	-3.113.100986	-29.3	-71.5	-87.5	-235.2	163.7	164.0
[C ₈ mim][Br]	-3.152.325444	-29.3	-91.6	-89.2	-263.6	172.0	170.8
^a Assessed values (see text). Values in bold are recommended for further thermochemical calculations.							

highly pure (99.9%) sample is required. Such amount of ILs is very expensive and also methods for purity attestations of the sample are still not sufficiently developed. Another issue-in order to get an acceptable accuracy of the results (with an uncertainty of 1–3 kJ·mol⁻¹ in $\Delta_{\rm f} H^{\circ}_{\rm m}$), the combustion energies have to be measured with an error of 0.01-0.02%. Such result is already achieved for C-, H-, O-, and N-containing compounds using the static bomb calorimeter.²⁷⁻²⁹ For the ILs additionally containing Cl, Br, I, and S atoms, a special procedure utilizing a rotating bomb calorimeter is required. This procedure has now succeeded for the S-containing ILs³⁰ and further development for the Cl-, Br-, and I-containing ILs is now in progress in our laboratory. In this context, we put focus of our efforts on the development of the new and concurring DSC-based thermochemical method leading to values of enthalpies of formation and further, indirectly, to vaporization enthalpies.

As a representative example, we consider once more the reaction according eq 1 to show the way how the enthalpy of reaction of synthesis of $[C_4mim][Br]$ is used to obtain its enthalpy of formation. According to Hess's Law the enthalpy of reaction is calculated as follows:

$$\Delta_{\rm r} H^{\circ}{}_{\rm m} = \Delta_{\rm f} H^{\circ}{}_{\rm m} ([C_4 \text{mim}][Br], \text{ liq})$$
$$- \Delta_{\rm f} H^{\circ}{}_{\rm m} (\text{MeIm, liq}) - \Delta_{\rm f} H^{\circ}{}_{\rm m} (\text{BuBr, liq})$$
(4)

where $\Delta_r H^{\circ}_{\ m}(liq)_{exp} = -(89.0 \pm 0.8) \text{ kJ} \cdot \text{mol}^{-1}$ was measured in this work using the DSC in the liquid phase, $\Delta_r H^{\circ}_{\ m}(MeIm,liq) = (70.7 \pm 1.1) \text{ kJ} \cdot \text{mol}^{-1}$ was measured using the combustion calorimetry recently,²⁶ and $\Delta_r H^{\circ}_{\ m}(BuBr,liq) = -(143.8 \pm 1.3) \text{ kJ} \cdot \text{mol}^{-1}$ was known from the literature.^{31,32} From eq 4 the enthalpy of formation of the IL was calculated:

$$\Delta_{f} H^{\circ}_{m} ([C_{4} \text{mim}][Br], \text{ liq}) = (-89.0) + (70.7) + (-143.8) = -(162.1 \pm 1.9) \text{ kJ} \cdot \text{mol}^{-1}$$

In the same way, the enthalpies of formation of other ILs $[C_n mim][Br]$ were estimated (see Table 2). These values can be used (together with results from ab initio calculations) to obtain the enthalpies of vaporization for these ILs indirectly.

3.3. Indirect Determination of Molar Enthalpies of Vaporization of $[C_n mim][Br]$ from DSC Results. Enthalpy of vaporization data should be intensively measured, as they are of paramount importance for the proper calibration and validation of new force fields used in computational simulations based

on MD techniques, as well as for anchoring parameters for pVT equations of state for neat ILs and their mixtures.³³ Unfortunately, the available data on vaporization enthalpies of ILs are rather a minefield than a consistent collection of data.³³ For example, the experimental results from different techniques reported for the most frequently studied homologues series [C_nmim][NTf₂] are in disagreement^{15,34} of 5–7 kJ·mol⁻¹, but the data from the direct drop-calorimetric study³⁵ differ even by 30–40 kJ·mol⁻¹. This fact shows clearly the necessity of a more conclusive investigation of the vaporization enthalpies of ILs using reliable experimental techniques. At the same time, any indirect option for obtaining enthalpies of vaporization from empirical, half-empirical, or theoretical methods is of high value to test the consistency of the data.

3.3.1. Vaporization Enthalpy from Enthalpy of Formation, $\Delta_f H^{\circ}_m(liq)$. One of the first indirect options to determine enthalpy of vaporization is the combination of combustion calorimetry with the high-level quantum chemical calculations. This method has turned out to be a valuable thermochemical option to derive vaporization enthalpies.^{2,27–31} The procedure is based on experimental results from combustion calorimetry and first-principles calculations according to the general equation

$$\Delta_{\rm f} H^{\circ}{}_{\rm m}({\rm g}) = \Delta_{\rm f} H^{\circ}{}_{\rm m}({\rm liq}) - \Delta_{\rm l}^{\rm g} H_{\rm m} \tag{5}$$

where $\Delta_{f}H^{\circ}_{m}(liq)$ is measured by combustion calorimetry and $\Delta_{f}H^{\circ}_{m}(g)$ is calculated by high-level first-principles calculations (e.g., CBS-QB composite method). Then the enthalpy of vaporization, $\Delta_{f}^{g}H_{m}$, of the IL can be estimated from eq 5

$$\Delta_l^g H^\circ{}_m = \Delta_f H^\circ{}_m(g) - \Delta_f H^\circ{}_m(liq) \tag{6}$$

Comprehensive studies of the thermochemical properties of $[C_n \min][N(CN)_2]$,^{2,29} $[C_n \min][NO_3]$,^{27,28} and $[C_{1,4}$ Pyrrolidinium] $[N(CN)_2]^{36}$ have been performed successfully for validation of this procedure.

In this work, we have extended this procedure for combination of the high-level quantum chemical calculations with the results from DSC as a valuable thermochemical option to derive vaporization enthalpies. Instead of the combustion calorimetry used earlier to derive $\Delta_t H^{\circ}_{m}(IL,Iiq)$ this concurring procedure is based on the DSC experimental determination of the reaction enthalpies (see section 3.1) and $\Delta_f H^{\circ}_{m}(IL,Iiq)$ (see section 3.2). As an example, for the ionic liquid $[C_4mim][Br]$ using the following data: $\Delta_f H^{\circ}_{m}(Iiq) = -162.1 \pm 1.9 \text{ kJ} \cdot \text{mol}^{-1}$ derived from DSC calorimetry (see chapter 3.2); and $\Delta_f H^{\circ}_{m}(g) =$ $-10.5 \pm 4.0 \text{ kJ} \cdot \text{mol}^{-1}$ calculated by *first-principles* calculations (CBS-QB3 method, see Table 2), the enthalpy of vaporization of the IL could be estimated from eq 6

$$\Delta_l^g H_m = \Delta_f H^\circ{}_m(g) - \Delta_f H^\circ{}_m(liq)$$
$$= 151.6 \pm 4.4 \text{ kJ} \cdot \text{mol}^{-1}$$

This indirect value is in a good agreement with the result $\Delta_l^{g}H_m([C_4mim][Br]) = 152.7 \pm 3.0 \text{ kJ} \cdot \text{mol}^{-1}$ measured with QCM in this work. This good agreement demonstrates in a convincing way the successful application of the DSC method developed in this work to obtain reliable vaporization enthalpies of ILs in the proposed indirect way.

3.3.2. Vaporization Enthalpy from the Enthalpy of Reaction, $\Delta_r H^{\circ}_m(liq)$, Measured by DSC. The indirect option to determine enthalpy of vaporization using eq 6 suggested in section 3.3.1 has one handicap: it is based on the value of the gaseous enthalpy of formation, $\Delta_{f}H^{\circ}_{m}(g)$, which is calculated using ab initio calculations. There are some ambiguities in respect to procedures of converting results of first-principles calculations (total energies E_0 at T = 0 K and enthalpies H_{298} at T = 298 K) into the desired value of $\Delta_{\rm f} H^{\circ}{}_{\rm m}(g)$. It is well established that in standard Gaussian-n theories, theoretical standard enthalpies of formation, $\Delta_f H^{\circ}_{\ m}(g)$, are calculated through atomization reactions, and isodesmic and bond separation reactions.³⁷ However, it has turned out^{37,38} that gaseous enthalpies of formation calculated from the standard atomization procedure deviate very often systematically from the available experimental results.³⁹ The deviation can be positive or negative, depending on the homologous series under study. It has been also often discussed that the enthalpies of formation obtained from the first-principles calculations are very sensitive for the choice of the bond separation or isodesmic reactions used for this purpose.^{38–40} Possible reasons for these deviations are usually given by different qualities and accuracies of the experimental data involved in the estimations, as well as a imbalance of electronic energies calculated for the reaction participants. That is why we are somewhat hesitant to use atomization reactions and isodesmic and bond separation reactions to obtain $\Delta_{\rm f} H^{\circ}{}_{\rm m}({\rm g})$ of ionic liquids without careful testing of these reactions. At the same time, the logic of the DSC experiment lends itself to an elegant solution of the aforementioned problem. Indeed, using the DSC we have measured the experimental reaction enthalpy in the liquid phase, e.g., for $[C_4 mim][Br]$ according to eq 1. It is apparent that the same reaction enthalpy, but in the gaseous phase, could be obtained from the first-principles calculations. In this work, we have calculated H_{298} at T = 298.15 K for all reaction participants in eq 1 using the CBS-Q3B composite method. According to the Hess law, the enthalpy of this reaction was calculated as follows:

$$\Delta_{\rm r} H^{\circ}{}_{\rm m}({\rm g}) = H_{298}([{\rm C}_4 {\rm mim}][{\rm Br}], {\rm g}) - H_{298}({\rm MeIm}, {\rm g}) - H_{298}({\rm BuBr}, {\rm g}) = -28.5 \text{ kJ} \cdot {\rm mol}^{-1}$$

It is important to realize and to emphasize that the $\Delta_r H^{\circ}_{m}(g)$ was obtained using first principles *directly* from the calculated H_{298} bypassing the conventional calculation of the enthalpies of formation with the help of atomization, isodesmic, or other procedures. As a consequence of this trick, the resulting value of $\Delta_r H^{\circ}_{m}(g)$ was not affected at all by any choice and quality of the auxiliary quantities commonly required for the atomization, bond separation, etc., reactions.

Article

Having established the values of $\Delta_r H^{\circ}_{m}(liq)_{exp}$ and $\Delta_r H^{\circ}_{m}(g)$, we have derived the vaporization enthalpy (e.g., for $[C_4 mim][Br]$) provided that the following balance holds:

$$\Delta_{\rm f} H^{\circ}{}_{\rm m}({\rm liq}) = \Delta_{\rm f} H^{\circ}{}_{\rm m}({\rm g}) - \Delta_{\rm l}^{\rm g} H_{\rm m} \tag{7}$$

The enthalpy of reaction was calculated using the Hess law:

$$\Delta_{r}H^{\circ}{}_{m}(\text{liq})_{exp} = [\Delta_{f}H^{\circ}{}_{m}(g)(\text{IL}) - \Delta_{l}^{g}H_{m}(\text{IL})] - [\Delta_{f}H^{\circ}{}_{m}(g)\text{MeIm}) - \Delta_{l}^{g}H_{m}(\text{MeIm})] - \Delta_{f}H^{\circ}{}_{m}(g)(\text{BuBr}) - \Delta_{l}^{g}H_{m}(\text{BuBr})]$$
(8)

From eq 6, the enthalpy of vaporization of the IL has been obtained in eq 9:

$$\Delta_{I}^{g} H_{m}(IL) = -\Delta_{r} H^{\circ}{}_{m}(Iiq)_{exp} + \Delta_{r} H^{\circ}{}_{m}(g) + \Delta_{I}^{g} H_{m}(MeIm) + \Delta_{I}^{g} H_{m}(BuBr)] = -(-89.0) + (-28.5) + (55.0) + (36.7) = 152.2 \pm 4.1 \text{ kJ} \cdot \text{mol}^{-1}$$
(9)

with values $\Delta_l^g H_m(MeIm) = 55.0 \pm 0.3 \text{ kJ} \cdot \text{mol}^{-1}$ measured in our lab recently,²⁶ and $\Delta_l^g H_m(BuBr)$] = 36.7 \pm 0.1 kJ \cdot mol⁻¹ available from the literature.⁴⁰

Thus, using the value $\Delta_r H^{\circ}_m(g)$ calculated with CBS-QB3 in the gas phase and enthalpies of vaporization of MeIm and alkyl bromides available from the literature (see Table S2, Supporting Information), and the enthalpy of reaction $\Delta_r H^{\circ}_m(\text{liq})_{exp}$ measured using the DSC in the liquid phase, the enthalpies of vaporization of the ILs under study have been derived (see Table 2).

In addition, we compared vaporization enthalpies derived using two DSC-based procedures: from eq 6 and from eq 9 (see Table 2). Both methods provide the values in very close agreement; however, we should recommend eq 9 because the $\Delta_r H^{\circ}_{m}(g)$ values for this procedure have been calculated *directly* from the H₂₉₈ avoiding any recalculating procedure.

3.4. Consistency of Enthalpies of IL Synthesis **Reactions.** Structure–property relations within a homologous series are always a valuable tool to get insight into the consistency of experimental and calculated results. The systematic study of the $[C_n \min][Br]$ family in the current work has allowed to correlate the enthalpies of IL synthesis reactions, $\Delta_r H^{\circ}_{m}$, in the liquid and in the gaseous phase (see Table 2) with the number of C atoms, N_c , in the alkyl chain of the cation, (see Figure 2). It is apparent that gaseous enthalpies, $\Delta_r H^{\circ}_{m}(g)$, calculated by using the CBS-QB3 composite method for reactions according to eq 1 show a quite linear dependence for $N_c \ge 3$. However, reaction enthalpies with methyl and ethyl bromides are noticeably less negative (see Figure 2). Enthalpies $\Delta_r H^{\circ}_{m}(liq)$ measured by DSC for $N_c = 4-8$ are obviously indistinguishable within the boundaries of their experimental uncertainties. But what trend for reaction enthalpies could be expected for $N_c < 4$ in the liquid phase? Unfortunately, methyl, ethyl, and propyl bromides are too volatile in order to perform the DSC studies properly. That is why we studied in this work only reactions with $N_c \ge 4$ (see Figure 2). However, it is quite interesting to assess at least the level of thermodynamic properties for $[C_1 mim][Br]$, $[C_2 mim][Br]$, and $[C_3 mim][Br]$, where the DSC experiments were not feasible. To do this, we assumed the similarity of tendencies for $\Delta_r H^{\circ}_{m}(g)$ and $\Delta_r H^{\circ}_{m}(liq)$ for



Figure 2. Enthalpies of reaction, $\Delta_r H^{\circ}_{m\nu}$ of $[C_n \min][Br]$ synthesis reaction: $(\Delta) \Delta_r H^{\circ}_m(g)$ for $N_c = 1-8$; (O) $\Delta_r H^{\circ}_m(liq)$ for $N_c = 4-8$; (\bullet) $\Delta_r H^{\circ}_m(liq)$ for $N_c < 3$.

 $N_{\rm c}$ < 4. The assessed values of $\Delta_{\rm r} H^{\circ}{}_{\rm m}$ (liq) are given in parentheses in Table 2. The latter values have allowed to estimate enthalpies of vaporization for $[C_1 \text{mim}][Br]$, $[C_2 \text{mim}][Br]$, and $[C_3 \text{mim}][Br]$ using eqs 6 and 8 (Table 2). The chain length dependence of vaporization enthalpy for the $[C_n \text{mim}][Br]$ series is presented in Figure 3. As can be seen in Figure 3,



Figure 3. Enthalpies of vaporization $\Delta_{\rm F}^{\rm e}H^{\circ}_{\rm m}(298 \text{ K})$, of $[C_n \text{mim}]$ -[Br]: (O) $[C_n \text{mim}][\text{Br}]$ with $N_{\rm c} = 1$ and 2; (\bullet) $[C_n \text{mim}][\text{Br}]$ with $N_{\rm c} \geq 3$.

the first representative, methyl bromide, is slightly out of the linear correlation. However, such an anomaly was also observed for vaporization enthalpies of the $[C_n mim][NTf_2]$ series of ionic liquids,⁴¹ as well as for the molecular liquids such as aliphatic esters^{42,43} and aliphatic nitriles⁴⁴ and this fact might be caused by the high dipole moments of these species. The vaporization enthalpy of $[C_2 mim][Br]$ already fits very well the linear behavior. The chain length dependence of the vapor-

ization enthalpy for $N_{\rm c} \geq 4$ is expressed by the following equation:

$$\Delta_1^{g} H_{\rm m}(298 \text{ K})/\text{kJ} \cdot \text{mol}^{-1} = 135.3 + 4.3N_{\rm c}$$

(r = 0.989)

from which enthalpies of vaporization of other representatives of the $[C_n \text{mim}][Br]$ series with $N_c \ge 4$ can be calculated.

3.5. Quantum Chemical Calculations. Gas-Phase Enthalpies of Reaction and Formation. Thermodynamic properties of the reaction 1 participants were calculated using high-level first-principles calculations. The CBS-QB3 composite method is one of the most powerful methods for calculation of large molecules of ILs in a reasonable time. A careful conformational analysis of the $[C_n mim]$ cations has been performed at the level RHF/3-21G* at 0 K. Molecular structures and relative energies of all conformations for the cations formed by rotation of alkyl groups around N-C and C-C bonds of the butyl group (CCCN and CCNC dihedrals) by 360° have been studied with 10° steps starting from the coplanar conformation. The conformers with the lowest energies were chosen for further CBS-QB3 calculations. The halogen anion was placed near the atoms with the highest positive charge. In this way, from 10 to 20 conformers of ionic liquids were generated, which were optimized on B3LYP/6-31+G(d,p) level of theory. After that, the conformers with the lowest energy were calculated on the CBS-QB3 level.

3.5.1. Enthalpy of Formation $\Delta_f H^{\circ}_m(g, 298 \text{ K})$: Improvement of the Atomization Procedure. We calculated the total energies E_0 at T = 0 K and enthalpies H_{298} at T = 298 K using the CBS-QB3 (Table 2). Atomization reactions are the simplest way to obtain theoretical standard enthalpies of formation, $\Delta_f H^{\circ}_m(g)$, from the ab initio results.^{37,46} A more sophisticated option is to use a set of isodesmic reactions, bond separation reactions, or homodesmic reactions to derive theoretical enthalpies of formation.³⁷ Unfortunately, for ionic liquids the choice of species with reliable thermodynamic data which could be involved in these reactions is very restricted. In this work, we applied the atomization procedure (AT), e.g., for [C₂mim][Br]:

$$[C_2 mim][Br] = 6C + 11H + 2N + 1Br$$
(10)

In contrast to the bond separation and isodesmic reactions, the atomization reaction suggests the constant quality of the data on the right side (the constituted atoms with the well established thermodynamic values) the same for all compounds under study.³⁷ However, the AT procedure for estimation of enthalpies of formation, $\Delta_{t}H^{o}_{m}(g,298 \text{ K})$, of ILs have to be tested for validity with the reliable experimental data. In Table S3 (in the Supporting Information), we collected a set of reliable enthalpies of formation for the molecular Br-containing compounds. Results of the CBS-QB3 calculations (Table S3) revealed that enthalpies of formation calculated from the atomization procedure are *systematically* less positive than those from the experimental data. But, a remarkable linear correlation was found between experimental and calculated by AT enthalpies of formation (see Table S3, and Figure 3):

$$\Delta_{\rm f} H^{\circ}{}_{\rm m}(g)(\exp)/kJ \cdot {\rm mol}^{-1} = 1.002 \times \Delta_{\rm f} H^{\circ}{}_{\rm m}(g)({\rm AT}) + 28.2 \qquad (r = 0.9981)$$
(11)

Using this correlation, the "corrected" enthalpies of formation of the $[C_n \min][Br]$ have been calculated (see Tables 2 and 3) and these values are now in good agreement with the

Table 3. Results of Calculation of the Enthalpy of Formation (in kJ·mol⁻¹) of Br-Containing ILs in the Gaseous Phase at 298 K, CBS-QB3

ILs	$\Delta_{\mathrm{f}} {H^{\circ}}_{\mathrm{m}}$ from AT	$\Delta_{\rm f} {H^{\circ}}_{\rm m}$ from ${ m AT}_{ m corr}$
$[C_1 mim][Br]$	39.7	68.0
$[C_2 mim][Br]$	5.4	33.6
[C ₃ mim][Br]	-17.6	10.6
$[C_4 mim][Br]$	-38.6	-10.5
[C ₅ mim][Br]	-60.6	-32.5
$[C_6 mim][Br]$	-79.6	-51.5
$[C_7 mim][Br]$	-99.6	-71.5
[C ₈ mim][Br]	-119.6	-91.9

experimental results. Having established this "modified atomization procedure", we could use eqs 11 and 6 for estimation of the enthalpies of formation of the Br-containing compounds from the CBS-QB3 energies without creating any "suitable" bond separation or isodesmic reactions. Thus, the CBS-QB3 method combined with the modified atomization procedure has been applied in this work for reliable calculations of $\Delta_{\rm f} H^{\circ}_{\rm m}$ (g, 298 K) of the ILs (see Tables 2 and 3).

3.5.2. Quantum Chemical Calculations for Degree of Dissociation of the lon Pair. Enthalpy of vaporization of $[C_4mim][Br]$ was measured in this work in the temperature range 427–467 K using the QCM. At such elevated temperatures, thermal dissociation of the ILs according to reaction R1

$$[C_2 \min][Br] \rightleftharpoons [C_2 \min]^+ + [Br]^-$$
(R1)

could be expected. However, in our recent studies^{2,27,29,36} we have shown that the aprotic ILs such as $[C_4 \text{mim}][N(\text{CN})_2]$, $[\text{Pyrr}_{1,4}][N(\text{CN})_2]$, and $[C_n \text{mim}][\text{NO}_3]$ exist in the gaseous phase as ion pairs and not as separated ions. In this work, calculations for the free cation $[C_2 \text{mim}]^+$, the free anion [Br], and the ion pair $[C_2 \text{mim}]^+[\text{Br}]^-$ have been performed (Table 4).

Table 4. CBS-QB3 Calculations of the Thermodynamic Properties of the Ions $[Br]^-$, $[C_2mim]^+$, and the Ionic Pair $[C_2mim][Br]$ Used for Prediction of the Equilibrium Constant K_p of Dissociation of the Ionic Liquid According to Reaction 1

	R	.1
properties	298 K	447 K
$\Delta_{\rm r} G^{\circ}_{\ { m m}'} \ { m kJ} \cdot { m mol}^{-1}$	779.8	617.9
$\Delta_{\rm r} H^{\circ}_{\rm m}$, kJ·mol ⁻¹	703.2	759.5
$\Delta_r S^{\circ}_{m'} J \cdot mol^{-1} \cdot K^{-1}$	-257.0	316.7
K _p	2.4×10^{-137}	6.7×10^{-73}

Results of the total electronic energy at 0 K, the molecular structures in the lowest energetic state, and all vibrational frequencies of each species have been obtained (Table 4). On the basis of these quantum mechanical results, the molar Gibbs energy, the molar enthalpy, and the molar entropy at 298 K have been calculated using standard procedures of statistical thermodynamics. The purpose of this procedure was to obtain values of the molar entropy of reaction $\Delta_r S^{\circ}_{m}$, and the molar reaction enthalpy $\Delta_r H^{\circ}_m$ for the process of dissociation of the ion pair, e.g., $[C_2 \text{min}]^+[\text{Br}]$, into ions in the gaseous phase according to reaction R1. The chemical equilibrium constant $K_p = 2.4 \times 10^{-137}$ (at 298 K) and $K_p = 6.7 \times 10^{-73}$ (at 447 K)

in the ideal gaseous state has been calculated (Table 4). These values are in accord with $K_p = 1.4 \times 10^{-54}$ (at 298 K) for $[C_4\text{mim}][N(\text{CN})_2]$ derived in our previous work.² Such extremely low values allow us to conclude with high reliability that the degree of dissociation of the ion pair is zero for the ionic liquids under study; i.e., $[C_n\text{mim}][\text{Br}]$ exist exclusively as ion pairs in the gaseous phase. This theoretical finding was proved by QCM measurements, where $[C_4\text{mim}][\text{Br}]$ was successfully measured without thermal decomposition (tested by ATR IR) and agreement between the direct measurement by QCM and indirect DSC result was the validation of all assumptions applied in this work.

3.6. Summary of Benefits for Using DSC for Indirect Evaluation of $\Delta_{p}^{o}H^{o}_{m}$. There are several very important advantages of using the DSC technique for the indirect evaluation of the vaporization enthalpies of ionic liquids:

- (1) Experimental $\Delta_r H^{\circ}_{m}(liq)_{exp}$ measurements using DSC are less demanding compared to the combustion calorimetry.
- (2) Purity requirements for the chemicals are less rigorous compared to the combustion calorimetry.
- (3) $\Delta_r H^{\circ}{}_{m}(g)$ is obtained using first principles *directly* from the calculated H₂₉₈ (avoiding the usual calculation of the enthalpies of formation with help of atomization, isodesmic, etc., procedures.
- (4) $\Delta_{g}^{e}H_{m}$ of the starting chemicals are well-known or easy to be measured.
- (5) As a rule, DSC calorimeter is available as basic equipment in the laboratories working with ILs.

4. CONCLUSIONS

Standard DSC equipment has been applied for the express determination of reaction enthalpies of ionic liquids synthesis reactions in the systems quaternary amine + R-Hal (Hal = Cl, Br, I). Experimental parameters important for the precise determination of the heat effects were carefully studied and the optimal conditions have been recommended. The combination of the DSC method with the high-level first-principles calculations provided a consistent set of molar enthalpies of vaporization and enthalpies of formation for the homologous series of the imidazolium-based ILs. The indirect procedure to derive vaporization enthalpies from DSC measurements was successfully validated with the experimental QCM method. Combination of differential scanning calorimetry with the firstprinciples calculations allows now a rapid accumulation of the needed thermodynamic data. This procedure provides indispensable data material for testing first-principles procedures and molecular dynamic simulations techniques in order to understand thermodynamic properties of ionic liquids on a molecular basis.

ASSOCIATED CONTENT

S Supporting Information

Table S1, the results of the temperature-dependent studies of df/dt using the QCM for $[C_4mim][Br]$. Table S2, the results for alkyl halides derived from CBS-QB3 and experimental values for $\Delta_1^{g}H_m^{\circ}$ alkyl halides. Table S3, results of calculation of the enthalpy of formation bromo-containing compounds in the gaseous phase at 298.15 K. Figure S1, the IR spectra for $[C_4mim][Br]$ during enthalpy of vaporization investigation with QCM method, and Figure S2, correlation between calculated and experimental enthalpies of formation of

bromo-containing compounds in the gaseous phase at 298.15 K. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: sergey.verevkin@uni-rostock.de. Fax: +49 381 498 6524. Tel: +49 381 498 6508.

Notes

The authors declare no competing financial interest.

[†]Department of Life, Light and Matter, Faculty of Interdisciplinary Research, University of Rostock.

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