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Ammonium-Based Ionic Liquids: Cross-Validation of Energetics Using Solution Calorimetry, Quartz Crystal Microbalance, Quantum Chemistry, and Structure–Property Relationships

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Abstract

The solution enthalpies of tetra-methyl- and tetra-butyl-ammonium tetrafluoroborates were measured using solution calorimetry. The sublimation enthalpies and vaporization enthalpies of ammonium-based ionic liquids with the anions [BF_4] and [NO_3] were derived from temperature dependencies of the vapour pressures, measured with a quartz crystal microbalance and adjusted to the reference temperature 298.15 K. The solution calorimetry results were used to derive the solid-phase enthalpies of formation of the compounds studied. The latter results were combined with the sublimation enthalpies to obtain the experimental gas-phase formation enthalpies of the ionic liquid containing [BF_4] and [NO_3] anions. The theoretical gas-phase formation enthalpies were calculated using the quantum chemical method G3MP2 and agree well with the experimental results. Different types of structure–property relationships were used to establish the consistency of the alkyl-ammonium-based ionic liquids studied in this work.

Keywords Ionic liquid · Enthalpy of vaporization · Enthalpy of formation · Enthalpy of solution · Structure–property relationship

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1 Introduction

Calorimetry is a powerful tool to study the energetics of molecules and materials. Of the various types of calorimetry (solution, combustion, differential scanning, etc.), isothermal titration calorimetry is the most recent to emerge. The main reason for this is the modern development of electronics, which has led to fantastic sensitivity of the devices and has been particularly important for biochemical processes. The crucial contribution of Prof. Jean-Pierre E. Grolier to the development of this calorimetric technique is widely recognized [1]. This paper is written for a Special Issue in Honour of J. P. Grolier (1936–2022). In this context, it is important to acknowledge his personal contributions to the development of the titration calorimetry in Rostock. Our laboratory directly benefited from his private advice in establishing the experimental technique in our pioneering studies on ionic liquids using titration calorimetry in early 2000 [2, 3]. The goal of this work is to show advances in the application of solution calorimetry in combination with other experimental and theoretical thermochemical methods to generate a consistent set of thermodynamic data for practically interesting aprotic ammonium-based ionic liquids, as shown in Fig. 1.

From a practical point of view, the selected series of tetra-alkyl-ammonium-based ionic liquids can be synthesized from the relatively cheap starting materials. These ILs are considered to be suitable electrolytes for redox flow batteries, which are being developed as high-capacity, scalable energy storage systems to integrate solar or wind power into the grid [4]. Furthermore, the ammonium-based ILs exhibit energetically favourable solid–solid-phase transitions and they are interesting for use as phase-change materials in modern thermal energy storage devices as they offer smooth on–off switching in thermal cycles [5]. Last but not least, the selected type of ionic liquids shows advantageous catalytic activity. For example, the typical Knoevenagel condensation was carried out smoothly in the presence of a basic ionic liquid of N,N,N´,N´-tetra-methyl-N´-hexyl-ethylene-diammonium tetrafluoroborate and 99% of yield [6].

Experimental physico-chemical properties of alkyl-ammonium-based ILs associated with the $[BF_4]$ anion are very limited and mainly related to thermal behavior and phase transitions (solid–solid and solid–liquid) [5, 7–10]. The pure alkyl-ammonium $[BF_4]$ salts exhibit highly disordered crystal phases, and these phases are often referred to as ionic plastic crystals and have attracted attention because they can be used as solid electrolytes in the construction of safe and reliable electrochemical devices [9, 10]. The only study dealing with the enthalpies of solution was found in the literature is dating back to 1987 work of Johnsson and Persson [11]. The focus of the present study is vaporization thermodynamics of alkyl-ammonium-based ILs. This knowledge is of importance for practical

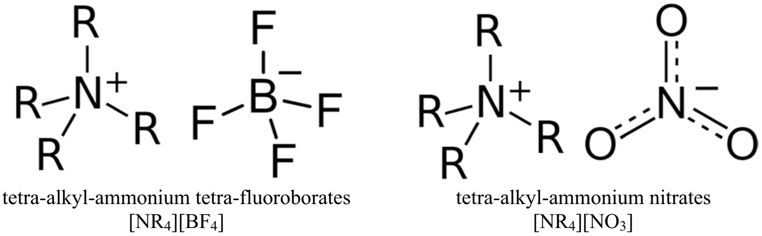

Fig. 1 Structures of tetra-alkyl-ammonium-based ionic liquids studied in this work with $R = CH_3$, C_2H_5, n-C_3H_7, and n-C_4H_9

applications of these ILs at elevated temperatures in batteries and phase-change materials. Furthermore, it was recently shown that the degree of purity of the [BF4]-containing ionic liquids significantly affects the thermal stability; with a purity greater than 99.9%, no decomposition is observed even in the temperature range around 500 K [12]. One of the established methods to purify ILs is a short-pass distillation [13], where the vaporization thermodynamics is essential to optimize practical conditions.

In this paper we used complementary experimental and theoretical methods to evaluate a consistent set of thermodynamic data for the $[NR_4][BF_4]$ series of ILs presented in Fig. 1, including standard molar solution enthalpies, standard molar vaporization enthalpies, and standard molar enthalpies of formation in the crystal and gas state. In addition, we used our previous thermochemical results [14] for the series $[NR_4][NO_3]$ of alkyl-ammonium-based ILs associated with the nitrate anion (see Fig. 1). The apparent structural similarity of molecules in the chosen series enabled the development and understanding of the structure–property relationships in the corresponding structures. The experimental and theoretical results were used for the determination of aqueous and solid-state enthalpies of formation of alkyl-ammonium ionic liquids connected with the $[BF_4]$ anion, as well as for validation of the high-level quantum chemical method G3MP2 for these series of ionic liquids.

It should be noted that all compounds in both the $[NR_4][BF_4]$ and $[NR_4][NO_3]$ series are solid at room temperatures. Nevertheless, we believe that conflicts in the definition of "the salt or the ionic liquid" were successfully resolved in 2010 [15]; hence, compounds shown in Fig. 1 are referred to as "ionic liquids" in this article. The similar logic we used in defining sublimation or vaporization thermodynamics. Throughout the text we have used "vaporization" because these thermodynamic properties are related by the equation:

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}} = \Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}} + \Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}, \tag{1}$$

where $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}$ is the standard molar enthalpy of fusion, easily measurable using differential scanning calorimetry (DSC). Both, the sublimation enthalpies, $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$, and vaporization enthalpies, $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}$, were derived from the vapour pressure–temperature dependences in this work. The latter values are commonly used to obtain the standard molar enthalpies of formation, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$, according to the equations:

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = \Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{liq}) + \Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}, \tag{2}$$

$$\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g}) = \Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr}) + \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}. \tag{3}$$

In the last decades, the $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$-values have been successfully calculated with a "chemical accuracy" of 1 $\mathrm{kcal \cdot mol^{-1}}$ using the high-level quantum chemical methods [14]. However, the reliability of these methods for properly calculating ionic liquids has yet to be proven with reliable experimental data derived through Eqs. 2 and 3. The enthalpies of formation in the condensed state, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr\ or\ liq})$, are usually measured by calorimetry; therefore, the experimental gas-phase enthalpies of formation, $\Delta_{\mathrm{f}} H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{g})$, obtained by Eqs. 1, 2 and 3 are valuable data for a mutual validation of experimental and quantum chemical results. The possible deviations are always a good starting point for troubleshooting in the experiment or in theory. In thermochemistry, it is common to adjust all enthalpies involved in Eqs. 1, 2, and 3 to $T = 298.15$ K as the reference temperature.

In our previous work [14], we measured the $\Delta_f H^o_m$(cr) of alkyl-ammonium-based ILs using combustion calorimetry. In this study, these values were alternatively derived from the infinite dilution enthalpies of solution in water, $\Delta_{sol}H^{\infty}_m$(IL), measured using high-precision solution calorimetry.

The way from $\Delta_{sol}H^{\infty}_m$(IL) to the $\Delta_f H^o_m$(cr)-values is straightforward as follows. The enthalpy of formation of an IL in aqueous solution, $\Delta_f H^o_m(\mathrm{IL}_{aq})$, is a sum of appropriate enthalpy contributions from the aqueous cation and the anion that make up the IL:

$$\Delta_f H^o_m(\mathrm{IL}_{aq}) = \Delta_f H^o_m\left(\mathrm{cation}^+_{aq}\right) + \Delta_f H^o_m\left(\mathrm{anion}^-_{aq}\right). \tag{4}$$

The reaction enthalpy Eq. 4 represents the standard molar enthalpy of solution of an IL in water at infinite dilution $\Delta_{sol}H^{\infty}_m$(IL). Fortunately, the aqueous enthalpies of formation of the cations, $\Delta_f H^o_m\left(\mathrm{NR}^+_{4aq}\right)$, and the anion, $\Delta_f H^o_m\left(\mathrm{BF}^-_{4\,aq}\right)$, are known from the literature [14, 16]. Therefore, the last step to obtain the required enthalpies of formation in the condensed state is according to Eq. 5:

$$\Delta_f H^o_m([\mathrm{NR}_4][\mathrm{BF}_4],\mathrm{cr}) = \Delta_f H^o_m\left(\mathrm{NR}^+_{4\,aq}\right) + \Delta_f H^o_m\left(\mathrm{BF}^-_{4\,aq}\right) - \Delta_{sol}H^{\infty}_m(\mathrm{IL}). \tag{5}$$

The latter results can now be compared with the experimental $\Delta^g_{cr}H^o_m$-values according to Eq. 3, and the final experimental gas-phase formation enthalpies are now ready for validation of those calculated using quantum chemistry. This guideline helps to follow the logic of combining experimental and theoretical methods applied in this work.

2 Materials and Methods

2.1 Materials

The tetra-methyl-ammonium tetrafluoroborate $[\mathrm{N}_{1111}][\mathrm{BF}_4]$ (TCI, ˃98%, CAS 661-36-9), tetra-butyl-ammonium tetrafluoroborates $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ (Sigma-Aldrich, 99%, CAS 429-42-5), and tetra-butyl-ammonium nitrate $[\mathrm{N}_{4444}][\mathrm{NO}_3]$ (TCI, ˃98%, CAS 1941-27-1) were of commercial origin with sufficient for thermochemical studies initial purity higher than 98%. Samples used for vaporization and dissolution experiments were subjected to vacuum inside the experimental chamber of a Quartz Crystal Microbalance (QCM) assembly at 435–440 K for at least 12 h. Traces of possible volatile contaminants were removed during this pre-conditioning process. The residual water content in ILs of 60 ppm was determined by Karl Fischer titration before the experiments. We used Mettler DL35 Karl Fischer Titrator with Hydranal Composite 2, Hydranal Methanol Dry, and Hydranal Eichstandard 5.0 (Riedel-de Haen). A certain amount of condensate was collected on the cold quartz sensor. The ATR-FTIR analysis of the initial sample and those after vaporization was used to detect possible traces of decomposition of the examined IL, but none were found.

2.2 Experimental and Theoretical Thermochemical Methods

A high-precision solution calorimeter was used to measure infinite dilution solution enthalpies of $[\mathrm{N}_{1111}][\mathrm{BF}_4]$ and $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ in water. The detailed description of experimental procedure can be found elsewhere [17]. Solution calorimetry is widely used for studies on molecular and ionic compounds. The method is simple, robust, and has only some limitations when the sample is hygroscopic. But even in this case, the use of the glovebox provides reliable measurements.

Vapour pressures at different temperatures and vaporization/sublimation enthalpies of $[N_{4444}][BF_4]$ and $[N_{4444}][NO_3]$ were derived by the QCM technique combined with the vaporization from an open surface described by the Langmuir equation. Details on the QCM-Langmuir technique are reported elsewhere [18]. The QCM method was specially developed for the investigation of compounds with extremely low vapour pressure, such as ionic liquids. This method allows reliable vapour pressure measurements from as low as 353 to 373 K. As with other methods, the upper temperature range is limited by the decomposition temperature.

Theoretical values of the gas-phase standard molar enthalpies of formation of $[NR_4][BF_4]$ and $[NR_4][NO_3]$ were calculated using the composite G3MP2 [19] method available in the Gaussian 09 software package [20] for calculations of enthalpies H_{298} which were finally converted to the $\Delta_f H^o_m$(g)-values and discussed. For quantum chemical calculations we used the most stable conformer of each IL. The well-established assumption "rigid rotator"-"harmonic oscillator" was used for the quantum chemical calculations. The G3MP2 method seems to be the most suitable for the calculation of ionic liquids, as the resources required to calculate the relatively large ion pairs are appropriate for the facilities usually available at the university computer centre. Short descriptions of experimental and computational techniques applied in this work are given in Supporting Information.

3 Results and Discussion

3.1 Experimental Thermodynamics of Solution, Vaporization, and Sublimation

The results from solution calorimetry are compiled in Table 1. As can be seen from this table, the experimental conditions were close to infinite dilution since the sufficient variations in sample masses (two- to fivefold) provided reproducible values of solution enthalpies. For comparison, our result for $[N_{4444}][BF_4]$ (see Table 1) was in the excellent agreement with the $\Delta_{sol}H^{\infty}_m = 6.3 \pm 1.2$ kJ·mol^{-1}, reported in Ref. [11].

The QCM results of sublimation/vaporization enthalpies determinations are presented in Table 2.

The experimental enthalpies of sublimation/vaporization, $\Delta^g_{cr/l}H^o_m\left(T_{av}\right)$, were derived from slopes of vapour pressure temperature dependences and adjusted to the reference temperature $T = 298.15$ K with help of Kirchhoff's equation:

$$\Delta^g_{cr/l}H^o_m(298.15\,\mathrm{K}) = \Delta^g_{cr/l}H^o_m(T_{av}) + \Delta^g_{cr/l}C^o_{p,m}\,(298.15\,\mathrm{K} - T_{av}), \tag{6}$$

where the values $\Delta^g_{cr/l}C^o_{p,m}$ are the difference between the molar isobaric heat capacities of the gaseous $C^o_{p,m}$(g) and the crystal or liquid $C^o_{p,m}$(cr or l) phase, which are given in Table S1 in the ESI.

3.2 Thermodynamics of Solid–Solid and Solid–Liquid-Phase Transitions

The thermal properties of $[NR_4][BF_4]$ and $[NR_4][NO_3]$, including melting and decomposition temperatures, as well as the temperatures and energetics of the solid–solid and

Table 1 Enthalpies of solution, $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$(IL), of ionic liquids in water measured at 298.15 K and atmospheric pressure

Ionic liquid	Mass of sample[a] g	Concentration mol·kg^{-1}	$\Delta_{\text{sol}}H_{\text{m}}^{\infty}$(IL) kJ·mol^{-1}
[N_{1111}][BF_4]	0.01375	0.00342	42.92
	0.01374	0.00341	43.30
	0.00790	0.00196	43.27
	0.00846	0.00210	42.81
			43.1 ± 0.5[b]
[N_{4444}][BF_4]	0.01103	0.00134	6.84
	0.02251	0.00273	6.29
	0.01335	0.00162	6.66
	0.01313	0.00160	6.75
			6.6 ± 0.5[b,c]

[a] Mass of IL sample loaded into the ampoule for each experiment

[b] Uncertainties are twice the standard deviation

[c] For comparison, $\Delta_{\text{sol}}H_{\text{m}}^{\infty} = 6.3 \pm 1.2$ kJ·mol^{-1} was reported in Ref. [11]

Table 2 Compilation of standard molar enthalpies of sublimation/vaporization for [R_4Am][BF_4] and [R_4Am][NO_3] series

IL	T-range K	T_{av} K	$\Delta_{\text{cr/l}}^{\text{g}}H_{\text{m}}^{\text{o}}(T_{\text{av}})$ kJ·mol^{-1}	$\Delta_{\text{cr/l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}$ [a] J·K^{-1}·mol^{-1}	$\Delta_{\text{cr/l}}^{\text{g}}H_{\text{m}}^{\text{o}}$ (298.15 K)[b] kJ·mol^{-1}
[N_{4444}][BF_4] (sub)	400–425	412.7	162.2 ± 2.0	– 40	166.8 ± 2.2
[N_{4444}][BF_4] (vap)	430–450	439.7	142.8 ± 2.0	– 88	155.3 ± 3.2
[N_{4444}][NO_3] (sub)	413–461	436.4	166.6 ± 1.1	– 40	172.1 ± 1.6
[N_{4444}][NO_3] (vap)	458–506	481.9	157.9 ± 1.0	– 60	168.9 ± 2.4

[a] The difference between the molar isobaric heat capacities of the gaseous $C_{\text{p,m}}^{\text{o}}$(g) and the crystal or liquid phase $C_{\text{p,m}}^{\text{o}}$(cr or l) given in Table S1

[b] Adjusted to 298.15 K using $\Delta_{\text{cr/l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}$–values from column 5, the final uncertainties of sublimation/vaporization enthalpies are expanded taking into account the uncertainty of the heat capacity difference $\Delta_{\text{l}}^{\text{g}}C_{\text{p,m}}^{\text{o}}$ assigned to be of ± 20 J·K^{-1}·mol^{-1}. Uncertainties of vaporization enthalpies are presented as the expanded uncertainties for confidence level = 0.95, k ≈ 2. The corresponding uncertainty of the average temperature determination is $U(T_{\text{av}}) = 0.02$ K

solid–liquid-phase transitions, have been reported several times in the literature [5, 7–9]. However, since these molecules are known as plastic crystals, the reproducibility of the reported thermal properties from source to source is very poor (see Tables S2 and S3). The reason for this is the significant influence of the kinetic factors (sample mass, heating rates, etc.) on the resulting thermodynamic parameters. The results of Bhatt and Gohil [5] are particularly different and we suspect that the rather insufficient purity of the self-made samples could be a reason for this. Compilation of phase transitions for [NR_4][BF_4] and [NR_4][NO_3] is given in Table 3.

Table 3 Phase transition thermodynamics of [R_4Am][BF_4] and [R_4Am][NO_3] (in kJ·mol^{-1})[a]

ILs	T_{fus}, K[b]	$\Delta_{tpce}^{l}H_{m}^{o\,b}$ at T_{fus}	$\Delta_{tpce}^{l}H_{m}^{o\,c}$ 298.15 K	$\Delta_{l}^{g}H_{m}^{o\,d}$ 298.15 K	$\Delta_{cr}^{g}H_{m}^{o}$(exp)[e] 298.15 K	$\Delta_{cr}^{g}H_{m}^{o}$(theor)[f] 298.15 K
[N_{1111}][BF_4]	716	49.4 ± 2.0	21.0 ± 4.7	143.6 ± 3.0	164.6 ± 5.6	163.7 ± 5.3
[N_{2222}][BF_4]	642	44.3 ± 2.0	20.9 ± 4.0	149.0 ± 2.1	169.9 ± 4.6	170.5 ± 6.0
[N_{3333}][BF_4]	511	35.5 ± 0.5	21.0 ± 2.2	152.5 ± 2.1	173.5 ± 3.1	165.8 ± 6.4
[N_{4444}][BF_4]	429	20.0 ± 0.5	11.1 ± 1.3	155.3 ± 3.2[g]	166.4 ± 3.5	166.8 ± 5.7
[N_{1111}][NO_3] [14]	683	54.4 ± 1.0	28.2 ± 4.1	152.1 ± 2.7	180.3 ± 4.9	180.6 ± 4.2
[N_{2222}][NO_3] [14]	553	40.9 ± 1.0	23.6 ± 2.8	161.2 ± 3.3	184.8 ± 4.3	184.4 ± 4.6
[N_{3333}][NO_3]	523	28.8 ± 2.0	13.5 ± 3.0	165.1 ± 3.0	178.6 ± 4.3	178.4 ± 5.2
[N_{4444}][NO_3]	390	14.8 ± 0.6	8.6 ± 1.1	168.9 ± 2.4[g]	177.5 ± 2.6	175.2 ± 4.7[h]

[a] Uncertainties are presented as expanded uncertainties (0.95 level of confidence with $k = 2$)

[b] Evaluated values from Tables S2–S5

[c] The "total phase change enthalpies" were adjusted to $T = 298.15$ K with the help of Eq. 7. Uncertainties in the temperature adjustment are estimated to account with 15% to the total adjustment

[d] Vaporization enthalpies evaluated from the structure–property correlations (see text)

[e] Calculated as the sum column 4 and 5 in this table

[f] From Table 6, column 7

[g] Experimental values of vaporization enthalpies (see Table 2)

[h] For comparison, the sublimation enthalpy $\Delta_{cr}^{g}H_{m}^{o}$(298.15 K) = 172.1 ± 1.6 kJ·mol^{-1} was measured by QCM (see Table 2)

Admittedly, for calculations, all thermodynamic quantities should be referred to the same temperature $T = 298.15$ K. The sublimation and vaporization enthalpies have been already adjusted to this temperature in Table 2. However, the experimental results for solid–solid-phase transitions and enthalpies of fusion have been reported at appropriate phase transition temperatures T_{tr} and at the melting temperature T_{fus}. According to the procedure developed by Chickos and Acree [21] for each compound, we need to combined the experimental phase transition enthalpies, $\Delta H_{\mathrm{m}}^{tr}$, and the experimental enthalpy of fusion, $\Delta_{\mathrm{cr}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}$, into a single term, called the "total phase change enthalpy", $\Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}$ (T_{fus}), and it has been adjusted to the reference temperature using Eq. 7 [21]:

$$\Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{m}^{o}(298.15\,\mathrm{K})/(\mathrm{J}\cdot\mathrm{mol}^{-1}) = \Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{m}^{o}(T_{\mathrm{fus}}/\mathrm{K}) + \Delta_{\mathrm{cr}}^{\mathrm{l}} C_{\mathrm{p,m}}^{\mathrm{o}} \times [(T_{\mathrm{fus}}/\mathrm{K}) - 298.15\mathrm{K}], \quad (7)$$

where $\Delta_{\mathrm{cr}}^{\mathrm{l}} C_{\mathrm{p,m}}^{\mathrm{o}} = 68\ \mathrm{J\cdot mol^{-1}\cdot K^{-1}}$ was evaluated to be essentially the same as for some common ionic liquids [14]. With this adjustment the total phase change enthalpies of the solid ammonium-based ILs $\Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$ were calculated (see Table 3). The energetics of the thermal behaviour is of interest for this work because for both relatively low-melting $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ and $[\mathrm{N}_{4444}][\mathrm{NO}_3]$ we could measure vapour pressures below and above the melting point (see Table 2). This means that the difference between the sublimation and vaporization enthalpy for each compound gives the enthalpy fusion (see Eq. 1). For example, for $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ (see Table 2), the difference between the experimental sublimation enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = 166.8 \pm 2.2\ \mathrm{kJ\cdot mol^{-1}}$ and the experimental vaporization enthalpy $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = 155.3 \pm 3.2\ \mathrm{kJ\cdot mol^{-1}}$ gives the value 11.5 $\mathrm{kJ\cdot mol^{-1}}$, which corresponds exactly to the $\Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = 11.1 \pm 2.2\ \mathrm{kJ\cdot mol^{-1}}$ (see Table 3) for this compound. For $[\mathrm{N}_{4444}][\mathrm{NO}_3]$ (see Table 2), the difference between the experimental sublimation enthalpy $\Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = 172.1 \pm 1.6\ \mathrm{kJ\cdot mol^{-1}}$ and the experimental vaporization enthalpy $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K}) = 168.9 \pm 2.4\ \mathrm{kJ\cdot mol^{-1}}$ gives the value $3.2 \pm 2.9\ \mathrm{kJ\cdot mol^{-1}}$, which also sufficiently (within the combined uncertainties) corresponds to the $\Delta_{\mathrm{tpce}}^{\mathrm{l}} H_{\mathrm{m}}^{\mathrm{o}}$ $(298.15\ \mathrm{K}) = 8.6 \pm 2.0\ \mathrm{kJ\cdot mol^{-1}}$ (see Table 3) for this compound. The observed agreement for the vaporization thermodynamics of both ILs could be taken as evidence for their data consistency.

3.3 Structure–Property Correlation Within Ionic Liquid Series

The experimental measurement of ionic liquids is a challenging task, since at low temperatures they have no detectable vapour pressures, but with rising temperature the risk of measuring vaporization and decomposition simultaneously increases. Therefore, any kind of empirical structure–property correlations for vaporization enthalpies are welcome. On the one hand, such correlations could be helpful for validating the available data, but at the same time they could also be used to assess not yet measured vaporization enthalpies for ILs. Only two experimental datasets on ammonium-based ILs are available in the literature for $[\mathrm{NR}_4][\mathrm{NO}_3]$ [14] and for $[\mathrm{NR}_4][\mathrm{NTf}_2]$ [22]. The experimental vaporization enthalpies for imidazolium-based ILs with $[\mathrm{NO}_3]$, $[\mathrm{NTf}_2]$, and $[\mathrm{BF}_4]$ are represented more [16, 23–25]. Are there empirical correlations between vaporization enthalpies for structurally similar series? It has turned out–yes! If we plot $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$ of $[\mathrm{C_n mim}][\mathrm{BF}_4]$ [16] versus $\Delta_{\mathrm{l}}^{\mathrm{g}} H_{\mathrm{m}}^{\mathrm{o}}(298.15\ \mathrm{K})$ of $[\mathrm{C_n mim}][\mathrm{NTf}_2]$ [24], a robust linear correlation is observed (see Table S6):

$$\Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][BF_4]) = 20.0 + 0.889 \times \Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][\mathrm{NTf}_2])\ \mathrm{with}\ \mathrm{R}^2 = 0.980. \tag{8}$$

If we plot $\Delta_l^g H_m^o$(298.15 K) of [$C_n$mim][BF_4] [16] versus $\Delta_l^g H_m^o$(298.15 K) of [$C_n$mim][NO_3] [23], a linear correlation is also observed (see Table S7):

$$\Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][\mathrm{BF}_4]) = -41.5 + 1.10 \times \Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][\mathrm{NO}_3])\ \mathrm{with}\ \mathrm{R}^2 = 0.971. \tag{9}$$

Finally, if we plot $\Delta_l^g H_m^o$(298.15 K) of [$C_n$mim][NO_3] [23] versus $\Delta_l^g H_m^o$(298.15 K) of [$C_n$mim][NTf_2] [24], a nearly perfect linear correlation is given by the equation (see Table S8):

$$\Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][\mathrm{NO}_3]) = 47.5 + 0.873 \times \Delta_l^g H_m^o(298.15\,\mathrm{K},\,[C_n\mathrm{mim}][\mathrm{NTf}_2])\ \mathrm{with}\ \mathrm{R}^2 = 0.998. \tag{10}$$

Such robust linear correlations are certainly evidence of the high consistency of the experimental data in each series. Just recently we reported vaporization enthalpies for a series of [NR_4][NTf_2] [22]. We have plotted the vaporization enthalpy of [N_{4444}][NTf_2] together with the enthalpy of vaporization of [N_{4444}][BF_4] (which is only available for the alkyl-ammonium [BF_4] series) to the correlation derived for the [$C_n$mim][BF_4] and [$C_n$mim][NTf_2] series (see Eq. 8). This point turned out to be right on their line, as shown in Fig. 2.

This perfect correspondence between different series led us to believe that [N_{1111}][BF_4], [N_{2222}][BF_4], and [N_{3333}][BF_4] also belong to this line. Therefore, the vaporization enthalpies of these three ILs were calculated (see Table S9) according to Eq. 8. To prove this assumption, we additionally correlated data for ammonium ILs with anions [BF_4] and [NO_3] (see Table S10) and interpolated vaporization enthalpies for [N_{2222}][BF_4] and [N_{3333}][BF_4] from this correlation (see Table S10). The barely distinguishable results for ammonium tetrafluoroborates (see Table S11) justified our assumption and provided the important for this work but missing enthalpies of vaporization of [N_{1111}][BF_4], [N_{2222}][BF_4], and [N_{3333}][BF_4], which are now involved in the thermochemical calculations in Table 3.

The final check for consistency of vaporization enthalpies in [NR_4][BF_4] and [NR_4][NO_3] homologous series is the correlation with the number of C-atoms in alkyl chains. For example, for the series [NR_4][NTf_2], the dependence of vaporization enthalpy on

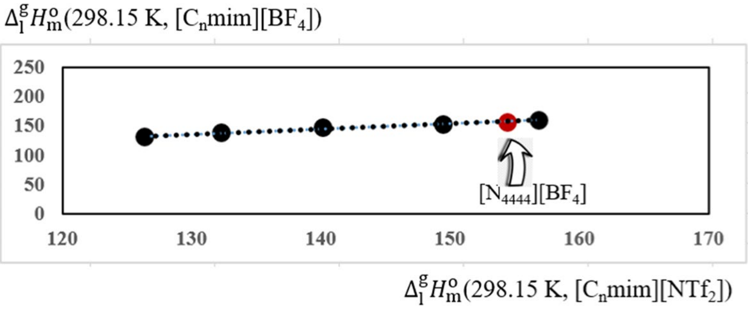

Fig. 2 Correlation of $\Delta_l^g H_m^o$(298.15 K) of [$C_n$mim][BF_4] and [$C_n$mim][NTf_2] (black points). The red point belongs to the pair from ammonium-based ILs: [N_{4444}][BF_4] and [N_{4444}][NTf_2] (Color figure online)

the total number of C-atoms, N_C, in the alkyl chains of the ammonium cation follows the equation [22]:

$$\Delta_l^g H_m^o(298.15\mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = 134.3 + 1.26 \times N_C(\mathrm{with}R^2 = 0.980), \tag{11}$$

from which the enthalpies of vaporization $\Delta_l^g H_m^o$(298.15 K) of other representatives of this series with different N_C can be calculated.

For the series $[NR_4][BF_4]$ investigated in this work, the vaporization enthalpies at the reference temperature (see Table 3, column 5) were approximated by the linear equation (for $N_C > 4$):

$$\Delta_l^g H_m^o\,(298.15\,\mathrm{K})/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = 142.2 + 0.788 \times N_C\,(\mathrm{with\,R}^2 = 0.996). \tag{12}$$

For the series $[NR_4][NO_3]$ the vaporization enthalpies (see Table 3, column 5) were approximated by the linear equation (for $N_C{}^{>}$ 4):

$$\Delta_l^g H_m^o\,(298.15K)/\mathrm{kJ}\cdot\mathrm{mol}^{-1} = 153.5 + 0.963 \times N_C\,(\mathrm{with\,R}^2 = 0.946). \tag{13}$$

It is important to note that the first members of these homologous series were excluded from correlations with the N_C. However, this phenomenon is already known for imidazolium-based ionic liquids [24]. It is also important to indicate that the slopes of Eqs. 11, 12, and 13 are very similar and generally representing a similar contribution of the CH_2 group to the vaporization enthalpy $\Delta_l^g H_m^o$(298.15 K). Interestingly, the CH_2 contribution is significantly lower than that of imidazolium-based ILs (*e.g.* 3.5 kJ·mol^{-1} [16] in $[C_n\mathrm{mim}][BF_4]$ and 3.9 kJ·mol^{-1} [24] in $[C_n\mathrm{mim}][NTf_2]$). The obvious reason for this decreasing contribution is the interweaving of the alkyl chains in the ammonium-based ILs due to strong dispersion interactions discussed in detail in our previous work [22]. When the CH_2 contributions to the vaporization enthalpy $\Delta_l^g H_m^o$(298.15 K) in $[NR_4][NTf_2]$, $[NR_4][BF_4]$, and $[NR_4][NO_3]$ series are similar, the intercepts are different and generally indicate that the volatility of the ammonium-based series is markedly different and the $[NR_4][NTf_2]$ family is the most volatile amongst them.

The consistent sets of vaporization enthalpies, $\Delta_l^g H_m^o$(298.15 K), for the $[NR_4][BF_4]$ and $[NR_4][NO_3]$ series evaluated in this section (see Table 3, column 5) together with the $\Delta_{tpce}^l H_m^o$(298.15 K)-values evaluated in this table (see Table 3, column 4) can now be used to derive "empirical" sublimation enthalpies $\Delta_{cr}^g H_m^o$(298.15 K) according to Eq. 1. These "empirical" values are given in Table 3, column 6 and can now be compared with the experimental values $\Delta_{cr}^g H_m^o$(298.15 K) measured by QCM (see Table 2). The empirical and experimental results for $[N_{4444}][BF_4]$ are hardly distinguishable (see Tables 2 and 3). The agreement for $[N_{4444}][NO_3]$ is less favourable, but is still good, considering generous uncertainties attributed to both empirical and experimental values. Therefore, the consistent sets of sublimation enthalpies, $\Delta_{cr}^g H_m^o$(298.15 K), for the $[NR_4][BF_4]$ and $[NR_4][NO_3]$ series were also evaluated in Table 3, column 6 and can now be used in combination with the crystal state enthalpies of formation, $\Delta_f H_m^o$(cr), to derive according to Eq. 3 the gas-state enthalpies of formation for these series.

3.4 Solution enthalpies for $\Delta_f H_m^o$(cr) calculations

The standard molar enthalpies of solution at infinite dilution, $\Delta_{sol} H_m^\infty$(IL), for $[N_{1111}][BF_4]$ and $[N_{4444}][BF_4]$ were measured in this work and given in Tables 1, 2, 3, and 4. The

Table 4 Estimation of aqueous enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{IL_{aq}})$, and crystalline enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, of alkyl-ammonium tetrafluoroborates at $T = 298.15$ K (in kJ·mol^{-1})[a]

IL	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty\ \mathrm{bb}}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}\left(\mathrm{NR}_{4\,\mathrm{aq}}^{+}\right)$ [14]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}\left(\mathrm{BF}_{4\,\mathrm{aq}}^{-}\right)$ [16]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{IL_{aq}})^{\mathrm{c}}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})^{\mathrm{d}}$
$[\mathrm{N}_{1111}][\mathrm{BF}_4]$	43.1 ± 0.5	− 103.9 ± 1.0	− 1571.5 ± 3.2	− 1675.4 ± 3.4	− 1718.5 ± 3.4
$[\mathrm{N}_{2222}][\mathrm{BF}_4]$	31.6 ± 2.1$^{\mathrm{e}}$	− 216.6 ± 2.1	− 1571.5 ± 3.2	− 1787.1 ± 3.8	− 1818.7 ± 4.4
$[\mathrm{N}_{3333}][\mathrm{BF}_4]$	18.9 ± 2.1$^{\mathrm{e}}$	− 317.5 ± 3.0$^{\mathrm{f}}$	− 1571.5 ± 3.2	− 1889.0 ± 4.0	− 1907.9 ± 4.9
$[\mathrm{N}_{4444}][\mathrm{BF}_4]$	6.5 ± 0.5	− 422.0 ± 2.2	− 1571.5 ± 3.2	− 1993.5 ± 3.9	− 2000.0 ± 3.9

[a] Uncertainties are presented as expanded uncertainties (0.95 level of confidence with k = 2)

[b] Measured in this work (see Table 1) or evaluated in this work from the structure–property relationships (see Table S12)

[c] Calculated according to Eq. 4

[d] Calculated according to Eq. 5

[e] From Table S12

[f] Interpolated from the chain length dependence: $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}\left(\mathrm{NR}_{4\,\mathrm{aq}}^{\ +}\right)/\mathrm{kJ{\cdot}mol^{-1}} = -\ 0.7\text{–}26.41 \times N_{\mathrm{C}}$ with $\mathrm{R}^2 = 0.9996$, obtained from the data given in this table. The N_{C} is the total number of C-atoms in alkyl chains

Table 5 Estimation of aqueous enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{IL_{aq}})$, and crystalline enthalpies of formation, $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$, of alkyl-ammonium nitrates at $T = 298.15$ K (in kJ·mol^{-1})[a]

IL	$\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$ [14]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}\left(\mathrm{NR}_{4\,\mathrm{aq}}^{+}\right)^{\mathrm{b}}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}\left(\mathrm{NO}_{3\,\mathrm{aq}}^{-}\right)$ [26]	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{IL_{aq}})^{\mathrm{c}}$	$\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})^{\mathrm{d}}$
$[\mathrm{N}_{1111}][\mathrm{NO}_3]$	19.8 ± 0.3	− 103.9 ± 1.0	− 206.9 ± 0.4	− 310.8 ± 1.1	− 330.6 ± 1.1
$[\mathrm{N}_{2222}][\mathrm{NO}_3]$	8.1 ± 0.1	− 216.6 ± 2.1	− 206.9 ± 0.4	− 422.5 ± 2.1	− 430.6 ± 2.1
$[\mathrm{N}_{3333}][\mathrm{NO}_3]$	− 6.2 ± 1.0$^{\mathrm{e}}$	− 317.5 ± 3.0	− 206.9 ± 0.4	− 524.4 ± 3.0	− 518.2 ± 3.2
$[\mathrm{N}_{4444}][\mathrm{NO}_3]$	− 19.8 ± 0.2	− 422.0 ± 2.2	− 206.9 ± 0.4	− 628.9 ± 2.2	− 609.1 ± 2.2

[a] Uncertainties are presented as expanded uncertainties (0.95 level of confidence with $k = 2$)

[b] From Table 4, column 3

[c] Calculated according to Eq. 4

[d] Calculated according to Eq. 5

[e] From Table S13, interpolated from the chain length dependence: $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}/\mathrm{kJ{\cdot}mol^{-1}} = 33.8\text{–}3.33 \times N_{\mathrm{C}}$ with $\mathrm{R}^2 = 0.998$, obtained from the data given in this table. The N_{C} is the total number of C-atoms in alkyl chains

$\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$(IL)-values for the $[\mathrm{NR}_4][\mathrm{NO}_3]$ series were reported in our previous work [14] and compiled in Table 5.

However, in order to use Eqs. 4 and 5 for calculations of $\Delta_{\mathrm{f}}H_{\mathrm{m}}^{\mathrm{o}}(\mathrm{cr})$ for the $[\mathrm{NR}_4][\mathrm{BF}_4]$ series, we are missing the $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$(IL) for $[\mathrm{N}_{2222}][\mathrm{BF}_4]$ and $[\mathrm{N}_{3333}][\mathrm{BF}_4]$. And again, the structure–property correlations help to get the necessary data. Indeed, we have already established [14] that the solution enthalpies for $[\mathrm{NR}_4][\mathrm{NO}_3]$ series depend linearly on chain length (see Table S13). With this prerequisite, the interpolation between experimental $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$(IL)-values for $[\mathrm{N}_{1111}][\mathrm{BF}_4]$ and $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ is expected to provide a rough estimate for the missing values, which are given in Table S14. However, to ascertain such structure–property relationships, we additionally correlated $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$(IL)-values of $[\mathrm{NR}_4][\mathrm{NO}_3]$ and $[\mathrm{NR}_4][\mathrm{BF}_4]$ series (see Table S14) and the interpolated $\Delta_{\mathrm{sol}}H_{\mathrm{m}}^{\infty}$(IL)-values for $[\mathrm{N}_{1111}][\mathrm{BF}_4]$ and $[\mathrm{N}_{4444}][\mathrm{BF}_4]$ agree well (see Table S15) with those from the chain length dependence. With good agreement for "empirical" solution enthalpies obtained independently (see Table S12), we averaged the $\Delta_{\text{sol}}H_{\text{m}}^{\infty}$(IL)-values for each $[\text{N}_{1111}][\text{BF}_4]$ and $[\text{N}_{4444}][\text{BF}_4]$ compound and used these results for thermochemical calculations in Table 4.

Now we have gathered all the necessary information to estimate the aqueous enthalpies of formation and crystalline enthalpies of formation of alkyl-ammonium tetrafluoroborates (see Table 4) and nitrates (see Table 5). Results of the calculations according to Eqs. 4 and 5 are shown in the last columns of these tables. The crystalline enthalpies of formation, $\Delta_{\text{f}}H_{\text{m}}^{\text{o}}$(cr), of alkyl-ammonium-based ILs (obtained in Tables 4 and 5) together with the evaluated sublimation enthalpies, $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$, given in Table 3, column 6, were used to derive according to Eq. 3 the experimental gas-phase enthalpies of formation for $[\text{NR}_4][\text{BF}_4]$ and $[\text{NR}_4][\text{NO}_3]$ series. The latter values are essential for the validation of quantum chemical methods, as will be shown in the next section.

3.5 Experimental and Theoretical Gas-Phase Standard Molar Enthalpies of Formation

Ionic liquids are large compared to the usual organic molecules. The high-level quantum chemical calculation of large molecules is a challenging task, not only due to the limitation of computational resources, but also due to a possible accumulation of systematic errors inherent in any calculation method. In our laboratory, we systematically apply the G3MP2 composite method [19] to calculate the gas-phase enthalpies of the molecular and ionic compounds. A good agreement between experimental and theoretical values was obtained for imidazolium- [23, 27] and ammonium [14]-based ILs. In the current study,

Table 6 Thermochemical data for $[\text{NR}_4][\text{BF}_4]$ and $[\text{NR}_4][\text{NO}_3]$ series (at $T = 298.15$ K, $p° = 0.1$ MPa, in kJ·mol^{-1})[a]

IL	$\Delta_{\text{f}}H_{\text{m}}^{\text{o}}$(cr)[b]	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$[c]	$\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g})_{\text{exp}}$[d]	$\Delta_{\text{f}}H_{\text{m}}^{\text{o}}(\text{g})_{\text{G3MP2}}$[e]	$\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}$(theor)[f]
$[\text{N}_{1111}][\text{BF}_4]$	− 1718.5 ± 3.4	164.6 ± 5.6	− 1553.9 ± 6.5	− 1554.8 ± 4.1	163.7 ± 5.3
$[\text{N}_{2222}][\text{BF}_4]$	− 1818.7 ± 4.4	169.9 ± 4.6	− 1648.6 ± 6.3	− 1648.2 ± 4.1	170.5 ± 6.0
$[\text{N}_{3333}][\text{BF}_4]$	− 1907.9 ± 4.9	173.5 ± 3.1	− 1734.4 ± 5.7	− 1742.1 ± 4.1	165.8 ± 6.4
$[\text{N}_{4444}][\text{BF}_4]$	− 2000.0 ± 3.9	166.4 ± 3.5	− 1833.6 ± 5.3	− 1833.2 ± 4.1	166.8 ± 5.7[g]
$[\text{N}_{1111}][\text{NO}_3]$	− 330.4 ± 1.1	180.3 ± 4.9	− 150.1 ± 5.0	− 150.0 ± 4.1	180.6 ± 4.2
$[\text{N}_{2222}][\text{NO}_3]$	− 430.7 ± 1.7	184.8 ± 4.3	− 245.9 ± 4.6	− 246.2 ± 4.1	184.4 ± 4.6
$[\text{N}_{3333}][\text{NO}_3]$	− 518.2 ± 3.2	178.6 ± 4.3	− 339.6 ± 5.3	− 339.8 ± 4.1	178.4 ± 5.2
$[\text{N}_{4444}][\text{NO}_3]$	− 607.0 ± 1.9	177.5 ± 2.6	− 429.5 ± 3.2	− 433.9 ± 4.1	173.1 ± 4.8[h]

[a] The uncertainty in this table are expressed as the twice standard deviation

[b] From Table 4 for $[\text{NR}_4][\text{BF}_4]$ and from Table S16 for $[\text{NR}_4][\text{NO}_3]$

[c] From Table 3, column 6

[d] Sum of column 2 and 3 in this table

[e] Calculated by the G3MP2 method using the atomization reaction for $[\text{NR}_4][\text{BF}_4]$ in this work and for $[\text{NR}_4][\text{NO}_3]$ calculated by the G3MP2 method in our previous work [14]

[f] Calculated as the difference between column 5 and 2 in this table

[g] For comparison the sublimation enthalpy $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\ \text{K}) = 166.8 \pm 2.2$ kJ·mol^{-1} was measured using QCM (see Table 2)

[h] For comparison the sublimation enthalpy $\Delta_{\text{cr}}^{\text{g}}H_{\text{m}}^{\text{o}}(298.15\ \text{K}) = 172.1 \pm 1.6$ kJ·mol^{-1} was measured using QCM (see Table 2)

the H_{298}-values for the [NR$_4$][BF$_4$] series were also calculated using the G3MP2 method and converted into the enthalpies of formation using atomization reactions. The theoretical enthalpies of formation for the [NR$_4$][NO$_3$] were taken from our previous work [14]. The experimental gas-phase enthalpies for both series are given in Table 6, column 4 and are compared to the theoretical enthalpies of formation given in column 5.

The comparison of the results exceeds all expectations, the agreement is significantly better than the boundaries of the uncertainties attributed to the final $\Delta_f H^o_m$(g)-values. On the one hand, this good agreement supports numerous assumptions used in our structure–property correlations to recover the missing thermodynamic data. On the one hand, this good agreement supports numerous assumptions used in our structure–property correlations to obtain the missing thermodynamic data. On the other hand, it must be emphasized that modern quantum chemical calculations are becoming an indispensable tool to establish mutual consistency between experimental and theoretical data.

To give an encore, we compare results shown in columns 6 and 7 of Table 3. In column 6 are the sublimation enthalpies were derived by summing “total phase change enthalpies” with the vaporization enthalpies of experimental or empirical origin. In this column these values are denoted as $\Delta^g_{cr} H^o_m$(exp) since at least the data for [N$_{4444}$][BF$_4$] and [N$_{4444}$][NO$_3$] were measured by QCM. It is evident that the experimental determination of the phase transitions reported in Table 3 is thwarted by complications and may not be free of bias due to the high-temperature decomposition of the studied ILs. What about column 7 with sublimation enthalpies, denoted there as $\Delta^g_{cr} H^o_m$(theor)? First, the results in columns 6 and 7 largely agree. Secondly, the $\Delta^g_{cr} H^o_m$(theor)-values were obtained in a much simpler way: to measure the enthalpy of solution and to calculate the enthalpies of formation in the gas phase. The risk of high-temperature decomposition is irrelevant for this route. This conclusion is essential for the further development of solution calorimetry as a valuable complementary tool for the reliable determination of thermochemical properties of ionic liquids. This idea was strongly supported by Prof. Jean-Pierre E. Grolier and we are grateful for his efforts to advance the development of solution calorimetry.

4 Conclusion

The tetra-alkyl-ammonium-based ionic liquids are interesting from a practical point of view because they can be synthesized from relatively cheap starting materials. They are considered suitable for energy storage systems, such as batteries or as phase-change materials. Therefore, knowledge of their physico-chemical and thermodynamic properties is essential for the development of appropriate technologies. The solution enthalpies of tetra-alkyl-ammonium tetrafluoroborates and nitrates were evaluated and used together with the sublimation/vaporization enthalpies derived by QCM to obtain the experimental gas-phase formation enthalpies for these homologous series. The latter values were compared with the theoretical values calculated using G3MP2. The mutual validation of the experimental and theoretical gas-phase enthalpies helped to establish consistency in the thermodynamic data for the alkyl-ammonium-based ionic liquids studied in this work. Furthermore, the combination of solution calorimetry with the quantum chemical methods shown in this work is important for the further development of complementary tools for the reliable determination of the thermochemical properties of ionic liquids.

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Author Contributions SPV and SVV developed the methodology and wrote the main manuscript text and ESI. DHZ performed the vapour pressure measurements and wrote the text and ESI. AVY performed the solution calorimetry experiments and wrote ESI. All authors reviewed the manuscript.

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Declarations

Conflict of interest The authors report no conflict of interest related to this manuscript.

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