# Thermochemistry of ammonium based ionic liquids: Tetra-alkyl ammonium nitrates – Experiments and computations

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ABSTRACT

In this work data of the molar enthalpies of formation of the ionic liquids $[R_4N][NO_3]$ were measured by means of combustion calorimetry. The thermal behavior of $[R_4N][NO_3]$ was studied using differential scanning calorimetry. First-principles calculations of the enthalpy of formation in the gaseous phase have been performed for the ionic species using the G3(MP2) theory. Enthalpies of formation of aqueous tetra-alkyl ammonium ions $\Delta_f H_m^\circ$ ($[R_4N]^+_{(aq)}$) derived in this work are useful for prediction thermochemical properties of the ammonium based ionic liquids.

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## 1. Introduction

*Ionic liquids* (ILs) have attracted much attention due to widespread potential for practical applications such as heat transfer and storage medium in solar thermal energy systems as well as for many areas such as fuel cells, rechargeable batteries and "green solvents". Quaternary ammonium cations form ILs with various anions. Because of the variety of side chains that can be connected to the central N+, many quaternary ammonium ILs could be prepared to "tune" the physical properties such as melting point, water miscibility, conductivity and viscosity by selection and modification of the anion and cation of the IL.

Tetra-alkyl ammonium ILs are one of the key compounds to clarify the structure of aqueous solution and the nature of hydrophobic solute-solvent interaction as well as for study of a thermodynamics of transfer of ions from water to other solvents [1]. Moreover, tetra-n-alkyl ammonium compounds form the clathrate hydrate crystals below ambient temperature without applying high pressures. This fact suggests the ammonium ions with long alkyl chains have a strong tendency to enable the surrounding water molecules to form the clathrate-like structure even in aqueous solution. Regarded for many years as harmful by the oil and gas industry because of their tendency to plug pipelines, clathrate hydrates are now considered propitious for various applications. They may be used for gas capture, storage, separation, and transportation, and the gas hydrates naturally found in deep seas and permafrost may provide large amounts of methane [2].

Experimental data on thermodynamic properties of ionic liquids are scarce [3–7,11]. These quantities are required for the validation and development of the molecular modeling and first-principles methods towards this new class of solvents. In this work we report the measurements (oxygen combustion calorimetry) of molar enthalpy of formation, $\Delta_f H_m^\circ$ (cr), of the ammonium based ionic liquids – tetra-methyl ammonium nitrate ($[Me_4N][NO_3]$); tetra-ethyl ammonium nitrate ($[Et_4N][NO_3]$), and tetra-butyl ammonium nitrate ($[Bu_4N][NO_3]$). The gaseous enthalpies of formation of the ionic liquids were obtained from first-principles calculations using the G3(MP2) method. The enthalpies of formation $\Delta_f H_m^\circ$ (aq) of the aqueous cations $[Me_4N]^+$, $[Et_4N]^+$ and $[Bu_4N]^+$ were evaluated by using $\Delta_f H_m^\circ$ (cr) of $[R_4N][NO_3]$ measured in this work and solution enthalpies $\Delta_{sol} H_m^\circ$ of $[R_4N][NO_3]$ taken from reference [7].

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## 2. Experimental section

### 2.1. Materials and chemicals

The samples of the ammonium based ionic liquids [R₄N][NO₃]: tetra-methyl ammonium nitrate [1941-24-8], tetra-ethyl ammonium nitrate [1941-26-0], and tetra-butyl ammonium nitrate [1941-27-1] used for the experiments were prepared and purified by *proionic Production of Ionic Substances GmbH* (Austria). Prior to using the samples were subjected to vacuum evaporation at 333 K and $10^{-2}$ mbar for more than 24 h to reduce possible traces of solvents and moisture. Purities of all samples [R₄N][NO₃] were >99.5%. The residual water contents in all [R₄N][NO₃] were determined by Karl Fischer titration shortly before the combustion experiments. An appropriate correction for water content in the sample was applied when the combustion results were evaluated. We used Mettler DL35 Karl Fischer Titrator with Hydranal Composite 2, Hydranal Methanol Dry and Hydranal Eichstandard 5.0 (Riedel-de Haen). Samples of the ILs were kept and handled under nitrogen stream.

### 2.2. Thermochemical measurements. Combustion calorimetry

An isoperibol static bomb calorimeter was used for the measurement of energies of combustion of [R₄N][NO₃]. Results are presented in tables 1 and S1 to S3 (supporting information). The detailed procedure has been described previously.[3] The combustion products were examined for carbon monoxide (Dräger tube) and unburned carbon, but none was detected. The energy equivalent of the calorimeter $\varepsilon_{calor} = 14816.0 \pm 0.9$ J K$^{-1}$ was determined with a standard reference sample of benzoic acid (sample SRM 39j, NIST). Correction for nitric acid formation was based on the titration with 0.1 mol dm$^{-3}$ NaOH (aq). For converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states, the conventional procedure [8] was applied. Values of the standard specific energies of combustion $\Delta_c u^\circ$, together with the necessary auxiliary quantities, are given in tables S1 to S3 and S4 (electronic supporting information). All three compounds under study were not sufficiently hygroscopic to require encapsulation of the tablets, but it was necessary to add polyethylene pieces as the auxiliary compound to insure completeness of combustion. To derive the molar standard enthalpy of formation, $\Delta_f H_m^\circ$ (cr), from the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$, molar enthalpies of formation of H₂O (l) and CO₂ (g) were used, as assigned by *CODATA* [9]. Experimental results for [R₄N][NO₃] are given in table 1. The total uncertainty was calculated according to the guidelines presented by Olofsson [10]. The uncertainty assigned to $\Delta_f H_m^\circ$ is twice the overall standard deviation and includes the uncertainties from calibration, from the combustion energies of the auxiliary materials, and the uncertainties of the enthalpies of formation of the reaction products H₂O and CO₂.

### 2.3. Phase transitions in the solid state: DSC-measurements

The thermal behavior of [R₄N][NO₃] including phase transitions and enthalpies of fusion were studied with a computer controlled differential scanning calorimeter Perkin–Elmer Pyris Diamond DSC. For all measurements, an empty pan was used as reference. The fusion temperature and enthalpy were determined as the peak onset temperature and by using a straight baseline for integration, respectively. The temperature and heat flow rate scale of the DSC was calibrated by measuring high-purity indium ($T_0 = 429.8$ K and $\Delta H_{ref} = 28.4$ J g$^{-1}$). The thermal behavior of the specimen was investigated at heating rate of 10 K min$^{-1}$. The uncertainty for temperature is ±0.5 K and for enthalpy of fusion ±1 J g$^{-1}$. The DSC measurements on the sample of [R₄N][NO₃] were repeated twice and values agreed within the experimental uncertainties ±0.2 kJ mol$^{-1}$ for the enthalpy of fusion and ±0.5 K for the melting temperature. Results of our DSC studies together with the available data from the literature are collected in table 2.

### 2.4. First-principles calculations

Standard first-principles molecular orbital calculations were performed using the Gaussian 03 Rev.04 program package [18]. Conformation analysis of the IL was performed using B3LYP/6-31+G(d,p) with help of the procedure developed in our previous work [3]. Optimized structure, and energy of the most stable conformer of the ionic pair was further obtained using the G3(MP2) composite method. The enthalpy values of [R₄N][NO₃] at $T = 298.15$ K were evaluated according to standard thermodynamic procedures [19].

## 3. Results and discussion

Generally, the enthalpy of formation in the gaseous phase of any compound is made up of two contributions:

$$\Delta_f H_m^\circ (g) = \Delta_f H_m^\circ (l) + \Delta_l^g H_m \tag{1}$$

$$\Delta_f H_m^\circ (l) = \Delta_f H_m^\circ (cr) + \Delta_{cr}^l H_m \tag{2}$$

where $\Delta_f H_m^\circ$ is the enthalpy of formation in the gas, crystalline or liquid state; $\Delta_{cr}^l H_m$ is the enthalpy of sublimation, and $\Delta_l^g H_m$ is the enthalpy of vaporization. In the current study we derived these properties from thermochemical measurements as follows.

### 3.1. Enthalpies of formation from combustion calorimetry

Results of combustion experiments on [R₄N][NO₃] are summarized in table 1 as well as in the supporting information. The values of the standard specific energy of combustion, $\Delta_c u^\circ$, the standard molar enthalpy of combustion, $\Delta_c H_m^\circ$, and the standard molar enthalpy of formation in the crystalline state $\Delta_f H_m^\circ$ (cr) were based on the reactions:

**TABLE 1**
Thermochemical data at $T = 298$ K ($p^\circ = 0.1$ MPa) for compounds studied in this work (in kJ mol$^{-1}$).

| Compounds 1 | $\Delta_c H_m^\circ$ (cr)[a] 2 | $\Delta_f H_m^\circ$ (cr) 3 | $\Delta_f H_m^\circ$ (l)[b] 4 | $\Delta_f H_m^\circ$ (g)[c] 5 | $\Delta_l^g H_m$[d] 6 |
|---|---|---|---|---|---|
| Tetra-methyl Ammonium nitrate | −2960.5 ± 0.9 | −331.0 ± 4.2 [11]−331.8 ± 1.0 [7]−328.5 ± 1.1[a](**−330.3 ± 1.0**)[e] | −302.1 ± 0.7 | −150.0 ± 2.6 | 152.1 ± 2.7 |
| Tetra-ethyl ammonium nitrate | −5573.4 ± 3.4 | −428.5 ± 4.0 [7]−433.0 ± 3.6[a](**−431.0 ± 2.7**)[e] | −407.4 ± 2.7 | −246.2 ± 1.9 | 161.2 ± 3.3 |
| Tetra-butyl ammonium nitrate | −10840.9 ± 3.2 | −600.2 ± 3.9[a] | −591.8 ± 3.9 | −433.9 ± 1.0 | 157.9 ± 4.0 |

[a] From combustion experiments, this work.
[b] From table 3.
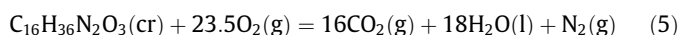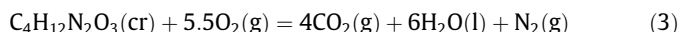[c] Calculated using the G3(MP2) method (see table 4).
[d] Calculated as the difference between column 5 and 4 in this table.
[e] The average was calculated as weighted value according to the procedure developed by Grossman *et al.* [47].

**TABLE 2**
Results from DSC study: enthalpies of phase transitions, $\Delta H_m^{tr}$ at $T_{tr}$ and enthalpies of fusion, $\Delta_{cr}^l H_m$, at $T_{fus}$.

| Compounds | Phase transition | | | Melting | | |
|---|---|---|---|---|---|---|
| | $T_{ongoing}$ (K) | $T_{peak}$ (K) | $\Delta H_m^{tr}$ ($T_{tr}$) (kJ mol$^{-1}$) | $T_{ongoing}$ (K) | $T_{peak}$ (K) | $\Delta_{cr}^l H_m$ ($T_{fus}$) (kJ mol$^{-1}$) |
| Tetra-methyl ammonium nitrate | 292 [14] | | 1.7 [14] | 683 [12] | | 37.2[b] |
| | 300 [14] | | 17.2 [14] | | | |
| | 299.6[a] | | 17.2[a] | | | |
| Tetra-ethyl ammonium nitrate | 365.7[a] | 371.5[a] | 10.8[a] | 553(dec) [16] | | 30.1[b] |
| Tetra-butyl ammonium nitrate | 359.8[a] | 361.4[a] | 0.2[a] | 388.4[a] | 391.1[a] | 14.3[a] |
| | | 362.3 [15] | 0.2 | 389.3 [15] | | 15.6 [15] |
| | | | | 392.2 [13] | | |

[a] From DSC experiments, this work.
[b] Calculated using the modified[17] Walden's rule: $\Delta_{cr}^l H_m$ ($T_{fus}$) = 54.4 (J K$^{-1}$ mol$^{-1}$) · $T_{fus}$ (K).

$$C_4H_{12}N_2O_3(cr) + 5.5O_2(g) = 4CO_2(g) + 6H_2O(l) + N_2(g) \qquad (3)$$

$$C_8H_{20}N_2O_3(cr) + 11.5O_2(g) = 8CO_2(g) + 10H_2O(l) + N_2(g) \qquad (4)$$

$$C_{16}H_{36}N_2O_3(cr) + 23.5O_2(g) = 16CO_2(g) + 18H_2O(l) + N_2(g) \qquad (5)$$

$\Delta_f H_m^\circ$ (cr) of [R$_4$N][NO$_3$] has been obtained from the enthalpic balance according to equations (3)–(5) and the Hess's law.

### 3.2. Thermal behaviour and enthalpies of phase transition of [R$_4$N][NO$_3$]

The tetra-methyl ammonium nitrate crystal showed a sharp phase transition at 283 K and a faint anomaly in the heating run at 428 K [20]. The following phase sequence has been observed by DSC:

phase III (292 K) → phase II(300 K) → phase I

The phase transitions, $\Delta H_m^{tr}$, values are 1.7 kJ mol$^{-1}$ for phase III → II transition and 17.2 kJ mol$^{-1}$ for phase II → I transition [14] (see table 3). The crystal structure of tetra-methyl ammonium nitrate at 303 K is tetragonal D$_{4h}$ [7] (P4/nmm) with Z = 2 and the nitrate ions are disordered [14,21]. Tetra-methyl ammonium nitrate begins to decompose at 636 K in conditions of the TGA measurements [22]. Nevertheless, the temperature of melting of 683 K was reported by Le Roux [12]. In our DSC experiments with tetra-methyl ammonium nitrate we have failed to measure its enthalpy of fusion due to decomposition around the melting point. In DSC study of tetra-ethyl ammonium nitrate we detected only the phase transition $\Delta H_m^{tr}$ at 365.7 K and we observed the decomposition around the melting point. The temperature dependence of the DSC signal for tetra-butyl ammonium nitrate crystal showed a very small phase transition at 359.8 K with the $\Delta H_m^{tr} = 0.2$ kJ mol$^{-1}$ following by melting at 388.4 K with the fusion enthalpy $\Delta_{cr}^l H_m = 14.3$ kJ mol$^{-1}$: this results are in acceptable agreement with the available in the literature DSC study [15] (see table 3). The rapid-scan TG-FTIR thermolysis studies of tetra-butyl

ammonium nitrate [23] revealed that the first gas products were detected at 643 K. These products were triethylamine and ethyl nitrate which are straightforward thermolysis products of tetra-butyl ammonium nitrate.

### 3.3. Determination of the liquid phase enthalpies of formation of [R$_4$N][NO$_3$]

Enthalpies of formation, $\Delta_f H_m^\circ$ (cr), of [R$_4$N][NO$_3$] derived from the combustion experiments are referred to the crystalline state at the reference temperature T = 298 K. However, using equation (2) we are able to calculate the standard molar enthalpy of formation in the liquid phase, $\Delta_f H_m^\circ$ (l), with help of the data on enthalpy of fusion discussed in chapter 3.1. All three compounds under study have the phase transitions, $\Delta H_m^{tr}$, above the reference temperature 298 K (see table 2) which should be also taken into account by using equation (2). As a rule, all four thermodynamic quantities in equation (2) should be referred to the same temperature, i.e., T = 298 K. However, experimental results for enthalpies of fusion, $\Delta_{cr}^l H_m$, and phase transitions, $\Delta H_m^{tr}$, of [R$_4$N][NO$_3$] measured by DSC (see table 2) were obtained at the melting temperatures $T_{fus}$ and $T_{tr}$ accordingly. For each compound under study, we have combined the experimental enthalpy of fusion, $\Delta_{cr}^l H_m$, and the experimental enthalpy of phase transition in a one term $\Delta_{tpce}^l H_m$ according to a procedure developed by Chickos [17]. Because of the difference from the reference temperature, this term $\Delta_{tpce}^l H_m$ have been adjusted to T = 298 K. The adjustment was calculated using equation (6) [17]:

$$\Delta_{tpce}^l H_m \ (298 \ K)/J \ mol^{-1} = \{\Delta_{cr}^l H_m(T_{fus}/K) + \Delta H_m^{tr}(T_{tr}) + 0.68 \cdot [(T_{fus}/K) - 298K]\} \qquad (6)$$

where $\Delta_{tpce}^l H_m$ (298 K) is the total phase change enthalpy of the solid from T = 298 K to $T_{fus}$ adjusted to T = 298 K. The difference between isobaric molar heat capacities of the solid and the liquid compounds ($C_p^{cr} - C_p^l$) = 68 J mol$^{-1}$ K$^{-1}$ in equation (6) was assessed to be essential the same as those for some common ionic liquids

**TABLE 3**
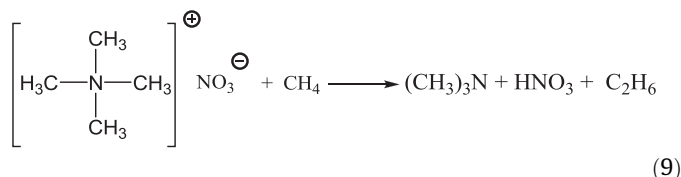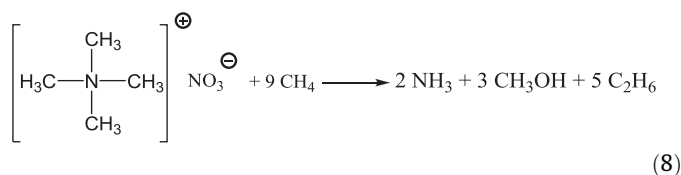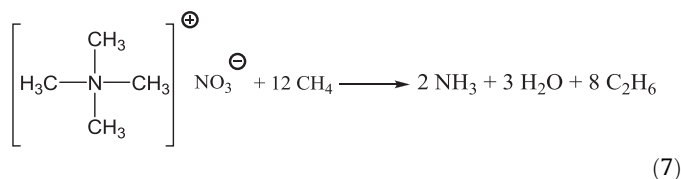Adjustment of the DSC data to the reference temperature T = 298.15 K, kJ·mol$^{-1}$.

| Compounds | $T_{fus}^a$, K | $\Delta_{cr}^l H_m(T_{fus})^a$ | $\Delta H_m^{tr}(T_{tr})^a$ | $\Sigma\Delta H_m$ ($T_{tr}$)$^b$ | $\Sigma\Delta H_m$ (298 K)$^c$ | $\Delta_f H_m^\circ$(cr) (298.15 K)$^d$ | $\Delta_f H_m^\circ$ (l) (298.15 K)$^e$ |
|---|---|---|---|---|---|---|---|
| 1 | 2 | 3 | 4 | 5 | 6 | 7 | 8 |
| Tetra-methyl ammonium nitrate | 683 | 37.2 | 17.2 | 54.4 | 28.2 | −330.3 ± 0.7 | −302.2 ± 0.7 |
| Tetra-ethyl ammonium nitrate | 553 (dec.) | 30.1 | 10.8 | 40.9 | 23.6 | −431.0 ± 2.7 | −407.4 ± 2.7 |
| Tetra-butyl ammonium nitrate | 388.4 | 14.3 | 0.2 | 14.5 | 8.4 | −600.2 ± 3.9 | −591.8 ± 3.9 |

[a] From table 2.
[b] Calculated as the sum of column 3 and 4.
[c] Adjusted to the reference temperature (see text).
[d] From table 1.
[e] Calculated as the sum of column 6 and 7.

(see table S5, ESI) measured in the recent work [24,25]. With this adjustment (the uncertainty of the correlation was not taken into account), the total phase change enthalpies of the solid, $\Delta_{\text{tpce}}^{l}H_m$ (298 K), were calculated (table 3). Substituting these values into equation (6) the standard molar enthalpies of formation of [R$_4$N][NO$_3$] in the undercooled metastable liquid phase, $\Delta_f H_m^{\circ}$ (l), have been derived (table 1). These values will be combined with the results from first-principles calculations in order to obtain vaporization enthalpies of [R$_4$N][NO$_3$].

### 3.4. Calculation of the gaseous phase enthalpies of formation of [R$_4$N][NO$_3$] using the first-principles methods

Results of the molar enthalpies of formation, $\Delta_f H_m^{\circ}$ (g), of [R$_4$N][NO$_3$] obtained by using first-principles methods have not been reported in the literature so far. We have calculated the enthalpies of formation of [R$_4$N][NO$_3$] using G3(MP2) method applying atomization reactions as well as bond separation reactions. For the latter method we have chosen the following three reactions:

$$\left[\begin{array}{c} CH_3 \\ | \\ H_3C-N-CH_3 \\ | \\ CH_3 \end{array}\right]^{\oplus} NO_3^{\ominus} + 12\ CH_4 \longrightarrow 2\ NH_3 + 3\ H_2O + 8\ C_2H_6$$

(7)

$$\left[\begin{array}{c} CH_3 \\ | \\ H_3C-N-CH_3 \\ | \\ CH_3 \end{array}\right]^{\oplus} NO_3^{\ominus} + 9\ CH_4 \longrightarrow 2\ NH_3 + 3\ CH_3OH + 5\ C_2H_6$$

(8)

$$\left[\begin{array}{c} CH_3 \\ | \\ H_3C-N-CH_3 \\ | \\ CH_3 \end{array}\right]^{\oplus} NO_3^{\ominus} + CH_4 \longrightarrow (CH_3)_3N + HNO_3 + C_2H_6$$

(9)

Using enthalpies of these reactions calculated by G3(MP2) and enthalpies of formation $\Delta_f H_m^{\circ}$ (g), for species involved in the reactions (7)–(9) recommended by Pedley et al. [26] (see table S6) enthalpies of formation of [R$_4$N][NO$_3$] have been calculated (see table 4). The quantum chemical calculations of the gaseous enthalpy of formation of ILs have been performed under the assumption that the gaseous phase of ionic liquid exists entirely of ion pairs. As it shown in table 4 the $\Delta_f H_m^{\circ}$ (g)-values calculated by G3(MP2) using the atomization procedure, as well as using equations (7)–(9) are

in good agreement, and we averaged them (see table 4) for further discussion and calculation of vaporization enthalpies of [R$_4$N][NO$_3$].

### 3.5. Enthalpies of vaporization $\Delta_l^g H_m$ of [R$_4$N][NO$_3$]

Enthalpies of vaporization of several ILs such as 1-butyl-3-methyl imidazolim dicyanoamide [C$_4$MIM][N(CN)$_2$] and 1-ethyl-3-methyl imidazolim bis(trifluoromethylsulfonyl)imide [C$_2$MIM][NTf$_2$] have successfully been determined using the method of transference [3]. In contrast, the ionic liquids 1-ethyl-3-methyl imidazolim nitrate [C$_2$MIM][NO$_3$] and 1-butyl-3-methyl imidazolim nitrate [C$_4$MIM][NO$_3$] were not stable enough during the transpiration experiments to measure vaporization enthalpy [5]. In this work we also have failed to measure the vaporization enthalpy of [R$_4$N][NO$_3$] by transpiration, hence, no experimental enthalpy of vaporisation could be determined using this technique. However, in the recent papers [5,6] we have developed an alternative procedure to obtain vaporization enthalpies of ILs using a combination of the traditional combustion calorimetry with the high-level first-principles calculations according to equation (1), which is for this purpose is re-written as follows:

$$\Delta_l^g H_m(298\ \text{K}) = \Delta_f H_m^{\circ}(g) - \Delta_f H_m^{\circ} \tag{10}$$

where $\Delta_f H_m^{\circ}$ (l) is the molar enthalpy of formation in the liquid state obtained by combination of results from the high precision combustion calorimetry with the results from DSC measurements (table 1, column 4) and $\Delta_f H_m^{\circ}$ (g) the gaseous enthalpy of formation calculated by the G3(MP2) composite method (table 1, column 5). Using equation (10), vaporization enthalpies of [R$_4$N][NO$_3$] have been obtained (table 1, column 6). The enthalpy of vaporization of tetra-methyl ammonium nitrate is as expected lower than those for tetra-ethyl- and tetra-butyl derivatives. In comparison with the enthalpies of vaporization (at 298 K) of other ionic liquids with the [NO$_3$] anion [5] $\Delta_l^g H_m$ ([C$_2$MIM][NO$_3$]) = 163.7 ± 5.3 kJ mol$^{-1}$ and $\Delta_l^g H_m$ ([C$_4$MIM][NO$_3$]) = 162.4 ± 5.7 kJ mol$^{-1}$ our results for ammonium based ionic liquids [R$_4$N][NO$_3$] seems to be also on the expected level.

### 3.6. The standard enthalpies of formation of the aqueous tetra-alkyl ammonium ions $\Delta_f H_m^{\circ}$ ([R$_4$N]$^+_{(aq)}$)

The enthalpies of formation of aqueous ions at infinite dilution are key constants in many fields of science and technology. They are needed to model aqueous solutions associated with the formation of hydrothermal ore bodies, geothermal systems, and marine chemistry. The transfer of the organic and inorganic ions from their isolated state in the gas phase into aqueous solutions is described by the standard molar enthalpy and entropy of hydration [27]. Enthalpies of formation of aqueous ions are also required for development of the Born–Fajans–Haber cycles for ionic liquids in order to gain insight into thermodynamic relations, for example between

**TABLE 4**
Results of calculation of the molar standard enthalpies of formation $\Delta_f H_m^{\circ}$ (g, 298.15 K) of tetra-alkyl ammonium nitrates (in kJ mol$^{-1}$).

| Compounds | G3(MP2) | | | | Average[b] |
|---|---|---|---|---|---|
| | Atomization | Reaction | | | |
| | | (7) | (8) | (9) | |
| Tetra-methyl ammonium nitrate | −142.6 | −150.4 | −153.4 | −153.6 | −150.0 ± 2.6 |
| Tetra-ethyl ammonium nitrate | −240.8 | −246.5 | −249.5 | −247.9 | −246.2 ± 1.9 |
| Tetra-butyl ammonium nitrate[a] | −431.6 | −433.2 | −436.1 | −434.6 | −433.9 ± 1.0 |

[a] Calculated by linear extrapolation with help of the data for the tetra-methyl ammonium nitrate and tetra-ethyl ammonium nitrate (see figure S1 and table S6).
[b] Uncertainties are standard deviation of the mean.

starting materials and products of a chemical reaction, or between different states of matter of the same substance [28–30].

In this context we decided to develop a valuable thermochemical option to derive enthalpies of formation of aqueous ions common for ionic liquids using combination of two kinds of calorimetry: the combustion calorimetry and the solution calorimetry. To set an example let us consider the ammonium based ionic liquid tetra-butyl ammonium nitrate [N(Bu)$_4$][NO$_3$]. The procedure consists of two experimental steps:

– the molar enthalpy of formation, $\Delta_f H_m^\circ$ ([N(Bu)$_4$][NO$_3$]$_{(cr)}$), of this compound in the crystal state was measured using the static bomb combustion calorimeter.
– the enthalpy of solution, $\Delta_{sol} H_m^\circ$, of this compound in the water is measured using a solution calorimeter.

The process of dissolution of [N(Bu)$_4$][NO$_3$] in water is ascribed for the following reaction:

$$[N(Bu)_4][NO_3]_{(cr)} + aq = [N(Bu)_4]^+_{(aq)} + [NO_3]^-_{(aq)} \quad (11)$$
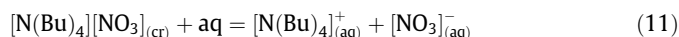
Applying the Hess's Law to this reaction we can define the enthalpy of solution using the enthalpies of formation of the reaction participants:

$$\Delta_{sol}H_m^\circ = \Delta_f H_m^\circ([N(Bu)4]^+_{(aq)}) + \Delta_f H_m^\circ([NO_3]^-_{(aq)}) - \Delta_f H_m^\circ([N(Bu)_4][NO_3]_{(cr)}) \quad (12)$$

From equation (12) the enthalpy of formation of tetra-butyl ammonium cation, $\Delta_f H_m^\circ$ [N(Bu)$_4$]$^+_{(aq)}$), can be calculated, provided that enthalpies of formation of other reaction participants are known (e.g., for the anion $\Delta_f H_m^\circ$ ([NO$_3$]$^-_{(aq)}$) the data is listed in the IUPAC-Tables [9]):

$$\Delta_f H_m^\circ([N(Bu)_4]^+_{(aq)}) = \Delta_{sol}H_m^\circ + \Delta_f H_m^\circ([N(Bu)_4][NO_3]_{(cr)}) - \Delta_f H_m^\circ([NO_3]^-_{(aq)}) \quad (13)$$

In the same way enthalpies of formation of two other ammonium based cations $\Delta_f H_m^\circ$ ([N(Me)$_4$]$^+_{(aq)}$) and $\Delta_f H_m^\circ$ ([N(Et)$_4$]$^+_{(aq)}$) have been derived using the data from combustion (see table 1) and solution calorimetry (see table 5) measurements on the tetra-alkyl-ammonium nitrates.

It has been also possible to derive enthalpies of formation of the $\Delta_f H_m^\circ$ ([N(R)$_4$]$^+_{(aq)}$) using the results published for enthalpies of combustion and enthalpies of solution of the tetra-alkyl-ammonium iodides [N(R)$_4$][I] with the R = Me, Et, and Bu [31]. The process of dissolution of [N(R)$_4$][I] in water is ascribed for the following reaction:



**FIGURE 1.** Standard enthalpies of formation of the solid tetra-alkyl ammonium ($C_nH_{2n+1})_4$ N nitrates (○: crystalline ionic liquids and ●: the aqueous ($C_nH_{2n+1})_4$ N cations). For comparison also given the standard enthalpies of formation of the liquid aliphatic tri-alkylamines ($C_nH_{2n+1})_3$N (△) and the standard enthalpies of formation of the solid tetra-alkyl ammonium iodides (▲).

$$[N(R)_4][I]_{(cr)} + aq = [N(Bu)_4]^+_{(aq)} + [I]^-_{(aq)} \quad (14)$$

Enthalpies of formation and enthalpies of solution of [N(R)$_4$][I] are given in table 5 and anion $\Delta_f H_m^\circ$ ([NO$_3$]$^-_{(aq)}$) is recommended by CODATA [9].

As can be seen in table 5, values of [N(R)$_4$]$^+_{(aq)}$ derived from nitrate and iodide series (column 4) are in good agreement and we averaged these values for each type of cations. These values (given in bold in table 5) could be recommended for further thermochemical calculations.

It has turned out that there are a remarkable linear correlation between the aqueous enthalpy of formation of the ammonium cation [N(R)$_4$]$^+_{(aq)}$ and the number of the C-atoms ($N_C$) in the alkyl chains (see figure 1):

$$\Delta_f H_m^\circ([N(R)_4]^+_{(aq)}) \text{ (in kJ mol}^{-1}) = -104.7N_C - 2.4 \quad (15)$$

Following, enthalpies of formation of symmetric ammonium based cations can be calculated with help of equation (15). Surprisingly, the similar linear correlations (see figure 1) have been found for the solid enthalpies of formation of the tetra-alkyl ammonium nitrates $\Delta_f H_m^\circ$ ([N(R)$_4$][NO$_3$]$_{(cr)}$) and for the solid enthalpies of formation of the tetra-alkyl ammonium iodides $\Delta_f H_m^\circ$ ([N(R)$_4$][I]$_{(cr)}$). The similar linear correlation of the enthalpies of formation, $\Delta_f H_m^\circ$ (l), of tri-substituted alkyl amines R$_3$N (data are from reference[26]) have been also observed (see figure 1). Such a nice linearity of thermodynamic properties under study provides an important test of consistency of the data obtained from the different experimental methods.

### 3.7. The standard enthalpies of formation of $\Delta_f H_m^\circ$ (cr), of the tetra-alkyl ammonium compounds

Having established the reliable values of enthalpies of formation of the aqueous cations $\Delta_f H_m^\circ$ ([N(R)$_4$]$^+_{(aq)}$) it is now possible

**TABLE 5**

Enthalpies of formation, $\Delta_f H_m^\circ$ (aq)$^+$, of the aqueous cations R$_4$N calculated with help of $\Delta_f H_m^\circ$ (cr) measured by combustion calorimetry and using enthalpies of solution $\Delta_{sol}H_m^\circ$ measured by solution calorimetry at 298.15 K (in kJ mol$^{-1}$).

| Compounds | $\Delta_f H_m^\circ$ (cr)$^a$ | $\Delta_{sol}H_m^\circ$ $^b$ | $\Delta_f H_m^\circ$ (aq)$^+$ for (R$_4$N) |
|---|---|---|---|
| [(Me)$_4$N][NO$_3$] | −330.4 ± 1.0 | 19.8 ± 0.3 | −103.7 ± 1.1 |
| [(Me)$_4$N][I] | −203.9 ± 2.7 [31] | 42.3 ± 0.3 | −104.9 ± 2.7 |
| | | | **−103.9 ± 1.0**$^c$ |
| [(Et)$_4$N][NO$_3$] | −430.8 ± 2.7 | 8.1 ± 0.1 | −215.8 ± 2.7 |
| [(Et)$_4$N][I] | −300.2 ± 3.2 [31] | 28.0 ± 0.5 | −215.4 ± 3.2 |
| | | | **−215.6 ± 2.1**$^c$ |
| [(Bu)$_4$N][NO$_3$] | −600.2 ± 3.9 | −19.8 ± 0.2 | −413.1 ± 3.9 |
| [(Bu)$_4$N][I] | −498.6 ± 2.7 [1] | 15.5 ± 0.5 | −426.3 ± 2.7 |
| | | | **−422.0 ± 2.2**$^c$ |

$^a$ From table 1.
$^b$ From table 6.
$^c$ Average value from nitrate and iodide series calculated as weighted value according to the procedure developed by Grossman *et al.* [47].
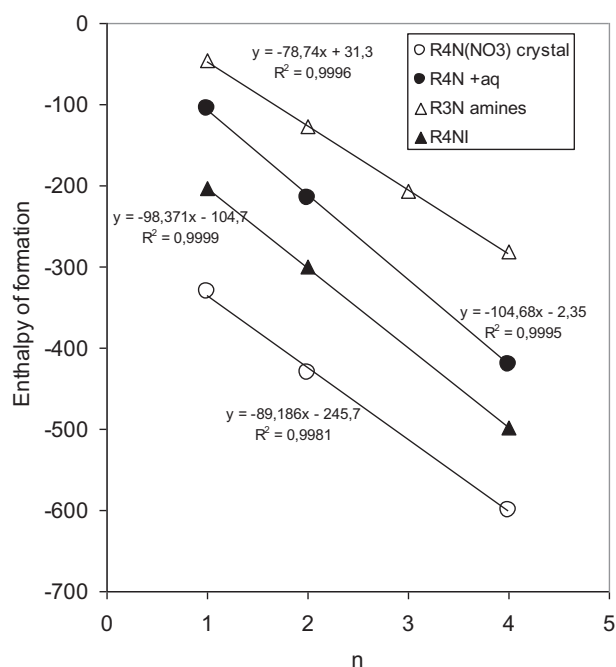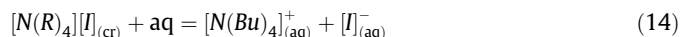
**TABLE 6**
Enthalpies of solution, $\Delta_{sol}H_m^\circ$, of [R$_4$N][X] at 298.15 K (in kJ mol$^{-1}$).

| | [Cl] | [Br] | [I] | [NO$_3$] |
|---|---|---|---|---|
| (Me)$_4$N | | 24.8 [35] | 42.1 ± 0.1 [38] | |
| | | 24.6 [32] | 42.2 [35] | |
| | 4.5 [32] | 24.3 ± 0.4 [33] | 42.4 [32] | |
| | 4.1 ± 0.3 [33] | 25.2 ± 0.1 [34] | 42.5 ± 0.2 [34] | 19.9 ± 0.2 [34] |
| | 3.9 ± 0.1 [34] | 24.6 ± 0.1 [36] | 41.8 ± 0.2 [39] | 19.6 ± 0.1 [7] |
| | **4.2 ± 0.2** (average)$^b$ | **24.7 ± 0.2** (average)$^b$ | **42.2 ± 0.1** (average)$^b$ | **19.8 ± 0.2** (average)$^b$ |
| (Et)$_4$N | | | 27.7 ± 0.1 [44] | |
| | | | 27.9 [35] | |
| | −12.8 [35] | 6.2 [35] | 28.7 [32] | |
| | −12.6 ± 0.3 [37] | 5.8 ± 0.3 [37] | 28.6 ± 0.5 [37] | |
| | −12.1 [40] | 6.2 [40] | 27.3 [40] | |
| | −12.8 ± 1.0 [41] | 6.2 [46] | 28.1 ± 0.6 [41] | |
| | −12.6 [42] | 6.1 ± 0.5 [41] | 28.2 [39] | |
| | **−12.6 ± 0.5** (average)$^b$ | **6.1 ± 0.1** (average)$^b$ | **28.1 ± 0.5** (average)$^b$ | **8.1 ± 0.1** [7] |
| (Pr)$_4$N | | −4.3 [42] | 11.5 ± 0.1 [44] | |
| | | −4.6 [32] | 11.6 [39] | |
| | | −4.9 ± 0.1 [36] | 11.6 ± 0.1[42] | |
| | −22.2 [42] | **−4.6 ± 0.2** (average)$^b$ | **11.6 ± 0.1** (average)$^b$ | (−32.7)$^a$ |
| (Bu)$_4$N | | −9.2 ± 0.1 [43] | | |
| | | −9.2 ± 0.1 [36] | | |
| | −30.5 ± 0.4 [43] | −8.4 [45] | | |
| | −29.9 [42] | −8.5 [42] | 15.9 ± 0.1 [43] | |
| | −28.9 [40] | −7.9 [40] | 15.0 [40] | |
| | **−29.8 ± 0.5** (average) | **−8.6 ± 0.3** (average) | **15.5 ± 0.5** (average) | **−19.8 ± 0.2** [1] |
| (Am)$_4$N | | 3.2 [42] | | |
| | | 2.7 [45] | | |
| | −38.2 [42] | **3.0 ± 0.3** (average)$^b$ | | (−6.1)$^a$ |

$^a$ Calculated using enthalpy of solution obtained from equation: $\Delta_{sol}H_m^\circ = -13.3n + 33.8$ with ($R^2 = 0.9983$) given for [(C$_n$H$_{2n+1}$)$_4$N][NO$_3$] ionic compounds in figure S2.
$^b$ Uncertainties are standard deviation of the mean.

**TABLE 7**
Enthalpies of formation, $\Delta_f H_m^\circ$ (cr), of [R$_4$N][X] calculated using equation (16)$^a$ (in kJ mol$^{-1}$).

| | X = Cl | X = Br | X = I | X = NO$_3$ |
|---|---|---|---|---|
| (Me)$_4$N | −275.6 | −250.4 | | |
| (Et)$_4$N | −370.1 | −343.1 | | |
| (Pr)$_4$N | −461.4$^b$ | −433.3$^b$ | −399.9$^d$ | −513.3$^d$ |
| (Bu)$_4$N | −557.0 | −532.5 | | |
| (Am)$_4$N | −654.8$^c$ | −650.3$^c$ | −596.7$^d$ | −691.7$^d$ |

$^a$ Values for $\Delta_f H_m^\circ$ (aq)$^+$ are those selected in table 5; values for $\Delta_f H_m^\circ$ (aq)$^-$ are from CODATA$^9$: [Cl$^-$] (aq) = −167.1 ± 0.1 kJ mol$^{-1}$; [Br$^-$](aq) = −121.4 ± 0.2 kJ mol$^{-1}$; [I$^-$](aq) = −56.8 ± 0.1 kJ mol$^{-1}$; values for $\Delta_{sol}H_m^\circ$ are those selected in table 6.
$^b$ Calculated using enthalpy of formation of the cation $\Delta_f H_m^\circ$ (aq, Pr$_4$N$^+$) = −316.5 kJ mol$^{-1}$ obtained from equation: $\Delta_f H_m^\circ$ (aq)$^+$ = −104.7$n$ − 2.4 ($R^2 = 0.9995$) see figure 1.
$^c$ Calculated using enthalpy of formation of the cation $\Delta_f H_m^\circ$ (aq, Am$_4$N$^+$) = −525.9 kJ mol$^{-1}$ obtained from equation: $\Delta_f H_m^\circ$ (aq)$^+$ = −104.7$n$ − 2.4 ($R^2 = 0.9995$) see figure 1.
$^d$ Calculated from equation: $\Delta_f H_m^\circ$ (cr) = −89.2$n$ − 245.7 ($R^2 = 0.9981$) given for [(C$_n$H$_{2n+1}$)$_4$N][NO$_3$] (see figure 1).

to predict enthalpies of formation, $\Delta_f H_m^\circ$ (cr), of different tetra-alkyl ammonium containing compounds using the simple thermodynamic equation:

$$\Delta_f H_m^\circ(cr) = \Delta_f H_m^\circ(aq) + \Delta_f H_m^\circ(aq) - \Delta_{sol}H_m^\circ \qquad (16)$$

The values for cations $\Delta_f H([N(R)_4]^+_{(aq)})$ are given in table 5, column 4. The values of solution enthalpies $\Delta_{sol}H_m^\circ$ have been collected and analyzed in table 6. Using equation (16) the enthalpies of formation of tetra-alkyl ammonium chlorides, bromides, iodides, and nitrates have been calculated (see table 7). Enthalpies of formation of aqueous tetra-alkyl ammonium cations $\Delta_f H_m^\circ$ ([R$_4$N]$^+_{(aq)}$) derived in this work in combination with the $\Delta_f H_m^\circ$ (aq)$^-$ of anions known from the literature are useful for prediction thermochemical prop-

erties of the ammonium based ionic liquids. In the similar way we a going to derive enthalpies of formation $\Delta_f H_m^\circ$ (aq)$^+$ for imidazolium, pyridinium, and pyrrolidinium based ionic liquids.

## 4. Conclusions

Combination of combustion calorimetry, differential scanning calorimetry, and solution calorimetry with the *first-principles* calculations allows to obtain the broad scope of the 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. Enthalpies of formation of aqueous tetra-alkyl ammonium ions $\Delta_f H_m^\circ$ ([R$_4$N]$^+_{(aq)}$) derived in this work are useful for prediction thermochemical properties of the ammonium based ionic liquids. This procedure also opens several thermochemical options to obtain values required for the Born–Fajans–Haber cycles for ionic liquids.

## Supporting information available

Results for typical combustion experiments of the tetra-alkyl ammonium nitrate (tables S1 to S3); auxiliary properties for combustion calorimetry and data treatment (tables S4 and S5); G3(MP2) total energies at 0 K and enthalpies at 298.15 K of the molecules studied in this work (table S6); correlations of enthalpies of ionic liquids with the chain length (Figs. S1 and S2).

## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jct.2012.02.035.

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