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Standard molar enthalpies of formation and lattice energies of 1-methylethyl, *n*-butyl and 2-methylpropyl ammonium halides

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Abstract

Standard molar enthalpies of formation of 1-methylethyl, $(CH_3)_2CHNH_3X$, *n*-butyl, $CH_3(CH_2)_3NH_3X$ and 2-methylpropyl, $(CH_3)_2CHCH_2NH_3X$, ammonium halides (X=Cl, Br, I) have been determined by solution-reaction calorimetry at 298.15±0.02 K. Heat capacities for solid and liquid phases were determined for the means of differential scanning calorimetry and estimated by gaseous phase through the generalized vibrational assignment method. Starting from the equivalent methyl cation derivative, the molar standard enthalpies of both cations were estimated by a group contribution method. From these values, the lattice energies of the salts have been calculated via a thermochemical cycle. The lattice energies decrease from chloride to iodide for all three series of compounds. Semi-empirical methods were used to determine the thermochemical cation radii. These values depend on the number of carbon atoms in the organic chain and the position of the attached methyl group on the branched carbon chain. © 1998 Elsevier Science B.V.

Keywords: 1-Methylethyl ammonium; *n*-Butyl ammonium; 2-Methylpropyl ammonium; Calorimetry; Cation radii; Lattice energy

1. Introduction

The importance of thermochemical data for alkylammonium cations is related to the behaviour of these salts in aqueous solution and their use as models to understand the hydrophobic interactions of large molecules in water [1]. The degree of substitution on nitrogen and the increase in size of the alkyl groups could affect these interactions by forming unusual hydrates containing a large number of water molecules per ammonium ion [2]. Also, from an experimental point of view, some of the salts may be useful in diverse solvent systems as precipitating agents in inorganic syntheses where the cations stabilize the desired anion via an electrostatic effect.

Based on the ionic cation–anion interaction, the lattice energy of crystals containing polyatomic ions can be estimated by empirical equations. For this purpose the standard molar enthalpy of formation of these solid compounds was initially determined by solution–reaction calorimetry [3–11]. This procedure was previously used to study a series with methyl groups substituted on the nitrogen of the amine [3–5].

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The standard molar enthalpies of formation and the respective lattice energies of the solid compounds decrease as the number of methyl groups attached to the nitrogen increases [3]. From this general behaviour, extrapolated data can be used to estimate some unknown properties of the quaternary salts [3]. The results of systematic investigations on other derivatives such as ethyl- [5,6], *n*-propyl- [7–10], dipropyl-, di-1-methylethyl- [8], di-*n*-butyl- and di-2-methylpropyl [9] ammonium halides have also been published.

The main purpose of this publication is to report determination of the standard molar enthalpies of formation of the solid 1-methylethyl ammonium halides, $(CH_3)_2CHNH_3X$, *n*-butyl ammonium halides, $CH_2CH_2CH_2CH_2NH_3X$, and 2-methylpropyl ammonium halides, $(CH_3)_2CHCH_2NH_3X$ (X=Cl, Br, I). The lattice energies of these salts were also calculated, enabling determination of the thermochemical radii for the cations.

2. Experimental

2.1. Chemicals

The solvents, 1-methylethylamine, *n*-butylamine and 2-methylpropylamine were dried over sodium hydroxide pellets and distilled before use [8,9].

2.2. Preparations

The salts $(CH_3)_2CHNH_3X$, $CH_3CH_2CH_2CH_2NH_3X$, and $(CH_3)_2CHCH_2NH_3X$ (X=Cl, Br, I) were prepared by reacting the pure amine with a 50% solution of the respective reagent grade acid, HX. After filtering, the white solids were recrystallized from ethanol, dried, and stored under nitrogen in a dessicator as before [10]. Melting temperatures were determined with a Microquímica model MQAPF-301 apparatus. The halides were titrimetrically analysed with a Quimis model Q-400 pH-meter. The nitrogen content of each compound was determined by the Kjeldahl method.

2.3. Other measurements

Thermogravimetric curves were obtained with a Shimadzu model TGA-50 thermobalance, at a heating rate of 0.17 K s^{-1} in a dry nitrogen flow of 0.33 $cm^3 s^{-1}$ in the temperature range 350–650 K. A Hewlett–Packard model 5988A spectrometer was used to obtain the mass spectra of the salts.

2.4. Calorimetric measurements

Reaction–solution calorimetric measurements were performed with an LKB 8700-1 isoperibol precision calorimetry system. Thin glass ampoules containing 20.0 to 100.0 mg of amine or the respective salts were prepared in a dry box. For each determination of the enthalpy of solution six to eigth ampoules were broken into the glass reactor vessel charged with 0.10 dm^3 of calorimetric solvent at 298.15±0.02 K. Details of the operational procedure, calculations and accuracy of the instrument have been described [13]. The uncertainty interval is quoted as twice the standard deviation of the mean.

The heat capacity of the solid form of the salts was determined with a Shimadzu model DSC-50 calorimeter at a heating rate of 0.17 K s^{-1} in a dry nitrogen flow of 0.83 $cm^3 S^{-1}$ [14–16]

3. Results and discussion

The nitrogen and halide elemental analyses of the salts are in good agreement with the expected values for the compounds as shown in Table 1. The melting points observed are consistent with the purity of these compounds, as indicated in Table 1, which also lists the decomposition temperature range for the thermogravimetric determinations. With the exception of $CH_3CH_2CH_2CH_2NH_3Cl$ and $(CH_3)_2CHCH_2NH_3I$, all the salts started to decompose before the melting point as shown by the thermogravimetric curves. Similar one-step decomposition curves were observed for all the salts and at the end of the thermal degradation process no residue was detected. Mass spectra revealed the parent ions only for both $CH_3CH_2CH_2CH_2NH_3Cl$ and $CH_3CH_2CH_2CH_2NH_3Br$.

The standard molar enthalpy changes ($\Delta_r H_m^0$) for reaction Eq. (1) where RNH_3X for R=$(CH_3)_2CH$, $CH_3(CH_2)_3$, $CH_3CH_2CH_2CH_2$ and X=Cl, Br, I were obtained by

Table 1
Mass percentage analysis found (calculated), melting temperatures T_{fus}, and temperature intervals TG determined by thermogravimetry for salts

Compound	N(%)	X(%)	T_{fus}/K	TG/K
$(CH_3)_2CHNH_3Cl$	14.61 (14.65)	37.05 (37.09)	477±1	515–549
$(CH_3)_2CHNH_3Br$	9.93 (9.99)	57.01 (57.04)	505±2	541–587
$(CH_3)_2CHNH_3I$	7.45 (7.50)	67.80 (67.85)	497±1	539–587
$CH_3CH_2CH_2CH_2NH_3Cl$	12.73 (12.78)	32.32 (32.34)	482±1	407–581
$CH_3CH_2CH_2CH_2NH_3Br$	9.02 (9.09)	51.75 (51.87)	473±1	530–586
$CH_3CH_2CH_2CH_2NH_3I$	6.85 (6.96)	63.00 (63.12)	441±2	461–617
$CH_3CH_2CH_2CH_2NH_3Cl$	12.74 (12.78)	32.23 (32.34)	449±1	483–528
$CH_3CH_2CH_2CH_2NH_3Br$	9.01 (9.09)	51.72 (51.87)	452±1	545–593
$CH_3CH_2CH_2CH_2NH_3I$	6.84 (6.96)	63.03 (63.12)	422±2	409–605

$$RNH_3X(cr) + OH^-(aq) = (RNH_2(l) + H_2O(l) + X^-)(aq);\ \Delta_r H^0_m \quad (1)$$

considering two independent series of experiments: (i) the salt RNH_3X is dissolved in a 0.10 dm^3 calorimetric vessel containing 0.10 mol dm^{-3} NaOH(aq) solution and (ii) the corresponding amine RNH_2 is dissolved in the same vessel now charged with 0.10 dm^3 of twice distilled water [6,7,10]. The experimental values are given in Table 2. The standard molar enthalpy of formation ($\Delta_f H^0_m$) of each compound can then be calculated from this set of $\Delta_r H^0_m$ values by means of Eq. (2):

$$\Delta_f H^0_m(RNH_3X, cr) = \Delta_f H^0_m(RNH_2) + \Delta_f H^0_m(H_2O, l) + \Delta_f H^0_m(NaX) - \Delta_f H^0_m(NaOH) - \Delta_r H^0_m \quad (2)$$

From breaking a series of ampoules charged with pure amines and the corresponding halides in twice distilled water the standard molar enthalpy of dissolution $\Delta_r H^0_m$ was determined for all considered compounds. The results are included in Table 2. By combining these values with the standard molar enthalpy of formation of the respective amines [17] listed in Table 3, gave: $\Delta_f H^0_m[(CH_3)_2CHNH_2] = -(129.95\pm 0.14)$, $\Delta_f H^0_m(CH_3CH_2CH_2CH_2NH_2) = -(149.87\pm 0.29)$ and $\Delta_f H^0_m$ $[(CH_3)_2CHCH_2NH_2] = -(157.07\pm 0.25)$ kJ mol^{-1}, respectively. By using these obtained values and the appropiate auxiliary data in Table 3, the standard molar enthalpies of formation of the alkylammonium salts were calculated and are reported in Table 4. The general behaviour previously observed with values is also observed here for this series of compounds, which values reflect a direct dependence on the radical attached to the nitrogen atom. So, the

Table 2
Standard molar enthalpy of dissolution of salts in 0.10 mol dm^{-3} NaOH(aq) and for pure amines in water at 298.15 K

Compound	Solvent	No. of Exp.	$-\Delta rH^0_m$/KJ mol^{-1}
$H_3CH_2CH_2CH_2NH_3Cl$(cr)	$NaOH_{(aq)}$	8	0.65±0.01
$CH_3CH_2CH_2CH_2NH_3Br$(cr)	$NaOH_{(aq)}$	6	4.69±0.07
$CH_3CH_2CH_2CH_2NH_3I$(cr)	$NaOH_{(aq)}$	7	6.85±0.19
$CH_3CH_2CH_2CH_2NH_2$(1)	H_2O	8	22.13±0.09
$(CH_{3)2}CHCH_2NH_3Cl$(cr)	$NaOH_{(aq)}$	7	6.09±0.02
$(CH_3)_2CHCH_2NH_3Br$(cr)	$NaOH_{(aq)}$	6	6.83±0.02
$(CH_3)_2CHCH_2NH_3I$(cr)	$NaOH_{(aq)}$	7	10.11±0.16
$(CH_3)_2CHCH_2NH_2$(l)	H_2O	6	19.50±0.06
$(CH_3)_2CHNH_3Cl$(cr)	$NaOH_{(aq)}$	7	2.43±0.02
$(CH_3)_2CHNH_3Br$(cr)	$NaOH_{(aq)}$	8	7.01±0.23
$(CH_3)_2CHNH_3I$(cr)	$NaOH_{(aq)}$	7	11.99±0.13
$(CH_3)_2CHNH_2I$	H_2O	7	17.62±0.04

Table 3
Auxiliary thermochemical data

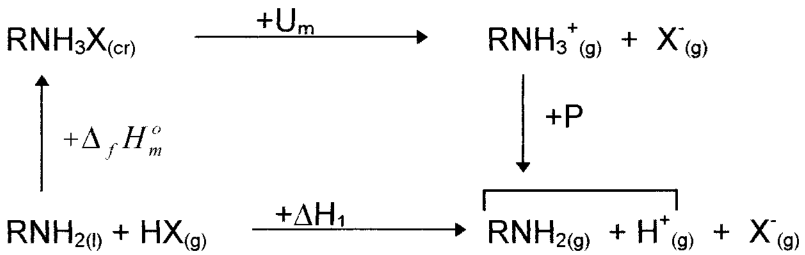
Compound	$-\Delta_f H^0_m$/kJ mol^{-1}	References
$H_2O_{(l)}$	285.83±0.04	[17]
NaOH	469.646±0.003	[17]
NaCl	407.066±0.003	[17]
NaBr	361.569±0.004	[17]
Nal	295.303±0.001	[17]
$(Ch_3)_2CHNH_{2(l)}$	112.33±0.14	[19]
$CH_3CH_2CH_2CH_2NH_{2(l)}$	127.74±0.29	[19]
$(CH_3)_2CHCH_2NH_{2(l)}$	137.57±0.25	[19]
$(CH_3)_2CHNH_{2(g)}$	83.82±0.17	[19]
$CH_3CH_2CH_2CH_2NH_{2(g)}$	95.04±0.40	[19]
$(CH_3)_2CHCH_2NH_{2(g)}$	106.34±0.40	[19]
$H^+_{(g)}$	−1536.20±0.01	[17]
$Cl^-_{(g)}$	233.13±0.01	[17]
$Br^-_{(g)}$	219.07±0.03	[17]
$I^-_{(g)}$	197±3	[17]

branched alkyl groups have larger $\Delta_f H^0_m$ values and within this series of halides, the values decrease from chloride to iodide [6–10].

The molar lattice energies ($U_m(T)$) were calculated for the salts by the following general equation [3,6–10]

$$U_m(T) = \Delta_f H^0_m(H^+, g) + \Delta_f H^0_m(X^-, g) + \Delta_f H^0_m(RNH_2, g) - \Delta_f H^0_m(RNH_3X, cr) - P - 2RT \quad (3)$$

derived from the thermodynamic cycle



where P is the proton affinity of the amines. The mean values of P for 1-methylethylamine, *n*-butylamine and 2-methylpropylamine are 934.91, 932.82 and 934.49 kJ mol^{-1}, respectively [18]. In this calculation the heat capacity contributions and thermal effects arising from polymorphism, order–disorder transitions, or internal rotations are neglected because these effects probably affect the energy value by only a few per cent [5]. The lattice energies values calculated with the thermochemical data listed in Table 3 are included in Table 4.

The lattice energies were also calculated [1] with a thermochemical cycle in which the heat capacity parameters are included as shown in Eq. (4)

$$U_m(T) = \Delta_f H^0_m(RNH_3{}^+, g) + \Delta_f H^0_m(X^-, g) - \Delta_f H^0_m(RNH_3X, cr) + \Sigma\Delta T + \int_0^{298,15} [C^0_{p,m}(RNH_3^+, g) - C^0_{p,m}(X^-, g)]dT \quad (4)$$

In the above equation the unkown values of molar standard enthalpies of formation for 1-methylethyl, *n*-butyl- and 2-methylpropylammonium cations were estimated to determine the respective lattice energies. This calculation was based on the known molar standard enthalpy of formation of methylammonium cation in gaseous phase, which value is tabulated as 604 kJ mol^{-1} [3]. From this value, the appropriate groups were added to reproduce those mentioned cations [16,19,20], which contributed to the above enthalpy data. Then, for 1-methylethyl-, *n*-butyl- and 2-methylpropyl ammonium cations the groups contribution were −60.54, −68.16 and −76.66 kJ mol^{-1}, respectively. From these contributions the molar standard enthalpies of formation for the same sequence of cations gave the values: 543, 535 and 527 kJ mol^{-1}, respectively.

The solid phase heat capacities ($C^0_{p,m}$) were determined by means of differential scanning calorimetry. The results are listed in Table 4. The corresponding gas-phase heat capacities for 1-methylethyl-, *n*-butyl- and 2-methylpropyl ammonium cations are: 0.107± 0.008, 0.105±0.010 and 0.105±0.006 kJ mol^{-1} K^{-1},

Table 4
Standard molar enthalpies of formation ($\Delta_f H^0_m$) in kJ mol^{-1}, heat capacity, ($C^0_{p,m}$), in kJ mol^{-1} K^{-1} for alkyl ammonium halides in solid state and their molar lattice energies (U_m) in kJ mol^{-1} and the thermochemical radii (r_c) in nm calculated for cations

Compound	$\Delta -_f H^0_m$	$C^0_{p,m}$	U_m[a]	U_m[b]	r_c
$(CH_3)_2CHNH_3Cl$(cr)	350.77±0.15	0.19±0.01	630	682	0.162
$(CH_3)_2CHNH_3Br$(cr)	300.70±0.27	0.24±0.02	594	658	0.169
$(CH_3)_2CHNH_3I$(cr)	231.45±0.20	0.34±0.02	547	640	0.179
$CH_3CH_2CH_2CH_2NH_3Cl$(cr)	372.47±0.29	0.12±0.01	643	675	0.155
$CH_3CH_2CH_2CH_2NH_3Br$(cr)	322.93±0.30	0.28±0.01	607	685	0.161
$CH_3CH_2CH_2CH_2NH_3I$(cr)	254.51±0.35	0.12±0.01	561	591	0.169
$CH_3CH_2CH_2CH_2NH_3Cl$(cr)	374.23±0.28	0.19±0.01	631	687	0.161
$CH_3CH_2CH_2CH_2NH_3Br$(cr)	327.99±0.25	0.22±0.02	599	664	0.165
$CH_3CH_2CH_2CH_2NH_3I$(cr)	258.45±0.30	0.24±0.01	552	623	0.175

[a] Calculated from standard molar enthalpy of formation.
[b] Calculated from standard molar enthalpy of formation and heat capacity.

as estimated by the method of generalized vibrational assignment [12,16,21]. The gas-phase heat capacities were assumed to be 0.021 kJ mol^{-1} K^{-1} for the halide anions [1] and the term $\Sigma\Delta T$ was assumed to be 1.0 kJ mol^{-1} in this work [1].

The lattice energies calculated from the standard molar enthalpies of formation are slightly lower than those including the heat capacity contribution, but the two series of results present a parallel sequence of values. This behaviour is well adjusted to the general ionic chemical bond approach, which is expected for this kind of acid-amine interaction to form the respective salt. The values listed in Table 4 show a decrease from chloride to iodide, correlating with the increase in the internuclear distance in the crystal, a consequence of the increase in anion radii [6–10]. Fig. 1

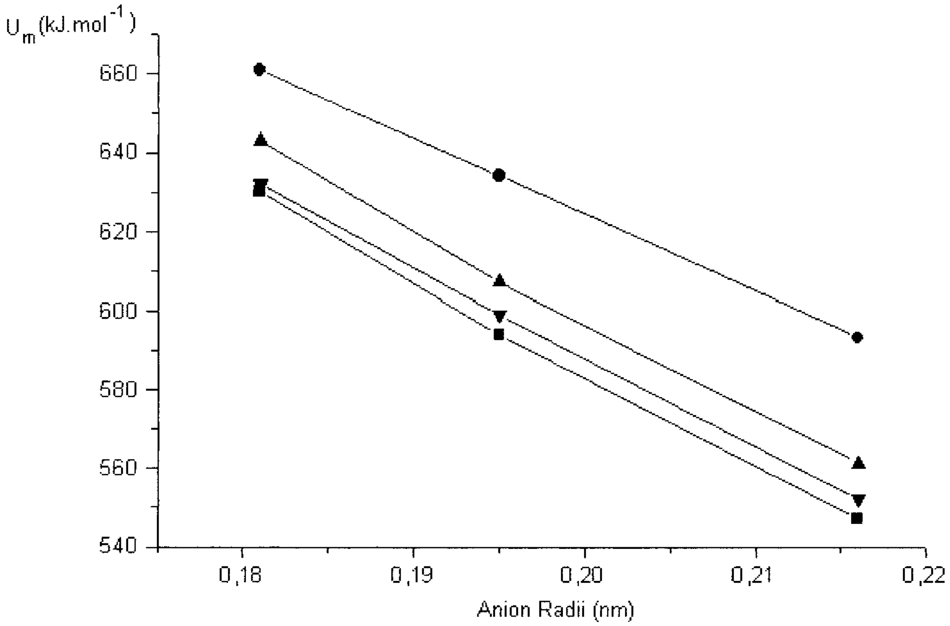


Fig. 1. Plot of lattice enthalpies (U_m) for 1-methylethyl-(■), *n*-propyl-(●), *n*-butyl-(▲) and 2-methylpropylammonium salts (▼) against anionic radii (r_a) of X$^-$ (Cl, Br, I).

illustrates this behaviour, including *n*-propyl ammonium halide data [10]. In all cases, the cation–anion electrostatic attraction in the crystal decreases as the distance becomes larger from chloride to iodide compounds. This plot shows that the sequence of lattice enthalpies from chloride to iodide for both of the linear alkylamines are larger than those form branched alkylamines for both set of salts. The difference is more pronounced for amines having propyl groups. These results suggest that lattice energy is affected by the methyl group position on the branched chain. Its location in 2-methylpropylamine caused a small decrease in comparison to *n*-butylamine. However, the largest shift for the branched 1-methylethylamine can be interpreted as due to the proximity of the methyl group to the nitrogen, which gives a less exothermic value for lattice energy.

The thermochemical radii of 1-methylethyl, *n*-butyl and 2-methylpropyl cations were calculated [6,10,22,23] by the Kapustinskii–Yatsimirskii Eq. (5)

$$U_{\mathrm{m}}(T_2) = 108.0 v \frac{Z^+ Z^-}{rc + ra} \tag{5}$$

which considers the number or ions as two with unitary charge for monocation and anion Z^+ and Z^- and the respective ionic radii r_c and r_a in nanometers. For this calculation $U_{\mathrm{m}}(a)$ was taken from Table 4 and Goldschmidt radii [24] of 0.181, 0.195 and 0.216 nm for chloride, bromide and iodide, respectively, were used. The thermochemical cation radii, r_c, obtained are given in Table 4.

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