

THERMOCHEMICAL DATA ON TETRAALKYLAMMONIUM SALTS. III *. TETRAETHYLAMMONIUM PERCHLORATE, CHLORIDE, BROMIDE AND IODIDE

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ABSTRACT

The standard enthalpies of formation

$$\Delta H_f^0(\text{NEt}_4\text{ClO}_4, \text{c}) = -408.80 \pm 6.4 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{Cl}, \text{c}) = -400.76 \pm 5.09 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{Br}, \text{c}) = -374.05 \pm 5.02 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{I}, \text{c}) = -331.53 \pm 5.11 \text{ kJ mole}^{-1} \quad (\text{Et} = \text{C}_2\text{H}_5)$$

have been calculated from calorimetric data on the enthalpies of solution of the salts in water at 298.15 K. By application of the Kapustinskii—Yatsimirskii procedure, the “thermochemical” radius of the NEt_4^+ ion (cryst.) has been derived and the lattice energies of the salts estimated.

INTRODUCTION

Quaternary ammonium salts have received considerable attention in recent years because of their abnormal behaviour in aqueous solution, such as their comparatively lower solubility in water than the corresponding alkali metal salts. This property is responsible for their wide use as precipitating agents in inorganic chemistry and as stabilizers of otherwise unstable anions and, in solution chemistry, as models for the study of “hydrophobic interactions” of large molecules (see for example ref. 1). The interest in the properties of these compounds has created a considerable literature on their enthalpies of solution in water from which values of their standard enthalpies of formation may be derived. Such values have been published for several tetramethylammonium salts [2–4]. However, apart from tetraethylammonium hexachlorophosphate and tetraethylammonium tetrabromophosphate, for which enthalpies of formation have been reported [5,6], no such literature exists for the other tetraethylammonium salts because the standard enthalpy of formation of the aqueous tetraethylammonium ion required for their calculation has only recently become available [5].

* Part II, see ref. 6.

This paper reports values for the standard enthalpies of formation and crystal lattice energies of tetraethylammonium perchlorate, chloride, bromide and iodide. Data required for the calculation of the standard enthalpies of formation have been obtained either from the literature or by experiment. The lattice energy calculations have been made here using the well-known Kapustinskii equation.

EXPERIMENTAL

Materials

Tetraethylammonium perchlorate $N(C_2H_5)_4ClO_4$ (Fluka, purum >99%) was recrystallized twice from water and dried at 333–353 K for 72 h in an electrically heated vacuum desiccator (Gallenkamp DK-720), and then over anhydrous calcium sulphate at room temperature in an evacuated laboratory desiccator for a further 48 h. The salt was stored inside a brown sample bottle and all handling was done in a dry nitrogen tent using P_2O_5 as desiccant.

The $N(C_2H_5)_4ClO_4$ was first reduced to the chloride by fusion with anhydrous sodium carbonate and then analyzed gravimetrically for chloride content. Duplicate analysis showed the salt to be better than 99 mole % pure. Found: Cl, 15.35 mass %; calcd. for $N(C_2H_5)_4ClO_4$: Cl, 15.43 mass %.

Double-distilled water from a Jobling 3 DWS all-glass still was used throughout.

Calorimetry

Enthalpy of solution measurements were made at 298.15 K using an LKB 8700-1 precision calorimetry system equipped with a 100 cm³ glass reaction vessel provided with a thermistor (2.4 k Ω) connected to a Wheatstone bridge circuit. The thermostat was an LKB 7603 precision thermostat connected to a proportional controller and cooled by circulating pre-cooled water at 2°C below the operating temperature through its cooling coil from a Gallenkamp WF 721 refrigerated bath. A constant-voltage transformer (Advance Industrial Electronics) was used to keep voltage variations within $\pm 2\%$. Temperature stability in the bath was ± 0.002 K over a 24 h period. The entire equipment was kept in a thermostated room, temperature constant within ± 0.5 K over a 24 h period.

A Hewlett-Packard 419A DC Null voltmeter was used to amplify the off-balance voltage from the Wheatstone bridge before presentation to a Bryans chart recorder (model 27000). The performance of the system was checked with the neutralization of tris(hydroxymethyl)aminomethane (THAM) in aqueous 0.100 mole dm⁻³ HCl, for which the mean of seven determinations was $\Delta H^\circ = -29.75 \pm 0.03$ kJ mole⁻¹, in good agreement with literature values [7].

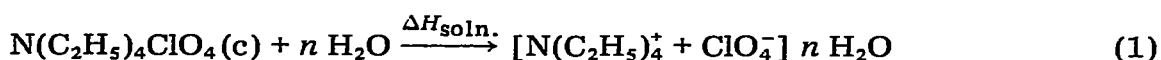
Accurately weighed amounts of the salt, obtained in glass ampoules (LKB 8727-1) and sealed with small silicone rubber bungs and wax, were broken

into 100 cm³ double-distilled water in the reaction vessel. The resistance—time curve was obtained as a trace on the chart recorder. The corrected resistance change (proportional to the temperature change) was calculated from the trace by Dickinson's graphical extrapolation procedure [8]. The calibration constant was determined after each reaction.

RESULTS AND DISCUSSION

Standard enthalpies of solution

For tetraethylammonium perchlorate, the enthalpy of solution was calculated from eqn. (1)



The results are given in Table 1. Within the concentration range studied, the enthalpies did not show any dependence on concentration, and in particular the enthalpies did not change at lower concentrations of the salt; they remained independent of the dilution N of the salt in water (where N is the mole ratio of H₂O to salt). Hence the mean of the enthalpy of solution values obtained was taken to represent the standard enthalpy of solution, $\Delta H_{\text{soln.}}^0$, at 298.15 K. This is within the limits of experimental error, the highest deviation from the mean being estimated at 0.58%, including systematic calibration errors.

There appears to have been no reported previous determination of the enthalpy of solution of this salt at 298.15 K with which to compare our results. The only experimental report was at 20°C (293.15 K) by Askew et al. [9] who obtained $\Delta H_{\text{soln.}}^0 = 30.04 \pm 0.40 \text{ kJ mole}^{-1}$. Abraham [10] estimates the enthalpy of solution of this salt at 298.15 K to be $30.71 \pm 0.1 \text{ kJ mole}^{-1}$ which is in good agreement with our experimental value of $30.90 \pm 0.10 \text{ kJ mole}^{-1}$. All literature data have been converted to SI units (1 cal_{th} = 4.1840 J).

TABLE 1

Enthalpy of solution in water of N(C₂H₅)₄ClO₄ at 298.15 K

Mass (g)	mmoles	Dilution (N)	$\Delta H_{\text{soln.}}$ (kJ mole ⁻¹)	Percentage max. deviation from mean
0.2283	0.9938	5574	31.04	0.45
0.2695	1.1734	4721	30.87	0.10
0.3278	1.4270	3882	30.72	0.58
0.4192	1.8247	3036	31.02	0.39
0.4795	2.0873	2654	30.89	0.03
0.6071	2.6430	2096	30.86	0.13
mean = 30.90 ± 0.10 kJ mole ⁻¹				

TABLE 2

Enthalpies of solution in water of NEt_4I , NEt_4Cl and NEt_4Br at 298.15 K

Salt	ΔH_{soln}^0		Ref.
	kcal mole ⁻¹	kJ mole ⁻¹	
NEt_4I	6.83 ± 0.12	28.58 ± 0.50	11
	6.67	27.91 ± 0.10	12
	6.67	27.91 ± 0.10	13
	6.67	27.91 ± 0.10	14
	6.62 ± 0.03	27.70 ± 0.13	15
	6.86	28.70 ± 0.00	16
	6.74 ± 0.06	28.20 ± 0.25	17
Mean = 28.13 ± 0.60 kJ mole ⁻¹			
NEt_4Cl	-3.02 ± 0.07	-12.64 ± 0.29	11
	-3.07	-12.84 ± 0.40	12
	-3.10	-12.97 ± 0.70	13
	-3.07	-12.84 ± 0.40	14
Mean = -12.82 ± 0.95 kJ mole ⁻¹			
NEt_4Br	1.411 ± 0.013	5.90 ± 0.05	1
	1.38 ± 0.08	5.77 ± 0.33	11
	1.49	6.23 ± 0.30	12
	1.50 ± 0.01	6.28 ± 0.04	18
Mean = 6.05 ± 0.45 kJ mole ⁻¹			

For tetraethylammonium chloride, bromide and iodide, calorimetrically determined standard enthalpies of solution of high precision and accuracy exist in the literature. Seven values [11–17] of the standard enthalpy of solution of tetraethylammonium iodide give $\Delta H_{\text{soln}}^0(\text{NEt}_4\text{I}) = 28.13 \pm 0.60$ kJ mole⁻¹ at 298.15 K. (Et = C₂H₅). The data used are summarized in Table 2, the experimental details are given in the literature [11–18]. A set of four closely agreeing values each for tetraethylammonium chloride [11–14] and tetraethylammonium bromide [1,11,12,18] imply that the standard enthalpies of solution of these salts are $\Delta H_{\text{soln}}^0(\text{NEt}_4\text{Cl}) = -12.82 \pm 0.95$ kJ mole⁻¹ and $\Delta H_{\text{soln}}^0(\text{NEt}_4\text{Br}) = 6.05 \pm 0.45$ kJ mole⁻¹, respectively.

Estimate of errors

In keeping with the proposal by Rossini [19], uncertainty intervals have been given as twice the standard deviation of the mean, \bar{s} , where $\bar{s} = [\Sigma(x - \bar{x})^2/n(n-1)]^{1/2}$. Where not expressly stated in the case of some data from the literature, uncertainty intervals have been assigned as 10 times the last figure reported [20]. The sum of the existing enthalpies of solution of each of the salts NEt_4Cl , NEt_4Br and NEt_4I was calculated and the mean taken as ΔH_{soln}^0 for that salt, the uncertainty in the value obtained being computed in terms of those of the components [21].

Standard enthalpies of formation

Combining the values of ΔH_{soln}^0 , reported above with

$$\Delta H_f^0(\text{ClO}_4^-, \text{aq.}) = -131.4 \pm 4.0 \text{ kJ mole}^{-1} \quad [22]$$

$$\Delta H_f^0(\text{Cl}^-, \text{aq.}) = -167.080 \pm 0.088 \text{ kJ mole}^{-1} \quad [23]$$

$$\Delta H_f^0(\text{Br}^-, \text{aq.}) = -121.50 \pm 0.15 \text{ kJ mole}^{-1} \quad [23]$$

$$\Delta H_f^0(\text{I}^-, \text{aq.}) = -56.90 \pm 0.84 \text{ kJ mole}^{-1} \quad [23]$$

$$\Delta H_f^0[\text{N}(\text{C}_2\text{H}_5)_4^+, \text{aq.}] = -246.5 \pm 5.0 \text{ kJ mole}^{-1} \quad [5]$$

the standard enthalpies of formation of the four salts were calculated from

$$\Delta H_f^0(\text{NEt}_4\text{X}, \text{c}) = \Delta H_f^0(\text{NEt}_4^+, \text{aq.}) + \Delta H_f^0(\text{X}^-, \text{aq.}) - \Delta H_{\text{soln}}^0 \quad (2)$$

(X = ClO₄, Cl, Br, I). Whence

$$\Delta H_f^0(\text{NEt}_4\text{ClO}_4, \text{c}) = -408.80 \pm 6.4 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{Cl}, \text{c}) = -400.76 \pm 5.09 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{Br}, \text{c}) = -374.05 \pm 5.02 \text{ kJ mole}^{-1}$$

$$\Delta H_f^0(\text{NEt}_4\text{I}, \text{c}) = -331.53 \pm 5.11 \text{ kJ mole}^{-1}$$

The main contribution to the uncertainty in $\Delta H_f^0(\text{NEt}_4\text{X}, \text{c})$ comes from $\Delta H_f^0(\text{NEt}_4^+, \text{aq.})$.

Calculation of lattice energies

The lattice energies of the salts were estimated via the Kapustinskii equation [24,25]

$$U_0 = \frac{121.4(\Sigma n) Z_1 Z_2}{r(\text{NEt}_4^+) + r(\text{X}^-)} \left[1 - \frac{0.0345}{r(\text{NEt}_4^+) + r(\text{X}^-)} \right] \text{ kJ mole}^{-1} \quad (3)$$

where (Σn) = total number of ions in the "molecule" (i.e. 2) and Z_1, Z_2 are the numerical values of the charges on the cation and anion (i.e. each 1). $r(\text{NEt}_4^+)$ and $r(\text{X}^-)$ are the crystal ion radii. $r(\text{NEt}_4^+)$ which is not available in the literature was calculated using Yatsimirskii's "thermochemical" radius principle [26,27]. For two salts $\text{NEt}_4\text{X}'$ and $\text{NEt}_4\text{X}''$ with a common cation, the difference in their lattice energies is given by

$$U_0' - U_0'' = \Delta H_f^0 \text{X}'^-(\text{g}) - \Delta H_f^0 \text{X}''^-(\text{g}) - \Delta H_f^0 \text{NEt}_4\text{X}'(\text{c}) + \Delta H_f^0 \text{NEt}_4\text{X}''(\text{c}) \quad (4)$$

Using the appropriate ancillary data from Table 3, the differences in lattice energies were calculated for the six pairs of salts: NEt_4ClO_4 and NEt_4Cl ; NEt_4ClO_4 and NEt_4Br ; NEt_4ClO_4 and NEt_4I ; NEt_4Cl and NEt_4Br ; NEt_4Cl and NEt_4I ; NEt_4Br and NEt_4I and were equated to the differences in the Kapus-

TABLE 3

Ancillary data for the calculation of $r(\text{NEt}_4^+)$

Species	ΔH_f^0 (kJ mole ⁻¹)	Cryst. ion radius (nm) ^a
ClO_4^-	-344 (g) ^b	0.236
Cl^-	-246.44 (g) ^c	0.181
Br^-	-233.89 (g) ^c	0.196
I^-	-196.65 (g) ^c	0.220
NEt_4^+	463 (g) ^d	
NEt_4ClO_4	-408.80 ± 6.4 (cryst.)	
NEt_4Cl	-400.76 ± 5.08 (cryst.)	
NEt_4Br	-374.05 ± 5.01 (cryst.)	
NEt_4I	-331.53 ± 5.11 (cryst.)	

^a Ref. 25; ^b ref. 28, ^c ref. 29; ^d ref. 5.

tinskii quantities (5)

$$U'_0 - U''_0 = 242.8 \left\{ \frac{1}{r(\text{NEt}_4^+) + r(\text{X}'^-)} \left[1 - \frac{0.0345}{r(\text{NEt}_4^+) + r(\text{X}'^-)} \right] - \frac{1}{r(\text{NEt}_4^+) + r(\text{X}''^-)} \left[1 - \frac{0.0345}{r(\text{NEt}_4^+) + r(\text{X}''^-)} \right] \right\} \quad (5)$$

The resulting quartic equation in $r(\text{NEt}_4^+)$ was solved using the Newton-Raphson iterative method [30]. Computer programs written for the Prime 750 computer and for the Hewlett-Packard HP-97 microcomputer were used to determine the roots of the equation. The mean of the positive real roots gave $r(\text{NEt}_4^+) = 0.356$ nm. This is consistent with the value of $r(\text{NMe}_4^+) = 0.300$ nm given by Kapustinskii [24].

Substitution of the appropriate values into eqn. (3) yields: $U_0(\text{NEt}_4\text{Cl}, c) = 422$ kJ mole⁻¹, $U_0(\text{NEt}_4\text{Br}, c) = 412$ kJ mole⁻¹, $U_0(\text{NEt}_4\text{I}, c) = 396$ kJ mole⁻¹ and $U_0(\text{NEt}_4\text{ClO}_4, c) = 386$ kJ mole⁻¹. It is probably not realistic to assign precise uncertainty limits to these values. An uncertainty in the lattice energy of approximately ±45 kJ mole⁻¹ is generated by a change of 0.05 nm in the value of $r(\text{NEt}_4^+)$. Differences in lattice energies are presumably much more precise than the absolute values.

Of the four salts, lattice energies have only been published for NEt_4I , for

TABLE 4

Lattice energies, U_0 (kJ mole⁻¹), of the ammonium, tetramethyl- and tetraethylammonium halides

	NH_4^+	NMe_4^+	NEt_4^+
Cl^-	692	502	422
Br^-	661	494	412
I^-	628	477	396
Ref.	3	33	This work

which Johnson and Martin [31] obtained $U_0 = 449 \text{ kJ mole}^{-1}$ from an equal weighting of the values calculated by Boyd [32] and Ladd [33]. This is in good agreement with our value of 441 kJ mole^{-1} . Values obtained on the basis of the Kapustinskii equation are generally lower than those from extended calculation procedures [27]. Table 4 compares the values for the tetraethylammonium halides with those of the ammonium and tetramethylammonium halides. The lattice energies decrease in the order $\text{NH}_4^+ > \text{NMe}_4^+ > \text{NEt}_4^+$ and $\text{Cl}^- > \text{Br}^- > \text{I}^-$, the larger values being associated with the smaller cations and anions.

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