Thermodynamic Properties of Tetra-alkylammonium Ions in Aqueous Solution

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The heat capacities of tetraethyl- and tetrapropyl-ammonium iodide have been measured in the temperature range 12—310 K. The solubilities of the two iodide salts have been determined at 298·15 K, and auxiliary data used to calculate values of 210 ± 3, 283 ± 4, and 336 ± 5 J K^{-1} mol^{-1} for the respective standard partial molar entropies of the ions $NMe_4^+(aq)$, $NEt_4^+(aq)$, and $NPr_4^+(aq)$, the value for the aqueous proton being taken as zero. Equations designed to reproduce the hydration energies of alkali and alkaline-earth metal ions are unsuitable for the tetra-alkylammonium ions.

RECENTLY there has been much interest in the thermodynamic properties of aqueous tetra-alkylammonium salts.[1-4] The abnormalities in these properties, which become apparent when comparisons are made with other electrolytes, have been attributed to the tendency of the ions to increase the hydrogen bonding between the water molecules.[1,2,5,6] Although this hypothesis lacks precision,[7,8] there is great interest in it because of the suggestion [9] that the native conformation of proteins might be strongly affected by hydrophobic bonding which avoids increased hydrogen bonding of the solvent around non-polar groups in the protein molecule. Solutions of tetra-alkylammonium salts have been suggested as models for the study of hydrophobic interaction in proteins.[10]

The solubilities of some tetra-alkylammonium salts also seem abnormal. The usual forms of expression for the lattice energies of ionic solids, and for the hydration energies of ions, is such that, if the anion is fixed and the size of the cation is increased from very small to very large values, the standard Gibbs energy of solution of a salt should rise to a maximum and thereafter decrease.[11] Good qualitative agreement is obtained for the salts of the alkali and alkaline-earth metals, but the solubilities of tetra-alkylammonium salts seem less than expected. This discrepancy is presumably connected with the wide use made of the tetra-alkylammonium ions as precipitating agents for the synthesis and analysis of inorganic anions.[12] The work described in this paper was undertaken in the hope of identifying the thermodynamic source of the discrepancy. Data required for the calculation of the standard partial molar entropies of the ions $NMe_4^+(aq)$, $NEt_4^+(aq)$, and $NPr_4^+(aq)$ have been obtained either from the literature or by experiment. The paper concludes with a tentative discussion of the thermodynamics of hydration of the gaseous ions.

EXPERIMENTAL

Tetraethylammonium iodide (B.D.H.) was recrystallized three times from water, the solution being cooled in ice. After each filtration the solid was washed with a little ice-cold water followed by acetone. The final product was dried to constant mass in a vacuum desiccator over P_2O_5. Tetrapropylammonium iodide (Fluka) was similarly recrystallized, but washed only with a little ice-cold water. The wet product was dried over P_2O_5 under vacuum for 4 days at room temperature, and then for 10 h at 80—100 °C. Iodide ion was determined gravimetrically as AgI (Found: I, 49·3. NEt_4I requires I, 49·35. Found: I, 40·5. NPr_4I requires I, 40·5%).

The adiabatic calorimeter used in the determination of the heat capacities has been described previously.[13] Solubilities were determined by gravimetric analysis of the compositions of saturated solutions at 298·15 K. Solutions containing an excess of solid were enclosed in a water bath maintained at 25·00 ± 0·01 °C, and stirred continually for 12 h. Samples of solution were withdrawn through a glass-wool plug into a pipette, weighed, and analysed gravimetrically for iodide ion.

RESULTS

Heat Capacity of Tetraethyl- and Tetrapropyl-ammonium Iodides.—Experimental molar heat capacities of the two solids obtained from the experimental observations are tabulated in Supplementary Publication No. SUP 20721 (4 pp., 1 microfiche).‡ Smoothed functions to fit these values were obtained by computer using orthogonal polynomials. The measured values had a standard deviation from the smoothed curves of ±0·5% below 50 K and ±0·1% above 50 K. Molar heat capacities of the two iodide salts were calculated for temperatures above 15 K from the smoothed functions and were extrapolated by 0 K by fitting Debye functions to the experimental values below 20 K.

Thermodynamic Properties.—*Solid-phase transitions.* Tetrapropylammonium iodide underwent a sluggish phase transition at 218·3 K as the plot of molar heat capacity against temperature shows (Figure). The enthalpy change was calculated from the area between the experimental results and the smoothed heat capacities in the temperature

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‡ For details see Notice to Authors No. 7 in *J. Chem. Soc. (A)*, 1970, Issue No. 20 (items less than 10 pp. are supplied as full size copies).

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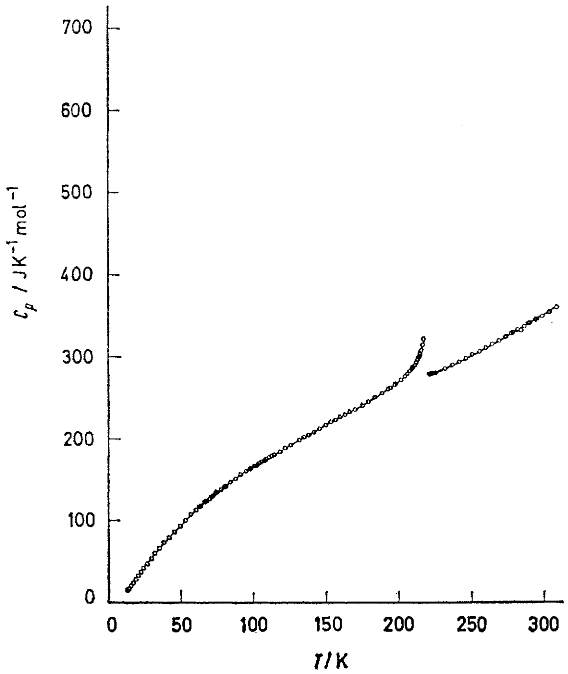
range of the transition. The entropy change was obtained from the enthalpy change and the transition temperature. These properties are given in Table 1. They agree with approximate values obtained by differential-scanning calorimetry.[14]



Variation of the molar heat capacity of tetrapropylammonium iodide with temperature

Tetraethyl- and tetrapropyl-ammonium iodide. Molar thermodynamic properties (Tables 2 and 3) were calculated from the smoothed heat capacities and the data in Table 1.

TABLE 1

Molar thermodynamic properties of the phase transition in tetrapropylammonium iodide

T/K	ΔH/J mol^{-1}	ΔS/J K^{-1} mol^{-1}
218·3	1 350 ± 10	6·18 ± 0·06

Solubilities of Tetraethyl- and Tetrapropyl-ammonium Iodide in Water at 25 °C.—For tetraethylammonium iodide, the results corresponded to a molality of 1·817 ± 0·005 mol kg^{-1}. For tetrapropylammonium iodide, the results corresponded to a molality of 0·619 ± 0·002 mol kg^{-1}.

CALCULATIONS

Values for the standard entropies of aqueous halide ions were taken from ref. 15. Auxiliary data from the literature have been converted into SI Units by using the factor 1 cal = 4·184 J. The standard state for solutes in aqueous solution is taken as the hypothetical ideal solution of unit molality.

Standard Molar Entropies.—The aqueous tetramethylammonium ion. Three independent routes exist for calculation of the standard molar entropy of the ion NMe_4^+(aq). The calculation based upon the iodide salt involves the most thoroughly investigated data. Five values [16–20] for the standard enthalpy of solution, $\Delta H_s^0(NMe_4I)$, imply that $\Delta H_s^0(NMe_4I) = 42{\cdot}2 \pm 0{\cdot}2$ kJ mol^{-1}. Three sets of activity-coefficient data,[16,21,22] and two determinations of the solubility at 25 °C,[16,21] agree closely. Levien's data [21] are representative and give $\Delta G_s^0(NMe_4I) = 9{\cdot}2 \pm 0{\cdot}4$ kJ mol^{-1} and $\Delta S_s^0(NMe_4I) = 110{\cdot}5 \pm 2$ J K^{-1} mol^{-1}. With the standard molar entropy of the solid,[16] and that of the iodide ion,[15] we obtain $S^0[NMe_4^+(aq)] = 211 \pm 4$ J K^{-1} mol^{-1}.

Boyd [19] reports unpublished work on NMe_4Cl which can be combined with the entropy of the solid chloride [23] to give a value of 205 J K^{-1} mol^{-1} in good agreement with the figure obtained from the iodide salt.

The data for the bromide salt present a problem in that the activity-coefficient data of Levien [21] differ somewhat from those of Lindenbaum and Boyd.[22] Closely agreeing values for the standard enthalpy of solution [17,24] suggest that $\Delta H_s^0(NMe_4Br) = 24{\cdot}69 \pm 0{\cdot}15$ kJ mol^{-1}. This figure, together with the solubility [21] and the entropy of the solid bromide salt,[23] can be combined with the activity-coefficient data of either Levien [21] or Lindenbaum and Boyd.[22] In the first case, the value obtained for the standard molar entropy of the aqueous cation is 217 J K^{-1} mol^{-1}; in the second, it is 212 J K^{-1} mol^{-1}. In view of the wealth of well documented data for the iodide salt, the value obtained from it has been doubly weighted against the figure obtained from the chloride and the mean of the two figures obtained from the bromide salt. Thus the chosen value is $S^0[NMe_4^+(aq)] = 210 \pm 3$ J K^{-1} mol^{-1}.

The aqueous tetraethylammonium ion. Five values for the standard enthalpy of solution of tetraethylammonium iodide are quite similar.[17,18,24–26] We have taken $\Delta H_s^0(NEt_4I) = 28{\cdot}3 \pm 0{\cdot}3$ kJ mol^{-1}. Two independent sets of activity-coefficient data [22,27] agree closely, and the value $f = 0{\cdot}205$ corresponds to the concentration of the saturated solution at 25 °C which was determined as described above. This gives $\Delta G_s^0(NEt_4I) = 4{\cdot}90 \pm 0{\cdot}2$ kJ mol^{-1} and $\Delta S_s^0(NEt_4I) = 78{\cdot}7 \pm 1{\cdot}5$ J K^{-1} mol^{-1}. Using the molar entropy of the solid iodide salt from Table 2, $S^0(NEt_4I) = 311{\cdot}1 \pm 1$ J K^{-1} mol^{-1}, we obtain $S^0[NEt_4^+(aq)] = 283 \pm 4$ J K^{-1} mol^{-1}.

The aqueous tetrapropylammonium ion. There exist three closely agreeing values [18,20,25] for the enthalpy of solution of tetrapropylammonium iodide. These imply that $\Delta H_s^0(NPr_4I) = 11{\cdot}5 \pm 0{\cdot}4$ kJ mol^{-1}. The solubility given earlier in this paper can be used to estimate, by a slight

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extrapolation, an activity coefficient[22] of 0·31 for the saturated solution at 25 °C. Then $\Delta G_s^0(NPr_4I) = 8{\cdot}2 \pm 0{\cdot}6$ kJ mol^{-1} and $\Delta S_s^0(NPr_4I) = 11 \pm 3$ J K^{-1} mol^{-1}. Using the molar entropy of the solid iodide salt from Table 3, $S^0(NPr_4I) = 432{\cdot}1 \pm 1$ J K^{-1} mol^{-1}, we obtain, $S^0[NPr_4^+(aq)] = 336 \pm 5$ J K^{-1} mol^{-1}.

Entropies of Gaseous Ions.—Accurate calculation of standard molar entropies of the gaseous tetra-alkylammonium ions by statistical mechanics is impossible, because the geometry of the gaseous ions is unknown. However, in structure and mass distribution, the ions should be almost identical with the molecules of those paraffins which are obtained by replacing the nitrogen atom with carbon and eliminating the positive charge. Moreover, Benson and his co-workers[28,29] have formulated accurate group-additivity methods for the estimation of entropies of gaseous organic molecules including the paraffins. Using Benson's group contributions with the appropriate symmetry factor[28] of 972, the following estimates are obtained: $S^0(CMe_4, g) = 305{\cdot}0$ J K^{-1} mol^{-1}; $S^0(CEt_4, g) = 462{\cdot}8$ J K^{-1} mol^{-1}; and $S^0(CPr_4, g) = 620{\cdot}5$ J K^{-1} mol^{-1}. In the case of neopentane, the S^0 value agrees closely with that obtained by statistical mechanics[29] (306·4 J K^{-1} mol^{-1}) and with the figure of 308·4 J K^{-1} mol^{-1} obtained by Boyd[19] for $S^0(NMe_4^+, g)$ using the geometry and fundamental frequencies of the ion *in a solid crystal.* This supports the belief that the group-additivity method forms a reliable basis for the estimation of entropies of gaseous ions. The values estimated above for CEt_4 and CPr_4 have therefore been used directly for the isoelectronic gaseous tetra-alkylammonium ions; they are recorded in column two of Table 6. The entropies of the gaseous alkali-metal cations were calculated from the Sackur–Tetrode equation, while the value for the tetramethylammonium ion is that given by Boyd.[19]

TABLE 2

Molar thermodynamic properties of tetraethylammonium iodide

T/K	C_p / J K^{-1} mol^{-1}	S^0 / J K^{-1} mol^{-1}	$(H - H_0^0)$ / J mol^{-1}	$(H - H_0^0)/T$ / J K^{-1} mol^{-1}	$-(G - H_0^0)/T$ / J K^{-1} mol^{-1}
10·00	3·345	1·115	8·362	0·836	0·279
15·00	11·98	3·766	42·47	2·831	0·935
20·00	22·99	8·730	130·1	6·504	2·227
25·00	33·40	14·99	271·4	10·85	4·138
30·00	42·95	21·94	462·6	15·42	6·519
35·00	51·61	29·22	699·4	19·98	9·240
40·00	59·43	36·63	977·4	24·43	12·20
45·00	66·51	44·05	1 292	28·72	15·23
50·00	72·97	51·40	1 641	32·83	18·57
60·00	84·51	65·75	2 430	40·50	25·24
70·00	94·78	79·56	3 327	47·54	32·02
80·00	104·2	92·84	4 323	54·04	38·80
90·00	112·9	105·6	5 409	60·10	45·52
100·00	121·1	117·9	6 580	65·80	52·15
110·00	128·9	129·9	7 830	71·18	58·67
120·00	136·3	141·4	9 156	76·30	65·09
130·00	143·4	152·6	10 560	81·19	71·39
140·00	150·4	163·5	12 020	85·89	77·58
150·00	157·3	174·1	13 560	90·42	83·66
160·00	164·0	184·4	15 170	94·81	89·64
170·00	170·6	194·6	16 840	99·07	95·51
180·00	176·9	204·5	18 580	103·2	101·3
190·00	183·1	214·3	20 380	107·3	107·0
200·00	189·2	223·8	22 240	111·2	112·6
210·00	195·3	233·2	24 160	115·1	118·1
220·00	201·5	242·4	26 150	118·9	123·5
230·00	207·9	251·5	28 200	122·6	128·9
240·00	214·4	260·5	30 310	126·3	134·2
250·00	221·1	269·4	32 480	129·9	139·4
260·00	227·7	278·2	34 730	133·6	144·6
270·00	234·4	286·9	37 040	137·2	149·7
273·15	236·5	289·6	37 790	138·3	151·3
280·00	241·1	295·5	39 420	140·8	154·8
290·00	248·2	304·1	41 860	144·4	159·8
298·15	254·2	311·1	43 920	147·3	163·8
300·00	255·6	312·7	44 380	147·9	164·7

DISCUSSION

In Table 4, the standard Gibbs energies of solution of the tetra-alkylammonium iodide salts are compared with those of the iodide salts of the alkali metals. The pattern which is of general application to alkali and alkaline-earth metal salts, that of a rough parabola with a single maximum when ΔG_s^0 is plotted against cation size,[11] is broken when the tetra-alkylammonium salts are introduced. In the case of the iodide salts, this is particularly apparent from the minimum at NEt_4I which is matched by a maximum in the solubility. Although precise data are not available for the other halide salts, rough values of the solubilities can be obtained from the maximum molarities to which Lindenbaum and Boyd[22] determined activity coefficients, and these allow calculation of approximate values of ΔG_s^0 which reveal a similar pattern. For instance, in the case of the chloride salts,

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TABLE 3

Molar thermodynamic properties of tetrapropylammonium iodide

T/K	$\frac{C_p}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^0}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{(H - H_0^0)}{\text{J mol}^{-1}}$	$\frac{(H - H_0^0)/T}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{-(G - H_0^0)/T}{\text{J K}^{-1}\text{ mol}^{-1}}$
10·00	7·500	2·582	19·29	1·929	0·653
15·00	19·92	7·876	86·67	5·778	2·098
20·00	32·70	15·37	218·5	10·92	4·448
25·00	44·80	23·98	412·6	16·50	7·480
30·00	56·13	33·16	665·2	22·17	10·99
35·00	66·73	42·62	972·7	27·79	14·83
40·00	76·68	52·19	1 331	33·29	18·90
45·00	86·08	61·77	1 739	38·63	23·13
50·00	95·01	71·30	2 191	43·83	27·47
60·00	111·7	90·12	3 226	53·77	36·35
70·00	127·1	108·5	4 421	63·16	45·35
80·00	141·1	126·4	5 763	72·04	54·37
90·00	153·9	143·8	7 239	80·43	63·35
100·00	165·5	160·6	8 837	88·37	72·24
110·00	176·2	176·9	10 550	95·87	81·01
120·00	186·4	192·7	12 360	103·0	89·66
130·00	196·2	208·0	14 270	109·8	98·18
140·00	206·1	222·9	16 280	116·3	106·6
150·00	216·1	237·4	18 400	122·6	114·8
160·00	226·1	251·7	20 610	128·8	122·9
170·00	236·4	265·7	22 920	134·8	130·9
180·00	245·5	279·5	25 330	140·7	138·8
190·00	257·3	293·2	27 860	146·6	146·5
200·00	270·9	306·7	30 500	152·5	154·2
210·00	289·5	320·3	33 290	158·5	161·8
220·00	400·0	338·0	37 100	168·6	169·4
230·00	285·0	350·6	39 920	173·6	177·0
240·00	293·0	362·9	42 810	178·4	184·5
250·00	301·6	375·0	45 780	183·1	191·9
260·00	310·7	387·0	48 840	187·9	199·2
270·00	320·3	398·9	52 000	192·6	206·3
273·15	323·5	402·6	53 020	194·1	208·5
280·00	330·4	410·8	55 250	197·3	213·4
290·00	340·8	422·5	58 610	202·1	220·4
298·15	349·5	432·1	61 430	206·0	226·1
300·00	351·5	434·3	62 070	206·9	227·4
310·00	361·9	446·0	65 640	211·7	234·2

the value for the tetrabutylammonium salt exceeds that for the tetramethylammonium salt, even though a clear maximum occurs at a smaller radius in the sequence of alkali-metal chloride salts. The standard Gibbs energies of solution of the heavier tetra-alkylammonium chloride, bromide, and iodide salts are thus greater than those values suggested by an extension of the pattern of variations observed for the alkali-metal halide salts.

TABLE 4

Standard Gibbs energies of solution of iodide salts at 25 °C [a]

Salt	ΔG_s^0/kJ mol^{-1}	Salt	ΔG_s^0/kJ mol^{-1}
LiI	−78	CsI	−0·4
NaI	−30·6	NMe_4I	9·2
KI	−11·7	NEt_4I	4·90
RbI	−8·4	NPr_4I	8·2

[a] Values for alkali-metal salts are taken from ref. 38.

The origin of this discrepancy may be sought in the models used to build up an expression for the standard Gibbs energy of solution. The latter is given by equation (1), where ΔG_L^0 is the standard Gibbs energy of sublimation of the lattice for conversion into the appropriate

$$\Delta G_s^0 = \Delta G_L^0 + \Delta G_h^0 \qquad (1)$$

gaseous ions in the ideal-gas state at 1 atm pressure, and ΔG_h^0 is the standard Gibbs energy of hydration of the ions. Expressions for ΔG_L^0 and ΔG_h^0 are obtained largely by using electrostatic models for monoatomic ions. It seems unlikely that the polyatomic nature of the tetra-alkylammonium ions alone would account for the observed discrepancy because, if the electrostatic models applied, the difference from the monoatomic-cation case should mainly show itself through the rotational entropy of the cation, and unexpectedly positive values of ΔG_s^0 would then arise only if the quenching of the rotational motion in solution were more substantial than in the solid salt. Thus the discrepancy is most likely due to a failure of the electrostatic models.

The models are used to derive expressions for the lattice energies of the salt and the hydration energy of the cation. The abnormal properties of solutions of tetra-alkylammonium salts [1-4] suggest the working assumption that the lattice energies of tetra-alkylammonium salts are 'normal,' and that the source of the discrepancy is the standard Gibbs energy of hydration of the tetra-alkylammonium ion. Values for the thermodynamic properties associated with the hydration of individual ions can only be assigned by using unproven assumptions founded upon models of the hydration process. However, various methods of assignment [30] have yielded quite similar results; the values used in this paper are based upon the

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work of Noyes.[31] They amount to the assignment of -1084 kJ mol^{-1} to the standard Gibbs energy of hydration of the hydrogen ion, of -1121 kJ mol^{-1} to the standard enthalpy of hydration of the hydrogen ion, and of -14 J K^{-1} mol^{-1} to the absolute standard entropy of the aqueous proton, $S_{\text{abs}}{}^0\,[\text{H}^+(\text{aq})]$.

Standard Molar Entropies of Hydration for Cations.—These were calculated by using equation (2), where

$$\Delta S_{\text{h}}{}^0(\text{M}^+) = S^0[\text{M}^+(\text{aq})] - S^0(\text{M}^+,\text{ g}) + S_{\text{abs}}{}^0[\text{H}^+(\text{aq})] \quad (2)$$

$S^0[\text{M}^+(\text{aq})]$ is the usual tabulated value referred to a scale on which $S^0[\text{H}^+(\text{aq})] = 0$.

Standard Enthalpies of Hydration for Cations.—Values for the alkali-metal ions can be obtained from equation (3).

$$\Delta H_{\text{h}}{}^0(\text{M}^+) = \Delta H_{\text{f}}{}^0[\text{M}^+(\text{aq})] - \Delta H_{\text{f}}{}^0(\text{M}^+,\text{ g}) + \Delta H_{\text{f}}{}^0(\text{H}^+,\text{ g}) + \Delta H_{\text{h}}{}^0(\text{H}^+) \quad (3)$$

In the case of the tetra-alkylammonium ions, this equation cannot be applied because experimental values of $\Delta H_{\text{f}}{}^0(\text{M}^+,\text{ g})$ and $\Delta H_{\text{f}}{}^0[\text{M}^+(\text{aq})]$ do not exist. Enthalpies of hydration can only be obtained by using theoretical calculations of the lattice energies of tetra-alkylammonium halide salts. The latter are used in equation (4), where it is assumed that the lattice energy at

$$-\Delta H_{\text{h}}{}^0(\text{M}^+) = U_0(\text{MX}) + 2RT - \Delta H_{\text{s}}{}^0(\text{MX}) + \Delta H_{\text{h}}{}^0(\text{X}^-) \quad (4)$$

temperature T, $U_{\text{T}}(\text{MX})$, is equal to $U_0(\text{MX})$. The lattice energies in this paper are presented in Table 5.

TABLE 6

Thermodynamic properties of ions at 25 °C

	$\frac{S^0(\text{M}^+,\text{ g})^a}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{S^0[\text{M}^+(\text{aq})]^b}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta S_{\text{h}}{}^{0\,c}}{\text{J K}^{-1}\text{ mol}^{-1}}$	$\frac{\Delta H_{\text{h}}{}^0}{\text{kJ mol}^{-1}}$	$\frac{\Delta G_{\text{h}}{}^{0\,d}}{\text{kJ mol}^{-1}}$
Li^+	132·9	14	-133	-545^e	-505
Na^+	147·9	59	-103	-436^e	-405
K^+	154·5	103	-66	-351^e	-331
Rb^+	164·2	124	-54	-327^e	-310
Cs^+	169·7	133	-51	-294^e	-278
$\text{NMe}_4{}^+$	308	210	-112	-192^f	-159
$\text{NEt}_4{}^+$	462	283	-193	-165^f	-107
$\text{NPr}_4{}^+$	620	336	-298	-157^g	-68

[a] See text for method of calculation. [b] Based on $S^0[\text{H}^+(\text{aq})] = 0$; data for alkali metals from ref. 38 (for other ions see text). [c] Obtained from equation (2) using the value of $S_{\text{abs}}{}^0[\text{H}^+(\text{aq})]$ given in ref. 31. [d] From equation (5). [e] Obtained from equation (3) using data from ref. 38 and the value of $\Delta H_{\text{h}}{}^0(\text{H}^+)$ derived in ref. 31. [f] Obtained by substituting the lattice energies of Table 5 into equation (4); hydration enthalpies of anions are taken from ref. 31, and heats of solution are given in this paper. [g] As footnote *f*, but $\Delta H_{\text{s}}{}^0(\text{NPr}_4\text{Br}) = -4{\cdot}48$ kJ mol^{-1} was used from refs. 19 and 20.

TABLE 5

Lattice energies of tetra-alkylammonium halide salts

Salt	U_0/kJ mol^{-1}	Salt	U_0/kJ mol^{-1}
NMe_4Cl	523	NEt_4I	449
NMe_4Br	516	NPr_4Br	452
NMe_4I	498		

The different values given by Boyd[19] for each salt have been averaged, and the resulting figures weighted equally with the values calculated by Ladd.[32] The two sets of lattice energies differ substantially in certain cases, but either set can be used to justify the conclusion reached in this paper.

Standard Gibbs Energies of Hydration for Cations.—These can be obtained from equation (5). Further

$$\Delta G_{\text{h}}{}^0 = \Delta H_{\text{h}}{}^0 - T\Delta S_{\text{h}}{}^0 \quad (5)$$

details of the calculations and final values of $\Delta S_{\text{h}}{}^0$, $\Delta H_{\text{h}}{}^0$, and $\Delta G_{\text{h}}{}^0$ are presented in Table 6. The absolute values are little more than suggestive because of the uncertainty in the values assigned to the hydrogen ion, but most of the argument that follows depends upon the *relative* values which are much more accurately known. This is particularly true of the entropies of hydration which in no case depend on the lattice-energy data.

The most striking feature of the thermodynamic properties for the individual ions is the change from an increase in the standard entropies of hydration from lithium to caesium (they become less negative) into a decrease in the sequence for the tetra-alkylammonium ions. In the case of the tetraethyl- and tetrapropylammonium ions, this change results in standard Gibbs energies of hydration which are markedly less negative than the usual theoretical treatments would suggest. These treatments mostly rely upon an empirical adjustment of the Born equation (6). If we consider an

$$\Delta G_{\text{h}}{}^0 = -\frac{z^2e^2}{2r}\left(1 - \frac{1}{\varepsilon}\right) \quad (6)$$

approach which uses the macroscopic value of the dielectric constant and adds a constant of 0·07—0·08 nm to the crystallographic radius,[33] values of r of about 0·5—0·6 nm are required to reproduce the figures for $\Delta G_{\text{h}}{}^0(\text{NEt}_4{}^+)$ and $\Delta G_{\text{h}}{}^0(\text{NPr}_4{}^+)$. Such radii are not consistent with the values of 0·25—0·35 nm suggested by the calculation of 'thermochemical radii' from the lattice energies of halide salts[19] and Kapustinskii-type equations,[34] or by the geometry of the ions in crystals.[35,36] Existing approaches, based upon adjustment of the value of ε to

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an extent depending on the radius of the cation,[31] are also incapable of accommodating the data. It seems, therefore, that a theoretical treatment of ionic hydration energies which embraces both the alkali-metal and tetra-alkylammonium ions will require increased sophistication.

The discordant values of ΔG_h^0 will tend to make the standard Gibbs energies of solution of tetra-alkylammonium salts less negative than expected. This will strongly influence the solubility, and it could well be that the special precipitating power of tetra-alkylammonium and tetraphenylarsonium ions in aqueous solution is as much dependent on the peculiar values of $\Delta G_h^0(M^+)$ as on the need to use large cations to precipitate large anions.[11,12]

As stated earlier, the factor which contributes most to the discordant values of ΔG_h^0 is the marked decrease in the standard entropies of hydration as one moves from the tetramethylammonium to the tetrapropylammonium ion. This contrasts with the increase with ionic radius from lithium to caesium. As explained above, inspection of the variation in the standard Gibbs energies of solution of halide salts suggests that the decrease cannot be completely accounted for by the quenching of rotational motion, and it is, of course, just the result that would be predicted on the basis of ' structure-enforcing ' models which are widely used to describe the effect of tetra-alkylammonium ions on water.[1,2,5,6] Like the invocation of covalent bonding around aqueous d^{10} cations,[31,37] this would be an example of an ion–water interaction which cannot be treated with an electrostatic model.

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