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Thermodynamic Studies in the Tetramethylammonium Iodide–Polyiodide and Tetraethylammonium Iodide–Polyiodide Systems

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The free energy of the reaction $R_4NI_x(s) + yI_2(s) = R_4NI_{x+2y}(s)$ was determined from emf measurements of solid-state cells of the type Ag|AgI|C, R_4NI_x–R_4NI_{x+2y}, where R_4NI_x–R_4NI_{x+2y} denotes the solid quarternary ammonium polyiodide systems $(CH_3)_4NI$–$(CH_3)_4NI_3$, $(CH_3)_4NI_3$–$(CH_3)_4NI_5$, $(CH_3)_4NI_5$–$(CH_3)_4NI_9$, $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$, and $(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$. For the temperature range 25–113.5° $\Delta G°$ values for this reaction are given by $\Delta G°(\text{kcal/mol}) = -A - B(T - 273)$ where A and B for the tetramethylammonium systems are 3.3 and 0.006 for R_4NI–R_4NI_3, 3.13 and 0.0032 for R_4NI_3–R_4NI_5, and 1.99 and 0.0062 for R_4NI_5–R_4NI_9; for the tetraethylammonium systems $A = 5.5$ for R_4NI–R_4NI_3 and for R_4NI_3–R_4NI_7 $A = 5.29$ and $B = -0.00092$. From these free energies and the vapor pressure of elemental iodine, dissociation pressure expressions for the polyiodides were obtained. From the enthalpy change of the above reaction and other thermodynamic data the following $\Delta H°$ values were calculated at 25°: the aqueous heats of solution of the triiodides, the $\Delta H°$ of the reaction $I^-(g) + I_2(g) = I_3^-(g)$, $\Delta H_f°$ of $I_3^-(g)$, and the enthalpy of hydration of I_3^-.

Introduction

Quaternary ammonium polyiodide systems have recently been proposed as cathodes[1] in solid-state batteries. To help utilize these systems for this purpose as well as to afford a comparison with the alkali and ammonium polyiodides, a knowledge of the thermodynamic properties is needed. In a previous study[2] thermodynamic data for the reaction

$$MI_x(s) + yI_2(s) = MI_{x+2y}(s) \qquad (1)$$

were obtained for the RbI–RbI_3, NH_4I–NH_4I_3, CsI–CsI_3, and CsI_3–CsI_4 systems from emf measurements of the solid-state galvanic cells

$$Ag|AgI|C,\ MI_x + MI_{x+2y} \qquad (I)$$

and

$$Ag|AgI|C,\ I_2(s) \qquad (II)$$

These measurements have now been extended to include the tetramethylammonium iodide–polyiodide systems, $(CH_3)_4NI$–$(CH_3)_4NI_3$, $(CH_3)_4NI_3$–$(CH_3)_4NI_5$, and $(CH_3)_4NI_5$–$(CH_3)_4NI_9$, and the tetraethylammonium iodide–polyiodide systems, $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$ and $(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$. Measurements on the system $(CH_3)_4NI_9$–$(CH_3)_4NI_{11}$, reported by Foote and Fleischer,[3] were also attempted but the results indicated that free iodine and not the $(CH_3)_4NI_{11}$ phase was present.

Experimental Section

Mallinckrodt silver iodide and iodine and Eastman tetramethylammonium iodide and tetraethylammonium iodide were used throughout. The polyiodides were synthesized by equilibrating stoichiometric amounts of the monoiodide and iodine at 70° in preevacuated, sealed tubes for 1 week. For the $(CH_3)_4NI_9$–$(CH_3)_4NI_{11}$ phases, preparation was attempted unsuccessfully by the above procedure as well as from toluene at 25° as described in the literature.[3]

For the electrochemical cell measurements, the configurations, electrodes, and techniques used were identical with those described in the earlier polyiodide study.[2] No contact between the AgI pellet and the polyiodide phases, contained in porous graphite cups, occurred in the cells except through the vapor phase. Except for those cases where the iodine pressure was too low to yield a well-poised electrode, the cells yielded emf's reproducible to ±0.3 mV over the temperature range of measurement, 25–115°. All measurements were made in an argon atmosphere at approximately 10° intervals with both ascending and descending temperatures. Constant and reproducible potentials were found to occur much more rapidly with increasing temperature for all the systems.

Results

The reaction measured by cells of type I with the M replaced by R_4N, which denotes the quaternary ammonium ion, is

$$2yAg(s) + R_4NI_{x+2y}(s) = 2yAgI(s) + R_4NI_x(s) \qquad (2)$$

where $x = 1, 3, 5$, or 9 for $R = CH_3$ and 1 or 3 for $R = C_2H_5$; in both systems $y = 1$ or 2. The emf values were found to be linear functions of temperature for all of the cells measured, except the $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$ cell, over most of the temperature range of measurement. The data are presented in Figure 1 and given in Table I in the form $E_I°(V) = \alpha + \beta(T - 273)$. The potentials measured below the lower temperature limits listed in Table I were not as reproducible as those at the other temperatures and those above the upper limits fell below the extrapolated linear values. The emf data for the $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$ cell must be regarded as questionable because of their very poor reproducibility; the iodine pressure corresponding to this potential appears to be too low to yield a poised electrode. In addition, the poor reproducibility for the $(CH_3)_4NI$–$(CH_3)_4NI_3$ system, as compared to the others, indicated that the data for this cell are also open to some question.

Cells with the stoichiometric mixture $(CH_3)_4NI_5$–

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[1] (a) B. B. Owens, "Solid State Electric Cell Utilizing as an Electron Acceptor Material an Organic Ammonium Polyiodide," U. S. Patent 3,476,605 (Nov 4, 1969); (b) M. De Rossi, G. Pistoia, and B. Scrosati, *J. Electrochem. Soc.*, **116**, 1642 (1969).

[2] L. E. Topol, *Inorg. Chem.*, **7**, 451 (1968).

[3] H. W. Foote and M. Fleischer, *J. Phys. Chem.*, **57**, 122 (1953).

TABLE I

DATA FOR THE EQUATION $E_I°(V) = \alpha + \beta(T - 273)$ for $Ag|AgI|C, R_4NI_x + R_4NI_{x+2y}$ Cells[a,b]

R_4NI_x–R_4NI_{x+2y}	α, V	$10^4\ \beta$, V deg^{-1}	Temp range, °C
$(CH_3)_4NI$–$(CH_3)_4NI_3$	0.611 ± 0.002	0.05 ± 0.01	60–110
$(CH_3)_4NI_3$–$(CH_3)_4NI_5$	0.6150 ± 0.0010	0.80 ± 0.07	55–110
$(CH_3)_4NI_5$–$(CH_3)_4NI_9$	0.6614 ± 0.0006	0.82 ± 0.05	45–110
$(CH_3)_4NI_9$–$(CH_3)_4NI_{11}$	*c*	*c*	25–110
$(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$	0.56 ± 0.02	*d*	80–115
$(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$	0.6255 ± 0.0012	1.60 ± 0.08	50–115

[a] The cell reaction is $2yAg(s) + R_4NI_{x+2y}(s) = 2yAgI(s) + R_4NI_x(s)$. [b] R denotes the alkyl group, CH_3 or C_2H_5. [c] The emf's indicated the presence of elemental iodine. [d] No value for β could be obtained from the measurements.

$(CH_3)_4NI_7$ yielded the same potentials as the $(CH_3)_4NI_5$–$(CH_3)_4NI_9$ cells indicating no other intermediate polyiodide is readily formed at these temperatures. Similarly, cells with the stoichiometric mixture $(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_5$ yielded the same results as the $(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$ cells showing no other intermediate to be present here also. The potentials found with variously prepared and analyzed stoichiometric mixtures of $(CH_3)_4NI_9$–$(CH_3)_4NI_{11}$ as well as of $(C_2H_5)_4NI_7$–$(C_2H_5)_4NI_9$ were identical with those measured in cell II and indicated that no compound with iodine content greater than that of the tetramethylammonium enneaiodide or of the tetraethylammonium heptaiodide, respectively, was present at room temperature or above.

TABLE II

VALUES OF $(E_I° - E_{II}°)^a$ AND $\Delta G°^a$ AS FUNCTIONS OF TEMPERATURE FOR QUARTERNARY AMMONIUM POLYIODIDE SYSTEMS

System	$(E_I° - E_{II}°)$,[b] V	$\Delta G°$, kcal
$(CH_3)_4NI$–$(CH_3)_4NI_3$	$-0.072 \pm 0.002 - 1.45 \pm 0.05(T - 273) \times 10^{-4}$	$-3.3 \pm 0.1 - 0.0067 \pm 0.0003(T - 273)$
$(CH_3)_4NI_3$–$(CH_3)_4NI_5$	$-0.0680 \pm 0.0013 - 0.70 \pm 0.09(T - 273) \times 10^{-4}$	$-3.13 \pm 0.06 - 0.0032 \pm 0.0004(T - 273)$
$(CH_3)_4NI_5$–$(CH_3)_4NI_9$	$-0.0216 \pm 0.0011 - 0.68 \pm 0.07(T - 273) \times 10^{-4}$	$-1.99 \pm 0.10 - 0.0062 \pm 0.0006(T - 273)$
$(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$	-0.12 ± 0.02	-5.5 ± 0.9
$(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$	$-0.0575 \pm 0.0015 + 0.10 \pm 0.09(T - 273) \times 10^{-4}$	$-5.29 \pm 0.14 + 0.0009 \pm 0.0008(T - 273)$

[a] These values are for the reaction $R_4NI_x(s) + yI_2(s) = R_4NI_{x+2y}(s)$. [b] $E_{II}°(V) = 0.6830 \pm 0.0009 + (1.50 \pm 0.05) \times 10^{-4}(T - 273)$ for the reaction $Ag(s) + 0.5I_2(s) = AgI(s)$.

TABLE III

VALUES OF $\Delta G°$, $\Delta S°$, AND $\Delta H°$ AT 25° FOR THE REACTION $R_4NI_x(s) + yI_2(s) = R_4NI_{x+2y}(s)$

System	$-\Delta G°$, kcal	$\Delta S°$, cal/deg	$-\Delta H°$, kcal
$(CH_3)_4NI$–$(CH_3)_4NI_3$	3.5 ± 0.1 (3.3)[a]	6.7 ± 0.3 (4.0)[a]	1.7 ± 0.1 (2.1)[a]
$(CH_3)_4NI_3$–$(CH_3)_4NI_5$	3.21 ± 0.06 (3.1)	3.2 ± 0.4 (4.7)	2.2 ± 0.1 (1.7)
$(CH_3)_4NI_5$–$(CH_3)_4NI_9$	2.14 ± 0.10 (2.2)	6.2 ± 0.6	0.3 ± 0.2
$(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$	5.5 ± 0.9	...	...
$(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$	5.27 ± 0.14	-0.9 ± 0.8	5.5 ± 0.3

[a] *The values in parentheses are calculated from the data of Foote and Fleischer.*[3]

From the potentials $E_I°$ for reaction 2 (in Table I) and $E_{II}°$ for cell II, where[2] $E_{II}°(V) = 0.6830 + 1.50 \times 10^{-4}(T - 273)$, and the relation

$$\Delta G° = -nF(E_{II}° - E_I°) \tag{3}$$

where $n = 2y$, the standard free energies $\Delta G°$ for reaction 1, where $M = R_4N$, can be found. Expressions for $(E_I° - E_{II}°)$ and $\Delta G°$ as functions of temperature for the range 50–113.5° (the melting point of I_2) are presented in Table II.

Extrapolation of the $\Delta G°$ relations in Table II to 25° yields the values of $\Delta G°$, $\Delta S°$, and $\Delta H°$ for reaction 1 at 25° and these results are given in Table III. For comparison, the thermodynamic values for the tetramethylammonium system calculated from the solubility data of Foote and Fleischer[3] in toluene are also listed, in parentheses, in this table.[4] It was assumed that the toluene solutions obey Henry's law.

Since no $\Delta G°$ or $\Delta H°$ data for the formation of the quarternary ammonium monoiodides from the elements are available, corresponding standard free energy and enthalpy of formation values for the polyiodides cannot be evaluated. However, the standard entropy $S°_{298.1°K}$ of $(CH_3)_4NI$ has been determined[5] as 49.7 ± 0.2 cal mol^{-1} deg^{-1}, and with $S°_{298.1°K} = 27.76$ cal mol^{-1} deg^{-1} for $I_2(s)$[4b] and the data in Table III, standard entropies of formation of the tetramethylammonium polyiodides can be derived. These $S°_{298.1°K}$ values are 84, 115, and 177 cal mol^{-1} deg^{-1} for $(CH_3)_4NI_3$, $(CH_3)_4NI_5$, and $(CH_3)_4NI_9$, respectively.

The iodine pressure over the polyiodide systems can be calculated by combining the free energy of reaction 1 per mole of I_2 with the $\Delta G°$ for the sublimation of elemental iodine, *i.e.*, for the reaction $I_2(s) = I_2(g)$. Thus employing eq 3 and the expression $\Delta G° = -RT \ln (p°/p)$, where $p°$ denotes the sublimation pressure of solid iodine and p the partial pressure of iodine in equilibrium with the $R_4NI_x + R_4NI_{x+2y}$ solid phases, one obtains the relation

$$\ln p = \ln p° + (2F/RT)(E_I° - E_{II}°) \tag{4}$$

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(4) (a) It should be noted that the values in Table III correspond to elemental iodine in the solid state whereas Foote and Fleischer gave their $\Delta H°$ data for gaseous iodine. The $\Delta H°$ values for the two standard states differ merely by the heat of sublimation of iodine at 25°, 14.92 kcal/mol.[4b] (b) *Nat. Bur. Stand.* (*U. S.*), *Tech. Note*, **No. 270-1**, Part I (1965).

(5) L. V. Coulter, K. S. Pitzer, and W. M. Latimer, *J. Amer. Chem. Soc.*, **62**, 2845 (1940).

(6) H. T. Gerry and L. J. Gillespie, *Phys. Rev.*, **40**, 269 (1932).

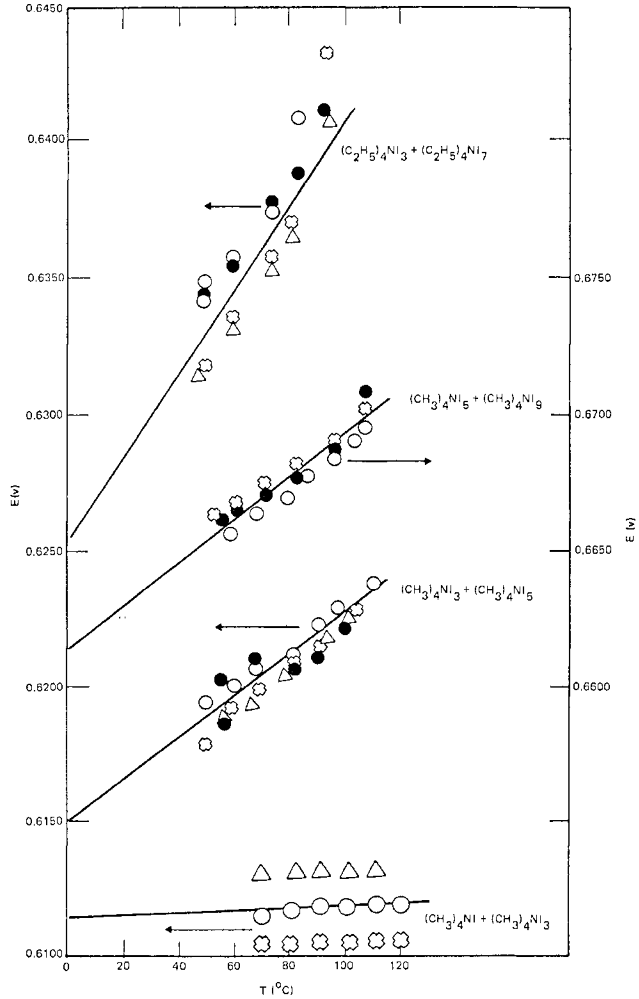

Figure 1.—Emf data for cells of the type Ag|AgI|C, R_4NI_x–R_4NI_{x+2y}. (The symbols denote different cells.)

The vapor pressure of elemental iodine[6] is given by

$$\log p°(\text{atm}) = \frac{-3512.8}{T} - 2.013 \log T + 13.3740 \quad (5)$$

and substituting this into eq 4, combining terms, and converting to Torr units yield

$$\log p(\text{Torr}) = \frac{-D(T)}{T} - 2.013 \log T + 16.2548 \quad (6)$$

for the dissociation pressures of the polyiodide systems from 25 to 113.5°. Expressions for $D(T)$ are given by $42.3 \times 10^2 + 1.4(T - 273)$, $4193 + 0.70(T - 273)$, and $3729 + 0.68(T - 273)$ for $(CH_3)_4NI$–$(CH_3)_4NI_3$, $(CH_3)_4NI_3$–$(CH_3)_4NI_5$, and $(CH_3)_4NI_5$–$(CH_3)_4NI_9$, respectively; for $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$ and $(C_2H_5)_4NI_3$–$(C_2H_5)_4NI_7$ $D(T) = 47 \times 10^2$ and $4088 - 0.10(T - 273)$, respectively.

The heat of solution $\Delta H_{\text{soln,t}}$ of $(CH_3)_4NI_3$ can be calculated from ΔH data for the following reactions

$$(CH_3)_4NI_3(s) \xrightarrow{\Delta H_d} (CH_3)_4NI(s) + I_2(s) \quad (7)$$

$$(CH_3)_4NI(s) + aq \xrightarrow{\Delta H_{\text{soln,m}}} (CH_3)_4N^+(aq) + I^-(aq) \quad (8)$$

$$I^-(aq) + I_2(s) \xrightarrow{\Delta H_a} I_3^-(aq) \quad (9)$$

Adding eq 7–9 yields

$$(CH_3)_4NI_3(s) + aq \xrightarrow{\Delta H_{\text{soln,t}}} (CH_3)_4N^+(aq) + I_3^-(aq) \quad (10)$$

Thus

$$\Delta H_{\text{soln,t}} = \Delta H_d + \Delta H_{\text{soln,m}} + \Delta H_a \quad (11)$$

where ΔH_d, the heat of dissociation of the solid triiodide, is given for 25° in Table III, $\Delta H_{\text{soln,m}}$, the heat of solution of the monoiodide, is 10.0 kcal/mol[5] at 25°, and ΔH_a, the heat of association of aqueous triiodide, is 0.9 kcal/mol.[4b] The heat of solution of $(CH_3)_4NI_3$ at 25° is calculated as 12.6 kcal/mol, somewhat larger than the alkali triiodide values.[2] For the solution reactions of the higher iodides

$$(CH_3)_4NI_{3+z}(s) + aq \longrightarrow (CH_3)_4N^+(aq) + I_3^-(aq) + (z/2)I_2(s) \quad (12)$$

where $z = 2$, 4, or 6, the heats at 25° can be obtained by merely adding to 12.6 kcal/mol the heats of reverse reaction 1, given in Table III, for $z = (x + 2y - 3) > 0$. Two of these heats of solution are listed in Table IV.

TABLE IV

CALCULATED ENERGY VALUES FOR SOME TRIIODIDE REACTIONS

Reaction	Energy, kcal
$(CH_3)_4NI_3(s) + aq \longrightarrow (CH_3)_4N^+(aq) + I_3^-(aq)$	$\Delta H = 12.6$
$(CH_3)_4NI_5(s) + aq \longrightarrow (CH_3)_4N^+(aq) + I_3^-(aq) + I_2(s)$	$\Delta H = 14.8$
$RbI_3(s) \longrightarrow Rb^+(g) + I_3^-(g)$	$L = 143.7^a$
$CsI_3(s) \longrightarrow Cs^+(g) + I_3^-(g)$	$L = 137.7^a$
$I^-(g) + I_2(g) \longrightarrow I_3^-(g)$	$\Delta H = -24.0$

[a] Calculated from the Kapustinskii equation with effective radii 2.25 and 2.45 Å (see text) for I^- and I_3^-, respectively.

Discussion

As was found in the previous study,[2] the $\Delta G°$ values at 25° for reaction 1 are in excellent agreement with those of Foote and Fleischer[3] (see Table III), but the agreement in $\Delta H°$ and $\Delta S°$ is somewhat poorer.

It should be noted, however, that the thermodynamic values derived from the solubility data in toluene[3] were obtained from measurements at only two temperatures, 6 and 25°, whereas in the present study many points were determined for each system over a long temperature range (except the $(CH_3)_4NI$–$(CH_3)_4NI_3$ and $(C_2H_5)_4NI$–$(C_2H_5)_4NI_3$ cells). The low iodine activities in these two systems not only made accurate absolute emf determinations difficult but also made the detection of the variation of potential with temperature virtually impossible. Thus, although the free energy values at 25° tabled for those two systems may be in some error, the entropy and enthalpy data are in greater doubt.

The results of this study as well as the former one[2] with the rubidium, cesium, and ammonium iodides are consistent with the stability of the polyiodides, as given by reaction 1, increasing with the size of the cation. However, unlike the alkali and ammonium salts the stability of the tetramethylammonium polyiodides with respect to solid iodine and the lower iodide increases with temperature. Furthermore, the entropy changes for the addition of solid iodine to the tetramethylammonium systems are both of opposite sign and larger magnitude than those observed in the other systems. The entropy change in the tetramethyl system per mole of I_2 added appears to be about 3 cal/deg except for the initial addition, the value for which (6 eu) may be in error. These $\Delta S°$ values indicate that the tetramethylammonium polyiodides formed by reaction 1 become more disordered in structure with each successive addition of iodine and this disorder helps stabilize the compounds.

Although the difference in cation size between Cs^+ and $(CH_3)_4N^+$ is large, 1.69[7] compared to 3.30 Å[8] (or 3.8 Å calculated from covalent and van der Waals radii[7]), there is no difference in $\Delta G°$ at 25° for reaction 1 for the two iodides. This is in contrast to the variation of $\Delta G°$ with cation size for the ammonium, rubidium, and cesium iodides as well as for the tetramethylammonium and tetraethylammonium ($r_+ = 4.65$[8] or 5.3 Å[7]) iodides. However, further additions of iodine to the triiodides can be achieved only with CsI_3, $(CH_3)_4NI_3$, and $(C_2H_5)_4NI_3$, and in the case of CsI_3, two molecules are required to combine with one iodine, *i.e.*, Cs_2I_8 is formed.[9] In addition, the formation of the next higher polyiodide after R_4NI_3 with the larger quarternary ammonium cationic salts involves much greater free energy changes than that for Cs_2I_8 for which $\Delta G°_{298\,°K} = 1.3$ kcal/mol of I_2.[2] Thus, not only is the stability of the triiodide with respect to the monoiodide increased as the cation size increases, but the combination with additional iodine is also enhanced. It is not obvious at present why polyiodides of similar stoichiometry do not form in the two quarternary ammonium systems. From the above observations it would appear that still more stable polyiodides could be synthesized from larger quarternary ammonium iodides, *e.g.*, tetrapropylammonium iodide, pyridinium iodide, etc.

The increasing stability of the polyiodides with cation size is due, at least in part, to the difference in lattice energies between lower and higher polyiodides. The enthalpy change for reaction 1, ΔH_1, is related to the lattice energies by the expression

$$\Delta H_1 = L_x - L_{x+2y} + \Delta H_{x,x+2y} \qquad (13)$$

where L_x and L_{x+2y} are the lattice energies for the lower and higher iodide, respectively

$$MI_x(s) \xrightarrow{L_x} M^+(g) + I_x^-(g) \qquad (14)$$

and $\Delta H_{x,x+2y}$ is the heat for the reaction

$$I_x^-(g) + yI_2(s) = I^-_{x+2y}(g) \qquad (15)$$

Since the lattice energy varies inversely as the interionic distance[7] d and since d_x is assumed to be smaller than $d_x + d_y$, the term $L_x - L_{x+2y}$ is expected to be positive. As is obvious from relation 13, the smaller the difference between L_x and L_{x+2y}, the more negative will ΔH_1 be since $\Delta H_{x,x+2y}$ is negative. The more negative the value of ΔH_1. the more stable the polyiodide $x + 2y$ will be (assuming $T\Delta S_1°$ is small). Compounds with large cations would be the most likely to have d_x nearly equal to d_{x+2y}[10] and have $L_x - L_{x+2y}$ small and thus form stable polyiodides. (It is also assumed that the Madelung constant is approximately equal for the two salts.[11])

Values of the lattice energies of the monoiodide and triiodide salts can be calculated by means of Kapustinskii's empirical equation.[12] With these data and eq 13 a value of $\Delta H_{x,x+2y} = \Delta H_{1,3}$ can be obtained. The Kapustinskii relation

$$L = \frac{287.2\sum nz_+z_-}{r_+ + r_-}\left[1 - \frac{0.345}{r_+ + r_-} + 0.00435(r_+ + r_-)\right] \qquad (16)$$

is the same for all crystal structures. Here Σn is the number of ions per molecule, z is the valence, and r is the effective or thermochemical ionic radius. The effective radii for simple monovalent ions can be taken equal to the crystallographic radii. If one of the radii is unknown, *e.g.*, for complex ions, it can be calculated from thermodynamic data.[13] Since the lattice energy is given by

$$L = \Delta H°_{M_+} + \Delta H°_{X_-} - \Delta H_f°(MX) \qquad (17)$$

$\Delta H°_{X-}$ (or $\Delta H°_{M+}$) can be eliminated by using two salts with a common ion, *e.g.*, MX and NX. Thus

$$\Delta L = \Delta H°_{M_+} - \Delta H_f°(MX) - \Delta H°_{N_+} + \Delta H_f°(NX) = 574.4\left[\frac{1}{r_M + r_X}\left(1 - \frac{0.345}{r_M + r_X}\right) - \frac{1}{r_N + r_X}\left(1 - \frac{0.345}{r_N + r_X}\right) + 0.00435(r_M - r_N)\right. \qquad (18)$$

and relation 18 is solved for r_X. For example, the enthalpies of formation[14] of RbI, $Rb^+(g)$, CsI, and $Cs^+(g)$ are −78.5, 118.3, −80.5, and 110.1 kcal, respectively, and the cation radii[7] are 1.48 and 1.69 Å. With these values and eq 18 an effective $r_I = 2.25$ Å (crystallographic $r = 2.19$ Å) is calculated. Inserting this effective r_I and the above r_M back into eq 16, one obtains $L_{RbI} = 149.4$ kcal/mol and $L_{CsI} = 143.4$ kcal/mol. These values are in excellent agreement with 149.8 and 143.6 kcal/mol calculated from eq 17 with $\Delta H°_{I^-(g)} = -47.0$ kcal/g-ion.[4b] In a similar procedure for RbI_3 and CsI_3, with $\Delta H_f° = -81.6$ and −84.2 kcal/mol,[2] respectively, an effective radius of 2.45 Å for I_3^- and $L_{RbI_3} = 143.7$ kcal/mol and $L_{CsI_3} = 137.7$ kcal/mol are derived. These two values are also listed in Table IV. The difference in the effective radii for I^- and I_3^-, 0.20 Å, compares very favorably with the

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(7) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1960.

(8) K. H. Stern and E. S. Amis, *Chem. Rev.*, **59**, 1 (1959), Table 23.

(9) E. E. Havinga, K. H. Boswijk, and E. H. Wiebenga, *Acta Crystallogr.*, **7**, 487 (1954).

(10) (a) For CsI, $d = 3.88$ Å, whereas for CsI_3, the average $d = 3.92$ Å: H. A. Tasman and K. H. Boswijk, *Acta Crystallogr.*, **8**, 59 (1955). (b) For NH_4I, $d = 3.62$ Å; for NH_4I_3 d of closest approach is 3.73 Å: R. C. L. Mooney, *Z. Kristallogr., Kristallgeometrie, Kristallphys., Kristallchem.*, **90**, 143 (1935).

(11) It should be noted that the only two triiodides, NH_4I_3 and CsI_3, which have been studied by X-ray techniques, have been found to be isostructural[10] and the other polyiodides were also reported to be structurally related: W. J. James, R. J. Hach, D. French, and R. E. Rundle, *Acta Crystallogr.*, **8**, 814 (1955).

(12) A. F. Kapustinskii, *Quart. Rev., Chem. Soc.*, **10**, 283 (1956).

(13) A. F. Kapustinskii and K. B. Yatsimirskii, *Zh. Obshch. Khim.*, **26**, 941 (1956).

(14) *Nat. Bur. Stand. (U. S.), Circ.*, **No. 500** (1952).

difference in interionic distance of closest approach, 0.1 Å, reported in X-ray studies.[10] Unfortunately, there is no way of judging the reliability of the lattice energy values. Since the triiodides have much more covalent character than the simple iodides and, in general, lattice energy calculations are most exact for simple ionic salts, the errors in the triiodide values may be appreciable. Due to the uncertainty in the value of $\Delta H_f°$ for $NH_4^+(g)$ and lack of data for the other iodides, no calculations were made for the other salts studied.

With the calculated lattice energies, $\Delta H_1°$ values[2] of -3.1 and -3.7 kcal for the rubidium and cesium systems, and eq 13, a value of $\Delta H_{1,3} = -9._1$ kcal is obtained for the monoiodide–triiodide reaction, eq 15. The heat of the reaction

$$I^-(g) + I_2(g) = I_3^-(g) \qquad (19)$$

with all three components in the gaseous state can be obtained by subtracting from $-9._1$ kcal the heat of sublimation of iodide and is $-24._0$ kcal (see Table IV).

In addition to the above, a $\Delta H_f°$ of $-56._4$ kcal is found for $I_3^-(g)$ from eq 17; for the reaction

$$I_3^-(g) \longrightarrow I_3^-(aq) \qquad (20)$$

the heat of hydration $\Delta H_h = \Delta H_{soln}(MI_3) - L - \Delta H_h(M^+)^{14} = 44._0$ kcal. This last value is about 10 kcal larger than ΔH_h for $I^-(aq)$, 33.8 kcal.[4b] From the Born equation[15]

$$\Delta G = \frac{Ne^2}{2r}(1 - 1/D) \simeq \Delta H \qquad (21)$$

where D is the dielectric constant of the medium and the difference in the heats of hydration is 10 kcal, the difference between the radii of the hydrated ions $I^-(aq)$ and $I_3^-(aq)$ is evaluated as about 0.3 Å or only 0.1 Å more than the calculated effective radii.

[15] M. Born, *Z. Phys.*, **1**, 45 (1920).

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Thorium Fluoride Complexes. Determination of the Stability Constants Using the Fluoride Ion Activity Electrode[1]

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Thorium(IV) in acidic media undergoes stepwise complexation with fluoride ion forming three soluble complexes, ThF_3^+, ThF_2^{2+}, ThF_3^+, and a precipitate, ThF_4. Using a titration technique and measuring the fluoride ion activity directly with a fluoride ion activity electrode, it was possible to evaluate the formation constants $^*\beta_n = [ThF_n^{4-n}][H^+]^n[Th^{4+}]^{-1}[HF]^{-n}$ for the complexes and the solubility product constant for the precipitate $^*K_{SO} = [Th^{4+}][HF]^4[H^+]^{-4}$ as $\log {}^*\beta_1 = 4.52 \pm 0.05$, $\log {}^*\beta_2 = 7.26 \pm 0.14$, $\log {}^*\beta_3 = 8.9 \pm 0.3$, and $\log {}^*K_{SO} = -15.17 \pm 0.15$. A calculation of the fraction of species present as a function of fluoride ion concentration using the value for $^*\beta_3$ indicates that the fraction of ThF_3^+ never exceeds 0.1 under the conditions investigated. Accordingly, the value for $^*\beta_3$ is at best approximate, and its elimination from the least-squares analysis of the data has almost no effect on the values of the other constants or on the standard deviations. Variation of the thorium ion concentration from 0.003 to 0.03 M indicates that polynuclear species do not play an important role. Experiments carried out at acid concentrations of 0.1 and 1.0 M show no evidence for acid–base equilibria of the thorium complexes.

Introduction

Thorium fluoride complexation has been previously investigated by several workers[3-6] using various indirect methods. Dodgen and Rollefson[3] employed the ferrous–ferric couple to determine the fluoride ion activity; Day and Stoughton[4] and Zebroski, Alter, and Heumann[5] made use of thenoyltrifluoroacetone extraction methods in their studies; and Tananaev[6] utilized both solubility and light-absorption methods to determine the stability of ThF_2^{2+} and ThF_3^+ complexes.

The development of the fluoride ion activity electrode has made possible the direct measurement of the fluoride ion activity (or concentration).[7,8] Recent studies by Mesmer and Baes[9] on beryllium fluoride complexes, by Bond and Hefter[10] on lead fluoride complexes, and by Bond and O'Donnell[11] on various 1+ and 2+ metal ions have shown the usefulness of the electrode in this type of investigation. Most recently the electrode membrane method has been employed for the study of thorium.[12]

In the present study we use the fluoride ion electrode to measure the fluoride ion activity during a titration

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[3] H. W. Dodgen and G. K. Rollefson, *J. Amer. Chem. Soc.*, **71**, 2600 (1949).

[4] R. A. Day, Jr., and R. W. Stoughton, *ibid.*, **72**, 5662 (1950).

[5] E. L. Zebroski, H. W. Alter, and F. K. Heumann, *ibid.*, **73**, 5646 (1951).

[6] I. V. Tananaev and L. Chzhao-Da, *J. Inorg. Chem.* (*USSR*), **4**, 961 (1959).

[7] M. S. Frant and J. W. Ross, Jr., *Science*, **154**, 1553 (1966).

[8] K. Srinivasan and G. A. Rechnitz, *Anal. Chem.*, **40**, 509 (1968).

[9] R. E. Mesmer and C. F. Baes, Jr., *Inorg. Chem.*, **8**, 618 (1969).

[10] A. M. Bond and G. Hefter, *ibid.*, **9**, 1021 (1970).

[11] A. M. Bond and T. A. O'Donnell, *J. Electroanal. Chem.*, **26**, 137 (1970).

[12] B. Noren, Thesis, University of Lund, Sweden, 1969; *Nucl. Sci. Abstr.*, **24**, 2051 (1970).