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Authors

Fuger, J.
Cunningham, B.B.

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Berkeley, California

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MICROCALORIMETRIC DETERMINATION OF THE ENTHALPY OF FORMATION OF THE COMPLEX IONS OF TRIVALENT PLUTONIUM, AMERICIUM AND LANTHANUM WITH EDTA *

J. Fuger† and B. B. Cunningham

Department of Chemistry and Lawrence Radiation Laboratory
University of California
Berkeley, California

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ABSTRACT

The heats of solution of anhydrous plutonium, americium and lanthanum trichlorides have been measured in solutions of EDTA (H_4Y) at a carefully chosen pH, and in inorganic solutions of the same ionic strength. From these data we have calculated the enthalpy change for the reaction:

$$MeCl_{3\,(c)} + 2HY^{3-}_{(aq)} \longrightarrow MeY^{-}_{(aq)} + H_2Y^{2-}_{(aq)} + 3Cl^{-}_{(aq)}$$

Using auxiliary data the thermodynamic quantities $\Delta H°$, $\Delta F°$, and $\Delta S°$ associated with the chelation are reported for 25°C and $\mu = 0.1$ and the results with actinides chelates are compared with literature values for the corresponding lanthanides.

INTRODUCTION

Quantitative data on actinide element complex species are relatively rare and often limited to stability constants determinations. No direct calorimetric measurement of the enthalpy of complexing have been published. In the present paper, we report such direct measurements for the complexing of Pu^{+3} and Am^{+3} with EDTA. We also report data on La^{+3} complexing for purposes of comparison.

From the enthalpy change and the formation constants (K_c) of the chelates, the entropy variation on complexing can be calculated:

$$\Delta F = - RT \ln K_c = \Delta H - T\Delta S$$

A number of thermodynamic studies of various EDTA complexes have been reported in the literature. From e.m.f. measurements at various temperatures, Carini and Martell(1) obtained thermodynamic data on alkaline earth chelates. Charles(2) made direct calorimetric determinations of the enthalpy of chelation of a number of mono- and divalent ions. Later, Staveley and Randall(3) made a similar study including 3 lanthanides. Using radioactive tracers, Betts and Dahlinger(4) investigated the temperature dependence of the chelation equilibrium of all the lanthanides except prometheum. While our work was in progress Mackey, Powell and Spedding(5) published their calorimetric data on all the lanthanides. More recently the calorimetric results of Anderegg,(6) on the complexing with EDTA and DCTA of various divalent ions and of lanthanum have appeared in the literature.

Large discrepancies exist between the results of direct measurements and those obtained from temperature dependence measurements. Because of the limited temperature range available, the latter are very sensitive to small experimental errors. Even direct enthalpy measurements by various investigators are hard to compare because of the diversity of experimental conditions and because of discrepancies in the auxiliary thermodynamic data used for the calculations. Within small variation two different methods have been used for the direct determination of the enthalpy of complexing with EDTA:

a) addition of a solution containing the cation studied to a solution of the tetrasodium or potassium salt of EDTA, in slight stoichiometric excess. A neutral salt (KNO_3, KCl) is used to maintain a constant ionic strength. This method requires a precise measurement of the initial and final pH of the solution in order to allow a correct evaluation of the reactions.

b) addition of a solution containing the cation studied to a solution of a neutral chelate of EDTA, also at constant ionic strength. Mackey, Powell and Spedding(5) who developed this method used the Mg^{++} chelate, which is much less stable(7) than the lanthanide chelates.

Method b) has the great advantage of being independent of pH measurements and hence allows a more direct comparison of the results with various cations.

For reasons that we shall give later, the method used by us is somewhat different. We have measured the heats of dissolution of crystalline anhydrous trichlorides in dilute solutions of EDTA at a fixed pH value, and compared these data with the heats of dissolution of the same chlorides in solutions of similar ionic strength, without EDTA. Under the experimental conditions, the equation:

$$MeCl_{3(c)} + 2HY^{3-}_{(aq)} \longrightarrow MeY^{-}_{(aq)} + 3Cl^{-}_{(aq)} + H_2Y^{--}_{(aq)} \quad \Delta H_1 \qquad (1)$$

unambiguously describes the reaction to better than 99.8%. From the known acid dissociation constants of EDTA(8,9) it may be shown by calculation that this condition is fulfilled when the pH of the EDTA solution remains between

7,4 and 6,6. Of course, the EDTA must be in large excess with respect to the cation concentration.

If we call ΔH_2 the heat of dissolution of the trichloride in a non complexing but otherwise identical medium;

$$MeCl_{3(c)} \longrightarrow Me^{3+}_{(aq)} + 3Cl^{-}_{(aq)} \quad \Delta H_2 \qquad (2)$$

and if we use the heats of the third and fourth dissociations of EDTA,

$$H_2Y^{2-}_{(aq)} \longrightarrow H^{+}_{(aq)} + HY^{3-}_{(aq)} \quad \Delta H_3 \qquad (3)$$

$$HY^{3-}_{(aq)} \longrightarrow H^{+}_{(aq)} + Y^{4-}_{(aq)} \quad \Delta H_4 \qquad (4)$$

the heat of complexing

$$Me^{3+}_{(aq)} + Y^{4-}_{(aq)} \longrightarrow MeY^{-}_{(aq)} \quad \Delta H_5 \qquad (5)$$

is easily calculated:

$$\Delta H_5 = \Delta H_1 - \Delta H_2 + \Delta H_3 - \Delta H_4 \qquad (6)$$

The method outlined above was chosen for two reasons: 1) it is easier to handle small crystals of the trichlorides (even though they are hygroscopic), than to prepare, and handle small volumes of solutions of these highly radioactive species; 2) due to its alpha activity, plutonium cannot be kept in a solely +3 state (in dilute acid solutions) for periods exceeding a few hours; moreover the oxygen formed by the radiolysis of water and accumulated in such solutions would immediately oxidize the plutonium in the chelate at the time of the reaction.

EXPERIMENTAL

A. Materials

Anhydrous trichlorides.

We have described elsewhere(10) the techniques for purification of the trichloride solutions: the obtaining of gram quantities of anhydrous single crystals by gradient solidification from the melt; and the preparation (handling and weighing) under dry nitrogen of the samples for calorimetry. Samples between 2 and 8 mg have been used.

100 μg samples showed no impurity when analyzed by the copper spark method (for sensitivity of the technique see ref (10)) in $PuCl_3$ and $AmCl_3$, while similar amount of 2 different batches of $LaCl_3$ showed 0.01 μg Mg and 0.03 μg Ca as the only impurities.

Reagents and solutions.

All inorganic reagents were of analytical grade. The EDTA was a Fisher Certified Reagent. It was further purified by recrystallization from hot water, in quartz vessels.

After drying in vacuum over P_2O_5, it was analyzed spectrographically. The only impurity detected was 2 p.p.m. of Na. Moreover, acidimetric and complexometric titrations (Mg^{2+}) showed that the composition of the reagent corresponded to the expected formula within the accuracy of these methods (± 0.3%). The EDTA solutions used were 2.5×10^{-2}M, neutralized at pH 7.27 with a KOH solution (0.9M) and made 0.1M in K^+ by adding KCl. For such a solution $\mu = 0.17$. Calculation shows that, when dissolving the trichlorides in the EDTA solution the ionic strength should decrease by a maximum of 0.02 units.

We have taken $\mu = 0.16$ as the mean ionic strength to report our results. The large (seven fold or greater) excess of EDTA holds the pH of the chelate solution within the required limits for the observation of the particular reaction corresponding to ΔH_1 given above. All the solutions used were prepared with de-aerated water in an argon atmosphere and kept in argon. Particular care was taken to prepare CO_2-free KOH solutions. As a routine measure, at the time of use the EDTA solution was again de-aerated with argon and the calorimeter was assembled in a gloved box which had been flushed with pure argon for several hours. Mass analysis of the atmosphere of the box at the time of loading indicated the oxygen content to be less than 0.02 vol %. This is important when studying the plutonium chelate because the +3 complex of plutonium (blue) is very sensitive to oxidation and is almost instantly oxidized to +4 (pink) by traces of oxygen. This is easily understandable if we consider that the +4 complex is of the order of 10^6 times more stable(11) than the +3 complex. The oxidation potential of the Pu^{+3}-Pu^{+4} couple is thereby made substantially more positive. The absence of Pu^{+4} complex in the calorimeter solutions was systematically checked using a Cary Model 14 Recording spectrophotometer. To do this, the calorimeter was disassembled and the cells loaded in an argon atmosphere. Within the limits of detection ($\leq$ 0.5%) no Pu^{+4} was found.

B. The calorimeter

The semi-adiabatic calorimeter used has been described(12,13) and recent modifications and improvements will be detailed elsewhere.(14)

Its heat capacity, when containing 8 ml of solution is about 9 calories per degree. The temperature sensitivity is approximately 1×10^{-5}C. Due to radioactive heating, stirring, and power input to the bridge the steady state temperature was from 0.1 to 0.3 C. higher than the temperature (25.03 C.) of the external bath. Methods of calculations and corrections used have been described.(10)

C. Units and limits of errors

In our thermochemical calculations we have taken the calorie to be equal to 4.1840 absolute joules.

The limits of error quoted for our experimental data are for the 95 per cent confidence interval, but we have not attempted to retain this limit when combining our data with that from other sources, for which we take the error to be that stated by the author.

The heat measurements reported here were made at temperatures a few tenths of a degree above 298.16°K, but within their limits of error they are not distinguishable from 298.16°K values. Hence, we have treated them as such. On the basis of mass analysis data we calculate 239.11 and 241.07 respectively, for the atomic weights of the plutonium and americium stocks used.

RESULTS AND DISCUSSION

Table 1 tabulates the experimentally observed heats of dissolution of the trichlorides into EDTA solutions (ΔH_1) and summarizes the experimental conditions.

As seen in table 1, the EDTA is always in large excess with respect to the cation studied and it can be calculated that conditions for reaction (1) are largely met in every case.

We have reported(10) the heat of dissolution of $PuCl_3$ in dilute $HClO_4$ ($\mu = 0.1$) and of $AmCl_3$ in various HCl concentrations. Our data on $PuCl_3$ agree very well with those of Westrum and Robinson(15) in dilute HCl (0.1M). The heat of dissolution of $LaCl_3$ in various concentrations of HCl has been measured by Spedding and Flynn.(16) Interpolation of the existing data will give without any appreciable error the heat of dissolution at $\mu = 0.16$. We therefore obtain, for $PuCl_3$, -31.65 ± 0.2; for $AmCl_3$, -33.05 ± 0.2; for $LaCl_3$, -32.65 ± 0.1 kcal. mole^{-1}, respectively. We shall use those values as ΔH_2 in our calculations.

The heats of the third and fourth dissociations of EDTA have been determined by Carini and Martell(17) from e.m.f. data at various temperatures. Recently Anderegg(6) measured these heats directly at $\mu = 0.1$ (KNO_3); a discrepancy of about 1 kcal/mole^{-1} exists between the two sets of data; we shall use the values of Anderegg: +4.34 and +5.65 kcal.mole^{-1}, respectively, neglecting in the calculations the heat of dilution of those species between $\mu = 0.1$ and $\mu = 0.16$.

Using the preceding data and also the existing formation constants for the chelates, the thermodynamic quantities for the formation of the complexes can be calculated. They are summarized in table 2. The K_c values have been obtained at $\mu = 0.1$; therefore in reporting the data, differences in ΔH between $\mu = 0.1$ and $\mu = 0.16$ will be neglected.

The data in table 2 show that the increase in entropy is the predominant factor responsible for the stability of the chelates, as has been found to be true for other EDTA chelates. Little more can be concluded from the magnitude of the entropy change because of the limited number of chelates investigated in the present study. If we compare our results on lanthanum with those of Mackey and co-workers,(5) we observe that a discrepancy of about 1.8 kcal. mole^{-1} exists. Differences in the auxiliary data used can account for deviations amounting to 0.5 kcal. mole^{-1}. On the other hand, if we compare plutonium and americium with the lanthanides having approximately the same ionic radii (praseodymium and neodymium), we note that the enthalpy change for the actinides is more negative by somewhat more than 1 kcal. mole^{-1}. If we attribute the disagreement between our data and those of Mackey and co-workers for lanthanum to a systematic error, application of the correction leads to an increased difference between the actinides studied and the lanthanides. We observe also that the stability constants of the Pu^{+3} and Am^{+3} chelates are about 10 times greater than those of the lanthanides(7) of similar ionic radii (Pr^{+3}, $\log_{10}K_c = 16.80$; Nd^{+3}, $\log 10K_c = 17.01$, after making the noted correction in table 2) and indeed the elution behavior(19) of mixtures of actinides and lanthanides in the presence of EDTA leads to the same conclusion. Therefore the increased stability of the actinide complexes is due mainly to a larger enthalpic term.

We believe it unlikely that structural differences exist between the complexes of the actinides studied and those of the corresponding lanthanides. Differences in stability must be due to other contributing factors in the interaction between the central ion and the ligands. Thermodynamic data on complexes of other trivalent actinides as well as studies using homologous chelating agents would no doubt be helpful in understanding the origin of the difference.

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FOOTNOTES AND REFERENCES

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Table 1. HEATS OF DISSOLUTION OF TRICHLORIDES INTO EDTA SOLUTIONS AT 298.3 ± 0.20 K (ΔH_1) EDTA 2.5×10^{-2}M, pH 7.27, 0.1M K^+ (KCl).

Sample	Weight of sample (mg)	Molarity of chelate	Heat evolved (cal.)	Final pH of solut.	ΔH_1 (kcal. mole^{-1})
$PuCl_3$	4.406 ± 0.005	1.594×10^{-3}	0.4389		-34.42
	2.610 ± 0.004	0.944×10^{-3}	0.2609		-34.54
	3.961 ± 0.004	1.433×10^{-3}	0.3964		-34.56
	4.066 ± 0.006	1.471×10^{-3}	0.4083		-34.69
					-34.55 ± 0.15
$AmCl_3$	5.069 ± 0.004	1.824×10^{-3}	0.5316		-36.44
	7.289 ± 0.006	2.622×10^{-3}	0.7643		-36.31
	7.606 ± 0.006	2.763×10^{-3}	0.7949		-36.31
					-36.39 ± 0.15
$LaCl_3$(a)	5.868 ± 0.004	2.990×10^{-3}	0.7779	6.74	-32.52
$LaCl_3$(b)	6.777 ± 0.005	3.454×10^{-3}	0.8946	6.68	-32.38
$LaCl_3$(b)	5.379 ± 0.004	2.741×10^{-3}	0.7140	6.80	-32.56
					-32.49 ± 0.15

[a,b] 2 different batches of $LaCl_3$

Table 2. THERMODYNAMIC QUANTITIES FOR THE FORMATION OF THE CHELATES WITH EDTA AT 25°C AND μ = 0.1.

Species	$\Delta H°$ (kcal. mole^{-1})	$\log_{10} K_c$	$\Delta F°$ (kcal. mole^{-1})	$\Delta S°$ (cal. mole^{-1}.°C^{-1})
PuY^-	-4.23 ± 0.25	18.07$^{(a)}$	-24.67	67.8 ± 2
AmY^-	-4.67 ± 0.25	18.16$^{(b)}$	-24.79	67.4 ± 2
LaY^-	-1.15 ± 0.20	15.88$^{(c)}$	-21.66	67.4 ± 2

[a] value from reference (2), corrected from 20°C to 25°C using the relation

$$\frac{d\ \ln K_c}{dT} = \frac{\Delta H}{RT^2}$$

[b] value from reference (18)

[c] value from reference (7) corrected from 20°C to 25°C and recalculated using Cabell's(9) dissociation constants for EDTA instead of Schwarzenbach's(8) in order to normalize K_c as well as possible. We have noted previously(18) that the two sets of EDTA dissociation constants lead to a discrepancy of about 0.4 in $\log_{10} K_c$ in the pH range considered.

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