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Complexes of Plutonium(III) with Acetate

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The complexity of the plutonium(III)-acetate system has been determined by means of potentiometric [H^+] measurements and a spectrophotometric check on the real oxidation state of the plutonium. A perchlorate medium of ionic strength $I=2$ M was used at 20°C.

Introduction

The literature on the coordination chemistry of plutonium in its various oxidation states is not extensive, and is often of a qualitative nature only.[1,2,3] One of the more interesting reasons for acquiring more quantitative data on the formation of complexes of plutonium, and of the actinides in general, is the possibility of comparison with the behaviour of the rare earths with a view to the idea that the 5f orbitals of the actinide elements might be more available for interaction with ligands than the 4f orbitals of the rare earths are. For a direct comparison, it would be useful to have data relating to the tervalent actinide elements.

A study of the formation of complexes of plutonium(III) with acetate in aqueous solution has been reported; this was carried out by means of a cation-exchange resin, using trace amounts of plutonium.[4] These authors give values for the stability constants of the complexes $Pu(Ac)_n^{3-n}$ ($n=1,2,3,4$) that appear surprisingly high when compared with those of analogous complexes of the rare earths.[5,6] It is very likely that the experimental methods adopted in this work were not suitable for obtaining reliable data.[7] Even if Pu^{III} is stable in aqueous solutions of perchloric and other inorganic acids, there is always the possibility that a more or less rapid oxidation of the Pu^{III} may occur if ligands that have a strong tendency to coordinate to Pu^{IV} are present, or if the solution is only slightly acid.

Taking this into consideration, we have studied the formation of plutonium(III)-acetate complexes in aqueous solution, determining the concentration of the free ligand by means of potentiometric [H^+] measurements. By using relatively concentrated solutions of plutonium, a spectrophotometric check on its real oxidation state was possible.

All measurements were made at a temperature of 20±0.1°C and in a perchlorate medium of ionic strength $I=2M$.

Experimental Section

Chemicals. Solutions containing known concentrations of Pu^{III}, $HClO_4$ and $NaClO_4$ ($I=2M$) were prepared as follows. A solution of Pu^{IV} (isotopic composition: ~99% ^{239}Pu and 1% ^{240}Pu) in approximately $1M$ HNO_3 was treated with SO_2 gas until there was total reduction of the Pu^{IV}. The Pu^{III} obtained was precipitated as hydroxide by addition of ammonia solution. The precipitate, after washing with water, was dissolved in $HClO_4$ (0.2 M) using slightly more than the volume required for complete dissolution. This solution was transferred to the cathode compartment of an electrolytic cell similar to one described previously.[8] An applied potential of about 1.5 volts rapidly yielded all the plutonium in the tervalent state.[8] This reduction was necessary because, in the precipitation and washing procedure described above, we have observed that partial oxidation of the Pu^{III} can occur.

The concentration of plutonium in solution as Pu^{III} was determined by potentiometric titration of a defined volume (1 ml, containing 10 to 13 mg Pu) with Ce^{IV} solution.[9]

The concentration of free perchloric acid in the plutonium solution was determined by passing a defined volume of the solution through the hydrogen ion form of the cation-exchange resin Dowex 50W-X4. The eluate was titrated with standard NaOH. If a total concentration of acid $[H^+]_t$ is found, then the original $[H^+]=[H^+]_t-3[Pu^{III}]$.

Using standard solutions of NaOH and $NaClO_4$, the solutions containing Pu^{III}, $HClO_4$ and $NaClO_4$ were eventually adjusted to the concentrations required for the measurements. The concentration of the stock solution of $NaClO_4$ (twice recrystallized) was checked by means of a cation-exchange column.

All chemicals used were of analytical grade.

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(1) J. J. Katz and G. T. Seaborg, «The Chemistry of the Actinide Elements», Methuen, London (1957).
(2) A. D. Gel'man, A. I. Moskvin, L. M. Zaitsev, M. P. Mefod'eva, «Complex Compounds of Transuranium Elements», Consultants Bureau, New York (1962).
(3) M. Taube, «Plutonium», Pergamon Press (1964).
(4) A. I. Moskvin, V. P. Zaitseva, and A. D. Gel'man, *Radiokhimiya*, *6*, 214 (1964).
(5) A. Sonesson, *Acta Chem. Scand.*, *12*, 165 (1958).
(6) A. Sonesson, *Acta Chem. Scand.*, *12*, 1937 (1958).
(7) G. N. Yakovlev and N. A. Lebedev, *Radiokhimiya*, *7*, 633 (1965).
(8) D. Cohen, *J. Inorg. Nucl. Chem.*, *18*, 207 (1961).
(9) I. M. Kolthoff and Ph. J. Elving, «Treatise on Analytical Chemistry», Part II, Vol. 9, Interscience Publ. (1962).

Measurements. The hydrogen ion concentration of the solutions was determined using the cell:

$$\mathrm{Ag}\;\Big|\;\mathrm{AgCl}\;\Big|\;\begin{array}{l}50\ \mathrm{m}M\ \mathrm{NaCl}\\ 1950\ \mathrm{m}M\ \mathrm{NaClO_4}\end{array}\;\Big\|\;\begin{array}{l}2.0\ M\\ \mathrm{NaClO_4}\end{array}\;\Big\|\;\begin{array}{l}C_M\ \mathrm{m}M\ \mathrm{Pu(ClO_4)_3}\\ C_H\ \mathrm{m}M\ \mathrm{HClO_4}\\ C_A\ \mathrm{m}M\ \mathrm{NaAc}\\ \mathrm{NaClO_4}\ (I=2\ M)\end{array}\;\Big|\;\text{glass electrode}\qquad(1)$$

The reference electrode and the bridge were of the «Wilhelm» type.[10] The silver-silver chloride electrode was of the thermal-electrolytic type.[11] The behaviour of the glass electrode was checked in the range with $NaClO_4$), usually both before and after a series of measurements. The e.m.f. is described by the equation $E=E^\circ+58.16\log[H^+]-0.033[H^+]$, (E in mV and $[H^+]$ in m*M*).

Cell potentials were read using a Leeds and Northrup k-5 potentiometer with a Cary 31-V electrometer as null point indicator. All the apparatus was contained in an oil bath thermostat maintained at 20±0.1°C.

The titrations of Pu^{III} solutions were made by adding, from a microburette, aliquots of a solution 0.5 *M* in NaAc ($I=2\ M$ with $NaClO_4$) to a known volume of the original solution (usually 7 ml). Equilibria were rapidly reached by bubbling through N_2, purified and presaturated with $NaClO_4$ (2 *M*) solution.

Under the same conditions, titrations have been done in the absence of Pu^{III}, with the aim of determining the K_c value of acetic acid.

The original solutions of Pu^{III} were examined spectrophotometrically before each titration, in order to check the absence of appreciable concentrations of plutonium in other oxidation states. The same control was made on the final solutions of the titrations. Preliminary spectrophotometric measurements were made in solutions of Pu^{III} in the presence of sodium acetate at different concentrations and pH-values, to ascertain the conditions under which plutonium is sufficiently stable in the tervalent state.

The titrations and the other operations with plutonium were performed in a well ventilated fume hood.

Treatment of Data. The following notation is used:

C_H = the total concentration of $HClO_4$;
C_M = the total concentration of Pu^{III};
C_A = the total concentration of NaAc.

Let us consider the possible equilibria and the relevant constants, assuming that merely mononuclear complexes exist, ($M=Pu^{III}$; $A=Ac^-$):

$$HA \rightleftarrows H^+ + A\,; \qquad K_c \qquad (2)$$

$$M + nA \rightleftarrows MA_n\,; \qquad \beta_n \qquad (3)$$

$$M + qHA \rightleftarrows M(HA)_q\,; \qquad \eta_q \qquad (4)$$

It must be that:

$$C_H = [H^+] + [HA] + \sum_{q=1}^{Q} q[M(HA)_q] \qquad (5)$$

The average number of ligands for each Pu^{III} is given by:

$$\bar{n} = \frac{C_A - [HA] - [A]}{C_M} \qquad (6)$$

If we neglect equilibrium (4) relating to the formation of complexes with the non-protolysed acid, from (5) we get:

$$[HA] = C_H - [H^+] \qquad (7)$$

$$\bar{n} = \frac{C_A + [H^+] - C_H - [A]}{C_M} \qquad (8)$$

Combination of equations (2) and (7) gives:

$$[A] = K_c \times \frac{C_H}{[H^+]} - 1 \qquad (9)$$

This allows us, knowing K_c, to determine the concentration of free ligand corresponding to the various experimental values of $[H^+]$, and therefore to determine $\bar{n}$ from (8). The $\bar{n}$ value so determined is a function of [A] and independent of C_M only if there is no appreciable formation of complexes with non-protolysed acid nor of polynuclear complexes.[10] For the calculation of the constants β_n, the Fronaeus method is adopted.

We can define the function:

$$X([A]) = 1 + \sum_{n=1}^{N} \beta_n [A]^n \qquad (10)$$

Then:

$$\frac{\bar{n}}{[A]} = \frac{\dfrac{dX([A])}{d[A]}}{X([A])} \qquad (11)$$

and integrating:

$$\ln X([A]) = \int_0^{[A]} \frac{\bar{n}}{[A]}\, d[A] \qquad (12)$$

For the graphical integration of the function $\dfrac{\bar{n}}{[A]} = f[A]$ we obtain the corresponding values of X([A]) and [A].

The stability constants β_n can be determined by extrapolation to $[A]=0$ of the functions defined by the equation:

$$X_j = \frac{X_{j-1} - \beta_{j-1}}{[A]} \qquad (13)$$

where $j=1, 2, 3, \ldots$; $X_0 = X$; $\beta_0 = 1$.

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(10) F. J. C. Rossotti and H. Rossotti, «The Determination of Stability Constants», McGraw-Hill Book Co., New York (1961).
(11) D. J. G. Ives and G. J. Janz, «Reference Electrodes, Theory and Practice», Academic Press, New York and London (1961).

Results and Discussion

The preliminary spectrophotometric measurements on Pu^{III} solutions containing NaAc at different pH values showed that Pu^{III} tends to oxidise to Pu^{IV}, in agreement with the observations of other authors.[12] The rate of oxidation increases with increasing acetate concentration and increasing pH. This is clearly in good agreement with the greater tendency of Pu^{IV} both to form complexes with Ac$^-$ and to give hydrolysis products. The presence of a reductant such as hydrazine does not prevent the oxidation in acetate solution. The conditions for the potentiometric titrations were fixed within limits of pH and acetate concentration indicated by the spectrophotometric measurements, such as to yield data that definitely refer to the formation of complexes of Pu^{III}. This has been achieved by spectrophotometric checks on the solutions before and after the titrations.

In Figure 1 the spectra relating to the solution used in titration (2nd) are shown; the spectrum (b), taken after adding acetate, shows that there is no appreciable quantity of Pu^{IV} present.

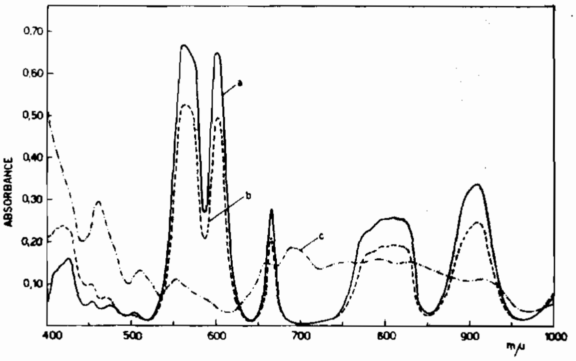

Figure 1. Absorbance curves for (a) solution of Pu^{III} before titration (2nd), (b) solution of Pu^{III} after adding acetate, (c) solution of Pu^{IV} (6.7 mM) and acetate (200 mM) at pH 3.7.

In Table I are reported the data relating to a titration for the determination of the dissociation constant of acetic acid in solution at $I = 2M$ and 20°C. For the suceeding calculations, the average value $K_c = 1.58 \times 10^{-5}$ was taken.

Table I. Determination of dissociation constant of acetic acid

C_A mM	C_H mM	E mV	[H$^+$] mM	[A] mM	$K_c \times 10^5$
0	11.78	+ 56.2	11.78	0	—
30.53	11.06	−124.7	9.02×10^{-3}	19.49	1.591
37.59	10.89	132.9	6.50	26.71	1.596
44.44	10.73	139.6	5.01	33.72	1.574
51.10	10.57	114.4	4.12	40.53	1.580
57.55	10.42	148.7	3.47	47.14	1.572
63.83	10.27	152.4	3.00	53.56	1.565
69.93	10.13	155.4	2.66	59.80	1.574

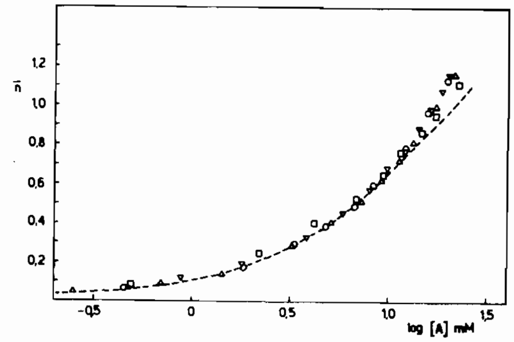

Figure 2. The complex formation curve of the Plutonium(III)-acetate system. The symbols relate to Table II.

Table II. Determination of corresponding values of $\bar{n}$ and [A]

C_M mM	C_H mM	C_A mM	E mV	[H$^+$] mM	[A] mM	$\bar{n}$
1st (○)						
26.00	11.87	0	+56.7	11.87	0	—
25.31	11.55	13.27	−29.6	38.9×10^{-2}	0.45	0.06
25.09	11.45	17.54	64.6	9.74	1.84	0.17
24.87	11.35	21.74	79.4	5.40	3.30	0.29
24.65	11.25	25.86	89.9	3.58	4.95	0.39
24.44	11.16	29.91	97.8	2.62	6.76	0.49
24.24	11.06	33.90	103.7	2.07	8.42	0.60
23.83	10.79	41.58	113.4	1.41	12.2	0.78
23.44	10.61	49.18	120.6	1.06	15.8	0.97
23.06	10.44	56.46	126.7	0.83	19.8	1.13
2nd (△)						
17.10	21.95	0	+71.5	21.95	0	—
15.73	20.19	20.00	− 1.4	1.19	0.25	0.05
15.61	20.03	21.82	27.1	42.99×10^{-2}	0.72	0.09
15.48	19.90	23.62	45.5	20.75	1.45	0.14
15.24	19.57	27.13	65.6	9.36	3.28	0.29
15.01	19.27	30.53	77.6	5.82	5.21	0.41
14.79	18.98	33.83	86.5	4.09	7.31	0.51
14.57	18.70	37.04	92.9	3.18	9.28	0.62
14.35	18.42	40.14	98.3	2.56	11.3	0.73
14.15	18.16	43.17	102.8	2.15	13.3	0.81
13.75	17.65	48.95	110.4	1.59	17.5	1.00
13.38	17.17	54.42	116.5	1.25	21.7	1.16
3rd (□)						
13.00	20.85	0	+70.2	20.85	0	—
12.45	19.97	20.96	−18.4	60.67×10^{-2}	0.49	0.08
12.35	19.81	25.00	56.2	13.58	2.29	0.25
12.25	19.64	28.92	72.1	7.24	4.27	0.42
12.15	19.48	32.79	84.6	4.41	6.96	0.52
12.05	19.32	36.58	92.7	3.20	9.52	0.64
11.95	19.17	40.32	98.9	2.50	12.07	0.76
11.86	19.01	44.00	104.2	2.03	14.8	0.86
11.76	18.86	47.62	108.7	1.70	17.5	0.96
11.58	18.57	54.69	116.2	1.26	23.2	1.11
4th (▽)						
8.70	13.85	0	+60.1	13.85	0	—
8.19	13.03	14.71	−43.2	22.72×10^{-2}	0.89	0.12
8.13	12.95	16.23	61.0	11.23	1.81	0.19
8.03	12.78	19.23	80.3	5.23	3.84	0.33
7.93	12.62	22.15	91.6	3.34	5.95	0.46
7.83	12.46	25.00	99.6	2.44	8.06	0.57
7.73	12.31	27.78	105.8	1.91	10.2	0.68
7.64	12.16	30.49	111.1	1.55	12.4	0.78
7.55	12.01	33.13	115.3	1.31	14.5	0.88
7.46	11.87	35.71	118.9	1.13	16.5	0.98
7.37	11.73	38.23	122.1	1.00	18.5	1.08
7.28	11.59	40.70	125.1	0.89	20.6	1.16

(12) Von E. Nebel and K. Schwabe, *Z. Phys. Chem.*, *224*, 29 (1963).

(13) I. Grenthe, *Acta Chem. Scand.*, *16*, 1695 (1962).

In Table II are reported the data relating to the four titrations with solutions containing Pu^{III}. The $\bar{n}$ values are reported as a function of log[A] in Figure 2. As can be seen, the limited interval of acetate concentration within which the system has been examined allows us to follow the formation of successive complexes up to a maximum value for $\bar{n}$ of about 1.2. Within these limits, the data relating to the four different initial concentrations of Pu^{III} show that $\bar{n}$ is, to a good approximation, only a function of the concentration of the free ligand, and is independent of that of the metal cation. This allows us to exclude any appreciable formation of polynuclear complexes or of complexes with non-protolysed acid.

Applying the relations (12) and (13), the value of the formation constant β_1 has been determined. The data relating to the calculation are reported in Table III. An approximate value of the constant β_2 was determined from the slope of the curve relative to the function X_1, since the data are insufficient for an accurate extrapolation of the function X_2.

The values obtained for the constants are:

$$\beta_1 = 105 \pm 4\ M^{-1};\quad \beta_2 = 2200 \pm 250\ M^{-2}$$

From these values some points on the dashed curve in Figure 2 have been calculated. The deviation from the experimental points for the higher values of log[A] may be due to the equilibrium formation of a third complex, and/or to the oxidation of a small amount of Pu^{III}.

As for the eventual hydrolysis of the metal cation, it may be neglected in the pH range examined by us, if we accept the reported order of magnitude[1] for the first hydrolysis constant of Pu^{III} in perchloric acid ($K_h = 7.5 \times 10^{-8}$).

For comparison, the values of our constants, together with those reported in the literature for the complexes of Pu^{III}, Sm^{III}, and $Am^{III}$with acetate ion, are reported in Table IV.

The cation Sm^{3+} has the same outer electronic structure as Pu^{3+}, apart from the principal quantum number. As can be seen, the values of the first two formation constants for the acetate complexes of these two cations are, under the same conditions of ionic strength and temperature, very close.

A comparison between the constants for Pu^{III} and Am^{III} (taken from different ionic strength solutions) seems to indicate a close analogy in the behaviour of the two consecutive actinide elements towards acetate ion.

With regard to the large discrepancy between our data and that reported elsewhere[4] for the Pu^{III}-acetate system, it must be observed that the latter were obtained using experimental conditions under which the Pu^{III} could undergo oxidation.

We feel that, in research on plutonium solutions, the necessity of effectively controlling the oxidation state of the metal cation must be stressed.

Table III. The functions X and X_1 for the plutonium(III)-acetate system

|A| m*M*	X	X_1
0	1	*105*
2	1.219	109.3
3	1.334	111.2
4	1.453	113.1
5	1.575	115.1
6	1.702	117.0
7	1.833	119.0
8	1.968	121.0
9	2.108	123.1
10	2.254	125.4
13	2.729	133.0
17	3.464	144.9
21	4.328	158.5

Table IV. The formation constants β_n for the acetate system of plutonium, samarium and americium

Cation	$\beta_1\ M^{-1}$	$\beta_2\ M^{-2}$	$\beta_3\ M^{-3}$	$\beta_4\ M^{-4}$	Ionic strength Temperature	Ref.
Pu^{III}	105 ± 4	$(2.2 \pm 0.25) \times 10^3$	—	—	2.0 *M*; 20°C	this work
	3.0×10^4	1.3×10^8	4.0×10^{12}	2.6×10^{16}	1.0 *M*; 20°C	(4)
Sm^{III}	103 ± 3	$(1.81 \pm 0.18) \times 10^3$	$(7.1 \pm 1.2) \times 10^3$	$\sim 7 \times 10^3$	2.0 *M*; 20°C	(6)
Am^{III}	98.5 ± 3	$(1.9 \pm 0.2) \times 10^3$	$(8 \pm 3) \times 10^3$	—	0.5 *M*; 20°C	(13)