

Complexes of Plutonyl Ion with Acetate

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The complex formation between plutonyl and acetate ion has been investigated by means of potentiometric $[H^+]$ measurements. The values of the complexity constants of the three mononuclear complexes have been determined in perchlorate medium of ionic strength $I=1M$ at $20^\circ C$.

Introduction

An interesting approach to deepening our knowledge of the chemical behaviour of the hexapositive actinide elements in relation to their electronic structure, would be to compare the coordination chemistry of the three cations UO_2^{2+} , NpO_2^{2+} , and PuO_2^{2+} .

While much information is already available on the formation in aqueous solution of complexes of the uranyl ion with ligands of varied nature, data on the behaviour of the plutonyl and neptunyl ions are insufficient and often inaccurate (see references (1), (2), and (3)).

We report here some research on the formation in aqueous solution of plutonyl-acetate complexes which was carried out by determining the concentration of the free ligand from pH measurements. All measurements were made at a temperature of $20^\circ C$ and in a perchlorate medium of ionic strength $I=1M$, to make the data comparable with those of uranyl-acetate complexes already studied under the same conditions.⁴

Experimental Section

Chemicals Used. Solutions containing known concentrations of PuO_2^{2+} , $HClO_4$ and $NaClO_4$ ($I=1M$) were prepared in the following way. A solution containing Pu^{IV} (isotopic composition: $\sim 99\%$ ^{239}Pu and 1% ^{240}Pu) in HNO_3 (about $1M$) was treated with SO_2 until total reduction of the Pu^{IV} had been effected.

The Pu^{III} formed was precipitated as hydroxide by addition of ammonia solution. The precipitate, after washing, was dissolved in $HClO_4$ (about $0.2M$) using slightly more than the volume necessary for complete

dissolution. The solution was transferred to the anode compartment of an electrolytic cell (electrodes of platinum wire; cathode and anode compartments separated by fine sintered glass discs; magnetic agitator in the anode compartment).

With an applied potential of 4-5 volts, all the plutonium can be obtained in a short time as PuO_2^{2+} .

The degree of oxidation was checked spectrophotometrically every time.

The concentration of plutonium in solution was determined by amperometric titration of a separated aliquot of the PuO_2^{2+} solution (1 or 2 ml) with Fe^{II} solution.⁵

The concentration of free perchloric acid in the plutonium solution was determined by passing a definite 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 $[H^+] = [H^+]_t - 2[PuO_2^{2+}]$.

Using standard solutions of $NaOH$ and $NaClO_4$, the solutions containing PuO_2^{2+} , $HClO_4$, and $NaClO_4$ were eventually adjusted to the concentrations required for the measurements.

Each solution so prepared was used for the e.m.f. measurements on the same day with the aim of minimising the self-reduction of the plutonium(VI) due to its α radiation.

The buffers were prepared using calculated quantities of acetic acid and sodium acetate. Then the exact concentrations of acid were determined alkalimetrically, and those of acetate ion acidimetrically. In the latter case, potentiometric indication of the end-point was used.

The concentration of the stock solution of $NaClO_4$ (twice recrystallized) was checked by means of a cation exchange column.

All chemical used were of analytical grade.

Measurements. The following notation is used:

C_M = total concentration of PuO_2^{2+} ;

C_H = concentration of $HClO_4$ in plutonyl solutions;

C'_{HA}, C'_A = stoichiometric concentrations of acetic acid and sodium acetate calculated from the amounts of buffer added;

δ = C'_{HA}/C'_A .

(1) J. J. Katz and G. T. Seaborg, «The Chemistry of the Actinide Elements», Methuen, London (1957).

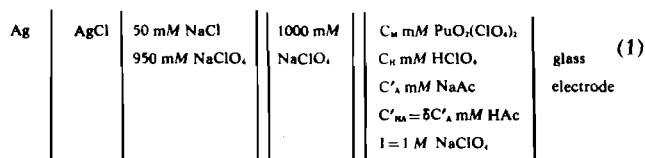
(2) A. D. Gel'man, A. I. Moskvin, L. M. Zaitsev, and M. P. Mefod'eva, «Complex Compounds of Transuranium Elements», Consultants Bureau, New York (1962).

(3) M. Taube, «Plutonium», Pergamon Press (1964).

(4) S. Ahrland, *Acta Chem. Scand.*, 5, 199 (1951).

(5) I. M. Kolthoff and Ph. J. Elving, «Treatise on Analytical Chemistry», Part II, Vol. 9, Interscience Publ. (1962).

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



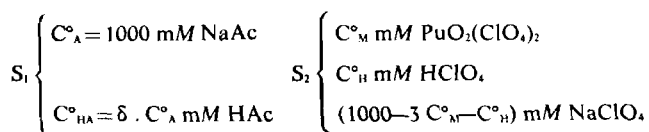
The reference electrode and the bridge were of the «Wilhelm» type.⁶

The silver-silver chloride electrode was of the thermal-electrolytic type.⁷

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 behaviour of the glass electrode was checked in the range 2.0 ≤ pH ≤ 3.0 with standard acid solutions (I = 1.0 M with NaClO₄) usually both before and after a series of measurements. The e.m.f. is described by the equation $E = E^{\circ} + 58.16 \log[H^+]$.

The solution in the right-hand half-cell was prepared by adding, with a microburette, known volumes of a buffer solution S₁ to a known volume (7.00 ml) of a solution S₂.



The measurements were performed with two different buffers, δ = 4 and δ = 2. For every buffer, besides the measurements for the [H⁺] determination in solutions containing PuO₂²⁺, measurements of E' have been carried out on solutions with C_M = 0. Equilibria were rapidly reached by bubbling through N₂ purified and presaturated with NaClO₄ (1 M) solution.

The absorption spectra of the solutions of PuO₂²⁺, in the range 360 to 1000 mμ, were determined with an Optica CF4-NI spectrophotometer.

All operations with plutonium solutions were performed in a well ventilated fume hood.

Treatment of Data. The treatment of the experimental data for the determination of the free ligand concentration [A] and the average number of ligands \bar{n} , and the calculation of the stability constants β_n, are essentially those used by other authors in the study of uranyl⁴ and rare earth⁸ complexes of acetate.

For a buffer solution free from PuO₂²⁺:

$$K_c = \frac{[H^+]' (C'_A + [H^+]')}{C'_{HA} - [H^+]'} \quad (2)$$

For the same buffer solution, in the presence of PuO₂²⁺ and HClO₄(C_H):

$$K_c = \frac{[H^+] [A]}{C'_{HA} + C_H - [H^+]} \quad (3)$$

By the combination of (2) and (3) we obtain:

$$[A] = \frac{[H^+]'}{[H^+]} \times \frac{(C'_A + [H^+]')(\delta \cdot C'_A + C_H - [H^+])}{\delta \cdot C'_A - [H^+]'} \quad (4)$$

The ratio $\frac{[H^+]'}{[H^+]}$ is calculated from:

$$E' - E = 58.16 \log \frac{[H^+]'}{[H^+]} \quad (5)$$

The average number of ligands \bar{n} is given by:

$$\bar{n} = \frac{C'_A + [H^+] - C_H - [A]}{C_M} \quad (6)$$

If there is formation only of mononuclear complexes MA_n, and hydrolysis of the metallic cation is negligible, the \bar{n} values are a function of [A] only.

Let us consider the formation constants of the single mononuclear complexes:

$$\beta_n = \frac{[MA_n]}{[M][A]^n} \quad (7)$$

We can define the function:

$$X([A]) = 1 + \sum_{n=1}^N \beta_n [A]^n \quad (8)$$

Then:

$$\frac{\bar{n}}{[A]} = \frac{dX([A])}{d[A]} \quad (9)$$

and integrating:

$$\ln X([A]) = \int_0^{[A]} \frac{\bar{n}}{[A]} d[A] \quad (10)$$

For the graphical integration of (10) we can 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 relation:

$$X_j = \frac{X_{j-1} - \beta_{j-1}}{[A]} \quad (11)$$

where j = 1, 2, 3, ...; X₀ = X; β₀ = 1.

(6) F. J. C. Rossotti and H. Rossotti, «The Determination of Stability Constants», McGraw-Hill Book Co., New York (1961).

(7) D. J. G. Ives and G. J. Janz, «Reference Electrodes, Theory and Practice», Academic Press, New York and London (1961).

(8) A. Sonesson, *Acta Chem. Scand.*, 12, 165, 1957 (1958).

Results and Discussion

Preliminary spectrophotometric measurements carried out on PuO_2^{2+} solutions containing sodium acetate at different pH values have shown that there is no appreciable reduction of Pu^{VI} over a period of 5-6 hours.

The actual oxidation state of the plutonium was checked before and after each titration by absorption spectroscopy in the range 360 to 1000 μm . The observed absorption spectra of PuO_2^{2+} with acetate were very similar to those already reported by other authors.⁹

The E' values for the different concentrations C'_A were determined by measuring the e.m.f. of the cell (1) with $C_M=0$ and $C_H=0$. The data obtained with the buffer solution used are reported in Table I.

Table I. Determination of E' as a function of C'_A , when perchlorate is exchanged for the two acetate buffers in solutions of $C_M=0$. Calculation of K_c in the medium used

Buffer C'_A mM	$\delta=4$		$\delta=2$	
	E' mV	$K_c \times 10^5$	E' mV	$K_c \times 10^5$
7.09	-77.8	2.37	-96.0	2.31
14.05	77.8	2.37	95.7	2.33
27.8	77.8	2.37	95.5	2.34
41.1	77.9	2.36	95.5	2.34
54.1	78.1	2.34	95.6	2.33
66.7	78.2	2.32	95.7	2.32
78.9	78.2	2.32	95.8	2.32
90.9	78.3	2.30	95.9	2.30
113.9	78.5	2.28	96.1	2.28

One can observe that E' changes slightly on increasing the buffer strength relative to that of perchlorate in the solution.

If E changes in the same way in the presence of the plutonyl ion, one can assume that, by applying (5) with values of E' and E relating to the same C'_A concentration, the variation will not influence the results of the measurements.

The data obtained from the measurements on solutions containing PuO_2^{2+} are reported in Table II for the buffer $\delta=4$, and in Table III for the buffer $\delta=2$.

In all the titrations carried out we have observed, at the highest concentrations of acetate, the formation of pink colored crystals. This is in agreement with the already observed formation of an almost insoluble salt complex $\text{NaPuO}_2(\text{CH}_3\text{COO})_3$.² Also, the formation of the corresponding salt complex has been observed for solutions of UO_2^{2+} under the same conditions,⁴ and this should be more soluble than the plutonyl one. The measurements reported in Tables II and III relate to solutions in which precipitation of the complex had certainly not yet begun.

In Figure 1 the values of \bar{n} vs. $\log[A]$ for the five series of measurements are reported. From all the data the formation of successive complexes with $\bar{n}=1, 2, 3$, is evident.

Table II. Determination of corresponding values of \bar{n} and $[A]$ at the pH of the buffer 4:1

C_M mM	C'_A mM	E mV	$[A]$ mM	\bar{n}
$C_M^0=15.00$ mM; $C_H^0=1.80$ mM; (○)				
14.90	7.09	-48.6	2.38	0.216
14.79	14.05	51.9	5.34	0.486
14.59	27.78	56.3	12.07	0.994
14.39	41.10	58.8	19.6	1.39
14.20	54.05	61.1	27.8	1.74
14.01	66.67	63.0	36.8	2.02
13.82	78.95	64.8	46.7	2.22
$C_M^0=7.31$ mM; $C_H^0=1.47$ mM; (△)				
7.26	7.09	-57.3	3.33	0.347
7.21	14.05	62.0	7.53	0.698
7.16	20.98	64.3	12.26	1.04
7.11	27.78	65.8	17.55	1.26
7.01	41.10	67.9	28.0	1.69
6.91	54.05	69.6	38.9	2.01
6.82	66.67	70.9	50.3	2.22
6.73	78.95	72.0	62.1	2.32
6.64	90.91	72.8	73.2	2.49

Table III. Determination of corresponding values of \bar{n} and $[A]$ at the pH of the buffer 2:1

C_M mM	C'_A mM	E mV	$[A]$ mM	\bar{n}
$C_M^0=15.40$ mM; $C_H^0=0.54$ mM; (□)				
15.33	4.27	-67.7	1.47	0.157
15.27	8.50	70.7	3.21	0.320
15.20	12.82	72.5	5.23	0.472
15.14	16.85	73.6	7.26	0.606
15.07	20.98	74.7	9.28	0.748
14.97	27.78	76.0	12.95	0.962
14.87	34.48	77.1	16.96	1.16
14.76	41.10	78.2	20.8	1.40
14.56	54.05	80.2	29.5	1.65
14.37	66.67	81.8	38.6	1.92
14.18	78.95	83.4	48.5	2.12
$C_M^0=8.98$ mM; $C_H^0=2.55$ mM; (●)				
8.94	4.27	-57.3	1.18	0.085
8.90	8.50	68.3	3.25	0.321
8.85	12.82	73.0	5.73	0.529
8.83	16.85	75.6	8.23	0.704
8.79	20.98	77.2	10.7	0.893
8.73	27.78	79.3	15.3	1.16
8.67	34.48	80.9	20.0	1.39
8.61	41.10	82.3	25.1	1.58
8.50	54.05	84.5	35.7	1.89
8.38	66.67	86.4	47.0	2.07
8.27	78.95	87.8	58.4	2.20
8.16	90.91	89.0	70.1	2.27
$C_M^0=6.16$ mM; $C_H^0=1.70$ mM; (▽)				
6.13	4.27	-67.9	1.67	0.170
6.10	8.50	76.7	4.34	0.421
6.08	12.82	79.8	7.29	0.648
6.06	16.85	81.7	10.2	0.840
6.03	20.98	83.0	13.2	1.02
5.99	27.78	84.6	18.6	1.27
5.95	34.48	85.9	24.1	1.47
5.91	41.10	86.8	29.7	1.67
5.83	54.05	88.4	41.3	1.92
5.75	66.67	89.7	53.2	2.07
5.67	78.95	90.6	65.0	2.19
5.60	90.91	91.4	76.8	2.26

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

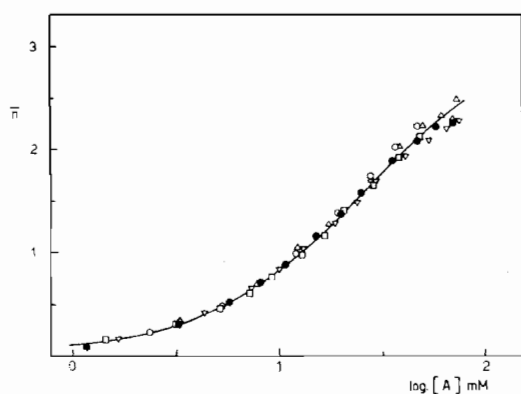


Figure 1. The complex formation curve of the plutonyl-acetate system. The symbols relate to Tables II and III. Full-drawn curve obtained from calculate complexity constants.

The good agreement of the formation curves obtained with the two different buffers shows that under these conditions the plutonyl ion does not undergo any hydrolysis reaction. This is in agreement with the low value of the equilibrium constant for the reaction $\text{PuO}_2^{2+} + \text{H}_2\text{O} \rightleftharpoons \text{PuO}_2\text{OH}^+ + \text{H}^+$ ($K = 1.95 \times 10^{-6}$) determined by K. A. Kraus *et al.*¹

Table IV. The X-functions of the plutonyl-acetate system

[A] mM	X([A])	X_1 M^{-1}	$X_2 \times 10^{-3}$ M^{-2}	$X_3 \times 10^{-4}$ M^{-3}
0	1.0000	112	3.500	9.2
1	1.1155	115.5		
3	1.3714	123.8		
5	1.6623	132.5		
7	1.9914	141.6		
9	2.363	151.4	4.377	
11	2.780	161.8	4.528	
13	3.251	173.2	4.710	
16	4.067	191.7	4.978	9.23
19	5.026	211.9	5.257	9.24
22	6.145	233.8	5.537	9.25
25	7.433	257.3	5.812	9.25
30	9.996	299.9	6.263	9.21
35	13.15	347.0	6.714	9.20
40	16.96	398.9	7.172	9.18
45	21.51	455.8	7.640	9.20
50	26.88	517.6	8.111	9.22
55	33.09	583.4	8.571	9.22
60	40.20	653.3	9.021	9.20
65	48.06	724.0	9.415	9.10

Table V. The formation constants β_n for the acetate system of plutonyl and uranyl

Cation	$\beta_1 M^{-1}$	$\beta_2 M^{-2}$	$\beta_3 M^{-3}$	Ionic strength Temperature	Ref.
PuO_2^{2+}	112 ± 4 1.86×10^3	$(3.5 \pm 0.5) \times 10^3$ 1.95×10^6	$(9.2 \pm 2.0) \times 10^4$ 2.29×10^7	1.0 M; 20°C 2 M; ?	this work (2)
UO_2^{2+}	240 ± 10	$(2.3 \pm 0.2) \times 10^4$	$(2.2 \pm 0.3) \times 10^6$	1.0 M; 20°C	(4)

Moreover the good overlap (within the limits of experimental error) of the formation curves obtained from measurements at different initial concentrations of PuO_2^{2+} shows that, at least in the range of the concentrations examined, we get formation of mono-nuclear complexes only.⁸

Applying (10) and (11), we have determined the values of the formation constants β_n for $\bar{n} = 1, 2$, and 3. The data relating to the calculation are reported in Table IV.

In Table V the formation constants determined by us are reported, for the sake of comparison, those of other authors for the same complexes² and for the analogous complexes with the UO_2^{2+} cation⁴ are included. The remarkable discrepancy between our values of the stability constants and those reported elsewhere² for plutonyl acetate complexes is difficult to explain solely in terms of the different ionic strengths of the solutions studied; it is more probable that the reason lies in the different methods used. There being no clear information concerning the experimental procedures in the paper cited,² we consider our results to be the more reliable.

Comparison of our data with the values of the stability constants of the UO_2^{2+} -acetate complexes,⁴ clearly shows that plutonyl has a lower tendency to coordinate acetate ions in aqueous solution than has uranyl.

If we consider one of the important factors in determining the stability of these complexes to be the ionic radius of the metal, we should find the relative stability to be the reverse of that obtained, since Pu^{VI} has the smaller ionic radius.

However, it is as well to note that the two cations UO_2^{2+} and PuO_2^{2+} exhibit the same relative tendency towards hydrolysis as towards complexation with acetate, *i.e.* uranyl forms hydrolysis products much more readily than plutonyl.¹⁰

To explain the latter behaviour an idea based on the packing of hard spheres about a uranyl group was proposed, *viz.* that «plutonyl behaves as a larger ion than uranyl towards oxygens or water molecules about the equator».¹¹

It is reasonable to invoke this idea to explain also their different tendencies towards the formation of acetate complexes, without however excluding the possibility that the different electronic structures of uranyl and plutonyl may have some importance.

(10) K. A. Kraus and J. R. Dam, National Nuclear Energy Series, «The Transuranium Elements», Div. IV, Vol. 14B, McGraw-Hill Book Co., Inc., New York (1949).

(11) R. E. Connick and Z. Z. Hugus, Jr., *J. Am. Chem. Soc.*, 74, 6012 (1952).