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STUDY OF OXALATE AND CARBONATE COMPLEXES OF PLUTONIUM (IV) IN AQUEOUS SOLUTIONS BY THE SOLUBILITY METHOD

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In the published literature on oxalate complexes of Pu(IV) there are only the data of Rice ([1]), who determined the solubility of Pu(IV) oxalate in oxalic acid of various concentrations (0.001–0.4 mol/l) in the presence of 0.75 M HNO_3. Information on the composition and stability of carbonate complexes of Pu(IV) is entirely lacking. There is only qualitative evidence for complex formation of Pu(IV) with carbonate ions (2 a, b).

Below are presented the results of determining the composition and instability constants of oxalate and carbonate complexes of Pu(IV) by the solubility method. Initially the solubility of Pu(IV) oxalate was determined in solutions of ammonium oxalate of various concentrations (0.001–0.35 mol/l) in the presence of 1.0 M HNO_3.

The experiments were carried out in a special apparatus for determining solubility, into which a solution with a freshly prepared precipitate of Pu(IV) oxalate was placed, the precipitate having first been washed with distilled water to remove excess precipitant, $H_2C_2O_4$. The precipitate was stirred with a mechanical stirrer for 4–6 hr at $20 \pm 0.02°$. As preliminary experiments showed, this time is quite sufficient for establishing equilibrium in the system solution–solid phase. The concentration of plutonium in the equilibrium solutions was determined throughout by the radiometric method.

Table 1

Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in mixed solutions HNO_3–$(NH_4)_2C_2O_4$ (μ 1), in mol/l

Concentration of $(NH_4)_2C_2O_4$	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$	Concentration of $(NH_4)_2C_2O_4$	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$
0.001	$6.19 \cdot 10^{-5}$	0.175	$2.38 \cdot 10^{-4}$
0.002	$5.02 \cdot 10^{-5}$	0.21	$3.35 \cdot 10^{-4}$
0.003	$4.58 \cdot 10^{-5}$	0.233	$4.18 \cdot 10^{-4}$
0.004	$4.06 \cdot 10^{-5}$	0.257	$5.36 \cdot 10^{-4}$
0.005	$3.55 \cdot 10^{-5}$	0.28	$6.87 \cdot 10^{-4}$
0.01	$4.3 \cdot 10^{-5}$	0.303	$8.92 \cdot 10^{-4}$
0.05	$5.77 \cdot 10^{-4}$	0.327	$1.135 \cdot 10^{-3}$
0.14	$1.8 \cdot 10^{-4}$	0.35	$1.37 \cdot 10^{-3}$

The experimental data are given in Table 1.

The solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, when the concentration of ammonium oxalate is increased from 0.001 to 0.005 mol/l, decreases, reaches a minimum value of $3.55 \cdot 10^{-5}$ mol Pu(IV) per 1 l, and then increases as a result of complex formation of Pu(IV) with oxalate ions. The solubility of Pu(IV) oxalate in oxalic-acid solutions may be expressed by an equation of the form:

Calculation ([3]) with the aid of equation (1) showed that in oxalate

$$S = \frac{PR}{[C_2O_4^{2-}]^2} \left\{ 1 + \frac{[C_2O_4^{2-}]}{K_{n_1}} + \frac{[C_2O_4^{2-}]^2}{K_{n_2}} + \dots \frac{[C_2O_4^{2-}]^m}{K_{nm}} \right\}. \qquad (1)$$

solutions Pu(IV) forms complex ions* $[Pu(C_2O_4)]^{2+}$,

* By the composition of the complex ions of Pu(IV) everywhere is meant the ratio cation/addend in the inner sphere of the complex.

$[Pu(C_2O_4)_2]^0$, $[Pu(C_2O_4)_3]^{2-}$ and $[Pu(C_2O_4)_4]^{4-}$, the overall instability constants of which are, respectively, equal to: $K_{n_1} = 1.8 \cdot 10^{-9}$, $K_{n_2} = 1.2 \cdot 10^{-17}$, $K_{n_3} = 4.0 \cdot 10^{-24}$ and $K_{n_4} = 3.3 \cdot 10^{-28}$. These instability constants correspond to the complete decomposition of the Pu(IV) complex ions according to the scheme:

$$[Pu(C_2O_4)_{n_i}^{4-2n_i} \rightleftarrows Pu^{4+} + n_{iC}2O_4^{2-}. \qquad (2)$$

The values of the overall instability constants were used to determine the stepwise instability constants of the oxalate complex ions of Pu(IV), which proved to be successively equal to: $K_1 = 1.8 \cdot 10^{-9}$, $K_2 = 6.7 \cdot 10^{-9}$, $K_3 = 3.3 \cdot 10^{-7}$ and $K_4 = 8.2 \cdot 10^{-5}$. These constants characterize the dissociation of the indicated Pu(IV) complex ions according to the equation:

Table 2

Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in water and acids

No.	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in water, mg/l	Concentration of H_2SO_4, N/l	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, mg/l	Concentration of HNO_3, mol/l	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, mg/l	Concentration of $HClO_4$, mol/l	Solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$, mg/l
1	53	0.025	68	0.025	25	0.1	29
2	60	0.1	97	0.1	30	0.5	53
3	50	0.5	260	0.25	54	1.0	82
4	Av. 54	1.0	418	0.5	72	–	–
5	–	–	–	1.0	144	–	–

$$[Pu(C_2O_4)_n^{4-2n_i}] \rightleftarrows [Pu(C_2O_4)_{n-1}^{6-2n_i}] + C_2O_4^{2-}. \quad (3)$$

In accordance with this, the complex-formation reactions of Pu(IV) occurring in solution may be expressed by the following equations:

$$Pu^{4+} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)]^{2+}, \quad (4)$$

$$[Pu(C_2O_4)]^{2+} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_2]^{0}, \quad (5)$$

$$[Pu(C_2O_4)_2]^{0} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_3]^{2-}, \quad (6)$$

$$[Pu(C_2O_4)_3]^{2-} + C_2O_4^{2-} \rightleftarrows [Pu(C_2O_4)_4]^{4-}. \quad (7)$$

Next, the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in water and in the acids H_2SO_4, HNO_3, and $HClO_4$ was determined. The results of the experiments are summarized in Table 2.

As is evident from Table 2, the solubility of $Pu(C_2O_4)_2 \cdot 6H_2O$ in the acids HNO_3 and $HClO_4$ at first decreases in comparison with the solubility in water, and then, as the acid concentration increases to approximately above $0.1\,N$, begins to increase again. According to A. A. Grinberg and G. I. Petrzhak[4], the decrease in the solubility of $U(C_2O_4)_2 \cdot 6H_2O$ at low acid concentrations is due to the presence of acidic properties of the substance itself. This explanation may also be applied to Pu(IV) oxalate. In terms of their interaction with $Pu(C_2O_4)_2 \cdot 6H_2O$ in aqueous solutions, the acids are arranged in the following

order: $H_2SO_4 > HNO_3 > HClO_4$. The pH of the saturated aqueous solution of Pu(IV) oxalate was found to be 4.4, and the molar electrical conductivity 470 Ω^{-1}.

The dissociation process of Pu(IV) oxalate (by analogy with U^{4+}) may be represented in the form of the scheme:

$$[Pu(C_2O_4)_2(H_2O)_n] \overset{70\%}{\rightleftarrows} [Pu(C_2O_4)(H_2O)_{n-1}OH]^+ + H^+ + C_2O_4^{2-} \quad (8)$$

$$[Pu(C_2O_4)_2(H_2O)_n] \overset{30\%}{\rightleftarrows} [Pu(C_2O_4)(H_2O)_n]^{2+} + C_2O_4^{2-}. \quad (9)$$

On the basis of the data from the determination of the pH and electrical conductivity of saturated

and dilute aqueous solutions of $U(C_2O_4)_2 \cdot 6H_2O$, it is assumed that for uranium(IV) oxalate the first process of acid dissociation proceeds to 70%, and the second (the process of salt dissociation) to 30% ([4]).

With this dissociation scheme, which approximately reflects the processes occurring in solution, the calculated electrical conductivity is close to that found experimentally for saturated and dilute aqueous solutions of $U(C_2O_4)_2 \cdot 6H_2O$ and $Pu(C_2O_4)_2 \cdot 6H_2O$. An estimate of the acid-dissociation constant of $Pu(C_2O_4)_2 \cdot 6H_2O$ gave a value of $\simeq 3 \cdot 10^{-5}$.

The solubility values of $Pu(C_2O_4)_2 \cdot 6H_2O$ in mixed $HNO_3 - (NH_4)_2C_2O_4$ solutions (see Table 1) were used to determine graphically the solubility product of plutonium(IV) oxalate, which proved to be $4 \cdot 10^{-22}$. Approximately the same value of $\Pi P_{Pu(C_2O_4)_2}$ was obtained by calculation from the solubility data for $Pu(C_2O_4)_2 \cdot 6H_2O$ in hydrochloric acid directly from equation ([5])

$$\Pi P_{Pu(C_2O_4)_2} = [Pu^{4+}][C_2O_4{}^{2-}]^2. \quad (10)$$

We then determined the solubility of plutonium(IV) hydroxide at constant ionic strength in aqueous K_2CO_3 solutions of different concentrations. To maintain constant ionic strength of the solutions ($\mu \simeq 10$), various amounts of KCl or $KClO_4$ were added to them. The pH of the carbonate solutions was brought to 11.5 with KOH or HCl. The solution under study was stirred with a freshly prepared precipitate of the hydroxide for 20-24 hours at a temperature of 20°. Preliminary data showed that the solubility of plutonium(IV) hydroxide practically reaches its equilibrium value during the indicated period. The experimental results are given in Table 3.

Table 3

Solubility of plutonium(IV) hydroxide in aqueous K_2CO_3 solutions at 20° ($\mu = \text{const}$), mol/l

K_2CO_3 concentration	Pu^{4+} solubility	K_2CO_3 concentration	Pu^{4+} solubility
0.362	$1.78 \cdot 10^{-4}$	2.896	$1.28 \cdot 10^{-3}$
0.724	$2.58 \cdot 10^{-4}$	3.261	$1.44 \cdot 10^{-3}$
1.448	$5.79 \cdot 10^{-4}$	3.62	$1.65 \cdot 10^{-3}$
2.172	$1.15 \cdot 10^{-3}$	–	–

At K_2CO_3 concentrations < 1.45 mol/l, the ionic strength of the solutions was maintained at about 7.

The solubility of plutonium(IV) hydroxide in a saturated aqueous KCl solution ($\mu \simeq 3.5$) is $6.92 \cdot 10^{-6}$ M/l.

As is evident from Table 3, the solubility of plutonium(IV) hydroxide increases as the K_2CO_3 concentration increases, owing to complex formation of Pu(IV) with carbonate ions. The calculation showed that, under these conditions, the complex ion $[Pu(CO_3)]^{2+}$ is formed, with a concentration instability constant of $1.1 \cdot 10^{-47}$.

In parallel, the absorption spectra of the carbonate-complex solutions of Pu(IV) formed were studied on an SF-4 spectrophotometer in the region 400–1100 mμ at room temperature. The absorption spectra of carbonate solutions of Pu(IV) have the most characteristic absorption maxima at the wavelengths: 426, 472, 487, 640, 690–695, 764, 794, 848–850, 1075 mμ.

Using data on the stability of plutonium oxalate complex ions in its various valence states, one can make a quantitative comparison of the relative tendency toward complex formation of Pu(III), Pu(IV), and Pu(VI). As is known, complex formation is influenced by the size, charge, and structure of the cation, as well as by other factors. The tendency toward complex formation increases with increasing polarizability of the ions, i.e., with an increase in formal charge and a decrease in radius. Table 4 gives the calculated values of the ionic potential $(^{2v})$

$\varphi = z/r$ (where z is the ion charge, r is the ionic radius in angstroms), which can be used when comparing the relative tendency toward complex formation of plutonium in different oxidation states.

Table 4

Ionic potentials of plutonium in various valence states

Cation	r, Å	φ
Pu^{3+}	1.03	2.91
Pu^{4+}	0.90	4.44
PuO_2^{+}	0.87	1.15

Cation	r, Å	φ
PuO_2^{2+}	0.81	2.47

It is evident from this that the tendency toward complex formation among the different plutonium ions should decrease in the following order:
$Pu^{4+} > Pu^{3+} \simeq PuO_2^{2+} > PuO_2^{+}$, i.e., in the order of decreasing ionic potentials given in Table 4. The influence of cation structure should have a strong effect on the stability of complex ions. This is especially noticeable for the plutonyl and plutyl ions. A comparison of the overall instability constants [(5)] for oxalate complex ions of Pu(III), Pu(IV), and Pu(VI) shows that the order of arrangement of Pu ions according to their tendency toward complex formation, predicted from Table 4, is justified:

Composition of the complex ion: $[Pu^{IV}(C_2O_4)_2]^0$, $[Pu^{III}(C_2O_4)_2]^-$, $[PuO_2^{VI}(C_2O_4)_2]^{2-}$.
Overall instability constants: $1.2 \cdot 10^{-17} > 4.9 \cdot 10^{-10} \simeq 5 \cdot 10^{-13}$.

The tendency of Pu toward complex formation in various valence states with anions of the type CO_3^{2-}, $C_6H_5O_7^{3-}$, $C_4H_4O_6^{2-}$, etc., will probably have the same order as in the case of oxalates.

Also of considerable interest is the question of the influence of the size, charge, and structure of the anions of various acids on the tendency toward complex formation. Using the data of Table 5, the anions may be arranged according to their tendency toward complex formation with Pu(IV) in the following order:
$CO_3^{2-} > C_4H_4O_6^{2-} > C_6H_5O_7^{3-} \simeq C_2O_4^{2-}$.

Table 5

Dissociation constants of organic acids and instability constants of complex ions of Pu(IV)

Acid	Acid dissociation constants	Composition of complex ions of Pu(IV)	Overall instability constants of complex ions of Pu(IV)	Method of determination	Determined by
HCO_3^-	$[[unclear]] \cdot 10^{-11}$	$[Pu(CO_3)]^{2+}$	$1.1 \cdot 10^{-47}$	By solubility	Gel' man and Moskvin
$HC_4H_4O_6^-$	$[[unclear]], 5 \cdot 10^{-5}$	$[Pu(C_4H_4O_6)_6]^{8-}$	$5.0 \cdot 10^{-32}$	Polarogr.	Vinogradov, Gryaznov
$H_2C_6H_5O_7^-$	$1.74 \cdot 10^{-5}$	$[Pu(C_6H_5O_7)_4]^{8-}$	$6.0 \cdot 10^{-28}$	Same	Same
$HC_2O_4^-$	$5.18 \cdot 10^{-5}$	$[Pu(C_2O_4)_4]^{4-}$	$3.3 \cdot 10^{-28}$	By solubility	Gel' man, Moskvin
			$3.2 \cdot 10^{-28}$	Polarogr.	Fomin et al.

Comparison of the overall instability constants (see Table 5) with the dissociation constants of organic acids confirms the viewpoint of I. Hindman [(2)] regarding the correspondence between the strength of the hydrogen acids and the strength of the complex ions of Pu(IV) formed by the anions of these acids.

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Note: Figure translations are in progress. See original paper for figures.