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A. D. GELMAN, N. N. MATORINA, and A. I. MOSKVIN

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Abstract

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STUDY OF THE CONDITIONS OF FORMATION AND STABILITY OF OXALATE COMPLEX COMPOUNDS OF Pu(III) IN AQUEOUS SOLUTIONS

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According to the literature data, Pu(III) exhibits a considerably smaller tendency toward complex formation than Pu(IV). Hindman and co-workers (1) studied the effect of changes in the concentration of perchloric, hydrochloric, nitric, and sulfuric acids on the absorption spectra of Pu(III). Although the changes in the spectra were small, nevertheless the tendency of the various acids toward complex formation with Pu(III) was presented by him in the following order:

$$\mathrm{ClO_4^-} < \mathrm{Cl^-} < \mathrm{NO_3^-} < \mathrm{SO_4^{--}}.$$

The data of Thomas and Werner (2) on the preparation of an oxalate complex of Pu(III) are called into question by Hindman, since the color of the solution (green instead of blue) and the conditions under which the experiments were carried out required additional evidence that the oxalate complex is formed by Pu(III), and not by Pu(IV).

We studied by the spectrophotometric method the resistance to oxidation by atmospheric oxygen of solutions of oxalate, carbonate, citrate, and ethylenediaminetetraacetate complex compounds of Pu(III). As a result of this study it was possible to show convincingly that Hindman' s doubts concerning the data (2) were justified. Complex compounds of Pu(III), of the typical bluish-blue color, were resistant to oxidation by atmospheric oxygen only when the experiments were carried out in an atmosphere of nitrogen or in the presence of a very strong reducing agent.

The absorption spectra of the above-mentioned complex compounds of Pu(III) have the most characteristic absorption maxima approximately at wavelengths of 565, 605, 665, 780-790, 905-910, and 1090 mμ, and are similar to the absorption spectrum of a nitric-acid solution of Pu(III). Such a similarity of the absorption spectra is consistent with Hindman' s suggestion (3) that complex formation may not produce noticeable changes in the absorption spectrum of

Pu(III) because of the strong screening of the 5*f*-electrons (the absorption spectra were measured at room temperature in the region 400–1100 mμ on a domestic SF-4 spectrophotometer).

Having established the conditions under which oxalate complexes of Pu(III) are resistant to oxidation by atmospheric oxygen, we decided to determine the composition and instability constants of the complex ions of Pu(III) with various complexing agents. Various physicochemical methods are widely used to determine the composition and stability of complex compounds (4–14). The present work sets forth results obtained in the study of oxalate complexes of Pu(III) by the solubility method (at pH ~ 8) and by the ion-exchange method (at pH 1.4–3.0). It should be noted that these methods do not make it possible to establish the true coordination number of the central atom; however, they do make it possible to determine the ratio central atom—addend and to calculate the instability constants of the complex ions formed.

Initially, the solubility of $Pu_2(C_2O_4)_3 \cdot 9H_2O$ was determined in aqueous solutions of $K_2C_2O_4$ (0.01–2.4 mol/L) at a temperature of 20° and constant ionic strength of the solution. Preliminary experiments showed that stirring for 4–6 h is quite sufficient to establish equilibrium between the solution and the solid phase. To prevent oxidation of Pu(III), a continuous stream of nitrogen was passed through the solution. The plutonium content in the solutions was determined by a radiometric method. The results of the solubility determinations are given in Table 1.

The solubility product L_p of Pu(III) oxalate, calculated from data on the solubility of $Pu_2(C_2O_4)_3 \cdot 9H_2O$ in water at 20 and 70°*, is, respectively, $1.62 \cdot 10^{-25}$ and $2.52 \cdot 10^{-22}$.

Table 1

Solubility of $Pu_2(C_2O_4)_3 \cdot 9H_2O$ in aqueous solutions of $K_2C_2O_4$ and $(NH_4)_2C_2O_4$

Concentration of $K_2C_2O_4$, mol/L	Solubility of Pu(III) oxalate, mol/L	Concentration of $(NH_4)_2C_2O_4$, mol/L	Solubility of Pu(III) oxalate, mol/L
0.01	$3.53 \cdot 10^{-5}$	0.07	$2.02 \cdot 10^{-4}$
0.025	$7.54 \cdot 10^{-5}$	0.13	$2.90 \cdot 10^{-4}$
0.05	$1.00 \cdot 10^{-4}$	0.225	$4.70 \cdot 10^{-4}$
0.075	$1.09 \cdot 10^{-4}$	0.28	$5.66 \cdot 10^{-4}$
0.10	$1.55 \cdot 10^{-4}$	0.35	$6.90 \cdot 10^{-4}$
0.2	$2.7 \cdot 10^{-4}$	0.41	$8.19 \cdot 10^{-4}$
0.3	$4.04 \cdot 10^{-4}$	0.49	$9.75 \cdot 10^{-4}$
0.6	$1.01 \cdot 10^{-3}$	0.56	$1.14 \cdot 10^{-3}$
0.8	$1.71 \cdot 10^{-3}$	0.62	$1.50 \cdot 10^{-3}$
0.9	$2.27 \cdot 10^{-3}$	0.66	$2.05 \cdot 10^{-3}$

Fig. 1. Effect of the concentration of the C_2O_4'' ion on the concentration of complex ions: I $-[Pu(C_2O_4)_2]^-$, II $-[Pu(C_2O_4)_3]^{3-}$, III $-[Pu(C_2O_4)_4]^{5-}$

Figure 1: Fig. 1. Effect of the concentration of the C_2O_4'' ion on the concentration of complex ions: I $-[Pu(C_2O_4)_2]^-$, II $-[Pu(C_2O_4)_3]^{3-}$, III $-[Pu(C_2O_4)_4]^{5-}$

Concentration of $K_2C_2O_4$, mol/L	Solubility of Pu(III) oxalate, mol/L	Concentration of $(NH_4)_2C_2O_4$, mol/L	Solubility of Pu(III) oxalate, mol/L
1.2	$3.46 \cdot 10^{-3}$	0.70	$2.25 \cdot 10^{-3}$
1.51	$5.91 \cdot 10^{-3}$		
1.81	$8.45 \cdot 10^{-3}$		
2.00	$1.06 \cdot 10^{-2}$		
2.41	$1.87 \cdot 10^{-2}$		

On the basis of the results obtained, the composition was established and the overall instability constants of the oxalate complex ions of Pu(III) were calculated by the least-squares method (^{6}). In the concentration range of $K_2C_2O_4$ studied, complex ions are formed (more precisely, the ratio between Pu(III) and the C_2O_4'' ion):

$$[Pu(C_2O_4)_2]^-, \quad [Pu(C_2O_4)_3]^{3-} \text{ and } [Pu(C_2O_4)_4]^{5-},$$

the overall concentration instability constants of which are, respectively, $4.9 \cdot 10^{-10}$, $4.1 \cdot 10^{-10}$, and $1.2 \cdot 10^{-10}$. The dependence of the concentration of these ions on the concentration of the complex-forming agent is shown in Fig. 1.

Fig. 1. Effect of the concentration of the C_2O_4'' ion on the concentration of complex ions: I $-[Pu(C_2O_4)_2]^-$, II $-[Pu(C_2O_4)_3]^{3-}$, III $-[Pu(C_2O_4)_4]^{5-}$

In an analogous way, the solubility of $Pu_2(C_2O_4)_3 \cdot 9H_2O$ was determined in aqueous solutions of $(NH_4)_2C_2O_4$ in the concentration range of ammonium oxalate from 0.07 to 0.7 mol/L at 70° (see Table 1). It was established that under these conditions complex ions of the same composition are formed, whose overall instability constants are, for $[Pu(C_2O_4)_2]^-$, $11.6 \cdot 10^{-9}$; for $[Pu(C_2O_4)_3]^{3-}$, $5.6 \cdot 10^{-9}$; and for $Pu + (C_2O_4)_4^{5-}$, $2.5 \cdot 10^{-9}$.

* The solubility of $Pu_2(C_2O_4)_3 \cdot 9H_2O$ in water at 20° is $4.32 \cdot 10^{-6}$ mol/L and at 70° $1.88 \cdot 10^{-5}$ mol/L.

The heat of formation of complex ions was also calculated for the reaction:

$$Pu^{3+} + nC_2O_4'' \rightleftarrows [Pu(C_2O_4)_n]^{3-2n} \tag{1}$$

Fig. 2. Effect of solution pH on ion concentration: I–Pu^{3+}, II–$[Pu(C_2O_4)_2]^-$, III–$[Pu(HC_2O_4)_4]^-$

Figure 2: Fig. 2. Effect of solution pH on ion concentration: I–Pu^{3+}, II–$[Pu(C_2O_4)_2]^-$, III–$[Pu(HC_2O_4)_4]^-$

It was found that ΔQ for the ion $[Pu(C_2O_4)_2]^-$ is 1300 cal., for $[Pu(C_2O_4)_3]^{3-}$ 1200 cal., and for $[Pu(C_2O_4)_4]^{5-}$ 1300 cal.

The data on complex formation of Pu(III) with C_2O_4'' ions, obtained by the solubility method, were confirmed by the ion-exchange method.

The distribution of Pu(III) between a one-molar solution of NH_4Cl and the cation exchanger KU-2 (15) was studied as a function of the pH of the solution. NH_4Cl was added to maintain the constancy of the ionic strength of the solutions ($\mu \simeq 1$).

Fig. 2. Effect of the solution pH on the concentration of ions:
I–Pu^{3+},
II–$[Pu(C_2O_4)_2]^-$,
III–$[Pu(HC_2O_4)_4]^-$

The distribution of Pu(III) between a 1 *M* solution of NH_4Cl and the cation exchanger in the presence of 0.005 *M* $H_2C_2O_4$ was also studied as the pH of the solution was varied from 1.4 to 3.0. Solutions with the adsorbent ($v = 25$ ml; resin sample 0.5 g) were shaken for 3 hours in a nitrogen atmosphere at a temperature of $20 \pm 1^\circ$ until equilibrium was established (the experiments were carried out with indicator amounts of plutonium). The experimental data are shown in Table 2.

In the pH interval studied, 1.4-3.0, both C_2O_4'' ions and HC_2O_4' ions can participate in complex formation. The concentrations of these ions were determined from the equations for the first and second stages of dissociation of oxalic acid at an ionic strength $\mu \simeq 1$, created by NaCl. The dissociation constants of $H_2C_2O_4$, found by us by potentiometric titration, proved to be:

$$K_1 = 1.4 \cdot 10^{-2} \quad \text{and} \quad K_2 = 1.5 \cdot 10^{-4}.$$

Calculation by the method of Schubert et al. (9) showed that in these solutions, in the pH interval 1.4-3.0, complex ions $[Pu(HC_2O_4)_4]^-$ and $[Pu(C_2O_4)_2]^-$ are formed, the overall instability constants of which are, respectively, $1.1 \cdot 10^{-11}$ and $7.1 \cdot 10^{-10}$. Figure 2 shows the dependence of the concentration of the complex ions $[Pu(HC_2O_4)_4]^-$ and $[Pu(C_2O_4)_2]^-$, as well as the concentration of free Pu^{3+} ions, on the pH of the solution.

Table 2

Distribution of Pu(III) between a 1 M solution of NH_4Cl and the cation exchanger at different pH values

In the absence of complexing agent	In the absence of complexing agent	In the absence of complexing agent	In the absence of complexing agent	In the presence of complexing agent	In the presence of complexing agent	In the presence of complexing agent
Equilibrium pH of the NH_4Cl solution	Concentration of Pu^{3+} in the equilibrium solution, in % of the initial, a_0	Adsorbed amount of Pu^{3+}, in % of the initial, q_0	$A = \frac{a_0}{q_0}$	Equilibrium pH of the solution	Total amount of Pu^{3+} in the equilibrium solution, in % of the initial, a	Adsorbed amount of Pu^{3+}, in % of the initial, q
1.63	28.4	71.6	0.40	1.47	35.8	64.2
2.00	28.6	71.4	0.40	1.60	42.6	57.4
2.29	28.5	71.5	0.40	1.73	56.8	43.2
2.40	27.8	72.2	0.39	1.80	64.4	35.6
2.95	29.0	71.0	0.41	1.90	72.3	27.7
3.18	30.6	69.4	0.44	2.00	79.0	21.0
3.34	27.4	72.6	0.38	2.35	94.0	6.0
3.48	29.1	70.9	0.41	2.40	95.0	5.0
				2.50	96.8	3.2
				2.65	98.0	2.0

The value of the overall instability constant of the complex ion $[Pu(C_2O_4)_2]^-$, obtained by the ion-exchange method, agrees satisfactorily with the value obtained by the solubility method.

Institute of Physical Chemistry
Academy of Sciences of the USSR

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