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Disproportionation of Pu(V) in Aqueous HCOOH Solutions

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Abstract—The behavior of Pu(VI), Pu(V), and Pu(IV) in the HCOOH–H_2O system was studied by spectrophotometry. The Pu(VI) absorption spectrum in solutions containing less than 1 mM $HClO_4$ changes on adding HCOOH to a concentration of 0.53 M. Along with a decrease in the intensity of the absorption maximum at 830.6 nm, corresponding to an *f–f* transition in the PuO_2^{2+} aqua ion, a new band arises with the maximum shifted to 834.5 nm. These transformations are due to formation of a Pu(VI) formate complex (1 : 1). The Pu(IV) absorption spectra in HCOOH solutions vary insignificantly in going from 3.0 to 9.0 M HCOOH and are similar to the spectrum of Pu(IV) in a 0.88 M HCOOH + 0.41 M NaHCOO + 0.88 M $NaClO_4$ solution, which indicates that the composition of the Pu(IV) formate complexes is constant. Pu(V) is unstable in HCOOH solutions and disproportionates to form Pu(VI) and Pu(IV). The reaction rate is approximately proportional to $[Pu(V)]^2$ and grows with an increase in [HCOOH]. The reaction products affect the reaction rate: Pu(IV) accelerates the process, and Pu(VI) decelerates the consumption of Pu(V) by binding Pu(V) in a cation–cation complex. The disproportionation occurs via formation of a Pu(V)–Pu(V) cation–cation complex whose thermal excitation yields an activated complex with its subsequent decomposition to Pu(VI) and Pu(IV).

Key words: plutonium(V), disproportionation, formic acid

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The Pu(V) disproportionation

$$2PuO_2^{+} + 4H^{+} = Pu^{4+} + PuO_2^{2+} + 2H_2O \tag{1}$$

and the related reaction

$$PuO_2^{+} + Pu^{4+} = Pu^{3+} + PuO_2^{2+} \tag{2}$$

determine the stability of Pu(V) in solutions of any composition. The rate of reaction (1) depends on the content of Pu(V), H^+ ions, water, and complexing ligands. The latter factor is important for the occurrence of reaction (2). In aqueous carboxylic acid solutions, the effect of all the above factors can be traced. In our previous paper [1], we considered the Pu(V) disproportionation in the CH_3COOH–H_2O system. In this study we examined the behavior of Pu(V) in solutions of formic acid, which is a stronger acid than acetic acid but forms (as anion) less strong complexes with Pu(VI) than do acetate ions {log β_1 at an ionic strength of 1.0 for $\cdot PuO_2(HCOO)^+$ and $PuO_2\cdot(CH_3COO)^+$ is 1.03 [2] and 2.05 [3], respectively}. The similar ratio should be observed for Pu(IV) complexes. Therefore, in dilute HCOOH solutions the hydrolysis of Pu(IV) is possible, especially at elevated temperatures.

EXPERIMENTAL

Working solutions of ^{239}Pu(VI) in 0.01 M $HClO_4$ were prepared by the known procedure [1]. HCOOH, HCOONa, and H_2O_2 were of analytically pure grade. All solutions were prepared in double-distilled water.

Plutonium(V) was prepared by two procedures. The first procedure is reduction of Pu(VI) with hydrogen peroxide in 0.02–0.03 M HCOONa:

$$2Pu(VI) + H_2O_2 = 2Pu(V) + 2H^{+}. \tag{3}$$

H_2O_2 was taken in a 10% excess relative to the stoichiometry, because H_2O_2 is also consumed in side reactions.

The second procedure is photochemical reduction of Pu(VI) in 0.2–0.3 M HCOOH. For this purpose, a quartz cell with a Pu(VI) solution was placed in a

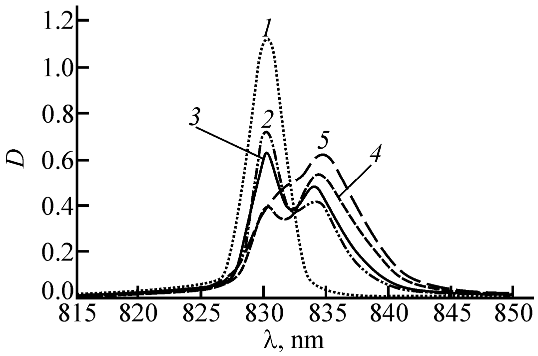

Fig. 1. Variation of the Pu(VI) absorption spectrum in aqueous HCOOH solutions. [Pu(VI)] = 2 × 10^{-3} M. (*1*) [$HClO_4$] = 1.0 M; [HCOOH], M: (*2*) 0.53, (*3*) 1.04, (*4*) 8.00, and (*5*) 26.10.

beam of UV and visible light from a VIO-1 installation with two super-high-pressure mercury lamps DRK-120. The irradiation was interrupted at regular intervals, and the absorption spectrum in the range 400–1000 nm, where the absorption bands of all the valence forms of Pu are located, was recorded. The irradiation was stopped after disappearance of approximately 80% of Pu(VI). Then the Pu(VI) reduction continued for several hours in the dark with the reductants accumulated in the system.

Table 1. Influence of the HCOOH concentration on the major absorption band of Pu(VI)

[HCOOH], M	First maximum		Second maximum	
	λ, nm	ε, l mol^{-1} cm^{-1}	λ, nm	ε, l mol^{-1} cm^{-1}
–	830.2	555		
0.53	830.2	356	834.0	210.8
1.04	830.2	311.7	834.1	239.1
2.02	830.2	269.6	834.1	261.2
2.93	830.2	247.4	834.1	266.9
4.56	830.2	225.3	834.1	273.6
6.00	830.2	210.2	834.1	273 ± 3
7.83	830.2	198	834.1	273 ± 3
8.00	830.4	195.8	834.4	273 ± 5
10.0	830.4	189.8	834.4	273 ± 5
12.1	830.4	188	834.4	273 ± 5
14.1	830.4	192	834.4	273 ± 5
17.8			834.5	273 ± 5
18.8			834.5	273 ± 5
20.6			834.5	278
22.6			834.5	282.6
24.3			834.5	292
25.2			834.5	301
25.7			834.5	306
26.1			834.5	315

The Pu(IV) solution was prepared as follows. From a nitric acid solution of Pu(IV), we precipitated $Pu(OH)_4$ with an ammonia solution. The precipitate was separated by centrifugation, washed with ice-cold double-distilled water, and dissolved in concentrated HCl. The $PuCl_4$ obtained after evaporation was dissolved in 2.75 M HCl.

The progress of Pu(VI) reduction and Pu(V) disproportionation was monitored by the Pu(VI) absorption in the range 830–850 nm. The disproportionation leads to the formation of Pu(IV), and its absorption is summed up with the Pu(VI) absorption. Therefore, initially we examined the spectra of Pu(VI) and Pu(IV) in HCOOH solutions at wavelengths of 400–1000 nm with a Shimadzu UV-3100 PC spectrophotometer (Japan). The kinetic studies were performed with an SF-46 spectrophotometer (Leningrad Optical and Mechanical Association, Russia) by the following procedure. In experiments performed at 18–20°C with solutions with [HCOOH] ≤ 6 M, Pu(V) was prepared directly in the spectrophotometric cell either by reduction of Pu(VI) with hydrogen peroxide or photochemically, after which an aliquot of anhydrous HCOOH was added to the cell. In experiments with [HCOOH] = 7–12 M at 20°C and with [HCOOH] = 2–6 M at 25–45°C, to 0.05–0.10 ml of the initial Pu(VI) solution we added 0.015 ml of 5 M $NaHCO_2$ and a calculated volume of 0.08–0.1 M H_2O_2. After 20–25 min, 0.1–0.2 ml of the Pu(V) solution was introduced into the cell with an HCOOH solution.

RESULTS AND DISCUSSION

Spectra of Pu(VI) and Pu(IV) in HCOOH Solutions

Figure 1 shows the spectra of Pu(VI) in 1 M $HClO_4$ solution and in HCOOH solutions containing about 0.1 mM $HClO_4$. With an increase in the HCOOH concentration in solution, the intensity of the absorption maximum at 830.6 nm, corresponding to an *f–f* transition in the PuO_2^{2+} aqua ion, decreases, and a new band arises with the maximum shifted to 834.5 nm. These transformations are due to formation of a 1 : 1 Pu(VI) formate complex:

$$\{PuO_2^{2+}\}\cdot 5H_2O + HCOO^- = \{PuO_2HCOO^+\}\cdot(5-n)H_2O + nH_2O. \tag{4}$$

The positions of the maxima and the molar extinction coefficients ε are given in Table 1.

In the range 5–22 M HCOOH, variation of the solution composition does not significantly affect ε. However, in 24–26 M HCOOH, ε increases. This is due to replacement of H_2O molecules in the PuO_2^{2+} equatorial sphere by HCOOH molecules.

Figure 2 shows the spectra of Pu(IV) in HCOOH solutions containing ~0.05 M NaCl. The positions and heights of the absorption maxima change insignificantly in going from 3.0 to 9.0 M HCOOH and to a 0.88 M HCOOH + 0.41 M $NaHCO_2$ + 0.88 M $NaClO_4$ solution, suggesting constant composition of the Pu(IV) formate complexes.

Kinetics of Pu(V) Disproportionation

In 4–12 M HCOOH solutions at 18–20°C, by the end of the reaction the sum of the Pu(VI) and Pu(IV) concentrations corresponded to the amount of Pu(VI) taken for the reduction to Pu(V). Only the absorption bands of Pu(IV) and Pu(VI) were present in the spectrum, whereas the Pu(III) bands were absent. It should be noted that Pu(V) slowly disproportionated in 0.5–2 M HCOOH solutions, but the arising Pu(IV) was in the hydrolyzed form and gave a suspension undergoing sedimentation with time.

In 4 M HCOOH at 25°C, in one experiment Pu(IV) underwent hydrolysis and polymerization, and in the other experiment it remained nonpolymerized, but at 27°C the Pu(IV) hydrolysis was observed in all the experiments. At the same temperature in several experiments Pu(IV) underwent hydrolysis in 6 M HCOOH also.

Figure 3 shows the kinetic curves of the Pu(VI) accumulation. These curves have induction periods observed in the majority of experiments. some curves are linearized in the semilog coordinates, which could suggest the first order of the reaction with respect to Pu(V). However, the slope of the linearized kinetic curves changes with an increase in the initial Pu(V) concentration. In a 6 M HCOOH solution containing by the end of the induction period 1.21, 1.52, and 3.26 mM Pu(V) (T = 20°C), the half-conversion times $\tau_{1/2}$ are 156, 130, and 65 s, respectively. It follows from these values that the reaction rate follows a second-order law, i.e., in the initial period reaction (1) prevails. The apparent first order is due to participation of the reaction products in the transformation of Pu(V) into Pu(VI) and Pu(IV).

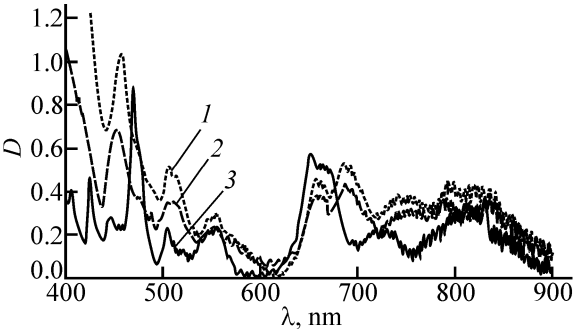

Fig. 2. Electronic absorption spectra of aqueous Pu(IV) solutions: (*1*) [HCOOH] = 25.7, [Pu(IV)] = 1.66×10^{-3} M; (*2*) [HCOOH] = 0.88, [HCOONa] = 0.41, [$NaClO_4$] = 0.88, [Pu(IV)] = 1.17×10^{-3} M; (*3*) [$HClO_4$] = 1.14, [Pu(IV)] = 1.58×10^{-3} M.

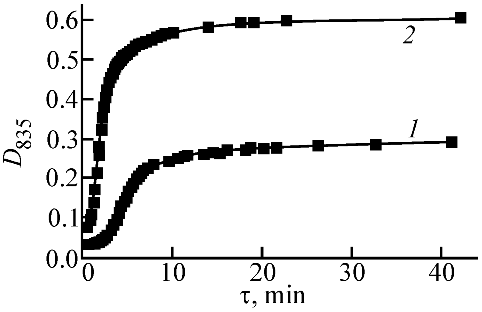

Fig. 3. Kinetic curves of Pu(VI) accumulation in Pu(V) disproportionation. T = 20°C, [HCOOH] = 6 M; $[Pu(V)]_0$, M: (*1*) 1.52 and (*2*) 3.26.

We performed experiments on Pu(V) disproportionation in solutions containing 3–4 mM Pu(VI) or 4 mM Pu(IV). The results of these experiments are given in Table 2.

It can be readily seen that Pu(VI) decelerates the loss of Pu(V). This is caused by formation of cation–cation complexes (CCCs):

$$\text{Pu(V)} + \text{Pu(VI)} \rightleftarrows \text{CCC(I)}. \quad (5)$$

Table 2. Effect of Pu(VI) and Pu(IV) on the Pu(V) disproportionation

[HCOOH], M	[Pu], mM			$\tau_{1/2}$, s
	Pu(VI)	Pu(IV)	Pu(V)	
4			1.45	600
4	4		1.47	1860
6			1.52	130
6	4		1.75	372
6		4.3	0.6	50
10			1.1–1.2	24–44
10	3		0.62	117
10	3		0.8	80

Table 3. Influence of the solution composition on k_{obs}

T, °C	[HCOOH], M	k_{obs}, l mol^{-1} s^{-1}
18	4	1.15 ± 0.2
19	4.6	1.36 ± 0.2
20	6	5 ± 1
25	6	4.35 ± 0.5
20	7	6.5 ± 1.5
20	8	10.6 ± 3
20	9	20 ± 10
20	10	24.4 ± 10
20	11	~48
30	6	5.7 ± 0.5
35	6	5.2 ± 0.5

The Pu(V) bound in the complex reacts more slowly or does not react at all with another Pu(V) ion. Similar phenomenon was observed in Pu(V) disproportionation in 15 M CH_3COOH but was not observed in 6 M CH_3COOH [1].

Pu(IV) accelerates the Pu(VI) accumulation in HCOOH in the same manner as it does in CH_3COOH solutions [1]. Therefore, it can be assumed that, in the HCOOH–Pu(V) system, reactions (1), (2), (6), and (7), postulated for acetic acid solutions, occur:

$$\mathrm{Pu(VI)} + \mathrm{Pu(III)} \rightarrow \mathrm{Pu(V)} + \mathrm{Pu(IV)}, \qquad (6)$$

$$\mathrm{Pu(V)} + \mathrm{Pu(III)} \rightarrow 2\mathrm{Pu(IV)}. \qquad (7)$$

The rate of the Pu(V) disappearance in reactions (1), (2), and (7) and the rate of its accumulation in reaction (6) are described by the equation

$$\begin{aligned} -d[\mathrm{Pu(V)}]/dt &= 2k_1[\mathrm{Pu(V)}]^2 + k_2[\mathrm{Pu(V)}][\mathrm{Pu(IV)}] \\ &+ k_7[\mathrm{Pu(V)}][\mathrm{Pu(III)}] - k_6[\mathrm{Pu(VI)}][\mathrm{Pu(III)}]. \end{aligned} \qquad (8)$$

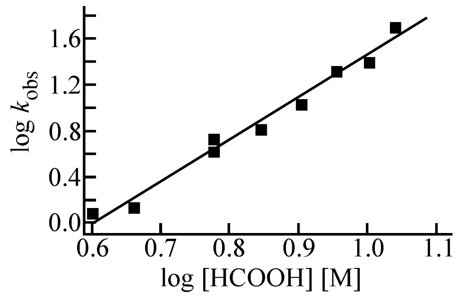

Fig. 4. log–log plot of k_{obs} vs. HCOOH concentration.

As a first approximation, Eq. (8) transforms into the expression

$$-d[\mathrm{Pu(V)}]/dt = 2d[\mathrm{Pu(VI)}]/dt = k_{obs}[\mathrm{Pu(V)}]^2, \qquad (9)$$

where k_{obs} is the observed second-order rate constant.

To evaluate the effect of the HCOOH concentration on the stability of Pu(V), we used the second-order rate constants found by the expression

$$k_{obs} = 1/([\mathrm{Pu(V)}]\tau_{1/2}), \qquad (10)$$

where $[\mathrm{Pu(V)}] = 2\{[\mathrm{Pu(VI)}]_\infty - [\mathrm{Pu(VI)}]\} = 2\Delta D/(\varepsilon l)$, $\Delta D = D_\infty - D_1$, D_1 and D_∞ are the solution optical densities by the end of the induction period and after the reaction completion, respectively; $\tau_{1/2} = \tau_2 - \tau_1$, τ_1 is the time of the end of the induction period and τ_2, time at which $D_2 = D_1 + \Delta D/2$; $\varepsilon = \varepsilon^{IV} + \varepsilon^{VI}$. The k_{obs} values are given in Table 3.

The above data show that the k_{obs} values obtained under similar conditions exhibit strong scatter. Most probably, this is due to the hydrolysis of Pu(IV). The point is that the components were mixed manually, and therefore it was impossible to standardize the mixing rate and avoid local effects, which could give rise to conditions for the formation of Pu(IV) hydroxide oligomers. In cases when these oligomers had no time to form, Pu(IV) participated in reaction (2) and increased the rate of Pu(VI) accumulation.

The k_{obs} values significantly increase with the HCOOH concentration. Figure 4 shows in the log–log coordinates the dependence of k_{obs} on [HCOOH], allowing determination of the reaction order with respect to HCOOH. It appeared to be equal to 3.7. In an aqueous $HClO_4$ solution, the rate of the Pu(V) disproportionation is directly proportional to $[H^+]$ [4]. If this trend were preserved in an aqueous HCOOH solution, where $[H^+] = (K_a[\mathrm{HCOOH}])^{0.5}$ and K_a is the HCOOH dissociation constant, k_{obs} would be proportional to $[\mathrm{HCOOH}]^{0.5}$. The stronger dependence observed should be attributed to participation of HCOOH molecules in the formation of an activated complex or its precursor, cation–cation complex of Pu(V) ions:

$$\mathrm{Pu(V)} + \mathrm{Pu(V)} \rightarrow \mathrm{CCC(II)}. \qquad (11)$$

Thermal excitation of the cation–cation complex yields an activated complex, in which charge transfer occurs:

$$\text{CCC(II)} \leftrightarrows \text{activated complex}, \tag{12}$$

$$\text{activated complex} \rightarrow \text{Pu(IV)} + \text{Pu(VI)}. \tag{13}$$

Thus, we found that Pu(V) is unstable in HCOOH solutions and disproportionates to form Pu(VI) and Pu(IV). The disproportionation rate is approximately proportional to $[\mathrm{Pu(V)}]^2$ and increases with an increase in [HCOOH]. Presumably, disproportionation of Pu(V) occurs via a cation–cation complex Pu(V)–Pu(V) whose thermal excitation yields an activated complex subsequently decomposing to Pu(VI) and Pu(IV). The reaction products affect the disproportionation rate: Pu(IV) accelerates the process, whereas Pu(VI) decelerates the Pu(V) consumption by binding Pu(V) in a cation–cation complex.

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