Journal of Alloys and Compounds 271–273 (1998) 813–816

Journal of
ALLOYS
AND COMPOUNDS

Behavior of plutonium(V) in alkaline media

N.A. Budantseva[a], I.G. Tananaev[a,*], A.M. Fedoseev[a], C.H. Delegard[b]

[a]Institute of Physical Chemistry, Russian Academy of Sciences, Leninski Prospect 31, Moscow, 117915, Russia
[b]Pacific Northwest National Laboratory, P.O. Box 999, Richland, WA, 99352, USA

Abstract

In alkaline solutions with NaOH concentration below 8 M, Pu(V) has been found to be unstable, disproportionating to form Pu(IV) hydrous oxide precipitate and dissolved Pu(VI). Sorption of Pu(V) on the freshly precipitating Pu(IV) hydrous oxide and partial reduction of Pu(VI) by water α-radiolysis products complicate disproportionation of Pu(V). Disproportionation and reproportionation equilibrium constants were measured in the range 4–8 M NaOH. The yield of disproportionation and reproportionation reaction products increase with temperature and sharply fall with NaOH concentration.

Keywords: Plutonium; Disproportionation; Formal potential; Alkaline solutions

1. Introduction

The stability of Pu(V) in acid to neutral solution is known to depend on hydrogen ion concentration and temperature [1]. However, studies of Pu(V) stability in basic solution are scarce and the data sometimes appear contradictory. Thus, Pu(V) hydrolyzes and disproportionates in high pH [2] and disproportionates in oxidation/reduction reactions in strong alkali [3]. In contrast, limited reproportionation of dissolved Pu(VI) with freshly precipitated Pu(IV) hydrous oxide occurs to give Pu(V) in 4 and 6 M NaOH [4]. Plutonium(V) is directly observed in 15 M NaOH solution in apparent equilibrium with Pu(IV) hydrous oxide [5].

Plutonium(V) disproportionation in alkali depends on the formal potential of the Pu(V)/Pu(IV) electrochemical pair. Reported potentials range from −0.61 to −1.03 V in 0.1 to 14.1 M NaOH (polarographic data) [6]; to 0.44 V in 4 M NaOH (electrochemical and spectrophotometric experiments) [4]; to 0.76 V in 1 M NaOH (estimated from measured acid potential and hydrolysis constants) [7].

The objective of the present work was to examine the stability of Pu(V) over a wide range of NaOH concentrations.

2. Instruments and reagents

Plutonium (primarily ^{239}Pu) was purified by anion exchange and oxalate precipitation. Plutonium(IV) was stabilized with hydrogen peroxide in 4 M HNO_3 solutions at 80°C, and Pu(VI) by fuming with perchloric acid. Preparation of alkaline Pu(V) solutions by chemical or electrochemical reduction of alkaline Pu(VI) solutions gave products contaminated with Pu(IV). Crystalline $NH_4PuO_2CO_3$, synthesized by known techniques [8], was used to prepare Pu(V) solutions. This compound had a white colour, which was not altered by exposure to neutral H_2O solutions.

Standardized NaOH solutions were prepared from 17.7 M NaOH kept sealed in a plastic vessel to prevent carbonate contamination. All reagents were pure and extra pure grade. Solutions were prepared from distilled water purified of CO_2 by pH 4 acidification and boiling. Plutonium valence was determined by spectrophotometry (Shimadzu UV-3100 PC, Japan).

3. Results and discussion

3.1. Pu(V) solubility in 8 M NaOH

Alkaline solutions of Pu(V) were prepared by dissolving crystalline $NH_4PuO_2CO_3$ in 8 M NaOH. After mixing of NaOH solution and $NH_4PuO_2CO_3$, the solid phase and

---

[*] Corresponding author. Fax: +7 95 3351778.

0925-8388/98/$19.00
PII: S0925-8388(98)00224-2

mother solution became pink. After 1.5 h of equilibration, Pu(V) concentration was measured by spectrophotometric titration with Pu(VII) prepared by electrochemical oxidation of 0.01 M Pu(VI) in 8 mol/l NaOH. The Pu(VII) concentration was measured by titration with standard $K_4[Fe(CN)_6]$ solution. The Pu(V) solubility was estimated as $(8\pm3)\times10^{-3}$ M at 12°C.

3.2. Pu(V) disproportionation

For each disproportionation test, 0.027 mmol of $NH_4PuO_2CO_3$ was precipitated in a plastic tube. The white sediment was washed free of occluded salts, 5 ml of alkali of selected concentration added, and the suspension stirred in a thermostat. Stirring was halted at hourly intervals and solution spectra recorded (1000 to 400 nm). The spectra showed absorptions at 620 to 630 nm inherent to Pu(VI); and at 500 to 600 nm and 800 to 810 nm assigned to Pu(V). Plutonium(IV) precipitates almost completely in NaOH solution and no corresponding spectrum is observed. After 5 h, the spectra became constant and the initial Pu(V) was judged to be at equilibrium with its disproportionation products. Fig. 1 illustrates the spectra as a function of NaOH concentration. The Pu(V) and Pu(VI) concentrations were evaluated based on measured molar extinction coefficients $\varepsilon_{810}^{V}=\varepsilon_{630}^{VI}=10$ l/(mol cm).

The total amount of dissolved Pu(V) and (VI) was calculated and the amount of Pu in the solid phase analyzed by redissolving to determine material balance.

Using the literature data about the species formations of Pu(VI) [9,10], (V) [5,10] and (IV) [11,12] in alkaline solutions, the ionic-molecular form disproportionation reaction could be presented as:

$$2PuO_2(OH)_4^{3-} + 2H_2O = PuO_2(OH)_4^{2-} + Pu(OH)_5^{-} + 3OH^{-} \qquad (1)$$

or

$$2PuO_2(OH)_4^{3-} + 2H_2O = PuO_2(OH)_4^{2-} + Pu(OH)_4 + 4OH^{-}\ . \qquad (2)$$

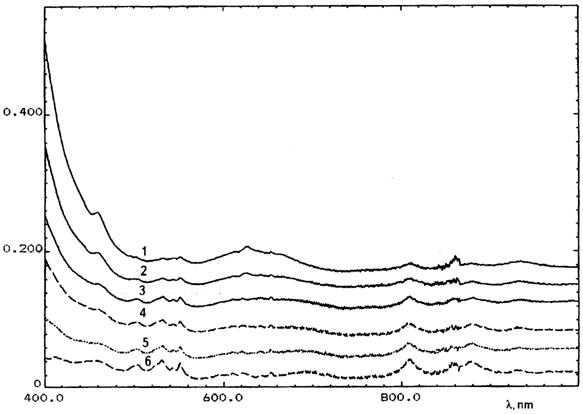

Fig. 1. Electron absorption spectra of equilibrium solutions of Pu(V) as a function of [NaOH] at 40°C. (1) 5.65 mol/l; (2) 6.10 mol/l; (3) 6.60 mol/l; (4) 7.00 mol/l; (5) 7.46 mol/l; (6) 8.02 mol/l.

To calculate the equilibrium constants, one should know the concentrations of all the valence forms of plutonium in solution. In this case, the Pu(IV) concentration is known from the solubility of Pu(IV) hydrous oxide (S) at 26°C as a function of NaOH concentration [12]. The temperature dependence of solubility has not been studied. Assuming that the Pu(IV) hydrous oxide solubility does not change in the interval 26–40°C, equilibrium constants can be calculated. Pu(VI) and Pu(V) concentrations are determined from spectrophotometric measurements. The disproportionation equilibrium constant was calculated as $K_d=[Pu(VI)]\cdot S\cdot[OH^-]^n/[Pu(V)]^2$ ($n=3$ or 4). In 1–4 M NaOH the disproportionation equilibrium reaction moves to the right side. Pu(V) concentration in these solutions was so low that we could not determine K_d values. In [NaOH] interval from 4 to 8 mol/l the equilibrium constants increase from 3.05 to 0.20 (reaction 1) and from 12.22 to 1.64 (reaction 2). In alkaline concentration higher than 8 mol/l plutonium(V) is stable for at least 1 week in solution. The dependence of K_d on NaOH concentration is linear in $\log(K_d)$–[NaOH] ordinates. The analytic form of this dependence has been calculated as: $K_d=K_d^0/e^{\alpha[NaOH]}$, when K_d^0 and α are constants.

3.3. Reproportionation of Pu(VI) and Pu(IV)

To investigate Pu(VI) and Pu(IV) reproportionation, known amounts of freshly precipitated Pu(IV) hydrous oxide and Pu(VI) in NaOH solution (1 to 10 M) were mixed at 40°C. The recorded absorption spectra stabilized after 4 h and the final Pu(VI) concentrations were determined. The equilibrium constant for the reproportionation, K_r, then was calculated by the formula:

$$K_r = [Pu(V)]^2/(S[Pu(VI)]\cdot[OH^-]^n)\ , \text{ where } n = 3 \text{ or } 4.$$

The K_d and $1/K_r$ in reactions 1 or 2 are linearly dependent on NaOH activity but are not identical. This disparity reveals complex mechanisms existing in the heterogeneous formation of plutonium hydrous oxide and its subsequent interactions with dissolved species. Related studies show sorption of Pu(V) on Pu(IV) hydrous oxide occuring in NaOH solution [13]; α-radiolytic reactions also may affect oxidation state at extended contact times.

3.4. The Pu(V)/Pu(IV) reduction potential

The dis- and reproportionation data may be used to calculate the potential of the Pu(V)/Pu(IV) electrode pair. The equilibrium constants, K_d and K_r, can be used to assess the thermodynamic characteristics of the disproportionation and reproportionation processes. The free energy, G, is related to the equilibrium constant and electrode

Table 1
Disproportionation/reproportionation equilibrium constants at 40°C and the formal potential of the Pu(V)/Pu(IV) pair. Disproportionation: 2Pu(V)=Pu(IV)+Pu(VI); $K_d=[\mathrm{Pu(VI)}]\cdot[\mathrm{Pu(IV)}]\cdot[\mathrm{OH}^-]^n/[\mathrm{Pu(V)}]^2$. Reproportionation: Pu(VI)+Pu(IV)=2Pu(V); $K_r=[\mathrm{Pu(V)}]^2/[\mathrm{Pu(VI)}]\cdot[\mathrm{Pu(IV)}]\cdot[\mathrm{OH}^-]^n$

[NaOH], M	[Pu(VI)] M	[Pu(V)] M	[Pu(IV)] = S[a], M	$E^b_{\mathrm{VI/V}}$, V	$E_{\mathrm{V/IV}}$, V from reaction (1) $n=3$	$E_{\mathrm{V/IV}}$, V from reaction (2) $n=4$
From disproportionation data						
4.00	6.0×10^{-3}	2.7×10^{-4}	5.8×10^{-7}	0.22	0.26	0.29
6.60	1.2×10^{-3}	9.3×10^{-4}	2.8×10^{-6}	0.215	0.21	0.27
8.02	6.7×10^{-4}	2.4×10^{-3}	3.4×10^{-6}	0.21	0.17	0.23
From reproportionation data						
4.00	1.9×10^{-3}	9.3×10^{-4}	5.8×10^{-7}	0.22	0.15	0.25
6.60	8.3×10^{-4}	1.2×10^{-3}	2.8×10^{-6}	0.215	0.20	0.19
8.02	9.0×10^{-4}	1.3×10^{-3}	3.4×10^{-6}	0.21	0.22	0.27

[a] Data from [12].
[b] Data from [4,14].

potential: $G=-RT\ln K_d=-nFE_f$; where n is the reaction's electron change (one in this case), F is the Faraday constant, and E_f is the potential change (in volts). Thus, $E_f=(0.000198T)\log K_d$ and $E_f=(-0.000198T)\log K_r$ for reproportionation data and equilibrium constant. The disproportionation reaction may be expressed as the sum of the respective oxidation and reduction half reactions for Pu(V)

$$\mathrm{Pu(V)} = \mathrm{Pu(VI)} + \mathrm{e}^-;\ E_{\mathrm{V/VI}}\text{, and } \mathrm{Pu(V)} + \mathrm{e}^- = \mathrm{Pu(IV)};\ E_{\mathrm{V/IV}}$$

to give

$$2\mathrm{Pu(V)} = \mathrm{Pu(VI)} + \mathrm{Pu(IV)} \text{ and } E_f = E_{\mathrm{V/VI}} + E_{\mathrm{V/IV}}.$$

Because the $E_{\mathrm{VI/V}}$ potential (which is the negative of $E_{\mathrm{V/VI}}$) has been measured in previous research [4,14] and E_f can be determined from K_d, the $E_{\mathrm{V/IV}}$ potential can be calculated and is $E_f-E_{\mathrm{V/VI}}$ or $E_f+E_{\mathrm{VI/V}}$. Results for disproportionation and similarly computed reproportionation data are listed in Table 1.

The calculated Pu(V) reduction potentials, $E_{\mathrm{V/IV}}$, given in Table 1 (from disproportionation data) indicate that Pu(V) should disproportionate in the range 4–8 M NaOH. This coincides with the experimental observations. The calculated $E_{\mathrm{V/IV}}$ from reproportionate data contradicts the experimental results and does not agree well with them. But we can make an important conclusion: the value of the oxidation potential of the pair Pu(V)/Pu(IV) in 4–8 M NaOH is in the range from 0.15 to 0.29 V. The large uncertainty in determination of $E_{\mathrm{V/IV}}$ is due to a lot of experimental difficulties of the studied system, especially there are questions about the behaviour of Pu(IV) in alkaline medium. It may be that Pu(IV) hydrous oxide has higher chemical activity under the experimental conditions in reactions with Pu(VI) and Pu(V). The actual Pu(IV) concentration (which determines the equilibrium) also may be greater than the solubility of Pu(IV) hydrous oxide exhibited in pure alkaline solutions.

Acknowledgements

This work was supported by the US Department of Energy, Office of Science and Technology, under the Office of Environmental Management.

References

[1] L.H. Gevantman, K.A. Kraus, Chemistry of plutonium(V). Stability and spectrophotometry, in: G.T. Seaborg, J.J. Katz, W.M. Manning (Eds.), The Transuranium Elements, National Nuclear Energy Series, Div. IV, vol. 14B, McGraw-Hill, New York, USA, 1949, pp. 500–518.

[2] K.A. Kraus, J.R. Dam, Hydrolytic behavior of plutonium(V). Acid constant of plutonyl ion, in: G.T. Seaborg, J.J. Katz, W.M. Manning (Eds.), The Transuranium Elements, National Nuclear Energy Series, Div. IV, vol. 14B, McGraw-Hill, New York, USA, 1949, pp. 478–485.

[3] V.P. Shilov, N.N. Krot, S.V. Kryutchkov, A.B. Yusov, N.A. Budantseva, A.G. Garnov, V.P. Perminov, L.N. Astafurova, L.I. Belyaeva, Investigation of some redox reactions of neptunium, plutonium, americium and technetium in alkaline media, WHC-EP-0886, Westinghouse Hanford Company, Richland, Washington, USA, 1996.

[4] J. Bourges, Preparation et identification du plutonium a l'etat d'oxydation-V en mileau basique, Radiochem. Radioanal. Lett. 12 (1972) 111–117.

[5] C.H. Delegard, Solubility of $\mathrm{PuO_2\cdot xH_2O}$ in alkaline Hanford high-level waste solution, Radiochim. Acta 41 (1987) 11–21.

[6] V.F. Peretrukhin, D.P. Alekseeva, Polarographic properties of higher oxidation states of plutonium in aqueous alkaline solutions, Sov. Radiochem. 16 (1974) 823–828.

[7] K.A. Kraus, Hydrolytic behavior of the heavy elements, in: Proceedings of the International Conference on the Peaceful Uses of Atomic Energy, Geneva, vol. 7, United Nations, New York, USA, 1956, pp. 304–318.

[8] J.P. Nigon, R.A. Penneman, E. Starizky, et al., J. Phys. Chem. 58 (1954) 403–404.

[9] I.G. Tananaev, Forms of existence of Pu(VI) and Am(VI) in alkaline medium, Sov. Radiochem. 31 (1989) 46–51.

[10] V.F. Peretrukhin, V.P. Shilov, A.K. Pikaev, Alkaline chemistry of transuranium elements and technetium and the treatment of alkaline radioactive wastes, WHC-EP-0817, Westinghouse Hanford Company, Richland, USA, 1995.

[11] V.F. Peretrukhin, S.V. Kryutchkov, V.I. Silin, I.G. Tananaev, C.H. Delegard, Stability of transuranium elements and technetium hydroxide compounds in NaOH solutions in the presence of redox- and complexing agents, in: Proceedings of the 211th American Chemical Society, New Orleans, USA, 1996, p. 204.

[12] V.F. Peretrukhin, S.V. Kryutchkov, V.I. Silin, I.G. Tananaev, Determination of the solubility of Np(IV)–(VI), Pu(III)–(VI), Am(III)–(VI) and Tc(IV),(V) hydroxo compounds in 0.5–14 M NaOH solutions, WHC-EP-0897, Westinghouse Hanford Company, Richland, Washington, USA, 1996.

[13] N.A. Budantseva, A.B. Bessonov, I.G. Tananaev, A.M. Fedoseev, C.H. Delegard, Capture of Pu(V), Np(V), and Pu(VI) from alkaline solutions by hydroxides of Pu(IV), Th(IV), and La(III), J. Alloys Comp. (1998) in press.

[14] V.P. Shilov, Oxidation of neptunium(VI) by plutonium(VI) in alkaline medium, Sov. Radiochem. 18 (1976) 592–593.