Plutonium in higher oxidation states in alkaline media

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Abstract

Experimental chemical and electrochemical properties of plutonium in strong alkaline solution are described. Using different chemical and electrochemical methods to determine plutonium oxidation state speciation, we suggest that during oxidation of Pu(VI) in alkaline media Pu(VIII) is produced in a mixture with Pu(VII). Probable values of molar extinction coefficient of Pu(VIII) at 635 nm, and Pu(VII) at 500–550 nm, were estimated as $\sim 2600 \pm 400$ and $\sim 100 \, M^{-1} \, cm^{-1}$, respectively. The yield of presumed Pu(VIII) in the experimental solution was estimated to be $\sim(15 \pm 5)\%$. From electrochemical calculations we estimate that the values of the reduction potential of Pu(VIII)/Pu(VII) and Pu(VII)/Pu(VI) pairs in 2 M NaOH are greater than 0.90 V, and 0.68 ± 0.05 V (vs. NHE), respectively. The possible presence of other unknown oxidations (such as Pu(VII) peroxo-compounds) that might give similar results are discussed. For uncontestable proof of existence of Pu(VIII) in alkaline solutions, advanced spectroscopic techniques should be employed.

Keywords: Actinides elements; Plutonium; Oxidation states; Stabilization

1. Introduction

In one of the earliest forms of the periodic system, Mendeleev illustrated a clear periodicity in the oxidation state of the elements [1], which in modern times is readily explained in terms of the electronic configuration and simple theories about chemical bonding. In the case of elemental plutonium, there are eight valence electrons with a valence electronic configuration of $5f^6 7s^2$ [2]. Plutonium forms compounds and complexes in oxidation states from Pu(III) to Pu(VII), but the penultimate oxidation state Pu(VIII), where all valence electrons have been removed, has never been definitively identified, in spite of various attempts over the past 40 years. In 2004, we reported that during oxidation of Pu(VI) with ozone in NaOH solutions to prepare Pu(VII), the electronic absorption spectra revealed time-dependent oscillations in the measured optical density of nearly 30% [3]. Pu(VII) in alkaline solution is characterized by a blue–black color and a distinct electronic absorption spectrum with a maximum at 635 nm [4,5]. The extinction coefficient is known to vary from 530 to 600 $L \, mol^{-1} \, cm^{-1}$, and this was historically attributable to experimental differences from different

laboratories. Changes in extinction coefficient reaching 30% had never been reported, and were likely due to the strong and vigorous ozonolysis conditions employed. Additional experiments employing strong ozonolysis conditions led to the conclusion that during Pu(VI) oxidation with ozone in alkaline solution, Pu(VII) is formed as the major product, and that a minor amount of Pu(VIII) is also produced [3]. In this report, we provide a series of new chemical and electrochemical experiments that more reliably support the proposal that Pu(VIII) can be prepared in small quantities during the preparation of Pu(VII) in alkaline solution.

2. Results and discussion

For complementary evidence for the possible formation of octavalent plutonium in a mixture with Pu(VII) in alkaline solutions, a number of additional experiments beyond those reported in reference [3] were performed.

2.1. Ozone oxidation of Pu(VI)

A 3.5 vol.% O_3/O_2 gas mixture (gas flow 5–7 dm^3/h) was added via bubbling to a pure solution of 2.9 mM Pu(VI) in 1.5 M NaOH at 20 °C over a 30 min period. This produces a

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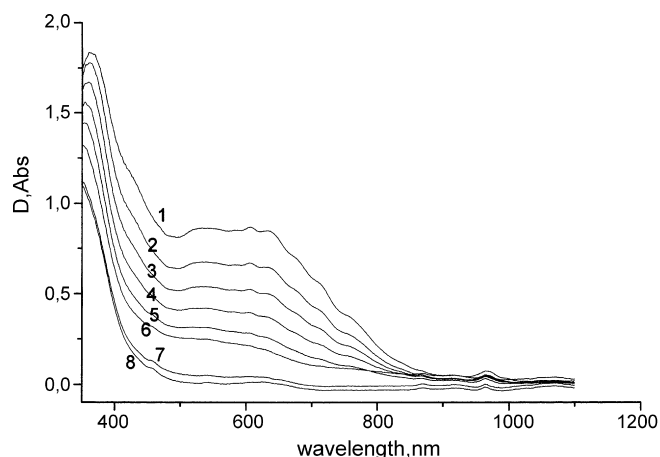*E-mail address:* tananaev@geokhi.ru (I.G. Tananaev).

Fig. 1. The absorption spectra of solution of 2.9 mM Pu(VI) in 1.5 M NaOH (1 ml) ozonizing within 60 min (1), and this mixture with 1.3 mM solution of Pu(VI) in 1.5 M NaOH: (2) 0.05 ml; (3) 0.1 ml; (4) 0.15 ml; (5) 0.2 ml; (6) 0.25 ml; (7 and 8) after storage within 30 and 90 min, respectively.

blue–black alkaline solution of nominal oxidation state Pu(VII) with a characteristic electronic absorption spectrum ($\lambda_{max} = 607$ and 635 nm) as reported previously [4,5]. Stepwise addition of 0.05-mL aliquots of a 1.3 mM Pu(VI) solution in 1.5 M NaOH to a 3 mL portion of the ozonized [colored, Pu(VII)] solution results in an immediate decrease in optical density of the blue–black solution. This decrease is proportional to the amount of Pu(VI) added (Fig. 1). One possible explanation for this unusual observation is that the ozonolysis of Pu(VI) in 1–3 M NaOH produces a mixture of Pu in two different oxidation states; of the previously known Pu(VII) and a small amount of hypothetical Pu(VIII). To account for the decrease in optical density with addition of Pu(VI), the proposed Pu(VIII) could react with Pu(VI) according to the stoichiometry of Eq. (1) as described previously [3].

$$Pu(VIII) + Pu(VI) \rightarrow 2Pu(VII) \tag{1}$$

Alternative explanations of the observed data include the possible formation of a mixed-valent Pu(VI)–Pu(VII) compound, or the formation of either ozonide or peroxy-complexes of Pu(VII), which can interact with the initial Pu(VI) under the stated conditions. To test for these possibilities, we prepared oxidized Pu(VI) solutions in the absence of ozone, and repeated the original experiments.

2.2. Electrochemical oxidation of Pu(VI)

Identical reactions between Pu(VI) and oxidized blue–black Pu solutions were carried out in 2 M NaOH solution, with the exception that the oxidation of Pu(VI) was performed electrochemically.

The electrochemical cell consisted of a Pt anode ($S = 81$ cm^2), Pt cathode ($S = 25$ cm^2), and Hg|HgO reference electrode; where the electrodes were separated from each other by porous glass frits. The reduction potential of Hg|HgO reference electrode in alkaline solution is known to be +0.0984 V relative to the Normal Hydrogen Electrode (NHE) in 1 M NaOH at 25 °C [6].

The electrochemical potentials were measured by an APPA-305 multimeter, and absorption spectra were recorded using a Cary 100 UV–vis spectrophotometer. A solution containing 3.85 mM Pu(VI) in 2 M NaOH was electrolyzed at 1.0 V (relative to Hg|HgO) for 150 min, during which time the initial yellow–green solution of Pu(VI) changed gradually to dark blue. To this freshly-prepared dark blue solution was added aliquots of the original (non-electrolyzed) Pu(VI) solution in 2 M NaOH as previously described [3].

As in the previous experiment, the optical absorbance between 500 and 700 nm of the electrochemically oxidized blue–black solution decreased instantly upon addition of small aliquots of the 3.85 mM Pu(VI) solution in 2 M NaOH. The observed changes in the electronic absorption spectra were identical to those observed when ozone was used as the oxidant. These data strongly suggest that the observed changes in optical density of the oxidized form of plutonium are not due to the presence of ozone or its reaction products.

The data obtained from both ozonolysis and electrochemical oxidation experiments support our original conclusion regarding the possibility of Pu(VIII) formation in oxidized alkaline solutions of Pu(VI) [3].

Knowing the initial Pu(VI) concentration in the first aliquot (0.05 mL $\times$ 1.3 mM = 6.5×10^{-5} mmol), and the magnitude of decrease in optical density of the mixture at 635 nm ($\Delta D \sim 0.18$) from Fig. 1, a probable value of the molar extinction coefficient (ε) of Pu(VIII) can be estimated as $\sim 2600 \pm 400$ M^{-1} cm^{-1}. The extinction coefficient of Pu(VII) in the 500–550 nm range was then found to be ~ 100 M^{-1} cm^{-1}. From these data the yield of presumed Pu(VIII) in the experimental solution was estimated to be $\sim (15 \pm 5)\%$ [3].

2.3. Neptunium analog studies

To further test for the possible presence of mixed-valent compounds, or complexes of ozone or peroxide, pure solutions of the analogous Np(VI) and Np(VII) ions in 1 M NaOH were studied. Heptavalent neptunium in 1.5 M NaOH was prepared by ozone oxidation of Np(VI) with 3.5 vol.% O$_3$/O$_2$ mixture (gas flow 5–7 dm^3/h, 20 °C) over a 30 min period using the same experimental conditions employed for oxidation of Pu(VI) [4]. The optical density of colored (ozonized) Np(VII) solution at 620 nm decreased only slightly because of the dilution of the experimental solution upon addition of Np(VI). If mixed-valent Np(VI)–Np(VII) compounds were formed under these conditions, their existence does not affect the optical density of neptunium solutions.

2.4. Redox reaction with Np(VI)

The interaction of 0.2-mL aliquots of freshly ozonized 1.8 mM Pu(VI) in 2 M LiOH with 1 mL of 5 mM Np(VI) in 2 M LiOH was examined. Addition of an ozonized Pu(VI) solution to Np(VI) results in the appearance of an electronic absorption band at 620 nm, typical for Np(VII) solutions (Fig. 2) [4]. Knowing the concentration of Pu in the added aliquot, and the concentration of Np(VII) in the test solution, it was possible to calculate the
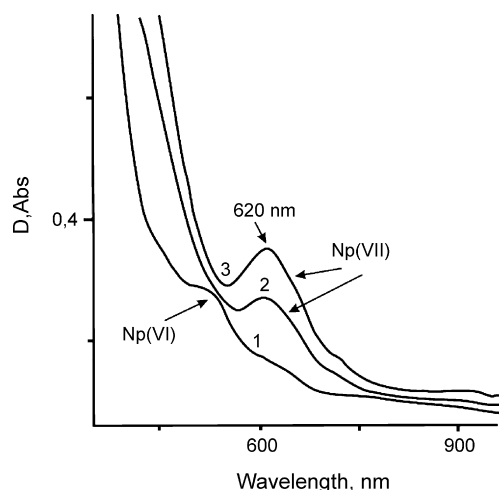
Fig. 2. Absorption spectra of 5 mM Np(VI) (0.9 ml) solution in 2 M LiOH (1); after consequent addition of 1.8 mM ozonized solution of Pu(VI): (2) 0.2 ml; (3) any more 0.2 ml.

ratio of Np:Pu $\sim$1.2 ± 0.1 (the results of three parallel experiments). Note, that if only Pu(VII) were present in ozonized 2 M LiOH solution, the resulting ratio of Np(VII):Pu(VI) in the experiments above must be 1:1 as indicated in Eq. (2).

$$Np(VI) + Pu(VII) \leftrightharpoons Np(VII) + Pu(VI) \qquad (2)$$
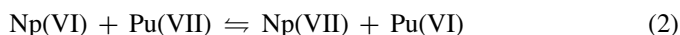
The fact that the observed Np(VII):Pu(VI) ratio was found to be 1.2 ± 0.1 (20% greater than the expected ratio of 1:1) suggests that there must be $\sim$20 ± 10% of Pu(VIII) or an unknown complementary oxidizing agent in the ozonized Pu(VI) solution. This closely mirrors the results of spectrophotometric titration of ozonized and non-ozonized solutions of Pu(VI) in alkaline media which suggested approximately 15 ± 5% of Pu(VIII) or an unknown oxidizing agent (see above).

2.5. Redox reactions with Fe(VI) and Fe(III)

The room temperature stepwise addition of two 0.2-mL aliquots of a 2 mM Pu(VI) solution in 1 M NaOH to 1 mL of 0.3 mM red–violet Fe(VI) solution in 1 M NaOH resulted in a $\sim$50% decrease in the optical density of the ferrate solution during the time of mixing (Fig. 3, spectra 1 and 3, respectively), and decolorization of the initial red–violet Fe(VI) solution (spectrum 3), respectively. The addition of a third 0.2-mL portion of 2 mM Pu(VI) in 1 M NaOH to the Fe(VI) solution caused no further change in the absorption spectrum (spectrum 4). These data indicate that complete reduction of Fe(VI) took place by Pu(VI) species. No change in the spectrum of a separate 0.3 mM Fe(VI) in 1 M NaOH solution was noticed during the time-frame of the experiment. Therefore, we conclude that Fe(VI) had oxidized Pu(VI) in 1 M NaOH to an oxidation state higher than Pu(VI). The plutonium absorption spectrum 3 (Fig. 3) attributed to oxidization by Fe(VI), had no intense absorbance bands attributable to Fe(VI), and corresponded to the spectra observed after interaction of equimolar amounts of ozonized and non-ozonized Pu(VI) solutions in alkaline media (see Fig. 1, spectra 7, and 8).
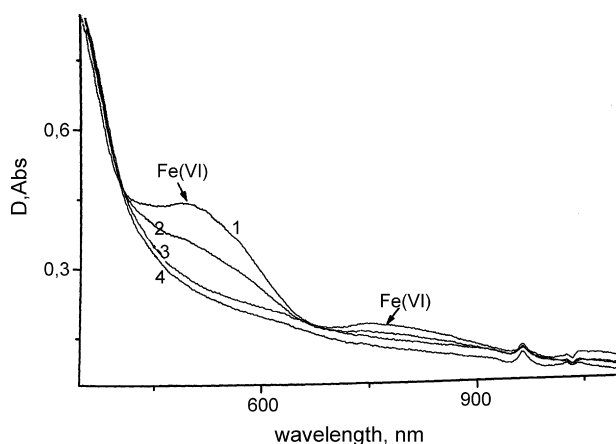

Fig. 3. The absorption spectrum of solution 0.3 mM Fe(VI) in 1 M NaOH (1 ml) (1); and a mixture of this solution with 2 mM Pu(VI) in 1 M NaOH: (2) 0.2 ml; (3) 0.4 ml; (4) 0.6 ml.

In a subsequent experiment it was found that addition of 0.05-mL aliquots of slightly acidic 1 mM Fe(III) to the blue–black just-ozonized solution of Pu(VI) in 1 M NaOH led to a decrease in optical density of the mixture (Fig. 4, spectrum 2). Further addition of 0.05-mL aliquots of 1 mM Fe(III) to the test solution resulted in considerable change in absorption spectra with a simultaneous color change of the solution to red–violet. The resulting absorption (Fig. 4, spectrum 3), and concomitant color change were attributable to the appearance of Fe(VI) ions in alkaline media. The decolorization of this solution proceeded only after $\sim$40 min at room temperature, probably due to the reduction of Fe(VI) by water. If we assume that the freshly ozonized blue–black solution of Pu(VI) in 1 M NaOH contains only heptavalent plutonium, then the reaction in Eq. (3) should
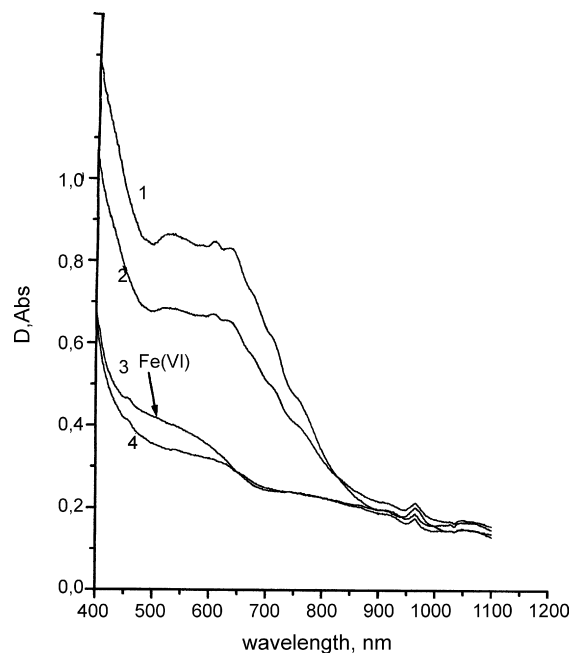

Fig. 4. The absorption spectra of ozonizing solution of Pu(VI) in 1 M NaOH (1) and this mixture with 1 mM Fe(III) solution in 1 M NaOH: (2) 0.05 ml; (3) 0.10 ml; (4) spectrum of mixture (3) after 40 min storage.
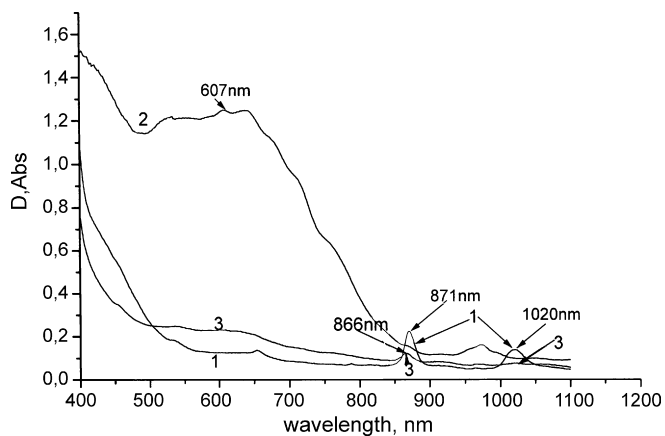
Fig. 5. Absorption spectra: initial 1.8 mM Pu(VI) in 0.45 M NaOH (1); the same solution after 1 h ozonization (2); ozonized solution after interaction with 0.05 ml 2 M NaNO$_2$ (3).

take place following the addition of Fe(III):

$$3Pu(VII) + Fe(III) \rightarrow 3Pu(VI) + Fe(VI) \qquad (3)$$

However, in the previous experiment it was found that coexistence of Pu(VI) and Fe(VI) ions was impossible, so that reaction (3) could not be realized. Hence, the appearance of Fe(VI) under these conditions suggests the presence of an additional oxidant, presumably Pu(VIII), in the blue–black just-ozonized solution of Pu in 1 M NaOH. Knowing that ferrate-ions oxidize Pu(VI) ions easily in 1 M NaOH solutions; and that $E_{Fe(VI)/Fe(III)}$ is 0.72 V (vs. NHE) [7,8], we could estimate the upper limit of the Pu(VII)/Pu(VI) oxidation potential under these conditions to be less than 0.72 V (NHE). Since the Am(VI)/Am(V) reduction potential in 1 M NaOH is equal to 0.65 V (vs. NHE) [5], and Am(VI) does not oxidize Pu(VI) under tested conditions, the lower limit of $E_{Pu(VII)/Pu(VI)}$ oxidation potential exceeds 0.65 V (vs. NHE). Hence, the value of $E_{Pu(VII)/Pu(VI)}$ is in the interval from 0.65 to 0.72 V, and the average value is 0.685 ± 0.35 V (vs. NHE) as was described earlier [9].

2.6. Redox reactions with nitrite and manganate(VI)

When an equimolar mixture of ozonized Pu(VI) solution is reacted with 0.1 M NO$_2^-$ in less than 1 M NaOH media, the electronic absorption spectrum shows neither intensive absorbance bands at 607, and 635 nm [proposed for the spectrum of Pu(VIII)], nor maxima of absorbance at 655, 871 and 1021 nm (known for alkaline solutions of Pu(VI) at the indicated concentrations of NaOH) (Fig. 5). Presumably, the initial ozonized solution comprises a mixture of Pu(VII) and Pu(VIII), but nitrite ions interact only with Pu(VIII) producing Pu(VII). Pu(VII) has weak absorption in the range of 500–800 nm, which corresponds to our data obtained earlier (see, for example, Fig. 1). During the interaction of the above solution with Mn(VI) (as MnO$_4^{2-}$ ions) in 0.5 M NaOH, the intensive crimson coloration of Mn(VII) was observed (Fig. 6, spectrum 3). In a parallel experiment, it was found that Pu(VI) did not interact with Mn(VI) under these solution conditions. Hence, it is suggested that the formation of
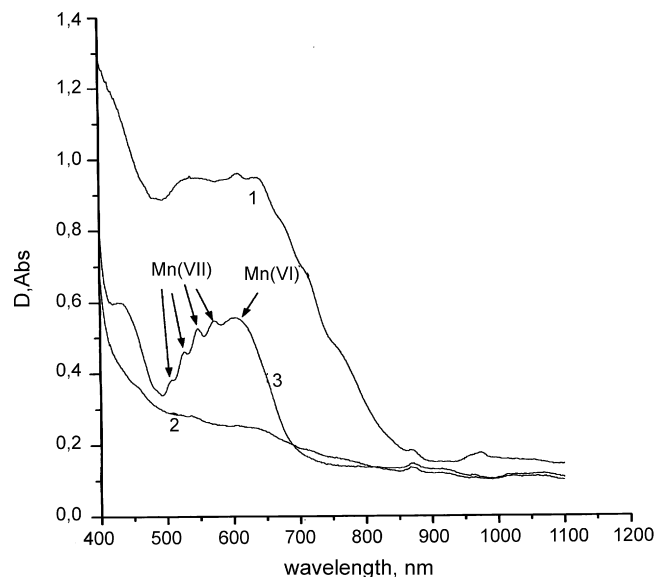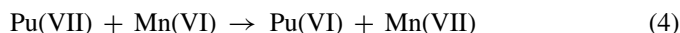

Fig. 6. Absorption spectra: 1 h ozonizing 1 mM Pu(VI) in 0.5 M NaOH (1); the same solution after addition of 0.005 mmol of NaNO$_2$ (2); with the following consequent introduction of 0.001 mmol of K$_2$MnO$_4$ (3).

Mn(VII) is explained only by Eq. (4).

$$Pu(VII) + Mn(VI) \rightarrow Pu(VI) + Mn(VII) \qquad (4)$$

All of the data strongly suggest that Pu(VIII) is formed during ozonizing of Pu(VI) in alkaline solutions. The alkaline solutions of Pu(VIII) has the characteristic absorption spectra with the main maxima at 607 and 635 nm, that earlier was attributed to absorption of Pu(VII) [4,5].

2.7. Direct electrochemical methods

After electrochemical oxidation of Pu(VI) in 2 M NaOH, chronopotentiometric measurements of the resulting solution were carried out in the current-off regime. The change in anode potential with time is shown in Fig. 7. The experimental plot consists of three parts, indicating that the reduction of the oxidized forms of Pu by water has a complicated character. At early time, the reaction starts out with a slow decrease of the anodic potential at the initial part of the curve (Fig. 7, part I). The curve
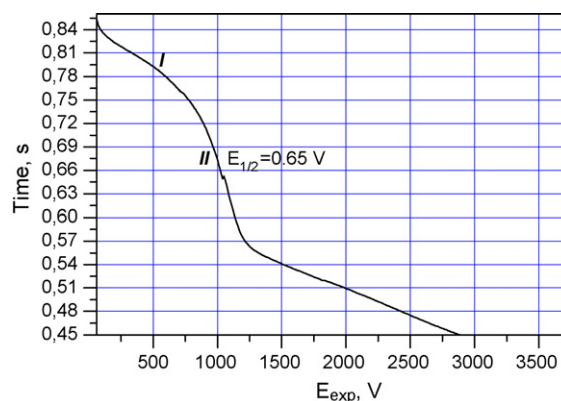

Fig. 7. The chronopotentiometric measurements of electrochemically oxidized Pu(VI) solution in 2 M NaOH. Changing of an anode potential in time.

then experiences a sharp change in the potential by $\sim$200 mV (Fig. 7, part II). We suggest that the chronopotentiometric curve indicates the presence of Pu in solution in at least two oxidation states, with reduction by water at different reaction rates. The values of reduction potentials of the Pu(VIII)/Pu(VII) and Pu(VII)/Pu(VI) couples were estimated to be higher than the reduction potential of oxygen release from water, therefore both components should be reduced by water molecules as outlined in Eqs. (5) and (6):

$$Pu(VIII) + H_2O \rightarrow Pu(VII) \qquad (5)$$

$$Pu(VII) + H_2O \rightarrow Pu(VI) \qquad (6)$$
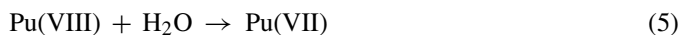
However, these processes do not explain the sharp change in the character of the process for parts (I) and (II) of the plot, seen clearly in Fig. 7. We suggest that the slow decline of the value of the anodic potential at the initial part of the plot (I) may be caused by the generation of an additional product with a high value of reduction potential, but which is lower than the potential of Pu(VIII). One pathway that might account for the observed results is the generation of additional Pu(VII) as outlined in Eq. (1) [3].

In this way, as the amount of Pu(VIII) decreases with time, the relative contributions of reactions (1) and (5) is also decreasing. At the same time, the contribution of reaction (6) is increasing, and that reaction causes a change in the character of the plot. Finally, when the concentration of Pu(VIII) becomes negligible, the change in anodic potential is defined only by the reaction (6) (part II of the chronopotentiometric curve). The beginning of the linear part of the curve (II) corresponds to the moment of disappearance of Pu(VIII) in solution ($E_{exp} = 0.69$ V), that was confirmed by parallel spectrophotometric measurements. This part of the chronopotentiometric curve can be stipulated only by the reaction (6). According to Eq. (7), the change of potential takes place only because of the change of concentration of Pu(VII) in solution.

$$E_{exp} = E_f + (RT)/T \ln([Pu(VII)]/[Pu(VI)]) \qquad (7)$$

Hence, it was necessary to find the point of equal concentrations of oxidized and reduced forms in order to estimate the value of the formal potential of the Pu(VII)/Pu(VI) couple ($E_{exp} = E_f$). The rate of change of reduction potential, found from the experiment for the linear part of the curve was 4.98×10^{-4} V/s. Therefore, differentiating Eq. (7) over time it is possible to determine the rate of reduction of Pu(VII) to Pu(VI) to be 1.87×10^{-5} M/s. In this way, we determined that $E_f = 0.638$ V + 0.098 V = 0.736 V (vs. NHE) for 2 M NaOH. The value of the formal reduction potential E_f for couple Pu(VII)/Pu(VI) using the spectrophotometric approach was estimated earlier as 0.68 ± 0.04 V (vs. NHE) [3], and these data are in close agreement with the E_f for Pu(VII)/Pu(VI) determined from the electrochemical results. As to the value of the reduction potential of Pu(VIII)/Pu(VII) pair, looking at Fig. 7, it is likely higher than 0.90 V (vs. NHE) in 2 M NaOH.

The chronopotentiometric technique has allowed us to distinguish clearly that two oxidized forms exist in alkaline solutions as a result of oxidation of Pu(VI). A similar result was difficult to obtain by spectrophotometry because either Pu(VIII) or Pu(VII) undergo reduction by water and the main absorbance bands of both forms are located in absorption spectra at the same wavelengths.

In summary, the series of chemical and electrochemical experiments is consistent with the existence of two oxidation states of plutonium after chemical oxidation of Pu(VI) by ozone, or electrochemical oxidation of Pu(VI) in alkaline media. We submit that these data further support our original proposal that oxidation of Pu(VI) in NaOH solution produces predominantly Pu(VII) and a small but significant concentration of Pu(VIII). The values of the molar extinction coefficients (ε) of Pu(VIII) at 635 nm, and Pu(VII) at 500–550 nm, were estimated as $\sim$2600 $\pm$ 400 and $\sim$100 M^{-1} cm^{-1}, respectively. The yield of the assumed Pu(VIII) in the experimental solution is estimated to be $\sim$(15 $\pm$ 5)%. Finally, we admit that it is impossible to completely exclude the possibility of formation of Pu(VII) peroxy-complexes during Pu(VI) oxidation by ozone or electrochemically. For uncontestable proof of the existence of Pu(VIII) in alkaline solutions, we look forward to the application of advanced spectroscopic techniques such as electronic paramagnetic resonance, EXAFS, XANES, Raman, or multinuclear NMR.

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