

Experimental data points to the existence of plutonium(VIII) in alkaline solutions

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The ozonising of an alkaline Pu^{VI} solution resulted in the formation of both Pu^{VII} and Pu^{VIII}, and the black-blue colour earlier was ascribed to Pu^{VII}.

The ozonization of hydroxide suspensions or a solution of Pu^{VI} in 1–3 M NaOH is the most widely used method for the preparation of Pu^{VII} solutions.^{1,2} As the result, blue-black solutions with a characteristic absorption spectrum ($\lambda_{\text{max}} = 635 \text{ nm}$) are formed. Previously,^{1–4} it was found that the reaction of Pu^{VI} with O₃ occurs with the yield of about 100%. On this basis, Krot and co-authors^{1–4} performed the redox titration of a plutonium solution after ozonization reaction by H₂O₂, and concluded that only Pu^{VII} was formed under these conditions. The molar extinction coefficient (ϵ_{635}) of plutonium solutions, obtained^{1–4} as the result of ozone oxidation of Pu^{VI}, is 530–600 dm³ mol^{−1} cm^{−1}.

We carried out experiments to oxidise Pu^{VI} by ozone in NaOH solutions using a Tekhnozon ozonizer (Russia), where the concentration of O₃ in a mixture with O₂ was 3.5 vol% and the gas flow rate was 5–7 dm³ h^{−1} at 20 °C. It was shown that oscillations of the optical density of plutonium solutions took place after oxidation of 2.9 mM Pu^{VI} in 1.5 M NaOH with ozone for ≥ 30 min. The oscillations reached up to 30% of the maximum absorbance (Figure 1) that is much more than the experiment accuracy (Shimadzu UV-160). The same data were obtained under ozonization of a Pu^{VI} suspension in 0.7 and 3.5 M NaOH solutions.

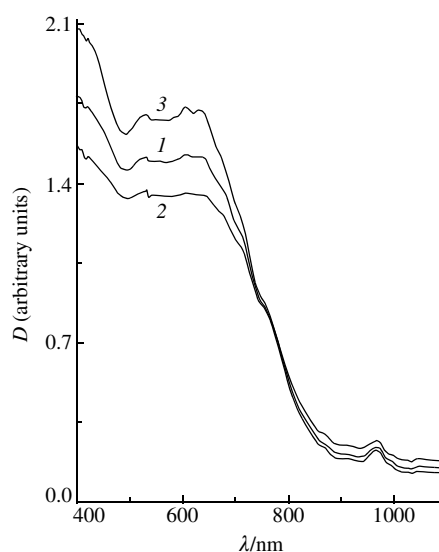


Figure 1 The absorption spectra of Pu^{VI} solution in 3.5 M NaOH during ozonization for (1) 42, (2) 45 and (3) 47 min.

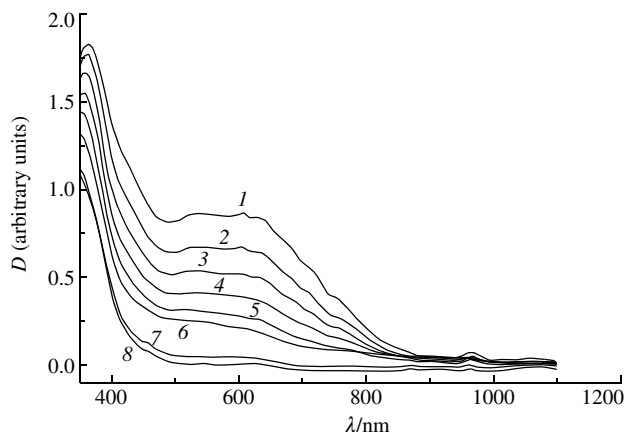


Figure 2 The absorption spectra (1) of solution of 2.9 mM Pu^{VI} in 1.5 M NaOH (1 ml), ozonised for 60 min, and its mixture with (2) 0.05, (3) 0.1, (4) 0.15, (5) 0.2, (6) 0.25 ml of 1.3 mM solution of Pu^{VI} in 1.5 M NaOH; and after storage for (7) 30 and (8) 90 min.

The data show that the previous determinations of the oxidation states of Pu after ozonization^{1–4} could not be accurate because a mixture of Pu^{IV} and Pu^{VII} has been used for redox titration. We carried out additional experiments in order to elucidate the nature of ozonization reactions with Pu^{VI}.

In the typical experiment at room temperature, the aliquots (0.05 ml) of a 1.3 mM Pu^{VI} solution in 1.5 M NaOH were added to 1 ml of a 2.9 mM Pu^{VI} solution, which was ozonised in 1.5 M NaOH for 60 min. The ozonised solution had a dark blue colour. The spectra of solutions were recorded at 400–800 nm (Figure 2). Another part of the ozonised Pu^{VI} solution was used as a reference. It was found that the optical density of a plutonium solution treated with ozone decreased proportionally to the amount of the added solution of Pu^{VI} (with a correction for dilution). No changes in the band positions or intensities were detected in the reference solution during the experiment. The results suggest the interaction between the ozonised plutonium(VI) solution in NaOH and the initial non-ozonised Pu^{VI}.

The above reaction also takes place if Pu^{VI} is applied as the solid-state Pu^{VI}O₃·H₂O hydroxide. The experiment is as follows: ~5 mg of Pu^{IV} hydroxide, precipitated by means of ammonia from a nitric acid solution and washed twice with distilled water, was synthesised. An aqueous suspension of Pu^{IV} hydroxide (pH ~ 7.5) was ozonised for 60 min. The completeness of Pu^{IV} hydroxide oxidation into PuO₃·H₂O was controlled by well-known spectrophotometric techniques.^{1–4} A part of the obtained

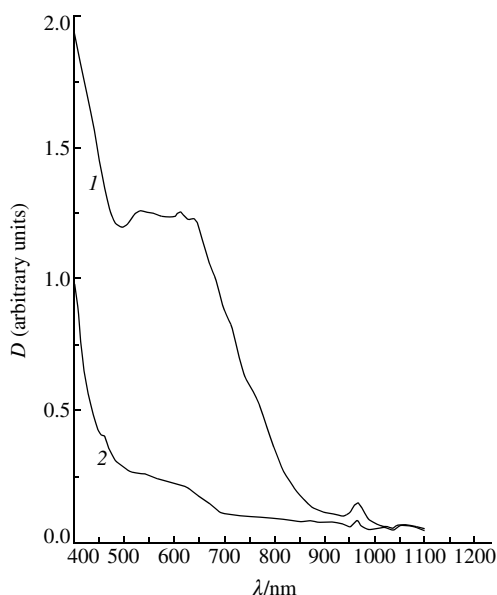


Figure 3 The absorption spectra of Pu^{VI} solution in 3.5 M NaOH (1) after ozonization for 42 min, 3.5 vol% O₃ and the gas flow 5–7 dm³ h⁻¹ at 20 °C; (2) after the interaction with excessive amount of solid state PuO₃·H₂O.

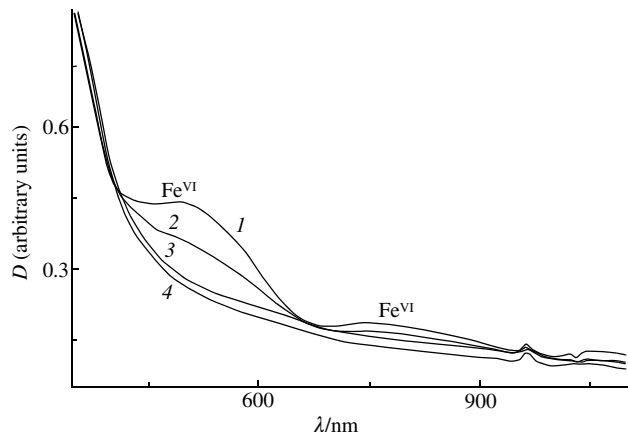


Figure 4 The absorption spectra of a mixture of solution 0.3 mM Fe^{VI} in 1 M NaOH (1 ml) and solution of 2 mM Pu^{VI} in 1 M NaOH: (1) 0, (2) 0.2, (3) 0.4 and (4) 0.6 ml.

PuO₃·H₂O precipitate was dissolved completely in 3 M NaOH. This solution of Pu^{VI} was ozonised for 40 min (the absorption spectrum of the solution is shown in Figure 3, spectrum 1). Then, the PuO₃·H₂O precipitate was treated with the ozonised Pu^{VI} solution. After mixing for ~10 s, the solution was centrifuged to record the absorption spectrum (Figure 3, spectrum 2). The absorbance in the wavelength range 500–700 nm decreased ~10 times as a result of the interaction between the ozonised solution and the PuO₃·H₂O precipitate. On the other hand, a noticeable amount of the precipitate remained unaffected.

It was supposed that the Pu^{VI} interacted with Pu^{VIII}, with accumulated in the plutonium-containing ozonising alkaline solution, by the following scheme:



This supposition is based on the possibility of formation of a Pu^{VII} and Pu^{VIII} mixture during plutonium(VI) ozonization in alkaline solution. Hence, spectrum 2 in Figure 2 can be considered as the characteristic spectrum of Pu^{VII} in 3 M NaOH. A short time of the experiment (< 5 min) allows us to believe that only a small excess of Pu^{VI} could be accumulated in the solution in spite of a rather high solubility of PuO₃·H₂O in alkaline solutions because the equilibrium state could not be reached in this time.

Additionally, the spectrophotometric titration of the product formed as the result of reaction (1) by hydrogen peroxide was carried out to identify its oxidation state. Aliquot portions

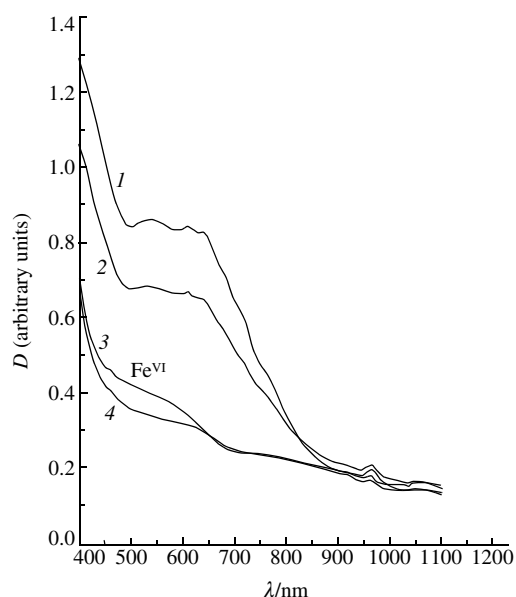
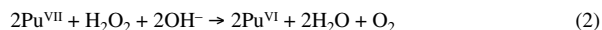


Figure 5 The absorption spectra of (1) ozonised solution of Pu^{VI} in 1 M NaOH and its mixture with 1 mM Fe^{III} solution in 1 M NaOH: (2) 0.05 and (3) 0.10 ml; (4) spectrum of a mixture (3) after 40 min storage.

0.05 ml of 5.2×10^{-3} M H_2O_2 were added to 1.5 ml of the plutonium solution obtained [reaction (1)]. The addition of H_2O_2 causes well-seen changes in the spectra of the test solution. The stoichiometric ratio $[\text{Pu}]:[\text{H}_2\text{O}_2]$, determined after the titration, was found to be 2.2:1. This ratio corresponds to the following reaction:



The data obtained can confirm that Pu in the tested solution was mainly in an oxidation state of +7. The slightly increased experimental value of the ratio $[\text{Pu}]:[\text{H}_2\text{O}_2]$ can be explained by the errors in the determination of reactant concentrations and by the presence of an inconsiderable amount of Pu^{VI} in solution. The total amount of Pu in the tested solution was determined after the treatment of the alkaline solution with 1 M HNO_3 by the absorbance at 830 nm. The spectrum did not show the presence of any valent forms of Pu, besides Pu^{VI} .

It was shown that the addition of 0.2 ml of a 2 mM Pu^{VI} solution in 1 M NaOH to 1 ml of 0.3 mM Fe^{VI} solution in 1 M NaOH at room temperature leads to a decrease in the optical density of ferrate solution down to ~50% during the time of mixing (Figure 4, spectra 1 and 2, respectively). The addition of the next aliquot (0.2 ml) of 2 mM Pu^{VI} in 1 M NaOH solution leads to decolouration of the solution (Figure 4, spectrum 3). The addition of the next portion of a 2 mM Pu^{VI} solution in 1 M NaOH (0.2 ml) did not change the absorption spectrum (Figure 4, spectrum 4); thus, the complete reduction of ferrate ions takes place. No changes in the spectrum of a reference solution of Fe^{VI} were detected during the time of the experiment.

On the basis of the obtained results, we conclude that ferrate ions oxidise Pu^{VI} in 1 M NaOH. This fact contradicts to the known information that redox potentials of the pairs $\text{Pu}^{\text{VII}}/\text{Pu}^{\text{VI}}$ and $\text{Fe}^{\text{VI}}/\text{Fe}^{\text{III}}$ in 1 M NaOH are equal to 0.85¹ and 0.72 V, respectively.^{5,6} In the typical experiment, the solution of Pu^{VI} in 1 M NaOH was ozonised for 60 min up to the formation of a bluish black solution, having a well-known absorption spectrum¹ (Figure 5, spectrum 1). After that, the aliquots (0.05 ml) of a slightly acidic 1 mM Fe^{III} solution were added to the ozonised blue-black solution of plutonium. It was found that the optical density decreased after the addition of the first aliquot (Figure 5, spectrum 2). The addition of the next 0.05 ml of a 1 mM Fe^{III} solution causes a further decrease in the absorbance. Simultaneously, the solution acquires a red-violet colour, and the bands characteristic of ferrate ions are observed in the spectrum of the solution (Figure 5, spectrum 3). The decolouration of the solution occurred during 40 min at room temperature, probably, due to the reduction of ferrate ions by water molecules.

Supposing that Pu^{VI} can be oxidised only to a heptavalent state under ozonization of an alkaline solution, the reaction



takes place after Fe^{III} addition. However, as it was found previously, Pu^{VI} can be easily oxidised by ferrate ions.

Based on the above data, we can make the following conclusions:

(1) The oscillations of the concentrations of plutonium ions, which reached 30% of a maximum value, take place under the ozonization of plutonium solutions (for more than 30 min) with NaOH concentrations of 0.7–3.5 M.

(2) Plutonium(VI) solutions, after oxidation by ozone in alkaline media, interact with non-ozonised Pu^{VI} solutions. We supposed that reaction (1) results in a mixture of Pu^{VIII} with Pu^{VII} .

(3) Pu^{VI} solutions can be oxidised by ferrate ions in 1.5 M NaOH. On the other hand, the ozonised plutonium solutions oxidise Fe^{III} to Fe^{VI} . These data contradict to the known behaviour of plutonium ions in the highest oxidation states in alkaline solutions. As ferrate ions oxidise Pu^{VI} ions, we conclude that the redox potential of the pair $\text{Pu}^{\text{VII}}/\text{Pu}^{\text{VI}}$ is lower than 0.72 V (vs. NHE). As the redox potential of the pair $\text{Am}^{\text{VI}}/\text{Am}^{\text{V}}$

in 1 M NaOH is equal to 0.65 V, and Am^{VI} does not oxidise Pu^{VI} under these conditions,¹ $E_{\text{Pu}^{\text{VII}}/\text{Pu}^{\text{VI}}}$ exceeds this value and, hence, lies in the range 0.685 ± 0.35 V (vs. NHE).

(4) Knowing the amount of Pu^{VI} that (Figure 2, spectra 1 and 2) interacted with plutonium treated with ozone (0.05 ml \times 1.3 mM = 6.5×10^{-5} mmol) and the decrease of the optical density of the mixture at 635 nm (~0.18), the molar extinction coefficient of Pu^{VIII} was estimated at 2600 ± 400 dm³ mol⁻¹ cm⁻¹. The value of $\epsilon_{\text{Pu}^{\text{VIII}}}$ at the chosen wavelength 500–550 nm was found to be ~100 dm³ mol⁻¹ cm⁻¹. It was supposed that the extinction coefficient of Pu^{VII} about 530 dm³ mol⁻¹ cm⁻¹ detected from the previous work¹ is the average value as the ϵ of a mixture of Pu^{VII} and Pu^{VIII} . Using the parameters $\epsilon_{\text{Pu}^{\text{VII}}} + \epsilon_{\text{Pu}^{\text{VIII}}} = 530$ dm³ mol⁻¹ cm⁻¹; $\epsilon_{\text{Pu}^{\text{VII}}} = 100$ dm³ mol⁻¹ cm⁻¹; and $\epsilon_{\text{Pu}^{\text{VIII}}} = 2600$ dm³ mol⁻¹ cm⁻¹, the $\epsilon_{\text{Pu}^{\text{VII}}}/\epsilon_{\text{Pu}^{\text{VIII}}}$ ratio must be about 0.25; from these calculations, the yield of Pu^{VIII} in the experimental solution was estimated at ~(15±5)%.

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