

## Specific oscillations upon $\gamma$ -radiolysis of alkaline aqueous solutions of neptunium and plutonium ions

Andrei V. Gogolev, Vladimir P. Shilov and Alexei K. Pikaev\*

Institute of Physical Chemistry, Russian Academy of Sciences, 117915 Moscow, Russian Federation. Fax: + 7 095 335 1778

$\gamma$ -Radiolysis of alkaline aqueous solutions of  $\text{Np}^{\text{VI}}$ ,  $\text{Np}^{\text{V}}$  and  $\text{Pu}^{\text{VI}}$  ions results in specific oscillation in the form of the periodic decrease and increase in the optical density of the solution.

An oscillation variation of the concentrations of radiolysis products takes place upon irradiation of aqueous solutions of  $\text{MgCl}_2$ ,  $\text{LiCl}$ ,  $\text{RbCl}$ ,  $\text{CsCl}$ ,  $\text{CaCl}_2$ ,  $\text{SrCl}_2$ ,  $\text{LiBr}$ ,  $\text{KBr}$ ,  $\text{SrBr}_2$  and  $\text{KI}$ ,<sup>1,2</sup> phosphomolybdic, silicomolybdic and silicotungstic acids,<sup>3</sup> aqueous and alcoholic solutions of  $\text{Co}^{\text{II}}$ ,  $\text{VO}^{2+}$ ,  $\text{Zn}^{\text{II}}$ ,  $\text{Mg}^{\text{II}}$  and  $\text{Mn}^{\text{II}}$  phthalocyanine complexes<sup>4,5</sup> and aqueous solutions of peroxidase from horseradish roots.<sup>6</sup> The oscillation variations in the rate of low-temperature radiation-induced chain hydrobromination of ethylene has also been described.<sup>7</sup>

We obtained specific oscillations consisting in the periodic decrease and increase in the optical density of the solution upon  $\gamma$ -radiolysis of alkaline aqueous solutions of neptunium and plutonium ions. This effect was due to the decrease in the optical density, caused by radiolytic reduction of  $\text{Np}^{\text{VI}}$ ,  $\text{Np}^{\text{V}}$  and  $\text{Pu}^{\text{VI}}$  and an increase in the optical density caused by the formation of a fine-disperse suspension and the subsequent decrease as a result of the formation of  $\text{Np}^{\text{IV}}$  and  $\text{Pu}^{\text{IV}}$  hydroxide precipitates.

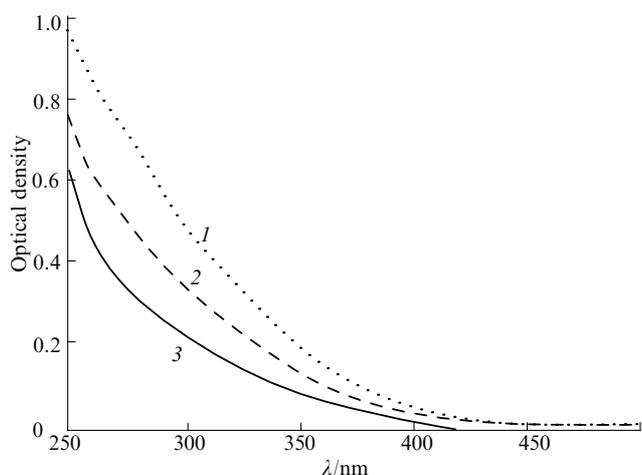
Alkaline solutions of  $\text{Np}^{\text{VI}}$ ,  $\text{Np}^{\text{V}}$  and  $\text{Pu}^{\text{VI}}$  were prepared by the addition of measured amounts of perchloric acid solutions of the respective actinide perchlorates to sodium hydroxide solutions of known concentration. All the solutions used were aerated. The maximum dose rate of  $^{60}\text{Co}$   $\gamma$ -rays was  $15 \text{ kGy h}^{-1}$ . Dosimetry was carried out with ferrosulfate or bichromate systems.<sup>8</sup> The difference in the densities of the dosimetric and studied solutions was taken into account in dose calculations. The valent states and concentrations of neptunium and plutonium were determined by spectrophotometry; a 'Shimadzu UV-3100-PC' spectrophotometer was used. The wavelength of 275 nm and the molar extinction coefficients given in refs. 9–11 or found by us were used in the measurements for  $\text{Np}^{\text{VI}}$  and  $\text{Pu}^{\text{VI}}$ . The coefficient varied within the range  $200\text{--}285 \text{ m}^2 \text{ mol}^{-1}$  with variation of the alkali

concentration from 1 to  $8.5 \text{ mol dm}^{-3}$ . In alkaline medium,  $\text{Np}^{\text{V}}$  has no optical absorption bands suitable for concentration determination; the concentration of  $\text{Np}^{\text{V}}$  was determined after acidification of the alkaline solutions or after dissolution of the precipitate separated by centrifuging in perchloric acid. The same method was used to determine the concentrations of  $\text{Np}^{\text{IV}}$  and  $\text{Pu}^{\text{IV}}$ .

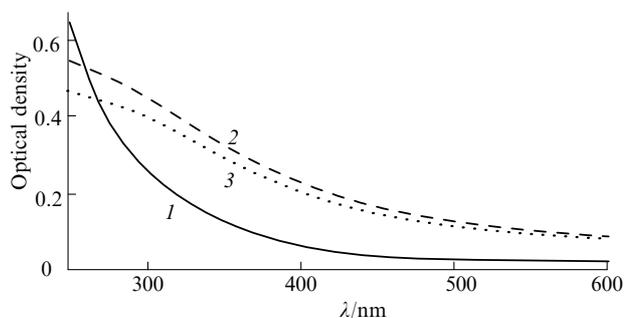
It was found that the decrease in optical density in the UV-region occurred upon  $\gamma$ -irradiation of alkaline ( $0.9\text{--}8.5 \text{ mol dm}^{-3}$   $\text{NaOH}$ ) aqueous solutions of  $\text{Np}^{\text{VI}}$  at comparatively low doses (approximately to  $2.4 \text{ kGy}$ ) (see Figure 1 for dose  $0.94 \text{ kGy}$ ). This was due to the radiolytic reduction of  $\text{Np}^{\text{VI}}$ . The radiation-chemical yields of the reduction at alkali concentrations of  $0.9\text{--}7 \text{ mol dm}^{-3}$  and at doses  $\leq 650 \text{ Gy}$  are equal to  $1.4\text{--}1.6 \text{ ion}/100 \text{ eV}$ . The reduction proceeds in reactions of  $\text{Np}^{\text{VI}}$  with hydrated electrons,  $e_{\text{aq}}^-$ , radical ions,  $\text{O}_2^-$  (the product of reaction between oxygen and  $e_{\text{aq}}^-$ ), and hydrogen peroxide  $\text{HO}_2$ . The formed  $\text{Np}^{\text{V}}$  ions are partially oxidized by radical ions  $\text{O}^-$  and  $\text{O}_3^-$  (the latter appears in the reaction of oxygen with  $\text{O}^-$ ). Some other reactions are also possible upon radiolysis of the system (for example, the reactions of  $\text{O}^-$  and  $\text{O}_3^-$  with  $\text{Np}^{\text{VI}}$ ,  $\text{Np}^{\text{VII}}$  and  $\text{Np}^{\text{V}}$ ). The important reaction is the subsequent reduction of  $\text{Np}^{\text{V}}$  to  $\text{Np}^{\text{IV}}$  by  $e_{\text{aq}}^-$  at high doses.

The spectra of the solutions irradiated at doses  $\leq 800 \text{ Gy}$  do not change for at least 20 h after  $\gamma$ -irradiation. However, further irradiation (doses over  $8 \text{ kGy}$ ) leads to an increase in optical absorption in the UV-VIS regions. The optical absorption decreases upon standing, but subsequent irradiation again gives rise to its increase. We thus have a system of specific oscillation. This is demonstrated more clearly upon radiolysis of alkaline solutions containing  $\text{Np}^{\text{V}}$  (see Figure 2).

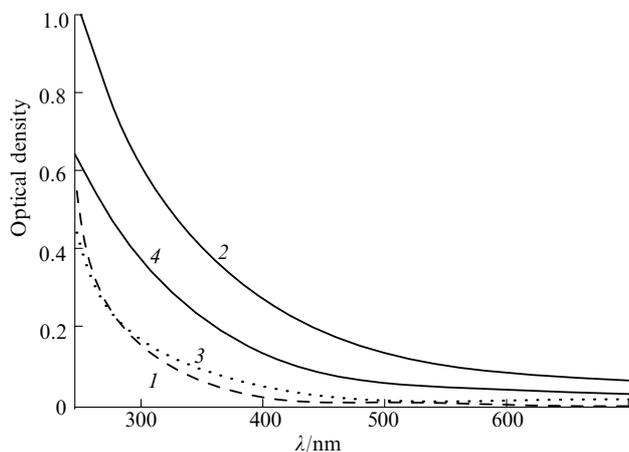
This discovered effect is due to the formation (at doses over  $8 \text{ kGy}$ ) of relatively stable, fine-disperse suspension. This is confirmed by the presence of a Tyndall cone, caused by the disperse particles scattering light. Besides, the intensity of optical absorption decreases with increasing time of centrifugation of the solution irradiated at doses over  $8 \text{ kGy}$ . This procedure leads to the separation of a precipitate predomi-



**Figure 1** Optical absorption spectra of an aerated solution containing  $2.74 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{Np}^{\text{VI}}$  and  $3.6 \text{ mol dm}^{-3}$   $\text{NaOH}$  irradiated at dose (kGy): (1) 0, (2) 0.47, (3) 0.94.



**Figure 3** Optical absorption spectra of an aerated solution containing  $1.9 \times 10^{-4} \text{ mol dm}^{-3}$   $\text{Pu}^{\text{VI}}$  and  $1.3 \text{ mol dm}^{-3}$   $\text{NaOH}$  irradiated at dose (kGy): (1) 0, (2) 4.3, (3) 8.6.



**Figure 2** Optical absorption spectra of an aerated solution containing  $1.54 \times 10^{-4} \text{ mol dm}^{-3} \text{ Np}^{\text{V}}$ ,  $1.2 \times 10^{-4} \text{ mol dm}^{-3} \text{ Np}^{\text{VI}}$  and  $6.9 \text{ mol dm}^{-3} \text{ NaOH}$  (1), after irradiation at 13 kGy (2), after subsequent standing of the irradiated solution for 17 h 10 min (3), after additional irradiation at 15 kGy (4).

nantly consisting of  $\text{Np}^{\text{IV}}$  (found from the spectra of solutions prepared by dissolution of a precipitate in perchloric acid). For instance, in the solution prepared by dissolution of a precipitate from an irradiated (dose 25 kGy) solution of  $\text{Np}^{\text{VI}}$  in  $7 \text{ mol dm}^{-3} \text{ NaOH}$ , the ratio  $[\text{Np}^{\text{IV}}]/[\text{Np}^{\text{V}}]$  is 8. Therefore, the formation of the slightly-soluble  $\text{Np}^{\text{IV}}$  hydroxide occurs mainly in the base of the oscillation process.

A similar phenomenon was detected upon  $\gamma$ -radiolysis of alkaline aqueous solutions of  $\text{Pu}^{\text{VI}}$ . The decrease in optical density of the solution connected with the reduction of  $\text{Pu}^{\text{VI}}$  (the radiation-chemical yields of this process at alkali concentrations of  $1.3\text{--}6.9 \text{ mol dm}^{-3}$  and doses  $< 1 \text{ kGy}$  are  $1.3\text{--}1.5 \text{ ion}/100 \text{ eV}$ ) is observed at low doses ( $0.2\text{--}0.4 \text{ kGy}$ ). The reduction yields of  $\text{Np}^{\text{VI}}$  and  $\text{Pu}^{\text{VI}}$  are the same; it testifies that the mechanism of the process is identical for both actinides. The difference seems only to be the disproportionation of  $\text{Pu}^{\text{V}}$  to  $\text{Pu}^{\text{VI}}$  and  $\text{Pu}^{\text{IV}}$ . As follows from the standard redox potentials of the  $\text{Np}^{\text{VI}}/\text{Np}^{\text{V}}$  and  $\text{Pu}^{\text{VI}}/\text{Pu}^{\text{V}}$  pairs (see, for example, ref. 11)  $\text{Np}^{\text{V}}$  is thermodynamically stable in an alkaline medium, whereas  $\text{Pu}^{\text{V}}$  is unstable and thereby disproportionates.

At relatively high doses (over *ca.* 2 kGy) the fine-disperse suspension causing the increase in optical density (see Figure 3) appears in the system. As found, the precipitate formed

upon standing or separated by centrifugation mainly consists of slightly-soluble  $\text{Pu}^{\text{IV}}$  hydroxide. For example, in a nitric acid solution, prepared by dissolution of the precipitate separated by centrifugation from an irradiated (10 kGy) solution of  $\text{Pu}^{\text{VI}}$  in  $1.3 \text{ mol dm}^{-3} \text{ NaOH}$ , the ratio  $[\text{Pu}^{\text{IV}}]/[\text{Pu}^{\text{VI}}]$  is  $\geq 12$ . It is most probable that the appearance of the suspension at lower doses in comparison with  $\text{Np}^{\text{VI}}$  solutions is explained by disproportionation of  $\text{Pu}^{\text{V}}$  to  $\text{Pu}^{\text{VI}}$  and  $\text{Pu}^{\text{IV}}$ .

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