The formation of a neptunium(V) peroxo complex upon γ-radiolysis of aqueous alkaline solutions of neptunium ions

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A neptunium(V) peroxo complex is formed upon γ-radiolysis of aerated aqueous alkaline solutions of Np(VI) or Np(V) ions containing nitrate; however, a Pu(V) peroxo complex is not formed under the same conditions.

There are many data on the radiolysis of aqueous solutions of actinide ions (see, *e.g.*, refs. 1,2). However, these data are restricted to acid and neutral solutions. In view of the practical importance of information on radiolytic conversions of actinides in alkaline media (*e.g.*, in relation to radioactive alkaline waste management), we started to study the radiolysis of these systems. In the course of our investigations we detected the formation of a Np(V) peroxo complex resulting from γ-irradiation of aerated Np(VI) or Np(V) aqueous alkaline solutions containing nitrate.

A cobalt-60 γ-radiation source with maximum dose rate 15 kGy h^{-1} was used in this work. Stock solutions of neptunium and plutonium ions were prepared *via* known procedures.[3] All solutions used were aerated. Dosimetry was performed with ferrosulfate or bichromate dosimetric solutions (the technique of dosimetry was described in detail in ref. 4). Optical absorption spectra of solutions were recorded on a 'Shimadzu UV-3100-PC' spectrophotometer.

It was found that γ-irradiation of aerated aqueous alkaline solutions of Np(VI) ions led to the formation of Np(V) and Np(IV). However, we did not observe the radiolytic reduction of Np(VI) in alkaline solutions containing nitrate at doses <2 kGy. We do not exclude the possibility that under these conditions the reduction proceeds in a comparatively low yield so that we could not measure the change in Np(VI) concentration. However, we did observe that a yellow–brown colour appeared at higher doses. The spectra of such solutions in the visible region coincided with the spectrum of the Np(V) peroxo complex.[5] The respective data are shown in Figure 1. The same spectrum is formed upon addition of a 2×10^{-4} M solution of Np(V) in 4 M NaOH to an equal volume of an irradiated (dose 19 kGy) solution containing 0.8 M $NaNO_3$ and 3.6 M NaOH. Acidification of the irradiated solutions yielded acid solutions of Np(V). Addition of EDTA or nitrite to an alkaline solution containing Np(V) peroxo complex had no effect on the position, shape and intensity of the optical absorption bands during 16 h. However, irradiation (dose 12 kGy) of the solutions prepared caused the complete disappearance of the complex. This effect in the case of $NaNO_2$ is illustrated in Figure 2.

It is possible to give the following qualitative explanation of the results obtained. In the solutions containing nitrate, all hydrated electrons react with NO_3^- ions:

$$e_{aq}^- + NO_3^- \longrightarrow NO_3^{2-} \tag{1}$$

The radical ion formed reacts with oxygen, regenerating the nitrate ion:

$$O_2 + NO_3^{2-} \longrightarrow O_2^- + NO_3^- \tag{2}$$

Reactions of NO_3^{2-} with O^-, O_2^- and O_3^- are also possible. Hydrogen peroxide seems to be decomposed in its reaction with O^-:

$$HO_2^- + O^- \longrightarrow O_2^- + OH^- \tag{3}$$

After reduction of a significant proportion of Np(VI) in reactions (4)–(6) the Np(V) formed can react with hydrogen peroxide forming the peroxo complex.

$$\mathrm{Np(VI)} + O_2^- \longrightarrow \mathrm{Np(V)} + O_2 \tag{4}$$

$$\mathrm{Np(VI)} + NO_3^{2-} \longrightarrow \mathrm{Np(V)} + NO_3^- \tag{5}$$

$$\mathrm{Np(VI)} + HO_2^- \longrightarrow \mathrm{Np(V)} + HO_2 \tag{6}$$

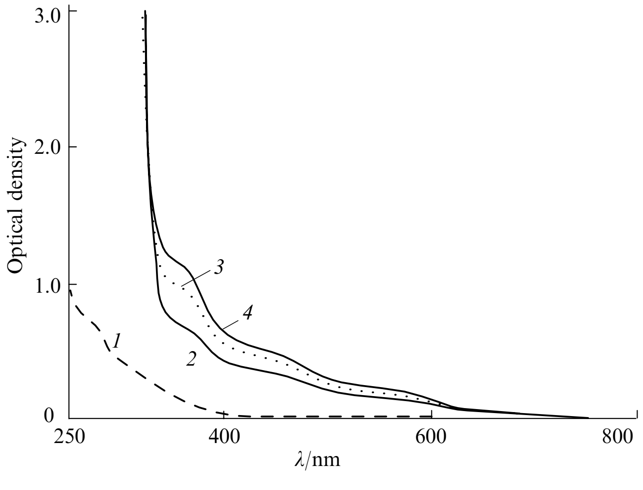

Figure 1 Optical absorption spectra of a non-irradiated solution containing 2.74×10^{-4} M Np(VI) and 8.5 M NaOH (*1*) and solution containing 3.2×10^{-4} M Np(VI), 0.7 M $NaNO_3$ and 7.7 M NaOH and irradiated with dose (in kGy): *2*, 15.2; *3*, 42.2; *4*, 58.8.

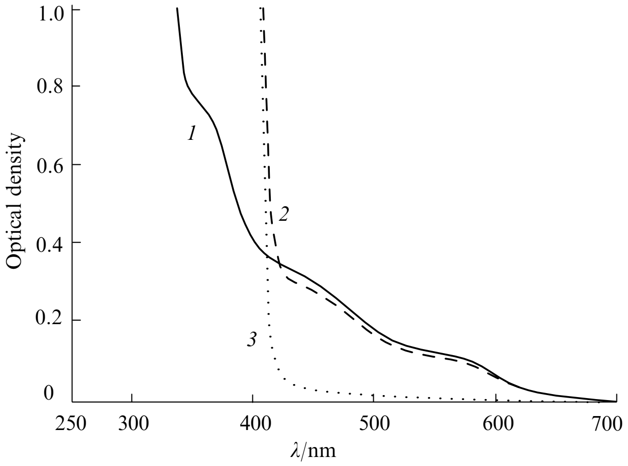

Figure 2 Optical absorption spectra of a solution containing 3.2×10^{-4} M Np(VI), 0.8 M $NaNO_3$ and 7.7 M NaOH irradiated with dose 42.9 kGy (*1*), the same solution 16 h after addition of 2.27 M $NaNO_2$ (*2*) and the previous solution, after additional irradiation to dose 12.9 kGy (*3*).

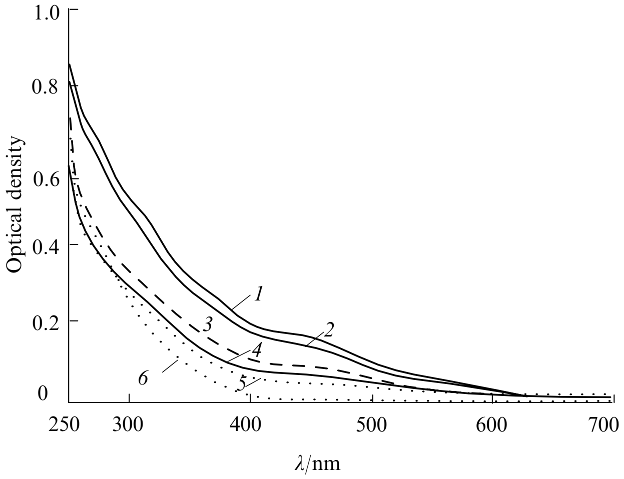

Figure 3 Optical absorption spectra of Np(V) peroxo complex in a solution containing 2.74×10^{-4} M Np(V), 3.9×10^{-4} M H_2O_2 and 4.2 M NaOH after γ-irradiation with dose (in kGy): *1*, 0; *2*, 2.15; *3*, 4.3; *4*, *5*, 6.45; *6*, 12.9.

In solutions containing Np(V) peroxo complex, nitrate and nitrite hydrated, electrons participate in reactions (1) and (7):

$$e_{aq}^- + NO_2^- \longrightarrow NO_2^{2-} \tag{7}$$

Radical ions O^- react with nitrite:

$$O^- + NO_2^- \longrightarrow NO_3^{2-} \tag{8}$$

Apparently, hydrogen peroxide and Np(V) peroxo complex can decompose in reactions with the product of reaction (7). Radiation-induced disappearance of Np(V) peroxo complex in the presence of EDTA seems to be caused by its reaction with a free radical which is the product of interaction between EDTA and O^-. Note that Np(V) peroxo complex prepared by the addition of hydrogen peroxide in small excess to an alkaline solution of Np(V) is decomposed upon irradiation (see Figure 3). Therefore, nitrate protects the complex from radiation-induced decomposition.

The same Np(V) peroxo complex spectrum is recorded in irradiated solutions initially containing Np(V) and nitrate. However, Pu(V) peroxo complex is not formed upon γ-radiolysis of aerated Pu(VI) alkaline solutions containing nitrate. One possible reason is that disproportionation of Pu(V) occurs upon reduction of Pu(VI) and proceeds considerably faster than the reaction of Pu(V) with hydrogen peroxide.

$$2\ Pu(V) \longrightarrow Pu(IV) + Pu(VI) \tag{9}$$

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