October, 1980] *Bull. Chem. Soc. Jpn.*, *53*, *2861—2864 (1980)*

The Determination of the Oxidation States of Neptunium in Sodium Hydroxide Solutions by Adsorption on Zirconium(IV) Hydroxide

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(Received March 4, 1980)

An adsorption method for determining the distribution of the oxidation states of neptunium in sodium hydroxide solutions is proposed. In the range of sodium hydroxide concentrations of 1—2 M (1 M=1 mol dm^{-3}), the Np(V) was almost entirely adsorbed on zirconium(IV) hydroxide, while both Np(VI) and Np(VII) remained in the supernatant. By means of this adsorption method, it was found that Np(V) in tracer quantities, though it was most stable in acidic or neutral solutions, was not the most stable state in sodium hydroxide solutions. Also, the oxidation and reduction of Np in sodium hydroxide solutions were investigated.

Since the discovery of heptavalent neptunium in sodium hydroxide solutions,[1] the chemical behavior of neptunium in those solutions has been investigated with interest. From the polarographic study, the oxidation states found in sodium hydroxide solutions were the penta-, hexa-, and heptavalent states.[2] In order to investigate this chemical behavior it is important to find a method both for preparing the oxidation state of interest and for determining the distribution of the oxidation states in sodium hydroxide solutions. Certainly there are some oxidants suitable for the preparation of heptavalent neptunium; also, we can satisfactorily confirm its existence by means of spectrophotometry.[1]

However, no reductant or oxidant suitable for preparing penta- and hexavalent neptunium in sodium hydroxide solutions has been found, though they have been prepared by electrolysis.[3,4] Unfortunately, spectrophotometry is quite insensitive for identifying these two oxidation states because of the low solubility and low molar-extinction coefficients.[5] The absorption spectra of neither penta- and hexavalent neptunium in sodium hydroxide solutions has yet been published. Thus, in order to determine the distribution of the oxidation states of neptunium in sodium hydroxide solutions, a method different from spectrophotometry and applicable to low concentrations of neptunium is required. For this purpose it is necessary to prepare the oxidation state of interest. However, neither the determination method nor the preparation method for the oxidation states of neptunium in sodium hydroxide solutions has been established except for heptavalent neptunium of an ordinary concentration.[1]

In the first step of the present work, the oxidation states of neptunium in sodium hydroxide solutions were tentatively divided into the "reduced state" and the "oxidized state." The "reduced state" was prepared by the addition of hydrazine, and the "oxidized state," by the addition of bromine. As a result of our examination, the difference in chemical behavior necessary for discriminating these two states was found in the adsorption on zirconium(IV) hydroxide. Second, the oxidation state of the reduced and oxidized neptunium was determined by the titration of heptavalent neptunium. Third, the oxidation and reduction of neptunium in sodium hydroxide solutions were examined by utilizing the adsorption on zirconium(IV) hydroxide.

Experimental

The stock solution of sodium hydroxide was prepared by filtrating its saturated solution through a Millipore Mitex filter with a pore size of 10 μm. In order to prevent the sodium hydroxide solutions from being contaminated by carbon dioxide or neptunium from being oxidized by air, the necessary experimental procedures were carried out in an atmosphere of nitrogen or argon gas.

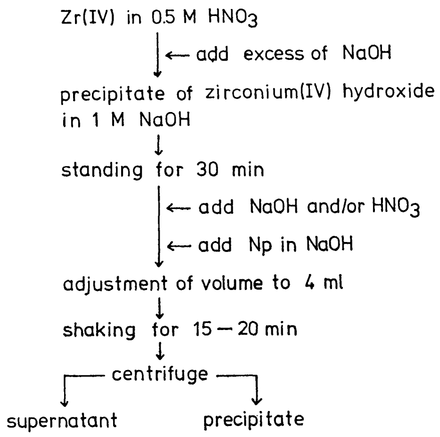

Fig. 1. Experimental procedures of the adsorption on zirconium (IV) hydroxide.

The reduced and oxidized neptunium in sodium hydroxide solutions were prepared by alkalizing a 0.5 M nitric acid solution of neptunium and by then adding hydrazine or bromine respectively. The ^{237}Np was obtained from The Radiochemical Centre, Amersham, while the ^{239}Np tracer was prepared by milking from ^{243}Am by the method of Espinosa.[6] In the preliminary experiments it was confirmed that the reduced and oxidized neptunium in sodium hydroxide solution were neither centrifuged nor adsorbed on glass.

The procedures for the adsorption on zirconium(IV) hydroxide are shown in Fig. 1. A suitable aliquot of a 0.5 M nitric acid solution of zirconium(IV) was transferred into a glass test tube equipped with a plug. In order to obtain zirconium(IV) hydroxide, a sodium hydroxide solution was added to an excess concentration of 1 M, and then, after 30 min, we added a sodium hydroxide solution and/or nitric acid solution in order to adjust the hydroxide ion-concentration. Then the sodium hydroxide solution of neptunium in the desired state was added, and the volume of the mixture was adjusted to 4 ml. The mixture was shaken for time enough to obtain an apparently constant adsorption. The recommended shaking time was 15—20 min. By measuring the ^{239}Np activity by means of a NaI scintillation or Ge detector in both the mixture and the supernatant obtained by centrifuging, the percentage of neptunium adsorbed was determined.

The procedures for the titration of heptavalent neptunium were as follows. Heptavalent neptunium of about 5×10^{-4} M was prepared by the passage of ozone into $^{237+239}$Np hydroxide in a 1 M sodium hydroxide solution, after which the excess ozone was swept out by argon-gas bubbling. The heptavalent solution (2—2.5 ml) was then transferred into a glass test tube equipped with a plug, and then 1×10^{-2} M hydrazine solution of 5—100 μl was added. After it was stood for 20—60 min at room temperature or 40 °C, this mixture was centrifuged, taking account of the low solubility of all the oxidation states except the heptavalent state. The supernatant was transferred into another test tube, and the adsorption on zirconium(IV) hydroxide was examined. In this experiment, the dissolved oxygen in the solution was swept out by the particularly careful passage of argon through just before use. The neptunium was determined by α- and γ-spectrometry, and the hydrazine, by iodometry.

Results and Discussion

Adsorption of the Reduced and Oxidized Neptunium on Zirconium(IV) Hydroxide. At first, the adsorption behavior on zirconium(IV) hydroxide under the various conditions was investigated for both the reduced and the oxidized neptunium in tracer quantities. Figure 2 shows the dependence of the adsorption on the amount of zirconium(IV) in a 0.96 M sodium hydroxide solution. In the range of 0.5—5 mg zirconium(IV), more than 95% of the reduced neptunium was adsorbed; on the other hand, the adsorbed fraction of the oxidized neptunium was less than 5%.

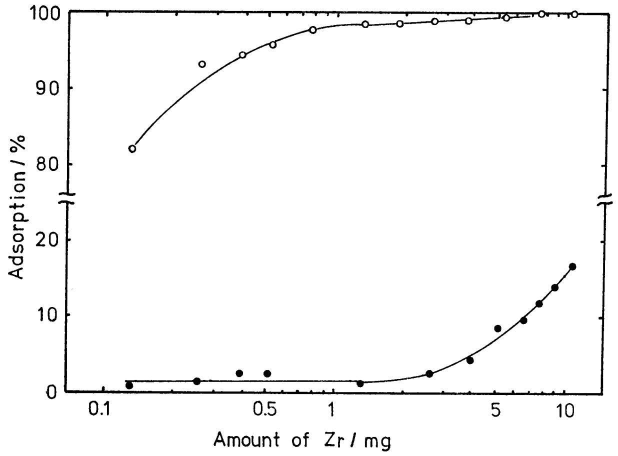

Fig. 2. Dependence of the adsorption on the amount of Zr(IV) at 0.96 M NaOH.
○: Np+$N_2H_4\cdot2HCl(1\times10^{-3}$ M),
●: Np+$Br_2(2\times10^{-2}$ M).

Figure 3 shows the dependence of the adsorption on the concentration of sodium hydroxide at a constant amount of zirconium(IV). For the reduced neptunium, the fraction adsorbed was about 99% in the range of the concentration of sodium hydroxide from 0.2 to 1 M; it decreased with the increase in the concentration, reaching about 95% at 2.5 M. For the oxidized state, the fraction adsorbed was less than 2% above the concentration of 1 M, but it increased below 1 M.

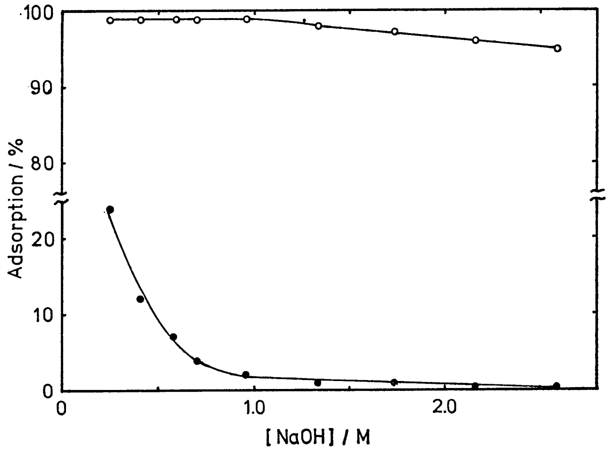

Fig. 3. Dependence of the adsorption on the concentration of NaOH using 2.9 mg Zr(IV).
○: Np+$N_2H_4\cdot2HCl(1\times10^{-3}$ M),
●: Np+$Br_2(1\times10^{-2}$ M).

Considering the dependency of the adsorption on both the amount of zirconium(IV) and the concentration of sodium hydroxide, as is shown in Figs. 2 and 3, it is possible to discriminate between the reduced and oxidized neptunium, if the adsorption is carried out with from 0.5 to 5 mg of zirconium(IV) per 4 ml of the mixture and at a sodium-hydroxide concentration from 1 to 2 M.

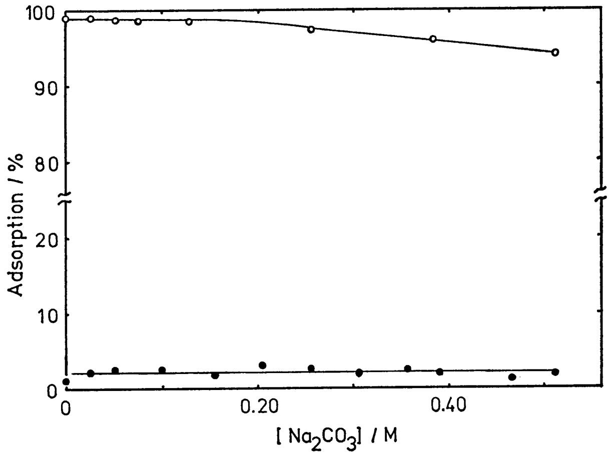

Fig. 4. Dependence of the adsorption on the concentration of Na_2CO_3 at 1.16 M NaOH using 2.6 mg Zr(IV).
○: Np+$N_2H_4\cdot2HCl(1\times10^{-3}$ M),
●: Np+$Br_2(2\times10^{-2}$ M).

The dependence of the adsorption on the concentration of the carbonate at a constant amount of zirconium(IV) and a constant concentration of sodium hydroxide is shown in Fig. 4. In the range of the carbonate concentrations examined, the fraction of the oxidized neptunium adsorbed remained constant, whereas that of the reduced neptunium was somewhat decreased

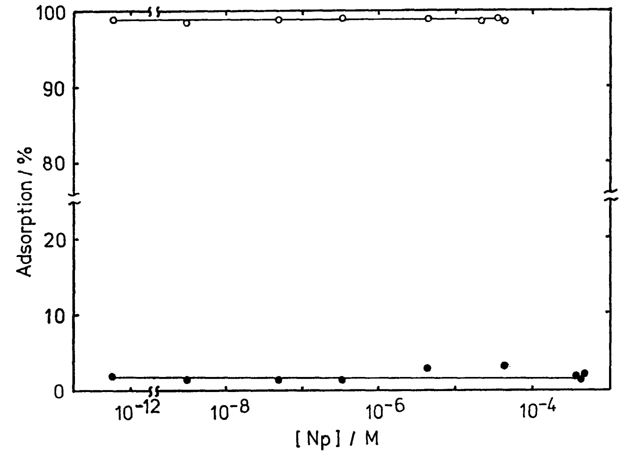

Fig. 5. Dependence of the adsorption on the concentration of Np at 1.25 M NaOH using 2.7 mg Zr(IV).
○: Np+N_2H_4·2HCl(1×10^{-3} M),
●: Np+Br_2(2.5×10^{-2} M).

above the concentration of 0.15 M. As is shown in Fig. 4, the adsorption is little affected by the existence of the carbonate, and so this adsorption procedure may be applicable in the atmosphere of air. In the present work, however, in order to prevent the results from being disturbed, all the procedures were carried out in an atmosphere of nitrogen or argon gas.

Though the results of Figs. 2, 3, and 4 are for the reduced and oxidized neptunium in tracer quantities, the dependence of the adsorption on the concentration of neptunium is shown in Fig. 5. As is shown in Fig. 5, the fraction adsorbed was almost constant for both the reduced and oxidized neptunium over a wide range of the neptunium concentrations. Because of the low solubility of neptunium in sodium hydroxide solutions, the concentrations of neptunium examined ranged up to about 5×10^{-4} M for the oxidized neptunium and up to about 5×10^{-5} M for the reduced neptunium.

Titration of Heptavalent Neptunium by Hydrazine.
As has been mentioned above, it is the only heptavalent state to be identified among some kinds of oxidation states of neptunium which occur in sodium hydroxide solutions. Therefore, if the reduced and oxidized neptunium can be prepared by adding an adequate reductant to heptavalent neptunium, it is possible to determine their oxidation states by considering the relationship between the amount of heptavalent neptunium and that of the reductant. We preferred hydrazine, which was able to reduce heptavalent neptunium quantitatively into hexavalent in sodium hydroxide solutions.[7]

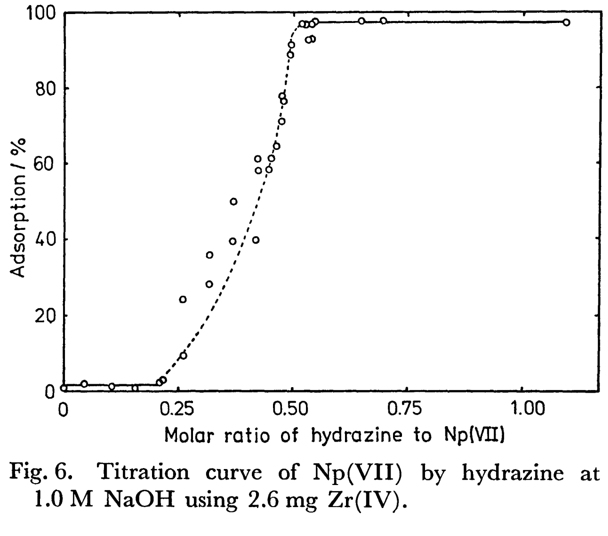

Fig. 6. Titration curve of Np(VII) by hydrazine at 1.0 M NaOH using 2.6 mg Zr(IV).

The results of the titration of heptavalent neptunium by hydrazine are shown in Fig. 6. As the equivalence point is the molar ratio of 0.25 for the reduction of heptavalent neptunium into hexavalent,[7] the adsorption at the molar ratio of 0 corresponds for heptavalent neptunium, and that at the molar ratio of 0.25, for hexavalent neptunium. Moreover, in the region of the molar ratios from 0 to 0.25, the adsorption corresponds for the mixture of hepta- and hexavalent neptunium. As is shown in Fig. 6, the fraction adsorbed in this region is very small. Consequently, both hepta- and hexavalent neptunium are hardly adsorbed at all on zirconium(IV) hydroxide.

On the other hand, the fraction adsorbed gradually increases in the region of the molar ratios between 0.25 and 0.50, and the neptunium is almost entirely adsorbed in the region of molar ratios more than 0.50. From this adsorption behavior, it is concluded that the neptunium in the oxidation state below the pentavalent state is almost entirely adsorbed on zirconium(IV) hydroxide. Moreover, if it is considered that the reduced rate of neptunium into the tetravalent state by hydrazine is negligibly small in the range of pH from weak acid to neutral solutions, and that the rate is rapid only in the strongly acid solutions,[8,9] the oxidation state of neptunium must be the pentavalent state in the region of molar ratios more than 0.5; therefore, the neptunium adsorbed on zirconium(IV) hydroxide must be in the pentavalent state.

In the region of the molar ratios between 0.25 and 0.50, the adsorption shows some scatter. This may be ascribed to the difference in the standing time and temperature on the reduction of heptavalent neptunium by hydrazine, because the solubility of hexavalent neptunium is about ten times as large as that of pentavalent neptunium in 1 M sodium hydroxide solutions, as is mentioned in the explanation of Fig. 5.

From the above discussion, it is apparent that the reduced neptunium prepared by hydrazine is in the pentavalent state, but the oxidized state cannot be assigned whether the hexavalent state, the heptavalent state, or a mixture.

Determination of the Oxidation State of Neptunium of Tracer Quantities. In the solution of neptunium without any foreign oxidants or reductants, the change of the oxidation state is as is shown in Table 1. Here, in addition to the adsorption on zirconium(IV) hydroxide, the oxidation state was determined by the adsorption on silica gel, in which hexavalent neptunium was quantitatively adsorbed, while pentavalent neptunium remained in the supernatant solution in the pH range of 6—7.[9]

At first, a solution of ^{239}Np in a 0.5 M nitric acid solution was prepared in the absence of foreign oxidants

Table 1. The variation in the oxidation state of neptunium in tracer quantities in relation to the pH

	Adsorption$^{a)}$/%		Oxidation state
	Silica gel pH 6—7	$Zr(OH)_4$ 1 M NaOH	
Np in 0.5 M HNO_3	2		V
Np in 1 M NaOH		18	VI+(V)
Np in acetate buffer (pH 6.35)	1		V

a) The amounts of silica gel and Zr(IV) were 100 mg and 2.7 mg respectively.

or reductants; its oxidation state was acertained to be the pentavalent from the results of the adsorption on silica gel. Second, a 1 M sodium hydroxide solution of neptunium was prepared by alkalizing a 0.5 M nitric acid solution; the oxidation state was then examined by means of the adsorption on zirconium(IV) hydroxide. Because neptunium is never oxidized by oxygen into the heptavalent state,[1] the results shown in Table 1 indicate that a large portion of the neptunium in the 1 M sodium hydroxide solution exists in the hexavalent state, and a small portion, in the pentavalent state. Third, the neutral solution of neptunium was prepared by adding an acetate buffer solution to a 1 M sodium hydroxide solution; its oxidation state was found to be pentavalent.

It is well known that the most stable oxidation state of neptunium is the pentavalent state, and it has been confirmed, not only by the present work, but also by Inoue *et al.*,[9] that the oxidation state of neptunium in tracer quantities is pentavalent in the region from an acidic to a neutral solution in the absence of foreign oxidants or reductants. However, in a 1 M sodium hydroxide solution of neptunium in tracer quantities, the most stable oxidation state is not the pentavalent state, but a mixture of the pentavalent and hexavalent states, because pentavalent neptunium must be oxidized by the oxygen dissolved in the solution.

Espinosa investigated the preparation and identification of penta-, hexa-, and heptavalent neptunium in tracer quantities in alkaline solutions by means of glass fiber-electrophoresis and solvent extraction.[6] He concluded that neptunium in a sodium hydroxide solution, in the absence of foreign oxidants or reductants, was pentavalent. However, as is shown in Table 1, his method of preparation and his identification of pentavalent neptunium is questionable.

Table 2. The reduction and oxidation of neptunium in tracer quantities in 1 M NaOH

Reductant and oxidant		Adsorption$^{b)}$/% Standing time	
		15—20 min	3 h
$N_2H_4 \cdot 2HCl$	1×10^{-2} M$^{a)}$	99	99
$NH_2OH \cdot HCl$	1×10^{-2} M	99	99
$SnCl_2$	1×10^{-2} M	99	99
$K_4Fe(CN)_6$	1×10^{-2} M	95	97
L-Ascorbic acid	1×10^{-2} M	92	93
H_2O_2	1×10^{-2} M	62	57
None		18	18
$KBrO_3$	1×10^{-2} M	16	15
$NaClO_2$	1×10^{-2} M	16	13
$K_2S_2O_8$	1×10^{-2} M	15	14
$K_2S_2O_8$(50 °C)	1×10^{-2} M		9
O_3	1.5 g/h		6
$K_3Fe(CN)_6$	1×10^{-2} M	5	2
$KMnO_4$	1×10^{-2} M	3	1
Br_2	4×10^{-2} M	2	2

a) The concentrations were at the stage of reduction and oxidation, and were reduced to 1/4 of the value given at the stage of adsorption. b) The amount of Zr(IV) was 2.7 mg.

The adsorption of neptunium in tracer quantities on zirconium(IV) hydroxide in the presence of some oxidants or reductants is shown in Table 2. The pentavalent neptunium in a 1 M sodium hydroxide solution can be prepared by adding hydroxylamine and tin(II) besides hydrazine. However, it is difficult to prepare pentavalent neptunium by the use of hexacyanoferrate(II), ascorbic acid, and hydrogen peroxide, which are known as reductants capable of reducing heptavalent neptunium quantitatively into hexavalent.[1,7] The adsorption of neptunium in the presence of bromate, chlorite, and peroxosulfate is nearly equal to that in the absence of any oxidants or reductants. Therefore, these three reagents are not effective oxidants in 1 M sodium hydroxide solutions. Neptunium in tracer quantities is oxidized only to some extent by peroxosulfate at 50 °C, and in the presence of ozone, though under the same conditions neptunium of an ordinary concentration is oxidized into the heptavalent state.[1] By the use of hexacyanoferrate(III), permanganate, and bromine, neptunium is oxidized into a hexavalent or heptavalent state, as is shown in Table 2.

As has been mentioned above, pentavalent neptunium is found to be selectively absorbed on zirconium(IV) hydroxide, and the method proposed is effective for determining the distribution of the oxidation state of neptunium in a sodium hydroxide solution.

References

1) V. I. Spitsyn, A. D. Gelman, N. N. Krot, M. P. Mefordiyeva, F. A. Zakharova, Yu. A. Komokov, V. P. Shilov, and I. V. Smirnova, *J. Inorg. Nucl. Chem.*, **31**, 2733 (1969).

2) V. P. Peretrukhin and D. P. Alekseeva, *Radiokhimiya*, **16**, 836 (1974).

3) G. A. Simakin, I. V. Matyashchuk, and N. A. Vladimirova, *Radiokhimiya*, **15**, 98 (1973).

4) A. J. Zielen and D. Cohen, *J. Phys. Chem.*, **74**, 394 (1970).

5) D. Cohen and S. Fried, *Inorg. Nucl. Chem. Lett.*, **5**, 653 (1969).

6) E. Espinosa, Report 1973, FRNC-TH-478.

7) V. P. Shilov and N. N. Krot, *Radiokhimiya*, **11**, 399 (1969).

8) G. A. Burney and R. M. Harbour, "Radiochemistry of Neptunium," U. S. Atomic Energy Commission (1974).

9) Y. Inoue and O. Tochiyama, *J. Inorg. Nucl. Chem.*, **39**, 1443 (1977).