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Studies on Actinoid Elements. V. The Determination of the Np(V)/Np(IV) Ratio in an Aqueous Solution by Means of the Partition Method

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The distribution study of neptunium ions in an aqueous solution containing Np(IV) and Np(V) was made using the metal chelate extraction system, TTA-benzene, or HDEHP-benzene at room temperature. The results obtained by this method were then compared with those obtained by spectrophotometry. In each system, a linear relationship was obtained between the fraction of the Np(V) ion and $1/(D+1)$, where D is the distribution ratio of neptunium. This analysis was performed with an accuracy of $\pm 5\%$ and was established within one minute in the case of the HDEHP-benzene system. The results obtained by this method were in good agreement with those obtained by spectrophotometry.

When a solution contains metal ions of different oxidation states, its composition is usually determined by spectrophotometry, potentiometry, *etc.* However, these methods, in which an appreciable concentration of the sample is required for measurement, appear not to be suitable for a nuclide like ^{239}Np, which is difficult to supply in so great a quantity which is difficult to handle because of its radioactivity.

In this experiment, we have attempted to use a radiochemical method, *i.e.*, a liquid-liquid partition of Np(IV) and Np(V) ions, to determine the oxidation state of neptunium.

Experimental

Reagents. Neptunium-237 oxide obtained from the Radiochemical Center, Amersham, was dissolved in nitric acid. The solution was then evaporated to dryness, and the residue was dissolved in 0.1 M hydrochloric acid. This solution served as the stock solution of neptunium. The neptunium-239 was prepared from neutron-irradiated uranium dioxide by the thenoyltrifluoroacetone(TTA) extraction method.[1,2] The radiochemical purities of ^{237}Np and ^{239}Np were confirmed by studying the γ-ray spectra with a $2''\phi\times 2''$ NaI(Tl) detector connected to a TMC 400-channel pulse-height analyzer. The chemical purity of ^{237}Np was also checked by spectrophotometry. The tributyl phosphate (TBP) and di(ethylhexyl)phosphoric acid (HDEHP) were purified from commercial chemicals by the usual method.[3,4] The other reagents used were of a G.R. grade.

The sample solution of tetravalent neptunium-239 was prepared by a TTA-extraction method,[2,5,6] and by oxidizing this solution with a warm perchloric acid solution, the neptunium-239 was changed to the pentavalent state. Both sample solutions were freshly prepared before each experiment.

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[2] F. L. Moore and J. E. Hudgens, *ibid.*, **29**, 1767 (1957).

[3] D. F. Peppard, G. W. Mason, J. L. Maier, and W. J. Driscoll, *J. Inorg. Nucl. Chem.* **4**, 334 (1957).

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[6] J. O. Lilienzin and J. Stary, *J. Inorg. Nucl. Chem.*, **32**, 1357 (1957).

Apparatus. The γ-activity of the neptunium-239 was measured with a $5''\phi\times 5''$ well-type NaI(Tl) scintillation counter. A Hitachi EPS-2U spectrophotometer was used to determine the absorption spectra of the neptunium-237. The sample (about 1 ml) was transferred into a quartz cell with a 1 cm path length. A Hitachi-Horiba pH meter, model M-5, was used for the pH measurement.

Procedures. *Liquid-liquid Partition Study*: After 4 ml of 1.0M perchloric acid and a 0.5M TTA benzene solution (4 ml) or a 0.16M HDEHP benzene solution (4 ml) had been transferred into the centrifuge tubes, sample solutions (50 μl each) of different Np(V)/Np(IV) ratios were added to the mixture. The air in the tubes was displaced with nitrogen gas. Then the tubes were shaken mechanically for 10 min at room temperature because it was already known by preliminary experiments that this period was sufficient to equilibrate the partition of Np(IV) and Np(V) ions. In the case of the 0.16M HDEHP/benzene extraction system, since the pre-equilibration was made between the organic and aqueous phases, the partition was accomplished within 1 min. After the shaking and the centrifugation, an aliquot (2 ml) of each phase was transferred into a polyethylene tube and the γ-activity was measured in order to determine the distribution ratio, D. The hydrogen-ion concentration of the aqueous phase was determined by a titration method after the γ-activity measurements.

Spectrophotometry and Partition Study. In the course of the reduction reaction, the changes in the oxidation states were simultaneously measured by spectrophotometry and the partition method. Into a spectrophotometer cell containing a solution of citric acid and pentavalent neptunium, a pentavalent neptunium-239 solution was added. The mixture was then irradiated with the light of a tungsten lamp, and the cell was kept in a thermostat maintained at 20°C. The reactions were followed at the same time by spectrophotometry and by radiometry, with a partition between 0.16M HDEHP/benzene and the 1.0M perchloric acid solution.

Results and Discussion

Calculation of the Neptunium(V) Fraction from the Partition Data. As is already known, in a liquid-liquid partition system of neptunium species, the distribution ratio, D, is represented by Eq. (1):

$$D = [\mathrm{Np}]_{\mathrm{org}}/[\mathrm{Np}]_{\mathrm{aq}} = \frac{\gamma\text{-activity of }{}^{239}\mathrm{Np/ml\ of\ organic\ phase}}{\gamma\text{-activity of }{}^{239}\mathrm{Np/ml\ of\ aqueous\ phase}} \qquad (1)$$

The fraction of pentavalent neptunium, X, is expressed as follows:

$$X = \frac{[\mathrm{Np(V)}]}{[\mathrm{Np(IV)}]+[\mathrm{Np(V)}]} \qquad (2)$$

If we assume that there is no change in the oxidation states of neptunium in the extraction procedure, the net distribution ratio can be defined as follows:

$$D = \frac{[\mathrm{Np(IV)}]_{\mathrm{org}}+[\mathrm{Np(V)}]_{\mathrm{org}}}{[\mathrm{Np(IV)}]_{\mathrm{aq}}+[\mathrm{Np(V)}]_{\mathrm{aq}}} \qquad (3)$$

The distribution ratios of the respective neptunium species are:

$$D^{\mathrm{IV}} = [\mathrm{Np(IV)}]_{\mathrm{org}}/[\mathrm{Np(IV)}]_{\mathrm{aq}} \qquad (4)$$

$$D^{\mathrm{V}} = [\mathrm{Np(V)}]_{\mathrm{org}}/[\mathrm{Np(V)}]_{\mathrm{aq}} \qquad (5)$$

A new function, Y, is defined by the following equation:

$$Y = 1/(1+D) \qquad (6)$$

The material balance equation can be thus expressed concerning the pentavalent neptunium:

$$[\mathrm{Np(V)}]_{\mathrm{aq}} + [\mathrm{Np(V)}]_{\mathrm{org}} = [\mathrm{Np(V)}] \qquad (7)$$

By introducing Eq. (5) into Eq. (7), Equation (8) is obtained:

$$[\mathrm{Np(V)}]_{\mathrm{aq}} = 1/(1+D^{\mathrm{V}})\cdot X/(1-X)\{[\mathrm{Np(IV)}]_{\mathrm{aq}} + [\mathrm{Np(IV)}]_{\mathrm{org}}\} \qquad (8)$$

From Equations (3), (4), and (8), Eqs. (9) and (10) are obtained:

$$1/D = 1/D^{\mathrm{IV}}\{1+(1+D^{\mathrm{IV}})/(1+D^{\mathrm{V}})\cdot X/(1-X)\} \qquad (9)$$

$$1 + D = (1+D^{\mathrm{IV}})\{(1+D^{\mathrm{V}})-D^{\mathrm{V}}X\}/\{(1+D^{\mathrm{V}}) + (D^{\mathrm{IV}}-D^{\mathrm{V}})X\} \qquad (10)$$

Since the $D^{\mathrm{V}}X$ term is sufficiently small compared to unity, Equation (10) can be simplified and the Y function can be expressed as follows:

$$Y = 1/(1+D^{\mathrm{IV}}) + [(D^{\mathrm{IV}}-D^{\mathrm{V}})/(1+D^{\mathrm{IV}})(1+D^{\mathrm{V}})]\cdot X \qquad (11)$$

When the partition process is performed under constant experimental conditions, the distribution ratios, D^{IV} and D^{V}, are both constant; therefore, it can be expected that Y can be expressed as a linear function of X.

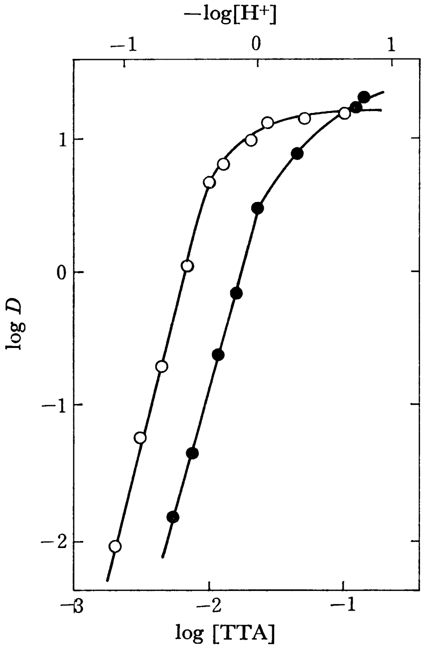

Fig. 1. Plots of log D *vs.* $-\log[\mathrm{H^+}]$ (●) and log D *vs.* log-[TTA] (○).

The Confirmation of the Valency State of the Neptunium Ion in the Sample Solution. The TTA extraction of the tetravalent neptunium ion was carried out in order to verify its valency state in a perchloric acid solution. The effect of the hydrogen ion concentration on the extraction was examined by using a 0.05M TTA benzene solution. As Fig. 1 shows, the relationship between log D and $-\log[\mathrm{H^+}]$ is linear, with a slope of 3.8, over the $-\log[\mathrm{H^+}]$ range from -0.6 to 0.0. The relationship between the TTA concentration and the distribution ratio was examined in 0.1M perchloric acid. As is shown in Fig. 1, the log-log plot of the distribution

Table 1. Distribution ratio of ^{239}Np for sample solution (D) and tetravalent state (D^{IV})

Partition system	Distribution ratio D	Distribution ratio D^{IV}
0.16M HDEHP -1M $HClO_4$	0.01±0.01	4.2±0.2
0.5M TTA -1M $HClO_4$	0.001±0.001	55 ±4

ratio and the TTA concentration shows a good linearity, with a slope of 4.0, over the TTA concentration range from 0.002 to 0.01M. These results indicate that the neptunium ion is tetravalent during the procedures.

The pentavalent neptunium ion was also confirmed by the partition method. The distribution ratio of ^{239}Np in the sample solution was measured with 0.16M HDEHP/benzene and 0.5M TTA/benzene *vs.* a 1M perchloric acid solution. The results obtained are given in Table 1, where the distribution ratios of Np(IV), D^{IV} are also shown as examples. These are mean values for three measurements. The differences between D^{IV} and D, 4×10^2 and 5×10^4, show that the neptunium exists in the form of an unextractable species. Since the hexavalent neptunium is extractable from the highly acidic solution,[1] the neptunium in the sample solution indicating such small D values may be considered to be in a pentavalent state, NpO_2^+.

The Rate of the Partition of Neptunium Ions. The partition rate of the neptunium ion between two phases may depend on various experimental conditions, such as the contact time, the way of shaking and the extracting reagent. Tests were made for tetra- and pentavalent neptunium ions using the two kinds of extractants, 0.50M TTA/benzene and 0.16M HDEHP/benzene, under constant shaking conditions and at a constant temperature. Same typical results are presented in Fig. 2. In the case of the TTA system, the partition was fairly rapid and gave reproducible data, while in the case of the HDEHP system, a pre-equilibration was necessary between an organic and an aqueous phase because the partition rate was appreciably small and the observed D value was not reproducible. As the contact time, 1 and 10 min were selected for the HDEHP and TTA systems respectively.

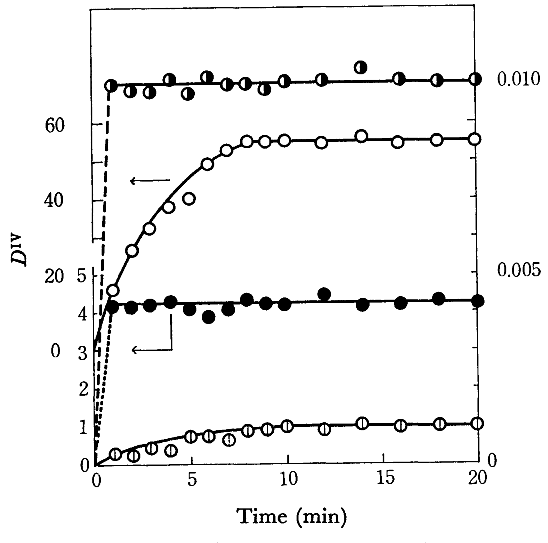

Fig. 2. The plot of D^{IV} or D^V *vs.* extraction time.
D^{IV}: ○ TTA, ● HDEHP, D^V: ⦶ TTA, ◑ HDEHP

Determination of the Pentavalent Neptunium Fraction, X, *from the Partition Data.* The results are shown in Figs. 3 (TTA-benzene system) and 4 (HDEHP-benzene system) as plots of Y *versus* X. As has been expected, the plots indicate a good linear relationship between Y and X in both cases. However, it was found that the air on the extractant should be removed because the oxygen caused a transformation from Np(IV) to Np(V) during the shaking for 10 min, as is indicated by the closed circles in Fig. 3. On the other hand, since the shaking time is only one minute for the HDEHP system, the variation between the two oxidation states might be sufficiently small,

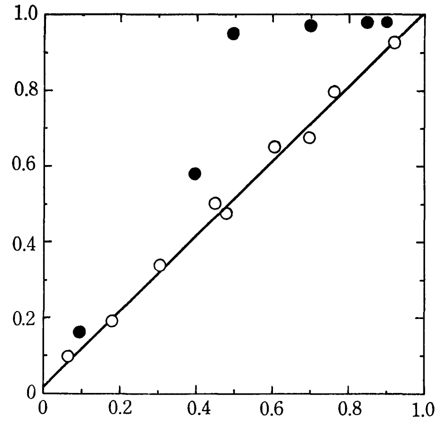

Fig. 3. The plot of $Y=1/1+D$ *vs.* X for TTA/benzene perchloric acid system.
○: Air replaced, ●: Unreplaced.

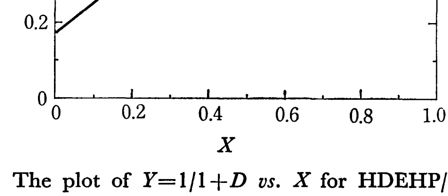

Fig. 4. The plot of $Y=1/1+D$ *vs.* X for HDEHP/benzene perchloric acid system.

The empirical equations were determined by a least-squares method as follows:

$Y=(0.015\pm0.003)+(0.983\pm0.001)\cdot X$; 0.50M TTA-benzene/1.0M $HClO_4$

$Y=(0.18\pm0.01)\pm(0.78\pm0.01)\cdot X$; 0.16M HDEHP-benzene/1.0M $HClO_4$.

Comparison of the Results from Two Different Analyses of Neptunium Ions. The spectrophotometry of neptu-

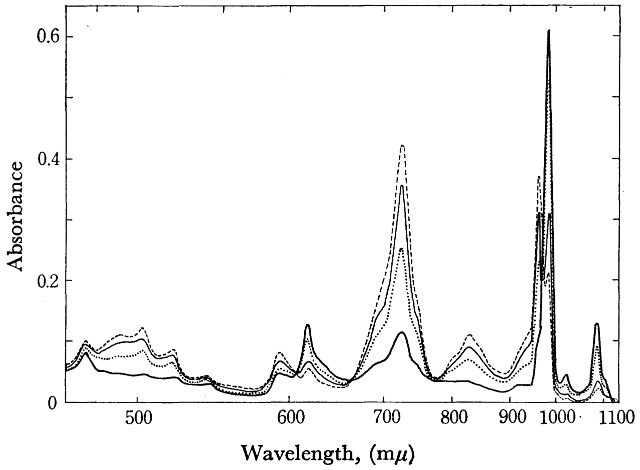

Fig. 5. Changes of absorption spectra of neptunium during the reduction with the reaction time.
Conditions; $[\mathrm{Np(V)}]_0=1.52\times10^{-3}$M, $[\text{citric acid}]_0=4.8\times10^{-2}$M, $[\mathrm{H^+}]=0.01$M, at 20°C.
Reaction time: — 2 min, ··· 9 min, — 25 min, --- 35 min.
Irradiation; at 30 cm from 300 W tungsten light.

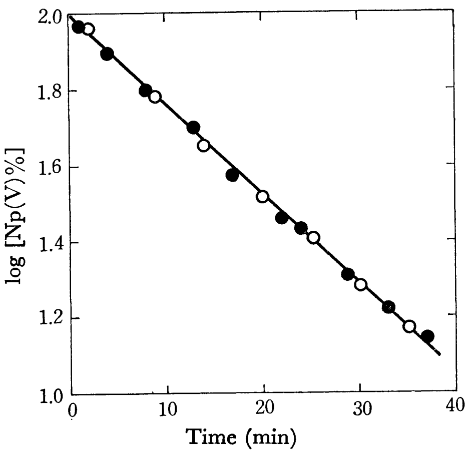

Fig. 6. Plots of the logarithm of neptunium (V) fraction *vs.* reaction time.
○: Spectrophotometry, ●: Partition method.

nium ions was carried out in order to compare the results with those from the partition method in the course of the kinetic run. A photochemical reduction of pentavalent neptunium ions was employed in this attempt. A mixture of $^{237}\mathrm{NpO_2}^+$, $^{239}\mathrm{NpO_2}^+$, and citrate ions was placed under the tungsten lamp and irradiated by visible light. The reduction of $\mathrm{NpO_2}^+$ then proceeded *via* some photochemical processes. The details of this reaction will be reported elsewhere.

The changes in the absorbance due to the neptunium-237 and the changes in the distribution ratio of the neptunium-239 in the reacting solution were simultaneously measured at appropriate intervals.

Figure 5 shows the changes in the absorption spectra of neptunium with the reaction time during the course of reduction; the absorbances at 617 and 980 mμ corresponding to Np(V) decrease, while those at 723 and 960 mμ corresponding to Np(IV) simultaneously increase. The logarithmic plots of the Np(V) fraction *versus* the reaction time are shown in Fig. 6, using the data from spectrophotometry (○) and those from the partition method (●). This figure, where the open circles and the closed circles are observed on the same line, confirms that the results from these two methods are essentially the same. From the good linear relationship obtained, the reaction can be said to obey first-order kinetics.

Thus, the partition method can be used to determine the pentavalent neptunium fraction in a mixture of Np(V) and Np(IV) ions, especially when their concentrations are in a tracer scale. Furthermore, it may be used in studying the kinetics of a reaction between penta- and tetravalent neptunium ions.