Distribution of Neptunium between TBP and Some Mineral Acids

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Tri-*n*-butyl phosphate*, an excellent solvent which plays an important role in the Purex process, attracts the attention of chemists. For example, the distribution of plutonium was studied by McKay et al.[1] in the TBP-nitric acid system. Peppard et al.[2-5] are aggressively studying the behaviors of both actinides and lanthanides in TBP-mineral acid systems.

Although the extraction of neptunium with TBP has caused deep concern in connection with the isolation of the element[6,7], systematic studies on the behavior of the element are not known. Besides, the existence of three kinds of oxidation states of the element, (IV), (V) and (VI) makes the study complicated.

In the present paper, extraction of neptunium with TBP is studied systematically with the emphasis on its oxidation states.

* Tri-*n*-butyl phosphate is denoted by "TBP" in the present paper.

1) G. F. Best, H. A. C. McKay and P. R. Woodgate, *J. Inorg. & Nucl. Chem.*, **4**, 315 (1957).

2) D. F. Peppard, G. W. Mason and J. L. Maier, ibid., **3**, 215 (1956).

3) D. E. Peppard, S. W. Moline and G. W. Mason, ibid., **4**, 344 (1957).

4) D. F. Peppard, W. J. Driscoll, R. J. Sironen and S. McCarty, ibid., **4**, 326 (1957).

5) D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, ibid., **4**, 334 (1957).

6) H. A. C. Mckay, "First United Nations International Conference on the Peaceful Uses of Atomic Energy", Vol. VII, P/441, United Nations Publication, New York (1956).

7) E. K. Hyde, ibid., Vol. VII, P/728.

Experimental

Sources of Materials.—Neptunium-239 tracer is prepared from uranyl nitrate hexahydrate irradiated by JRR-1 reactor for 2 hr. After cooling several hours, the irradiated uranyl salt is converted into chloride and dissolved in 0.5 M hydrochloric acid solution. After reduction by a small amount of granulated zinc**, neptunium is extracted by about 5% TTA***-benzene. After rinsing with a small portion of 0.5 M hydrochloric acid solution, the benzene layer is contacted with >3 N hydrochloric, nitric, perchloric or sulfuric acid according to preference. Neptunium is thus obtained as acid solution. The TTA which might go into the tracer solution is removed by contact with benzene. The radiochemical purity of the tracer is checked by both gamma spectrometry and the decay measurement. Separation from fission products is excellent. But a small remaining amount of uranium was still found by a color reaction with hydrogen peroxide.

Protactinium-233 is isolated from irradiated thorium nitrate by solvent extraction. Irradiation is carried out in conditions similar to those mentioned above. Protactinium is separated from thorium by contacting concentrated nitric acid solution with 10% TBP-toluene. In this separation protactinium is extracted into the organic phase leaving thorium in the aqueous phase. After washing with concentrated nitric acid, protactinium is recovered by shaking with water. The resultant solution of protactinium-233 gives no precipitate by adding aqueous ammonia, showing that practically thorium does not remain. The radiochemical purity of protactinium-233 thus prepared is checked again by both γ-spectrometry and the measurement of the decay curve.

Hafnium-181 received from Oak Ridge National Laboratory is used without further purification.

Thorium-234 is prepared according to Dyrssen's[8] method. The radiochemical purity is checked by determining its half life of 24.1 days.

Determination of Distribution Ratios. — In the determination of the distribution ratio, *Kd*, of a specific nuclide, defined as the concentration of nuclide in the organic phase divided by that of nuclide in the aqueous phase of two equilibrated liquid phases, a portion of aqueous acid of the indicated concentration containing a radioactive nuclide is equilibrated against a portion of solvent which is previously pre-equilibrated with respect to the corresponding barren aqueous acid. Every contact is carried out on a milliliter scale. For example, a 2.5 ml. portion of 10.1 M nitric acid containing approximately 10^5 cpm neptunium-239 is equilibrated with a 2.5 ml. portion of undiluted TBP which was previously contacted with three successive equal-volume portions of barren 10.1 M nitric acid. All solvent pre-equilibrations are made immediately before the use to avoid any complications arising from solvent hydrolysis. Aliquots of each phase are pipetted into small glass tubes for gamma counting. Gamma counting is made by means of Philips' scintillation counter with bed type head. Scrubbings are carried out both for aqueous and organic phases, if necessary. The *Kd* values are calculated dividing cpm of the organic phase by that of the aqueous phase after making a correction for natural counting.

Results and Discussion

Nitric Acid-TBP System. — Nitric acid solution of neptunium tracer prepared as mentioned above contains both neptunium (IV) and (V). The relative abundance between neptunium(IV) and (V) varies according to the treatment of the tracer solution. The freshly prepared solution contains only a very small amount of neptunium(V), whereas standing for a few days or warming in boiling water makes neptunium(V) rich.

Nitric acid solution containing both neptunium(IV) and (V) is contacted with TBP. The resultant organic or aqueous

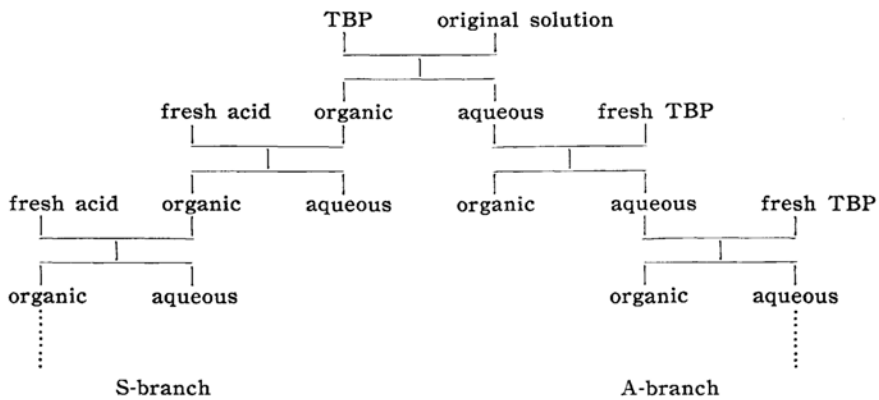

Fig. 1. The extraction scheme of neptunium.

** In order to avoid reduction of uranyl ion, reduction with zinc should be carried out at room temperature for only a few minutes.

*** Thenoyltrifluoroacetone

8) D. Dyrssen, *Svensk. Kem. Tid.*, **62**, 153 (1950).

phases are scrubbed with fresh acid solution or TBP, respectively. Scrubbings are carried out as shown in Fig. 1, until *Kd* values become practically constant, keeping the acidity of aqueous solution the same all through the procedures. Thus two values of *Kd*, Kd^{IV} and Kd^{V}, are obtained from S- and A-branches of the scrubbing scheme. Species which give Kd^{IV} and Kd^{V}, are assigned to neptunium (IV) and (V) respectively by the chemical behaviors against zinc, potassium bromate or TTA-benzene, to be mentioned below.

(*a*) *Oxidation with potassium bromate.* — The species which gives Kd^{IV} can not be oxidized with potassium bromate. At 0.5 N nitric acid Kd^{IV} value is 2.5. After adding the oxidant and scrubbing with a few portions of fresh acid, the *Kd* value remains almost constant, 2.7, showing that the species which gives Kd^{IV} is not practically oxidized.

On the other hand, Kd^{V} which is about 0.026 at 1 N nitric acid becomes about 16.3 after oxidation with potassium bromate and scrubbing with fresh acid solution. This change shows that the species which gives Kd^{V} is easily oxidized by potassium bromate. Besides that, the new third *Kd* value is also different from Kd^{IV} value of the same acidity. Accordingly this third value is supposed to be assigned to the hexavalent state. It is well known that neptunium(V) is easily oxidized by potassium bromate to neptunium(VI) state, whereas neptunium(IV) is not[9].

(*b*) *Reduction with zinc metal.* — Kd^{IV} value (6.92 at about 1 N) remains almost the same after adding zinc and heating on a water bath, whereas Kd^{V} value (0.026 at 1 N) becomes 7.8 after reduction with zinc metal****. This value almost coincides with that of Kd^{IV} at the same acidity, showing that the species which gives Kd^{V} is reduced to another species which gives Kd^{IV}.

(*c*) *Extraction with TTA.* — The comparison of extraction behaviors of the two species are given in Table I. The difference shown in the table again shows that the species which gives high Kd^{IV} in TBP-nitric acid system has high *Kd* in TTA extraction and is assigned to tetravalent[10], whereas another species which gives low Kd^{V} in TBP-nitric acid system has low *Kd* in TTA extraction and is assigned to quinquevalent[10].

TABLE I. THE BEHAVIOR OF NEPTUNIUM ON TTA EXTRACTION AT 1 N NITRIC ACID

Concn. of TTA in benzene (%, w/v)	*Kd* for the species which gives Kd^{IV} in $TBP\text{-}HNO_3$ system	*Kd* for the species which gives Kd^{V} in $TBP\text{-}HNO_3$ system
5.0	4.11	0.017
2.5	0.95	0.021
1.25	0.31	0.011

The variation of Kd^{IV} or Kd^{V} caused by changing the acidity of aqueous phase is shown in Fig. 2. In Fig. 3 acid dependences of neptunium(IV) and (V) are compared with those of hafnium(IV), thorium(IV), protactinium(V) and plutonium(IV). The thorium line is written according to Peppard et al.[2] and that of plutonium(IV) is rewritten based upon the values of McKay et al.[1] The behavior of neptunium(IV) shows strong similarity to that of plutonium(IV). However, *Kd* value of neptunium(IV) always lies below that of plutonium(IV) at the same acidity. *Kd* values of neptunium(IV) and thorium are almost the same at acidities less than 10 N. But the neptunium(IV) curve shows a maximum at about 9 N while that foi

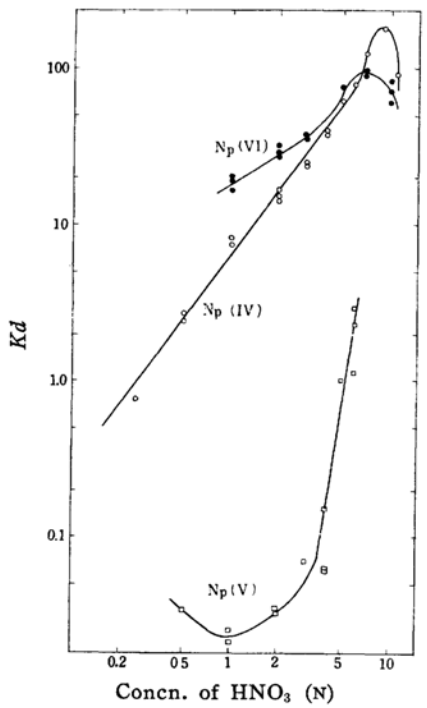

Fig. 2. The *Kd* values of neptunium in HNO_3-100% TBP.
—●— Np(VI) —○— Np(IV) —□— Np(V)

9) G. T. Seaborg and J. J. Katz, "The Chemistry of the Actinide Elements", Methuen and Co., Ltd., London (1957), p. 231.

**** The solution gives *Kd*=0.064 after heating on a water bath without zinc.

10) F. L. Moore, *Anal. Chem.*, **29**, 941 (1957).

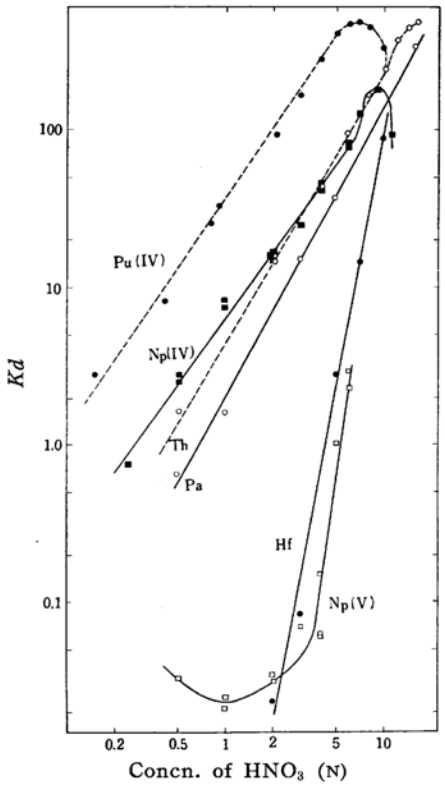

Fig. 3. The *Kd* values of neptunium, plutonium, thorium, protactinium and hafnium.
---●--- Pu(IV) —■— Np(IV) —●— Hf
---○--- Th —□— Np(V) —○— Pa

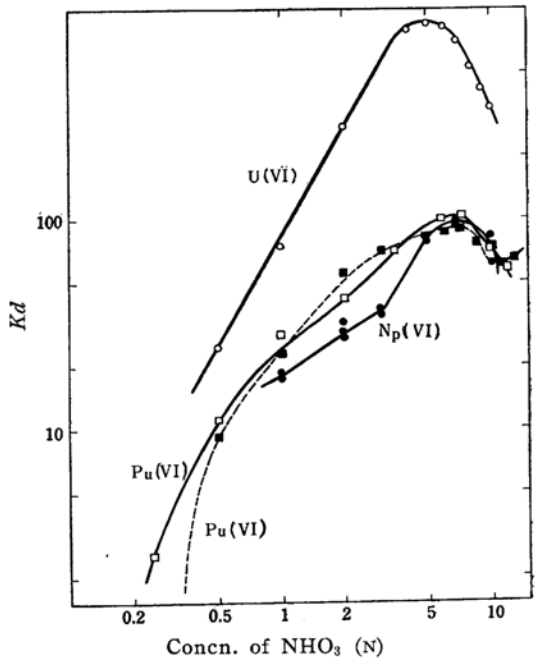

Fig. 4. The *Kd* values in HNO_3–100% TBP system.
—○— U(VI) —□— Pu(VI)
—●— Np(VI) —■— Pu(VI)

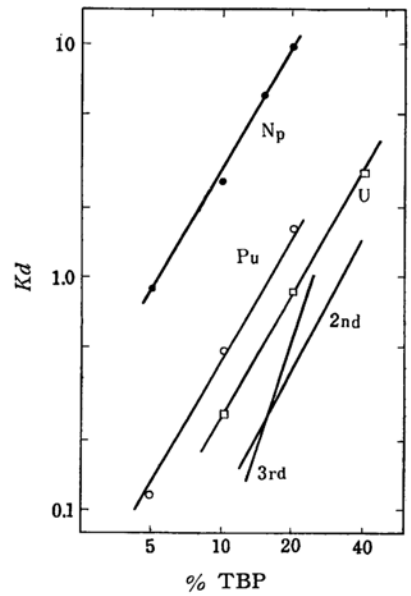

Fig. 5. The solvent dependence of *Kd* values in HNO_3–100% TBP system.
—●— Np(VI) at 10 N HNO_3
—○— Pu(VI) at 11.5 N HNO_3
—□— U(VI) at 0.27 N HNO_3

thorium does not. Hafnium shows a quite different behavior from that which neptunium(IV) does.

The behavior of neptunium(V) resembles that of hafnium(IV) more than that of protactinium(V).

As mentioned already neptunium(VI) is prepared easily by oxidation of neptunium (V) with potassium bromate and scrubbing of TBP phase with fresh acid solution in order to remove neptunium(V). Alternatively ceric ammonium nitrate works well as the oxidant in this case. The acid dependence of *Kd* value for neptunium(VI) is also given in Fig. 2. A comparison of *Kd* values for uranium(VI), neptunium(VI) and plutonium(VI) is also seen in Fig. 4. Naito[11] gave *Kd* values for macro amounts of uranium in 20% TBP in carbon tetrachloride-nitric acid system. He also found second power dependence of *Kd* in this system. Accordingly the present authors rewrite uranium (VI) curve of Fig. 4 multiplying Naito's *Kd* value with the factor of 25 in order to make it represent *Kd* values for 100% TBP-nitric acid solution system. Broken plutonium(VI) curve of Fig. 4 is rewritten

in a similar way correcting the values of McKay et al.[1] which were obtained with diluted TBP. The other plutonium(VI) curve represents values obtained by one of the present authors. As is known very well, correction with solvent dependence is not so satisfactory. Besides that, there might be some differences between behaviors of macro and micro amounts of actinide elements. Therefore, the comparison with each other of 3 curves in Fig. 4 will not be valid for a strict discussion. But it is remarkable that all of them show a maximum *Kd* value at about 6 or 7 N.

Solvent dependence of *Kd* value for neptunium is checked at 10 N nitric acid. As shown in Fig. 5, neptunium(VI) shows second power dependence. The figure shows also second power solvent dependences of uranium(VI) and plutonium(VI) according to the values obtained by Naito for uranium[11] and Mckay et al. for plutonium[1]. Here again strong similarity is shown among hexavalent uranium, neptunium and plutonium.

Hydrochloric Acid-TBP System. — Neptunium(VI) prepared by oxidizing neptunium(IV) and (V) with potassium chlorate and heating in boiling water shows *Kd* values as shown in Fig. 6. *Kd* values of uranium obtained by using uranium-233 as the tracer in the form of uranyl chloride are also show in the same figure in order to compare them with those for neptunium(VI). The acid dependences of these two elements are very similar in the shape indicating strong similarity in the chemical behaviors of these two species. However, neptunium(VI) is more extractable than uranium(VI) all through the acidity range investigated.

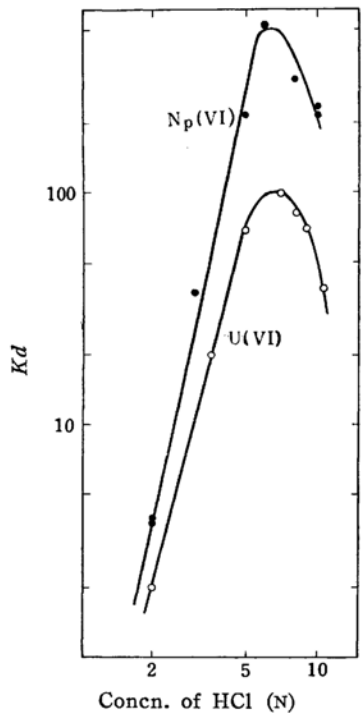

Fig. 6. The acid dependence of *Kd* values for neptunium and uranium.
—●— Np(VI) —○— U(VI)

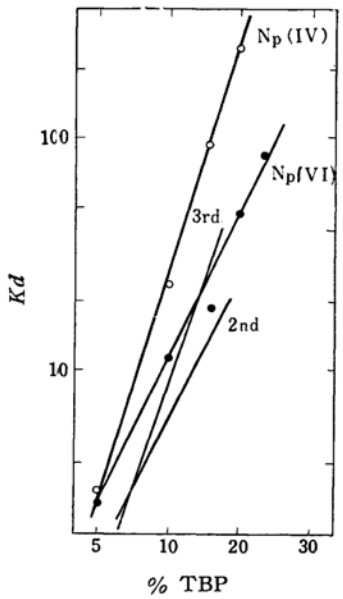

Fig. 7. The *Kd* values in diluted TBP–HCl system.
—●— Np(VI) at 6 N HCl
—○— Np(IV) at 8 N HCl

The solvent dependence of *Kd* for neptunium is studied at 6 N hydrochloric acid and found to be of second power as is seen in Fig. 7. Diluent used is toluene and TBP concentration is shown in volume per cent.

Neptunium(V) is prepared in hydrochloric acid solution by reducing neptunium(VI) with hydrazine sulfate. On the other hand, a solution of neptunium (IV) is prepared by recovering neptunium from TTA-benzene with hydrochloric acid (>3 N) and then treating it with hydroxylamine hydrochloride, granulated zinc or ascorbic acid in order to reduce neptunium(V) which comes into the solution in very small amount. Fig. 8 shows acid dependences of *Kd* values for both neptunium(V) and (IV) as well as those for hafnium, thorium and protactinium. The

11) K. Naito, In press.

neptunium(V) line is quite different from that of protactinium(V). In the range of 9~4 N, *Kd* of neptunium(IV) shows almost the same slope as those of thorium(IV) and hafnium(IV). It is notable that the acid dependence of neptunium(IV) shows a maximum at about 8 N.

The solvent dependence of *Kd* values for neptunium(IV) is studied at 8 N using toluene as the diluent. The result shows third power dependence as given in Fig. 7.

Sulfuric Acid-TBP System.—Neptunium (VI) in sulfuric acid solution is prepared by oxidation of the mixture of neptunium (IV) and (V) with ceric sulfate, while neptunium (V) is prepared by reducing neptunium (VI) with hydrazine sulfate. Variation curves of *Kd* values for both neptunium (V) and (VI) caused by the variation of the acidity in aqueous phases are given in Fig. 9. Extraction can not be carried out in the acidity range over about 20 N, because TBP becomes miscible with aqueous phase at such high acidity. Generally *Kd* values for both neptunium(V) and (VI) are small, their highest values being only about 2.5. The acid dependence of *Kd* values for protactinium is shown in Fig. 9 in order to compare it with that for neptunium(V).

Neptunium(IV) is prepared by contacting sulfuric acid solution with TTA-benzene which contains neptunium. In order to prevent contamination of neptunium (V), the resultant acid solution is treated

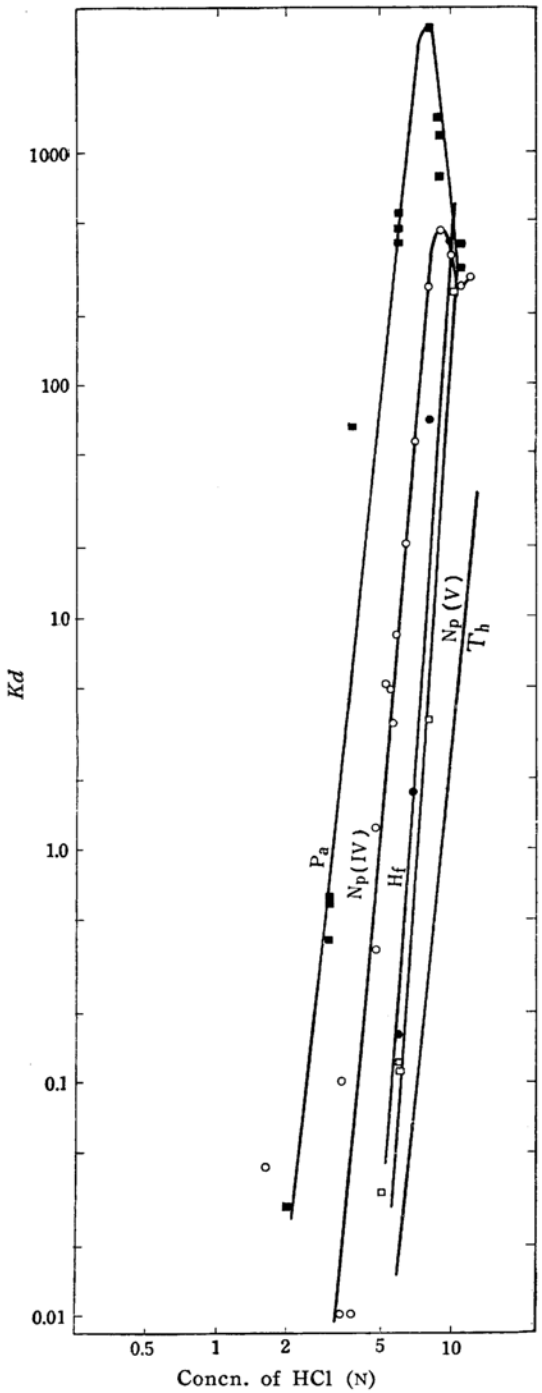

Fig. 8. The *Kd* values in HCl-100% TBP system.
—○— Np(IV) —□— Np(V) —— Th
—●— Hf —■— Pa

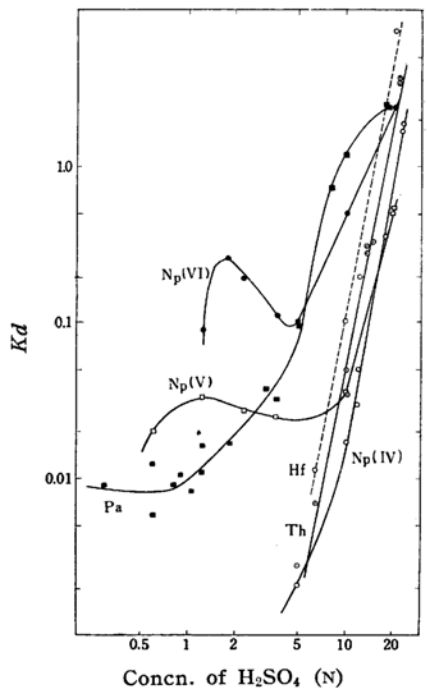

Fig. 9. The *Kd* values in H_2SO_4-100% TBP system.
—●— Np(VI) —■— Pa ---○--- Hf
—○— Np(IV) —□— Np(V) —⊙— Th

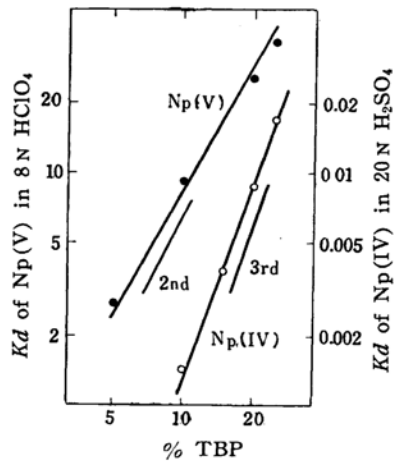

Fig. 10. The *Kd* values in diluted TBP-$HClO_4$ or H_2SO_4 system.
—●— Np(V) at 8 N $HClO_4$
—○— Np(IV) at 20 N H_2SO_4

with hydroxylamine hydrochloride and ferrous sulfate or 0.1 M hydroquinone and potassium iodide at higher acidities, while it is treated with granulated zinc at lower acidities. Acid dependence of *Kd* values for neptunium(IV) can also be seen in Fig. 9 where those for hafnium and thorium are added for comparison. These three curves resemble each other considerably. It is noted that in the range of lower acidities neptunium (IV) gives lower *Kd* values than neptunium(V) does.

The solvent dependence of *Kd* values for neptunium(IV) is studied at 20 N sulfuric acid and found as a third power. (Fig. 10).

Perchloric Acid-TBP System.—Perchloric acid (>3 N) solution obtained by contacting with neptunium solution in TTA-benzene contains only neptunium(V). This assignment is based on the following experiments:

(a) 3.4 N perchloric acid containing neptunium(V) is contacted with almost equal volume of TBP pre-equilibrated with 9 N hydrochloric acid. The resultant organic phase is equilibrated with many portions of 9 N hydrochloric acid successively. In this way, the system is converted to hydrochloric acid-TBP system. Finally *Kd* value approaches that of neptunium(V) at 9 N hydrochloric acid. (b) By oxidation with silver peroxide this species becomes another species which could be assigned to neptunium(VI).

The acid dependences of *Kd* values for both neptunium(V) and (VI) are given in Fig. 11 as well as that of protactinium.

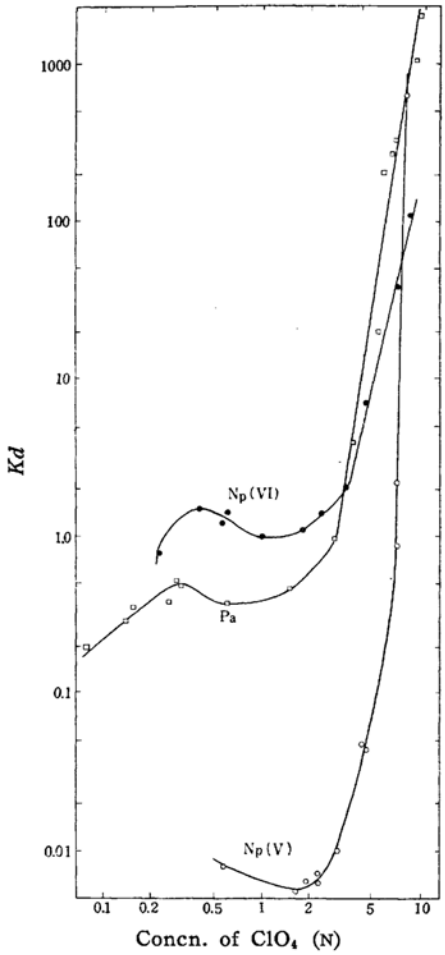

Fig. 11. The *Kd* values of neptunium and protactinium in $HClO_4$-100% TBP system.
—●— Np(VI) —□— Pa —○— Np(V)

It is characteristic that the neptunium(V) curve shows very rapid increase in *Kd* at the range of 3~8 N acidity. As will be shown later, this can be utilized for isolation of neptunium from irradiated uranyl nitrate.

As 8 N perchloric acid, the solvent dependence of *Kd* values for neptunium(V) is studied. The result is shown in Fig. 10.

The Reduction of neptunium(V) with hydroquinone and potassium iodide, hydrogen peroxide, granulated zinc or 3% zinc amalgam is not successful. Accordingly *Kd* values which could be assigned to the tetra-positive state can not be found.

Isolation of Neptunium from Irradiated Uranyl Nitrate. — As Fig. 11 shows, *Kd* for neptunium(V) in perchloric acid-TBP system varies from 800 at 8 N to 0.006 at 2 N. This is utilized in the isolation of

neptunium without introducing any other reagent.

Procedure. — Neutron irradiated uranyl nitrate hexahydrate is dissolved in a small volume of concentrated perchloric acid. The solution is heated under an infrared lamp in order to expel nitric acid. The residue is taken up by a few ml. of concentrated perchloric acid and the resultant solution is heated by dipping in boiling water for about 10 min. After cooling, it is shaken with 100% TBP. The organic phase contains neptunium(V) and uranium, while most of the fission products remain in the aqueous phase. The separated organic phase is shaken with 3 portions of 2 N perchloric acid. The resultant aqueous phase contains neptunium(V) and a small amount of uranium, while a large amount of uranium remains in organic phase. The resultant aqueous phase is washed with benzene in order to remove TBP, dried up under the infrared lamp, and dissolved into concentrated perchloric acid. The whole procedure is repeated as shown in Fig. 12.

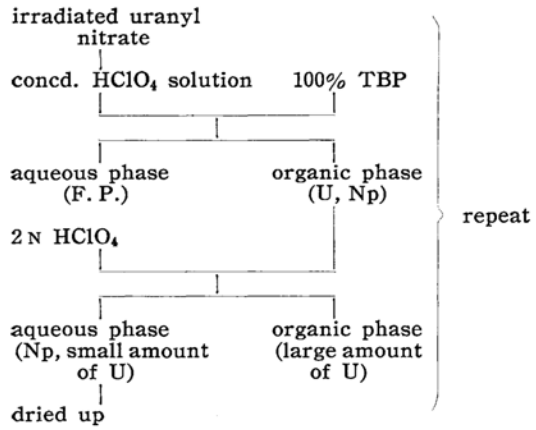

Fig. 12. Scheme for isolation of Np.

The yield of neptunium is 99%, and the decontamination of fission products is excellent. A very small amount of uranium remains.

Summary

Neptunium-239 is used as the tracer for studies on solvent extraction behaviors of neptunium in the following system:

1. Nitric acid solution and TBP.
2. Hydrochloric acid solution and TBP.
3. Sulfuric acid solution and TBP.
4. Perchloric acid solution and TBP.

Kd values are measured by combinations of scrubbing techniques and chemical treatments. In nitric, hydrochloric and sulfuric systems, neptunium gives three kinds of *Kd*, distribution ratio which could be assigned to oxidation states of (IV), (V) and (VI). On the other hand, in the perchloric system neptunium does not show *Kd* value which should be assigned to the oxidation state(IV).

Some of these results are compared with those of uranium, plutonium and other elements. In the nitric system, neptunium(VI) shows an acid dependence of *Kd* value similar to those of uranium (VI) and plutonium(VI). *Kd* values of neptunium(IV) and plutonium(IV) vary in almost the same way against the acid concentration of nitric acid. There is also a strong similarity between acid dependences of uranium(VI) and neptunium (VI) in the hydrochloric system.

Behavior of neptunium(V) are compared with those of protactinium.

Finally a simple method for isolation of neptunium from irradiated uranyl salt is stated.

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