Distribution of Neptunium between Di-(2-ethyl hexyl)-phosphoric Acid and Mineral Acids

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Solvent extraction studies on neptunium have been carried out using tri-*n*-butyl phosphate[1-4], tertiary amines[5], thenoyl tri-fluoro acetone[6], diethyl ether[7] or methyl isobutyl ketone[7], as an extractant.

However, the extraction behavior of neptunium using di-(2-ethyl hexyl)-phosphoric acid, HDEHP, has not been reported. The experimental results in the works referred to above have usually been complicated unless careful precautions were taken, because the neptunium tracer solution often contains neptunium in two or three oxidation states. Giving special attention to the oxidation states of neptunium, the extraction behavior of quadri-, quinqui- and sexi-valent neptunium in the system of diluted HDEHP vs. hydrochloric or perchloric acid was studied in this work.

Di-(2-ethyl hexyl)-phosphoric acid has been proved to be useful as a solvent extracting agent for uranium(VI) and other metals. Some works about this extracting agent have been published by a number of investigators[8-10]. Recently a comprehensive study on the extraction of metal ions from hydrochloric acid solution has been reported by Kimura[11]. According to these previous works, it seems that HDEHP behaves as a cation extracting reagent in the low acidity region. In other words, HDEHP-metal ion complex is formed with the inorganic cation in the aqueous phase, and extracted into the organic phase which is composed of the organic diluent and HDEHP. The neptunium(IV), (V) and (VI) cations also seemed to be extracted as the HDEHP-neptunium(IV), (V) or (VI) cation complex.

Experimental

Reagents.—The HDEHP received from Virginia Chemicals, Co. Ltd. was purified by the method of Peppard et al.[12] It was diluted with toluene, C. P.

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1) T. Ishimori and E. Nakamura, This Bulletin, 32, 713 (1959).

2) H. A. C. McKay, J. S. Nairn and M. B. Waldron, *Second United Nations International Conference on the Peaceful Uses of Atomic Energy*, p/304 (1958).

3) J. S. Nairn, D. A. Collins, H. A. C. McKay and A. G. Maddock, ibid, p/1458 (1958).

4) W. H. Lewis, ibid, p/537 (1958).

5) J. C. Sheppard, HW-51958 (1957).

6) L. B. Magnusson, J. C. Hindman and T. J. LaChapell, ANL-4066 (1947).

7) J. Kooi, *First United Nations International Conference on the Peaceful Uses of Atomic Energy*, Vol. VII, p/929, United Nations Publication, New York (1956).

8) C. F. Baes, Jr., R. A. Zingaro and C. C. Coleman, *J. Phys. Chem.*, 62, 129 (1958).

9) D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, *J. Inorg. & Nucl. Chem.*, 7, 276 (1958).

10) D. F. Peppard and J. R. Ferraro, ibid., 10, 275 (1959).

11) K. Kimura, This Bulletin, 33, 1038 (1960).

12) D. F. Peppard, G. W. Mason, J. L. Maier and W. J. Driscoll, *J. Inor. & Nucl. Chem.*, 4, 334 (1957).

grade, in this work. Hydrochloric and perchloric acids, analytical grade, were used as received.

Carrier-free 2.3d-neptunium-239, 27.5d-protactinium-233 and 24.1d-thorium-234 were prepared as described in the previous paper[1,13]. The activities of these nuclides were measured by a gamma-scintillation counter. Zirconium-niobium-95 imported from the Oak Ridge National Laboratory, Tenn. USA, was used as received and measured the hard beta-rays of zirconium-95 cutting off the soft beta-rays of niobium-95.

The radiochemical purity of the tracers was checked by gamma-spectrometry, beta-ray absorption and decay.

According to the method written in the previous work[1], the quadri-, quinqui- and sexi-valent neptunium tracers were prepared. In the case of quadrivalent neptunium, hydrochloric acid was used as the aqueous medium, because neptunium(IV) is unstable in a perchloric medium[1].

Distribution Measurement.—All experiments were carried out with radioactive tracers. The distribution ratio, K_d, of a given nuclide was determined in the usual way[1,11]. The scrubbing techniques were used in every case in order to obtain the K_d values exactly. In all cases both acid and solvent dependence of the K_d values were determined.

Results and Discussion

Distribution of Sexivalent Neptunium in the System of HDEHP vs. Perchloric Acid.—The distribution ratios of sexivalent neptunium were determined in the system of about 0.6% (v/v) HDEHP-toluene vs. perchloric acid varying the acidity from 0.1 to 0.5 N. Experimental results are shown in Fig. 1 where the curve for uranium(VI), taken from the work of Baes et al.[8], is also given for comparison. Baes et al. determined the distribution ratio of uranium in the system of 0.1 M (3.33% v/v) HDEHP-hexane vs. perchloric acid changing the acidity from 0.01 to 2.0 N.

From these results it is found that both sexivalent neptunium and uranium are extracted very well with HDEHP from perchloric acid solution. As Fig. 1 shows, both lines for neptunium and uranium have the slope of −2, suggesting a close similarity between uranium (VI) and neptunium(VI) ions.

The solvent dependence of K_d values for sexivalent neptunium was determined at 0.52 N perchloric acid concentration using toluene as the diluent. Experimental results for neptunium(VI) are shown in Fig. 2 together with the solvent dependence curve for uranium at 1 N perchloric acid, which is quoted from the work of Baes et al.[8] The distribution ratios of neptunium(VI) and uranium(VI) show the second power dependence on the HDEHP concentration, again suggesting the similarity

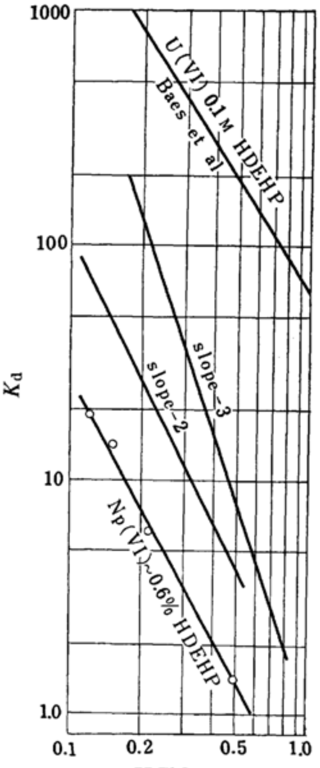

Fig. 1. The acid dependence of K_d values for neptunium(VI) and uranium(VI).

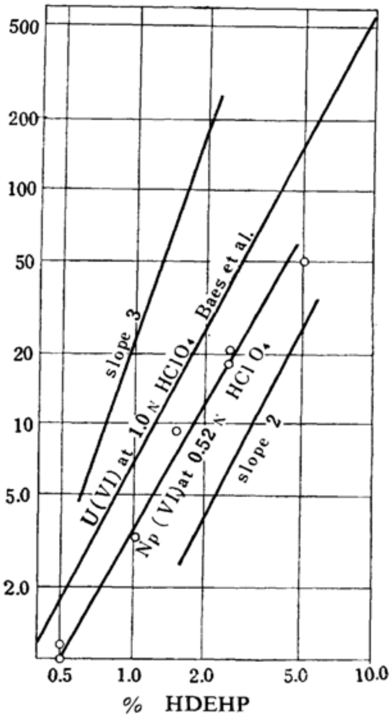

Fig. 2. The solvent dependence of K_d values for neptunium(VI) and uranium(VI).

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[13] T. Ishimori, K. Watanabe and E. Nakamura, This Bulletin, 33, 636 (1960).

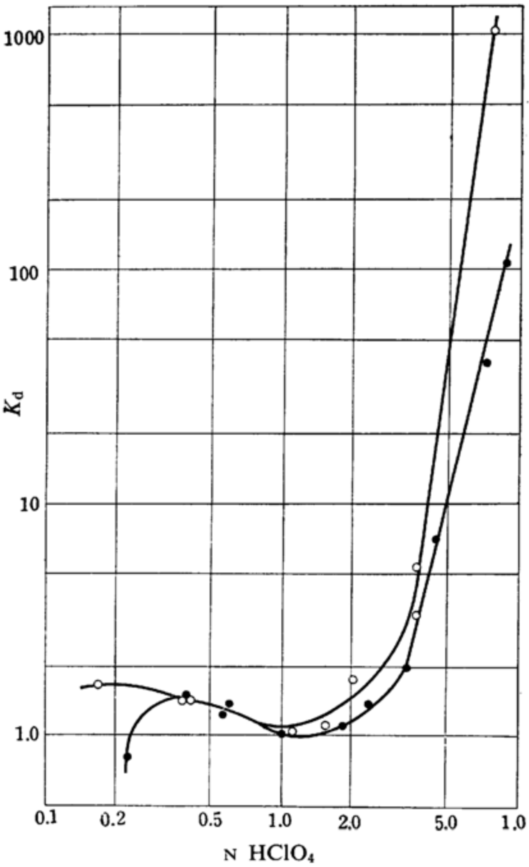

Fig. 3. The variation of the K_d values for sexivalent neptunium[5] and uranium[14] in the system of 100% TBP vs. perchloric acid.

—○— U(VI) by Naitō —●— Np(VI)

between the chemistry of sexivalent neptunium and uranium in an acid solution.

The similarity between sexivalent neptunium and uranium is also found in other systems:

The acid dependence curves for neptunium(VI)[1] and uranium(VI) in the system of 100% TBP vs. perchloric acid are given in Fig. 3 which shows that the behavior of sexivalent neptunium resembles that of uranium quite well, where the uranium curve is taken from the work of Naito[14]. Besides that found in the perchloric acid system similar behavior is also found in the nitric acid system. The acid dependence curve for neptunium(VI) also resembles that for uranium(VI)[1,2] in 100% TBP* vs. nitric acid system or in the trioctylamine vs. nitric acid system[5]. Thus it is likely that sexivalent ions of neptunium and uranium show almost the same behavior in the distribution experiments discussed above. In other words, the extraction mechanism of neptunium(VI) seems to be analogous to that of uranium(VI).

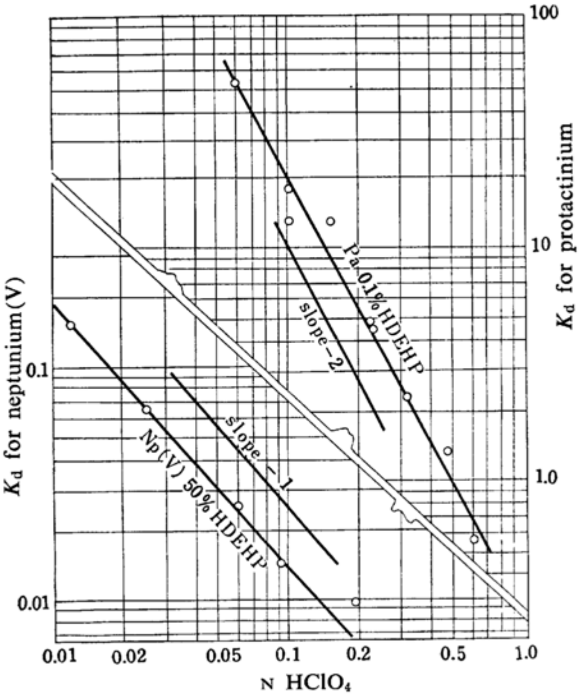

Fig. 4. The acid dependence of K_d values for neptunium(V) and protactinium.

According to Baes et al.[8], who discussed the composition of uranium-HDEHP complex based on the acid and the solvent dependence of the K_d values for uranium in the system of HDEHP vs. perchloric acid, the uranium-HDEHP complex is $UO_2A_4H_2$, where HA represents HDEHP molecule. As mentioned above, both acid and solvent dependence of K_d values for neptunium(VI) in the HDEHP vs. perchloric acid system coincide with those of uranium(VI), so that it is presumed that the neptunium(VI) ion is extracted forming the neptunium(VI)-HDEHP complex, $NpO_2A_4H_2$.

Distribution of Quinquivalent Neptunium in the System of HDEHP vs. Perchloric Acid.— The distribution ratios of quinquivalent neptunium were determined in the system of 50% HDEHP-toluene vs. perchloric acid varying the acidity from 0.01 to 0.2 N. The results obtained are given in Fig. 4, where the K_d values for protactinium are also shown. The K_d values for protactinium were so high that the relationship between the acidity and the K_d values for protactinium could not be found clearly using 50% HDEHP with which the extraction of neptunium(V) was studied. Therefore, 0.1% HDEHP-toluene was chosen as the extractant in the determination of the K_d values for

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* Tri-*n*-butyl phosphate.

[14] K. Naito, This Bulletin, 33, 363 (1960).

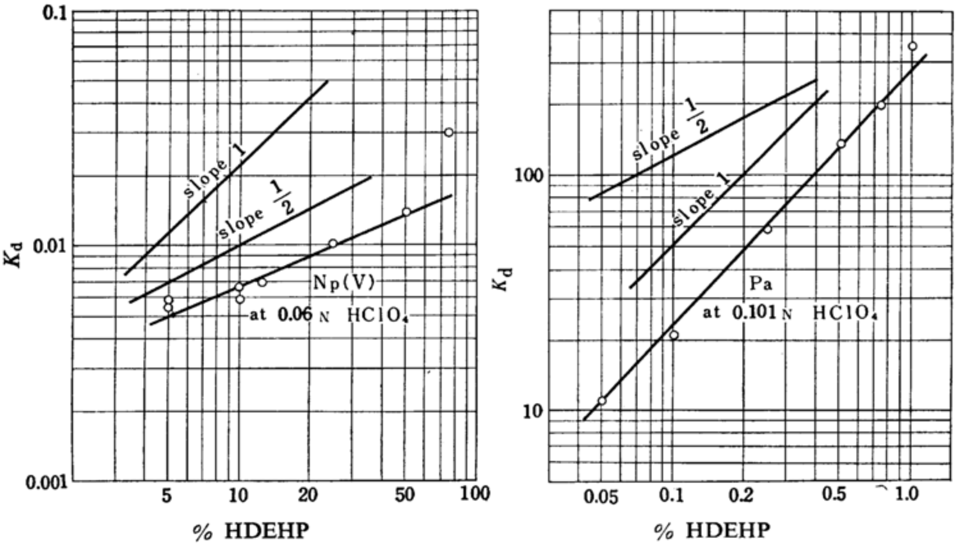

Fig. 5. The solvent dependence of K_d values for neptunium(V) and protactinium.

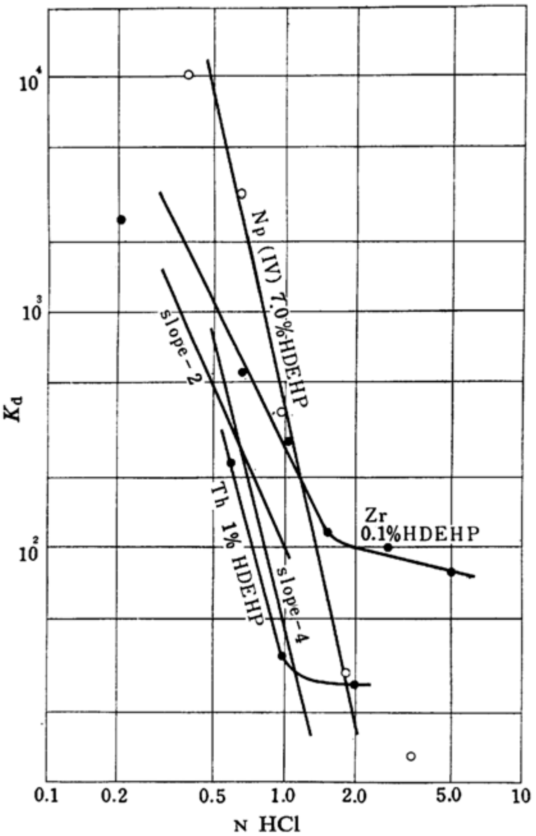

Fig. 6. The acid dependence of K_d values for neptunium(IV), thorium and zirconium.

protactinium varying the acidity of perchloric acid from 0.05 to 1.0 N. As Fig. 4 shows, the slope of the line for neptunium(V) is −1, whereas that for protactinium is −2. Thus it is likely that the neptunium(V) ion behaves differently from the protactinium ion in a dilute perchloric acid medium.

The variation of the K_d values of neptunium(V) and protactinium with the concentration of HDEHP in the organic phase, keeping the concentration of perchloric acid in the aqueous phase constant, is shown in Fig. 5. As Fig. 5 shows, the line for neptunium(V) has the slope of 1/2, whereas that for protactinium has the slope of 1. Assuming that the solvent dependence of K_d values for protactinium is kept at the first power up to 50% HDEHP at 0.1 N perchloric acid solution, it is calculated that the K_d value for protactinium is about 10^4, 500 times that of the K_d value shown in Fig. 4. On the other hand, in the 0.1 N perchloric acid-50% HDEHP system quinquivalent neptunium shows the K_d value of about 10^{-2} (Fig. 4). The difference of the K_d values between neptunium(V) and protactinium, 10^4 and 10^{-2}, shows that quinquivalent neptunium is less extractable than protactinium with the organic extractant from the aqueous phase. Similar relationships are seen in other cases like the system of 100% TBP vs. some mineral acids[1].

As mentioned above, the both acid and solvent dependence of K_d values for neptunium(V) show different values from those of protactinium. These facts suggest the difference between the chemistry of quinquivalent neptunium and protactinium.

Distribution of Quadrivalent Neptunium in the System of HDEHP vs. Hydrochloric Acid. —The distribution ratio of quadrivalent neptunium was determined in the system of 7.0%

HDEHP vs. hydrochloric acid varying the acidity from 0.5 to 3.0 N. The results are shown in Fig. 6, where the K_d values for thorium and zirconium are also given. The behavior of thorium was studied in the acidity range from 0.6 to 2.0 N using 1% HDEHP-toluene solution. Although zirconium is not a member of the actinide elements, the behavior of zirconium was studied as a quadrivalent species in the system of 0.1% HDEHP vs. hydrochloric acid varying the acidity from 0.2 to 4.0 N, where the K_d values for zirconium are so high that HDEHP-toluene solution had to be diluted to 0.1%.

From these results, it is found that thorium and zirconium are more extractable than quadrivalent neptunium. As is shown in Fig. 6, the lines for neptunium(IV) and thorium both have the slope of -4. The behavior of thorium had been studied by Peppard and Ferraro who had also found negative fourth power dependence of the K_d values on the acidity of hydrochloric acid[10]. On the other hand, zirconium shows a negative second power dependence on the acidity. The difference between the neptunium(IV) and zirconium ion seems to be greater than that between the neptunium(IV) and thorium ion.

The K_d values for quadrivalent neptunium in the system of 0.5 N hydrochloric acid vs. HDEHP-toluene are studied, the HDEHP concentration being varied. In Fig. 7, the neptunium(IV) curve is compared with those for thorium and zirconium. The behavior of thorium is taken from the work of Ishimori[15] in the system of 0.5 N perchloric acid vs. HDEHP-toluene. Peppard and Ferraro had also given a third power dependence of the K_d values for thorium on the hydrochloric or perchloric acid concentration. On the other hand, the results for zirconium obtained presently fall on a line of slope 2 in Fig. 7. Thus it is shown again that the quadrivalent neptunium ion behaves in a manner more nearly similar to thorium ion than to zirconium ion in the hydrochloric acid solution.

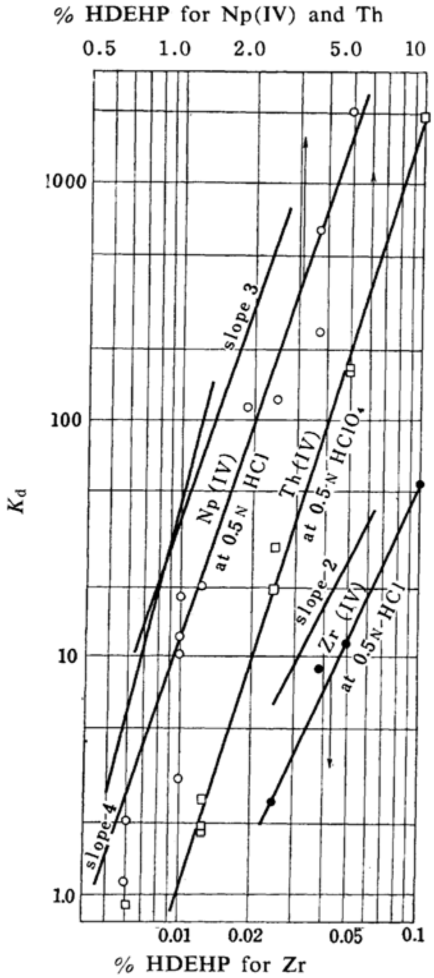

Fig. 7. The solvent dependence of K_d values for neptunium(IV), thorium and zirconium.

It is likely that the HDEHP extraction mechanism of neptunium(IV) from hydrochloric acid is similar to that of thorium ion, because both acid and solvent dependence of K_d values for neptunium(IV) coincide with those of thorium. That is to say, neptunium(IV)-HDEHP complex is supposed to have an iso-morphous structure with that of thorium(IV)-HDEHP complex. As the formula for the thorium complex, Peppard and Ferraro gave $ThA_2(HA_2)_2$ which was proposed from the results of the infrared spectra and the elementary analysis, where HA denotes the HDEHP molecule. Therefore it might be reasonable to give $NpA_2(HA_2)_2$ for the neptunium(IV)-HDEHP complex.

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[15] Unpublished work performed during the writer's stay in the Argonne National Laboratory, Lemont, Illinois, USA.