Inorganic Extraction Studies on the System between Bis(2-ethyl hexyl)-orthophosphoric Acid and Hydrochloric Acid. II

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(Received July 25, 1960)

In the previous paper¹⁾, was reported the influence of acid concentration on the solvent extraction of about fifty elements in the system of 50 percent bis(2-ethyl hexyl) orthophosphoric acid (HDEHP)-aqueous hydrochloric acid. As is well known in solvent extraction studies²⁾, the distribution ratio, K_d, is much affected by the solvent concentration in a way similar to that by the acid concentration.

Accordingly, a study on the influence of solvent concentration in organic phase is very important for the purpose of determining the suitable concentration for a given separation procedure. Besides that, the relationship

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

2) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons Inc., New York (1957), p. 52.

between K_d values of a given ion and solvent concentrations gives some suggestions on the chemistry of the extraction.

Along this line, have been published many studies[3-5] on the chemical mechanisms of thenoyltrifluoroacetone extraction or the chemical composition of the thenoyltrifluoroacetates. Concerning HDEHP extraction, the solvent dependence of the distribution ratios was already studied for lanthanide elements[6-8], uranium[8-9], iron and a few other chemical elements[8]. However, no comprehensive study on the extraction from a given mineral acid solution has been reported. In the present paper, the influence of solvent concentration is presented, discussing the extraction carried out from hydrochloric acid solution of a given acidity containing each of about fifty elements.

Experimental

Sources of Materials. — The bis(2-ethyl hexyl)-orthophosphoric acid received from Virginia Chemicals Co. was purified and checked on its purity as reported in the previous study[1]. The work reported here was carried out using HDEHP diluted with toluene of guaranteed reagent grade.

Radioisotopes used were the same as those which were reported previously[1] except for the following: The nuclides 19day ^{86}Rb and 40day ^{103}Ru were imported and used as received. The radioactive tracers of neodymium, samarium, europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium and lutetium contributed for counting were mainly 11.3day ^{147}Nd, 47 hr. ^{153}Sm, 9.2hr. ^{152}Eu, 18.0hr. ^{159}Gd, 73day ^{160}Tb, 2.32hr. ^{165}Dy, 9.4day ^{169}Er, 129day ^{170}Tm and 6.8day ^{177}Lu, respectively[10]. These were prepared by the neutron irradiation of highly-purified oxides in JRR-1. In the cases of gadolinium and erbium, the radioactivities caused by the radioactive daughters (6.75day ^{161}Tb and 680day ^{171}Tm) of simultaneously yielded short half-lived nuclides (3.73 min. ^{161}Gd and 7.5hr. ^{171}Er) were corrected from the total activities of gadolinium and erbium by the results of their decay measurements, respectively. The nuclide 27.4day ^{233}Pa was obtained as a by-product of uranium-233 processings[11].

The radiochemical purity of these nuclides was checked by their half-lives, γ-ray spectra, and/or β-ray absorption curves with aluminum foils.

Determination of Distribution Ratios.—The distribution ratio, K_d, of a given nuclide was radiometrically determined. The details and some remarks of the method written about in the previous report[1] were also adopted in the present study. Most of the data in this experiment were obtained after shaking the two layers for three minutes.

Although the HDEHP concentration in the organic layer was varied usually in the range from 0.5 to 50 volume percent, it was extended to 0.01 volume percent in some cases. The extraction with barren toluene containing no HDEHP was also checked. On the other hand the acidity in the aqueous layer was kept constant in a series of extractions of a given element.

Results and Discussion

The results are summarised in Fig. 1 as a series of graphs of log K_d vs. log (% HDEHP) where K_d is the distribution ratio and % HDEHP the concentration of HDEHP in volume percentage.

As reported previously[1], K_d values for each cation usually depend on inverse power of hydrogen ion concentration, and furthermore K_d values for mono-, di-, tri-, and tetra-valent cation decrease with the following general sequence; $M^{4+} > M^{3+} > M^{2+} > M^{+}$. Meanwhile, K_d values for the ion ready to form an anion are usually low. Therefore, it is desired that the acidity should be changed according to the valence of the ion concerned.

Although the acidity of aqueous phase was kept constant at 0.5 N for most of the elements, it was 0.05 N for the alkali and alkaline earth elements, 0.3 N for the rare earth elements, and 0.1 N or 2 N for some other elements. In some cases, the extractions of ion from the solutions of two different acidities were undertaken. The Arabic numeral in each graph shows the acidity taken.

Fig. 1 was compiled from some published and unpublished results. Data for lead and bismuth were taken from the observation of Ishimori[12]. Data for yttrium, promethium, thulium and americium were taken from the work of Peppard et al[6]. The K_d values for selected lanthanide cation(III) in HDEHP-hydrochloric acid system are inverse third power dependent on the hydrogen ion concentration of the aqueous phase. Therefore, K_d values for yttrium, promethium, thulium and americium were obtained correcting Peppard's value (at 0.552 M, 0.146 M, 0.552 M, and 0.275 M, respectively) for 0.3 N hydrochloric acid solution.

As is seen in Fig. 1, the K_d values for each

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[3] R. E. Connick and W. H. McVey, *J. Am. Chem. Soc.*, **71**, 3128 (1949).

[4] E. H. Hyffman and L. J. Beaufait, ibid., **71**, 3179 (1949).

[5] J. C. Sullivan and J. C. Hindman, ibid., **76**, 5931 (1954).

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

[7] D. F. Peppard, G. W. Mason, W. J. Driscoll and R. J. Sironen, ibid, **7**, 276 (1958).

[8] C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman and J. C. White, "Proceedings of the International Conference on the Peaceful Uses of Atomic Energy", Vol. 28, United Nations, Geneva (1958), p. 289.

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

[10] K. Kimura, "Hoshasen Data Book", Chijin Shokan, Tokyo (1958) p. 92.

[11] T. Ishimori et al., unpublished.

[12] T. Ishimori, unpublished.

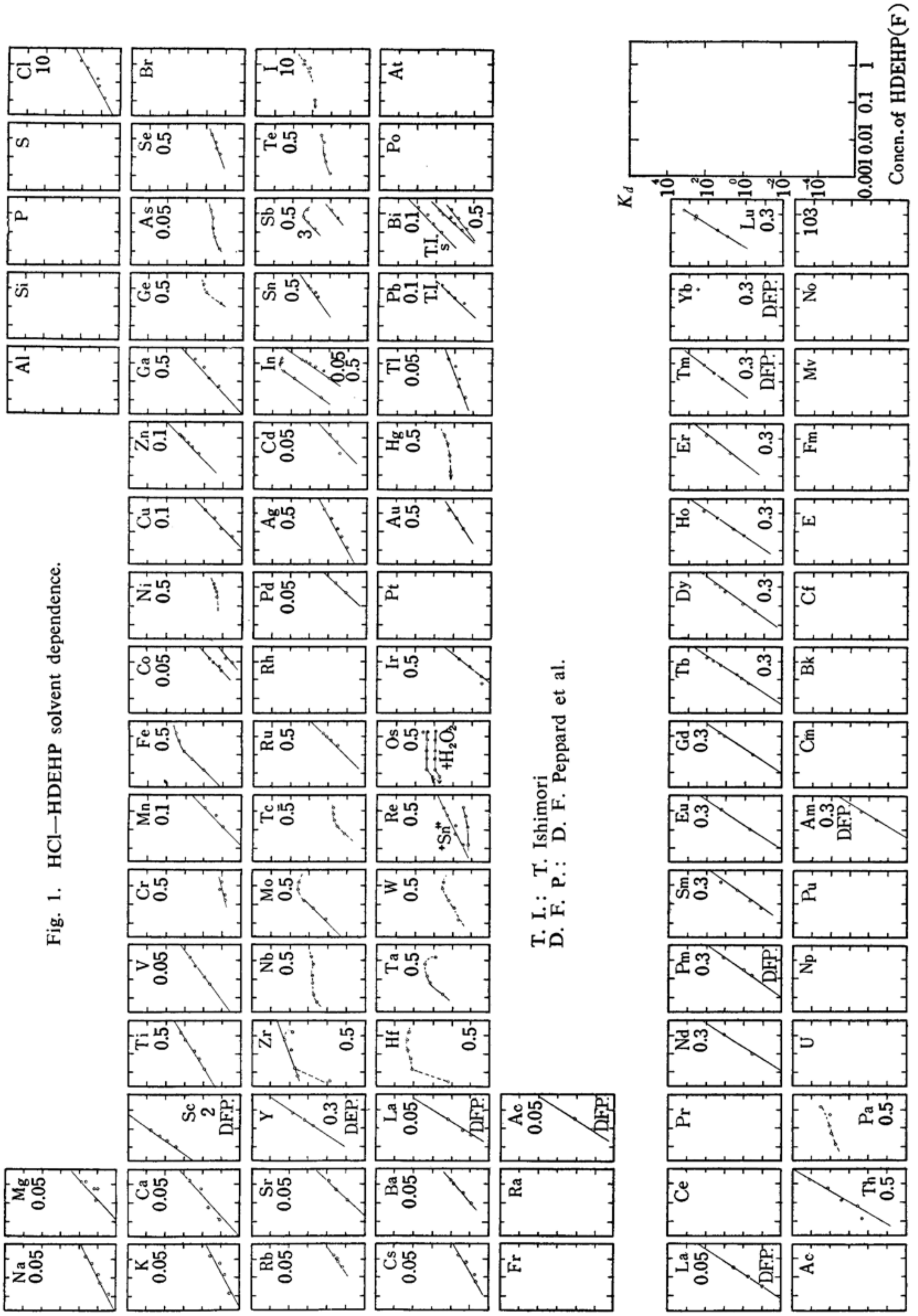

Fig. 1. HCl—HDEHP solvent dependence.

T. I.: T. Ishimori
D. F. P.: D. F. Peppard et al.

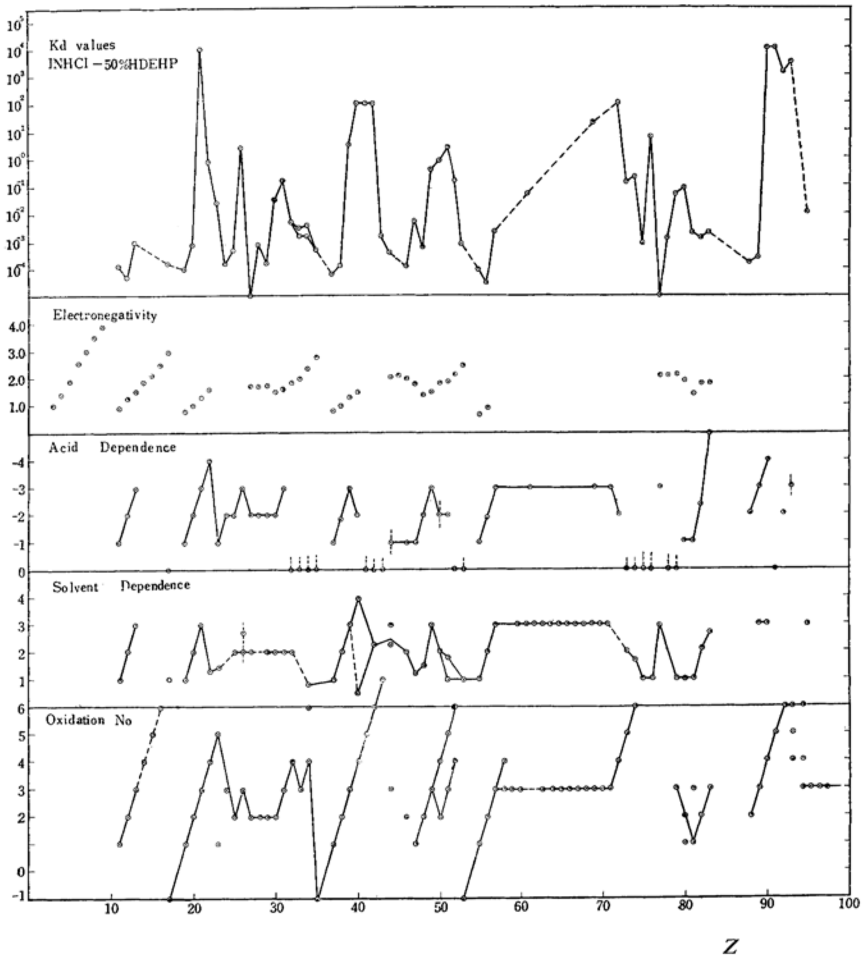

Fig. 2. *Z* dependences.

of almost all the elements increase as the concentration of HDEHP in the toluene phase increases. A similar relationship is observed generally in many solvent extraction systems.

The K_d values for alkali metals, alkaline earth metals and lanthanide elements show the first, second and third power dependence on the HDEHP concentration in the toluene phase, respectively. A similar relationship holds for some other elements: silver and thallium(I) indicate the first power solvent dependence, manganese, cobalt, copper, zinc and cadmium the second dependence, and indium indicates the third. The K_d values for iron and gallium follow the second power solvent dependence and those for thorium the third dependence.

The K_d values for zirconium remain nearly constant in almost the whole range of the solvent concentration. Although the strange behavior of zirconium is not clearly explained, it might be caused by both the hydrolysis of zirconium ion and its high K_d values. Scadden and Ballou[13] reported that only zirconium and indium are completely extracted with 0.06 M dibutylphosphoric acid (HDBP) for 1 M nitric, hydrochloric, or perchloric acid; and Ishimori et al[14] reported that only zirconium is extracted with dilute tributyl phosphate (1%. toluene diluent) from 8 M hydrochloric acid solution of the fission products. Furthermore, White[15] reported that zirconium is completely extractable from 1 M hydrochloric acid solution with 0.1 M trioctylphosphine oxide and partially extractable with 0.1 M tris-2-ethylhexyl phosphine oxide. This high extractability of zirconium with many alkyl phosphorous reagents is noteworthy as compared with the very low solubility of zirconium phosphate in mineral acids. Hafnium, niobium and protactinium resemble zirconium in the solvent dependence of their K_d values.

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[13] E. M. Scadden and N. E. Ballou, *Anal. Chem.*, **25**, 1602 (1953).

[14] T. Ishimori K. Umezawa and K. Watanabe, *J. Atomic Energy Soc. Japan* **1**, 299 (1955).

[15] J. C. White, USAEC TID-7555, 249 (1958).

The K_d values for osmium are relatively high and kept nearly constant. Besides that, osmium can be extracted with pure toluene fairly well, giving the K_d value of 1.31. This K_d value is as low as about one tenth of the K_d values for toluene containing HDEHP. The K_d value is shown with open circles attached with arrow in Fig. 1. The addition of hydrogen peroxide to the tracer solution makes all the K_d values for osmium low, keeping the shape of the curve unchanged. This would be explained as a partial reduction of the readily extractable species of osmium. Thus, the relatively high K_d values for osmium might be explained assuming the extraction of a neutral molecule such as osmium tetroxide. Futhermore, the higher K_d values with the HDEHP toluene solution might indicate that HDEHP promotes the extraction to some extent.

The K_d value for mercury with pure toluene is also high. It appears as if the extraction of mercury is partially based on the extraction of a neutral molecule such as $HgCl_2$, which is slightly ionized in the low concentration region of chloride.

In the case of iodine, the K_d values for the acid range up to 5 N were very low[1]. However, the slightly high K_d value is obtained at 10 N. Similarly the K_d value for pure toluene at 10 N hydrochloric acid remains high. It may be based on the oxidation of tracer quantity of iodide ion with the micro-amount of chlorine. Scadden and Ballou[13] reported that the neutral iodine molecule, I_2, showed a high extractability with dibutyl phosphate.

The different slopes of solvent dependence curve for bismuth are obtained varying the acid concentration of aqueous phase. Because it is known that bismuth forms a series of chloride complexes in hydrochloric acid solution[16], and that the ratios among these chloride complexes vary with the chloride concentration, it may be natural that the slope is changed according to the acid concentration.

On the other hand, the slopes of the K_d curves for indium and rare earth elements are not dependent on the acid concentration. For instanse, the K_d values for thulium follow the third power solvent dependence both at 0.552 M[6] and at 0.3 N hydrochloric acid. Concerning the K_d values for indium, a similar relationship also holds at 0.5 N and 0.05 N hydrochloric acid. The K_d values for cobalt are very low, but similar results are obtained at 0.5 N and 0.05 N, using a larger amount of radioactive cobalt-60.

The slopes of the solvent dependence and of the acid dependence and the oxidation number are plotted against the atomic number, Z, in Fig. 2. The graph of the "best values of electronegativity"[17] vs. Z and that of the K_d values between 50% HDEHP and 1 N hydrochloric acid vs. Z are attached to Fig. 2. The values of electronegativity of cobalt, nickel, ruthenium, rhodium, palladium, iridium and platinum are taken from Haïsinsky's data[18].

As mentioned above, the solvent dependence is studied at one of the several definite acidities. Accordingly the data of the solvent dependence may not be suitable for detailed discussion, because the formation of chlorocomplexes differs both with the acidity and with the element. However, the data may be applicable to general discussion. The vertical dotted lines indicate that the slope could not be clearly obtained. Almost all of the elements showed the slope defined as "the second type" in the previous paper indicate the slope of zero in the graph of the acid dependence vs. Z.

As is seen in Fig. 2, the slopes and the oxidation numbers vary regularly in Na–Mg–(Al), K–Ca–Sc, Rb–Sr–Y, and Cs–Ba–La, showing the increasing lines with increasing Z. Although the Fr–Ra–Ac–line is not studied, it may follow the similar relationship. Concerning the Ib–IIb–IIIb group of the periodic table, only the Ag–Cd–In line is satisfied with this increasing relation. On the other hand, the Cr–Zn line or La–Lu line is nearly horizontal. The curves indicate some complicated relationships for the ranges of the IVb–Vb–VIb group and of the platinum group in the periodic table.

Fig. 2 shows that the relation among the slopes of the dependences and the oxidation number is roughly divided into two types.

The first type is characteristic in the fact that the relation which the slope of the solvent dependence has equals that of the acid dependence and further that the oxidation number does so also. Scandium, yttrium, or lanthanum are satisfied with this relationship. This tendency is generally observed in the solvent extraction system where chelation plays an important role:

$$M^{m+}{}_{(aq.)}+m\mathrm{HR}_{(org.)}\rightleftarrows \mathrm{MR}_{m(org.)}+m\mathrm{H}^{+}{}_{(aq.)} \tag{1}$$

In Eq. 1, the distributio ration of M is given:

$$K_d=K[\mathrm{HR}]^{m}{}_{(org.)}[\mathrm{H}^{+}]^{-m}{}_{(aq.)} \tag{2}$$

Baes and Peppard[6,7] assumed the following

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[16] L. S. Newman and D. N. Hume, *J. Am. Chem. Soc.*, **79**, 4576 (1957).

[17] H. O. Pritchard and H. A. Skinner, *Chem. Revs.* **55**, 767 (1955).

[18] M. Haïsinsky, *J. Phys.* **7**, 7 (1946); *J. Chim. Phys.* **46**, 298 (1949).

equilibrium for the reaction between uranium(VI) or lanthanide elements in perchloric acid solution and HDEHP, considering that the HDEHP molecule is essentially completely dimerized in the toluene phase:

$$M^{m+}{}_{(aq.)}+m(HDEHP)_{2\,(org.)} \rightleftarrows MH_m(DEHP)_{2m(org.)}+mH^{+}{}_{(aq.)} \quad (3)$$

where the K_d value of M is given as:

$$K_d=K[(HDEHP)_{2(org.)}]^{m}[H]^{-m}{}_{(aq.)} \quad (4)$$

It is assumed that the alkali metal cation(I) and the alkaline earth metal cations(II) follow Eq. 3, showing the first and second power solvent dependence and the inverse first and second power acid dependence, respectively. Because manganese(II), cobalt(II), copper(II), zinc(II), silver(I), cadmium(II), indium(III) and thallium(I) also show the relationship of equal figures, it seems that they are also satisfied with Eq. 3.

K_d values of iron(III) are approximately second-power dependent on the HDEHP concentration for 0.5~0.05% HDEHP in the organic phase and are inverse third-power dependent on the acid concentration in the aqueous phase. Thus, iron belongs to a modified first type. Blake et al.8) postulate the following equilibrium for the partition of ferric iron:

$$Fe^{3+}+2(HDEHP)_2+HOH \rightleftarrows Fe(OH)H_2(DEHP)_4+3H^{+} \quad (5)$$

Besides that, Peppard and Ferraro19) mentioned that the solvent extraction of thorium is approximately third-power dependent on the HDEHP concentration and inverse forth-power dependent on the HDEHP concentration and inverse forth-power dependent on the acid concentration, and that these tentative dependencies are consistent with either or both of the following equilibria:

$$M^{4+}{}_{(aq.)}+3H_2DEHP_{2\,(org.)} \rightleftarrows MDEHP_2(HDEHP_2)_{2\,(org.)}+4H^{+}{}_{(aq.)} \quad (6)$$

and

$$M^{4+}{}_{(aq.)}+3H_2DEHP_{2\,(org.)}+HOH \rightleftarrows M(OH)(HDEHP_2)_{3\,(org.)}+4H^{+}{}_{(aq.)} \quad (7)$$

It seems that the solvent extraction of gallium also follows similar equilibria, showing the second-power solvent dependence and the inverse third-power acid dependence. A similar relationship also holds for the extraction of titanium.

On the other hand, the second type is characteristic both in the acid dependence with the slope of zero defined as "the second type" 1) and in the solvent dependence with the slope of one or more. These tendencies are commonly seen in the solvent extraction, in which the ion association plays an important role20) such as TBP extraction of uranyl ion21).

Chlorine, selenium, molybdenum, tungsten and gold, which form anions easily and have a relatively high value of electronegativity, are typical for the second type. Accordingly, it appears that the solvent extraction of these elements is based on partition as is found in the extraction with TBP. As for the electonegativity, it is noticed that the more extractable element generally has a value between 1.0 and 2.0.

Thanks are due to Dr. Tomitaro Ishimori for his guidance and suggestions, to Dr. Kenjiro Kimura and Dr. Toshio Nagai for their encouragement, and also to Mr. Ikuo Suzuki for his assistance.

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19) D. F. Peppard and J. R. Ferraro, *J. Inorg. Nucl. Chem.*, 10, 275 (1959).

20) G. H. Morrison and H. Freiser, Ref. 2, p. 59.

21) K. Naito, This Bulletin, 33, 363 (1960).