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

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During the last decade, alkyl esters of orthophosphoric acid as liquid-liquid solvent extraction reagents have been investigated widely for both chemical and chemical engineering purposes. A number of review articles on this subject(1,2) have been published. Among the esters, tributyl phosphate is beneficially used in several processes of the recovery of uranium and plutonium as well as in many other chemical separation techniques.

Bis(2-ethyl hexyl)-orthophosphoric acid, commonly abbreviated as HDEHP or D2EHPA, has been employed as a liquid-liquid extraction reagent primarily for uranium by Blake et al.(3) at Oak Ridge National Laboratory, and furthermore by Peppard et al. for berkelium(IV)(4) and lanthanides(5). Some physicochemical studies have also been performed by Peppard(6,7), Baes and others(8). Recently, some metal complexes of this reagent were prepared by Peppard and Ferraro(9) and their infrared spectra were also surveyed.

However, no comprehensive study on the

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1) C. A. Blake, Jr., C. F. Baes, Jr., K. B. Brown, C. F. Coleman and J. C. White, "Proceeding of the Second International Conference on the Peaceful Uses of Atomic Energy", A/Conf. 15/P/1550 (1958).

2) G. H. Morrison and H. Freiser, "Solvent Extraction in Analytical Chemistry", John Wiley & Sons. Inc., New York (1957), p. 146.

3) C. A. Blake, D. J. Crouse, C. E. Coleman, K. B. Brown and A. D. Klemers, USAEC ORNL-2172 (1956).

4) D. F. Peppard, S. W. Moline and G. W. Mason, *J. Inorg. Nucl. Chem.*, **4**, 344 (1957).

5) D. F. Peppard, G. W. Mason and S. W. Moline, ibid., **5**, 141 (1957).

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

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

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

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

extraction from a given mineral acid solution has been reported. In the present paper, the influence of acid concentration is presented and discussed when the extraction is carried out from hydrochloric acid solution containing each of about fifty elements.

Experimental

Solvent.—The bis(2-ethyl hexyl)-orthophosphoric acid received from Virginia Chemicals, Co. was purified according to the method of Peppard[7,10]. All treatments were manually performed using two separatory funnels. The purity of the solvent was checked by the determination of the distribution ratio, K_d, for lanthanum and iron[1,6]. The work reported here was carried out using HDEHP diluted to 50 volume percent with toluene of chemically pure grade.

Determination of Distribution Ratios. — The distribution ratio, K_d, of a given nuclide (or nuclides), defined as the concentration of nuclide in the organic layer divided by that in the aqueous layer, was determined radiometrically. In the determination, a portion of an aqueous acid solution of a given concentration containing the radioactive tracer was shaken with a portion of the solvent which had been previously equilibrated with the corresponding barren aqueous acid.

Details of the method of the determination were as follows. Two millilitres each of aqueous acid and pre-equilibrated HDEHP were placed in a 5 ml. glass-stoppered measuring-cylinder, and shaken vigorously. After the two layers were transferred together into a centrifuge tube, the content was centrifuged at 4000 rpm for 1 min. Nearly all of the aqueous layer was transferred with a transfer pipette to a new centrifuge tube. Both tubes were centrifuged for 1 min. again. Aliquots of each layer were taken into two glass-stoppered tubes for the radioassay. The quantity of the aliquots taken was usually 1 ml.

In several cases, a portion of the organic extract obtained was transferred to a new 5-ml. cylinder, shaken with an equal volume of fresh aqueous acid, and treated again as mentioned above. Further scrubbings were made in a few cases. By these scrubbings and the following redetermination of K_d values, difficulties caused by the undesired metal hydrates were obviated.

The greater part of the data was obtained by γ-ray scintillation counting. The counter was a Philips Model PW 4022-52-32 counting unit and the scintillator was a well-type Na(Tl)I crystal "7F8" made by Harshow Chemicals Co. In cases of β- and α-ray emitters aliquot portions from both layers were carefully dried up on small stainless steel or platinum disks, under an infrared lamp or in an induction furnace avoiding any loss of activity and dissolution of stainless steel in hydrochloric acid. β-Counting was performed with a G-M counter having a mica window of 2.1 mg./cm^2 thick made by Rikagaku Kenkyujo, and α-rays with a proportional counter of Nuclear Measurement Corp. or with an α-ray scintillation counter of Nihon-Musen Irigaku Kenkyujo.

Remarks on the Determination.—Almost all data in this experiment were obtained after shaking the two layers for two minutes. According to Peppard and his co-workers[7], the equilibrium of extraction of ^{147}Pm was attainable in a mixing period of less than 30 sec. Thus the equilibrium might be attained within two minutes for almost all elements. The K_d values for magnesium, aluminum, titanium, vanadium and silver were obtained by one minute shaking, because their half-lives are short.

The range of acidity of the aqueous hydrochloric acid solution covered mainly from 0.01 to 2 N. In some cases, it was extended to 12 N. The acidity was determined volumetrically, when necessary. Although the amount of the elements in the initial 2 ml. of the hydrochloric acid solutions was made as small as possible, it varied from tracer amount to about 1 mg. Details are shown in Table I. In all cases, the specific activity was higher than 10^4 cpm/mg. under a given condition of measurement.

All experiments were carried out at 21±3°C. Within this range, the variations in K_d values have been shown to be within experimental error.

Radioisotopes Used. — The radioactive isotopes used in this experiment were mainly prepared by irradiation of high purity targets in a water-boiler type reactor (Japan Research Reactor I, (neutron flux: 5×10^{11} n/sec. cm^2), whereas some of the isotopes were imported from Oak Ridge National Laboratory, U.S.A. or Radiochemical Centre, U.K.

The radiochemical purity of the isotopes was checked by their half-lives, γ-ray spectra, and/or β-ray absorption curves with aluminum foils. The γ-ray spectrograms were obtained with an RCL 256 channel γ-ray spectrometer or a single channel spectrometer made by Tokyo Shibaura Denki Co.

Table I[14-21] shows the radio-isotopes used[11], together with their half-lives and mass numbers, the target materials or sources, the method of checking the radiochemical purity, and the weight of the materials added in the initial 2 ml. of hydrochloric acid solutions.

Usually the irradiated targets were dissolved in hydrochloric acid and used without further treatment. For example, lanthanum oxide, magnesium

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[10] D. C. Stewart and H. W. Crandall, *J. Am. Chem. Soc.*, 73, 1377 (1951).

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

[12] N. Shibata and K. Yoshihara, This Bulletin, 32, 422 (1959).

[13] H. Ebihara and K. Yoshihara, ibid., in press.

[14] K. A. Kraus and F. Nelson," Proceeding of the International Conference on the Peaceful Uses of Atomic Energy", Geneva, A/Conf. 8/p/837 (1955); Vol. VII, United Nations Publication, New York (1956), p. 118.

[15] Green and Kafalas, *J. Chem. Phys.*, 22, 760 (1954).

[16] T. Ishimori, E. Nakamura and K. Watanabe, This Bulletin, in press.

[17] T. Nakai and S. Yajima, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, 79, 1267 (1958).

[18] T. Ishimori, H. Umezawa and K. Watanabe, *J. Atomic Energy Soc. Japan*, 1, 299 (1959).

[19] S. Yajima, This Bulletin, 31, 699 (1958).

[20] K. A. Kraus and G. E. Moore, *J. Chem. Soc.*, 72, 4293 (1950).

[21] C. J. Rodden, editor in chief, "Analytical Chemistry of the Manhattan Project", McGraw Hill, New York (1950), p. 83.

TABLE I. RADIOISOTOPES USED

Nuclide	Target material or source	Radiochemical purity was checked by	Weight	Remarks
15.0 hr. Na-24	$NaNO_3$, G. R.	γ-spec., γ-decay	100 γ	
9.45 min. Mg-27	Mg metal, 99.99%	γ-decay	250 γ	
2.27 min. Al-28	Al metal, 99.99%	γ-decay, γ-spec.	250 γ	
37.3 min. Cl-38	NH_4Cl, G. R.	γ-decay	250 γ	
12.51 hr. K-42	KNO_3, G. R.	γ-spec., γ-decay	100 γ	
164 d. Ca-45	imported		60 γ	$CaCl_2$ in HCl soln.
85 d. Sc-46	imported		60 γ	$ScOl_3$ in HCl soln.
5.80 min. Ti	Ti-hydroxide	γ-decay	250 γ	
3.76 min. V-52	NH_4VO_3, G. R.	γ-decay	5 γ	
27.8 d. Cr-51	Cr-dye, R. I.		～tracer	
2.58 hr. Mn-58	MnO_2, G. R.	γ-decay	250 γ	
3.0 y. Fe-55 45.1 d. Fe-59	imported		10 γ	$FeCl_3$ in HCl soln.
5.2 y. Co-60	imported			$CoCl_2$ in HCl soln.
2.56 hr. Ni-65	Ni metal	γ-decay	0.5 mg.	Co-58 was removed by ion exchange[14].
12.8 hr. Cu-64	Cu metal, 99.9%	γ-decay	100 γ	
245 d. Zn-65	imported		5 γ	$ZnCl_2$ in HCl soln.
14.2 hr. Ga-72	Ga_2O_3, J. M.	γ-spec., γ-decay	100 γ	
11.4 d. Ge-71	Ge metal, 99.9%	γ-decay	500 γ	Separated from As-77 by benzene extraction[15].
26.5 hr. As-76	As_2O_3, G. R.	γ-decay	500 γ	
127 d. Se-75	Se metal, G. R.	γ-decay, γ-spec.	300 γ	
4.5 hr. Br-80 m 35.9 hr. Br-82	NH_4Br, G. R.	γ-decay	250 γ	
19 d. Rb-86.	RbCl, G. R.	γ-decay	1 mg.	Cooled for five hours.
28 y. Sr-90	imported		tracer	$SrCl_2$ in HCl soln.
64 hr. Y-90	imported Sr-90	β-abs., β-decay	tracer	
65 d. Zr-95	imported		tracer	Oxalate, β-activity of Nb-95 was eliminated with a 17.6 mg./cm² Al absorber.
17.0 hr. Zr-97	UO_2-Oxalic acid	γ-spec.	tracer	Separated by method 17) and 18). Counted at 0.65～0.8 MeV.
35 d. Nb-95	imported Zr-95	β-decay, β-abs.		Oxalate; separated by Yajima's method[19].
67 hr. Mo-99	$(NH_4)MoO_4$, G. R.	γ-spec., β-decay		
2.12×10^5 y. Tc-99	imported		tracer	Sodium pertechnetate in KOH soln.
1.0 y. Ru-106	imported			$RuCl_3$ in HCl soln.
17 d. Pd-103 13.6 d. Pd-109	Pd metal, J. M.	γ-decay	250 γ	
2.3 min. Ag-108	Ag metal, 99.9%	γ-decay	50 γ	
53 hr. Cd-115 43 d. Cd-115 m	Cd metal, J. M.	γ-spec.	210 γ	
54.0 min. In-116 m	$In(OH)_3$, R. I.	γ-spec, β-decay	100 γ	
112 d. Sn-113	Sn metal, 99.997%	γ-spec.	750 γ	
2.75 d. Sb-122	Sb metal, 99.99%	γ-decay	750 γ	
33.5 d. Te-129 m, etc.	Te metal, G. R.		1 mg.	
8.06 d. I-131	imported		tracer	
30 y. Cs-137	imported		tracer	CsCl in HCl soln.
85 min. Ba-139	$BaCO_3$, J. M.	γ-decay	50 γ	
40.2 hr. La-140	La_2O_3, J. M.	γ-decay	100 γ	
46 d. Hf-181	imported		～tracer	$HfOCl_2$ in HCl soln.
111 d. Ta-182	imported			Potassium tantalate in KOH soln.

TABLE I (Continued)

23.9 hr. W-187	W oxinate, R. I.	γ-decay	~tracer	
3.87 d. Re-186 17 hr. Re-188	Re metal, J. M.	γ-decay	500 γ	
15 d. Os-191 31 hr. Os-193	Os metal, J. M. or imported Os-191	γ-decay	250 γ	Na_2CO_3-$NaNO_3$ fusion Osmate in NaOH soln.
74.4 d. Ir-192 19 hr. Ir-194	Ir metal, J. M.	γ-decay	50 γ	Na_2O_2 fusion.
4.5 d. Pt-193 18 hr. Pt-197	Pt metal, 99.9%	β, γ-decay	50 γ	
2.69 d. Au-198	Au metal, 99.9%	γ-decay	10 γ	
48 d. Hg-203	imported		5 γ	$Hg(NO_3)_2$ in HNO_3 soln.
4.0 y. Tl-204	imported		tracer	
3.64 d. Ra-224	imported Th-228	α-decay	tracer	Separated by TBP extraction[16].
24.1 d. Th-234	uranyl chloride	γ-spec. γ-decay	tracer	Separated by TBP extraction[16].
27.4 d. Pa-233	ThO_2	γ-spec. γ-decay	tracer	Separated by ion exchange[20].

G. R.: Guaranteed reagent.
J. M.: "Spec-pure" standard source produced by Johnson-Matthey Chemicals Co.
R. I.: High purity target produced by the Radioisototope Production Group, JAERI.

metal, sodium nitrate and barium carbonate were simply dissolved in hydrochloric acid after irradiation. Some of the irradiated targets were dissolved in nitric acid, aqua regia or sodium hydroxide solution and converted into hydrochloric acid solution. For example, rhenium and silver were primarily dissolved in nitric acid, platinum and gold in aqua regia, and arsenous oxide was dissolved in sodium hydroxide solution.

It is likely that the K_d values for arsenic were not largely affected by sodium chloride resulting from sodium hydroxide, for only one drop of tracer solution was added into 2 ml. of the aqueous phase.

Chromium and tungsten tracers were prepared by Yoshihara and Ebihara[12,13], Radioisotope Production Group, Japan Atomic Energy Research Institute. Both were of a high specific activity. On the other hand, most of the imported tracers were used as received.

Some special precautions taken both for the preparation of tracers and for the measurement of distribution ratios are given below in detail:

Vanadium.—Irradiated ammonium metavanadate was dissolved in hot 5 N hydrochloric acid and used without any further treatment. Hence, the chemical form of the vanadium tracer was not clearly known. It might have remained in the V(V) state. *Selenium.* — Irradiated selenium was dissolved in nitric acid containing bromine water, and then converted into a hydrochloric acid solution. The resultant solution was used without heating, as selenic tracer, whereas selenous tracer was obtained by heating the solution in 3 N hydrochloric acid. *Molybdenum.*—Irradiated ammonium molybdate showed a pale purple tint, and the hydrochloric acid solution colored blue-green. It was likely that this color came from a certain reduced chemical form. However, the solution was used without any further treatment, e. g., oxidation. *Antimony.*—Irradiated antimony was dissolved in hydrochloric acid containing a small volume of nitric acid. In an acid range below 2 N, obvious hydrolysis occurred. As the K_d values for 3 N acid is fairly high, being as high as 0.2, the HDEHP solution of antimony that had been prepared by extracting antimony(III) from 3 N hydrochloric acid solution was used as the organic phase. *Tantalum.*—Tantalum-182 solution was acidified with hydrochloric acid, and hydrated tantalum precipitate was centrifuged off. The supernatant solution was used as the tracer solution. *Iridium.*—Fusion with sodium peroxide was more rapid and complete than sodium nitrate-carbonate fusion. *Mercury.*—A dilute nitric acid solution of imported mercury tracer was dropped into hydrochloric acid of known concentration, and used without any further treatment. Both phases were clear after the contact. *Thallium.*—Thallic chloride solution was prepared by oxidation of Tl(I) solution with ceric ammonium nitrate or potassium bromate. *Uranium.* — K_d values for uranium were obtained photometrically[21].

Results and Discussion

The results are summarized in Fig. 1 as a series of graphs of $\log K_d$ vs. $\log N$, where K_d is the distribution ratio and N the acidity in normality. Fig. 1 was compiled from some published and unpublished results. Data for lead, bismuth and americium were taken from the observation of Ishimori[22]. Data for neptunium were taken from the work of Nakamura[23].

Peppard and his coworkers reported that the K_d values for selected lanthanide and actinide cations (III) in the system of HDEHP—perchloric acid are inverse third power dependent on the hydrogen ion concentration in the aqueous phase (0.15 M HDEHP—toluene solution) and direct third power dependent on

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[22] T. Ishimori, unpublished.

[23] E. Nakamura, unpublished.

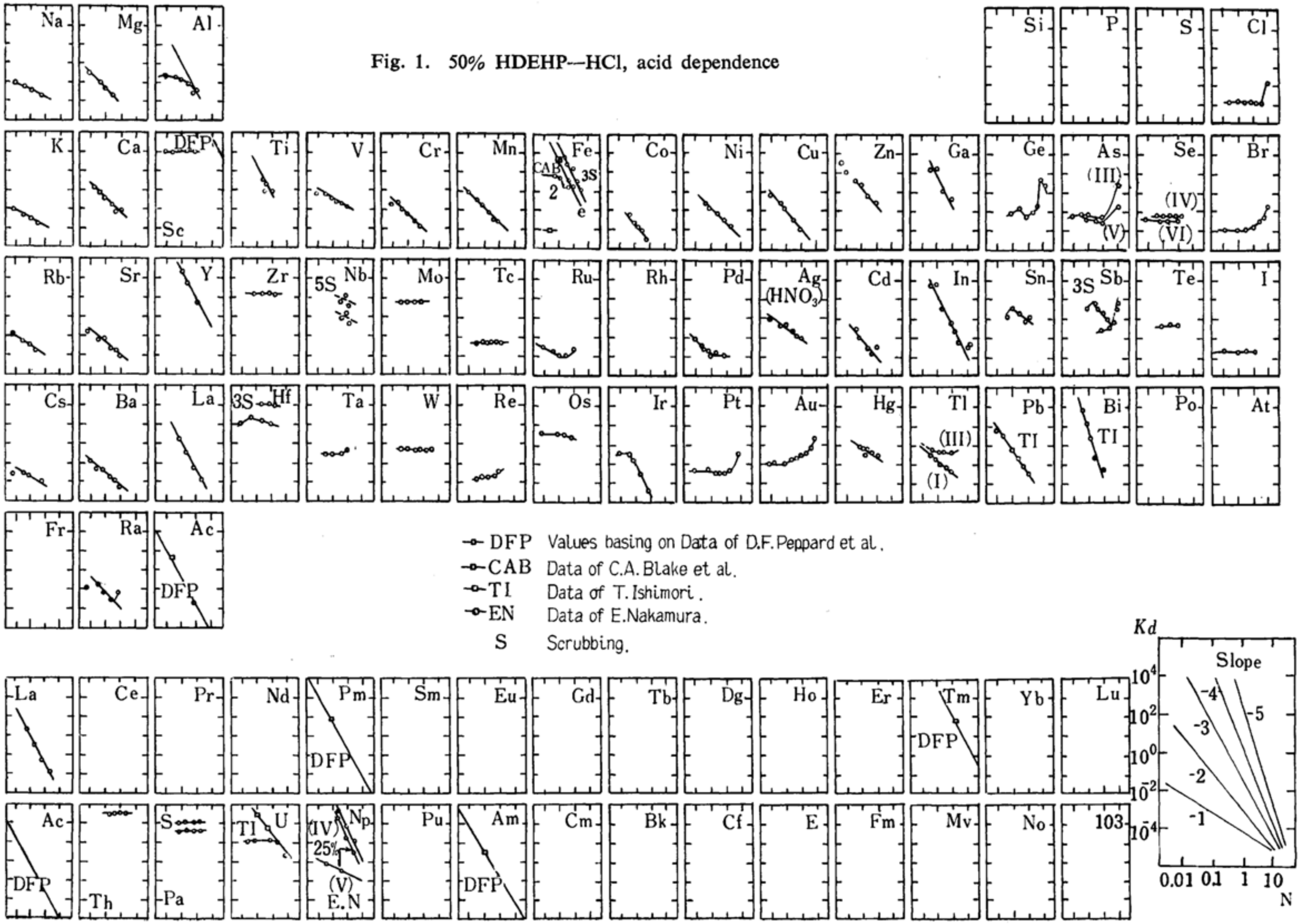

Fig. 1. 50% HDEHP—HCl, acid dependence

the solvent concentration. The results for yttrium and lanthanum of the present author agree with those of Peppard in K_d values. Therefore, K_d values for thulium, promethium, actinium and americium were taken from their data corrected for 50% HDEHP (1.5 M) assuming that the solvent dependence remains unchanged at this high concentration.

According to Peppard and his coworkers[6,9] and Baes et al.[8], the K_d values for scandium, thorium and uranium for diluted HDEHP solution are inverse third, fourth and second power dependent on the hydrogen ion concentration in the aqueous phase, respectively. However, the concentration of HDEHP is so high in this experiment that the K_d values for these elements show almost horizontal curves. It is caused by the limitation of the method of determination. The fact that the horizontal K_d curve for uranium is lower than those for thorium and scandium is mainly brought about by the difference in the method of K_d determinations. The same can be said for protactinium, zirconium and hafnium, whereas the fourth power acid dependence of K_d values is obtained for titanium. Ishimori's data for uranium in the system of 0.75 M HDEHP solution and hydrochloric acid solution are also added after correction for the concentration of HDEHP. The K_d values show inverse second power dependence on the hydrogen ion concentration in the aqueous phase.

As Fig. 1 shows, the shape of the curves is roughly divided into two types. The first type consists of those in which the absolute figures of the slope are identical with the ionic charges or at least the figures are below minus one. On the other hand, the K_d values of the second type are unaffected by the hydrogen ion concentration in the aqueous phase in the acid range below about 2 N.

The K_d values for alkali metals, alkaline earth metals and lanthanide elements are characteristic of the first type, showing first, second and third power dependence on the hydrogen ion concentration in the aqueous phase, respectively. A similar relationship holds for the elements of Ib, IIb and IIIb group in the periodic table except in the case of gold.

The extraction of metal cation with HDEHP is expressed generally in the following equation[1,6]:

$$M^{m+}{}_{(aq)}+m(\mathrm{HDEHP})_{2\,(org)} \rightleftarrows$$

$$\mathrm{MH}_m(\mathrm{DEHP})_{2m\,(org)}+m\mathrm{H}^{+}{}_{(aq.)}$$

$$K_d=K\cdot[(\mathrm{HDEHP})_{2\,(org)}]^{m}\cdot[\mathrm{H}^{+}{}_{(aq)}]^{-m} \qquad (1)$$

where, K is the constant of the above equilibrium. In this equation, $(\mathrm{HDEHP})_{2\,(org)}$ represents the dimer of HDEHP in the organic phase[24]. Eq. 1 indicates that an ion with $+m$ charge shows a curve of $-m$ slope. It appears as if an element giving a K_d curve of the first type behaves as a cation in the given system.

On the other hand, the K_d curves for chlorine, bromine and iodine are typical of the second type. Germanium, arsenic, platinum and gold give curves of a similar shape. Almost all of these elements give higher K_d values in an acid solution over 2 N than in 1 N. It is likely that the extraction of these elements is not based on the chelation mentioned above, but on partition, as is found in the case of extraction with TBP[25].

Although the three light elements of Va, VIa and VIIa group, vanadium, chromium and manganese, show the characteristic curves of the first type, the heavy elements of the groups, niobium, molybdenum, technetium, tantalum, tungsten and rhenium, show those of the second type. This appears to be in accord with the fact that Cr(III) and Mn(II) are apt to behave in cationic state in hydrochloric acid media, whilst niobium, molybdenum, technetium, tantalum, tangsten and rhenium are not. The present K_d values for vanadium were relatively low. Vanadinyl(IV) ion in the system HDEHP-sulfate solution, however, shows high K_d values which depend on the hydrogen ion concentration with a slope of ca. -2[1].

Chromium resembles manganese more than it does molybdenum or tungsten as regards the type of acid concentration-K_d value relation. Besides, the slope of ca. -2 for chromium gives a suggestion that chromium exists as a mixture of hydrated chloro-complexes. K_d values for molybdenum and niobium are relatively high, while those for technetium and rhenium are very low.

In contrast with the Va, VIa and VIIa groups, the light elements of IVb, Vb and VIb group, germanium, arsenic and selenium, show K_d curves of the second type, while heavy elements, lead and bismuth, show that of the first type.

It is known that iron(III) and aluminum require a long time to attain extraction equilibrium[1]. In graph "Fe" in Fig. 1, curve 2 shows K_d values for 2 min. shaking, line 3s those for three times scrubbing, line e those for thirty hours shaking. Line e has a slope of -3. In all three cases, iron gives high K_d values, while cobalt and nickel give low values throughout the acidity range. For aluminum,

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[24] D. F. Peppard, J. R. Ferraro and G. W. Mason, *J. Inorg. Nucl. Chem.*, **4**, 371 (1957).

[25] D. Dyrssen and F. Krasovec, *Acta Chem. Scand.*, **13**, 568 (1959).

the K_d values for the equilibrium were not obtained, because the aluminum tracer used was short-lived.

It is difficult to account for the difference in the behavior of the platinum elements because the methods used in preparing the tracers were quite different. The K_d values for osmium are relatively high, those for iridium show -4th power acid dependence, and those for others are low.

Indium gives a straight line of slope ca. -3 over the acidity range from 0.05 to 10 N. Copper, silver, zinc, cadmium and gallium also behave similarly giving the slope of $-m$. It is generally accepted that these elements form chloro-complexes easily. However, the absolute figures of the slopes for these are nearly equal to those of ionic charges in such condition that the elements do not form chloro-complexes.

As was mentioned by Peppard and his coworkers[6], Eq. 1 is principally analogous to that of the equilibrium found for the extraction of metals with thenoyl trifluoroacetone, HTTA. Figs. 2 and 3 show the comparison between HDEHP and HTTA extraction for

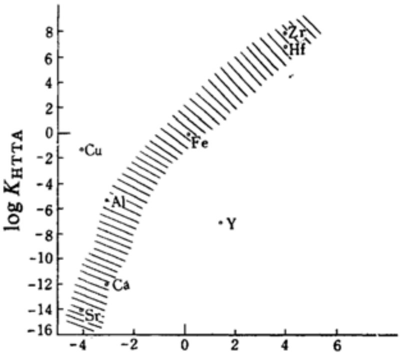

Fig. 2. Relation between K_d HDEHP and K_{HTTA} values.

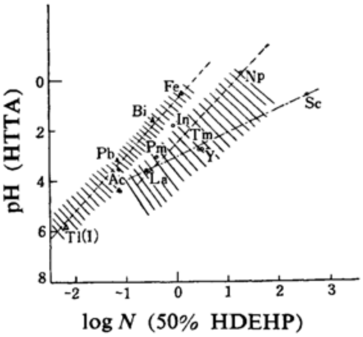

Fig. 3. Relation between log $N_{1/2}$ for HDEHP system and $pH_{1/2}$ for HTTA system.

○ 0.5 M HTTA ; △ 0.25 M HTTA

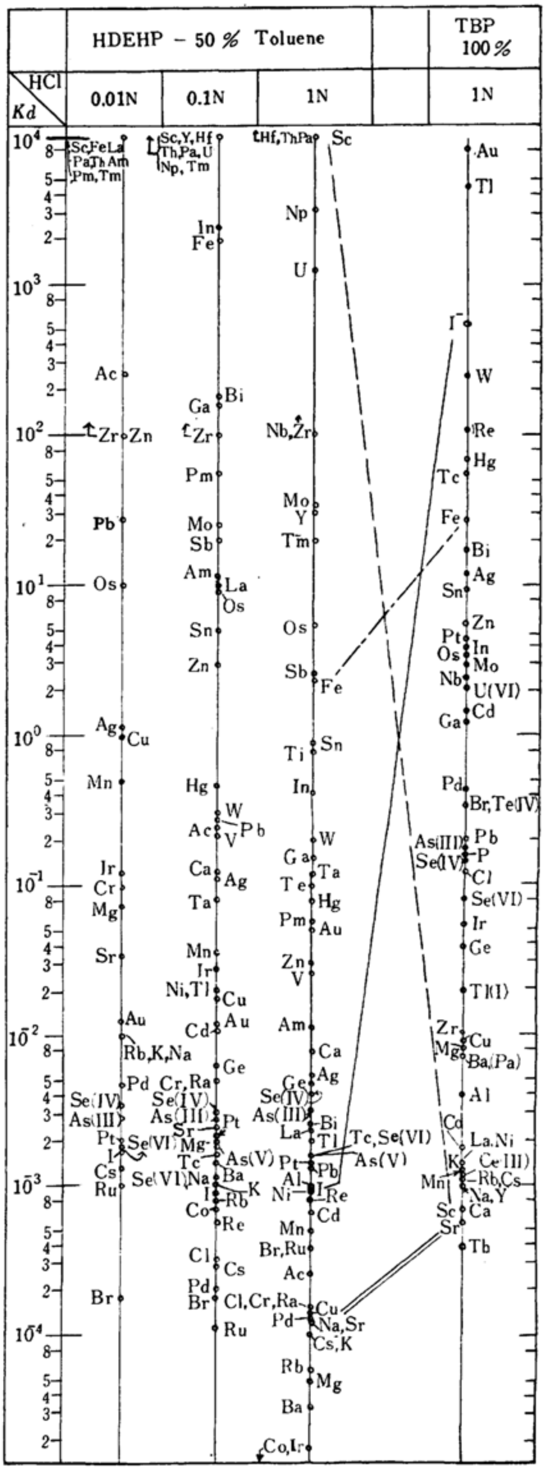

Fig. 4. K_d values in 50% HDEHP—0.01 ~1 N HCl and comparison with 100% TBP—1 N HCl.

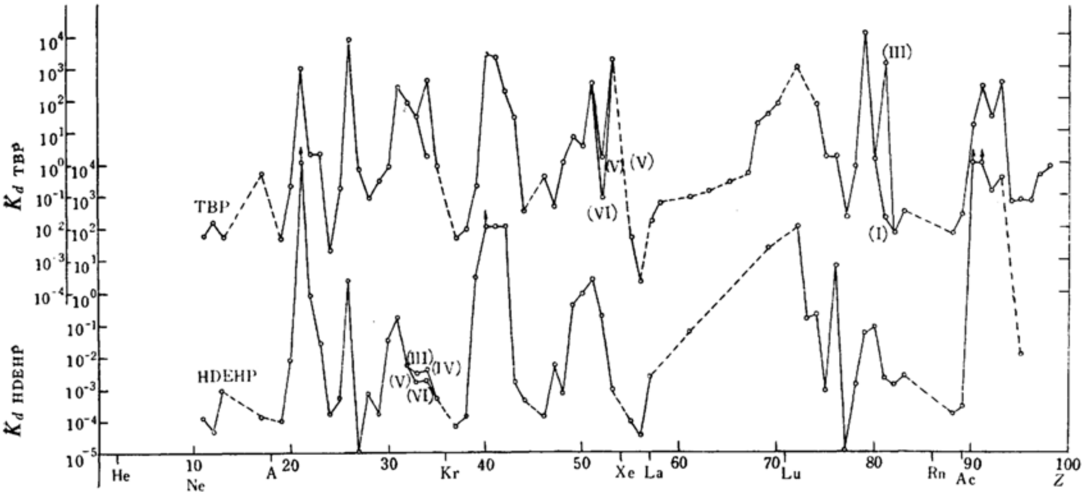

Fig. 5. Relation between K_d values and Z.

some cations. The K_d values for 50% HDEHP at 1 N hydrochloric acid are plotted against K_{HTTA} values[*][26,27]. In Fig. 3, the acidity given by log $K_d=0$ with HDEHP are plotted against the pH values giving 50% extraction with HTTA[27-29]. As Fig. 2 shows, the plots for zirconium, hafnium, iron, aluminum, calcium and strontium appear in the hatched band. Besides, as seen in Fig. 3, Fe-Bi-Pb-Tl and Np-In-La-lines show a straight line of slope ca. $+2$, showing that mutual difference of the values for these elements are larger in the HTTA system rather than in the HDEHP system. The Sc-Y-Tm-Pm-La-Ac-line of Fig. 3, however, gives a slope of $+1$. In all cases, it is found that these cations extractable into HTTA phase are also readily extracted into HDEHP.

Fig. 4 gives K_d values in 50% HDEHP (toluene) vs. 1, 0.1 and 0.01 N HCl systems together with K_d values in 100% TBP—1 N hydrochloric acid system. Alkali and alkaline earth metals are situated in a range of low K_d values both for the systems of HDEHP and TBP—1 N hydrochloric acid. It is very interestingthat K_d values for scandium, thorium and protactinium are very high for HDEHP, but very low for TBP. In contrast with this fact K_d values for zinc, cadmium and gold are very high for TBP, but relatively low for HDEHP. However, it is found that iron and indium have relatively high K_d values both for HDEHP and TBP.

K_d values between 50% HDEHP and 1 N hydrochloric acid are plotted against the atomic number, Z, in Fig. 5. The figure shows that the K_d values vary regularly to some extent, giving two peaks in a given long period of the periodic table. A similar regularity is also found in the system of 50% HDEHP vs. 0.1 N and 0.01 N hydrochloric acid. Although an obvious exception for this regularity is the peak for iron(III), this peak may become low by adopting the K_d value for iron(II) which is more suitable for this consideration from the viewpoint of the electron configuration. Blake et al.[1] mentioned that iron(II) is less extractable. In Fig. 5, K_d values at 12 N hydrochloric acid and 100% TBP are also plotted on the same scale for comparison. It is clear and somewhat noticeable that the readily extractable ions are almost common for systems 100% TBP-12 N hydrochloric acid and 50% HDEHP-1 N hydrochloric acid. It appears as if the extraction of ions with HDEHP is not only based on chelation, but also based on partition as in the extraction with TBP. A notable exception is the case of iodine. Iodine shows remarkably high K_d values for TBP, but low for HDEHP.

As can be seen in Figs. 1 and 5, the K_d values for Ia, IIa and IIIa groups in low acidity region decrease according to the following sequence: Sc > Ca > K, Y > Sr > Rb and La > Ba > Cs. These are analogous to the sequence of relative affinity K^* for cation exchange resin Dowex 50 or Diaion SK:

$$\mathrm{M}^{4+} > \mathrm{M}^{3+} > \mathrm{M}^{2+} > \mathrm{M}^{+}$$

However, the order of the extractability with HDEHP for cations of the same valence is

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[*] $K_{\mathrm{HTTA}}=(\mathrm{MT}_m)_{\mathrm{org}}\cdot(\mathrm{H}^+)^m_{\mathrm{aq}}\cdot(\mathrm{M}^{m+})^{-1}_{\mathrm{org}}\cdot(\mathrm{HT})^{-m}_{\mathrm{org}}$.

26) E. H. Huffman and L. J. Beaufait, *J. Am. Chem. Soc.*, 71, 3179 (1949).

27) R. A. Bolomy and L. Wish, ibid., 72, 4483 (1950).

28) F. Hageman, ibid., 72, 768 (1950).

29) W. W. Meinke, Progress Report 7, Univ. of Michigan, No. 1 (1958).

[*] $K=[\mathrm{MR}_m]_{\mathrm{resin}}\cdot[\mathrm{H}^+]^m_{\mathrm{aq}}\cdot[\mathrm{HR}]^{-m}_{\mathrm{resin}}\cdot[\mathrm{M}^{m+}]^{-1}_{\mathrm{aq}}$.

TABLE II. COMPARISON OF THE ORDER OF SELECTIVITY

Cation(III)	
HDEHQ	Sc>Tm>Y>In>Ga>Pm>Am>La>Ac, (Al)
Resin	Ac>La>……>Dy>Y>Ho>……>La>Sc>Al
TBP(max)	Fe, Tl>Sc>Ga>In>Yb>Tm>Er>Ho>Y>Tb>Eu,Pm,Am>Ce>La>Al
TBP	Tl>Fe>In>Ga>Al>La>Ce>Y
Cation(II)	
HDEHP	UO_2, Zn>Ga>Pb>Mn, Cu>Cd, Ni>Mg, (Ra)>Ba, Sr, Co
Resin	Ra>Ba>Pb>(Sr, Be_2O)>Ca>(Mg, Zn, Cu, Ni, Co, Mn, UO_2, Cd)>Be
TBP(max)	UO_2, Zn>Cd>Cu, Pb>Ca, Co>Mn, Mg>Ra>Ni>Ba, Sr
TBP	Zn>Cd>UO_2>Pb>Cu, Mg, Ba>Co>Mn, Ni
Cation(I)	
HDEHP	Ag>Tl>Na>K>Rb>Cs
Resin	Tl>Ag>Cs>Rb>K=NH_4>Na>H>Li
TBP(max)	Ag>Tl>Alkali metals
TBP	Ag>Tl>(K>Rb, Cs>Na)

reverse to that of the relative affinity for cation exchange resin. A similar reversal had been found in the pairs of mono(2-ethyl hexyl)-orthophosphoric acid and sulfonated cation exchange resin for selected lanthanides and actinides(30), of HDEHP and mono(heptadecyl) sulfuric acid for K, Na, and Li(30) and of phosphonic resin and sulfonic resin for K, Na and Li(31).

Table II shows the comparison of the orders of selectivity. In the table, the heading HDEHP and TBP stand for the values in the systems of 100% TBP-1 N hydrochloric acid and of 50% HDEHP-1 N hydrochloric acid, respectively. The TBP(max) for the maximum K_d values.

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30) D. F. Peppard, G. W. Mason and R. J. Sironen, *J. Inorg. Nucl. Chem.*, **10**, 117 (1959).

31) J. I. Bregman and Y. Murata, *J. Am. Chem. Soc.*, **74**, 1867 (1952).