Solvent Extraction of Inorganic Nitrates with Diphosphonate Ester. I.
Zirconium, Yttrium and Lanthanide Nitrates

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Various extracting agents have been investigated on the solvent extraction of many elements. Much attention has been paid to such extracting agents as organophosphorus compounds (tri-*n*-butyl phosphate and others) and β-diketones (thenoyltrifluoroacetone and others).

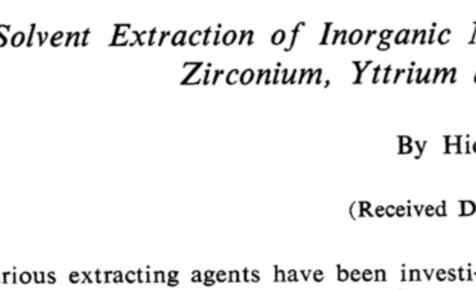

Fig. 1. The structural formulae of ketone (I), β-diketone (II), tri-*n*-alkyl phosphate (III) and diphosphonate ester (IV).

The extractability of various metal ions with β-diketone (Fig. 1-II) is much higher than that with ketone (Fig. 1-I), though both ketone and β-diketone are used for the solvent extraction. From the similarity of structural formulae as shown in Fig. 1, it is expected that diphosphonate ester (Fig. 1-IV) may show better extractability than tri-*n*-alkyl phosphate (Fig. 1-III). Thus, in the present paper tetra-*n*-butyl ethylenediphosphonate* (TBEDP), $(BuO)_2\cdot P(O)(CH_2)_2(O)P(BuO)_2$, was chosen, and the extractability of zirconium, yttrium and several lanthanide elements (cerium, promethium, europium and lutetium) was studied on the system between TBEDP-kerosene and various nitric acid concentrations.

Although Kennedy et al.[1] reported the solvent extraction of uranium with diphosphonate esters, the extracting behavior was not studied in detail. Since then, no investigations on the diphosphonate esters extraction of some elements other than uranium have been reported.

Experimental

Solvent.—TBEDP purchased from the Tama Chem. Co., Tokyo, Japan, was used without any further purification. TBEDP was diluted with kerosene to 0.1 or 0.2 M according to the experimental requirements. Kerosene used here had flash point above 60°C and was not specially purified. Nitric acid solutions were prepared by diluting concentrated nitric acid, special grade. The acidity range of the solution covered from 0.01 to 13 M. The acidity was determined volumetrically, whenever necessary.

Determination of Distribution Ratios. — The distribution ratio of a given nuclide, defined as the concentration of the nuclide in the organic phase divided by that in the aqueous phase, was determined radiochemically.

Five millilitres of nitric acid solution containing the radioactive tracer and the equal volume of TBEDP diluted with kerosene were placed together in a 30 ml. glass-stoppered cylinder, and shaken vigorously in a thermostat kept at 25 ± 0.5°C. Shaking was continued for 30 min. Preliminary

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* Tetra-*n*-butyl ethylenediphosphonate is abbreviated as TBEDP.

[1] T. V. Healy and J. Kennedy, *J. Inorg. & Nucl. Chem.*, **10**, 128 (1959).

tests showed that the equilibrium was attained in less than 10 min. Then, the two phases were separated by the use of a separating funnel.

Aliquots from organic or aqueous phases were taken into small stainless steel dishes and carefully dried under an infrared lamp.

Radioactivity of Y-91, Ce-144, Pm-147, Eu-152-154 and Lu-177 was measured with a G.-M. counter having a window of 3.10 mg./cm^2 thick. As it took at least about four hours to evaporate aliquots to dryness, Ce-144 and its daughter, Pr-144 reached the radioactive equilibrium completely when the activities were counted. Amounts of Zr-95 were measured at the Zr-95 (0.754 and 0.722 MeV.) photopeaks by an Argonne Type 256 Channel Pulse Height Analyzer with a 3'' diameter ×3'' NaI(Tl) crystal.

Radioisotopes Used.—The radioisotopes used in this experiment were Zr-95, Y-91, Ce-144, Pm-147, Eu-152-154 and Lu-177. These tracers were imported from Oak Ridge National Laboratory, U.S.A. or Radiochemical Centre, U. K.

Ce-144 and Eu-152-154 received as nitrates were used without further treatments. However, Y-91, Pm-147 and Lu-177 were converted into nitrates by a cation exchange technique**, because they were imported as chlorides. The cerium tracer was always kept in the trivalent state.

Zr-95 tracer[2] was freed from Nb-95 as follows: Zr-95 was first extracted into a 0.5 M TTA (thenoyltrifluoroacetone)-xylene solution from 2 M nitric acid solution containing Zr-Nb-95. The Zr-95 tracer was stripped into 8 M nitric acid solution from the organic phase diluted with xylene by a factor of 10 or more. The solution was used immediately after the separation.

Results and Discussion

Effect of Nitric Acid Concentration.— The results obtained are plotted in Figs. 2-4, where other authors' results[3-6] for each element in the extraction with TBP (tri-*n*-butyl phosphate) from nitric acid are added for comparison.

Fig. 2 shows the variation of distribution ratio, K_d, of zirconium in the range of nitric acid concentration from 0.01 to 13 M, keeping the TBEDP concentration 0.1 M. As Fig. 2 shows, the acid-dependence curves for TBP and TBEDP have a similar tendency concerning the fact that the distribution ratios increase with increasing acidity in both cases.

Fig. 3 also shows the variation of K_d of yttrium and lutetium in the same acidity range

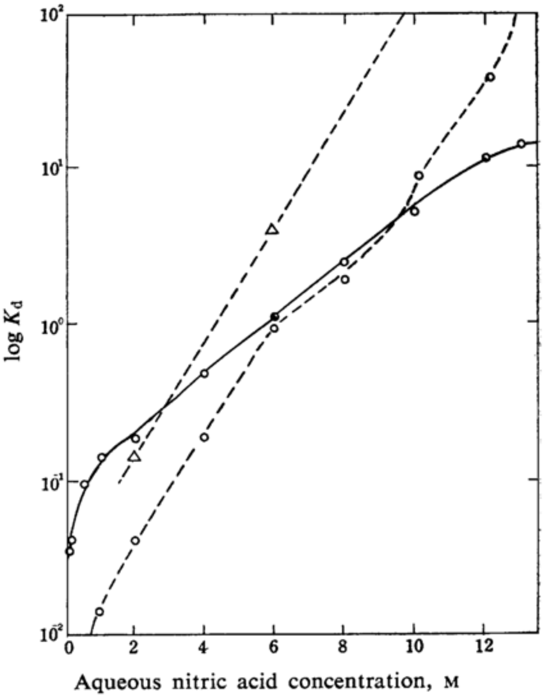

Fig. 2. The K_d values of zirconium.

—○—: 0.1 M TBEDP in kerosene
--○--: McKay et al.[3], 19% TBP in kerosene
--△--: Peppard et al.[4], 100% TBP

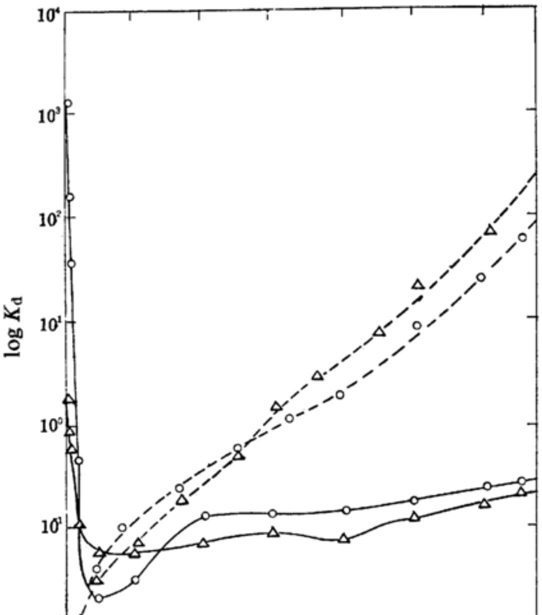

Fig. 3. The K_d values of yttrium and lutetium.

——: 0.2 M TBEDP in kerosene
----: McKay et al.[5,6], 100% TBP
○ : Yttrium △ : Lutetium

** The radioactive tracer was adsorbed on the resin Dowex 50-X8, H form column and then eluted with nitric acid solution.

2) F. L. Moore, *Anal. Chem.*, **28**, 997 (1956).

3) K. Alcock, F. C. Bedford, W. H. Hardwich and H. A. C. McKay, *J. Inorg. & Nucl. Chem.*, **4**, 100 (1957).

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

5) D. Scargill, K. Alcock, J. M. Fletcher, E. Hesford and H. A. C. McKay, ibid., **4**, 304 (1957).

6) E. Hesford, E. E. Jackson and H. A. C. McKay, ibid., **9**, 279 (1959).

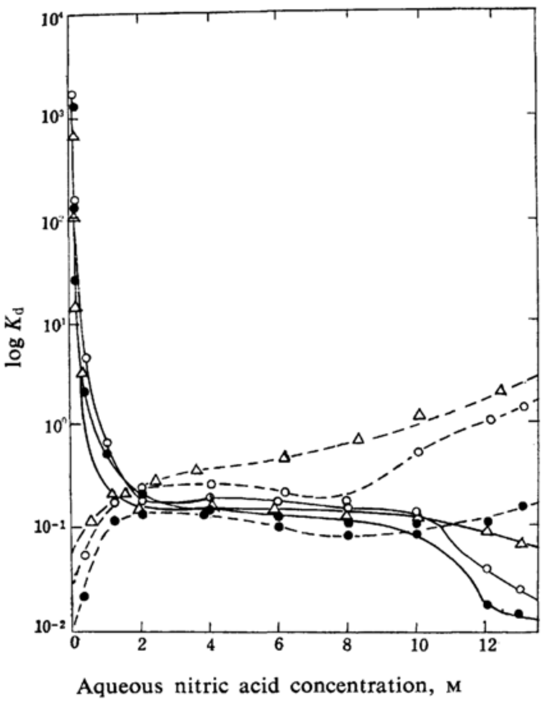

Fig. 4. The K_d values of cerium, promethium and europium.

——: 0.2 M TBEDP in kerosene
----: McKay et al.5,6), 100% TBP
● : Cerium ○ : Promethium
△ : Europium

as in the case of zirconium, keeping the TBEDP concentration 0.2 M. As shown in Fig. 3, there is a remarkable difference between TBP and TBEDP in the very low acidity range below about 0.5 M nitric acid. In TBEDP extraction the K_d values are very high at 0.01 M nitric acid and decrease sharply with increasing acidity up to about 1 M nitric acid. In the higher acidity range the K_d values by TBEDP tend to increase gradually, while those by TBP increase rapidly. Similarity in the extraction of yttrium and lutetium with TBEDP appears to be in accordance with the fact that they belong to the yttrium group.

Fig. 4 indicates the results for cerium, promethium and europium under the same experimental conditions as the case for yttrium and lutetium. In the low acidity region the extracting behavior of cerium, promethium and europium is very similar to that of yttrium and lutetium; the K_d values of these three elements decrease sharply with increasing acidity. On the contrary in the higher acidity the K_d values have decreasing tendency, though those by TBP increase in this region. It is interesting for the author that the sequence of the K_d values by TBEDP in the region agrees with that by TBP.

From the above-mentioned facts, it may be said that this extracting agent is very excellent for the extraction of trivalent elements such as lanthanide elements especially in the low acidity region. The difference between K_d values for a lanthanide element and zirconium is so great in the low acidity region that a lanthanide element may be separated from zirconium very easily.

Effect of Nitrate Concentration on Extraction of Zirconium.—The results obtained with 0.1 M TBEDP concentration are given in Table I. This table shows that the distribution ratios can increase when other nitrates are added to nitric acid. This fact suggests that the extraction of zirconium by TBEDP depends on nitrate ion concentration to some extent. The results also indicate that zirconium is extracted much more readily from nitric acid solution containing aluminum nitrate, than from pure nitric acid solution of the same total nitrate ion concentration.

TABLE I. EFFECT OF NITRATE CONCENTRATION ON EXTRACTION OF ZIRCONIUM
(0.1 M TBEDP IN KEROSENE)

Molarity					Distribution
HNO_3	NH_4NO_3	$Ca(NO_3)_2$	$Al(NO_3)_3$	Total NO_3	ratio
4	—	—	—	4	0.50
8	—	—	—	8	2.85
4	4	—	—	8	1.43
4	—	2	—	8	2.81
4	—	—	1.33	8	3.45
10	—	—	—	10	5.40
4	6	—	—	10	1.93
4	—	3	—	10	3.49
4	—	—	2	10	6.53
12	—	—	—	12	10.75
4	8	—	—	12	3.45
4	—	4	—	12	8.09
4	—	—	2.66	12	11.10

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