

Solvent Extraction of Inorganic Nitrates with Diphosphonate Ester. II. Thorium and Uranyl Nitrates

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In the previous paper¹⁾, was studied the solvent extraction behavior of zirconium, yttrium and several lanthanide elements (cerium, promethium, europium and lutetium) with tetra-*n*-butyl ethylene-diphosphonate* (TBEDP), $(\text{BuO})_2\text{P}(\text{O})(\text{CH}_2)_2(\text{O})\text{P}(\text{BuO})_2$. The distribution ratio of each element between nitric acid solution and TBEDP diluted with kerosene was determined in the range of nitric acid concentration from 0.01 to 13 M and TBEDP concentration from 0.1 to 0.2 M. The extractability of zirconium increased with increasing acidity. However, in the extraction of yttrium and lanthanide elements, the distribution ratios were very high in the low acidity region and decreased sharply with increasing acidity. This extracting reagent is very excellent for the extraction of trivalent elements such as lanthanide elements especially in the low acidity region.

The present paper describes in detail the solvent extraction behavior of thorium and uranium in the system of TBEDP-kerosene and nitric acid solution.

Infrared absorption studies have also been undertaken to obtain the information on the organic phase containing uranium.

Experimental

Sources of Materials.—TBEDP received from the Tama Chem. Co., Tokyo, Japan was used without any further purification. TBEDP was diluted to the desired concentrations with kerosene, which had its flash point above 60°C and was not specially purified. Nitric acid solutions were prepared by diluting concentrated nitric acid, special grade. The acidity was checked volumetrically, whenever necessary.

Uranyl nitrate was of guaranteed reagent grade, and was used as 1.24×10^{-3} M solution in the whole acidity region studied.

Thorium-234 (UX_1) separated from uranium was chosen to study the extractability of thorium by TBEDP. Thorium-234 tracer²⁾ was obtained as nitrate by means of the usual ethyl ether extraction method followed by cation exchange.

Determination of Distribution Ratios.—The details of the method used in the previous report¹⁾

were also adopted in the present study. The distribution ratio was measured after shaking the two phases for thirty minutes in a thermostat kept at $25 \pm 0.5^\circ\text{C}$.

The uranium concentration in the aqueous phase was determined colorimetrically or by fluorimetry and that in the organic phase was measured in the same way after extraction into an aqueous solution of sodium carbonate. For colorimetry, the ordinary hydrogen peroxide method³⁾ was employed. The method adopted for fluorimetry was similar to that of Grimaldi et al.⁴⁾ The procedure was as follows: Aliquot portions containing uranium were transferred to a small platinum dish and carefully dried up under an infrared lamp. Fluoride flux was then added to the dish and the flux was melted for about five minutes in an electric furnace kept at 700°C. After cooling the melt, the fluorescence was measured, using excitation by radiation of 365 mμ wavelength. A blank and a standard were run at the same time. The fluoride flux used here consisted of 9% sodium fluoride, 45.5% sodium carbonate and 45.5% potassium carbonate, which were fused in platinum at about 500°C and then thoroughly ground and mixed. Both colorimetric and fluorimetric measurements were made with a Shimadzu recording photoelectric spectrophotometer, type RS.

Amounts of thorium-234 were determined radiochemically in the same way as those described in the previous paper¹⁾. Infrared spectra were measured with a Hitachi EPI-II double-beam infrared spectrophotometer equipped with a sodium chloride prism. All the measurements were made in the liquid state.

Results and Discussion

Effect of Nitric Acid Concentration.—Figures 1 and 2 show the variation of distribution ratio, K_d , of uranium(VI) and thorium(IV) in the range of nitric acid concentration from 0.1 to 13 M, keeping the TBEDP concentration 0.1 M. Other authors^{5,6)} results for both elements in the extraction with TBP from nitric acid are added for comparison.

3) C. J. Rodden, editor-in-chief, "Analytical Chemistry of the Manhattan Project" (NNE8 VIII-1), McGraw-Hill Book Co., Inc., New York (1950), p. 83.

4) F. S. Grimaldi, I. May, M. H. Fletcher and J. Titcomb, "Collected Papers on Methods of Analysis for Uranium and Thorium", United States Government Printing Office, Washington (1954), p. 43.

5) K. Alcock, G. F. Best, E. Hesford and H. A. C. McKay, *J. Inorg. Nucl. Chem.*, **6**, 328 (1958).

6) E. Hesford, H. A. C. McKay and D. Scargill, *ibid.*, **4**, 321 (1957).

1) H. Saisho, This Bulletin, **34**, 859 (1961).

* Tetra-*n*-butyl ethylene-diphosphonate is abbreviated as TBEDP.

2) D. Dyrssen, *Svensk. Kem. Tidskr.*, **62**, 153 (1950).

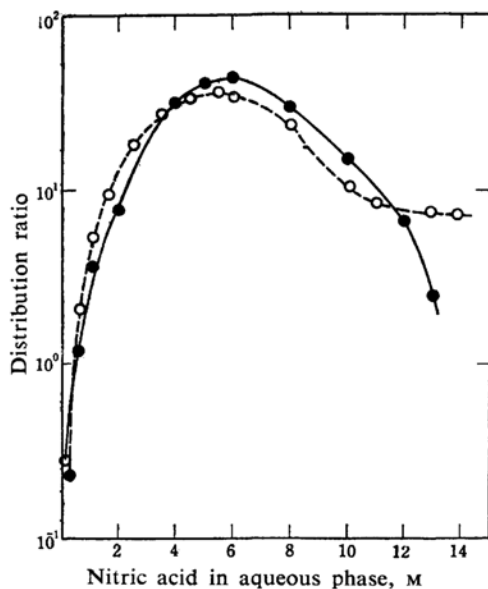


Fig. 1. Distribution ratio of uranium(VI).
 —●—●—: 0.1 M TBEDP in kerosene
 ---○---: McKay et al.^{5),} 19% TBP in kerosene

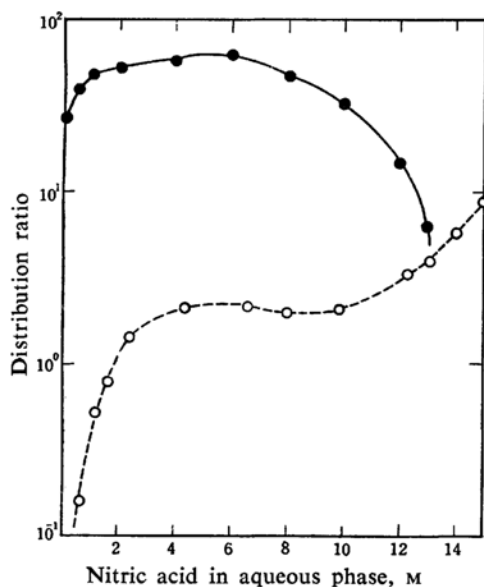


Fig. 2. Distribution ratio of thorium(IV).
 —●—●—: 0.1 M TBEDP in kerosene
 ---○---: McKay et al.^{6),} 19% TBP in kerosene

As shown in Fig. 1, the acid dependence curves for TBEDP and TBP have a considerable resemblance; maximum extractions of uranium(VI) from nitric acid solutions are observed at about 6 M nitric acid concentration in both cases.

As Fig. 2 shows, similarity in the shape of

the acid dependence curves for TBEDP and TBP is also found in the acidity range up to about 6 M nitric acid; the K_d values for thorium(IV) increase with increasing acidity. In the higher acidity range, the K_d values by TBEDP tend to decrease gradually, whereas those by TBP have an increasing tendency, especially in the acidity region over about 10 M nitric acid.

Effect of TBEDP Concentration on Extraction of Uranium(VI).—Figure 3 shows two series of results in the range of 1×10^{-3} to 1×10^{-1} M TBEDP concentration in the organic

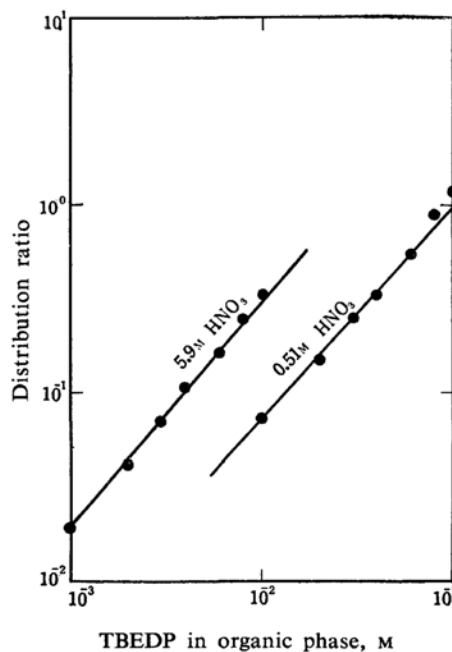


Fig. 3. Power dependence of distribution ratio on TBEDP concentration.

phase, keeping the acidity of the aqueous phase constant. In the plots of $\log K_d$ vs. logarithmic TBEDP concentration, the slope of the lines through the points is 1.1 for both 0.51 and 5.9 M nitric acid up to about 6×10^{-2} M TBEDP concentration. The first power dependence of the K_d values on the TBEDP concentration indicates the 1:1 TBEDP to uranium ratio. The complex formed in the organic phase may be $\text{UO}_2 \cdot (\text{NO}_3)_2 \cdot \text{TBEDP}$, analogous to the corresponding uranium(VI) compound in TBP extraction^{5,7)}. It is in good agreement with the results obtained by Healy and Kennedy⁸⁾ for benzene solutions of diphosphoryl reagents containing the group $-\text{P}(\text{O})\text{Y}(\text{O})\text{P}-$ (where Y

7) H. A. C. McKay, "Proceedings of International Conference on Peaceful Uses of Atomic Energy", Vol. VII, p.441, United Nations Publication, New York (1956).

8) T. V. Healy and J. Kennedy, *J. Inorg. Nucl. Chem.*, 10, 128 (1959).

is oxygen, methylene or ethylene), saturated with uranyl nitrate.

Infrared Studies on the Organic Phase.—

Infrared absorption studies may provide some information on the extracting behavior of uranyl nitrate by TBEDP. Infrared spectra were recorded for the following samples: (I) kerosene, (II) pure TBEDP, (III) 0.2 M kerosene solution of TBEDP, (IV) 0.2 M kerosene solution of TBEDP after being shaken with 6 M nitric acid, and (V) 0.2 M kerosene solution of TBEDP after being shaken with 0.5 M uranyl nitrate solution in 6 M nitric acid. The spectra in the region of 900 to 1700 cm^{-1} are illustrated in Fig. 4.

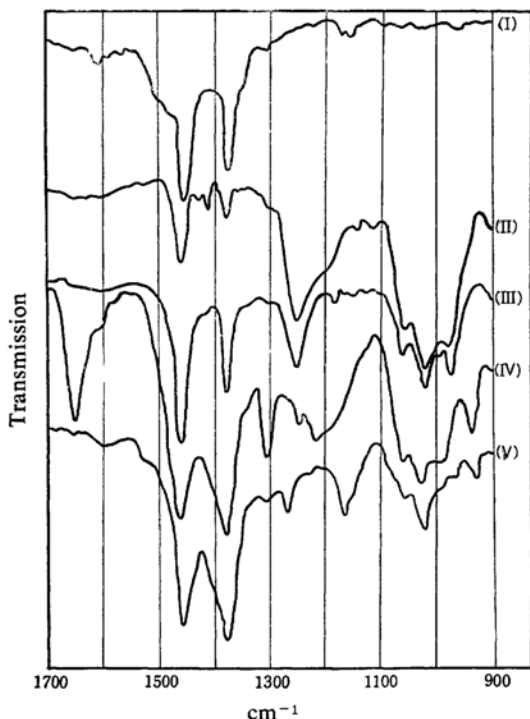


Fig. 4. Infrared absorption spectra of samples I—V.

- (I) Kerosene
- (II) Pure TBEDP
- (III) 0.2 M Kerosene solution of TBEDP
- (IV) 0.2 M Kerosene solution of TBEDP after being shaken with 6 M nitric acid
- (V) 0.2 M Kerosene solution of TBEDP after being shaken with 0.5 M uranyl nitrate in 6 M nitric acid

The spectrum of the sample III can be explained as a mixture of the samples I and II. In the spectrum of III, the bands at 1462 and 1380 cm^{-1} are assigned to the deformation vibrations of methyl groups in TBEDP and kerosene. The band at 1255 cm^{-1} and the bands in the region of 1100 to 950 cm^{-1} are due to

TBEDP. The 1255 cm^{-1} band is assignable to the P=O stretching frequency, while the other bands are associated with the stretching vibrations of the P—O—C linkage and the C—C bond.

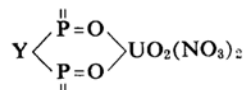
In the spectrum of IV, three new absorption bands were observed at 1649, 1305 and 944 cm^{-1} . According to Peppard et al.⁹⁾, four absorption bands are found in the infrared spectrum of 100% nitric acid at 1680, 1308, 924 and 769 cm^{-1} . The addition of water to 100% nitric acid causes the appearance of bands at 828 and 1380–1410 cm^{-1} which have been attributed to the nitrate ion^{10–13)}. Thus, these three new bands are possibly due to nitric acid. The band due to the nitrate ion in the 1380–1410 cm^{-1} region appears to overlap the 1380 cm^{-1} band observed for TBEDP. These results indicate that nitric acid is extracted into the TBEDP organic phase.

The P=O stretching band, which appears at 1255 cm^{-1} in pure TBEDP, shifts to about 1220 cm^{-1} . The corresponding band in the spectrum of V is observed at 1169 cm^{-1} . On the other hand, the bands near 1030 cm^{-1} do not show any change in the spectra for III, IV and V. Therefore, the P—O bond takes part in the extractability of nitric acid and uranyl nitrate by TBEDP, but the P—O—C linkage does not appear to participate.

It is noticeable that the strong band of nitric acid observed at 1649 cm^{-1} for IV disappears in the spectrum of V. The bands at 1305 and 944 cm^{-1} , which are also due to nitric acid, can not be found. Consequently, nitric acid seems to be nearly absent in V. These results suggest that uranium(VI) is extracted into the TBEDP organic phase more predominantly than nitric acid.

A band at 937 cm^{-1} is observed in the spectrum of V instead of the absence of 944 cm^{-1} . This band may be assignable to the U=O stretching frequency^{14–16)}.

Healy and Kennedy⁸⁾ have proposed the structure



9) D. F. Peppard and J. R. Ferraro, *ibid.*, **15**, 365 (1960).

10) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules", Van Nostrand, New York (1945), p. 322.

11) D. Redlich and L. E. Nielsen, *J. Am. Chem. Soc.*, **65**, 654 (1943).

12) D. K. Ingold and D. J. Millen, *J. Chem. Soc.*, **1950**, 2612.

13) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions", Academic Press, New York (1959).

14) G. K. T. Conn and C. K. Wu, *Trans. Faraday Soc.*, **34**, 1483 (1938).

15) L. H. Jones, *J. Chem. Phys.*, **23**, 2105 (1955).

16) B. M. Gatehouse and A. E. Comyns, *J. Chem. Soc.*, **1958**, 3965.

for the chelate complex formed between diphosphoryl reagents and uranyl nitrate. This model is consistent with the present results.

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