Inorganic Extraction Studies on the System of Tri-n-butyl Phosphate—Nitric Acid

By Tomitaro ISHIMORI and Kenju WATANABE

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Tri-*n*-butyl phosphate*, an excellent extracting agent for inorganic salts, has been widely used for the reprocessing of reactor fuel, the separation of some actinide elements from fission products and the analysis of uranium.

Results on the distribution of inorganic salts between TBP and nitric acid solution have been published by a number of investigators. Peppard et al. studied the behavior of scandium[1], yttrium[2], zirconium[1], lanthanide elements[2,3,4,5] and some actinide elements[1,3,5-7] in the extraction from nitric acid solution. McKay et al. also studied in detail the extraction of nitrates of yttrium[8], zirconium[9], lanthanide elements[8,10] and some actinide elements[11-16] with both diluted and undiluted TBP.

Distribution of uranyl[13-31] and thorium nitrate[1,7,11,15,16,20,23-25,32-39] between TBP and nitric acid solution has been studied at various concentrations of TBP, and nitric acid and/or nitrate using aluminum nitrate[18,23,25,26,33],

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* Tri-*n*-butyl phosphate is abbreviated as TBP in the present paper.

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sodium nitrate[15,18] or calcium nitrate[7,17] as the salting-out agent. In some cases sulfate[27,37], phosphate[27,37] or fluoride[27,33] was added in order to observe the influence of these anions on the partition of the objectives.

Distribution data for protactinium[40], neptunium[13,16,24,64] and plutonium[12,13,15,16,24,28,41,42] were also presented in the extraction with diluted TBP. According to Yakovlev and Kosyakov[43] extractabilities of americium and curium increase with the concentration of nitrate as salting-out agent in the aqueous solution. Behavior of lanthanide elements[20,23,34,35,44-49] has been often studied in the presence of uranium and/or thorium. The extraction of tetravalent cerium[48,50] from nitric acid solution with TBP was very easy in comparison with other trivalent lanthanide elements. Diluted TBP was used in order to separate zirconium from hafnium[51-53]. The extraction of fission products[23,41,42,48,54] with TBP has been evaluated for the decontamination of fissionable materials. Krieger et al.[48], who presented the extraction data of major long-lived fission products (Cs, Sr, Ru, Zr-Nb and lanthanide elements), observed that cesium was not extracted at all while strontium was extracted very slightly from a solution containing aluminum nitrate. They also mentioned that ruthenium and niobium could be extracted in a yield more than 99% into undiluted TBP. According to Bruce[54], molecular iodine was easily extracted with many diluents for TBP, but iodine extraction may have been minimized by maintaining iodine in the reduced valence state. The extractability of zirconium and niobium, given by Scadden et al.[55], from nitric acid solution containing oxalic acid into undiluted TBP was lower than that from nitric acid alone[1]. Morrison and Beaumont[20] showed that distribution ratio of molybdenum between 30% TBP-kerosene and 1 M nitric acid was 0.060 to 0.088. Diamond's observation[56] shows that molybdenum(VI) is not extracted with TBP from nitric acid. It was reported that the distribution of vanadium was very low between 25% TBP and 5 N nitric acid[57]. The distribution coefficients of ferric, cupric, nickel and chromic nitrate between TBP and nitric acid solution were given by Bartlett[18]. McKay et al[14,58,59] and Tuck[60] studied the system of TBP-diluent-nitric acid.

In this paper are presented the comprehensive and systematic studies on the distribution of ions between undiluted TBP and nitric acid of various concentration.

Experimental

The general techniques used were described in the previous paper[61]. TBP was purified in the usual way[1-3,8-13], and was used without any dilution. Nitric acid solutions were prepared by diluting concentrated chemically pure nitric acid. The acidity was determined volumetrically whenever necessary. Tracers of sodium and potassium were prepared by irradiation of the nitrates while those of manganese, nickel, germanium and tellurium were prepared from irradiated metals. A nickel tracer was separated from radiochemical impurities by an anion-exchange technique[62]. Germanium and tellurium tracers were used immediately after the separation from their daughters, respectively arsenic and iodine, by solvent extraction[63]. The imported tracers, Rb-86, Sb-124, and Os-191 were used as received. The sources of radioactive tracers other than mentioned above were the same as those shown in the previous paper[61].

The specific counting rate of these radiochemical tracers was higher than 10^4 count per min. per 100 μg. Although in some cases the oxidation state and the chemical form of the tracer could not clearly be defined, the most familiar chemical forms were chosen as far as possible. Distribution

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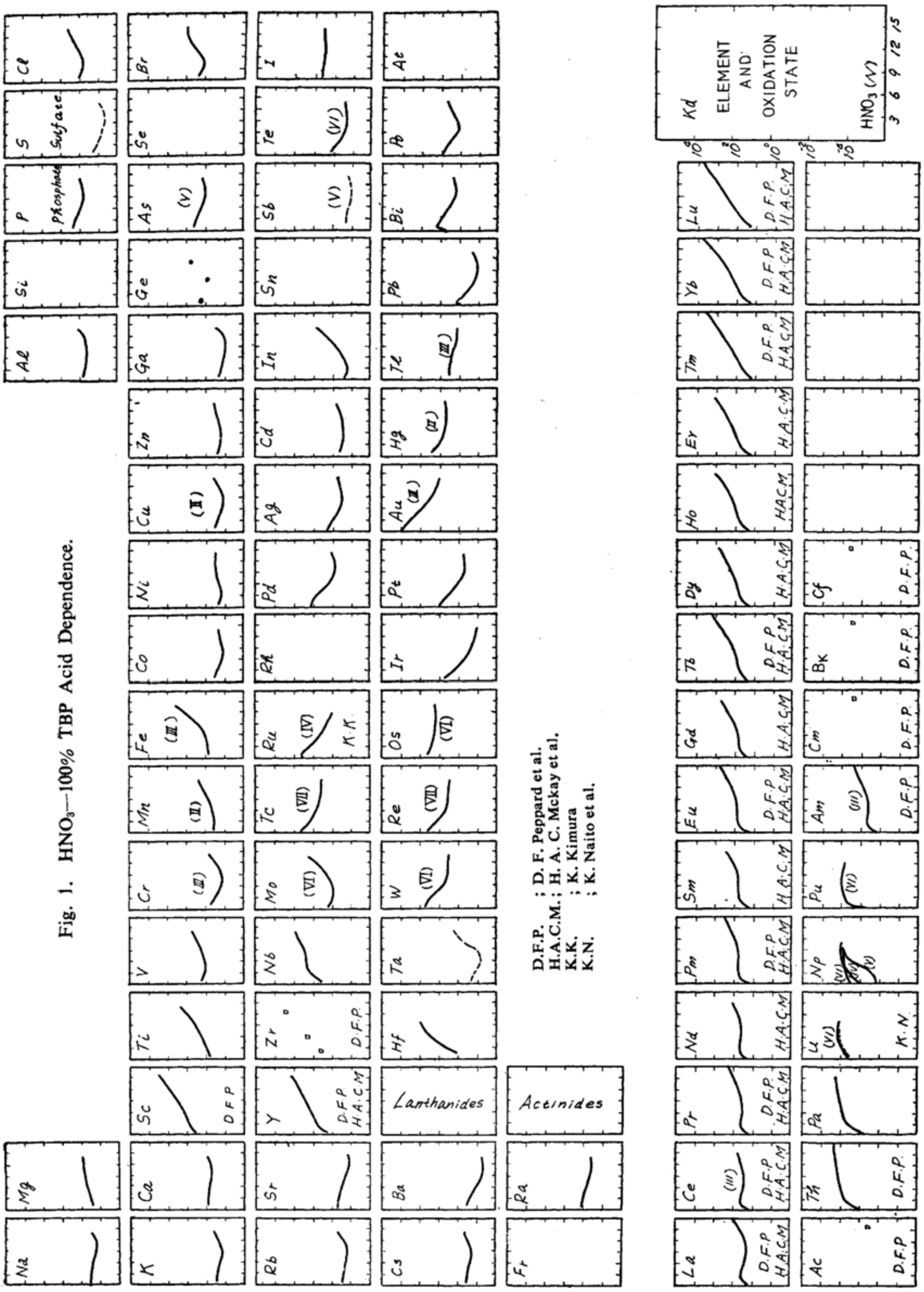

Fig. 1. HNO$_3$—100% TBP Acid Dependence.

D.F.P. ; D. F. Peppard et al.
H.A.C.M. ; H. A. C. Mckay et al.
K.K. ; K. Kimura
K.N. ; K. Naito et al.

ratios were determined radiometrically in the ordinary way[1,3,61,64].

Results and Discussion

The results are summarized in Fig. 1 as a series of graphs of log K_d vs. N, where K_d is the distribution ratio and N the acidity of nitric acid in normality. Some of the graphs in Fig. 1 were compiled from some published and unpublished results. Data for scandium[1], zirconium[1], thorium[1], americium[3] and some other actinide elements[5] are taken from the work of Peppard and his coworkers. Curves for yttrium[2,8] and lanthanide elements[2,3,8,10] are quoted from the reports of Peppard et al. and McKay et al. Data for ruthenium[65] and uranium(VI)[66] are cited from the observations of Kimura and Naito, respectively. A dotted line for uranium(VI) is based on the result by Bartlett[18]. The curves for hafnium, protactinum and neptunium are taken from the paper[64] of Nakamura et al. The data for plutonium(VI), lead and bismuth were obtained by one of the present authors (T. I.) during his stay in the Argonne National Laboratory, U. S. A.

The K_d values for sulfate and antimony could not be determined exactly, because the activities extracted into the organic phase were very low.

As Fig. 1 shows, four alkali elements behave in a similar way, showing always very low K_d values. There are some similarities in the shape of the acid-dependence curves for chloride and bromide; ruthenium, palladium and platinum. The K_d values of scandium, yttrium and lanthanum increase with the decreasing atomic number, Z. Calcium, strontium and barium also show a similar relationship between K_d vs. Z in a high acidity range. As far as these fifteen elements, namely, alkali metals, chloride, bromide, ruthenium, palladium, platinum, calcium, strontium, barium, scandium, yttrium and lanthanum, are concerned, there is a remarkable difference in the shape of log K_d vs. N curve between TBP-nitric and TBP-hydrochloric acid system. On the other hand, the group of alkali metals, chloride and bromide, ruthenium, palladium and platinum, calcium, strontium and barium, and scandium, yttrium and lanthanum shows a similar K_d vs. Z relationship between TBP-nitric and TBP-hydrochloric system. Among zirconium, hafnium and thorium, thorium gives the highest extractability into TBP from a nitric acid solution while it shows the lowest into TBP from a hydrochloric acid solution.

Concerning the group of zinc, cadmium and mercury, there is a marked similarity both in the shape of acid dependence curve and in values of K_d in the hydrochloric acid system[61]. In the nitric acid system, howerver, the K_d values of these three elements increase with atomic number, showing a noticeable difference between the shape of the acid-dependence curve for mercury and that for two other elements.

The K_d values for 12 N nitric acid were

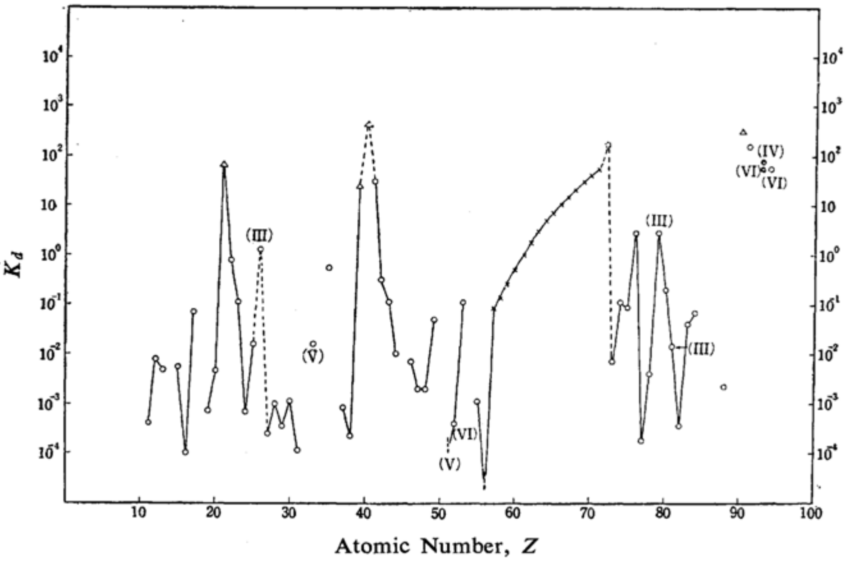

Fig. 2. Relationship between atomic number and K_d values at 12 N HNO_3.

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plotted against the atomic number Z, in Fig. 2. The values for lanthanides are quoted from the paper of McKay et al.[10] The values for scandium, yttrium, ruthenium and thorium are taken from both published and unpublished works[1-3,65]. There were no data for zirconium, hafnium and neptunium in 12 N nitric acid in the original papers. Accordingly the present authors indicate the values with dotted marks which are estimated from the original data. A regularity in the variation of K_d values seen in Fig. 2 is analogous to that in the TBP-hydrochloric acid system[61]. In $\log K_d$ vs. Z relationship, however, one peak for one long period of the periodic table is seen in the nitric acid system, whereas two peaks are found in the hydrochloric acid system.

Niobium and ferric nitrate give relatively high K_d values in the extraction with TBP from a concentrated nitric acid, while technetium, ruthenium, tungsten, rhenium, osmium and gold are extractable from nitric acid in low concentrations. Protactinum, uranium, neptunium(IV) and -(VI) and plutonium are extracted easily from a nitric acid solution of more than about 3 N.

Fig. 3 gives K_d values for 100% TBP-nitric acid system. This will be convenient for checking the possibility and the efficiency of a mutual separation of a couple of elements chosen arbitrarily. For example, technetium-99 will be separated with TBP from a irradiated molybdenum in 1 N nitric acid solution, because the K_d value for technetium is 18.7 in 1 N nitric acid, while that for molybdenum is 0.02.

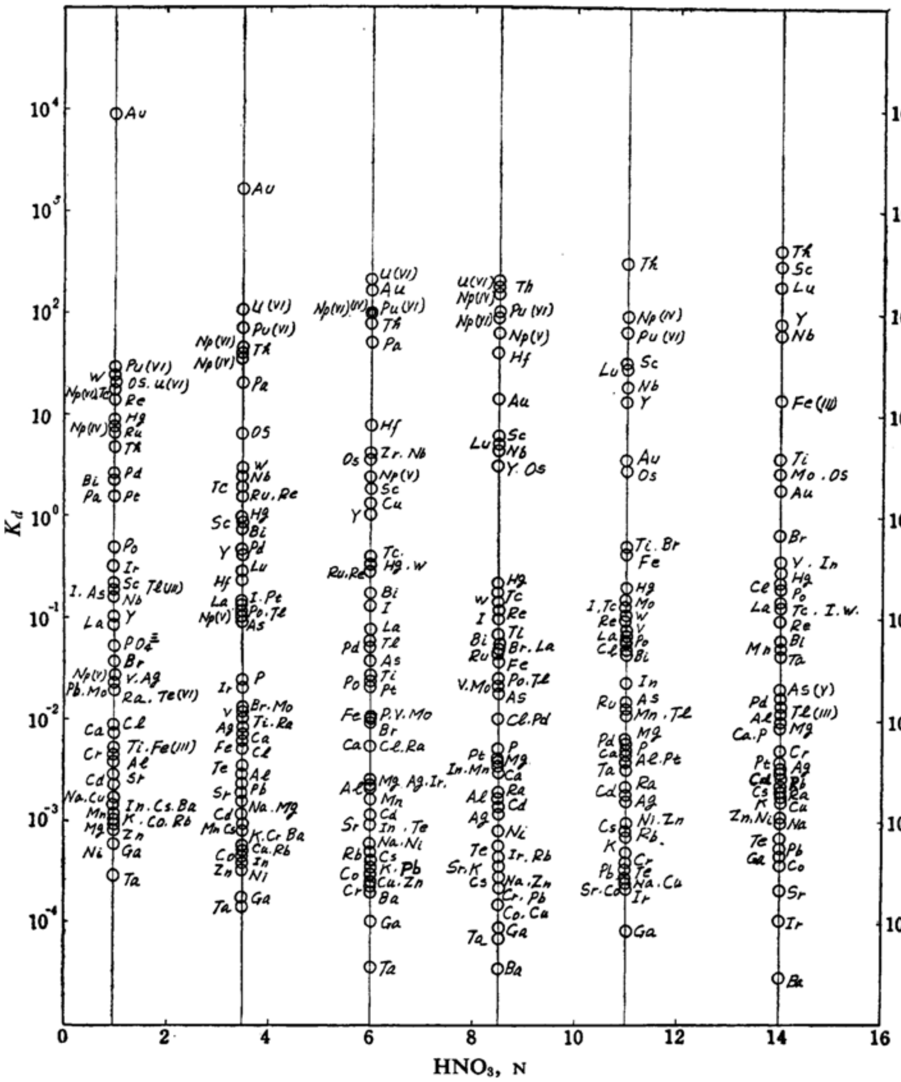

Fig. 3. K_d values in 100% TBP—HNO_3 System.

As the K_d values were obtained with a tracer in the present work, the optimum conditions of separation found in Fig. 3 will well fit a chemical separation on a tracer scale. However, some cautions must be paid in macro-scale separations.

Generally most elements give lower K_d values in the TBP-nitric acid system than in the hydrochloric acid system. In other words, it would be easy to find out a favorable condition, where many kinds of element remain in the aqueous phase after TBP extraction from nitric acid solution, while a few kinds of element are extracted into the organic phase. Accordingly, the extraction from nitric media could be applied to a chemical or a radiochemical separation not so widely as that from hydrochloric acid media could be. However, this means that a small number of elements could be isolated selectively. Isolation and group separation of scandium, yttrium, zirconium, hafnium, some actinide and lanthanide elements are promising, according to the TBP extraction data from nitric acid solution of a high acidity. Similarly, extraction from dilute nitric acid well be favorable for the isolation and group separation of technetium and ruthenium.

Chemistry Division, Tokai Laboratory
Japan Atomic Energy Research Institute
Tokai, Ibaraki-ken