A Study on Anion Exchange aud Amine Extraction of Rare Earth Elements in Nitric Acid

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The use of amine extraction for uranium, thorium and many other elements has recently been developed by a number of investigators[1-7]. It is reported that the mechanism of amine extraction is similar to that of anion exchange and the former is called commercially liquid anion exchanger. The author previously reported[8] the amine extraction and anion exchange of uranium, protactinium and thorium in nitric, hydrochloric and sulfuric acid. Peppard, Mckay and their coworkers[9-12] reported on the extraction of rare earth nitrates with tri-*n*-butyl phosphate.

In the present paper, the distribution coefficients of rare earth elements between anion exchange resin and nitric acid are compared with those between amine and nitric acid. Based on the resuls from these distribution studies, the mechanism of amine extraction is discussed.

Experimental

Materials.—Dowex 1, X8 (100~200 mesh), converted into nitrate form by nitric acid, is used as an anion exchange resin. Primene JM-T, Amberlite LA-2 and tri-*n*-octyl amine are respectively used as primary, secondary and tertiary amine. Amines are diluted with kerosene, and octyl alcohol is added to this solution to avoid the third phase formation, making phase separation clear. These amine solutions are converted into the nitrate form with 8 N nitric acid, as shown in the following equation.

$$RR'NH+HNO_3 \rightleftarrows RR'NH_2NO_3$$

Promethium-147 is used as a tracer of Pm. Other radioactive tracers of rare earth elements are prepared by neutron irradiation of rare earth oxides in J. R. R.-1 Reactor or by separation from isotopes of alkaline earth elements which are in a state of equilibrium with their daughter nuclides. The irradiated oxides are dissolved in 8 N nitric acid. The γ-ray spectrograms of these samples are obtained with a single channel pulse height analyzer and the radioactivities of these samples are measured by γ-ray or β-ray counting.

Table I shows the radioisotopes used in this experiment and the method for radioactivity measurement.

TABLE I. RADIOISOTOPES OF RARE EARTH ELEMENTS

Nuclide	Preparation	Counting method
^{140}La	Imported ^{140}Ba→^{140}La, coprecipitation with $Fe(OH)_3$, extraction of Fe by Amberlite LA-1 from 6 N HCl	γ
^{141}Ce	(n, γ)	γ
^{142}Pr	(n, γ)	β
^{147}Nd	(n, γ)	γ at 0.092 MeV. of ^{147}Nd
^{147}Pm	imported	β
^{152}Eu+^{154}Eu	(n, γ)	γ
^{159}Gd	(n, γ)	γ at 0.364 MeV. of ^{159}Gd
^{160}Tb	(n, γ)	γ
^{165}Dy	(n, γ)	γ
^{166}Ho	(n, γ)	γ
^{170}Tm	(n, γ)	γ
^{175}Yb	(n, γ)	γ at 0.396 MeV. of ^{175}Yb
^{176m}Lu+^{177}Lu	(n, γ)	γ

Sm and Er are omitted from this experiment because their γ-ray spectra resemble those of the daughters'.

Procedure.—The distribution coefficients in both anion exchange and amine extraction are measured by the batch method. Half a gram of dried resin is immersed in 5 ml. of nitric acid solution of rare earth elements and then shaken for 20 hr. at a constant temperature so that a state of equilibrium is attained. Then the sample is filtered and the activity of 1 ml. of the filtrate is compared with that of a reference solution.

In the case of the amine extraction, 2 ml. of 30% kerosene solution of amine is shaken for 1 min. with 2 ml. of nitric acid solution of rare earth element. Then resulting solution is then centrifuged and two phases are separated. The activity of both organic and aqueous solutions are measured. The distribution coefficient is calculated from the data which are obtained in these experiments.

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[1] D. J. Crouse et al., ORNL-2099 (1956).
[2] J. C. Sheppard, HW-51958 (1957).
[3] C. F. Coleman et al., A/Conf. 15/p/510 (1958).
[4] K. B. Brown et al., ORNL-2269 (1957).
[5] A. Preuss and J. Saunders, RMO-2533 (1955).
[6] A. S. Wilson, A/Conf. 15/p/544 (1958).
[7] D. J. Crouse and J. O. Denis, ORNL-1859 (1955).
[8] F. Ichikawa and S. Uruno, This Bulletin, 33, 569 (1960).
[9] D. P. Peppard et al., *J. Phys. Chem.*, 57, 294 (1953).
[10] D. F. Peppard et al., *J. Am. Chem. Soc.*, 75, 6063 (1953).
[11] H. A. C. Mckay et al., *J. Inorg. Nucl. Chem.*, 4, 304 (1957).
[12] H. A. C. Mckay et al., idid., 9, 279 (1959).

Results

Distribution coefficients (K_d) of lanthanum, promethium and holmium are measured for the nitric acid solution of various concentrations.

Results are shown in Figs. 1—4. In the concentration range from 1 to 8 N nitric acid, the K_d value of anion exchange increases slowly and then decreases in acidities over 8 N. The distribution coefficients in primary amine extraction increases with the increase in the concentration of nitric acid. As is shown in Fig. 1, the maximum value of K_d decreases with increasing atomic number. In order to confirm this trend, values of K_d for rare earth elements in 8 N nitric acid is determined at 20°C. Fig. 5 shows the result of this experiment. For rare earth elements from lanthanum to gadolinium the K_d value decreases with increasing atomic number. The difference in the K_d value for rare earth elements of higher atomic number is very small and the relation between the K_d value and the atomic number is complicated.

In the case of amine extraction, the K_d values for rare earth elements are very small. Results are shown in Figs. 6—8. K_d decreases slowly from lanthanum to dysprosium in

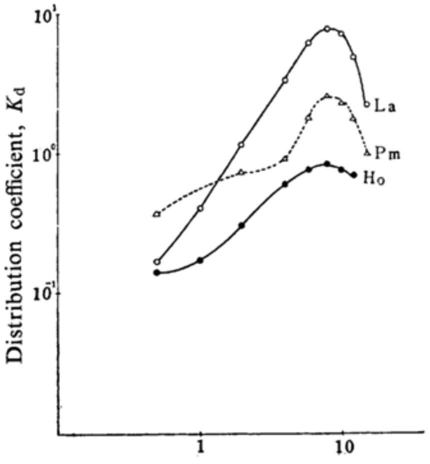

Fig. 1. Distribution coefficients of La, Pm and Ho between Dowex 1 and nitric acid.

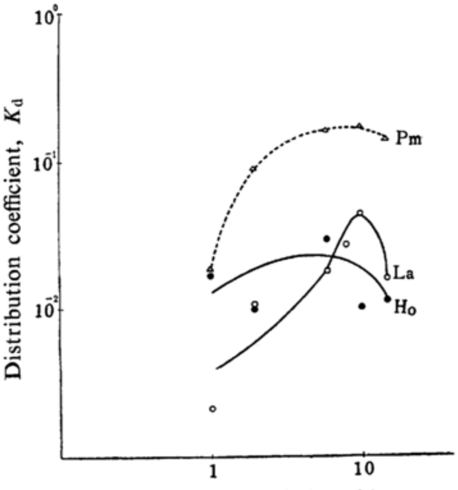

Fig. 3. Distribution coefficients of La, Pm and Ho between 30% Amberlite LA-2 and nitric acid.

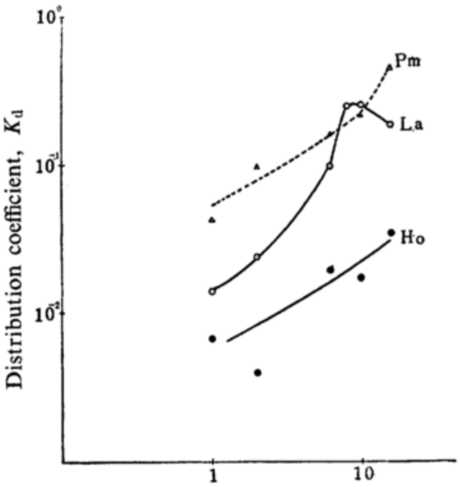

Fig. 2. Distribution coefficients of La, Pm and Ho between 30% Primene JM-T and nitric acid.

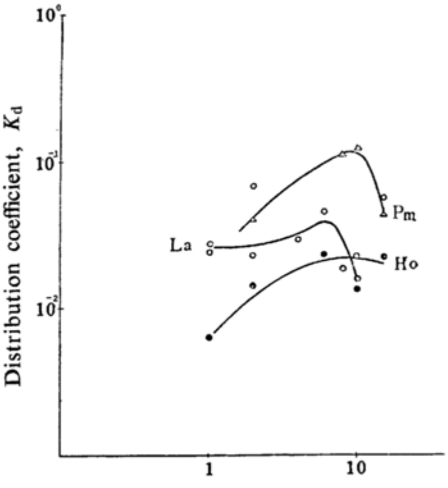

Fig. 4. Distribution coefficients of La, Pm and Ho between 30% tri-*n*-octyl amine and nitric acid.

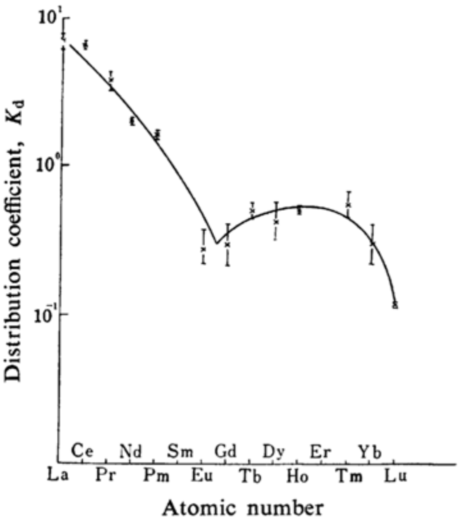

Fig. 5. Distribution coefficients of rare earth elements between Dowex 1 and 8 N nitric acid.

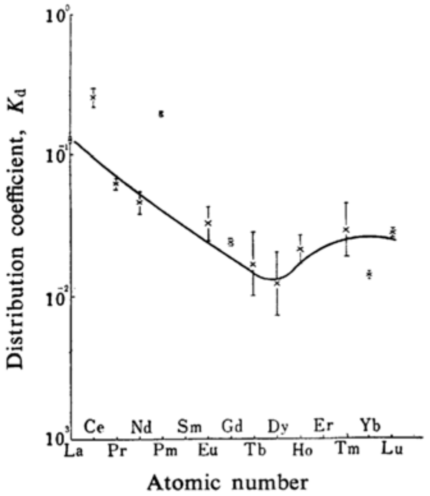

Fig. 6. Distribution coefficients of rare earth elements between 30% Primene JM-T and 8 N nitric acid.

primary amine extraction. From holmium to lutetium, the difference in K_d value is very small. This is a tendency similar to that observed in anion exchange. As to the secondary amine extraction, a small decrease in K_d is found. But no significant variation in K_d is observed in tertiary amine extraction.

To compare these results, the extraction of rare earth elements by 100% TBP from 8 N nitric acid solution is studied. Fig. 9 shows the result. K_d value increases with increasing atomic number and this result is very different from those in anion exchange or amine extraction.

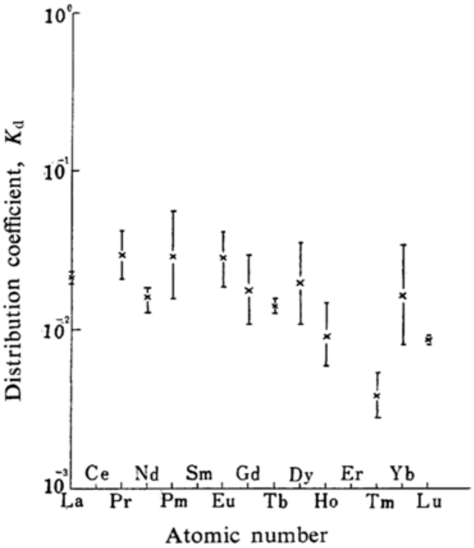

Fig. 7. Distribution coefficients of rare earth elements between 30% Amberlite LA-2 and 8 N nitric acid.

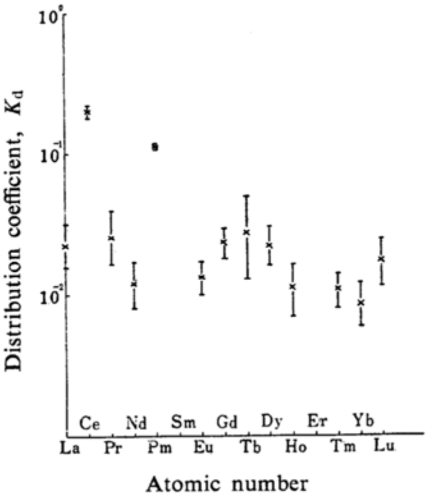

Fig. 8. Distribution coefficients of rare earth elements between 30% tri-*n*-octyl amine and 8 N nitric acid.

Discussion

Peppard and his coworkers[9,10] found the tendency of the increase in the extractability of rare earth nitrates by TBP with increasing atomic number. Mckay and his coworkers[11,12] reported that this trend is not always found in the subgroup from Gd to Lu. In the present experiment, the extractability of rare earth elements by 100% TBP from 8 N nitric acid solution also increased with increasing atomic number and some difference is found between lower and higher subgroups.

On the contrary, anion exchange study shows

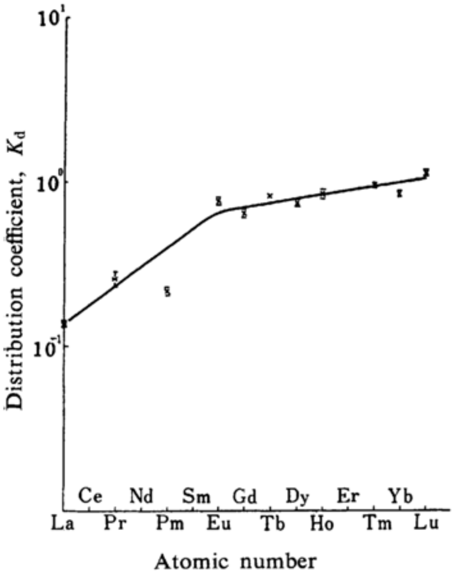

Fig. 9. Distribution coefficients of rare earth elements between 100% TBP and 8 N nitric acid.

decreasing of K_d value with increasing atomic number for rare earth elements of lower subgroup.

The different behavior of these two subgroups is probably due to the ionic radius, electronic structure and other characters. The reverse trend observed in TBP extraction and anion exchange might be due to the different probability of neutral complex formation and anionic complex formation in each circumstance.

From these points of view, the amine extraction behavior of these elements is very interesting. As is shown in Figs. 6—8, the difference in K_d value between rare earth elements of lower and higher atomic number is greater in the case of primary amine extraction than in secondary amine extraction. But, in both cases, decrease in K_d value with increasing atomic number is observed. It is suggested from these facts that the mechanism of amine extraction of rare earth elements resembles more the mechanism of anion exchange than TBP extraction does.

Summary

The amine extraction of rare earth elements in nitric acid is compared with anion exchange and TBP extraction with respect to the increase or decrease in K_d value with increasing atomic number of rare earth elements.

Concerning the relationship between distribution coefficient and atomic number of rare earth element, a similar trend is observed in anion exchange and amine extraction. The distribution coefficient decreases with increase in the atomic number. In TBP extraction, however, the corresponding value increases with increasing atomic number. It seems that the mechanism of amine extraction for rare earth element is similar to that of anion exchange.

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