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Separation of rare earth elements by tertiary pyridine type resin

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Abstract

The novel separation method of rare earth elements by using the tertiary pyridine type resin with methanol and nitric acid mixed solution was developed. The separating operation in this method is very simple and easy, and the waste generation in this method is expected to be low. The adsorption and separation behaviors of rare earth elements were investigated with changing the nitric acid concentration, the methanol concentration, and the alcoholic species. It was confirmed that the rare earth elements can be well separated mutually.

Keywords: Rare earth elements; Lanthanides; Tertiary pyridine; Nitric acid; Alcohol

1. Introduction

The separation of rare earths is difficult because of the similarity of their chemical properties derived from their same valence and similar ion radii. The rare earth elements, however, are required to be mutually separated in many fields because of the peculiar physical, chemical, and nuclear properties of themselves or their compounds. The separations of rare earth elements are carried out or are developed for the industrial use of rare earth elements [1,2], for the pretreatment for the analyses of rare earths in the some chemical fields such as a geochemistry [3,4], and for the analyses and the partitioning of rare earth elements including the fission products generated in nuclear reactors [5,6]. The separation methods are variously conducted, but the following types are basically categorized, i.e., solvent extraction [1,2,6], and ion exchange chromatography [3–5]. In each conventional separation methods, there are some problems, such as complicated operation, tight separability condition, remain of organic material, restriction on separable rare earth elements, and so on.

We have proposed the simple separation technique based on the chromatography using the tertiary pyridine resin with alcoholic inorganic acid solution system. Our proposal technique is freed from the described above problems. The separation method in hydrochloric acid/alcohols mixed solution system were already studied [7–9]. In the hydrochloric acid solution system, it has been confirmed that the separation of rare earth elements and actinides is available, but the mutual separation of rare earth elements is insufficient. In the present study, the adsorption behaviors of rare earths elements on the tertiary pyridine resin in the nitric acid solution system were investigated. The effects of the nitric acid concentration, the methanol concentration, and the alcoholic species on the adsorption were explored in order to separate the rare earth elements under optimal conditions.

2. Experimental

2.1. Tertiary pyridine resin

The resin used in the present experiment was highly porous tertiary pyridine type resin embedded in silica beads. This resin was produced by our research group of Research Lab-

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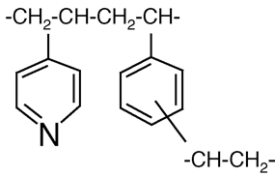

Fig. 1. Chemical structure of tertiary pyridine type resin.

oratory for Nuclear Reactors, Tokyo Institute of Technology [10]. The chemical structure of this resin is presented in Fig. 1. The average diameter of this resin is 60 μm. The total exchange capacity of the resin is 1.94 meq/g(dry) in Cl^- form. The cross-linkage is 20%. The tertiary pyridine has two functions; one is anion exchange function, and another is extract agent function.

2.2. Chromatography

The mixture of rare earth elements, which chemical forms were nitrides or oxides, was dissolved in alcoholic nitric acid solutions, which are adjusted to desirable concentrations. The concentration of each rare earth elements was 10 mmol/dm^3. A 10 cm^3 portion of this solution was fed into a 50 cm column with a water jacket, packed with pyridine type resin. This column was kept the temperature of 293 K. The column was preliminarily conditioned with the 200 cm^3 alcoholic nitric acid solution similar in composition to feed solution. The elution experiment was carried out at flow rate of 100 cm^3/h. The 2 cm^3 portions of the eluate were fractionally collected. Rare earth elements in these eluate samples were analyzed by ICP-AES (OPTIMA 3000, Perkin Elmer Inc.).

3. Results and discussion

3.1. Separation behavior in the present system

The typical result of rare earth separation by using chromatogram are shown in Fig. 2. This chromatography experiment was carried out with using the methanolic nitric acid solution of composition ratio, concentrated nitric acid solution:deionized water:methanol = 3:3:4. The lanthanides are eluted in reverse order of atomic number. In this separation experiments, yttrium was also used, although its peak was not shown in Fig. 2 because the yttrium peak overlapped the lutetium peak. The distribution coefficients calculated from this chromatogram, including yttrium, are shown in Fig. 3. The distribution coefficients are defined as, $K_d = (V_M - V_S)/V_R$, where V_M, V_S, and V_R are the volume of effluent at elution peak, the dead volume of resin column, and the volume of resin, respectively. The ionic radii [11] of rare earth elements were used as x-axis in this graph. This result shows that the elements with large ionic radii have the high distribution coefficients. The eluted order of rare earth elements in Fig. 2 was governed by the ionic radii, i.e. the

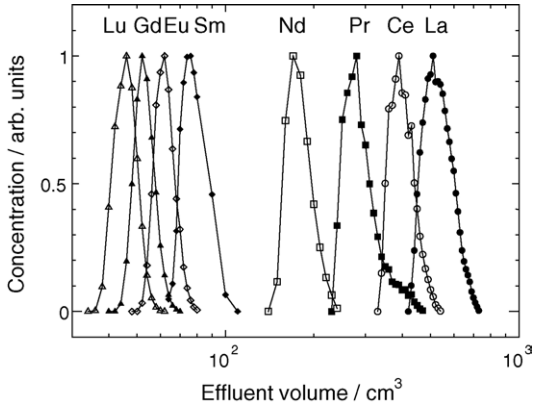

Fig. 2. Typical chromatogram of rare earth elements. Eluent was the nitric acid and methanol mixed solvent, the volume ratio of conc. HNO_3:H_2O:MeOH is 3:3:4.

charge densities of rare earth ions. This fact means that the tertiary pyridine type resin acts as anion exchange resin in the alcoholic nitric acid solutions. This behavior is different in the alcoholic hydrochloric acid solutions [8].

3.2. Solvent effects

The chromatography experiments with constant the mixture ratio of concentrated nitric acid, 30 vol.%, were carried out with changing the adding methanol ratio. The methanol concentration effects on distribution coefficient of rare earth elements are shown in Fig. 4. The distribution coefficients of all rare earth elements exponentially increase with the increase of the methanol ratio. The separation factors, which can be calculated by the ratio of distribution coefficients, also increase with the increase of the methanol ratio.

The chromatography experiments with constant the mixture ratio of methanol, 30 vol.%, were carried out with changing the nitric acid concentration. The nitric acid

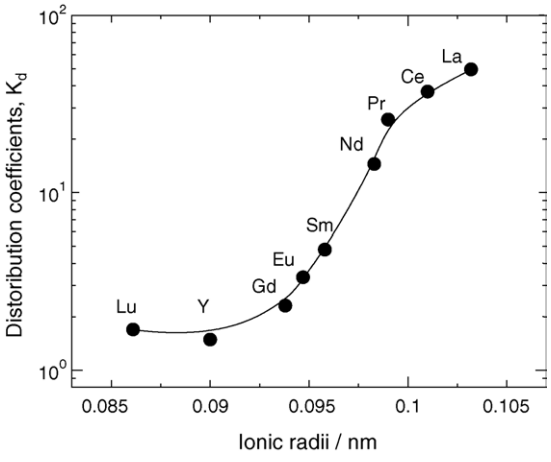

Fig. 3. Relation of distribution coefficients and ionic radii of rare earth elements. Distribution coefficients were calculated by results of chromatography described in Fig. 2.

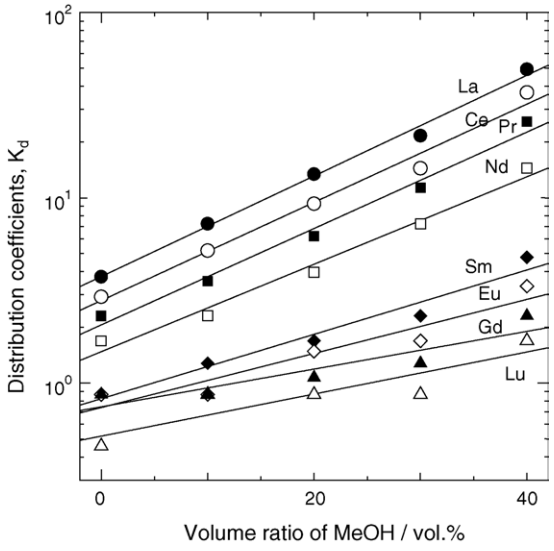

Fig. 4. Methanol effects on distribution coefficients. Volume ratio of concentrated nitric acid was kept in 30 vol.%.

concentration effects on the distribution coefficients are shown in Fig. 5. From this figure, we can see that the distribution coefficients of the heavier lanthanides, from samarium to lutetium, monotonically increase with the increase of nitric acid concentration, while the distribution coefficients of the lighter lanthanides, from lanthanum to neodymium, have the peak. The positions of peak are moved to the higher ratio of methanol with the increase of atomic number, i.e. from lanthanum to neodymium. We expect that the heavier lanthanides have also peak of distribution coefficient in the higher methanol concentration solution. The tendency of these adsorption behaviors are similar to the adsorption behavior of rare earth elements on the general strongly basic anion exchange resin, i.e., quaternary ammonium type resin,

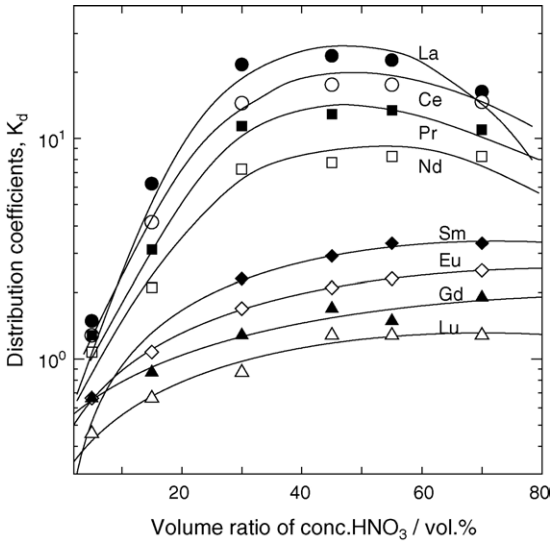

Fig. 5. Nitric acid concentration effects on distribution coefficients. Volume ratio of methanol was kept in 30 vol.%.

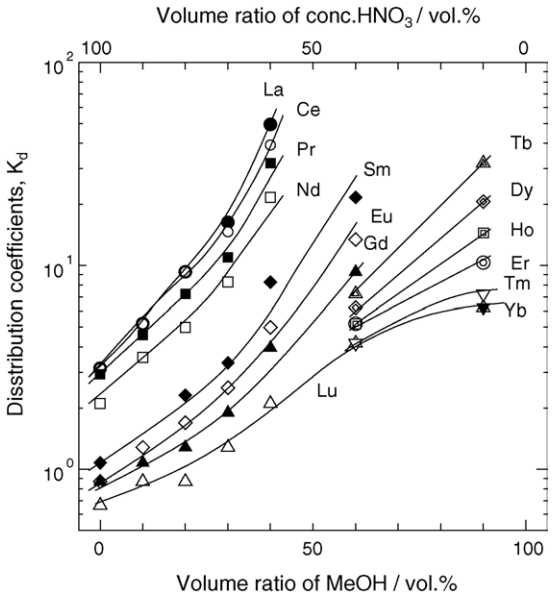

Fig. 6. Distribution coefficients with varying the mixture ratio of concentrated nitric acid solution and methanol.

in nitric acid solution. The separation factors have same tendency of distribution coefficients.

The chromatography experiments were carried out with changing the mixture ratio of the concentrated nitric acid solution and the methanol. The distribution coefficients with varying the mixture ratio of concentrated nitric acid and methanol are shown in Fig. 6. The distribution coefficients and the separation factors increase with the increase of the methanol volume ratio. We confirmed that the heavier lanthanides can be sufficiently separated by increasing the methanol ratio. The chromatogram of heavier lanthanides carried out with 90 vol.%-methnaol/nitric acid mixed solution is shown in Fig. 7. In additional remark, the lighter lanthanides than gadolinium were strongly adsorbed on the pyridine type resin, and so these elements were eluted by the diluted nitric acid solution. In this figure, the heavier

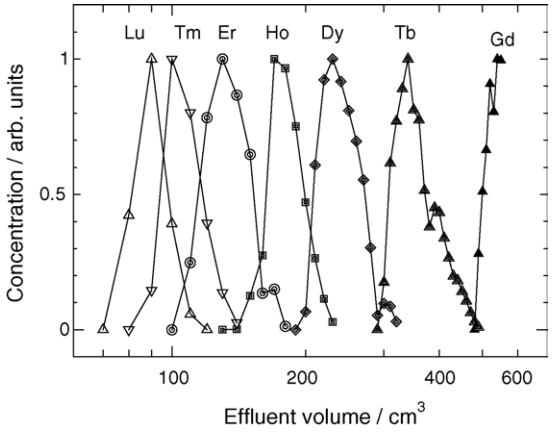

Fig. 7. Chromatogram of heavy lanthanides in the separation experiment with highly adding methanol into the nitric acid solution. Mixture ratio of HNO_3 and MeOH is 1:9 in volume ratio.

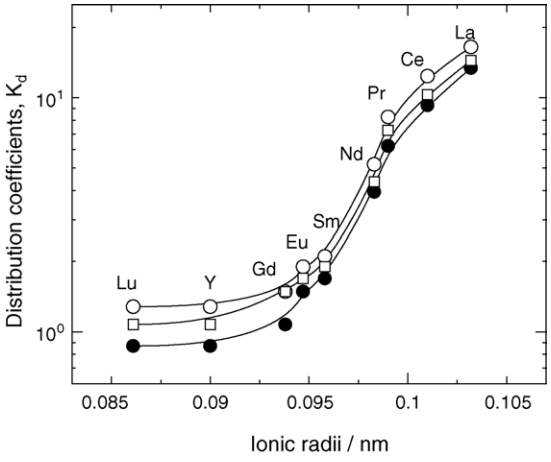

Fig. 8. Influence of alcoholic species on adsorption behaviors. ●: methanol, ◯: ethanol, □: 1-propanol. The mixture ratio of alcohol is 20 vol.%. The volume percent of concentrated nitric acid solution is 30%.

lanthanides are well separated, especially from erbium to gadolinium, these elements are almost completely separated. Although the lutetium and the ytterbium is not separated in Fig. 6 and the elements from erbium to lutetium are not completely separated in Fig. 7, it is expected that the resolution is able to be made higher by adding the methanol of the extra higher mixture ratio.

From the above results, the mixture ratio of methanol was confirmed to affect the adsorption behavior of rare earth elements on the tertiary pyridine type resin. Arisakam et al. was confirmed by using the time-resolved laser-induced fluorescence spectroscopy that the number of hydrations in the inner sphere of europium decreases with the addition of methanol in hydrochloric acid solution with lithium chloride system [12]. In the nitric acid solution system, similar phenomenon is expected to be also observed. We infer that the coordination of nitrate ions in inner sphere of rare earth ions are promoted as a result of the dehydrations from the rare earth ions by adding the methanol into the nitric acid solution.

The chromatography experiments were carried out with the changing the additional alcoholic species, i.e., methanol, ethanol, and 1-propanol. The mixture ratios of alcohol, concentrated nitric acid solution, and deionized water are 20, 30, and 50 vol.%, respectively. The obtained distribution coefficients were shown in Fig. 8. The most effective alcohol in increasing the distribution coefficients is ethanol, second is 1-propernol, and third is methanol. This result shows that the alcohol with high organicity is not exactly high effective in the dehydration from rare earth elements. This alcoholic species effect on the adsorption and separation is similar to the behavior of lanthanides and actinides in alcoholic hydrochloric acid solutions [9].

4. Conclusion

The chromatographic separations of rare earth elements by using the tertiary pyridine type resin with the alcoholic nitric acid solution were investigated. We confirmed that the rare earth elements can be separated in this simple and easy system. The distribution coefficients of rare earth elements are governed by the ionic radii of their elements in the nitric acid solution system, and this result shows that the tertiary pyridine works as anion exchange functional group in the nitric acid solution system. The distribution coefficients and the separation factors strongly depend on the methanol concentrations. Most suitable composition of methanol and nitric acid has to be varied by separating objects, the light lanthanides or heavy lanthanides. The alcohol with highest distribution coefficients is ethanol. This fact means that the distribution coefficients are not exactly increased by the addition of the solvent with high organicity.

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