

## 18-Crown-6와 Azacrown Compound에 의한 란탄족 원소의 용매추출

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### Solvent Extraction of Lanthanide by 18-Crown-6 and Azacrown Compound

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Rare earth metals are abundant in the earth, but they have been used rarely because of the difficulties in separation and refining. The demand for these materials is now uprising for applications in electronics, atomic reactors, metallurgy, glass industry, ceramic industry, and so on. In a nuclear power plant, lanthanide ions should be removed to increase the efficiency of thermal neutrons since they have large absorption cross sections for thermal neutrons.

The methods known for chemical separation of these elements from each other were very slow and tedious. Considerable advances have been made in the last few years, among them the solvent extraction method based on the use of crown ethers for separation of lanthanide ions seems to be the most effective<sup>1</sup>. In this method, the crown ether is used as a synergistic extracting agent to selectively extract the lanthanide ions from the aqueous into the organic phase<sup>2</sup>. It has been noted that the complexation ability of a crown compound and the stability of the resulting complex depend on the relative sizes of the diameter of the cavity in crown compound and the radius of cation. They are also influenced not only by the charge and hardness of the cation but also by the kinds of donor atoms present in the crown compound<sup>3</sup>.

In this study, 18-crown-6 and azacrown containing three nitrogen atoms were used as extracting agent to extract the lanthanide ions such as Yb<sup>3+</sup>, Tb<sup>3+</sup>, Eu<sup>3+</sup>, and Nd<sup>3+</sup>. The pyridino diazacrown used was synthesized by methods shown in Scheme 1<sup>4,5</sup>.

The distribution coefficient,  $D$  of the extraction is given by the following equation,

$$\text{Ln}^{3+} + n\text{CE} + m\text{B}^- = [\text{Ln}(\text{CE})_n \text{B}_m]^{(3-m)+} \quad (1)$$

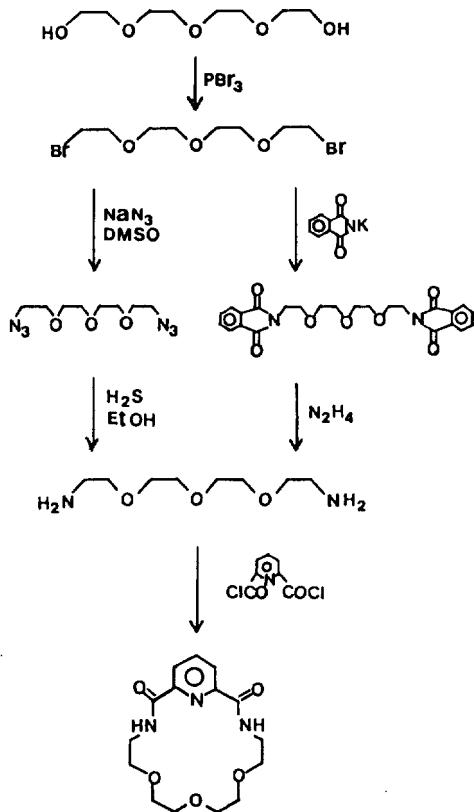
$$D = \frac{\sum [\text{Ln}]_{\text{org}}}{\sum [\text{Ln}]_{\text{aq}}} = \frac{[\text{Ln}(\text{CE})_n \text{B}_m^{3-m}]_{\text{org}}}{[\text{Ln}^{3+}]_{\text{aq}} + [\text{Ln}(\text{CE})_n^{3+}]_{\text{aq}}} \quad (2)$$

Where Ln<sup>3+</sup>, CE, and B<sup>-</sup> are the rare earth, crown ether, and benzoate anion, respectively.

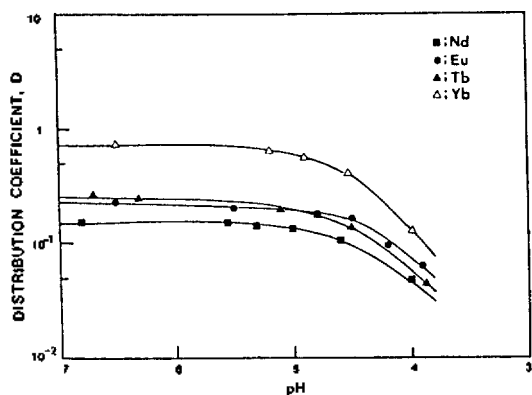
The distribution coefficient,  $D$  can be determined by measuring the concentrations of the lanthanide ion in the ethylacetate and in the aqueous phases<sup>6</sup>.

In this experiment, the extractabilities of several lanthanide ions were changed with varying the pH and the concentration of benzoate as a counter ion and crown ethers. Especially, a comparison has been made between commercial 18-crown-6 and the pyridino diazacrown compound.

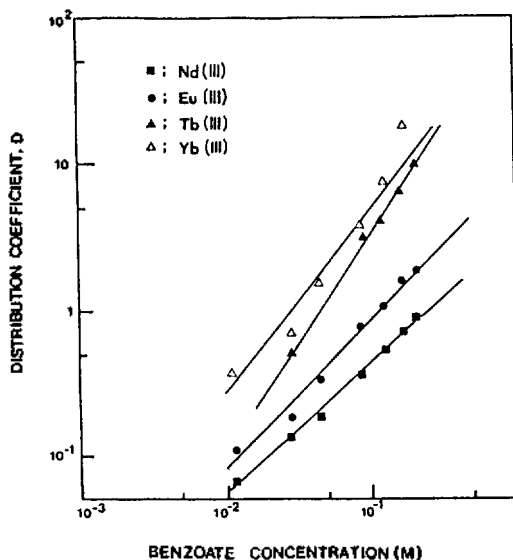
To test the pH effect on the extraction with adding an appropriate amount of lithium benzoate



Scheme 1

Fig. 1. Plot of pH vs.  $D$  at  $0.05 M$  18-crown-6 and  $0.024 M$  benzoate-benzoic acid solution.

and benzoic acid,  $1 \text{ ml}$  of  $0.001 M$  lanthanide solution was transferred into  $15 \text{ ml}$  of centrifugal tube. During being kept the concentration of benzoate constant, pH was varied from 4 to 7 by adding  $0.05 M$  LiOH. Distilled water was added to make

Fig. 2. Plot of benzoate concentration vs.  $D$  at  $0.05 M$  18-crown-6.

final volume  $5 \text{ ml}$ . After  $5 \text{ ml}$  of  $0.05 M$  crown ethers in ethylacetate was added, the solution was vigorously shaken for  $40 \text{ min}$  at room temperature, centrifuged, and separated into two phases<sup>5</sup>. The extracted lanthanide elements in the organic phase were analyzed with a colorimetric method by using Arsenazo-III<sup>7</sup>.

The distribution coefficient until pH 5 was increased with increasing the value of pH of the solution, but there was no further its increment at above pH 7, as shown in Fig. 1. Considering the  $pK_a$  value of benzoic acid in aqueous solution, in pH 5 to 7 range, benzoic acid, HB mainly exist as a dissociated form,  $B^-$ , whereas  $[B^-]$  is abruptly reduced at below pH 5. Thus the pH effect in this extraction may due to change in benzoate concentration.

At the same condition, while the pH 7 was kept with  $0.05 M$  LiOH solution, benzoate concentration was varied by adding different amounts of lithium benzoate solution from  $0.05 M$  to  $0.1 M$ . There is no a drop of pH with increasing lithium benzoate concentration. The extractability for all  $\text{Ln}^{3+}$  ions was gradually increased with increasing benzoate concentration, as shown in Fig. 2. Thus the concentration of benzoate as a counter ion seems to

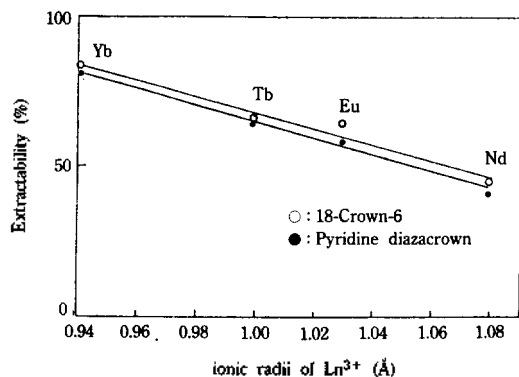


Fig. 3. Relation between extractability and ionic radii of lanthanide ions at 0.05M crown ethers.

be important factor in this solvent extraction.

Their extractabilities were investigated by using 18-crown-6 and pyridino diazacrown compound, which was synthesized as the extractant containing three nitrogen atoms. As shown in Fig. 3, there was no significant difference on the extractability of Nd(III), Eu(III), Tb(III), and Yb(III) ions with 18-crown-6 and pyridino diazacrown compound. It was found that the smaller the ionic radii of lanthanide element, the more stable the complex was formed with an extractant. This result was consistent with the previous results reported by Tran *et al.*<sup>6</sup> and Nakagawa *et al.*<sup>8</sup>, even though there was a little difference in their extractabilities. It seemed that the cavity size of pyridino diazacrown compound was just close to that

of 18-crown-6. As a result, it was suggested that the extraction of lanthanides are influenced much by the cavity size of crown ether than by the species of donor atoms. For further research, it will be studied about the extractabilities for the crown ethers with another donor atoms and various cavity sizes.

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