SYNERGISTIC EXTRACTION OF LANTHANIDE IONS WITH
DIBUTYLMONOTHIOPHOSPHORIC ACID AND
1,10-PHENANTHROLINE

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Measurement of the extraction equilibria of samarium and europium in acetate media with dibutylmonothiophosphoric acid (HR) in toluene diluent was carried out at 303 K. It was found that lanthanide ions (La^{3+}) are extracted according to the following equation.

\[ \text{Ln}^{3+}_{aq} + 3	ext{HR}_{org} = \text{LnR}_{3,org} + 3\text{H}^+_{aq} \]

The extraction equilibrium constants of the metals were obtained. The separation factor between the two metals was a very low 1.1.

A synergistic extraction of the metals with the mixed extractant of dibutylmonothiophosphoric acid and 1,10-phenanthroline (phen) was also conducted to separate the metals efficiently. In this case, the lanthanide ions were extracted according to the following equation.

\[ \text{Ln}^{3+}_{aq} + 3	ext{HR}_{org} + \text{phen}_{org} = \text{LnR}_{3,org} \cdot \text{phen}_{org} + 3\text{H}^+_{aq} \]

The extraction equilibrium constants were obtained, and from them the separation factor was calculated as 1.3. It was found that the factor is improved by the synergistic effect.

Introduction

A solvent extraction technique as an effective and selective separation method for rare-earth metals has attracted practical interest from the viewpoint of energy conservation. In developing such a high-separation process, elucidation of the mechanism of metal extraction is very important.

A number of studies of extraction of the rare-earth metals have been carried out, using di-(2-ethylhexyl)phosphoric acid (abbreviated as D2EHPA) \cite{1,2,5,10,11,13,14,16} or other acidic organophosphorus extractants. \cite{3,5,11,16} However, few studies of the synergistic extraction of lanthanide ions have been reported. Hirashima et al. \cite{4} studied the synergistic extraction of some lanthanide ions with a mixture of D2EHPA and thonyl trifluoroacetone (HTTA) and concluded that the magnitude of synergistic enhancement is relatively small. Nag et al. \cite{12} carried out the synergistic extraction of neodymium with a mixture of 1,1,1-trifluoro-4-(2-thienyl)-4-mercaptobut-3-en-2-one (HSTTA) and some neutral donors such as dipiridyl and clarified the extracted species by synergism. Yamada et al. \cite{15} studied the equilibrium extraction behavior of lanthanide ions with a mixed extractant of Kelex 100 and 1,10-phenanthroline, concluding that the formation of mixed complexes with a mixture of the two chelating extractants improves both extraction efficiency and separation capability.

The authors reported previously that europium ion is extracted by an extractant (HR) as EuR_{3} in the case of didodecylmonothiophosphoric acid (DDTPA) \cite{7} or as EuR_{3}, 3HR in the case of diodecylphosphoric acid (DPDA). \cite{8} In the present study, the synergistic extraction of samarium and europium with a mixed extractant of dibutylmonothiophosphoric acid and 1,10-phenanthroline is carried out to clarify the extracted species and further to improve the efficiency of separation of the two metals from one another. The extraction of the metals with dibutylmonothiophosphoric acid alone is also carried out. The extraction equilibrium constants of the metals in the two systems are obtained and the separation factor between the two metals is discussed.

1. Experimental

1.1 Reagents

The extractant, dibutylmonothiophosphoric acid (hereafter abbreviated as DBTTPA), was synthesized as its ammonium salt by the interaction of dibutyl phosphate and sulfur under ammoniacal atmosphere
at 350 K in the same manner as described in a previous paper. The product was identified by IR, NMR and elementary analysis. The results of elementary analysis were as follows. Found: C, 39.32; H, 9.09; N, 5.81%. Calcd. for C₈H₁₂NO₃S₈: C, 39.49; H, 9.11; N, 5.76%. The aqueous and organic phases were prepared by the same method as mentioned in the previous paper. All organic and inorganic chemicals used, that is, toluene, 1,10-phenanthroline (abbreviated as phen), sulfuric acid, hydrochloric acid, sodium acetate, hexahydrates of samarium chloride and europium chloride were guaranteed reagent grade.

1.2 Measurement of distribution ratio of DBTPA

The extractant, DBTPA, is apt to distribute in water because of its short alkyl-chain length. So the distribution ratio of DBTPA between toluene and water was measured. The organic phase was prepared in the same manner as mentioned above. The pH of the aqueous solution was adjusted using 1000 mol/m³ hydrochloric acid-sodium acetate buffer solution. Equal volumes (20 cm³) of the aqueous and organic phases were shaken in a flask immersed in a thermostated water bath (303 K), and allowed to attain equilibrium. After about 24 hours, the two solutions were separated and removed by a pipette. The pH of the aqueous solution was measured with a Hitachi-Horiba F-75S pH meter. The organic phase was then contacted sufficiently with an aqueous solution containing palladium of known concentration. After equilibration, the palladium concentration in the aqueous solution was determined by a Shimadzu AA-646 atomic absorption spectrophotometer. The DBTPA concentration in the organic phase was calculated by mass balance considering that a complex of palladium 1: DBTPA 2 is formed in this system.

1.3 Measurement of distribution ratio of phen

The distribution ratio of phen between toluene and water was also measured. The pH of the aqueous solution was adjusted using 1000 mol/m³ hydrochloric acid-sodium acetate buffer solution containing phen of known concentration. Equal volumes of the aqueous solution and toluene were shaken at 303 K for about 24 hours to attain equilibrium. After phase separation, phen in the organic phase was redistributed into 1000 mol/m³ hydrochloric acid. The phen concentrations in the two aqueous solutions were determined by a JASCO UVICORD-670 spectrophotometer.

1.4 Measurement of extraction equilibria of samarium and europium

First the extraction equilibria of the two metal ions with DBTPA alone were measured. The organic phase was prepared by the method mentioned above. An aqueous solution containing samarium and europium ions was prepared in the same manner as described in the previous paper. The pH of the aqueous solution was adjusted by using 100 mol/m³ hydrochloric acid and 100 mol/m³ sodium acetate solutions. Then measurement of the synergistic extraction of the metals was carried out. The organic phase was prepared by further dissolving phen in toluene containing DBTPA. The experimental procedure was the same as that described in the previous paper. The concentration of the lanthanide ions was determined by a SEIKO SPS-1200VR ICP radiation spectrophotometer.

2. Results and Discussion

2.1 Distribution equilibrium of DBTPA

The distribution ratio of DBTPA, $D_{HR}$, between toluene and water is defined as

$$D_{HR} = \frac{C_{HR,org}}{C_{HR,aq} + C_{R,org}}$$

(1)

where $C_{HR}$ and $C_{R}$ are the concentrations of DBTPA and its anion, respectively. Defining the partition constant of DBTPA, $K_{D,HR}$, by Eq. (2),

$$K_{D,HR} = \frac{C_{HR,org}}{C_{HR,aq}}$$

(2)

the following equation is obtained;

$$D_{HR} = \frac{K_{D,HR}}{1 + K_{a,HR}/C_H}$$

(3)

where $K_{a,HR}$ is the dissociation constant of DBTPA and $C_H$ is the hydrogen-ion concentration.

Figure 1 shows the relation between $D_{HR}$ and pH. From the results and Eq. (3), the values of $K_{D,HR}$ and $K_{a,HR}$ were obtained by non-linear regression as follows;

$$K_{D,HR} = 20 \pm 4$$

$$K_{a,HR} = 79 \pm 21$$ mol/m³

The solid line in Fig. 1 is the calculated one by using the values of $K_{D,HR}$ and $K_{a,HR}$.

2.2 Distribution equilibrium of phen

Phen is protonated to phen·H⁺ in acidic aqueous solution. So the distribution ratio of phen, $D_{ph}$, is defined by Eq. (4),

$$D_{ph} = \frac{C_{ph,org}}{C_{ph,aq} + C_{phH,aq}}$$

(4)

where $C_{ph}$ and $C_{phH}$ are the concentrations of phen and phen·H⁺ respectively. Defining the partition constant of phen, $K_{D,ph}$, by Eq. (5),

$$K_{D,ph} = \frac{C_{ph,org}}{C_{ph,aq}}$$

(5)

the following equation is obtained.
Fig. 1. Effect of pH on distribution ratio of dibutylmono-
nothiophosphoric acid

\[ D_{\text{ph}} = \frac{K_{D,ph}}{1 + C_{\text{H}}/K_{a,ph}} \]  

(6)

where \( K_{a,ph} \) is the acid dissociation constant of phen·H⁺.

The relation between \( D_{\text{ph}} \) and pH is shown in Fig. 2. The values of \( K_{D,ph} \) and \( K_{a,ph} \) were obtained from Fig. 2 and Eq. (6) by non-linear regression as follows.

\[ K_{D,ph} = 3.6 \]

\[ K_{a,ph} = 2.0 \times 10^{-2} \text{ mol/m}^3 \]

The solid line in Fig. 2 is the calculated one by using the values of \( K_{D,ph} \) and \( K_{a,ph} \).

2.3 Extraction equilibria of samarium and europium with DBTBA alone

The characteristics of extraction equilibria of the lanthanide ions with DBTBA is shown in Fig. 3. Considering the results of the extraction of europium with DDTPA, Eq. (7) is assumed for the extraction equilibria of the lanthanide ion.

\[ \text{Ln}^{3+} + 3\text{HR}_{\text{org}} \rightleftharpoons \text{LnR}_{3,\text{org}} + 3\text{H}^+_{\text{aq}} \]  

(7)

The distribution ratio, \( D \), of the lanthanide ion based on the free, that is, non-complexed ion with acetate anion is expressed by Eq. (8). The concentration of the free lanthanide ion was calculated by the same method as mentioned in the previous paper,7) using the stability constants9) with acetate anion.

\[ D = K_{\text{ex}}C_{\text{HR,org}}^1/C_{\text{H}}^1 \]  

(8)

Here \( K_{\text{ex}} \) is the extraction equilibrium constant.

Figure 4 shows the relations between \( DC_{\text{H}}^1 \) and \( C_{\text{HR,org}}^1 \) for samarium and europium, where \( C_{\text{HR,org}} \) was calculated according to a method which will be mentioned later. Good linear relations were obtained, from which the \( K_{\text{ex}} \) values were calculated as follows.

\[ K_{\text{ex,Sm}} = 2.5 \times 10^{-3} \]

Fig. 2. Effect of pH on distribution ratio of phenanthroline

Fig. 3. Relation between fractional extent of metal extracted and pH

Fig. 4. Relation between distribution ratio of metal, \( DC_{\text{H}}^1 \), and extractant concentration

\[ K_{\text{ex,Eu}} = 2.7 \times 10^{-3} \]

In this case, the separation factor, \( \alpha \), defined by Eq. (9) is 1.1, so that the separation between the two metals
is considered to be very difficult.

\[ \alpha = \frac{K_{ex, Eu}}{K_{ex, Sm}} = 1.1 \]  
\[ (9) \]

2.4 Synergistic extraction equilibria of samarium and europium with a mixture of DBTPTA and phen

The experimental results are shown in Fig. 3, along with the results in the case of DBTPTA alone. It is found that the addition of phen significantly enhances the extraction efficiency.

Figure 5 shows the results of extraction of europium with phen alone, from which it is considered that extraction by phen alone is negligibly small. Assuming that the lanthanide ions are extracted as a monomer complex \(^7\) of composition, \( \text{LnR}_3 \cdot x\text{HR} \cdot y\text{phen} \), with the mixed extractants from the aqueous solution, the synergistic extraction equilibrium can be expressed as

\[ \text{Ln}^{3+} + (3 + x)\text{HR} + y\text{phen} \rightarrow \text{LnR}_3 \cdot x\text{HR} \cdot y\text{phen} + 3\text{H}^+_{aq} \]  
\[ (10) \]

The synergistic extraction equilibrium constant, \( K_{ex, syn} \), is written as,

\[ K_{ex, syn} = \frac{[\text{LnR}_3 \cdot x\text{HR} \cdot y\text{phen}]_{org}[\text{H}^+]_{aq}^3}{[\text{Ln}^{3+} + \log[\text{HR}]_{org}[y\text{phen}]_{org}]_{aq}} \]  
\[ (11) \]

Denoting free lanthanide-ion and hydrogen-ion concentrations in the aqueous solution, and DBTPTA, phen and lanthanide concentrations in the organic phase by \( C_{\text{Ln,aq}} \), \( C_{\text{H},aq} \), \( C_{\text{HR,org}} \), \( C_{\text{ph,org}} \), and \( C_{\text{Ln,org}} \), respectively, Eq. (11) is rewritten as

\[ K_{ex, syn} = \frac{DC_H^3}{C_{\text{HR, org}}C_{\text{ph, org}}} \]  
\[ (12) \]

\[ D = \frac{C_{\text{Ln, org}}}{C_{\text{Ln, aq}}} \]  
\[ (13) \]

By assuming that \( x = 0 \), Eq. (14) is obtained.

\[ \log \left( \frac{DC_H^3}{C_{\text{HR, org}}} \right) = \log K_{ex, syn} + y \log C_{\text{ph, org}} \]  
\[ (14) \]

The experimental results, rearranged using Eq. (14), are shown in Fig. 6. Straight lines with a slope of unity were obtained in a low range of \( C_{\text{ph, org}} \), which indicates that \( y = 1 \). However, in a relatively high range of \( C_{\text{ph, org}} \) the slope tends to decrease slightly. The reason is not clear and is now under consideration.

Since DBTPTA and phen are distributed between the aqueous and organic phases as mentioned above, \( C_{\text{HR, org}} \) and \( C_{\text{ph, org}} \) were calculated by using the following equations.

\[ C_{\text{HR, org}} = \frac{C_{\text{HR, org}} - 3C_{\text{Ln, org}}}{1 + 1/K_{D,HR} + K_{a,HR}/(K_{D,HR}C_{\text{H},aq})} \]  
\[ (15) \]

\[ C_{\text{ph, org}} = \frac{C_{\text{ph, org}} - C_{\text{Ln, org}}}{1 + 1/K_{D,ph} + K_{a,ph}/(K_{D,ph}C_{\text{H},ph})} \]  
\[ (16) \]

where \( C_{\text{Ln,org}} \) is the total concentration of lanthanide ions in the organic phase. Metal complex existing in the aqueous solution is neglected in Eqs. (15) and (16) because of its high hydrophobicity. Substituting \( y = 1 \) into Eq. (12), the following equation is obtained.

\[ \log \left( \frac{DC_H^3}{C_{\text{HR, org}}} \right) = \log K_{ex, syn} + (3 + x) \log C_{\text{HR, org}} \]  
\[ (17) \]

The experimental results are rearranged using Eq. (17), and are shown in Fig. 7. As is evident from the figure, good linear relations were obtained. The slope of the straight line is three, which indicates that \( x = 0 \).

From the above results, the equation for the synergistic extraction equilibrium of the lanthanide ions is considered to be

\[ \text{Ln}^{3+} + 3\text{HR} + \text{phen} \rightarrow \text{LnR}_3 \cdot \text{phen} + 3\text{H}^+_{aq} \]  
\[ (18) \]

The synergistic extraction equilibrium constants were obtained from Fig. 7 as

\[ K_{ex, syn, Sm} = 44 \text{ m}^3/\text{mol} \]
Fig. 7. Relation between distribution ratio of metal, $D(C^3_{HR,org}/C_{ph,org})$, and extractant concentration

$$K_{ex,syn,Eu} = 57 \text{ m}^3/\text{mol}$$

The solid lines in Figs. 6 and 7 are the calculated results by using the values of $K_{ex,syn,Sm}$ and $K_{ex,syn,Eu}$. The separation factor in the synergistic extraction defined as the ratio between the two constants was obtained as

$$\alpha_{syn} = 1.3$$

The separation factor was found to be improved to some extent by the synergistic effect compared with the result of Eq. (9).

The relations between $D(C^3_{HR,org}/C_{ph,org})$ and pH are shown in Fig. 8. Good linear relations with a slope of three were obtained. The calculated results agree well with the experimental ones, indicating that Eq. (18) is reasonable.

2.5 Comparison of this study with other synergistic systems

Hirashima et al.\textsuperscript{4)} reported that a species of LnR\textsubscript{2}·TTA·2HR is extracted into the organic phase in a synergistic system of Ln-D2EHPA (HR)-HTTA, whereas a species of LnR\textsubscript{3}·3HR is extracted with D2EHPA only. Motomizu et al.\textsuperscript{11)} reported an extracted species of LnR\textsubscript{3}·phen·HR in a synergistic system of Ln-D2EHPA-phen. These results are different from one another, showing that a synergistic reagent plays an important role on the extraction. Whereas both the results introduced above are different from our results, results similar to ours have been reported for the following systems. Nag et al.\textsuperscript{12)} reported that a species of LnR\textsubscript{3}·dip is extracted in a synergistic system of Ln-HSTTA(HR)-diprydyl (dip). The same type of extracted species was reported by Yamada et al.\textsuperscript{13)} in a system of Ln-Kelex 100-phen. In these examples, the extracted species in the corresponding non-synergistic system was LnR\textsubscript{3}.

Conclusion

The synergistic extraction of samarium and europium with a mixed extractant of dibutylmophosphonic acid and 1,10-phenanthroline was carried out. It was found that one molecule of synergistic agent is added to the extracted species of the corresponding non-synergistic system. The synergistic extraction equilibrium constants of the metals were obtained.

The separation factor, defined as the ratio between the two extraction equilibrium constants, was found to be improved to some extent compared with that of the corresponding non-synergistic system.

Nomenclature

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Unit</th>
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<tbody>
<tr>
<td>C</td>
<td>concentration</td>
<td>[mol/m\textsuperscript{3}]</td>
</tr>
<tr>
<td>D</td>
<td>distribution ratio</td>
<td>[-]</td>
</tr>
<tr>
<td>E</td>
<td>fractional extent of metal extracted</td>
<td>[-]</td>
</tr>
<tr>
<td>$K_e$</td>
<td>partition constant</td>
<td>[mol/m\textsuperscript{3}]</td>
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<td>$K_{ex}$</td>
<td>extraction equilibrium constant</td>
<td>[-]</td>
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<tr>
<td>$K_{ex,syn}$</td>
<td>synergistic extraction equilibrium constant</td>
<td>[m\textsuperscript{3}/mol]</td>
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</tbody>
</table>
\[ x \quad = \quad \text{number of additional molecules of extractant in extracted species} \]
\[ y \quad = \quad \text{number of additional molecules of phenanthroline in extracted species} \]
\[ \alpha \quad = \quad \text{separation factor} \]

**Subscripts**
- \( aq \): aqueous phase
- \( Eu \): europium
- \( H \): hydrogen ion
- \( HR \): extractant
- \( Ln \): lanthanide ion
- \( org \): organic phase
- \( \text{ph} \): protonated phenanthroline
- \( \text{phH} \): phenanthroline
- \( R \): extractant anion
- \( Sm \): samarium
- \( \text{syn} \): synergism
- \( t \): total
- \( 0 \): initial value

**Literature Cited**