EQUILIBRIUM AND NON-EQUILIBRIUM EXTRACTION SEPARATION OF RARE EARTH METALS IN PRESENCE OF DIETHYLENEDIAMINEPENTACETIC ACID IN AQUEOUS PHASE

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Key Words: Solvent Extraction, Rare Earth Metal, Diethylene triaminepentaacetic Acid, Non-equilibrium Separation, Organophosphorus Extractant

Equilibrium and non-equilibrium extraction separations of rare earth metals were carried out in the presence of chelating agent in the aqueous phase. The separation systems of the rare earth metal mixtures used were Y/Dy, Y/Ho, Y/Er and Y/Tm, and the chelating agent and the extractant were diethylene triaminepentaacetic acid (DTPA) and bis (2,4,4-trimethylpentyl) phosphinic acid (CYANEX® 272), respectively. For Y/Dy and Y/Ho systems, higher selectivities were obtained in equilibrium separation compared with those in non-equilibrium separation. On the other hand, the selectivities in non-equilibrium separation were higher for Y/Er and Y/Tm systems. In the separation condition suitable to each system, the addition of DTPA to the aqueous phase was found to be very effective for obtaining higher selectivities. The distribution ratios of the rare earth metals and the selectivities in the equilibrium separations obtained experimentally were thoroughly analyzed by considering various equilibria such as the extraction equilibrium and the complex formation equilibrium between rare earth metals and DTPA in the aqueous phase. Moreover, the extraction rates and the selectivities in the non-equilibrium separations were also analyzed by the extraction model considering the dissociation reactions of the rare earth metal-DTPA complexes in the aqueous stagnant layer. Based on these analyses, we presented an index which is useful for selecting the optimum operation mode, that is, for determining whether equilibrium or non-equilibrium separation should be employed. Using this index, we can predict that the selectivities under equilibrium conditions are higher than those under non-equilibrium conditions for Y/Dy and Y/Ho systems, while for Y/Er and Y/Tm systems, higher selectivities are obtained under non-equilibrium conditions. The experimental results were in agreement with predictions by this index. Further, the selectivities in various systems including other chelating agents and extractants were discussed based on this index.

Introduction

It is well known that the mutual separation of rare earth metals (abbreviated as M) is very difficult because of their similar physical and chemical properties. The selectivities for nearest neighbors of rare earth metals by the solvent extraction are generally very low. Pierce and Peck (1963) reported the extractabilities of rare earth metals by bis (2-ethylhexyl) phosphoric acid (B2EHPA) and found that the average separation factors for nearest neighbors was about 2.4. Recently, extraction separations by either tri-n-octylmethylammonium nitrate (TOMAN) or TOMAN mixed with β-diketone were carried out (Komasawa and Miyamura, 1991). Although other extractants such as tri-n-butylphosphate (TBP) and 2-ethylhexylphosphonic acid mono-2-ethylhexyl ester (EHPA) have been investigated, the selectivities were very low and almost the same as reported by Pierce and Peck (1963).

It was reported that the addition of chelating agents to the aqueous phase was very effective for enhancing the selectivities of the rare earth metals under equilibrium conditions (Weaver and Kappelmann, 1968; Al-Fared et al., 1988; Kopunc and Kovalancik, 1989; Hirai and Komasawa, 1991). Weaver and Kappelmann (1968) investigated the effects of the addition of chelating agents such as diethylene triaminepentaacetic acid (DTPA) and ethylenedia- minetetraacetic acid (EDTA) in the extraction of lanthanides and trivalent actinides by B2EHPA. Equilibrium separation of cerium and europium was also reported by Kopunc and Kovalancik (1989) for the extraction system including EDTA, DTPA and 1,2-diaminocyclohexanetetraacetic acid (DCTA) in the aqueous phase. Because there are many combinations of chelating agents and extractants, it is time-consuming to carry out separation experiments for each system. Therefore, analysis of the equilibrium separation in the presence of the chelating agents is very important because the optimum system and condition can be predicted by such analysis. However, very few analytical studies on the extraction equilibrium in the presence of chelating agents have been reported.

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purity were purchased from Mitsuwa Chemicals Co., Ltd. DTPA and bis (2,4,4-trimethylpentyl) phosphonic acid (CYANEX® 272, abbreviated as BTMPPA) used as the extractant was purchased from Dojindo Laboratories Co., Ltd. and supplied by Cymanid Canada Inc., respectively. Aqueous and organic stock solutions were prepared by the same procedures as described in the previous works (Matsuyama et al., 1989a, 1989b). The aqueous solutions for the extraction experiments were prepared by mixing M²⁺ stock solution and DTPA stock solution so that [DTPA] might be slightly higher than [M²⁺]. The extractant CYANEX® 272 was purified according to the procedure of Partridge and Jensen (1969). n-Heptane was used as the diluent.

1.2 Equilibrium and non-equilibrium extraction

The distribution measurements under equilibrium conditions were carried out by the usual method both in the absence and in presence of DTPA. The extraction rates under non-equilibrium conditions were measured by using a stirred transfer cell with a constant interfacial area, which was the same as that used in the previous study (Miyake et al., 1990). The volumes of aqueous and organic phases were 200 cm³ and 25 cm³, respectively, and the interfacial area was 12.6 cm². The agitation speeds of both phases were controlled at 1.67 s⁻¹. Samples removed from the organic phase at certain time intervals were stripped with 3.5 mol/dm³ HNO₃ solutions, and the rare earth metal concentrations were analyzed by an inductively coupled plasma emission spectrophotometer (Shimadzu Co., Ltd., ICPS 1000 III).

In all experiments, temperature was controlled at 298 K and the ionic strength of the aqueous phase was maintained at 0.1 mol/dm³ by the addition of KClO₄. Details of the experimental conditions are shown in the captions of the following figures.

2. Results and Discussion

2.1 Extraction equilibrium constant

The extraction equilibrium of a rare earth metal with an organophosphorus extractant is widely recognized to obey the following equation (Pierce and Peck, 1963; Zikovsky, 1973).

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**Table 1** Extraction equilibrium constants and ratios of the constants

<table>
<thead>
<tr>
<th></th>
<th>( K_{e} ) [( M^{2+} )]</th>
<th>( K_{e}^{M^{1+}}/K_{e}^{M^{2+}} ) [( M^{2+} )]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dy</td>
<td>0.052</td>
<td>1.92</td>
</tr>
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<td>Ho</td>
<td>0.10</td>
<td>1.40</td>
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<tr>
<td>Y</td>
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<td>Er</td>
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</tr>
<tr>
<td>Tb</td>
<td>0.54</td>
<td>2.49</td>
</tr>
</tbody>
</table>

M₁ and M₂ denote lower and upper rare earth metal in this table
a) Pierce and Peck (1963)
b) Matsuyama et al. (1989b)
Fig. 2 Schematic mechanism of equilibrium extraction of rare earth metal in the presence of DTPA

\[
\begin{align*}
M^{3+} + 3[(HR)_3 \rightleftharpoons & MR_3[(HR)_3] + 3H^+ \\
K_e &= \frac{[MR_3[(HR)_3]]}{[(HR)_3]} \\
&= D(H^+)^3/[(HR)_3] \\
\end{align*}
\]

Here, \((HR)_2\) is a dimer of the extractant, and \(K_{ex}\) and \(D\) denote the extraction equilibrium constant and the distribution ratio, respectively. The overbar denotes the organic phase species. In the previous work, BTMPMA was found to form trimer in addition to dimer in an aliphatic diluent such as n-heptane (Matsuyama et al., 1989b). By considering the dimerization and trimerization reactions (Eqs. (2) and (3)) and neglecting the monomer concentration, \([(HR)_2]\) can be estimated by Eq. (4) (Matsuyama et al., 1989b).

\[
\begin{align*}
2[(HR)_2] & \rightleftharpoons [(HR)_3]; K_2 = [(HR)_3]/[(HR)_2]^2 \\
[(HR)_2] + HR & \rightleftharpoons [(HR)_3]; K_3 = [(HR)_3]/([(HR)_2][HR]) \\
C_{HR} &= 2[(HR)_3] + (3K_3/\sqrt{K_2})[(HR)_2]^{1.5} \\
\end{align*}
\]

Here, \(C_{HR}\) is an initial extractant concentration as the monomer unit.

Figure 1 shows the relationships between \(D(H^+)^3\) and \([(HR)_2]\) for various rare earth metals. In all cases, third order dependences were observed, which shows that the equilibrium reactions represented by Eqs. (1)-(3) are valid. The extraction equilibrium constants obtained are listed in Table 1. The order of the extractability is Dy < Ho < Y < Er < Tm, which is in accordance with the usual order for the organophosphorus extractant reported previously. In this table, the selectivities, that is, the ratios of the extraction constants, are also included. The selectivities are generally very low, and are comparable to those obtained with B2EHPA as the extractant (Pierce and Peck, 1963).

2.2 Equilibrium separation in the presence of DTPA

Figure 2 schematically shows the mechanism of the equilibrium extraction of the rare earth metal in the presence of DTPA. In this equilibrium extraction system, the following equilibrium reactions are considered.

1. DTPA complex and protonated DTPA complex formation reactions in the aqueous phase (Moeller and Thompson, 1962)

\[
\begin{align*}
M^{3+} + D^{5-} & \rightleftharpoons MDTPA^{2-}; \\
K_{MDTPA} &= [MDTPA^{2-}]/[[M^{3+}][D^{5-}]] \\
\end{align*}
\]

2. Dissociation reactions of DTPA

\[
\begin{align*}
H_3D & \rightleftharpoons H_2D^+ + H^+; K_{a1} = [H^+][H_2D^+]/[H_3D] \\
H_3D & \rightleftharpoons H_2D^+ + H^+; K_{a2} = [H^+][H_2D^+]/[H_3D] \\
H_2D^+ & \rightleftharpoons HD^++ H^+; K_{a3} = [H^+][HD^+]/[H_2D^+] \\
HD^+ & \rightleftharpoons D^++ H^+; K_{a4} = [H^+][D^+]/[HD^+] \\
\end{align*}
\]

3. Extraction reaction (Eq. (1))

4. Association reactions of the extractant in the organic phase (Eqs. (2) and (3))

Here, H$_3$D$^n$ is an abbreviation of DTPA with m proton and n valence.

Because \([H^+]\) was known from the measured pH value, all these equations could be solved simultaneously by taking account of the mass balance equations of
DTPA and rare earth metals, and the concentrations of rare earth metals in the organic phase ([(MR₃(HR)₃)]) and those in the aqueous phase ([M³⁺], [MDTPA⁻²] and [MHDTPA⁺]) could be determined. The equilibrium constants used in the calculation are listed in Table 2.

The distribution ratio of the rare earth metal in the presence of DTPA, D' is expressed as follows:

\[
D' = \frac{[\text{MR}_3(\text{HR})_3]/([\text{M}^3+] + [\text{MDTPA}^{-2}] + [\text{MHDTPA}^+])]}{([\text{MR}_3(\text{HR})_3]/[\text{M}_1\text{DTPA}^-])}
\]

(12)

The concentration of M³⁺ is negligibly small compared with [MDTPA⁻²] when [DTPA] is large because K_{MDTPA} is extremely large as listed in Table 2. This condition lead to the following simplified distribution ratio:

\[
D' = \frac{[\text{MR}_3(\text{HR})_3] / ([\text{MDTPA}^-] (1 + K_{MHDTPA} [H^+]))}{([\text{MR}_3(\text{HR})_3]/[\text{M}_1\text{DTPA}^-])}
\]

(13)

Then, the selectivity for two rare earth metals M₁ and M₂ in the equilibrium separation, S_{eq}' is expressed by Eq. (14).

\[
S_{eq}' = \frac{D_{M_1}}{D_{M_2}} = \frac{([\text{MR}_3(\text{HR})_3]/[\text{M}_1\text{DTPA}^-])}{([\text{MR}_3(\text{HR})_3]/[\text{M}_2\text{DTPA}^-])}
\]

\[
\times (1 + K_{MHDTPA} [H^+]) / (1 + K_{MHDTPA} [H^+])
\]

(14)

The values of K_{MHDTPA} [H⁺] were comparable to unity or less than unity in the present pH region described below. Further, the values of K_{MHDTPA} are not so much different for each rare earth metal, as shown in Table 2. Therefore, in the rough approximation, the ratio of (1+K_{MHDTPA} [H⁺]) to (1+K_{MHDTPA} [H⁺]) can be regarded as unity. This assumption leads to the following equation by considering Eqs. (1), (5) and (14).

\[
S_{eq}' = \left( \frac{K_{M_1}^{\text{M}_1}}{K_{M_2}^{\text{M}_2}} \right) \left( \frac{K_{\text{EDTPA}}}{K_{\text{MHDTPA}}} \right)
\]

(15)

**Figures 3 and 4** show the effect of [DTPA] on the distribution ratios and the selectivities for various separation systems. As [DTPA] increases, the distribution ratios decrease due to the decrease in [M³⁺] brought about by complexation with DTPA. This effect is known as the masking effect. Yttrium, having a lower stability constant of the DTPA complex, showed a higher distribution ratio due to the higher free metal concentration except for the Y/Tm system. In the low [DTPA] region for the Y/Tm system, the distribution ratio of Tm is higher than that of Y because \( K_{\text{Y}}^{\text{Tm}} / K_{\text{Y}}^{\text{Y}} \) is much larger than unity, nevertheless \( [\text{Tm}^{3+}] / [\text{Y}^{3+}] \) is less than unity. The selectivities increased with the increase in [DTPA]. For the Y/Dy system, the selectivity reached as high as 19. In the low [DTPA] region where [DTPA] is lower than total rare earth metal concentration, [M³⁺] cannot be neglected compared with [MDTPA⁻²], which results in the low selectivity.
because free yttrium concentration \( [Y^{3+}] \) is larger due to the lower stability constants of Y-DTPA complex. Therefore, the selectivities in the high [DTPA] region correspond to the values expressed by Eq. (15).

The effect of proton concentration on the distribution ratios was not so remarkable as that of [DTPA] as shown in Fig. 5. With the increase in \([H^+]\), the distribution ratios increase slightly and then decrease rapidly. In order to understand these results, it is necessary to take account of the following two effects. With increasing \([H^+],[D^{5+}]\) decreases because the degree of dissociation of DTPA decreases. This leads to an increase in the distribution ratio. On the other hand, \([M^{3+}]\) increases with increasing \([H^+]\) as expected by the dependence of \(D\) in Eq. (1) on \([H^+]\), which results in the decrease in the distribution ratio. In the low \([H^+]\) region, \(D\) in Eq. (1) is so large that \([M^{3+}]\) is negligibly small. Therefore, the distribution ratio slightly increases with increasing \([H^+]\) due to the decrease in \([D^{5+}]\). Since the increase in \([M^{3+}]\) is remarkable compared with the decrease in \([D^{5+}]\) in the high \([H^+]\) region, the distribution ratio decreases rapidly. The increase in \([M^{3+}]\) makes the selectivities lower for the same reason as described above. Therefore, the selectivities decrease in the high \([H^+}\) region. These behaviours are definitively observed in Fig. 6.

The solid lines in Figs. 3-6 are the calculated results using the constants listed in Table 2. They are in satisfactory agreement with the experimental data. Thus, the extraction equilibria in the presence of DTPA could be quantitatively analyzed in this work.

### 2.3 Non-equilibrium separation in the presence of DTPA

In non-equilibrium separation, the selectivity based on the difference in the extraction ratios is utilized. In the previous work, we clarified the extraction kinetics of the rare earth metal in the presence of DTPA, and analyzed the extraction rates and the selectivity for a Y/Er system (Matsuyama et al., 1989b). According to this work, the extraction rate in the presence of DTPA, \(J_M\), was found to be expressed by Eq. (16) where the resistance of the mass transfer accompanied by the dissociation reaction of DTPA complex in the aqueous stagnant layer \(R_a\), the extraction reaction resistance at the interface \(R_i\) and the mass transfer resistance in the organic stagnant layer \(R_o\) is connected in series.

\[
J_M = \frac{[M^{3+}]_b}{(R_i + R_a + R_o)} \quad (16)
\]

Subscript b denotes the species in the bulk phase. \(R_a\) and \(R_i\) are given by the following equations (Matsuyama et al., 1989b).

\[
R_a^{-1} = \left( k_{\text{HR}} + k_{\text{R}} - K_{[H^+]_{\text{b}}}ight)
\]

\[
R_i^{-1} = (k_{\text{HR}} + k_{\text{R}} - K_{[H^+]_{\text{b}}}) \sqrt{\frac{\Gamma^* K_{HR}^* \sqrt{K_{[HR_b]}}}{\sqrt{1 + (K_{HR}^* + \sqrt{K_{[HR_b]}}) (1 + K_{[H^+]_{\text{b}}} (\Gamma_{HR}^*)^{0.5})}}} \quad (18)
\]
Table 3  Highest selectivities obtained in equilibrium and non-equilibrium separations

<table>
<thead>
<tr>
<th></th>
<th>Y/Dy</th>
<th>Y/Ho</th>
<th>Y/Er</th>
<th>Y/Tm</th>
</tr>
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<tbody>
<tr>
<td>Seq</td>
<td>19.4</td>
<td>9.43</td>
<td>4.10</td>
<td>1.12</td>
</tr>
<tr>
<td>Seq (cal.) a)</td>
<td>15.8</td>
<td>7.52</td>
<td>3.43</td>
<td>1.22</td>
</tr>
<tr>
<td>Se^eq</td>
<td>5.55</td>
<td>6.03</td>
<td>5.50 c)</td>
<td>4.13</td>
</tr>
<tr>
<td>Se^non-eq (cal.) b)</td>
<td>5.55</td>
<td>6.20</td>
<td>5.24</td>
<td>4.54</td>
</tr>
<tr>
<td>I_{eq}</td>
<td>0.35</td>
<td>0.83</td>
<td>1.53</td>
<td>3.72</td>
</tr>
</tbody>
</table>

a) Calculated by Eq.(15), b) Calculated by Eq.(21)
c) Matsuyama et al. (1989b)

\[
R_{eq}^{-1} = \left(k_{eq} \left[HR^\cdot\right]\right)/\left[H^+\right]^3
\]  (19)

The symbols in the equations are listed in the nomenclature. Equation (17) was derived by solving the diffusion equation of M^{3+} in the aqueous stagnant layer, where the dissociation reaction of DTPA complex, that is DMTPA^2- + 2H^+ ⇌ M^{3+} + H^2D^3 occurs. Equation (18) was obtained by considering the interfacial extraction reaction between M^{3+} and HR or R^+ adsorbed at the interface. Equation (19) denotes the reciprocal of the usual mass transfer resistance in the organic stagnant layer.

The selectivity in the non-equilibrium operation, S_{non-eq} is defined as

\[
S_{non-eq} = \frac{(J_{M1})}{(J_{M2})} = \frac{(J_{[M1]}/[M1]_0)}{(J_{[M2]}/[M2]_0)}
\]  (20)

Because R_{eq} is predominant under the usual conditions, the following equation can be derived under the condition that almost the entire amount of rare earth metal ions is consumed by complexation with DTPA (Azis et al., 1995).

\[
S_{non-eq} = \sqrt{\left(k_{M1}^{[M1]}K_{EDTPA}\right)} / \left(k_{M2}^{[M2]}K_{MDTPA}\right)
\]  (21)

**Figure 7** shows the effect of [H^+] on the extraction rates for various systems. For all rare earth metals, the extraction rates increased with the increase in [H^+] because the dissociation rates of the DTPA complexes increase in proportion to [H^+]^2 (Azis et al., 1995). The extraction rate of Y is larger than that of other rare earth metals for every system. This is because the dissociation rate of YDTPA^2- is larger than those of other DTPA complexes (Azis et al., 1995), and the free concentration of Y is also higher due to the lower stability constants of the Y-DTPA complexes. The obtained ratios of the extraction rates, that is, the selectivities, are almost the same in every system, and are in the range from 4 to 6.

The solid lines in Fig.7 are the calculated results by Eqs.(16)-(19). The interfacial concentrations such as \([HR^\cdot]_0\) and \([H^+]\), in Eqs.(18) and (19) were determined by considering the conservation equations of the extractant and H^+, and the equation showing that total DTPA flux is zero. The procedure was the same as described previously (Matsuyama et al., 1989b). The parameters used in the calculations are included in Table 2. Although for the Y/Dy system, the dependences on [H^+] in the experimental data are slightly lower than those of the calculated lines, the calculated results are approximately in agreement with the experimental data in every case, which indicates that our extraction model is applicable to various cases.

2.4 Determination of operating conditions for the highest selectivity

The highest selectivities obtained in each extraction method are summarized in Table 3. The addition of DTPA in the aqueous phase was confirmed to result in enhancement in the selectivities. For Dy, Ho, Er and Tm, the stability constants and the dissociation rates of the DTPA complexes are almost the same (Moeller and Thompson, 1962; Azis et al., 1995). This leads to similar selectivities in non-equilibrium separation for Y/Dy, Y/Ho, Y/Er and Y/Tm systems. The order of the extractability by BTMPPA is Dy < Ho < Y < Er < Tm and that of the stability constants of the DTPA complexes is Y < Tm < Er < Ho < Dy. Therefore, in the equilibrium separation, both the masking effects by DTPA and the large ratios of the extraction equilibrium constants result in high selectivities for Y/Dy and Y/Ho systems as understood by Eq. (15). On the other hand, for Y/Er and Y/Tm systems, the two effects are compensated, which lowers the selectivities.

From the above tendencies, the equilibrium separations in the presence of DTPA are favorable for obtaining higher selectivities for Y/Dy and Y/Ho systems. On the other hand, non-equilibrium separations are favorable for Y/Er and Y/Tm systems. Therefore, in order to obtain higher selectivities, the optimum operation mode should be selected. In the cases of equilibrium and non-equilibrium separations in the presence of DTPA, the selectivities calculated based on Eqs. (15) and (21) are also listed in Table 3. These values are in rough agreement with the experimental results. Therefore, we present the following index

Table 4  Predicted values of S_{eq}, S_{non-eq} and I_{eq} for various cases

<p>| | | | | | |</p>
<table>
<thead>
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<td>chelating agent</td>
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<td>S_{non-eq}</td>
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<td>Y/Ho</td>
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<td>4.30</td>
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<td>Y/Er</td>
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<td>8.85</td>
<td>1.63</td>
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<td>18.5</td>
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<td>Y/Ho</td>
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<td>5.46</td>
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<td></td>
<td></td>
<td>Y/Tm</td>
<td>2.01</td>
<td>8.44</td>
<td>4.20</td>
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</table>

a) Extraction equilibrium constants (Pierce and Peck, 1963)
b) Stability constants of rare earth metals (Schwenk and Martell, 1964 for Dy and Ho, Moeller, 1963 for Y, Er and Tm)
c) Stability constants of rare earth metals (Spedding et al., 1956)
\( I_{\text{opt}} \), which can be conveniently used for selecting the optimum operation mode.

\[
I_{\text{opt}} = \frac{S_{\text{non-eq}}}{S_{\text{eq}}} = \frac{K_{\text{ex}}^{M^2} \sqrt{k_d^{M^1} K_{\text{MDTPA}}}}{K_{\text{ex}}^{M^1} \sqrt{k_d^{M^2} K_{\text{MDTPA}}}}
\]  \(22\)

When the \( I_{\text{opt}} \) value is less than unity, equilibrium separation is favorable. Otherwise, non-equilibrium separation must be chosen. As shown in Table 3, the values of \( I_{\text{opt}} \) are less than unity for Y/Dy and Y/Ho systems, and are larger than unity for Y/Er and Y/Tm systems. The experimental results described above are in agreement with the prediction by this criteria.

By using this \( I_{\text{opt}} \) values, the optimum extraction mode can also be selected for other systems containing other chelating agents and/or other extractants. The \( I_{\text{opt}} \) values and the selectivities calculated using Eqs. (15), (21) and (22) are listed in Table 4 for various cases. According to our previous work (Azis et al., 1995), the ratios of \( k_d \) values of respective rare earth metals for each chelating agent were estimated as follows. Since the ratios of the complex formation rate constants between M and DTPA are considered to be equal to those between M and murexide, they are estimated from the complex formation rate constants between M and murexide (Geier, 1968). By using the estimated ratios and the stability constants of the DTPA complexes, the ratios of \( k_d \) values were obtained.

Each extraction system has its own optimum extraction mode. Generally speaking, B2EHPA is more favorable in equilibrium separation than BTMPPA, and with respect to the chelating agent, DTPA is the best among DTPA, EDTA, DCTA and N-hydroxyethyl ethylenediaminetriacetic acid (HEDTA). It should be noted that the predicted value of \( S_{\text{non-eq}} \) for Y/Tm system using EDTA and BTMPPA is as high as 18.

**Conclusion**

Equilibrium and non-equilibrium extractions using BTMPPA as the extractant were carried out for Y/Dy, Y/Ho, Y/Er and Y/Tm systems in the presence of DTPA in the aqueous phase. For Y/Dy and Y/Ho systems, higher selectivities were obtained in the equilibrium separations. Especially, the obtained selectivity reached more than 19 for Y/Dy system. On the other hand, the non-equilibrium separation was found to be favorable for Y/Er and Y/Tm systems.

The distribution ratios and the selectivities in equilibrium separations were quantitatively analyzed by considering several equilibrium processes. The extraction rates and the selectivities in non-equilibrium separation were also analyzed by our extraction model.

We presented an index which is useful for selecting the optimum operation mode, that is, for determining whether equilibrium separation or non-equilibrium separation is desirable. Using this index, the optimum conditions and the selectivities for the system including various chelating agents and extractants were discussed.

In this paper, the increase in selectivity by addition of chelating agents in the aqueous phase was focused on. The extraction rate decreased by the addition of them. In actual extraction operations, compromise between the selectivity and the extraction rate must be considered for choosing the optimum extraction conditions.

**Nomenclature**

- \( C_{HR} \) = analytical monomer concentration of extractant [mol/dm³]
- \( D \) = distribution ratio in absence of DTPA [-]
- \( D' \) = distribution ratio in presence of DTPA [-]
- \( \sqrt{D} \) = diffusivity of \( M^n \) [cm²/s]
- \( H_0^{D^2} \) = abbreviation of DTPA with m proton and n-valence [-]
- \( I_{\text{opt}} \) = index for selecting optimum operation mode defined by Eq.(22) [-]
- \( J_M \) = extraction rate of rare earth metal [mol/(cm²s)]
- \( K_s \) = dissociation constant of extractant [mol/dm³]
- \( K_{HR} \) = dissociation constant of DTPA (\( H_0^{D^2} \)) [mol/dm³]
- \( k_{ex} \) = extraction equilibrium constant [-]
- \( k_{HR} \) = Langmuir adsorption constant of extractant [cm³/mol]
- \( K_{MDTPA} \) = stability constant of DMDTPA³⁻ [dm³/mol]
- \( K_{MDHTPA} \) = stability constant of MDHTPA [dm³/mol]
- \( K_2 \) = dimerization constant of extractant [mol²/dm³]
- \( K_3 \) = trimerization constant of extractant [mol³/dm³]
- \( k_2 \) = dissociation rate constant of MDTPA²⁻ [dm³/(mol-s)]
- \( k_{HR} \) = extraction rate constant between \( M^{n+} \) and HR [dm³/(mol-s)]
- \( k_0 \) = mass transfer coefficient of extracted species in organic stagnant layer [cm/s]
- \( k^R \) = extraction rate constant between \( M^{n+} \) and R⁻ [dm³/(mol-s)]
- \( M \) = abbreviation of rare earth metal [mol/dm³]
- \( R_s \) = resistance of mass transfer with dissociation reaction of DTPA complex in aqueous stagnant layer [s/cm]
- \( R_i \) = resistance of extraction reaction at interface [s/cm]
- \( R_o \) = resistance of mass transfer in organic stagnant layer [s/cm]
- \( R^* \) = abbreviation of acid-dissociated extractant [-]
- \( S_{eq} \) = selectivity in equilibrium separation [-]
- \( S_{non-eq} \) = selectivity in non-equilibrium separation [-]
- \( \Gamma^* \) = saturated interfacial excess quantity of extractant [mol/dm³]

**<Subscripts>**

- \( b \) = bulk phase
- \( f \) = feed total values
- \( i \) = interface
- \( o \) = initial total values

**<Superscript>**

- \( \text{org} \) = organic phase

**Literature Cited**


18) Sillen, L.G. and A.E. Martell; The Stability of the Rare Earth Complexes, 2nd ed., The Chemical Society, London (1964)

