

DISSOCIATION RATES OF VARIOUS HEAVY RARE EARTH METAL-DIETHYLENETRIAMINEPENTAACETIC ACID COMPLEXES

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Key Words: Chemical Reaction, Rare Earth Metal, Exchange Reaction, Diethylenetriaminepentaacetic Acid, Solvent Extraction

In relation to the separation of rare earth metal ions (M^{3+}) by solvent extraction in the presence of diethylenetriaminepentaacetic acid (DTPA) in an aqueous phase, the rate of dissociation of rare earth metal-DTPA complex, i.e., $MDTPA^{2-} + 2H^+ \rightleftharpoons M^{3+} + H_2DTPA^{3-}$, was determined by the analysis of the rate of exchange reaction between $MDTPA^{2-}$ and Eu^{3+} , which is described by $MDTPA^{2-} + Eu^{3+} \rightleftharpoons EuDTPA^{2-} + M^{3+}$ ($MDTPA^{2-}$; $DyDTPA^{2-}$, $HoDTPA^{2-}$, $TmDTPA^{2-}$). The exchange rate could be expressed by the following equation and the parameters α , β and γ in the equation were determined.

$$\text{Rate} = \alpha [MDTPA^{2-}] [H^+]^2 + \beta [MDTPA^{2-}] [Eu^{3+}] + \gamma [MDTPA^{2-}] [H^+] [Eu^{3+}]$$

A method for estimating approximate values of α , that is, the rate constants of proton-catalyzed dissociation of $MDTPA^{2-}$ for various rare earth metals was proposed. Based on the dissociation rate constants of DTPA complexes obtained, selectivities in solvent extraction in the presence of DTPA were estimated for various cases.

Introduction

In the separation of rare earth metal ions by solvent extraction, addition of polyaminopolycarboxylic acids such as diethylenetriaminepentaacetic acid (DTPA) to an aqueous phase has been found to be effective for enhancing the separation factor in non-equilibrium operation (Minagawa *et al.*, 1977; Minagawa *et al.*, 1980), where the difference in the extraction rates is utilized for the separation. In a previous study by the present authors on the extraction of Er^{3+} and Y^{3+} with an organophosphorus extractant in the presence of DTPA in the aqueous phase, it was found that the rate of dissociation of rare earth metal-DTPA complexes $MDTPA^{2-}$ into free metal ions M^{3+} and DTPA, which is expressed by $MDTPA^{2-} + 2H^+ \rightleftharpoons M^{3+} + H_2DTPA^{3-}$, has a decisive effect on the overall extraction rate and selectivity (Matsuyama *et al.*, 1989b).

It was also found that the rate expression for the dissociation of $MDTPA^{2-}$ can be obtained by analysis of the exchange reaction between rare earth metals and their DTPA complexes, i.e., $MDTPA^{2-} + Eu^{3+} \rightleftharpoons EuDTPA^{2-} + M^{3+}$ and also that the observed rate of exchange reaction for $ErDTPA^{2-}$ - Eu^{3+} and $YDTPA^{2-}$ - Eu^{3+} systems could be satisfactorily explained by a proposed rate equation (Matsuyama *et al.*, 1989a). The dissociation rate constants obtained were, however, restricted to the values for $ErDTPA^{2-}$, $YDTPA^{2-}$ and $EuDTPA^{2-}$.

In this paper, the kinetics of the exchange reaction between Eu^{3+} and $MDTPA^{2-}$ (M ; Dy , Ho , Tm) were studied to obtain the rate equations of the dissociation of heavy rare earth metal-DTPA complexes. Furthermore, a method

for estimating the dissociation rate of $MDTPA^{2-}$ for various rare earth metals is proposed. These results are useful to discuss the rate and selectivity in the extraction of rare earth metals in the presence of DTPA in the aqueous phase, as will be described in our next paper.

1. Experimental

1.1 Materials

Aqueous solutions of rare earth metals (Dy , Ho , Tm and Eu) were prepared by dissolving Re_2O_3 of 99.9% purity (Mitsuwa Chemicals Co., Ltd.) in aqueous $HClO_4$ solutions. DTPA stock solutions were prepared by adding appropriate amounts of aqueous KOH solutions to weighed amounts of H_5DTPA (purity: 99%, Dojindo Laboratories Co., Ltd.). The solutions of rare earth metal-DTPA complexes, $MDTPA^{2-}$ were prepared by mixing aqueous rare earth metal solutions with aqueous DTPA solutions so that the concentrations of rare earth metal ions were slightly higher than those of DTPA. The pH of the solution was adjusted in the range from 4.0 to 5.0 with $HClO_4$ or KOH and the ionic strength was controlled at 0.1 mol/dm^3 by adding $KClO_4$.

1.2 Procedure

The experimental procedure was the same as described in our previous paper (Matsuyama *et al.*, 1989a). The molar extinction coefficients of chemical species were measured by a Hitachi UV3200 spectrophotometer using a UV cell of 10 cm path length. The rates of the exchange reactions for $DyDTPA^{2-}$ - Eu^{3+} , $HoDTPA^{2-}$ - Eu^{3+} and $TmDTPA^{2-}$ - Eu^{3+} systems were measured spectrophotometrically. As described below, since the molar extinction coefficient of $EuDTPA$ complex which is

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** Presented at the 26th Autumn Meeting of the Society of Chemical Engineers of Japan, Kyoto, October 1993.

Table 1. Molar extinction coefficients of chemical species at 248 nm

species	molar extinction coefficients [dm ³ /(mol·cm)]
Eu ³⁺	0.38 ^{a)}
Dy ³⁺	0.13
Ho ³⁺	0.16
Tm ³⁺	0.49
EuDTPA ²⁻	181 ^{a)}
DyDTPA ²⁻	1.10
HoDTPA ²⁻	4.30
TmDTPA ²⁻	1.23

a) Matsuyama *et al.* (1989a)

Table 2. Molar extinction coefficients and stability constants of binuclear complexes and protonated complexes

species	molar extinction coefficients at 248 nm [dm ³ /(mol·cm)]	stability constants of complex ^{c)} [dm ³ /mol]
EuDTPAEu ⁺	231 ^{a)}	127 ^{a)}
DyDTPAEu ⁺	57.9	102
HoDTPAEu ⁺	51.9	121
TmDTPAEu ⁺	48.1	162
ErDTPAEu ⁺	52.8 ^{a)}	175 ^{a)}
YDTPAEu ⁺	53.0 ^{a)}	153 ^{a)}
EuHDTPA ⁺	212 ^{a)}	141 ^{b)}
DyHDTPA ⁺	-	155 ^{b)}
HoHDTPA ⁺	-	178 ^{b)}
TmHDTPA ⁺	-	79 ^{b)}

a) Matsuyama *et al.* (1989a)

b) Moeller and Thompson (1962)

c) $K_{\text{MDTPAEu}} = [\text{MDTPAEu}^+] / ([\text{MDTPA}^{2-}][\text{Eu}^{3+}])$

$K_{\text{MHDTPA}} = [\text{MHDTPA}^+] / ([\text{MDTPA}^{2-}][\text{H}^+])$

formed in the exchange reaction is much higher than those of other chemical species at 248nm, the absorbance of the solution obtained by mixing the solutions of MDTPA²⁻ and Eu³⁺ increases as the reaction proceeds. The absorbance at this wave length was followed continuously in the UV cell of 10 cm path length. The temperature in the cell chamber was maintained at 298 K.

2. Results and Discussion

2.1 Stability constant of binuclear complexes

The extinction coefficients of the rare earth metal ions and their DTPA complexes measured in this study, along with those which had been reported so far (Matsuyama *et al.*, 1989a), are shown in **Table 1**. The molar extinction coefficient of EuDTPA complex was remarkably high, compared with those of other DTPA complexes, which makes it possible for the exchange reaction to be measured spectrophotometrically.

The method for analyzing the equilibrium constant (stability constant) K_{MDTPAM} for the formation of binuclear complex MDTPAM⁺, which is expressed by Eq. (1), was the same as described in the previous paper (Matsuyama *et al.*, 1989a).



It has already been found that when an aqueous solution of rare earth metal ions M³⁺ is mixed with an aqueous solution of rare earth metal-DTPA complex MDTPA²⁻, a

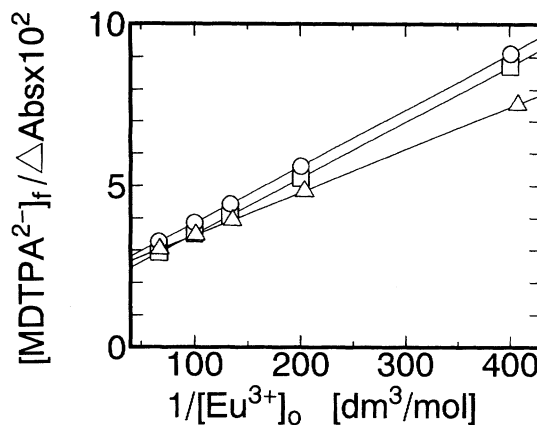


Fig. 1 Relation between $[\text{MDTPA}^{2-}]_x / \Delta \text{Abs}$ and $1/[\text{Eu}^{3+}]_0$.
pH = 4.5, $[\text{MDTPA}^{2-}]_f = 9.25 \times 10^{-4} \text{ mol/dm}^3$
□ DyDTPA²⁻-Eu³⁺ system
○ HoDTPA²⁻-Eu³⁺ system
△ TmDTPA²⁻-Eu³⁺ system

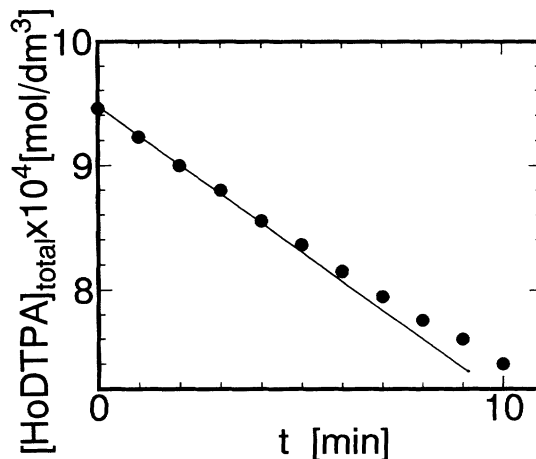


Fig. 2 An example of semilog plot of $[\text{HoDTPA}]_{\text{total}}$ against time
pH = 4.0, $[\text{HoDTPA}]_{\text{total}, f} = 1.85 \times 10^{-3} \text{ mol/dm}^3$,
 $[\text{Eu}^{3+}]_f = 7.37 \times 10^{-3} \text{ mol/dm}^3$

binuclear complex MDTPAM⁺ forms almost instantaneously followed by the slow exchange reaction. The absorbance of the solution immediately after mixing equal volumes of an Eu³⁺ solution and a MDTPA²⁻ solution, Abs₀, is larger than Abs_f, half the sum of the absorbances of the two solutions which have been mixed together. The difference between these absorbances, $\Delta \text{Abs} = \text{Abs}_0 - \text{Abs}_f$, is due to the very rapid formation of a binuclear complex MDTPAEu⁺ having higher molar extinction coefficient and is expressed as follows:

$$\Delta \text{Abs} = \epsilon_{\text{MDTPAEu}} [\text{MDTPAEu}^+]_0 + \epsilon_{\text{MDTPA}} ([\text{MDTPA}^{2-}]_0 - [\text{MDTPA}^{2-}]_f) + \epsilon_{\text{Eu}} ([\text{Eu}^{3+}]_0 - [\text{Eu}^{3+}]_f) \quad (2)$$

Here, the subscripts *f* and *0* refer to the values before and immediately after the formation of the binuclear complex in the mixed solution, respectively.

The stability constant of MDTPAEu⁺ is expressed as follows:

$$K_{\text{MDTPAEu}} = [\text{MDTPAEu}^+]_0 / ([\text{MDTPA}^{2-}]_0 [\text{Eu}^{3+}]_0) \quad (3)$$

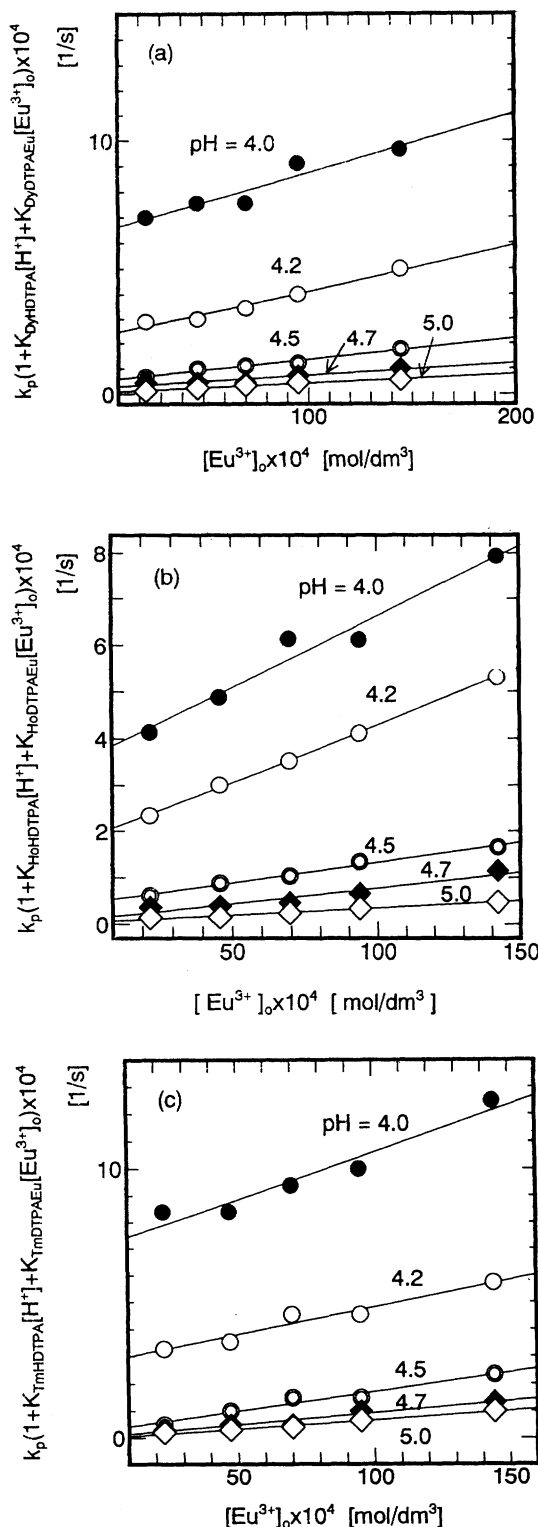


Fig. 3 Relation between $k_p(1 + K_{MHDTPA}[H^+] + K_{MDTPAEu}[Eu^{3+}]_0) \times 10^4$ [1/s] and $[Eu^{3+}]_0$ and $[Eu^{3+}]_0$ and $[MDTPA^{2-}]_f = 9.25 \times 10^{-4}$ mol/dm³
 (a) DyDTPA²⁻–Eu³⁺ system
 (b) HoDTPA²⁻–Eu³⁺ system
 (c) TmDTPA²⁻–Eu³⁺ system

By using the mass balance of DTPA and Eu³⁺, the following equation is obtained from Eqs. (2) and (3).

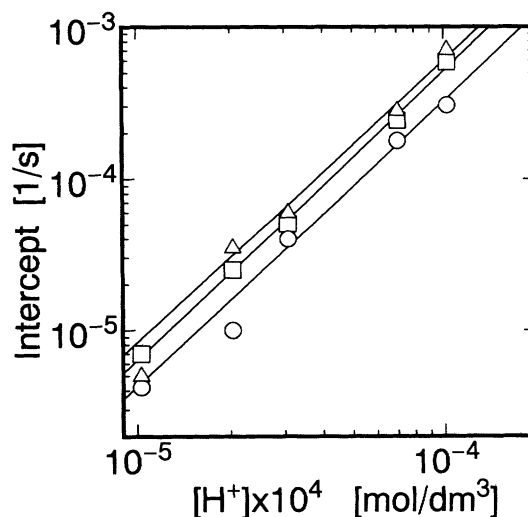


Fig. 4 Relation between intercept of the plot of Fig. 3 and $[H^+]$

□ DyDTPA²⁻–Eu³⁺ system
 ○ HoDTPA²⁻–Eu³⁺ system
 △ TmDTPA²⁻–Eu³⁺ system

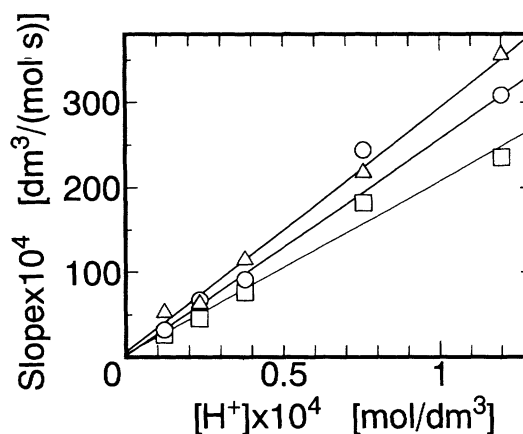


Fig. 5 Relation between slope of the plot of Fig. 3 and $[H^+]$

□ DyDTPA²⁻–Eu³⁺ system
 ○ HoDTPA²⁻–Eu³⁺ system
 △ TmDTPA²⁻–Eu³⁺ system

$$\frac{[MDTPA^{2-}]_f}{\Delta Abs} = \frac{1}{K_{MDTPAEu} \epsilon' [Eu^{3+}]_0} + \frac{1}{\epsilon'} \quad (4)$$

$$\epsilon' = \epsilon_{MDTPAEu} - \epsilon_{MDTPA} - \epsilon_{Eu} \quad (5)$$

The plots of $[MDTPA^{2-}]_f / \Delta Abs$ vs $1/[Eu^{3+}]_0$ for the three exchange reactions are shown in **Fig. 1**. In all cases, linear relations were obtained. From the slopes and the intercepts of the plots, the values of $K_{MDTPAEu}$ and $\epsilon_{MDTPAEu}$ (M; Dy, Ho, Tm) were obtained and are listed in **Table 2**. The values of $K_{MDTPAEu}$ for Dy, Ho and Tm were comparable to those for Er and Y obtained previously (Matsuyama *et al.*, 1989a).

2.2 Rate of exchange reaction

The exchange reaction is expressed as follows:



Table 3 Apparent rate constants in Eq. (9)

System	α [dm ⁶ /(mol ² ·s)]	β [dm ³ /(mol·s)]	γ [dm ⁶ /(mol ² ·s)]
DyDTPA ²⁻ /Eu ³⁺	4.2×10 ⁴	2.8×10 ⁻³	2.0×10 ²
HoDTPA ²⁻ /Eu ³⁺	3.0×10 ⁴	1.7×10 ⁻⁴	2.7×10 ²
ErDTPA ²⁻ /Eu ³⁺ ^{a)}	3.8×10 ⁴	2.0×10 ⁻³	2.9×10 ²
TmDTPA ²⁻ /Eu ³⁺	4.9×10 ⁴	9.3×10 ⁻⁴	2.8×10 ²
YDTPA ²⁻ /Eu ³⁺ ^{a)}	2.2×10 ⁵	1.4×10 ⁻²	7.1×10 ²

a) Matsuyama *et al.* (1989a)**Table 4** Stability constants, dissociation rate constants of MDTPA²⁻ and complex formation rate constants of MDTPA²⁻ and M-murexide

complex	log K_{MDTPA} ^{a)} [dm ⁶ /(mol ² ·s)]	$\alpha = k_d$ ^{b)} [dm ³ /(mol·s)]	k_f ^{b)} [dm ³ /(mol·s)]	k^f (murexide) ^{c)} [dm ³ /(mol·s)]
DyDTPA	22.82	4.2×10 ⁴	1.8×10 ⁸	1.7×10 ⁷
HoDTPA	22.78	3.0×10 ⁴	1.2×10 ⁸	1.4×10 ⁷
ErDTPA ^{d)}	22.74	3.8×10 ⁴	1.4×10 ⁸	1.0×10 ⁷
TmDTPA	22.72	4.9×10 ⁴	1.7×10 ⁸	1.1×10 ⁷
YDTPA ^{d)}	22.05	2.2×10 ⁵	1.6×10 ⁸	1.3×10 ⁷

a) Moeller and Thompson (1962)

b) Values calculated by Eq. (11) using the values of K_{MDTPA} in this table and $K_{H_2DTPA} = 10^{19.18}$ (Moeller and Thompson, 1962)

c) Geier (1968)

d) Matsuyama *et al.* (1989a)

This is the simplified reaction expression. Actually, binuclear complexes and protonated complexes MHDTPA⁻ also exist. The molar extinction coefficients and stability constants of the protonated complexes are also included in Table 2.

It was generally confirmed that the exchange reaction between rare earth metal ions and their polyaminopolycarboxylic acid complexes proceeds through two different paths (Asano *et al.*, 1970; Brucher and Laurenczy, 1980; Choppin and Williams, 1973; Glentworth *et al.*, 1968; Nyssen and Margerum, 1970). One is a proton-catalyzed reaction. In this reaction, ReDTPA²⁻ first dissociates into free M⁺ and DTPA. This is followed by a fast reaction between Eu³⁺ and DTPA to form the complex EuDTPA²⁻. Therefore, this reaction corresponds to the reverse reaction of the complex formation between M³⁺ and DTPA. Another reaction is considered to proceed through a binuclear intermediate that has not been identified.

The initial rates of the exchange reaction between YDTPA²⁻ and Eu³⁺ and also those between ErDTPA²⁻ and Eu³⁺ have been found to be expressed by the following equation (Matsuyama *et al.*, 1989a).

$$-d[\text{MDTPA}]_{\text{total}}/dt = k_p [\text{MDTPA}]_{\text{total}} \quad (7)$$

Here, $[\text{MDTPA}]_{\text{total}}$ is expressed as follows:

$$[\text{MDTPA}]_{\text{total}} = [\text{MDTPA}^{2-}] + [\text{MHDTPA}^{-}] + [\text{MDTPAEu}^{+}] \quad (8)$$

$$= (1 + K_{\text{MHDTPA}} [\text{H}^{+}] + K_{\text{MDTPAEu}} [\text{Eu}^{3+}]) [\text{MDTPA}^{2-}]$$

The constant k_p is an apparent pseudo-first order rate constant and is a function of $[\text{H}^{+}]$ and $[\text{Eu}^{3+}]$ (Matsuyama *et al.*, 1989a).

$$k_p = \frac{\alpha [\text{H}^{+}]^2 + (\beta + \gamma [\text{H}^{+}]) [\text{Eu}^{3+}]}{1 + K_{\text{MHDTPA}} [\text{H}^{+}] + K_{\text{MDTPAEu}} [\text{Eu}^{3+}]} \quad (9)$$

Because $[\text{Eu}^{3+}]_0$ was considerably higher than $[\text{MDTPA}^{2-}]_0$ and also because the solution containing DTPA had a buffer

Table 5 Selectivities in various cases

	Y/Dy	Y/Ho	Y/Er	Y/Tm
Non-equilibrium separation in the presence of DTPA	5.55	6.27	5.24	4.54
Usual equilibrium separation ^{a)}	3.20	1.65	0.75	0.30

a) Pierce and Peck (1963). Bis (2-ethylhexyl) phosphoric acid was used as an extractant

capacity, the concentrations of proton and Eu³⁺ were almost constant at the initial stage of the exchange reaction. Therefore, k_p could be considered to be constant.

The values of $[\text{MDTPA}]_{\text{total}}$ during the reaction were calculated from the observed absorbance of the reaction solutions by the procedure described previously (Matsuyama *et al.*, 1989a). A typical plot of $[\text{HoDTPA}]_{\text{total}}$ vs. time t is shown in Fig. 2. It is seen that a linear relation is observed in the early stage and the value of k_p was calculated from the slope. The deviation of the plot from the straight line in the later stage is due to the contribution of the reverse reaction.

By similar experiments, the values of k_p at various initial proton and Eu³⁺ concentrations were obtained for the three exchange reaction systems, i.e., DyDTPA²⁻-Eu³⁺, HoDTPA²⁻-Eu³⁺ and TmDTPA²⁻-Eu³⁺ systems. The plots of $k_p (1 + K_{\text{MHDTPA}} [\text{H}^{+}] + K_{\text{MDTPAEu}} [\text{Eu}^{3+}]_0)$ vs $[\text{Eu}^{3+}]_0$ with pH as the parameter are shown in Fig. 3 (a)-(c). These plots are based on Eq. (9), and the intercept corresponds to $\alpha [\text{H}^{+}]^2$ and the slope to $\beta + \gamma [\text{H}^{+}]$. Figure 4 shows a plot of the intercept vs $[\text{H}^{+}]$. As anticipated, straight lines of slope two were obtained. From these plots, the values of α for the three exchange reactions were obtained. The plots of the slopes of Fig. 3 vs $[\text{H}^{+}]$ are shown in Fig. 5. Each plot shows a linear relation and from the slope and the intercept, the values of β and γ were obtained. The values of α , β and γ for the three reaction systems thus obtained, together with the values for the exchange reaction systems which had been reported before (Matsuyama *et al.*, 1989a), are shown in Table 3.

From Eqs. (7)-(9), the rate of the exchange reaction rate is expressed as follows:

$$-d[\text{MDTPA}]_{\text{total}}/dt = k_p [\text{MDTPA}]_{\text{total}} = \{ \alpha [\text{H}^{+}]^2 + (\beta + \gamma [\text{H}^{+}]) [\text{Eu}^{3+}] \} [\text{MDTPA}^{2-}] \quad (10)$$

The first term on the right-hand side of Eq. (10) represents the rate of proton-catalyzed reaction (Matsuyama *et al.*, 1989a), in which MDTPA²⁻ dissociates into M³⁺ and DTPA followed by the fast complex formation reaction between Eu³⁺ and DTPA. Therefore, this rate constant corresponds to k_d , the rate constant of the dissociation reaction of MDTPA²⁻ expressed by $\text{MDTPA}^{2-} + 2\text{H}^{+} \rightleftharpoons \text{M}^{3+} + \text{H}_2\text{DTPA}^{3-}$. Although DTPA exists in six forms: DTPA⁵⁻, HDTPA⁴⁻, H₂DTPA³⁻, H₃DTPA²⁻, H₄DTPA⁻ and H₅DTPA, under our experimental conditions, the predominant species is H₂DTPA³⁻. The second and the third terms of Eq. (10) represent the rates via the binuclear intermediate. Because the free rare earth metal concentrations are usually very low in the solvent extraction in the presence

of DTPA, the rate via the binuclear intermediate can be neglected when analyzing extraction rates.

The stability constants, dissociation rate constants and the complex formation constants are summarized in **Table 4**. The rate constant of the proton-catalyzed dissociation k_d corresponds to α in Eq. (10) (Matsuyama *et al.*, 1989a). Therefore, the values of k_f are calculated from the values of K_{MDTPA} and K_{H_2DTPA} using the following relation.

$$K_{MDTPA} = \frac{[MDTPA^{2-}]}{[M^{3+}][DTPA^{5-}]} = \frac{k_f}{k_d} K_{H_2DTPA} \quad (11)$$

Here, K_{H_2DTPA} is the stability constant of the reaction $2H^+ + DTPA^{5-} \rightleftharpoons H_2DTPA^{3-}$ and the value is available in the literature (Moeller and Thompson, 1962). The values of k_f (murexide) listed in Table 4 are the reported values for complexation of rare earth metals with murexide ion (Geier, 1968). The complex formation reaction of rare earth metal ion is considered to follow a multistep mechanism, which involves diffusion-controlled ion-pair formation followed by the rate-determining displacement of water molecule by the ligand (Purdie and Vincent, 1967). The obtained values of k_f in the present study are one order of magnitude higher than those for murexide ion, probably because H_2DTPA^{3-} is more negatively charged than murexide⁻ and ion-pair formation occurs more easily. However, it can be seen that the ratios of k_f values for the complex formation between M^{3+} and H_2DTPA^{3-} to those between M^{3+} and murexide⁻ are almost constant. Therefore, the values of k_f for the complex formation between H_2DTPA^{3-} and other rare earth metals can be approximately estimated from the values of k_f determined in the present study and the available values of k_f for the complex formation of M^{3+} with other complexing agents such as murexide ion. This, in turn, suggests that the rate constants of the dissociation of $MDTPA^{2-}$, k_d can be estimated for various rare earth metals from the estimated values of k_f using Eq. (11).

The extraction rate in the presence of DTPA, J_M , was found to be expressed by the following equation where the resistance of 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 are connected in series (Matsuyama *et al.*, 1989b).

$$J_M = [M^{3+}]_b / (R_a + R_i + R_o) \quad (12)$$

Subscript b denotes the species in the bulk phase. In the usual conditions, R_a , given by Eq. (13) is predominant.

$$R_a^{-1} = \sqrt{k_d [MDTPA^{2-}]_b [H^+]_b^2 / ([M^{3+}]_b D_M)} \quad (13)$$

Here, D_M is the diffusivity of the rare earth metal ion. The selectivity in the presence of DTPA in non-equilibrium operation S is defined as

$$S = (J_M / [M]_b) / (J_{M'} / [M']_b) \quad (14)$$

Under the condition that almost the entire amount of rare earth metal ions are consumed by complexation with DTPA, the following equation is obtained for the ratio of free ion concentrations.

$$\frac{[M^{3+}]}{[M'^{3+}]} = \frac{K_{M'DTPA} [MDTPA^{2-}]}{K_{MDTPA} [M'DTPA^{2-}]} = \frac{K_{M'DTPA} [M]_b}{K_{MDTPA} [M']_b} \quad (15)$$

From Eqs. (13)-(15), Eq. (16) is derived.

$$S = \sqrt{\frac{k_d [MDTPA^{2-}]_b / [M^{3+}]_b}{k_d' [M'DTPA^{2-}]_b / [M'^{3+}]_b}} \times \frac{K_{M'DTPA}}{K_{MDTPA}} \quad (16)$$

Using the k_d values obtained in this work, the selectivities for various systems can be estimated. The calculated values are listed in **Table 5**. When organophosphorus extractant was used as an extractant, the selectivities in the absence of DTPA were reported to be in the range of 1.3-3.3 for Y/Dy, Y/Ho, Y/Er and Y/Tm systems (Pierce and Peck, 1963). Compared with these values, the selectivities in the presence of DTPA were much improved, which suggests that the addition of DTPA is very useful in the various separations between Y and the heavy rare earth metals. The experimental results on separation by solvent extraction in the presence of DTPA will be described in our next paper.

Conclusion

The kinetics of the exchange reaction $MDTPA^{2-} + Eu^{3+} \rightleftharpoons EuDTPA^{2-} + M^{3+}$ (M; Dy, Ho, Tm) were studied spectrophotometrically. The exchange rate followed the rate expression Eq. (10) which had been reported previously by the present authors for the $ErDTPA^{2-}$ - Eu^{3+} and $YDTPA^{2-}$ - Eu^{3+} systems. The rate consists of the rate by proton-catalyzed process and the rate via binuclear complex intermediate. It was found that the rate constants of dissociation of the complex $MDTPA^{2-}$ into M^{3+} for rare earth metals other than those investigated in this study can be approximately estimated using the present results and the rate constants of complex formation between rare earth metals and complexing agents such as murexide ion which are available in the literature. Based on the dissociation rate constants obtained, selectivities of extraction in the presence of DTPA were estimated for various cases.

Nomenclature

Abs	= absorbances	[-]
D_M	= diffusivity of M^{3+}	[cm ² /s]
J_M	= Extraction rate of M^{3+}	[mol/(cm ² ·s)]
K_{H_2DTPA}	= stability constant of H_2DTPA^{3-}	[dm ⁶ /(mol) ²]
K_{MDTPA}	= stability constant of $MDTPA^{2-}$	[dm ³ /(mol)]
$K_{MDTPAM'}$	= stability constant of $MDTPAM'^+$	[dm ³ /(mol)]
K_{MHDTPA}	= stability constant of $MHDTPA^-$	[dm ³ /(mol)]
k_d	= dissociation rate constant of $MDTPA^{2-}$	[dm ³ /(mol·s)]
k_f	= complexation rate constant of $MDTPA^{2-}$	[dm ³ /(mol·s)]
k_p	= apparent pseudo-first order rate constant	[1/s]
M	= abbreviation of rare earth metal	
R_a	= 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]
S	=	selectivity defined by Eq. (14)	[-]
t	=	time	[s]
α	=	rate constant in Eq. (9)	[dm ⁶ /(mol ² ·s)]
β	=	rate constant in Eq. (9)	[dm ³ /(mol·s)]
γ	=	rate constant in Eq. (9)	[dm ⁶ /(mol ² ·s)]
ΔAbs	=	difference between absorbances	[-]
$\varepsilon, \varepsilon'$	=	molar extinction coefficient	[dm ³ /(mol·cm)]

<Subscripts>

b	=	values in the bulk phase
f	=	feed values
total	=	total values
o	=	values immediately after mixing rare earth metal solutions and DTPA complex solutions

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