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# Novel Synergistic Agent for Selective Separation of Yttrium from Other Rare Earth Metals

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## ABSTRACT

An oil-soluble synergistic agent has been developed for the selective separation of yttrium (Y) from the other rare earth metals. The synergistic agent is a polyaminocarboxylic acid alkylderivative and has interfacial activity like that of surfactants. Separation of yttrium from heavy rare earth metals [erbium (Er) and holmium (Ho)] in the presence of the synergistic agent was carried out with 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester as a carrier using a hollow-fiber membrane extractor. The new agent shows a synergistic effect on the permeation rate of rare earth metals at the oil–water interface. By the addition of a small amount of the agent, the selectivity for yttrium from the two rare earth metals was enhanced remarkably, because the permeation rate of Y was selectively decreased compared with those of Er and Ho. The synergistic effect is discussed from the viewpoint of the stability constant for rare earth metals and the interfacial activity of the synergistic agent. The difference in interaction between the synergistic agent and rare earth ions at the oil–water interface results in an increase in the separation efficiency.

## INTRODUCTION

Research on the separation and purification of rare earth metals has been carried out intensively for producing new advanced materials. Ultrapurified rare earth metals show unique electronic, optical, and magnetic

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properties. However, for the preparation of high-purity products, the separation process for rare earth metals requires a huge energy because the separation of adjacent elements in the rare earth series is very difficult. A conventional solvent extraction by a multistage mixer-settler is considered to be the best method for the treatment of a large amount of rare earth ore. However, even in this process, a great deal of solvent and extractant are required to obtain the high-purity products. Thus a new method to enhance the separation efficiency is desirable to simplify the separation process.

A number of studies have been carried out on the separation of adjacent rare earth metals. In these studies, solvent extraction using aqueous-soluble chelating agents such as diethylenetriamine-*N*,*N*,*N*′,*N*″,*N*″-pentaacetic acid (abbreviated as DTPA) is a useful method for increasing the separation factors of rare earth metals (1–5). However, there is a crucial defect in this method. For use on an industrial scale, it is necessary to recover the chelating agents from the product solution because these chelating agents are very expensive. However, the recovery of the chelating agents from the aqueous solution is very difficult.

From the viewpoint of recovery and reuse of the synergistic agents, oil-soluble agents are available as an enhancer. In a previous paper (6) we found that EDTA (ethylene diamine tetraacetic acid) alkyl derivatives are very useful for enhancing the separation efficiency in the lanthanides, and further, two long-alkyl chains are required to dissolve such chelating agents in an organic phase. Therefore, in this study we have synthesized several EDTA dialkylderivatives which are oil-soluble. We applied the synergistic agents to the selective separation of yttrium from heavy rare earth metals. It is well-known that the separation of yttrium is one of the most difficult in the lanthanide series.

A membrane extractor is very useful when using a synergistic agent, such as the surfactant in this study, because membrane extraction has several advantages compared with conventional solvent extraction (7, 8). It has a very large interfacial area per unit of extractor volume and no problems concerning emulsification or flooding because the aqueous and organic solutions are not mixed directly. Therefore, we used a membrane extractor for the separation system using the new synergistic agent. First, we studied in detail the properties of the new synergistic agents, and then the effect of the synergistic agent on the separation of yttrium from erbium and holmium was investigated using a membrane extractor consisting of a hollow fiber. The synergistic mechanism is especially discussed from the viewpoint of the stability constants of the synergistic agents for rare earth metals and their interfacial activity. The point we want to make is that the new agents show a synergistic effect at the oil–water interface.

## EXPERIMENTAL

### Reagents

An extractant, 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester [commercial name PC-88A, denoted as HR for the monomeric species and $(HR)_2$ for the dimeric species hereafter] supplied by Daihachi Chemical Industry Co., was used without further purification. Reagent-grade rare earth metal chlorides (purity above 99.99%) were also used as received. Analytical grade toluene was used as an organic diluent. Other inorganic reagents were nitric acid, sodium nitrate, and sodium acetate.

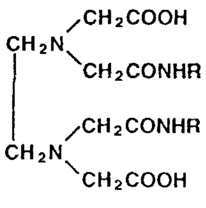
Figure 1 shows the molecular structure and abbreviation of the new synergistic agents synthesized in this study. Four kind of EDTA dialkyl derivatives were synthesized from the EDTA-anhydride and the respective alkylamines by amidation. The final products were identified by IR, $^1$H-NMR, and elementary analysis. Among them, EDTA-*N*,*N*′-DOLA was soluble in some organic solvents; however, EDTA-*N*,*N*′-DPRA, EDTA-*N*,*N*′-DBUA, and EDTA-*N*,*N*′-DAMA were not soluble in organic solvents. Therefore we used these three agents to examine some properties in aqueous solutions as the model compounds of EDTA-*N*,*N*′-DOLA.

### Aggregation Equilibrium of Extractant and Synergistic Agent in Toluene

The aggregation equilibrium of the extractant PC-88A and EDTA-*N*,*N*′-DOLA in toluene was investigated by vapor-pressure osmometry. The osmometric measurements were carried out using a CORONA molecular weight apparatus (Model 117).

### Interfacial Tension of Extractant and Synergistic Agents

Interfacial tension between the aqueous and organic phases was measured at 303 K by the drop volume method and the pendant drop method



-R : n-propyl
Ethylenediamine-N,N'-diacetic acid-N,N'-di(n-propyl)amide diacetate
(EDTA-N,N'-DPRA)
: n-buthyl
Ethylenediamine-N,N'-diacetic acid-N,N'-di(n-buthyl)amide diacetate
(EDTA-N,N'-DBUA)
: n-amyl
Ethylenediamine-N,N'-diacetic acid-N,N'-di(n-amyl)amide diacetate
(EDTA-N,N'-DAMA)
: oleyl
Ethylenediamine-N,N'-diacetic acid-N,N'-di(n-oleyl)amide diacetate
(EDTA-N,N'-DOLA)

FIG. 1 Molecular structures and abbreviations of new synergistic agents.

to examine the interfacial adsorption equilibrium of the extractant and the new synergistic agents.

### Acid Dissociation Constant of Synergistic Agents

Acid dissociation constants of the synergistic agents were calculated from titration data in the absence of metal ions. The solutions of the agents were titrated with sodium hydroxide solution under argon atmosphere at 303 K. Ionic strength was adjusted to 0.1 M with potassium chloride. For pH measurements, a Kyoto Electronics automatic titrator (Model AT-117) was used. The pH meter was calibrated in terms of hydrogen-ion concentration.

### Stability Constants between Rare Earth Metals and Synergistic Agent

Stability constants between three rare earth metals (Er, Ho, and Y) and EDTA-DPRA, which is the most soluble in aqueous solution, were determined by titrating with sodium hydroxide solution. The experimental procedure used was the same as that described above.

### Extraction Rate of Rare Earth Metals Using a Membrane Extractor

The extraction rate of rare earth metals was measured at 303 K with the membrane extractor shown in Fig. 2. The figure also indicates the properties of the membrane used. The extractor consisted of a hollow-fiber membrane inserted in a cylindrical glass tube made of poly(tetrafluoroethylene). The membrane was supplied by Japan Goretex Co. The aqueous and organic solutions are fed cocurrently along the inner and outer sides of the hollow fiber, respectively. Because the hollow-fiber membrane is made of poly(tetrafluoroethylene) and is hydrophobic, the interface between the aqueous and organic phases is formed on the inner surface of the membrane. The detailed experimental procedure is the same as that described in a previous paper (9). The concentrations of metal ions in the aqueous solution and after backextraction with 2000 mol/m$^3$ nitric acid were determined by inductively coupled plasma-atomic emission spectroscopy (abbreviated as ICP-AES) (SEIKO SPS-1200VR). The initial concentrations of rare earth metals were 0.5 mol/m$^3$.

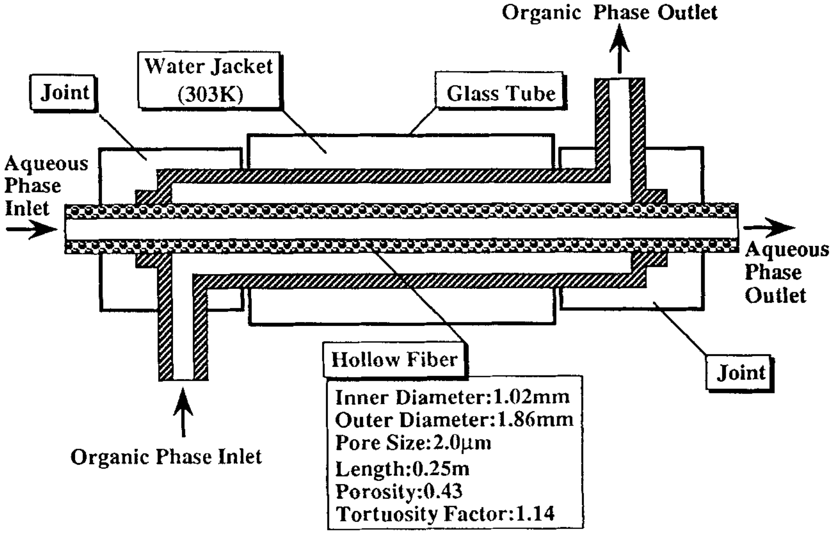


FIG. 2 Schematic diagram of membrane extractor using a hollow fiber.

## RESULTS AND DISCUSSION

### Aggregation Equilibrium of Extractant and Synergistic Agent

We measured the apparent molecular weights of the extractant PC-88A and EDTA-*N*,*N*′-DOLA in toluene to determine the aggregation properties in an organic solvent. The decrease in vapor pressure is proportional to the molar ratio of the solute as follows:

$$\Delta V/(C_T \cdot M_{HR}) = K/M_W \tag{1}$$

where $C_T$ is the analytical concentration of the agent and $\Delta V$ is the potential difference. $M_W$ and $M_{HR}$ denote the apparent molecular weight of the agent and the molecular weight of the monomer, respectively. $K$ is the characteristic constant for this apparatus. In a nonpolar solvent, the relation between the monomer and the dimer of the agent is expressed as follows:

$$2HR = (HR)_2 \colon K_D \tag{2}$$

where $K_D$ is the dimerization constant of the agent.

From Eqs. (1) and (2), Eq. (3) is derived:

$$K^2 \cdot C_T - K \cdot \Delta V = K_D \cdot (2\Delta V - K \cdot C_T)^2 \qquad (3)$$

From Eq. (3) and experimental results, the value of the dimerization constant, $K_D$, can be obtained by the linear least-squares method. A linear relationship was obtained for the extractant PC-88A, and the value of $K_D$ was determined to be 0.28 $m^3$/mol in toluene. On the other hand, the results for EDTA-*N*,*N'*-DOLA indicated that the agent is a monomer. We found that the extractant exists as a dimer but EDTA-*N*,*N'*-DOLA exists as a monomer in toluene in the concentration range of interest.

## Interfacial Tension of Extractant and Synergistic Agents

Figure 3 shows the relation between interfacial tension and the concentration of dimeric PC-88A and four synergistic agents. The interfacial activity of EDTA-*N*,*N'*-DOLA is much higher than those of the other synergistic agents having different alkyl chains and also extractant PC-88A. The synergistic agents having a carbon number of more than 5 (EDTA-*N*,*N'*-DAMA) show interfacial activity.

The adsorption equilibrium of the synergistic agent is expressed as follows:

$$H_2S_{org} = H_2S_{ad}\colon K_{H_2S} \qquad (4)$$

where $K_{H_2S}$ is the adsorption equilibrium constant of the synergistic agents.

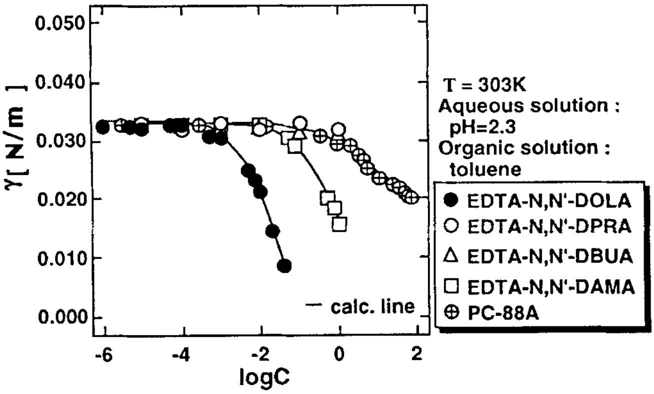


FIG. 3 Relation between interfacial tension and concentration of dimeric PC-88A and new synergistic agents.

The relation between interfacial tension, $\gamma$, and the concentration of the agent in the organic phase, $C_{H_2S}$, is derived from the Gibbs equation for adsorption assuming the Langmuir adsorption isotherm as follows:

$$\gamma = \gamma_0 - (RT/S_{H_2S}) \ln(1 + K_{H_2S}C_{H_2S}) \tag{5}$$

where $\gamma_0$ is the interfacial tension between pure toluene and the aqueous phases, and $S_{H_2S}$ is the interfacial area occupied by a unit mole of the agent. Similarly, we can obtain the adsorption equilibrium constant for the dimeric species of the extractant. From the experimental results shown in Fig. 3 and Eq. (5), the values of $K_{(HR)_2}$, $K_{H_2S}$, $S_{(HR)_2}$, and $S_{H_2S}$ are obtained by the nonlinear least-squares method. The results are presented in Table 1. It is found that the adsorption constant of EDTA-*N*,*N*′-DOLA at the interface is seventy times larger than that of the extractant. In addition to this, we find that EDTA-*N*,*N*′-DOLA can closely align at the oil–water interface based on its *S* value.

## Acid Dissociation Constant of Synergistic Agents

The acid dissociation constants of the synergistic agents (EDTA-*N*,*N*′-DPRA, EDTA-*N*,*N*′-DBUA, EDTA-*N*,*N*′-DAMA) were determined. However, we could not obtain the value for EDTA-*N*,*N*′-DOLA due to poor solubility in the aqueous solution. The acid dissociation of the agent having two carboxylic acid groups is expressed as follows:

$$H_2S = HS^- + H^+ : K_{a1} \tag{6}$$

$$HS^- = S^{2-} + H^+ : K_{a2} \tag{7}$$

The values of $K_{a1}$ and $K_{a2}$ for each agent were calculated from the titration data using the computer program PKAS (10). The obtained values of p$K_{a1}$ and p$K_{a2}$ are listed in Table 2. The values of the new agents are very different from those of the conventional complexing agent, IDA or

TABLE 1
The Adsorption Equilibrium Constants, $K_i$, and the Interfacial Area Occupied by Unit Mole, $S_i$

| Agents | $K_i$ (m$^3$/mol) | $S_i$ (m$^2$/mol) | $S_i$ (Å$^2$/molecule) |
|---|---|---|---|
| PC-88A | 3.28 | $1.07 \times 10^6$ | 166 |
| EDTA-*N*,*N*′-DPRA | — | — | — |
| EDTA-*N*,*N*′-DBUA | — | — | — |
| EDTA-*N*,*N*′-DAMA | 9.67 | $3.61 \times 10^5$ | 60 |
| EDTA-*N*,*N*′-DOLA | $2.01 \times 10^2$ | $2.31 \times 10^5$ | 38 |

EDTA (11). As shown in Table 2, the acid dissociation constants are not affected by the length of the alkyl chain in the synergistic agents. These results means that the acid dissociation constant of EDTA-*N*,*N*′-DOLA is almost the same as those of the other synergistic agents. As a result, the synergistic agent EDTA-*N*,*N*′-DOLA is deduced not to be in an acid dissociation state in the pH range of interest (less than pH 3).

## Stability Constants of Synergistic Agent for Rare Earth Metals

The stability constants of the synergistic agent for each metal offer a key to understanding the synergistic mechanism. The aqueous-soluble EDTA-*N*,*N*′-DPRA was used as a model compound because EDTA-*N*,*N*′-DOLA was not soluble in water. The equilibrium reactions between rare earth metal ions and the agent were defined by the following reactions:

$$M^{3+} + S^{2-} = MS^{+}: K_{MS} \tag{8}$$

$$MS^{+} + S^{2-} = MS_2^{-}: K_{MS_2} \tag{9}$$

The stability constants ($K_{MS}$, $K_{MS_2}$) of the agent for rare earth metals are described as follows:

$$K_{MS} = C_{MS}/(C_M \cdot C_S) \tag{10}$$

$$K_{MS_2} = C_{MS_2}/(C_{MS} \cdot C_S) \tag{11}$$

From Eqs. (6), (7), (10), and (11), the function of Bjerrum's formation can be obtained as follows:

$$n = (St - (C_H^2/(K_{a1} \cdot K_{a2}) + C_H/K_{a2} + 1) \cdot C_S)/Mt \tag{12}$$

where

$$St = C_{H_2S} + C_{HS} + C_S + C_{MS} + C_{MS_2} \tag{13}$$

$$Mt = C_M + C_{MS} + C_{MS_2} \tag{14}$$

TABLE 2
Acid Dissociation Constants of Synergistic Agents

| Agents | p$K_{a1}$ | p$K_{a2}$ | p$K_{a3}$ | p$K_{a4}$ |
|---|---|---|---|---|
| EDTA-*N*,*N*′-DPRA | 3.72 | 7.05 | — | — |
| EDTA-*N*,*N*′-DBUA | 3.79 | 7.24 | — | — |
| EDTA-*N*,*N*′-DAMA | 3.89 | 7.27 | — | — |
| IDA | 2.98 | 9.89 | — | — |
| EDTA | 2.0 | 2.8 | 6.2 | 10.3 |

From the formation curves of Eq. (12), we can determine the stability constants between rare earth metals and EDTA-*N*,*N*′-DPRA. The stability constants obtained were shown in Fig. 4. The stability constants of the synergistic agent are similar to those of iminodiacetic acid (abbreviated as IDA) (12), and the order was Y < Ho < Er. These results mean that the synergistic agent possesses considerably large stability constants for the three rare earth metals.

## Extraction Rate of Rare Earth Metals by a Hollow-Fiber Extractor

Based on the experimental results, the permeation rate of rare earth metals, $P_M$ (m/s), is obtained as follows:

$$P_M = (C_{M,org} \cdot Q_{org})/(\pi d_i L) \qquad (15)$$

where $C_{M,org}$ is the concentration of the rare earth metals in the organic solution at the outlet of the membrane extractor, and $Q_{org}$ is the volumetric flow rate of the organic solution. Further, $d_i$ denotes the inner diameter of the hollow fiber, and $L$ denotes the effective length of the membrane extractor. Separation factors between yttrium and other rare earth metals, $\beta_{M_i/Y}$, are defined as follows:

$$\beta_{M_i/Y} = P_{M_i}/P_Y \qquad (16)$$

where $M_i$ represents Er or Ho.

Figure 5 shows the relation between the permeation rate of three rare earth metals (Y, Ho, and Er) and pH when EDTA-*N*,*N*′-DOLA was added

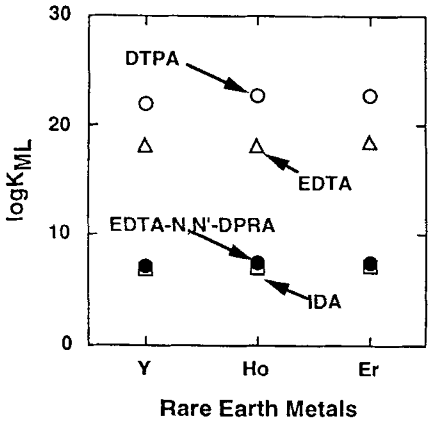


FIG. 4 Stability constants of new synergistic agent for rare earth metals.

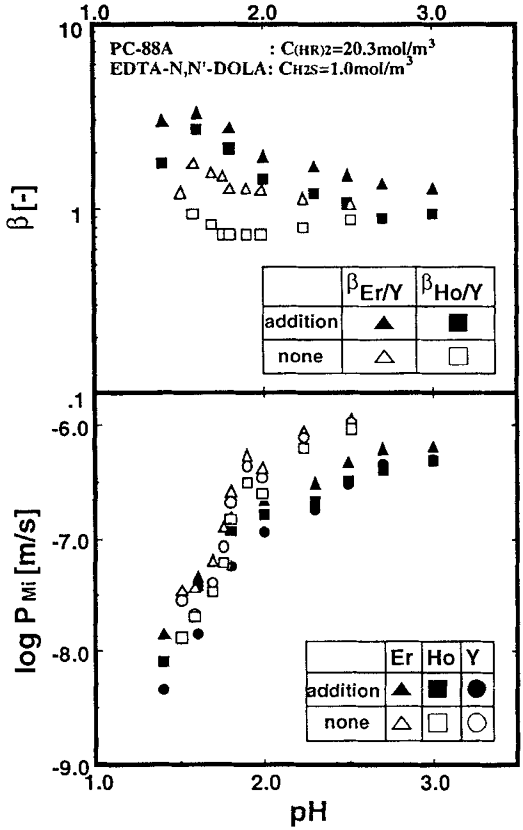


FIG. 5 Relation between permeation rate of rare earth metals and pH.

or not added to the organic phase. In the low-pH range, the rate strongly depends on the pH value, although the rate is not affected by pH in the high-pH range. These results suggest that the extraction rate is controlled by the interfacial reaction at low pH and by the diffusion of chemical species at high pH (8). From the experimental results shown in Fig. 5, we find that the synergistic agent increases the separation factor in the low-pH range. The synergistic agent is effective in the range controlled by the interfacial reaction because the selectivity can be enhanced by utilizing the difference in interaction between the synergistic agent and the metal ions at the interface.

Figure 6 shows the relation between the permeation rate of each metal and the dimer concentration of PC-88A when the concentration of EDTA-

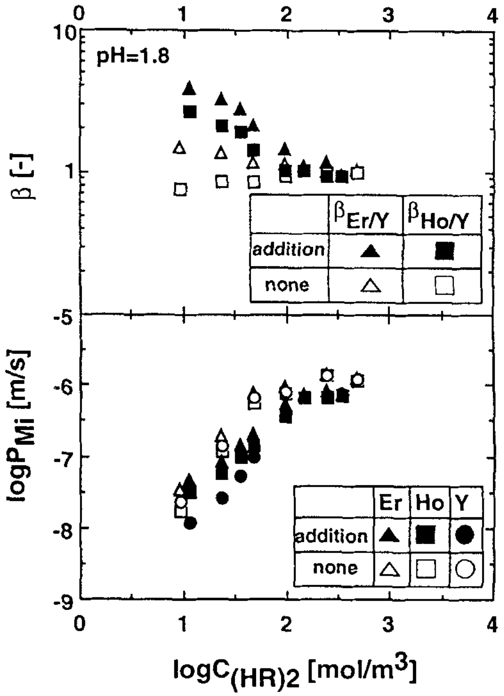


FIG. 6 Relation between permeation rate and dimer concentration of extractant.

*N*,*N*′-DOLA is constant (1 mol/m$^3$). The values of $P_M$ increase with increasing extractant concentration but scarcely depend on the concentration in the range of high concentration. With decreasing concentration of the extractant, the separation factors are enhanced by the synergistic effect of EDTA-*N*,*N*′-DOLA. In particular, the separation factor between Er and Y was remarkably enhanced and reached about 4, which is three times the value of 1.37 in conventional solvent extraction (13). From the results of interfacial tension in Table 1, we can represent the occupied ratio of the synergistic agent and the extractant at the oil–water interface as shown in Fig. 7. In the low concentration range of the extractant, the synergistic agent preferentially occupied the interface, and the separation factors increased with increasing ratio of EDTA-*N*,*N*′-DOLA at the interface. This result suggests that the synergistic effect of EDTA-*N*,*N*′-DOLA occurred at the oil–water interface and that the interfacial activity of the synergistic agent is a key factor in obtaining the synergistic effect at the interface.

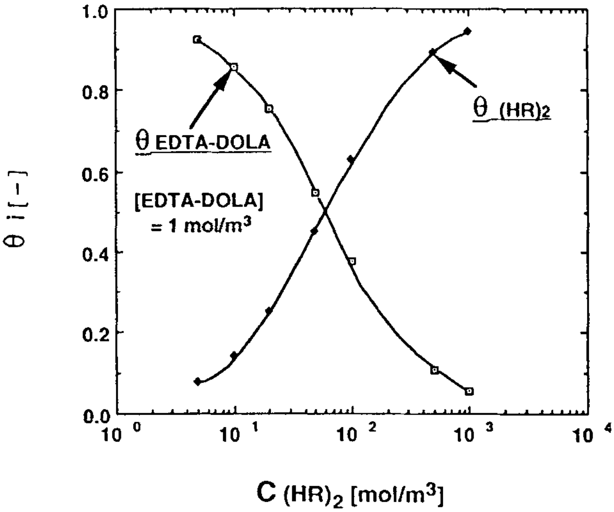


FIG. 7 Relation between the occupied ratio of the agent and the concentration of dimer extractant at the oil–water interface.

Figure 8 shows a schematic diagram of the synergistic mechanism of EDTA-*N*,*N*′-DOLA on the permeation rate of rare earth metals. First, rare earth ions in the aqueous phase interact with the adsorbed EDTA-*N*,*N*′-DOLA at the oil–water interface (Step 1 in the figure). Intermediate complexes between the rare earth ions and the agent are then formed at the interface (Step 2). In the next step (Step 3), the rare earth ions are extracted by the dimer of the extractant from the interface into the organic phase, because the extractability of the extractant PC-88A is higher than that of EDTA-*N*,*N*′-DOLA. In the final step (Step 4), rare earth ions form a very stable complex in the organic phase. It is well-known that the stable conformation of the rare earth complex with PC-88A is composed of one metal ion and three dimers of the extractant (13). Based on the results of the stability constants in Fig. 4, we can deduce that the interaction of Er and Ho with the synergistic agent is greater than that of Y. Therefore, Er and Ho are concentrated preferentially at the oil–water interface. As a result, the permeation rate of Y was decreased compared with those of Er and Ho. Therefore, the enhancement of the selectivity for yttrium is considered to be caused in Step 3 by the difference in the stability constants between the rare earth metals and EDTA-*N*,*N*′-DOLA at the interface. The point we wish to emphasize is that the agent developed in this study is a new type of synergistic agent showing a synergistic effect at

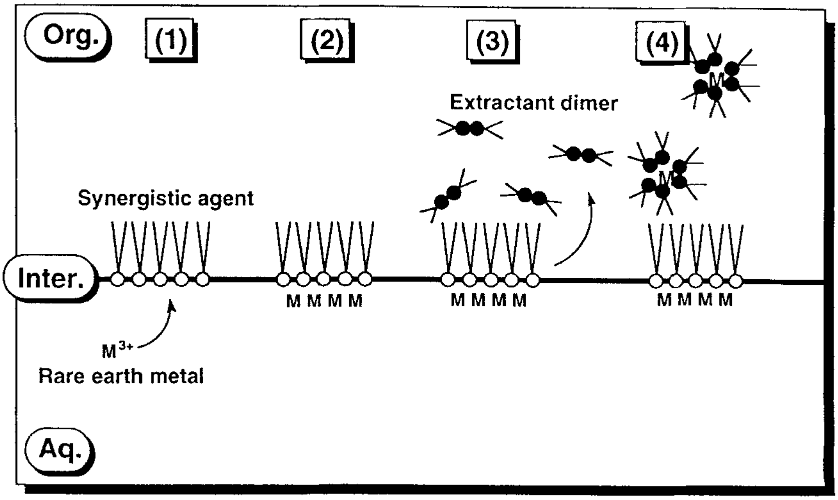


FIG. 8 Schematic diagram of the synergistic mechanism of EDTA-*N*,*N*′-DOLA at the oil–water interface.

the oil–water interface. For application of this system on an industrial scale, a membrane separation process using hollow-fiber modules is effective and is a promising method for the selective separation of yttrium.

## CONCLUSIONS

We have synthesized a new type of synergistic agent and determined some properties of the agents. The agents show a synergistic effect on the extraction rate of rare earth metals at the oil–water interface. Studies on the separation of yttrium from the other heavy rare earths in the presence of the synergistic agent were carried out using a hollow-fiber membrane extractor. The enhancement of the selectivity was considered to be caused by the difference in the stability constants between the rare earth ions and the synergistic agent at the oil–water interface. Therefore, the adsorption ability of the synergistic agents is one of the key factors in the synergistic effect. The difference in the degree of interaction between the metal ions and the agent at the interface results in an increase in the separation efficiency. These results lead to the conclusion that the extraction method using the new synergistic agent is very effective and is a promising method for the separation of yttrium from the other rare earth metals.

## NOMENCLATURE

| | |
|---|---|
| $C_i$ | concentration of species $i$ (mol/m$^3$) |
| HR | monomer species of extractant |
| $(HR)_2$ | dimer species of extractant |
| $H_2S$ | synergistic agent |
| $HS^-$ | synergistic agent ($H^+$ dissociation) |
| $S^{2-}$ | synergistic agent ($2H^+$ dissociation) |
| $K$ | characteristic constant for vapor-pressure osmometry ($V \cdot m^3 \cdot mol^{-1}$) |
| $K_{a1}$ | first step dissociation constant of synergistic agent ($mol \cdot m^{-3}$) |
| $K_{a2}$ | second step dissociation constant of new synergistic agent ($mol \cdot m^{-3}$) |
| $K_D$ | dimerization constant (—) |
| $K_i$ | interfacial adsorption constant of species $i$ ($m^3 \cdot mol^{-1}$) |
| $K_{MS}$ | stability constant between rare earth metal and synergistic agent (M:S = 1:1) ($m^3 \cdot mol^{-1}$) |
| $K_{MS_2}$ | stability constant between rare earth metal and synergistic agent (M:S = 1:2) ($m^3 \cdot mol^{-1}$) |
| $L$ | effective length of hollow-fiber membrane (m) |
| $M_{HR}$ | molecular weight of monomer |
| $Mt$ | analytical concentration of rare earth metals |
| $M_W$ | molecular weight |
| $P$ | permeation rate of metals (m/s) |
| $Q$ | volumetric flow rate (m$^3$/s) |
| $R$ | gas constant ($N \cdot m \cdot mol^{-1} \cdot K^{-1}$) |
| $r$ | inner radius of hollow-fiber membrane (m) |
| $S_i$ | interfacial area occupied by unit mole of species $i$ ($m^2 \cdot mol^{-1}$) |
| $St$ | analytical concentration of synergistic agent |
| $V$ | potential (V) |

### *Greek Letters*

| | |
|---|---|
| $\gamma$ | interfacial tension ($N \cdot m^{-1}$) |
| $\beta$ | separation factor defined by Eq. (16) (—) |
| $\Delta$ | variation |

### *Subscripts*

| | |
|---|---|
| ad | adsorption state |
| aq | aqueous phase |
| $i$ | species |
| org | organic phase |

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