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# Advanced liquid–liquid extraction systems for the separation of rare earth ions by combination of conversion of the metal species with chemical reaction

Syouhei Nishihama, Takayuki Hirai,* and Isao Komasawa

*Department of Chemical Science and Engineering, Graduate School of Engineering Science, and Research Center for Solar Energy Chemistry, Osaka University, Machikaneyama-cho 1-3, Toyonaka 560-8531, Japan*

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## Abstract

Advanced liquid–liquid extraction combined with the conversion of the metal species with chemical reactions has been investigated. The complex formation reaction with water-soluble complexing reagent and the photochemical redox reaction for metal ions are focused. In the case of complex formation reaction, ethylenediaminetetraacetic acid (EDTA) was added to the aqueous phase of the extraction system. The separation of adjacent rare earth metals improves, due to the difference of the complex formation ability between metals and EDTA. The design of separation process of the metals with countercurrent mixer-settler cascade was also investigated with simulation based on the extraction equilibrium, determined up to high loadings of the extractant, and the material balance equations. In the case of photochemical redox reaction, the photoreductive stripping of Eu from Sm/Eu/Gd mixture and the photooxidative extraction of Ce from La/Ce/Pr mixture were carried out. The extractability of the target metals changes dramatically when their valences are changed, and then the effective separation can be achieved.

*Keywords:* Liquid–liquid extraction; Rare earth metal; Separation; Water-soluble complexing reagent; Photochemical reaction

## 1. Introduction

Liquid–liquid extraction is presently one of the major techniques for separation, purification, and recovery of metal components, including rare earth metals, on industrial scale. However, the separation of adjacent rare earth metals by the use of conventional extraction system is still difficult, because such extractive separation processes are based on only the differences in the complex formation ability between the rare earth metals and their extractant. In these cases, the conversion of metal species by functional chemical reaction during actual extraction has proved very effective in improving the separation obtained for such metal species. There are three reactions for the species in the aqueous phase and three reactions for the species in the organic phase [1]. In the present paper, the complexing reaction of the metal ions in the aqueous phase with water-soluble complexing agents and the redox reaction of the metal ion in the aqueous phase will be focused, for improving the separation ability of the rare earth metals.

Modification of the aqueous phase species by adding a water-soluble complexing agent is known to be one of the effective methods for improving the separation ability of the metals. The most general water-soluble complexing agents employed in the extraction system are amino polyacetates, such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA). In the case of rare earth metals except for Y, the complex formation ability, between the metals and the complexing agent, increases with increase in the atomic number of the metals. Therefore, the masking effect with the agent can be obtained when the extractant, such as quaternary ammonium salt extractant, of which extractability for the rare earth metals decreases with increase in the atomic number, is used. In the case of Y, the extractability with several acidic extractants is between Ho and Er, while the complex formation ability is much lower than the other two

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*Corresponding author. Fax: +81-6-6850-6273.
*E-mail address:* hirai@cheng.es.osaka-u.ac.jp (T. Hirai).

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**Nomenclature**

| | |
|---|---|
| $C$ | flow rate of the aqueous phase in the scrubbing section, L/min |
| $D$ | distribution ratio |
| $E$ | flow rate of the organic phase, L/min |
| $f$ | overall decontamination factor |
| $F$ | flow rate of the aqueous phase in the extraction section, L/min |
| $K_f$ | complex formation constant |
| L | dissociated ligand of EDTA |
| Ln | rare earth metal |
| $P$ | number of extraction stages |
| $Q$ | number of scrubbing stages |
| $(RH)_2$ | dimeric species of the extractant |
| $\beta$ | separation factor |
| $\rho$ | overall fractional recovery |

*Subscript*

| | |
|---|---|
| E | extraction section |
| C | scrubbing section |
| $i$ | component (Ho, Y, or Er) |
| feed | aqueous or organic feed solution |
| $t$ | total value |

*Superscripts*

| | |
|---|---|
| $\overline{\phantom{x}}$ | organic-phase species |

metals. In the present paper, the selective extraction of Y from Ho/Y/Er mixture with EHPNA (2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester) in the presence EDTA [2] and the separation of adjacent rare earth metals with TOMAN (tri-*n*-octylmethylammonium nitrate) in the presence of EDTA [3] have been investigated. In both cases, the extraction equilibrium formulations in the absence and presence of EDTA were investigated. The method for design of the separation process with countercurrent mixer-settler cascade, using a simulation based on the extraction equilibrium formulation determined and material balance, was also investigated.

Introduction of the redox reaction for metals during extraction is also known to be effective for improving the separation ability, since the ions of different valences behave like different elements with respect to their extractability. In the case of organophosphorus acid extractant system, the distribution ratio for metal ions having a larger valence is larger than that for ions with a smaller valence. Therefore, the selective stripping of the target metal is expected to be carried out, when the metal is reduced in the stripping section, and the selective extraction is expected to be carried out, when the metal is oxidized in the extraction section. As for the reaction source, there are three possible ways to produce the redox reaction in an extraction system: (a) chemical reaction with chemical reagent, (b) electrochemical reaction, and (c) photochemical reaction. Photochemical reaction has advantages of little discharge of waste and good integration to the extraction system. In the present paper, therefore, photoreductive stripping of Eu from Sm/Eu/Gd mixture [4] and photooxidative extraction of Ce from La/Ce/Nd [5] were investigated.

## 2. Experiment

Tri-*n*-octylmethylammonium nitrate (TOMAN) was procured from Koei Kagaku Kogyo Co., Ltd. and was diluted in xylene prior to use. Bis(2-ethylhexy)phosphoric acid (D2EHPA) and 2-ethylhexyl phosphonic acid mono-2-ethylhexyl ester (EHPNA) were obtained from Daihachi Chemical Industry Co. Ltd. D2EHPA was diluted in cyclohexane and EHPNA was diluted in kerosene. Ethylenediaminetetraacetic acid (EDTA) was supplied by Dojin Chemical Industries as the disodium salt. In the case of the extraction in the presence of EDTA, the aqueous solution, containing appropriate rare earth metal and EDTA, and the organic solution containing extractant were shaken at a volume ratio of 1:1, and equilibrated at 298 K. In the case of the photoreductive stripping of Eu, the aqueous stripping solution and organic solution (D2EHPA/cyclohexane) following extraction of the metals were contacted in the glass bottle, and then were irradiated with a 20 W low-pressure mercury lamp (LPML; Eikohsha Co. Ltd.). In the case of photooxidative extraction of Ce, the aqueous solution following photooxidation of Ce with LPML was contacted with the organic solution. The concentrations of rare earth metals were determined by the use of a Nippon Jarrell-Ash ICAP-575 Mark II emission spectrometer.

## 3. Results and discussion

### 3.1. Extraction system combined with the masking effect with EDTA

### 3.1.1. EHPNA system

The extraction equilibrium formulations for rare earth metals with EHPNA/kerosene in the absence of EDTA have been investigated up to high loading ratio of the extractant as Eqs. (1) and (2), and the values of the corresponding extraction equilibrium constants were determined [6].

$$\mathrm{Ln}^{3+} + 3\overline{(\mathrm{RH})_2} \leftrightarrow \overline{\mathrm{LnR}_3(\mathrm{RH})_3} + 3\mathrm{H}^+ \tag{1}$$

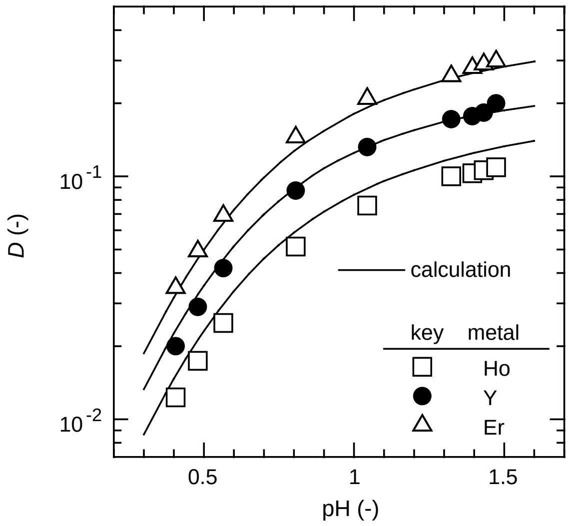

Fig. 1. Effect of pH on distribution ratios for the rare earth metals in a Ho/Y/Er ternary system. Comparison of experimental data with prediction, as shown by the solid lines: $\overline{[(RH)_2]}_{feed} = 0.05$ mol/L and $[Ln_i]_{feed} = 0.03$ mol/L.

$$Ln^{3+} + \overline{LnR_3(RH)_3} + 2\overline{(RH)_2} \leftrightarrow \overline{(LnR_3)_2(RH)_4} + 3H^+. \tag{2}$$

This extraction equilibrium is also able to apply for the Ho/Y/Er ternary system. Fig. 1 shows the effect of pH value on the distribution ratio of the three rare earth metals in ternary system without EDTA. The data are seen to agree well with the calculated value, shown by solid lines, based on the extraction equilibrium formulations and constants determined.

In the case of extraction system in the presence of EDTA, the rare earth metals complexed with EDTA are insensitive to the extraction. It is known that the ability of EDTA ($H_4L$) to complex with the rare earth metals depends on the pH value of the aqueous solution [7], since the only dissociated ligand of EDTA ($L^{4-}$) forms a complex with rare earth metals. The dissociated ligand of EDTA then makes a complex with rare earth metal is shown as

$$Ln^{3+} + L^{4-} \leftrightarrow LnL^-, \quad K_{f,i}. \tag{3}$$

The concentrations of the individual free rare earth metals are expressed as

$$[Ln_i^{3+}] = \frac{[Ln_i]_t}{1 + K_{f,i}[L^{4-}]}. \tag{4}$$

With EDTA, the rare earth metal, when complexed with EDTA as $Ln_iL^-$, is assumed not to take part in the extraction, and thus, the distribution ratio of each rare metal is determined only by the free rare earth metals in the aqueous phase, $Ln_i^{3+}$. The material balance of each rare earth metal in the extraction system in the presence of EDTA is expressed as

$$\begin{aligned}[Ln_i]_{feed} &= [Ln_i]_t + \overline{[Ln_i]}_t \\ &= [Ln_i^{3+}] + [Ln_iL^-] + \overline{[Ln_iR_3(RH)_3]} \\ &\quad + 2\overline{[(Ln_iR_3)_2(RH)_4]}.\end{aligned} \tag{5}$$

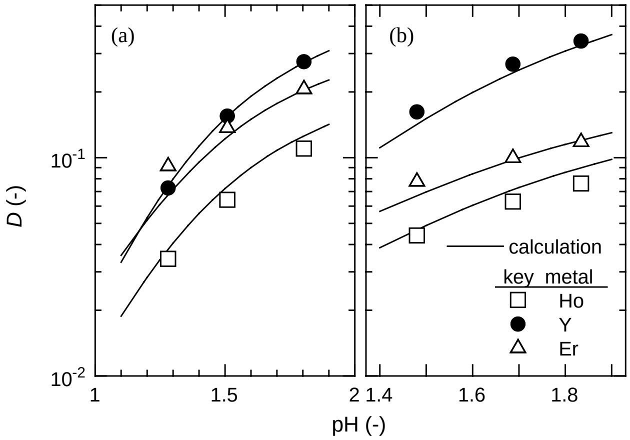

Fig. 2. Effect of pH on distribution ratios for the rare earth metals in a Ho/Y/Er ternary system in the presence of EDTA. Comparison of experimental data with prediction, as shown by the solid lines. $\overline{[(RH)_2]}_{feed} = 0.01$ mol/L, $[Ln_i]_{feed} = 0.005$ mol/L, and [EDTA] = (a) 0.005 mol/L and (b) 0.01 mol/L.

The distribution ratio for each rare earth metal in the presence of EDTA is also expressed as

$$D_i = \frac{\overline{[Ln_i]}_t}{[Ln_i]_t} = \frac{\overline{[Ln_i]}_t}{[Ln_i^{3+}] + [Ln_iL^-]}. \tag{6}$$

Based on the above assumption, an apparent distribution ratio, $D_{a,i}$, defined as $\overline{[Ln_i]}/[Ln_i^{3+}]$, can be calculated, enabling a predicted value of the distribution ratio, $D_i$, in the presence of EDTA to be calculated. The effect of pH on the distribution ratios for Ho, Y, and Er in the ternary system, in the presence of EDTA, is plotted in Fig. 2, together with the calculated distribution ratios, as shown by the solid lines. The experimental data are seen to cluster on the respective predicted lines, thus indicating that the proposed extraction scheme can be used to describe the extraction system, in the presence of EDTA. As shown in Fig. 2a for [EDTA] = 0.005 mol/L, the distribution ratios for Ho and Er are suppressed more than those for Y, with a masking effect occurring at the high pH region. With an increased concentration of 0.01 mol/L EDTA (Fig. 2b), the masking effect for Ho and Er increases, and the order of extraction between Y and Er is reversed, as compared to Fig. 1, and enhances the selective extraction of Y.

Based on the above equilibrium studies, a simulation of the separation of Y from a Ho/Y/Er mixture solution by a countercurrent mixer-settler cascade can be carried out, using the extraction equilibrium formulations and the material balance formulations for the each component. A schematic flowsheet for a countercurrent

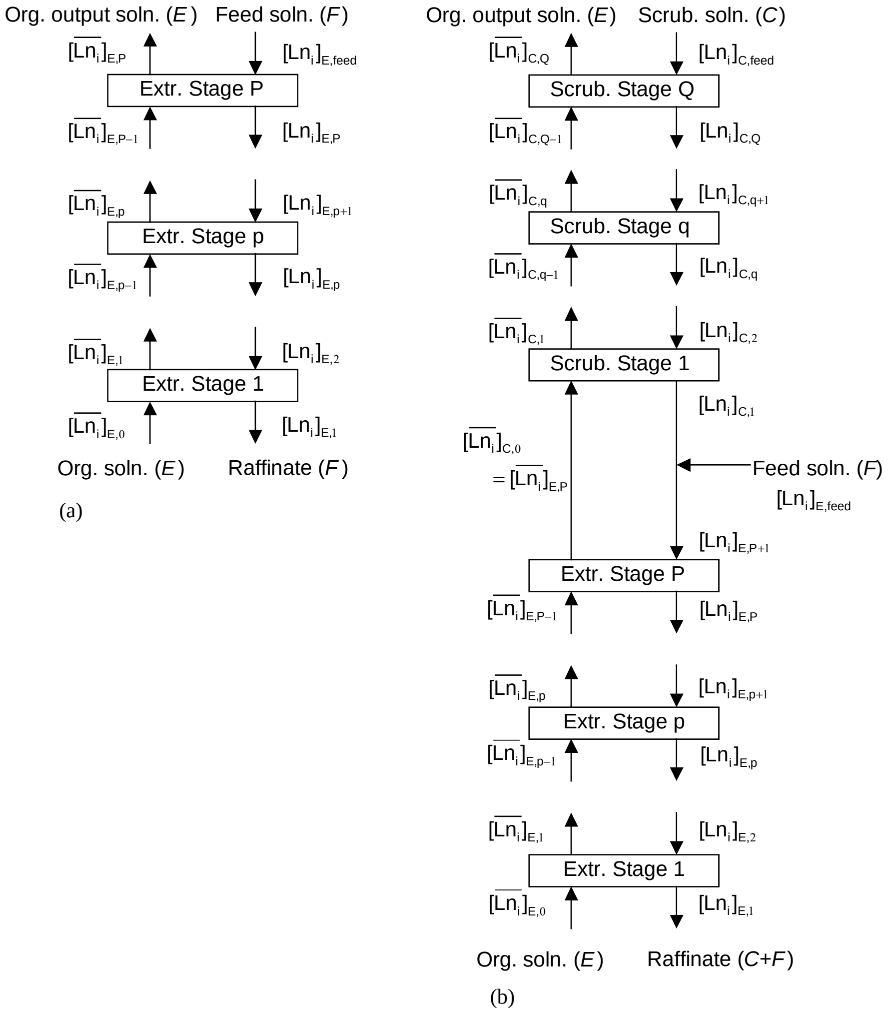

Fig. 3. Schematic flowsheets for the countercurrent mixer-settler cascade with (a) extraction only and (b) combined extraction and scrubbing sections.

mixer-settler cascade is shown in Fig. 3. First, separation with only an extraction section (Fig. 3a) was carried out. In this simulation, the input values of $F$ $(=1\,\mathrm{L/min})$, $E$ $(=1\,\mathrm{L/min})$, $[\mathrm{Ln}_i]_{\mathrm{E,feed}}$ $(=0.01\,\mathrm{mol/L})$, $[\overline{\mathrm{Ln}_i}]_{\mathrm{E},0}$ $(=0\,\mathrm{mol/L})$, $[\mathrm{H}^+]_{\mathrm{E},1}$, [EDTA] $(=0.02\,\mathrm{mol/L})$, and $[\overline{(\mathrm{RH})_2}]_{\mathrm{feed}}$ $(=0.02\,\mathrm{mol/L})$ were applied. The calculation was done as described in previous papers [6,8] as follows. When temporary values of $[\mathrm{Ln}_i]_{\mathrm{E},1}$ and $[\mathrm{H}^+]_{\mathrm{E},1}$ are given, $D_{i,1}$ is calculated using Eqs. (4)–(6), and then $[\overline{\mathrm{Ln}_i}]_{\mathrm{E},1}$ is calculated. The values of $[\mathrm{Ln}_i]_{\mathrm{E},2}$ and $[\mathrm{H}^+]_{\mathrm{E},2}$ are thus calculated based on the material balance formulations in each stage. These calculations are carried out in a similar way from stages 1 to $P$ repeatedly, until the resulting value of $[\mathrm{Ln}_i]_{\mathrm{E,feed}}$ becomes equal to the given $[\mathrm{Ln}_i]_{\mathrm{E,feed}}$ by changing the value of $[\mathrm{Ln}_i]_{\mathrm{E},1}$ based on the material balance formulations in the cascade. Fig. 4 shows the resulting organic-phase rare earth concentrations for the case of a 10-stage extraction cascade. With an aqueous feed pH value of 1.57 (Fig. 4a), the pH values in stages 5–10 hardly deviate from the feed value and the overall fractional recovery of Y, $\rho_{\mathrm{Y}} = E[\overline{\mathrm{Y}}]_{\mathrm{E,P}}/F[\mathrm{Y}]_{\mathrm{feed}}$, obtained is of low order. For a feed pH value of 2.92 (Fig. 4b), the pH values increase with increasing stage number, and an effective overall fractional recovery of $\rho_{\mathrm{Y}} = 0.491$ can be obtained. In addition, the masking effect for Ho and Er increases with the increasing pH, making the concentrations for Ho and Er in the organic phase decrease slightly with increasing stage number for stages 3–10. However, the overall decontamination factor, $f = \rho_{\mathrm{Y}}/(\rho_{\mathrm{Ho}} + \rho_{\mathrm{Er}})$, is not increased drastically, thus indicating that a scrubbing section is needed in the extraction cascade in order to achieve an effective separation for Y.

The effect of an additional scrubbing section was therefore investigated. Fig. 3b shows the schematic flowsheet for both the extraction and scrubbing sections. In this simulation, values of $F$ $(=1\,\mathrm{L/min})$, $E$ $(=1\,\mathrm{L/min})$, $C$ $(=1\,\mathrm{L/min})$, $[\mathrm{Ln}_i]_{\mathrm{E,feed}}$ $(=0.02\,\mathrm{mol/L})$, $[\mathrm{Ln}_i]_{\mathrm{C,feed}}$ $(=0\,\mathrm{mol/L})$, $[\overline{\mathrm{Ln}_i}]_{\mathrm{E},0}$ $(=0\,\mathrm{mol/L})$, $[\mathrm{H}^+]_{\mathrm{E},1}$,

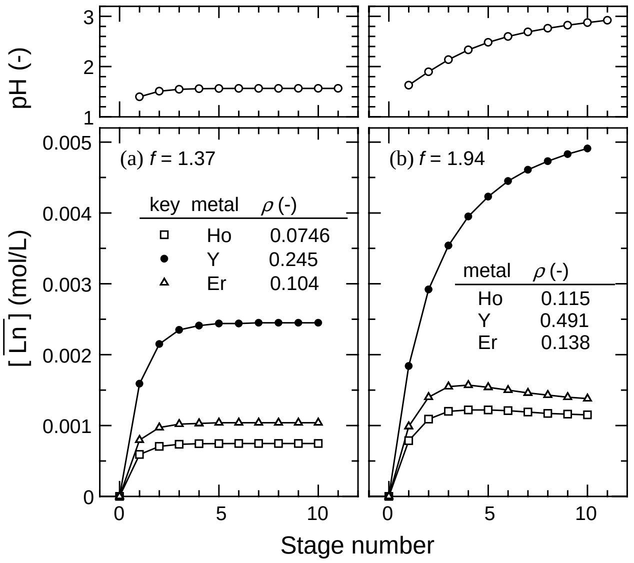

Fig. 4. Simulation studies for separation of Y from a Ho/Y/Er mixture by a countercurrent mixer-settler cascade with 10 extraction stages for the conditions $F$:$E$ = 1:1, $\overline{[(\mathrm{RH})_2]}_{\mathrm{feed}} = 0.02$ mol/L, $[\mathrm{Ln}_i]_{\mathrm{E,feed}} = 0.01$ mol/L, and $[\mathrm{EDTA}]_{\mathrm{E}} = 0.02$ mol/L.

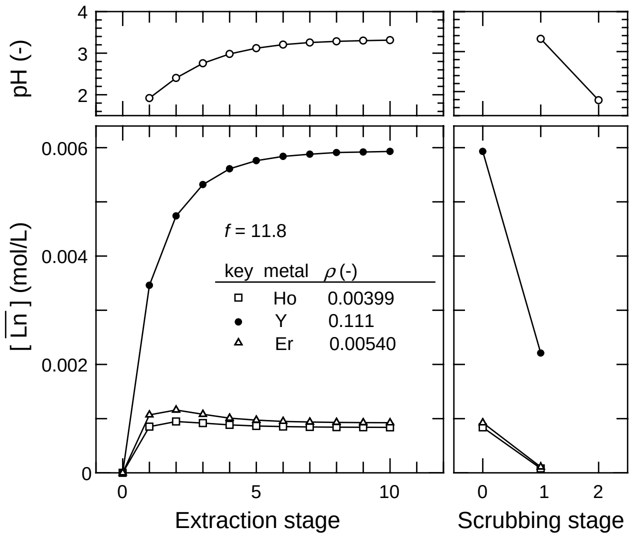

Fig. 5. Simulation studies for separation of Y from a Ho/Y/Er mixture by a countercurrent mixer-settler cascade with 10 extraction stages and a single scrubbing stage for the conditions $F$:$E$:$C$ = 1:1:1. $\overline{[(\mathrm{RH})_2]}_{\mathrm{feed}} = 0.02$ mol/L, $[\mathrm{Ln}_i]_{\mathrm{E,feed}} = 0.02$ mol/L, $[\mathrm{EDTA}]_{\mathrm{E}} = 0.04$ mol/L, $[\mathrm{Ln}_i]_{\mathrm{C,feed}} = 0$ mol/L, and $[\mathrm{EDTA}]_{\mathrm{C}} = 0.008$ mol/L.

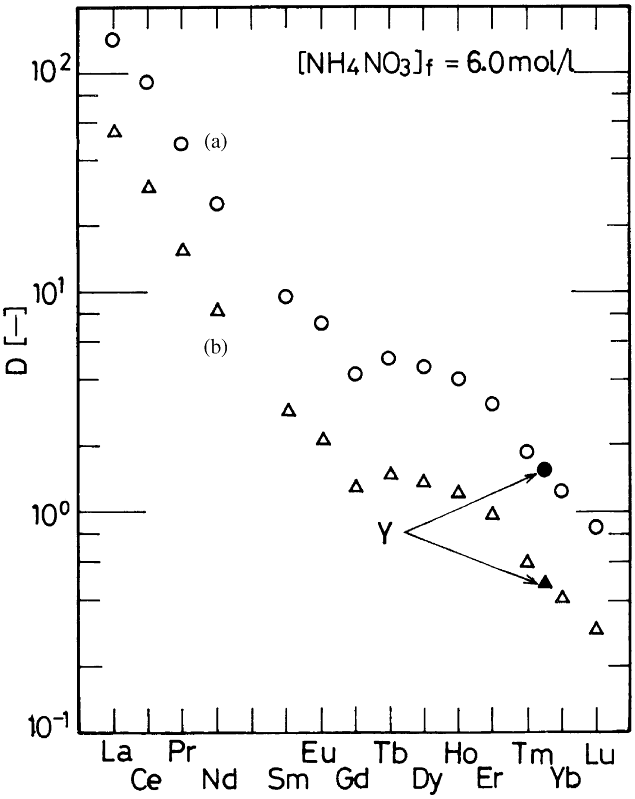

Fig. 6. Variation of distribution ratios of rare earth metals with atomic number. [TOMAN] = (a) 1.0 mol/L and (b) 0.4 mol/L.

$[\mathrm{EDTA}]_{\mathrm{E}}$ (= 0.04 mol/L), $[\mathrm{EDTA}]_{\mathrm{C}}$ (= 0.008 mol/L), and $\overline{[(\mathrm{RH})_2]}_{\mathrm{feed}}$ (= 0.02 mol/L) apply. The calculated rare earth metal concentrations in the organic phase for a cascade of 10 extraction stages and a single scrubbing stage are shown in Fig. 5. In this simulation, the pH value at the output of the scrubbing section, $[\mathrm{H}^+]_{\mathrm{C,0}}$, was set equal to that at the input to the extraction section, $[\mathrm{H}^+]_{\mathrm{E,11}}$. Although the fractional recovery value, $\rho_{\mathrm{Y}}$ $(= E\overline{[\mathrm{Y}]}_{\mathrm{C,Q}}/(F[\mathrm{Y}]_{\mathrm{E,feed}} + C[\mathrm{Y}]_{\mathrm{C,feed}}))$, was decreased to 0.111, the recovery efficiencies for Ho and Er were decreased substantially to 0.00399 and 0.00540, respectively, because of the scrubbing effect obtained with the EDTA-containing solution and resulted in an effective separation with the overall decontamination factor $f = 11.8$. With an increase in the scrubbing stage number from 1 to 2, the separation of Y is much improved with $f = 63.3$, while the recovery decreased with $\rho_{\mathrm{Y}} = 0.0490$ (where $\mathrm{pH}_{\mathrm{C,3}} = 1.675$).

### 3.1.2. TOMAN system

The extraction equilibrium formulations for rare earth metals with TOMAN/xylene in the absence of EDTA have also been investigated up to high loading ratio of the extractant as Eqs. (7) and (8), where $\bar{R}$ denotes the monomeric species of TOMAN [9]:

$$\mathrm{Ln}^{3+} + 3\mathrm{NO}_3^- + 5\overline{\mathrm{R}} \leftrightarrow \overline{\mathrm{Ln(NO_3)_3 \cdot 5R}}, \tag{7}$$

$$\mathrm{Ln}^{3+} + 3\mathrm{NO}_3^- + \overline{\mathrm{Ln(NO_3)_3 \cdot 5R}} \leftrightarrow \overline{\{\mathrm{Ln(NO_3)_3}\}_2 \cdot 5\mathrm{R}}. \tag{8}$$

Stepwise equilibria hold for all rare earth metals over the whole range of loadings of the extractant. The extractability of TOMAN for all rare earth metals under identical conditions is shown in Fig. 6. The extractability decreases continuously with increase in the atomic number with the exception of a slight increase from Gd

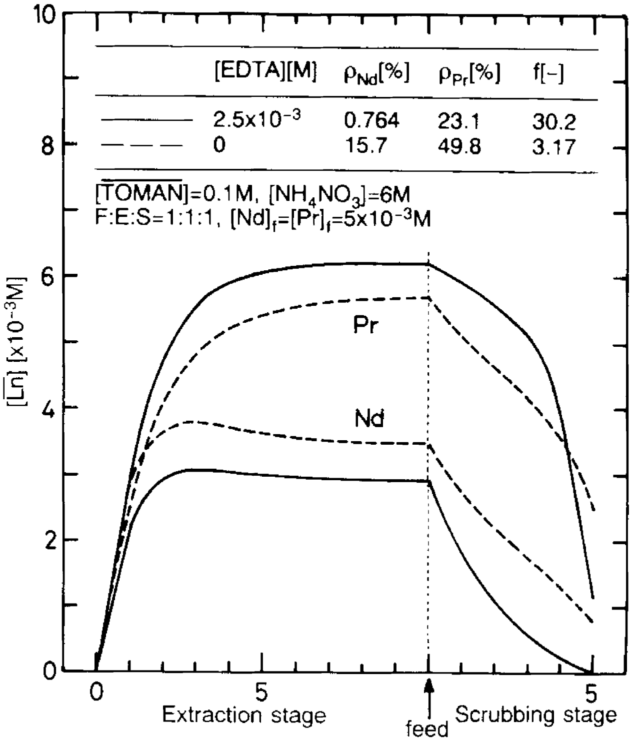

Fig. 7. Simulation of Pr/Nd separation in TOMAN and TOMAN-EDTA systems by countercurrent mixer-settler cascade of 10 extraction stages and five scrubbing stages in the case of $F{:}E{:}S = 1{:}1{:}1$.

to Tb. Therefore, the combination effect of masking reaction with EDTA is expected to be obtained in the extraction system employing TOMAN.

The extraction equilibrium formulation of rare earth metals with TOMAN in the presence of EDTA was then investigated. In this extractant system, it is also assumed that the complexed rare earth metal is inactive for the extraction. All of the EDTA in the aqueous phase is considered to be formed by the complex with rare earth metals, since the pH value of the aqueous phase in the TOMAN system is high (pH > 3) and all of the EDTA exist as the dissociated ligand, $L^{4-}$, as shown in Eq. (9).

$$[\mathrm{EDTA}] = [\mathrm{L}^{4-}] = [\mathrm{LnL}^{-}]. \tag{9}$$

The extraction behavior for the rare earth metals in the presence of EDTA can be expressed using the extraction equilibrium formulation determined. The simulation studies of separation of Pr/Nd by the countercurrent mixer-settler cascade, shown in Fig. 3, was carried out. In this case, the calculation was carried out with the same procedure for the extraction system of EHPNA. Fig. 7 shows the resulting organic phase rare earth concentrations for the case of 10 extraction stages and five scrubbing stages with and without EDTA. Although $\rho_{\mathrm{Pr}}$ is reduced to 0.231 by addition of EDTA, $\rho_{\mathrm{Nd}}$ is further reduced to 0.00764, thus obtained the overall decontamination factor, $f$, of 30.2.

### 3.2. Extraction system combined with the photochemical reaction for metal ions

### 3.2.1. Photoreductive stripping of Eu from Sm/Eu/Gd mixture

The photochemical reduction of $Eu^{3+}$ in the separate aqueous solution was first investigated. The $EuCl_3$ has the $C-T$ band from $H_2O$ to $Eu^{3+}$ at 188 nm, while the additional absorption band appears, when $SO_4^{2-}$ is in the aqueous solution, around 235 nm. This indicates that a longer-wavelength light as well as a shorter-wavelength light might be employed for the photochemical reduction. The photochemical reduction of $Eu^{3+}$ from the aqueous solution containing $(NH_4)_2SO_4$ by LPML (184.9 + 253.7 nm) progressed in the presence of radical scavenger (isopropyl formate, formic acid, or 2-propanol), and the reduced $Eu^{2+}$ was precipitated as $EuSO_4$.

The photochemical reduction of $Eu^{3+}$ was then applied to the stripping system, and the photoreductive stripping of Eu was carried out. In this case, the organic solution (0.2 mol/L D2EHPA), following extraction of Sm/Eu/Gd (5 mmol/L each), and aqueous stripping solution, containing 1 mol/L of $(NH_4)_2SO_4$ and radical scavenger, were agitated vigorously and irradiated using LPML. Fig. 8 shows the time-course variation for the precipitation of $EuSO_4$ and the stripping yields of Sm and Gd in D2EHPA/cyclohexane system. Eu ions extracted into the organic phase were stripped selectively and were precipitated as $EuSO_4$, while most of Sm and Gd remained in the organic phase. In the case of isopropyl formate used as the radical scavenger, the dielectric constant of the organic solution increases with the addition of the scavenger, and thus the extraction ability decreases. The addition of isopropyl formate also decreases the pH value of the aqueous phase. These results increase the stripping efficiency of Sm and Gd, compared to those obtained from other two radical scavenger systems. In the case of formic acid system, the photoreductive stripping occurred rapidly, because the $COOH\cdot$ formed by the photodecomposition of formic acid acts as a reducing agent. As for the 2-propanol system, the stripping yields of Sm and Gd were low, since the pH value of the aqueous phase was maintained greater than a value of 3. The stripping efficiency of these two rare earths became much lower when the amount of the 2-propanol was decreased (1.5 mL) because of the decrease in the dielectric constant of the organic phase. The high purity of the precipitate (ca. 99%) thus obtained as shown by the filled symbols in Fig. 8c.

The reusability of the organic phase after photo-irradiation was investigated. Table 1 shows the typical result obtained in the case of 2-propanol. The performance of the second and third extractions and subsequent photoreductive stripping was quite similar

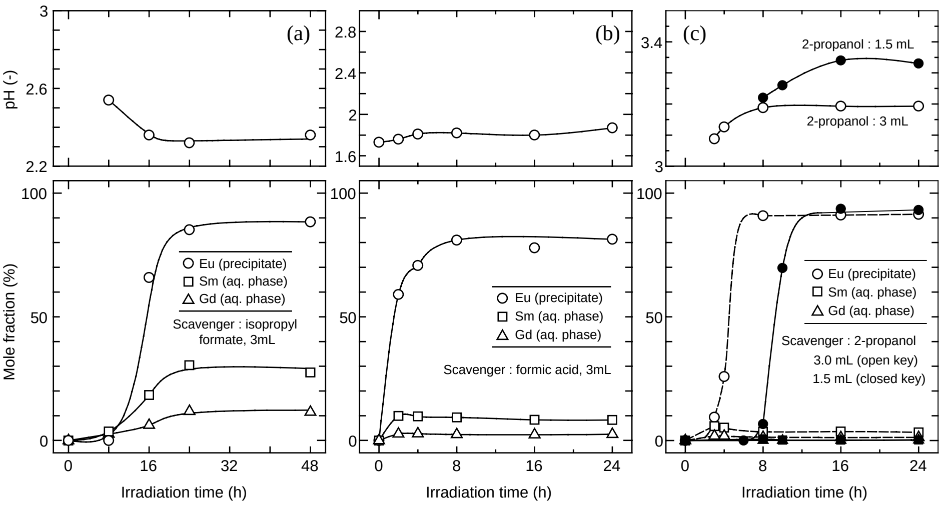

Fig. 8. Effect of irradiation time on precipitation of $EuSO_4$, stripping yield of Sm and Gd, and aqueous phase pH in the presence of radical scavenger: (a) isopropyl formate, (b) formic acid, and (c) 2-propanol.

Table 1
Reusability of organic phase: Scavenger: 2-propanol (1.5 mL); stripping: 16 h irradiation by LPML

| | Extraction (%) | | | Stripping (precipitation) | |
|---|---|---|---|---|---|
| | Sm | Eu | Gd | Eu (%) | Purity (%) |
| First | 99.0 | 99.5 | 99.7 | 93.7 | 98.8 |
| Second | 98.9 | 99.5 | 99.7 | 93.8 | 99.0 |
| Third | 98.9 | 99.5 | 99.7 | 92.5 | 99.0 |

to that of the first extraction-stripping, indicating that the organic phase can be reused for the repeated use.

### *3.2.2. Photooxidative extraction of Ce from La/Ce/Pr mixture*

The photooxidation of Ce(III) in the aqueous solution was reported to progress with photoirradiation of about 250 nm light [10]. In this case, therefore, LPML was used as the light source, and the 184.9 nm line was cut off by a glass filter. A weak oxidizing reagent, $KBrO_3$, was added to the aqueous solution, since the photochemical oxidation of Ce(III) hardly occurs with only photoirradiation. The addition of $KBrO_3$ remarkably enhances the photooxidation of Ce(III), and the yield of Ce(IV) reached 98% after 8 h irradiation at $[KBrO_3] = 0.02$ mol/L ($[Ce] = 0.01$ mol/L).

The extraction of Ce from La/Ce/Pr was then investigated. In this case, the aqueous solution, containing three rare earth metals (0.01 mol/L each), after photoirradiation for 3 h was contacted with 0.3 mol/L D2EHPA/cyclohexane. Fig. 9 shows the effect of initial proton concentration and $KBrO_3$ concentration before photochemical oxidation on the extraction efficiency and separation factor, $\beta$, which is defined as ratio of the distribution ratios. Ce was extracted preferentially, with La and Nd remaining in the aqueous phase. The separation factors of 270–400 for La/Ce and 70–350 for Ce/Nd were obtained. The reusability of the organic phase after photooxidation–extraction–stripping process was investigated. Fig. 10 shows the metal concentration in the organic phase during the repeated processes. The organic phase showed sufficient loading and stripping capacities in the repeated processes. Since Ce(IV) is not stripped quantitatively, some accumulation of Ce in the organic phase was seen. This problem may be solved by adding the washing stages of the organic phase to remove the remaining metals after the stripping stages.

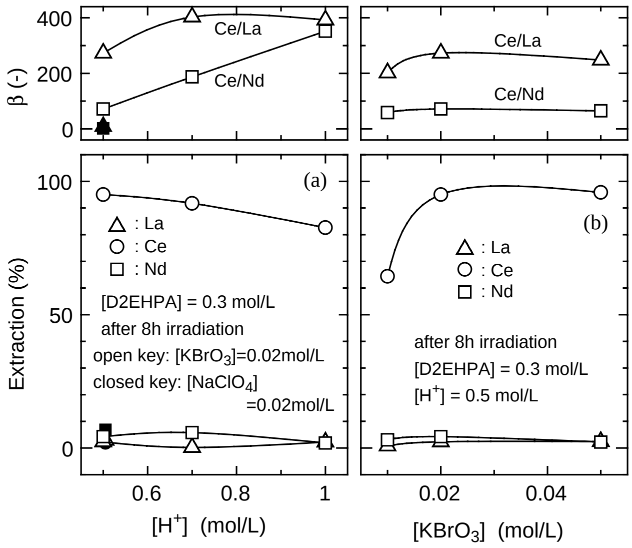

Fig. 9. Extraction percentages of the rare earth metals and separation factor, $\beta$. Effect of feed concentration of (a) $H^+$ and (b) $KBrO_3$.

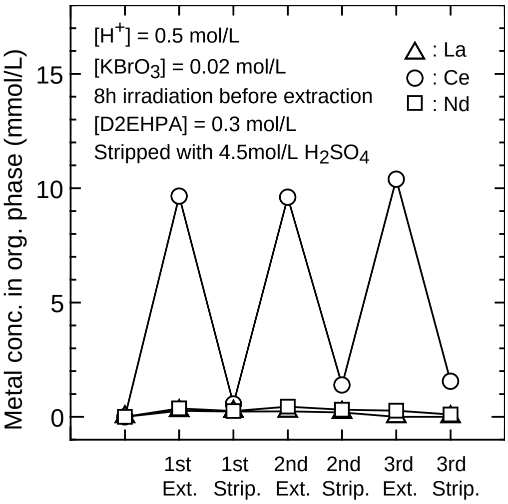

Fig. 10. Rare earth metal concentration in the organic phase during repeated photooxidation–extraction–stripping processes.

## 4. Conclusion

The advanced liquid–liquid extraction systems for the separation of rare earth ions by combination of conversion of the metal species with chemical reaction have been investigated with the following results:

(1) The improvement of the separation ability was successfully achieved by adding the water-soluble complexing agent, EDTA, into the aqueous phase of the extraction system. In the case of EHPNA system, the masking effect for Ho and Er was obtained, and thus the selective extraction of Y was carried out. In the case of TOMAN system, the masking effect for Pr was obtained and the improvement of the separation ability for Pr/Nd was achieved. The method for design of the separation process with countercurrent mixer-settler cascade was proposed.

(2) The separation ability for the rare earth metals was improved by the introduction of the photochemical redox reaction of the target rare earths. In the case of the photoreductive stripping of Eu from Sm/Eu/Gd mixture, the selective stripping of Eu progressed, while most of Sm and Gd remained in the organic phase, and $EuSO_4$ with high purity was obtained. In the case of photooxidative extraction of Ce from La/Ce/Pr mixture, oxidized Ce(IV) was selectively extracted into the organic phase.

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