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Selective Separation of Rare Earth Metals by Solvent Extraction in the Presence of New Hydrophilic Chelating Polymers Functionalized with Ethylenediaminetetraacetic Acid. II. Separation Properties by Solvent Extraction

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ABSTRACT

The selective separation of rare earth metals by solvent extraction including chelating polymers in the aqueous phase was investigated. The chelating polymers were synthesized in this laboratory by introducing ethylenediaminetetraacetic acid (EDTA) onto water-soluble polyallylamine. The highest selectivity obtained for the Y/Er separation system was 14.7, which was much higher than that in conventional solvent extraction (about 1.4) and also higher than that in extraction including EDTA (about 5.0). This means that the number of extraction stages required can be considerably reduced by the addition of chelating polymers. The effects of several experimental conditions such as pH, extractant concentrations, chelating polymer concentrations, and initial total rare earth metal concentrations on the separation factors and the distribution ratios for the Y/Er system were studied in detail. Furthermore, this extraction method was applied to other separation systems (Y/Dy, Y/Ho, Y/Tm). A remarkably high separation factor (12.6) was obtained for the Y/Tm system and the Y/Er system, although the separation factors were comparable to those in the presence of EDTA in the Y/Dy and Y/Ho systems.

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INTRODUCTION

To enhance the separation factors in solvent extraction of rare earth metals, several studies which add such chelating agents as ethylenediaminetetraacetic acid (EDTA) or diethylenetriaminepentaacetic acid (DTPA) to the aqueous phase have been attempted recently (1–6). These methods have succeeded, to some extent, in enhancing the separation factors. One of the problems with this extraction system, however, is recovery of the chelating agents. Because the chelating agents are usually precipitated by the addition of a large amount of acid for recovery, the cost for the acid used and the additional precipitation operation restrict the usefulness of this extraction system.

In Part I of this work we reported the development of new hydrophilic chelating polymers (7). The new chelating polymers were synthesized by introducing EDTA onto a water-soluble polyallylamine (PAA). These polymers were naturally precipitated in the presence of rare earth metals, which suggested that the recovery of the polymers is easy from solvent extraction systems that include them in the aqueous phase. The adsorption properties of Y^{3+} and Er^{3+} to these polymers were also investigated.

For this paper we studied the separation properties of rare earth metals by solvent extraction systems containing the new chelating polymers. Because the chelating polymers were synthesized through the formation of amido group between EDTA and PAA, the unit structures of the chelating polymers are different from the structure of EDTA, which may make it possible to obtain a higher separation factor than in the case adding EDTA. The effects of several experimental conditions, such as pH, the concentration of the chelating polymer, and the concentration of the extractant, on the distribution ratios and the separation factors are described here.

EXPERIMENTAL

Rare earth stock solutions were prepared by the same method described previously (7). The extraction equilibrium experiments were carried out by the usual method. The aqueous solutions contained both rare earth metals and the chelating polymer. The ionic strength of the aqueous solutions were adjusted at 0.1 mol/dm^3 by the addition of $KClO_4$. The organic solution used was *n*-heptane containing di(2,4,4-trimethylpentyl) phosphinic acid (CYANEX 272) as the extractant. It is known that the extractant forms the dimer or trimer in an aliphatic solvent (*n*-heptane) (3). The initial concentration of the extractant as the monomer was constant at 0.295 mol/dm^3 except for the experiments with varying extractant concentrations. After mixing the aqueous and organic solutions, the solutions were stirred for more than 12 hours in a water bath thermostated at 298 K, and extraction equilibrium was achieved. The organic solutions were stripped with 2.7 mol/dm^3 HNO_3 solution, and the concentrations of the rare earth metals in the strip solutions were measured by an inductively coupled plasma emission spectrophotometer (Shimadzu Co Ltd., ICPS 1000III).

RESULTS AND DISCUSSION

Effect of Addition of PAA

The overall extraction reaction of the rare earth metal with the acidic organophosphorus extractant is generally expressed as

$$Re^{3+} + 3\overline{(HR)_2} \rightleftharpoons \overline{ReR_3(HR)_3} + 3H^+ \qquad (1)$$

$$\begin{aligned} K_{ex} &= [\overline{ReR_3(HR)_3}][H^+]^3/([Re^{3+}][\overline{(HR)_2}]^3) \\ &= D[H^+]^3/[\overline{(HR)_2}]^3 \end{aligned} \qquad (2)$$

where Re^{3+} represents a rare earth metal ion and $(HR)_2$ denotes the dimer of the extractant. K_{ex} and D are the extraction equilibrium constant and distribution ratio, respectively, and an overbar denotes an organic phase species.

Figure 1 shows the effect of the addition of PAA on the extraction equilibrium. The results of the extraction equilibria in the absence of PAA

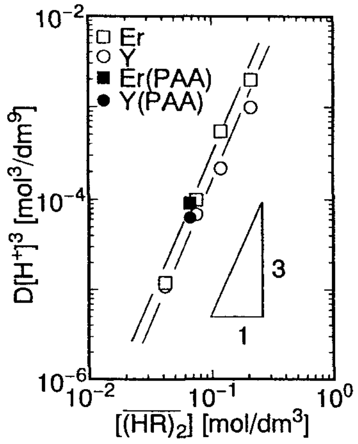

FIG. 1 Effect of the addition of polyallylamine on extraction equilibria. ■, ●: pH 2.25. The concentrations of $(HR)_2$ were estimated by considering the equilibria of dimer and trimer of the extractant (3).

are also included (3). These data show a third-order dependence in the relation between $D[H^+]^3$ and $[\overline{(HR)_2}]$, which verifies the relation of Eqs. (1) and (2). The extraction equilibria were hardly influenced by the addition of PAA (■, ●). We reported earlier that the rare earth metals adsorbed little on PAA (7). This low adsorption brought about no effect of PAA on the extraction equilibria. It was confirmed that the addition of PAA was not useful in enhancing the separation factor.

Effect of Addition of New Chelating Polymers on Separation of Er and Y

Figure 2 shows the effects of the addition of the chelating polymers (Polymer 1 or Polymer 2) on the realation between the distribution ratio *D* and pH. Polymer 1 and Polymer 2 symbolize the synthesized polymers with higher and lower solubilities in water, respectively. The characteristics of the polymers have been described (7). The dotted lines in Fig. 2 denote the results calculated in Ref. 3 for the case of the absence of polymers by using values of 0.2 and 0.14 as the extraction constants for Er and Y, respectively. The distribution ratios for Er and Y decreased upon the addition of the chelating polymers. This is because the concentrations of the free rare earth metal ions which can be extracted by acidic organophosphorus extractants decreased due to complexation with the chelating polymers in the aqueous phase. At low pH, *D* decreased because of the low extraction power of the extractant as expected from Eq. (2).

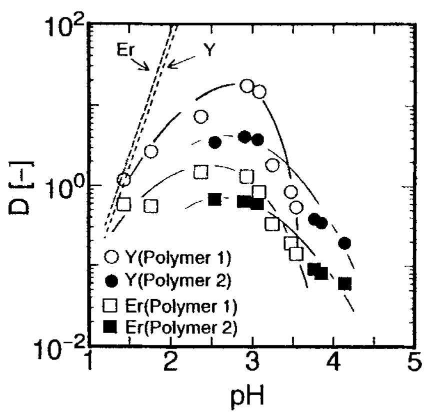

FIG. 2 Relation between distribution ratio *D* and pH in Y/Er separation system. The dotted lines are for extraction without the polymers. $[Y]_0 = [Er]_0 = 0.001$ mol/dm^3, [polymer] = 2.4 g/dm^3, $[\overline{(HR)_2}] = 0.0731$ mol/dm^3.

At high pH, *D* also decreased because the concentrations of the free rare earth metal ions decreased due to the increase of the complexability of the chelating polymers accompanied by further dissociations of the carboxylic groups of the polymers. These two effects led to the maxima of *D* shown in Fig. 2. Because the adsorption abilities of Er were higher than those of Y (7), the free Y concentration becomes higher, permitting the higher distribution ratio of Y in Fig. 2. This tendency is opposite to that in the absence of the polymers, shown in Fig. 1. The adsorption abilities of rare earth metals on Polymer 2 were found to be lower than on Polymer 1 (7). This is the reason for the higher distribution ratios at high pH in the case of the addition of Polymer 2.

The effect of pH on the separation factor β is shown in Fig. 3. β is defined as the ratio of *D* for Y to that for Er. The highest separation factor obtained was about 14.7, which is much higher than that in the presence of EDTA (= 5.0), described below. Note that the addition of the new chelating polymers is useful for obtaining the higher separation factor as well as for their easy recovery. Because the separation factor in the absence of the chelating polymer is about 1.4 [= K_{ex}^{Er}/K_{ex}^{Y} = 0.2/0.14 (3)], the selectivity increased remarkably by the addition of the chelating polymer. In the usual multistage operation of solvent extraction, the total selectivity is given by the separation factor of a single stage raised to a power equal to the number of stages used. Therefore, in this extraction method involving a chelating polymer, much fewer stages are required compared with either the case where a chelating agent (EDTA) is used or by the conventional extraction method.

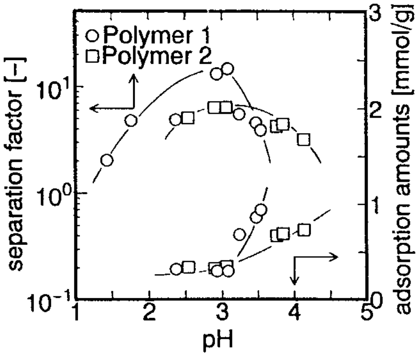

FIG. 3 Effect of pH on separation factor and adsorption amounts in Y/Er separation system. $[Y]_0$ = $[Er]_0$ = 0.001 mol/dm^3, [polymer] = 2.4 g/dm^3, $[(HR)_2]$ = 0.0731 mol/dm^3.

Although the separation properties by adsorption on the polymers were comparable to those by EDTA (7), higher seperation factors were obtained in solvent extraction involving chelating polymers for the following reason. The chelating polymers contain various types of ligands, similar to EDTA (7), and each ligand is considered to have a different chelating ability. Generally, the ligand with low chelating ability also has low selectivity for rare earth metals. For example, the stability constants and the selectivities for rare earth metals are known to increase in the order of imminodiacetic acid (IMDA), nitrilotriacetic acid (NTA), and EDTA (8). The total free rare earth metal concentrations in the aqueous phase in the extraction system cannot be measured directly due to complexation with the polymer, but they can be estimated from Eq. (2) by using the measured organic metal concentrations and the extraction equilibrium constants. For example, the total metal concentration at pH 3.0 in the case of the addition of Polymer 1 is 1.8×10^{-8} mol/dm^3, which is much lower than that in the adsorption experiments in the previous work (10^{-2}–10^{-3} mol/dm^3) (7). Because the free rare earth metal concentrations in the aqueous phase in this extraction system are very low at high pH due to the high distribution ratios, only ligands with a high chelating ability (that is, with high selectivity) can complex with metal ions. This leads to higher separation factors compared with the case of adsorption. This explanation is supported by the experimental result that the amounts of adsorption to the polymers in the extraction system at pH 3.0, where the highest selectivity was obtained, are much lower than the adsorption capacity of Polymer 1 [1.5 mmol/g, (7)], as shown in Fig. 3. β also showed the maxima against pH, similar to the distribution ratios. As shown in Fig. 3, the amount of adsorption increased with an increase in pH because of an increase in the chelating ability due to dissociation of the carboxyl groups of the polymers. Therefore, at a lower pH, β decreased due to a decrease in the effective chelating polymer concentration. On the other hand, β also decreased at higher pH because ligands with a low chelating ability with the polymer (which probably have low selectivity, as described above) complexed with the rare earth metals, accompanied by an increase of their chelating ability.

The effects of extractant concentration on the distribution ratios, the separation factors, the amount of adsorption and the total free rare earth metal concentrations in the aqueous phase, which were estimated as described above, are shown in Fig. 4. As the extractant concentrations increased, the distribution ratios and the separation factors increased. With an increase of the extractant concentration, the total free metal concentration in the aqueous phase decreased due to the increase in the distribution ratios, as expected by Eq. (2). Therefore, only ligands with a high chelating

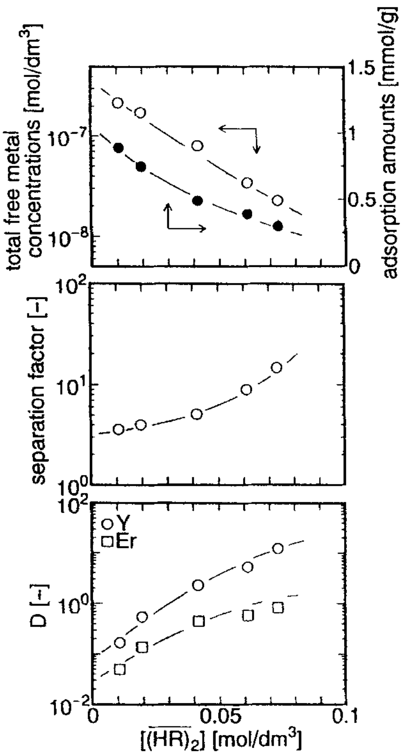

FIG. 4 Effect of extractant concentrations in Y/Er separation system. Polymer: Polymer 1, pH 3.0, $[Y]_0 = [Er]_0 = 0.001$ mol/dm^3, [Polymer 1] = 2.4 g/dm^3.

ability and a high selectivity can complex with metal ions, and this probably leads to higher separation factors with higher extractant concentrations. The experimental result that adsorption decreased with an increase in extractant concentration substantiates this explanation.

Figure 5 shows the effect of chelating polymer concentrations. As the polymer concentrations increased, the distribution ratios decreased because the free metal concentrations in the aqueous phase decreased. On the other hand, β was nearly constant. This is attributable to the constant chelating ability of the polymer, which is supported by the experimental result of the nearly constant adsorption amounts.

Figure 6 shows the effect of the initial total rare earth metal concentrations. The distribution ratios increased and the separation factors de-

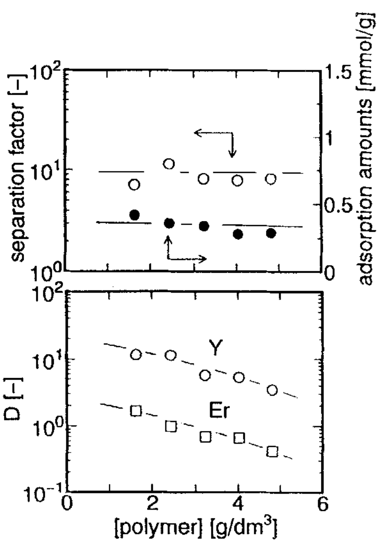

FIG. 5 Effect of polymer concentration in Y/Er separation system. Polymer: Polymer 1, pH 3.0, $[Y]_0 = [Er]_0 = 0.001$ mol/dm³, $[(HR)_2] = 0.0731$ mol/dm³.

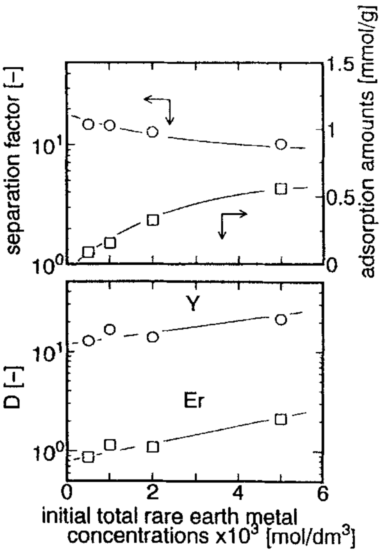

FIG. 6 Effect of initial total rare earth metal concentrations in Y/Er separation system. Polymer: Polymer 1, [Polymer 1] = 2.4 g/dm³, pH 3.0, $[Y]_0 = [Er]_0$, $[(HR)_2] = 0.0731$ mol/dm³.

creased with an increase in metal concentrations. As the metal concentrations increased, the adsorption amounts increased, but the rate of the increase was lower than linear. This means that the degree of complexation decreases relative to the unit mass of the rare earth metals in the aqueous phase, which leads to an increase in the distribution ratios. The increase in the chelating ability of the polymer at higher metal concentrations makes ligands with low selectivity able to complex with metal ions and lowers the separation factors.

Application to Y/Dy, Y/Ho, and Y/Tm Separation Systems

The separation factors in Y/Dy, Y/Ho, Y/Er, and Y/Tm systems obtained by solvent extraction in the presence of chelating polymers are summarized in Table 1. For comparison, extraction experiments in the presence of EDTA in the aqueous phase were also carried out, and the resulting separation factors are also included in the table. β in the presence of EDTA is given by

$$\beta = \left(\frac{[\overline{\mathrm{ReR_3(HR)_3}}]}{[\mathrm{Re}^{3+}] + [\mathrm{ReEDTA}]}\right) \Bigg/ \left(\frac{[\overline{\mathrm{Re'R_3(HR)_3}}]}{[\mathrm{Re'}^{3+}] + [\mathrm{Re'EDTA}]}\right) \tag{3}$$

where ReEDTA and Re'EDTA denote the complexes between a rare earth metal and EDTA in the aqueous phase. Under these experimental conditions, the concentrations of the free rare earth metals in the aqueous phase are negligible compared with the concentrations of the EDTA complexes because the distribution ratios are very high. Therefore, β is simplified to

TABLE 1
Separation Factors in Various Systems

	Y/Dy	Y/Ho	Y/Er	Y/Tm
EDTA:[a]				
Experiment	5.0	6.2	5.0	3.5
Predicted	4.4	6.3	4.0	4.4
Polymer 1[b]	3.5	6.2	14.7	12.6
Polymer 2[b]	6.6	6.0	6.4	11.0

[a] $[\mathrm{Y}]_0 = [\mathrm{Re}]_0 = 1.0 \times 10^{-3}$ mol/dm^3, [EDTA] $= 1.6 \times 10^{-3}$ mol/dm^3, pH 3.0, $[\overline{(\mathrm{HR})_2}] = 0.0731$ mol/dm^3.

[b] $[\mathrm{Y}]_0 = [\mathrm{Re}]_0 = 1.0 \times 10^{-3}$ mol/dm^3, [polymer] $= 2.4$ g/dm^3, pH 3.0, $[\overline{(\mathrm{HR})_2}] = 0.0731$ mol/dm^3.

TABLE 2
Stability Constants of EDTA and Methyl–EDTA Complexes and Extraction Equilibrium Constants

	Y	Dy	Ho	Er	Tm
K_{ReEDTA}[a] [dm^3/mol]	$10^{18.09}$	$10^{18.30}$	$10^{18.74}$	$10^{18.85}$	$10^{19.32}$
$K_{\mathrm{ReEDTA}}/K_{\mathrm{YEDTA}}$	—	1.62	4.47	5.75	17.0
$K_{\mathrm{Remethyl\text{-}EDTA}}$[b] [dm^3/mol]	$10^{18.78}$	—	$10^{19.30}$	$10^{19.61}$	$10^{20.08}$
$\dfrac{K_{\mathrm{Remethyl\text{-}EDTA}}}{K_{\mathrm{Ymethyl\text{-}EDTA}}}$	—	—	3.31	6.76	20.0
K_{ex}[c] [—]	0.14	0.052	0.10	0.20	0.54

[a] Schwarzenbach et al. (9).
[b] Pribil (10).
[c] Azis et al. (11).

$$\begin{aligned}\beta &= ([\overline{\mathrm{ReR_3(HR)_3}}]/[\mathrm{ReEDTA}])/([\overline{\mathrm{Re'R_3(HR)_3}}]/[\mathrm{Re'EDTA}]) \\ &= (K_{\mathrm{ex}}^{\mathrm{Re}}/K_{\mathrm{ex}}^{\mathrm{Re'}})/(K_{\mathrm{ReEDTA}}/K_{\mathrm{Re'EDTA}})\end{aligned} \qquad (4)$$

where K_{ReEDTA} is the stability constant for the EDTA complex. The separation factors calculated using Eq. (4) and the constants shown in Table 2 are listed in Table 1. The calculated results are approximately in agreement with the experimental data using EDTA.

The separation factors in the presence of chelating polymers in Y/Er and Y/Tm systems were much higher than those in the presence of EDTA, although the former values were comparable to those of the latter in Y/Dy and Y/Ho systems. Therefore, the use of chelating polymers has a significant advantage, especially for Y/Er and Y/Tm separation systems. As shown in Table 2, the ratios of the stability constants of Er or Tm to the constant of Y are larger for 1,2-diaminopropane-*N*,*N*,*N'*,*N'*-tetraacetic acid (methyl-EDTA), which is a chelating agent with one methyl group bonded to EDTA, than those for EDTA (10). Thus, the complex-forming abilities and selectivities change with a slight structural change of the chelating agent. It was previously found that the ligand structures of the chelating polymers were different from EDTA (7). This structural difference may bring about the higher selectivities of this chelating polymer.

CONCLUSIONS

The effects of the addition of chelating polymers to the aqueous phase in the separation of Er and Y by solvent extraction were investigated.

The highest selectivity obtained was 14.7, which was much higher than that in the conventional solvent extraction (about 1.4), and also than that in the presence of EDTA (about 5.0). This means that the number of the extraction stages required can be significantly decreased by the addition of a chelating polymer. The effects of such experimental conditions as pH, the extractant concentrations, the chelating polymer concentrations, and the initial total rare earth metal concentrations on the separation factors and the distribution ratios were studied in detail. The separation factors showed a maximum against pH and increased with an increase of the extractant concentrations and with a decrease in the rare earth metal concentrations. The chelating polymer concentrations hardly influenced the separation factors. These effects are explained by the variety of ligands on the chelating polymer.

This solvent extraction method involving a chelating polymer was applied to other separation systems (Y/Dy, Y/Ho, and Y/Tm). Remarkably high separation factors were obtained in the Y/Tm and Y/Er systems. The separation factors in the Y/Dy and Y/Ho systems were comparable to those in the presence of EDTA.

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SYMBOLS

D	distribution ratio
HR	acidic organophosphorus extractant
K_{ex}	extraction equilibrium constant
K_{ReEDTA}	stability constant of EDTA complex (dm^3/mol)
$K_{Remethyl\text{-}EDTA}$	stability constant of methyl–EDTA complex (dm^3/mol)
Polymer 1	chelating polymer with higher solubility in water
Polymer 2	chelating polymer with lower solubility in water
Re	rare earth metal
ReEDTA	complex between rare earth metal and EDTA

Subscript

0	initial concentration

Superscript

—	species in organic phase

Greek

β	separation factor

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