This article was downloaded by:
On: *25 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Separation Science and Technology
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713708471

# Selective Separation of Rare Earth Metals by Solvent Extraction in the Presence of New Hydrophilic Chelating Polymers Functionalized with Ethylenediaminetetraacetic Acid. I. Development of New Hydrophilic Chelating Polymers and Their Adsorption Properties for Rare Earth Metals

Hideto Matsuyama[a]; Yoshikazu Miyamoto[a]; Masaaki Teramoto[a]; Masahiro Goto[b]; Fumiyuki Nakashio[b]
[a] DEPARTMENT OF CHEMISTRY AND MATERIALS TECHNOLOGY KYOTO, INSTITUTE OF TECHNOLOGY MATSUGASAKI, SAKYO-KU, KYOTO, JAPAN [b] DEPARTMENT OF CHEMICAL SCIENCE AND TECHNOLOGY, KYUSHU UNIVERSITY 6-10-1, HAKOZAKI, FUKUOKA, JAPAN

**To cite this Article** Matsuyama, Hideto , Miyamoto, Yoshikazu , Teramoto, Masaaki , Goto, Masahiro and Nakashio, Fumiyuki(1996) 'Selective Separation of Rare Earth Metals by Solvent Extraction in the Presence of New Hydrophilic Chelating Polymers Functionalized with Ethylenediaminetetraacetic Acid. I. Development of New Hydrophilic Chelating Polymers and Their Adsorption Properties for Rare Earth Metals', Separation Science and Technology, 31: 5, 687 — 704

**To link to this Article: DOI:** 10.1080/01496399608000713

**URL:** http://dx.doi.org/10.1080/01496399608000713

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

SEPARATION SCIENCE AND TECHNOLOGY, 31(5), pp. 687–704, 1996

# Selective Separation of Rare Earth Metals by Solvent Extraction in the Presence of New Hydrophilic Chelating Polymers Functionalized with Ethylenediaminetetraacetic Acid. I. Development of New Hydrophilic Chelating Polymers and Their Adsorption Properties for Rare Earth Metals

---

HIDETO MATSUYAMA,* YOSHIKAZU MIYAMOTO,
and MASAAKI TERAMOTO
DEPARTMENT OF CHEMISTRY AND MATERIALS TECHNOLOGY
KYOTO INSTITUTE OF TECHNOLOGY
MATSUGASAKI, SAKYO-KU, KYOTO 606, JAPAN

MASAHIRO GOTO and FUMIYUKI NAKASHIO
DEPARTMENT OF CHEMICAL SCIENCE AND TECHNOLOGY
KYUSHU UNIVERSITY
6-10-1, HAKOZAKI, FUKUOKA 812, JAPAN

Downloaded At: 11:52 25 January 2011

## ABSTRACT

New hydrophilic chelating polymers were synthesized by introducing ethylenediaminetetraacetic acid (EDTA) onto water-soluble polyallylamine. The selective separation of rare earth metals by solvent extraction including these chelating polymers in the aqueous phase is the goal of this work. The polymers were characterized by IR analysis, elemental analysis, gel permeation chromatography (GPC) measurement, and pH titration. Two kinds of polymers with different solubilities in water were produced using different solvents. Both polymers were naturally precipitated in the presence of rare earth metals. This suggests that in the solvent extraction system including these chelating polymers, the recovery of the polymers is easy. Adsorption properties of $Y^{3+}$ and $Er^{3+}$ on these polymers were also investigated. The separation properties by adsorption on the polymers were comparable to those by EDTA. The chelating polymers had the characteristics that their separation factors decreased by adsorption and the total amount adsorbed

* To whom correspondence should be addressed.

Copyright © 1996 by Marcel Dekker, Inc.

increased with increasing pH or initial metal concentrations, although in the presence of EDTA these properties were found to be almost constant.

## INTRODUCTION

Rare earth metals are important elements for producing high technology materials such as advanced semiconductors, superconductors, crystals for lasers, etc. However, it is well known that their mutual separation is very difficult because the chemical and physical properties of adjacent elements among the rare earth metals are very similar.

Solvent extraction has been extensively applied to the practical separation of rare earth metals because it is suitable for a large-scale operation. However, with solvent extraction using an organophosphorus extractant, the separations of Er/Y, Nd/Pr, and Gd/Eu are especially difficult (1) and require a large number of stages in order to obtain these elements in high purity. This situation motivated us to develop new extraction systems.

It has been reported that the addition of chelating agents such as ethylenediaminetetraacetic acid (EDTA) and diethylenetriaminepentaacetic acid (DTPA) to the aqueous phase is very effective for enhancing the separation factors in the solvent extraction of rare earth metals. This work is summarized in Table 1. Although in the group separation of transplutonides from lanthanides the usefulness of the extraction methods (including the water-soluble complexing agents) has been known for more than two decades (10), it was only recently that this extraction method was applied to the mutual separation of rare earth metals. Minagawa et al. first reported that a preferential extraction of Y from other heavy rare earth metals was successfully carried out in a nonequilibrium state by the addition of DTPA to the aqueous phase (2, 3). Hirai and Komasawa investigated the equilibrium separation of rare earth metals in EDTA/water and tri-*n*-octylmethylammonium nitrate (TOMAN)/xylene systems by utilizing the characteristic that the extractabilities of TOMAN for rare earth elements decreased with the atomic number, in contrast to those of organophosphorus extractants (8). We previously elucidated the extraction mechanism of Er and Y in the presence of DTPA (6). The schematic extraction mechanism is shown in Fig. 1 for Er/Y separation using an acidic organophosphorus extractant. Rare earth metals complex with DTPA in the aqueous phase, and their electric charges become negative. Because the acidic organophosphorus is a cation-exchange-type extractant, only free rare earth metal ions, which have positive charges, can be extracted. The free ion concentration of Y is higher than that of Er due to the lower stability constant of the Y–DTPA complex (11); thus permit-

Downloaded At: 11:52 25 January 2011

TABLE 1
Previous Studies on Separation of Rare Earth Metals by Solvent Extraction in the Presence of Chelating Agents in the Aqueous Phase[a]

| Investigators | Year | Separation system | Chelating agent | Extractant | Operation |
|---|---|---|---|---|---|
| Minagawa et al. (2) | 1977 | Y/Er, Ho, Dy, etc. | DTPA | B2EHPA | Nonequilibrium extraction |
| Minagawa et al. (3) | 1980 | Y/Er, Ho, Dy | DTPA or EDTA | B2EHPA | Nonequilibrium extraction |
| Danesi and Cianetti (4) | 1982 | Eu alone | DTPA or HEDTA and lactic acid | B2EHPA | Nonequilibrium extraction |
| Al-Fared et al. (5) | 1988 | Ce/Nd, Pm, Sm, Eu | NTA or DTPA | TBP etc. | Equilibrium extrcation |
| Matsuyama et al. (6) | 1989 | Y/Er | DTPA | BTMPPA | Nonequilibrium extraction |
| Kopunec and Kovalancik (7) | 1989 | Ce/Eu | EDTA, DCTA, DTPA | TBP | Equilibrium extraction |
| Hirai and Komasawa (8) | 1991 | Tb/Dy, Ho | EDTA | TOMAN | Equilibrium extraction |
| Minagawa and Yajima (9) | 1992 | Y/Er | DTPA | B2EHPA | Nonequilibrium extraction |

[a] DTPA = diethylenetriaminepentaacetic acid; EDTA = ethylenediaminetetraacetic acid; HEDTA = *n*-(2-hydroxyethyl)ethylenediaminetriacetic acid; NTA = nitrilotriacetic acid; DCTA = 1,2-diaminocyclohexanetetraacetic acid; B2EHPA = bis(2-ethylhexyl)phosphoric acid; TBP = tributylphosphate; BTMPPA = bis(2,4,4-trimethylpentyl)phosphinic acid; TOMAN = tri-*n*-octylmethylammonium nitrate.

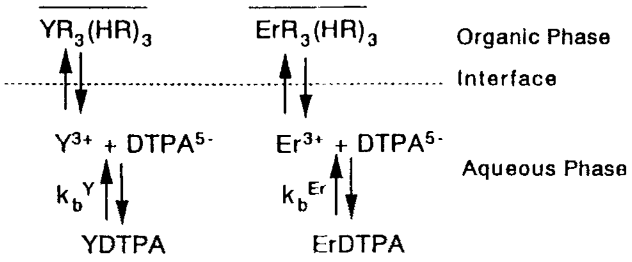


FIG. 1 Schematic extraction mechanism in the presence of DTPA for Er/Y separation. HR, acidic organophosphorus extractant; $k_b$, dissociation rate constant of DTPA complex; superscript—, species in the organic phase. The ratio of the stability constant of Er–DTPA complex to that of Y–DTPA complex is 4.9 (11). The ratio of $k_b^Y/k_b^{Er}$ is 5.8 (12).

Downloaded At: 11:52 25 January 2011

ting the preferential extraction of Y. This is known as a masking effect. Moreover, because the Y–DTPA complex dissociates 5.8 times faster than the Er–DTPA complex (12), such a difference in the dissociation rate brings about an improvement in the separation factor in a nonequilibrium state. We elucidated the conditions where the two effects are present (6).

One of the problems with this extraction system is the recovery of the chelating agents from the solutions. The chelating agents are usually precipitated by the addition of a large amount of acid to the solution. However, the cost of the acid used and the additional operation for precipitation restrict the usefulness of this extraction system.

To extend this extraction system further, we proposed a new system containing a hydrophilic chelating polymer in the aqueous phase. In this system it is expected that the chelating polymer can be easily recovered by sedimentation or a simple membrane operation. The chelating polymer must be hydrophilic in order not to dissolve in the organic phase. We attempted to synthesize the hydrophilic chelating polymer by introducing EDTA onto water-soluble polyallylamine. In this part of the study we describe the development of the new hydrophilic chelating polymer. We also investigated its affinity for Er and Y.

Part II of this study will deal with the separation of Er and Y by an extraction system containing the chelating polymer in the aqueous phase. The effects of several experimental conditions will be discussed.

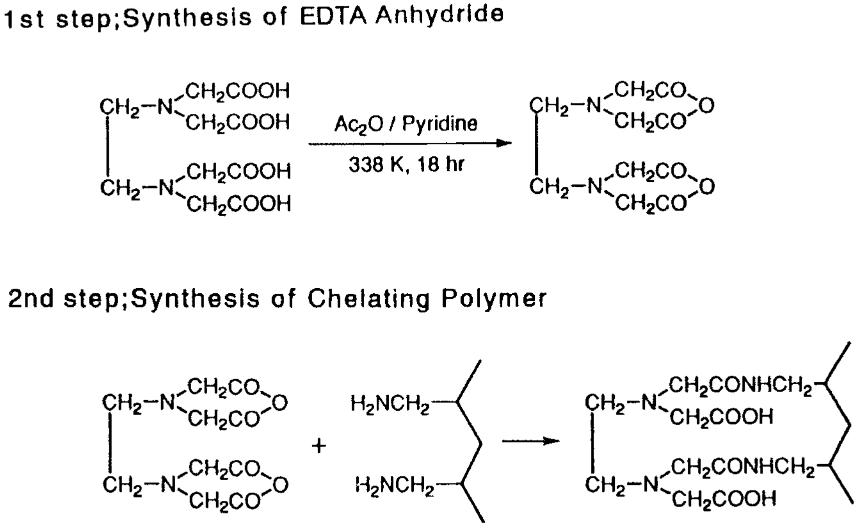
Downloaded At: 11:52 25 January 2011

## EXPERIMENTAL

### Synthesis of New Hydrophilic Chelating Polymer

The hydrophilic chelating polymer was synthesized by introducing EDTA (Nacalai Tesque Inc., Reagent grade) onto polyallylamine [Nitto Boseki Co., PAA-L (20 wt% aqueous solution), nominal molecular weight: 10,000]. The synthesis scheme is shown in Fig. 2. EDTA anhydride was synthesized by a procedure reported previously (13). The product was identified by IR analysis.

The second step described in Fig. 2 is an ideal reaction. In practice, it is thought that polymers might also be produced with the portions shown in Figs. 3(a) and 3(b). Therefore, we synthesized two kinds of chelating polymers using two different solvents. As mentioned below, the two polymers had different solubilities in water. Hereafter, we identify the polymer with higher solubility in water and that with lower solubility as Polymer 1 and Polymer 2, respectively.


1st step;Synthesis of EDTA Anhydride

2nd step;Synthesis of Chelating Polymer

FIG. 2 Synthesis scheme for chelating polymer.

## *Synthesis of Polymer 1*

In a flask, 3.0 g of 20 wt% polyallylamine (PAA) aqueous solution (1.05 × $10^{-2}$ mole of equivalent weight) was dissolved in 480 mL of a 62.5 vol% acetone/water mixture, and the flask was placed in a water bath

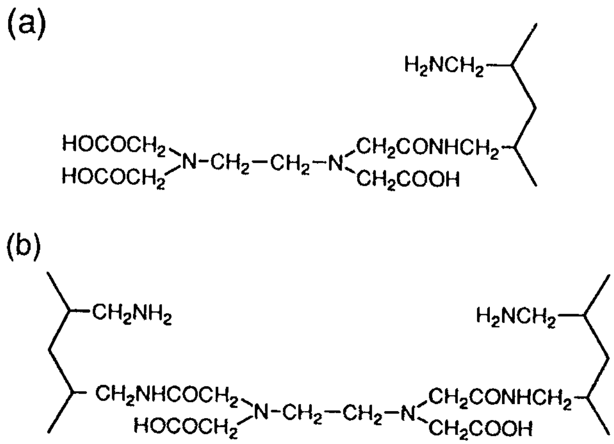


FIG. 3 Possible structures in bonding between polyallylamine and EDTA.

Downloaded At: 11:52 25 January 2011

thermostated at 298 K. EDTA anhydride solution was prepared by dissolving 2.7 g ($1.05 \times 10^{-2}$ mole) of EDTA anhydride in 45 mL of dimethylsulfoxide (DMSO). The mole ratio of PAA estimated by using an equivalent molar weight to that of EDTA anhydride was set at unity. The EDTA anhydride solution was added dropwise to the PAA solution, and the mixture was stirred for 10 minutes. After allowing the mixture to stand for 10 minutes, the product was filtered and dried under vacuum. The product yield was 2.45 g.

### *Synthesis of Polymer 2*

In a four-necked flask equipped with a reflux condenser and a $CaCl_2$ tube, 3.0 g of PAA solution was dissolved in DMSO. After the flask was placed in an oil bath thermostated at 338 K, the EDTA anhydride solution, which was the same as that described above, was added dropwise with stirring, and the mixture was refluxed for 1.5 hours. After cooling the mixture to room temperature, the product was filtered. The product was then washed with acetone, filtered, and dried under vacuum. The yield was 2.57 g.

Downloaded At: 11:52 25 January 2011

## Analytical Measurement of the Chelating Polymers

The chelating polymers were indentified by IR analysis (Japan Spectroscopic Co., IR-810) and elemental analysis. The amount of EDTA introduced onto PAA was investigated by pH titration. Gel permeation chromatography (GPC) measurements (pump: Shimadzu Co., LC-5A; detector: Shimadzu Co., RID-2A; mobile phase: 0.4 mol/dm$^3$ NaCl solution at pH 11.5) were carried out for Polymer 1 (column: Toso Co., TSK gel G5000PWXL) and for PAA (column: Asahi Chemical Industry Co., Asahi-Pack GS-320). GPC measurement could not be carried out for Polymer 2 because of its low solubility in water.

## Adsorption Properties of the Chelating Polymers

$Er^{3+}$ and $Y^{3+}$ aqueous stock solutions were prepared by dissolving $Er_2O_3$ and $Y_2O_3$ (Mitsuwa Chemical Co.) in $HClO_4$ solution and were standardized by titration against the disodium salt of EDTA using arsenazo III as the indicator. A batchwise technique was used to determine the adsorption equilibrium. A mixture (100 mL) containing rare earth metals (both $Er^{3+}$ and $Y^{3+}$ or $Y^{3+}$ alone) and the chelating polymer was stirred for 12 hours at 298 K. The ionic strength of the solution was maintained at 0.1 mol/dm$^3$ by the addition of $KClO_4$. After equilibrium was attained, the solution was filtered using an ultrafilter (UF) membrane. UF experiments were carried out in a stirred cell (Advantec Co., UHP-43K), and the membrane used was Advantec UK-10 (molecular weight cutoff: 10,000). The effective membrane area was 9.1 cm$^2$, and the applied pressure was 5 bar, gauge-controlled by nitrogen gas. The rejection of PAA by this membrane was found to be more than 0.95. After the first portion (about 5 mL) of the permeate was discarded, the rare earth metal concentrations in the next 5 mL of the permeate were analyzed by an inductively coupled plasma emission spectrophotometer (Shimadsu Co., ICPS-1000III).

## RESULTS AND DISCUSSION

### Characteristics of the Chelating Polymers

Figure 4 shows the IR spectra of PAA, Polymer 1, and Polymer 2. The IR spectrum of PAA solution was measured with a Nocolet 205 FT-IR spectrometer by the ATR method (ZnSe). In both polymers the absorption assignable to the amide group (C=O stretching and N—H deformation) was observed at about 1650 cm$^{-1}$, although the spectra of PAA had no such absorption. This shows that EDTA was introduced onto PAA by the formation of the amide bond, as shown in Figs. 2 and 3.

Downloaded At: 11:52 25 January 2011

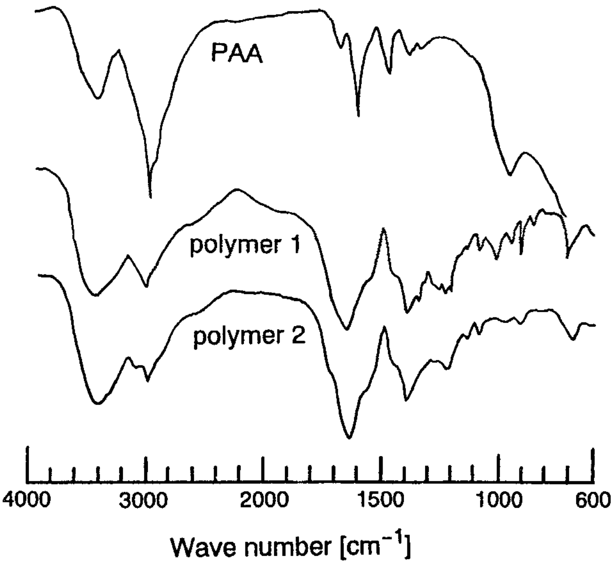


FIG. 4 IR spectra of PAA, Polymer 1, and Polymer 2.

TABLE 2
Elemental Ratios, Chelating Capacities, and Fraction of the Amounts of EDTA Introduced

|  | Polymer 1 | Polymer 2 | 1:1 Bonding case | 1:2 Bonding case |
|---|---|---|---|---|
| C/N ratio | 3.60 | 3.49 | 3.71 | 3.43 |
| Chelating capacity [mmol/g] | 2.90 | 2.77 | 3.03 | 2.70 |
| Fraction of the amounts of EDTA introduced | 80% | 61% | 100% | 50% |

Downloaded At: 11:52 25 January 2011

The results of elemental analysis are shown in Table 2. Because the polymers are hygroscopic, compositions of O and H were not reliable, so only C/N ratios are listed in Table 2. When all EDTA bonds to PAA are at a 1:1 mol ratio, that is, the bonding shown in Fig. 3(a) is formed, the C/N ratio must be 3.71. On the other hand, when all EDTA bonds to PAA are at a 1:2 mol ratio, that is, the bonding shown in Figs. 2 and 3(b) is formed, the C/N ratio becomes 3.43. The C/N ratios obtained for Polymer 1 and Polymer 2 are intermediate between 3.71 and 3.43, which suggests that both polymers contain a mixture of the bondings shown in Figs. 2 and 3. If we assume that for all amino groups in PAA bonded to EDTA in any form,* the chelating capacity and the fraction of the original EDTA that is involved in 1:1 bondings can be calculated from the measured C/N ratios. These values are also included in Table 2. Polymer 1 had a higher chelating capacity and a higher fraction of the EDTA attached than Polymer 2. The EDTA anhydride forms carboxyl groups in the presence of water by hydrolysis. In the synthesis of Polymer 1, the solvent contained more water, as described above. Therefore, Polymer 1 has a greater possibility of forming the 1:1 bonding unit shown in Fig. 3(a). In our opinion, this is the reason for the higher chelating capacity of Polymer 1.

Figure 5 shows the conditions of the aqueous polymer solutions in the absence and presence of $Y^{3+}$. Polymer 1 alone could be dissolved in water and did not precipitate. Polymer 2 had a low solubility in water and was gelatinous in water. After the stirring was stopped, Polymer 2 precipitated. In the presence of $Y^{3+}$, Polymer 1 also became insoluble in water and

---

* Free amino groups, which did not bond to EDTA, probably exist in the chelating polymers. However, because a pair of free amino groups and a 1:1 bonding unit are almost equivalent to the 1:2 bonding unit with respect to the molecular weight, the assumption is useful.

Downloaded At: 11:52 25 January 2011

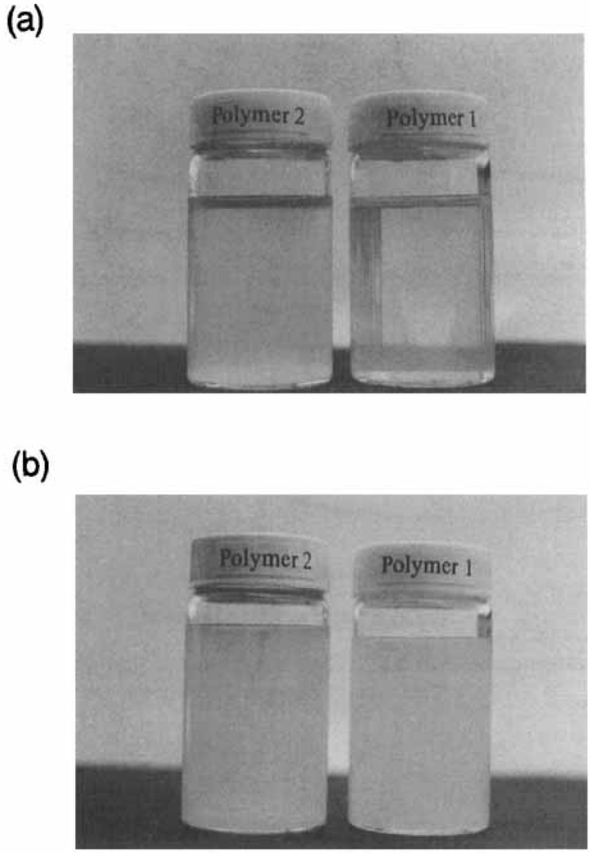


FIG. 5 Conditions of aqueous polymer solutions. (a) Polymer alone (2.0 g/dm$^3$). (b) Both polymer (2.0 g/dm$^3$) and $Y^{3+}$ ($1.0 \times 10^{-3}$ mol/dm$^3$).

precipitated after the stirring was stopped. This is probably because the availability of hydrophilic groups in the polymer decreased due to chelation with $Y^{3+}$. These results demonstrated that Polymer 1 as well as Polymer 2 can be easily recovered by simple sedimentation.

It is well known that the pH titration curve of EDTA has two infection points (14). One of them corresponds to the neutralization of —COOH and the other to that of $—N^{+}HCOO^{-}$. This means that the number of moles required for titration between the two infection points is equal to that of EDTA. Figures 6(a)–(c) shows the pH titration curves and their

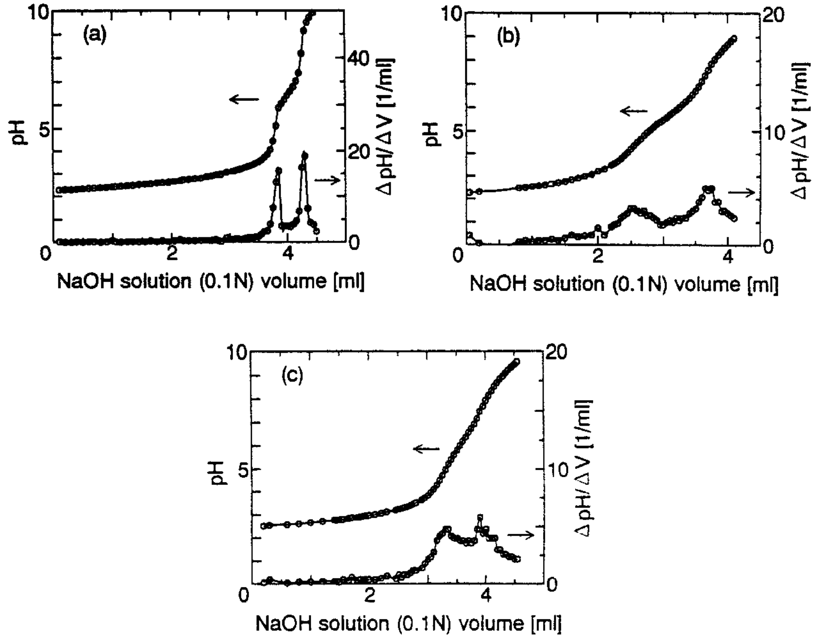


FIG. 6 pH titration curves and their differential forms. (a) EDTA (0.013 g), (b) Polymer 1 (0.077 g), (c) Polymer 2 (0.045 g).

differential forms for EDTA, Polymer 1, and Polymer 2. It was confirmed from the data for EDTA that the number of moles required for titration between the two inflection points agreed with that of EDTA. The infection points of Polymers 1 and 2 in the titration curves were less clear. However, the two peaks were recognized in both differential curves. The chelating capacities obtained from the amounts of titration between the two peaks were 1.55 mmol/g for Polymer 1 and 1.2 mmol/g for Polymer 2. These values are lower than those shown in Table 2. This is probably because all the EDTA introduced onto PAA, which exists in several forms, is not necessarily neutralized in this pH region. The less inflection points for the polymers may also be due to the diversity of the structures of EDTA introduced onto PAA.

The results of GPC measurements are shown in Fig. 7. For PAA, the average molecular weight estimated using polyethylene glycol as a standard was found to be about 20,000, which is roughly equal to the nominal value. On the other hand, the GPC data for Polymer 1 had a broader peak

Downloaded At: 11:52 25 January 2011

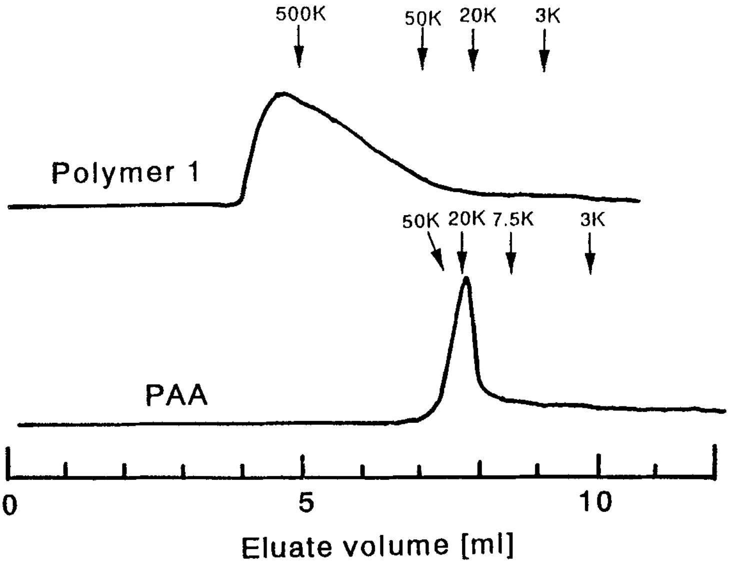


FIG. 7 Results of gel permeation chromatography measurements. The arrows denote the positions at which polyethylene glycols with different molecular weight were eluted.

Downloaded At: 11:52 25 January 2011

compared to that of PAA. The top position of the peak corresponded to a molecular weight of more than 500,000. Even if all the EDTA bonds to PAA at a 1 : 1 mol ratio and the average molecular weight of PAA is 20,000, the molecular weight of the chelating polymer becomes only 70,000. The results of GPC measurements indicate that PAA was crosslinked via EDTA. This is evidence of the formation of the bonding type shown in Fig. 3(b). Polymer 2 contained less 1:1 bonding units. This leads us to presume that Polymer 2 was highly crosslinked and had a higher molecular weight so that it was less hydrophilic.

Figure 8 shows the adsorption isotherm for various initial $Y^{3+}$ concentrations. The solid line in this figure denotes the adsorption amounts in the case where all the initial rare earth metal was adsorbed. It was confirmed from the preliminary experiment that $Y^{3+}$ hardly adsorbed on PAA where [PAA] was 2.0 g/dm$^3$ and [$Y^{3+}$] was $1.0 \times 10^{-3}$ mol/dm$^3$ at pH 6.2. In the low $Y^{3+}$ concentration region, almost all $Y^{3+}$ adsorbed on Polymer 1, which indicates that the adsorption ability of the polymer was increased greatly by introducing EDTA onto PAA. As the $Y^{3+}$ concentration increased, Y adsorption approached a constant value, which corre-

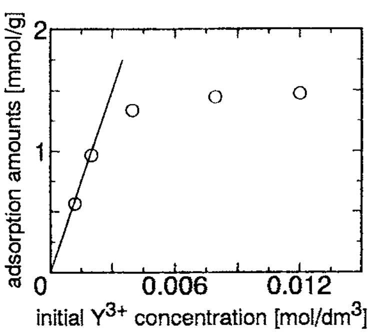


FIG. 8 Adsorption isotherm for $Y^{3+}$. Polymer: Polymer 1, pH 3.0; [Polymer 1] = 2.0 g/ $dm^3$. The solid line denotes the adsorption amounts in the case where all initial rare earth metal adsorbed.

Downloaded At: 11:52 25 January 2011

sponds to the adsorption (chelating) capacity. The measured chelating capacity was about 1.5 mmol/g and was close to that measured by pH titration. Only EDTA bonded to PAA which can be neutralized by the pH titration may be able to chelate with the rare earth metal. However, further investigation is necessary to examine this in detail.

## Separation Properties by Adsorption on the Chelating Polymers for Er and Y

Figure 9 shows the effects of pH on the selectivity (β) and the total adsorption ($T$). β is defined as

$$\beta = ([\mathrm{Er}]_{\mathrm{ad}}/[\mathrm{Er}^{3+}])/([\mathrm{Y}]_{\mathrm{ad}}/[\mathrm{Y}^{3+}]) \quad (1)$$

where the subscript ad denotes the species adsorbed. For comparison, we calculated β and $T$ for the case of EDTA by considering the following complexations between rare earth metals and EDTA, the dissociation of EDTA, and the mass balance with respect to metals and EDTA.

$$K_{\mathrm{ErEDTA}} = [\mathrm{ErEDTA}^-]/([\mathrm{Er}^{3+}][\mathrm{D}^{4-}]) \quad (2)$$

$$K_{\mathrm{YEDTA}} = [\mathrm{YEDTA}^-]/([\mathrm{Y}^{3+}][\mathrm{D}^{4-}]) \quad (3)$$

$$K_1 = [\mathrm{H_3D}^-][\mathrm{H}^+]/[\mathrm{H_4D}] \quad (4)$$

$$K_2 = [\mathrm{H_2D}^{2-}][\mathrm{H}^+]/[\mathrm{H_3D}^-] \quad (5)$$

$$K_3 = [\mathrm{HD}^{3-}][\mathrm{H}^+]/[\mathrm{H_2D}^{2-}] \quad (6)$$

$$K_4 = [\mathrm{D}^{4-}][\mathrm{H}^+]/[\mathrm{HD}^{3-}] \quad (7)$$

Downloaded At: 11:52 25 January 2011

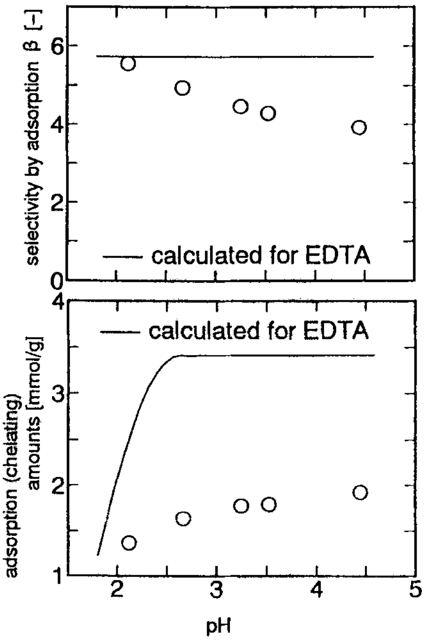


FIG. 9 Effect of pH on total adsorption amounts and selectivity by adsorption in Y/Er separation system. Polymer: Polymer 1, $[Y]_0 = [Er]_0 = 2.0 \times 10^{-3}$ mol/dm$^3$; [Polymer 1] = 2.0 g/dm$^3$.

$$[Er]_0 = [Er^{3+}] + [ErEDTA^-] \tag{8}$$

$$[Y]_0 = [Y^{3+}] + [YEDTA^-] \tag{9}$$

$$\begin{aligned}[EDTA]_0 = [ErEDTA^-] + [YEDTA^-] + [H_4D] + [H_3D^-] \\ + [H_2D^{2-}] + [HD^{3-}] + [D^{4-}]\end{aligned} \tag{10}$$

Here, $K_{\mathrm{ErEDTA}}$ and $K_{\mathrm{YEDTA}}$ are the stability constants of EDTA complexes, and $K_1$–$K_4$ are the dissociation constants of EDTA. EDTA is abbreviated as $H_4D$, and the subscript 0 denotes the initial total concentration. The protonations of EDTA complexes were ignored because their stability constants are small (15). The constants used for the calculation are summarized in Table 3. The solid lines in Fig. 9 are the calculated results. For the initial EDTA concentration, we used the value of $3.86 \times 10^{-3}$ mol/dm$^3$, which is equal to the effective concentration of EDTA introduced onto PAA at pH 4.5 [(1.93 mmol/g) × (2.0 g/dm$^3$)].

TABLE 3
Value of Constants Used for the Calculations

| | |
|---|---|
| $K_{\mathrm{ErEDTA}}$ [dm$^3$/mol] | $10^{18.85}$[a] |
| $K_{\mathrm{YEDTA}}$ [dm$^3$/mol] | $10^{18.09}$[a] |
| $K_1$ [mol/dm$^3$] | $10^{-2.07}$[b] |
| $K_2$ [mol/dm$^3$] | $10^{-2.75}$[b] |
| $K_3$ [mol/dm$^3$] | $10^{-6.24}$[b] |
| $K_4$ [mol/dm$^3$] | $10^{-10.34}$[b] |

[a] Schwarzenbach et al. (16).
[b] Wikberg and Ringbom (17).

Downloaded At: 11:52 25 January 2011

As pH increased, β decreased while $T$ increased. When a usual chelating agent such as EDTA is used, β must be constant and $T$ must also be constant for almost all EDTA complexes with metal ions. This behavior is observed in the calculated results. At a low pH, the calculated results for $T$ decrease. This is because [$D^{4-}$] is extremely low due to the protonation of EDTA. In our opinion, the results for the chelating polymer are explained as follows. The chelating polymer contains various types of ligand like EDTA, as described above. Although each ligand has a different chelating ability, even a ligand with low ability is able to chelate with metal ions at some higher pH because the chelating ability increases due to dissociation of the carboxyl groups. This is the reason why adsorption due to chelating increased with pH. Generally, a ligand with a low chelating ability also has a low selectivity for each rare earth metal. For example, the stability constants and the selectivities for each rare earth metal are known to increase in the order of imminodiacetic acid (IMDA), nitrilotriacetic acid (NTA), and EDTA (18). Therefore, β might decrease when the adsorption amounts increase at higher pH; that is, a ligand with low chelating ability begins to chelate with the rare earth metals. The separation properties of the synthesized chelating polymer were comparable to that of the starting EDTA. This suggests that the chelating polymer has the possibility of functioning effectively for separation by solvent extraction when it is included in the aqueous phase.

Figure 10 shows the effects of the initial rare earth metal concentrations on β, $T$, and the ratios of residual free metal concentrations $R$. The solid lines are also the calculated results in the case of EDTA when using the value of $3.92 \times 10^{-3}$ mol/dm$^3$ as the initial EDTA concentration, which is equal to the effective concentration of EDTA introduced onto PAA at the largest $T$. For both Polymers 1 and 2, β decreased slightly while $T$ increased with an increase in the initial metal concentrations. As the metal

Downloaded At: 11:52 25 January 2011

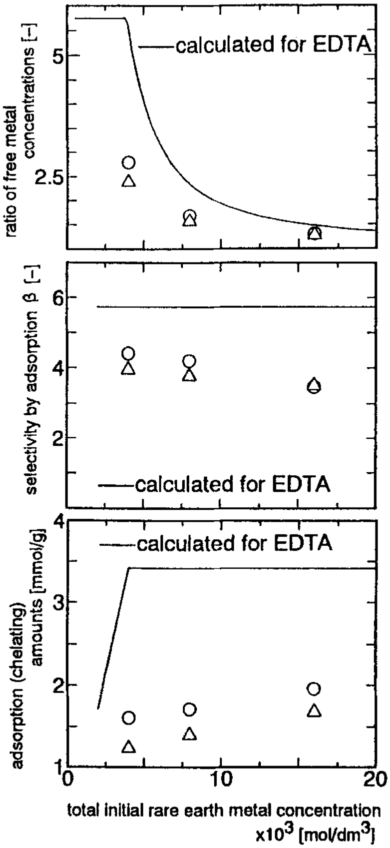


FIG. 10 Effect of initial rare earth metal concentrations on total adsorption amounts, selectivity by adsorption, and ratios of residual free metal concentrations in Y/Er separation system. (O) Polymer 1, (Δ) Polymer 2, $[Y]_0 = [Er]_0$, pH 3.0, [polymer] = 2.0 g/dm$^3$.

concentrations increase, the degree of chelation of the polymer increases. Therefore, the above-mentioned explanation is also useful in this case to explain the results. The values of $T$ for Polymer 2 were lower than those for Polymer 1. This agrees with the fact that Polymer 2 has a lower chelating capacity, as shown in Table 2. Polymer 2 also showed a slightly lower β. Polymer 2 consisted of more structures like those shown in Figs. 2 and 3(b). Because these ligands have fewer carboxyl groups, their chelating abilities are low, which may lead to the low selectivity of Polymer 2.

In solvent extraction involving a chelating agent in the aqueous phase, only the free rare earth metal ions can be extracted when a cation-exchange-type organophosphorus extractant is used (6). Therefore, the ratios of the free metal concentrations in the presence of a chelating polymer are important in considering the separation factor in the extraction. In the presence of EDTA, $R$ ($[Y^{3+}]/[Er^{3+}]$), is given by

$$R = (K_{ErEDTA}/K_{YEDTA})([Y]_{ad}/[Er]_{ad}) \tag{11}$$

When $[Y]_0$ is equal to $[Er]_0$ and the initial total rare earth metal concentration is smaller than $[EDTA]_0$, almost all metals complex with EDTA so that the highest value of $R$, which is equal to $K_{ErEDTA}/K_{YEDTA}$ (= 5.75), is obtained. As the initial total metal concentrations increase and become larger than $[EDTA]_0$, the ratio $[Y]_{ad}/[Er]_{ad}$ becomes lower than unity. This leads to a decrease in $R$. These tendencies are clearly observed in the calculated solid line in Fig. 10. When chelating polymers were used, $R$ also decreased with an increase in the initial metal concentrations. In the low metal concentration regions, the values of $R$ for the chelating polymers decreased more compared to the case for EDTA because the total adsorption by the polymers was not constant and decreased.

Downloaded At: 11:52 25 January 2011

## CONCLUSIONS

New hydrophilic chelating polymers were synthesized by introducing EDTA onto polyallylamine. The polymers were analyzed by IR analysis, elemental analysis, GPC measurement, and pH titration. It was found that the structures of EDTA introduced varied and the polyallylamines were crosslinked. Although the two kinds of polymers produced using different solvents had different solubilities in water, both polymers were naturally precipitated in the presence of rare earth metals. This suggests that in a solvent extraction system including these chelating polymers, the recovery of the chelating agent is easier than in a system including the usual low molecular weight chelating agents.

The adsorption properties of $Y^{3+}$ and $Er^{3+}$ on these polymers were investigated. For comparison, we also calculated the chelating properties of EDTA. The separation properties due to adsorption on the chelating polymers for $Y^{3+}$ and $Er^{3+}$ were comparable to those by EDTA. The chelating polymers had separation factors that decreased and total adsorptions that increased with increasing pH or initial metal concentrations. However, these properties were constant in the presence of EDTA.

## ACKNOWLEDGMENTS

We wish to thank Prof. A. Oku, Kyoto Institute of Technology, and members of his research group for their guidance in the synthesis technique for the chelating polymer. We also thank Nitto Boseki Co. Ltd. for supplying the polyallylamine solution.

## SYMBOLS

| | |
|---|---|
| HR | acidic organophosphorus extractant |
| $K_{\mathrm{ErEDTA}}$ | stability constant of Er–EDTA complex ($\mathrm{dm^3/mol}$) |
| $K_{\mathrm{YEDTA}}$ | stability constant of Y–EDTA complex ($\mathrm{dm^3/mol}$) |
| $K_1$–$K_4$ | dissociation constants of EDTA ($\mathrm{mol/dm^3}$) |
| $k_b$ | dissociation rate constant of DTPA complex [$\mathrm{dm^6/(mol^2 \cdot s)}$] |
| PAA | polyallylamine |
| Polymer 1 | chelating polymer with higher solubility in water |
| Polymer 2 | chelating polymer with lower solubility in water |
| $R$ | ratio of residual free metal concentrations in Y/Er separation system |
| $T$ | total adsorption amounts (mmol/g) |

### Subscripts

| | |
|---|---|
| ad | species adsorbed |
| 0 | initial concentration |

### Superscript

| | |
|---|---|
| — | species in organic phase |

### Greek

| | |
|---|---|
| $\beta$ | selectivity by adsorption in Y/Er separation system |

## REFERENCES

1. T. B. Pierce and P. F. Peck, *Analyst*, *88*, 217 (1963).
2. Y. Minagawa, T. Kaneko, F. Yajima, K. Yamaguchi, and T. Yoshitome, Japan Patent Kokai 52-150717 (1977).
3. Y. Minagawa, K. Kojima, T. Kaneko, F. Yajima, K. Yamaguchi, T. Miwa, and T. Yoshitome, *Rare Earth Mod. Sci. Technol.*, *2*, 139 (1980).
4. P. R. Danesi and C. Cianetti, *Sep. Sci. Technol.*, *17*(7), 969 (1982).
5. S. Al-Fared, F. Zantuti, and Y. S. Krylov, *J. Radioanal. Nucl. Chem.*, *125*(2), 381 (1988).
6. H. Matsuyama, T. Okamoto, Y. Miyake, and M. Teramoto, *J. Chem. Eng. Jpn.*, *22*, 627 (1989).
7. R. Kopunec and J. Kovalancik, *J. Radioanal. Nucl. Chem.*, *129*(2), 295 (1989).
8. T. Hirai and I. Komasawa, *J. Chem. Eng. Jpn.*, *24*, 731 (1991).

Downloaded At: 11:52 25 January 2011

9. Y. Minagawa and F. Yajima, *Bull. Chem. Soc. Jpn.*, *65*, 29 (1992).
10. B. Weaver and F. A. Kappelmann, *J. Inorg. Nucl. Chem.*, *30*, 263 (1968).
11. T. Moeller and L. C. Thompson, *Ibid.*, *24*, 499 (1962).
12. H. Matsuyama, T. Okamoto, and M. Teramoto, *J. Chem. Eng. Jpn.*, *22*, 460 (1989).
13. T. Miyata, F. Kubota, M. Goto and F. Nakashio, *Proceedings of Symposium on Solvent Extraction*, 1991, pp. 67–74.
14. K. Urano, *Nyumon Kireto Kagaku* (in Japanese), Nankodo, Tokyo, 1969, pp. 67–70.
15. E. Brucher, C. E. Kukri, and L. Zekany, *J. Inorg. Nucl. Chem.* *36*, 2620 (1974).
16. G. Schwarzenbach, R. Gut, and G. Anderegg, *Helv. Chim. Acta*, *37*, 937 (1954).
17. H. Wikberg and A. Ringbom, *Suom. Kem.*, *41*, 177 (1968).
18. A. Ringbom, *Complexation in Analytical Chemistry*, Wiley, New York, 1963.

*Received by editor December 14, 1994*
*Revision received May 23, 1995*

Downloaded At: 11:52 25 January 2011