

# Studies on Selective Adsorption Resins. XXXIII. Behavior of Macroreticular Chelating Resins Containing Phosphinic and/or Phosphonic Acid Groups in the Adsorption of Trivalent Lanthanides

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## SYNOPSIS

The effect of the crosslinking and the porosity of the chelating resins containing phosphinic and/or phosphonic acid groups (RSP and RCSP) on uptake of trivalent lanthanides was studied; RSP and RCSP were prepared by hydrolysis of condensation products of phosphorus trichloride with styrene–divinylbenzene copolymer beads (RS) and with chloromethylated RS, respectively. From a series of RSs synthesized by systematically changing the amount of the crosslinker (divinylbenzene) or the porogen (2,2,4-trimethylpentane), RSPs and RCSPs with different degrees of crosslinking and with different porosities were derived. Measurements of their uptake of La(III), Gd(III), or Yb(III) have clarified that RSP and RCSP with moderately crosslinked highly porous structures exhibit high capacities toward the lanthanides. Using these optimized RSP and RCSP and their respective oxidized derivatives RSPO and RCSP, the distribution of all lanthanides(III) except for Pm(III) from aqueous hydrochloric acid solutions (0.1–1M) was examined. The distribution of each lanthanide(III) at a given concentration of the acid increases in the order RCSP  $\approx$  RCSP < RSPO < RSP. Their lanthanide selectivity patterns resemble one another; the selectivity increases with increasing the atomic number of the lanthanides except for the elements from Sm to Ho. In order to illustrate usefulness of these resins in the separation of lanthanides, the chromatographic separation of La(III), Nd(III), and Sm(III) was conducted using columns packed with RCSP. The three lanthanides were successfully separated by the elution with 0.5M hydrochloric acid solution without use of any organic complexing reagents, such as EDTA. © 1994 John Wiley & Sons, Inc.

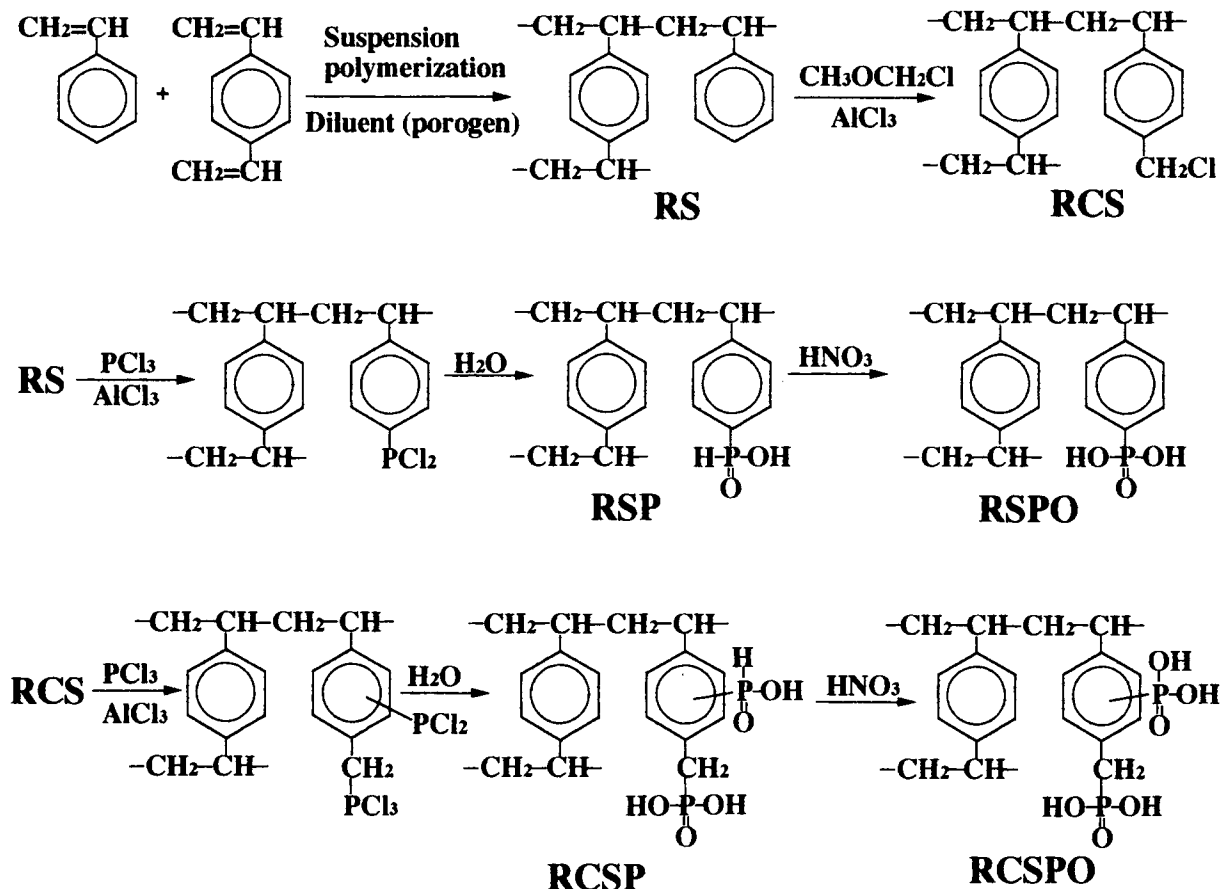
## INTRODUCTION

In previous studies,<sup>1,2</sup> we have reported that macroreticular chelating resins containing phosphinic and/or phosphonic acid groups exhibit large capacities as well as high selectivity toward hard Lewis acid cations, such as uranyl and ferric ions. More recently, Alexandratos et al. have also reported the similar phenomena.<sup>3</sup> Since hardness of lanthanide ions as the Lewis acid increases with an increase in their atomic numbers,<sup>4</sup> of interest is the adsorption behavior of these resins toward lanthanides(III).

Chelating or cation exchange resins based on oxyacids of phosphorus have been reported from as early as the mid-1950s.<sup>5–14</sup> However, detailed works on their adsorption behavior toward lanthanides(III) are rare; especially, little is known about the effect of macroreticular structures (physical pore structures) of the resins on the uptake of lanthanides(III).

In this work, a series of the chelating resins containing phosphinic and/or phosphonic acid groups (RSP and RCSP) with various degrees of crosslinking as well as with different physical pore structures has been prepared (Scheme 1),<sup>1,2</sup> and their adsorption behavior toward lanthanides(III) was studied in order to clarify the effect of the crosslinking as well as the porosity on the uptake of lan-

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**Scheme 1** Routes for the preparation of the chelating resins RSP, RSPO, RCSP, and RCSP.

thanides(III). From these RSPs and RCSPs (12 kinds of each), RSP and RCSP with the optimized performances were selected, and their respective oxidized derivatives RSPO and RCSP were prepared. The distribution of all lanthanides(III) except for Pm(III) from aqueous hydrochloric acid media was studied using these four resins, and one of the RCSPs was applied to the chromatographic separation of La(III), Nd(III), and Sm(III). Hereafter, lanthanides(III) are represented by omitting their valency for simplicity.

## EXPERIMENTAL

### Preparation of Chelating Resins and Their Fundamental Properties

Scheme 1 shows routes for the preparation of the four kinds of chelating resins: RSP, RSPO, RCSP, and RCSP. Detailed procedures of the preparation were reported elsewhere.<sup>1,2</sup> Properties of the result-

ing chelating resins, such as phosphorous contents, cation exchange capacities, and so on, were also evaluated according to the reported methods.<sup>1,2</sup> A series of RSP(*X*)-*Y* were derived from RS(*X*)-*Y*. Here, *X* means nominal mole percent of divinylbenzene (degree of crosslinking) and *Y* is volume percent of 2,2,4-trimethylpentane (porogen) per the monomeric mixtures in the suspension polymerization. Similarly, a series of RCSP(*X*)-*Y* were prepared from their precursory copolymers RCS(*X*)-*Y*, which were obtained by the chloromethylation of RS(*X*)-*Y*.<sup>1</sup> The properties of the resulting RSP(*X*)-*Y* and RCSP(*X*)-*Y* are summarized in Tables I and II, respectively. The moderately cross-linked highly porous RSP(10)-100 and RCSP(10)-100 were prepared in a large scale for the selectivity and separation studies as well as for the preparation of their respective oxidation derivatives RSPO(10)-100 and RCSP(10)-100. Properties of these four resins are listed in Table III with those of a conventional cation exchange resin SP-120. All resins

**Table I Properties of Chelating Resins RSPs**

Symbol for Chelating Resin <sup>a</sup>	Specific Surface Area (m <sup>2</sup> /g)	Phosphorous Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt-splitting Capacity (meq/g)	Volume of Dry Resin (mL/g)	Volume of Wet Resin (mL/g)
RSP(3)-100	—	5.39	5.3	2.8	1.5	1.7
RSP(5)-100	5.7	5.29	5.2	2.5	1.6	1.9
RSP(10)-100	36.2	4.77	4.4	2.1	2.4	2.9
RSP(15)-100	53.7	3.97	4.0	1.7	2.5	2.6
RSP(20)-100	67.6	3.74	3.6	1.5	2.9	3.3
RSP(30)-100	93.4	3.19	3.1	1.3	2.8	3.3
RSP(10)-0	—	2.52	2.1	1.0	1.5	1.6
RSP(10)-30	—	4.19	3.9	1.9	1.5	1.7
RSP(10)-60	1.2	4.13	3.7	1.9	1.5	1.7
RSP(10)-80	25.1	4.29	4.3	1.9	1.8	2.1
RSP(10)-120	24.4	3.97	4.2	1.8	3.2	3.9
RSP(10)-140	3.0	3.65	4.0	1.7	4.1	4.9

<sup>a</sup> For meanings of the symbols, refer to the experimental section of the text.

were used in the H form and their particle size was 32–60 mesh, unless otherwise specified.

#### Adsorption Capacity for Lanthanides

Into an Erlenmeyer flask (100 mL), 0.125 g of a dry resin and 50 mL of 0.01 M ( $M = \text{mol}/\text{dm}^3$ ) aqueous solution of a lanthanide trichloride were taken. After the flask was shaken with a mechanical shaker at 30°C for 24 h, the resin and the solution were im-

mediately separated. An aliquot of the separated solution was titrated against a standardized EDTA solution. From the concentration decrease in the solution, the uptake of the lanthanide was calculated.

#### Adsorption Rate

Adsorption rates were measured for RCSP(10)-100 and RSP(10)-140. In the case of RCSP(10)-100, which took up lanthanides rapidly, 0.2 g of the dried

**Table II Properties of Chelating Resins RCSPs**

Symbol for Chelating Resin <sup>a</sup>	Specific Surface Area (m <sup>2</sup> /g)	Phosphorous Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt-splitting Capacity (meq/g)	Volume of Dry Resin (mL/g)	Volume of Wet Resin (mL/g)
RCSP(3)-100	0.1	4.90	9.3	2.8	1.4	2.5
RCSP(5)-100	0.1	4.84	9.2	2.6	1.3	2.6
RCSP(10)-100	25.5	4.19	7.2	2.1	2.3	3.2
RCSP(15)-100	38.6	3.77	5.9	1.7	2.4	3.1
RCSP(20)-100	48.8	3.52	5.1	1.5	2.5	3.1
RCSP(30)-100	79.7	2.81	3.9	1.2	2.8	3.2
RCSP(10)-0	—	1.10	0.8	0.5	1.5	1.6
RCSP(10)-30	—	0.52	0.2	0.2	1.5	1.5
RCSP(10)-60	0.2	3.19	5.3	1.6	1.7	2.2
RCSP(10)-80	4.5	4.19	7.3	2.0	1.7	2.5
RCSP(10)-120	19.7	4.13	6.7	1.9	2.8	3.7
RCSP(10)-140	5.1	3.87	6.1	1.7	3.8	4.5

<sup>a</sup> For meanings of the symbols, refer to the experimental section of the text.

**Table III Properties of Resins Used in the Selectivity and Separation Studies of Lanthanides**

Symbol for Chelating Resin <sup>a</sup>	Specific Surface Area (m <sup>2</sup> /g)	Phosphorous Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt-splitting Capacity (meq/g)	Volume of Dry Resin (mL/g)	Volume of Wet Resin (mL/g)
RSP(10)-100 <sup>a</sup>	32.4	4.90	4.9	2.1	2.5	3.0
RSPO(10)-100 <sup>b</sup>	19.9	3.84	7.7	2.3	2.3	2.7
RCSP(10)-100 <sup>a</sup>	23.7	4.19	7.4	2.1	2.2	3.1
RCSP(10)-100 <sup>b</sup>	19.6	3.87	7.8	2.3	1.8	3.2
SP-120 <sup>c</sup>	24.7	—	3.6	3.6	2.2	3.2

<sup>a</sup> RSP(10)-100 and RSP(10)-100 shown here were separately prepared from those described in Tables I and II.

<sup>b</sup> RSPO(10)-100 and RCSP(10)-100 were derived from RSP(10)-100 and RSP(10)-100 given in this table, respectively.

<sup>c</sup> Macroreticular strong-acid cation exchange resins containing sulfonic acid groups.

resin and 40 mL of water were taken into a three-necked flask (300 mL) equipped with a stirrer. After the temperature of the mixture was attained at 30°C, 40 mL of a lanthanide trichloride solution (0.02 M) previously maintained at 30°C was added to the stirred mixture. Then, an aliquot of the stirring solution was sampled at pertinent intervals, and the concentration of the lanthanide in the sampled solution was determined by means of inductively coupled plasma-atomic emission spectrometry (ICP-AES). From the concentration decrease in the solution, the lanthanide uptake at the sampled time was calculated.

In the case of RSP(10)-140, which showed slow adsorption kinetics, 0.2 g of the resin and 80 mL of a 0.01 M lanthanide trichloride solution were taken into a 100-mL flask with a ground joint stopper, and the flask was shaken with a mechanical shaker at 30°C for a long while (80 days). The lanthanide uptake was determined at pertinent intervals as described above.

### Distribution Study

Into an Erlenmeyer flask (100 mL), 40 mg of a dry resin and 25 mL of an aqueous solution of a lanthanide trichloride (0.0001 M) were taken, and the flask was shaken at 30°C for 15 h; here, the acidity of the solution was adjusted with hydrochloric acid. Then, the concentration of the lanthanide in the supernatant was determined by means of ICP-AES. From a decrease in the concentration of the lanthanide in the solution, an adsorption percentage and a distribution coefficient ( $K_D$ ) were calculated. Here,  $K_D$  is designated as follows:

$$K_D = \frac{\text{amount of metal ion in resin (mmol/g)}}{\text{amount of metal ion in solution (mmol/ml)}}$$

### Breakthrough Study

A glass column (inner diameter 1.0 cm) was packed with 1 mL of wet settled RCSP(10)-100. An aqueous solution containing La or three lanthanides (La, Gd, and Yb) was downflow supplied to the column at a constant flow rate. The column effluent was fractionated by a fraction collector, and the concentration of each lanthanide in all fractions was determined by means of ICP-AES. The flow rate of solutions is represented by a space velocity ( $h^{-1}$ ), which is the ratio of flow rate of the solution (mL/h) to resin bed volume.

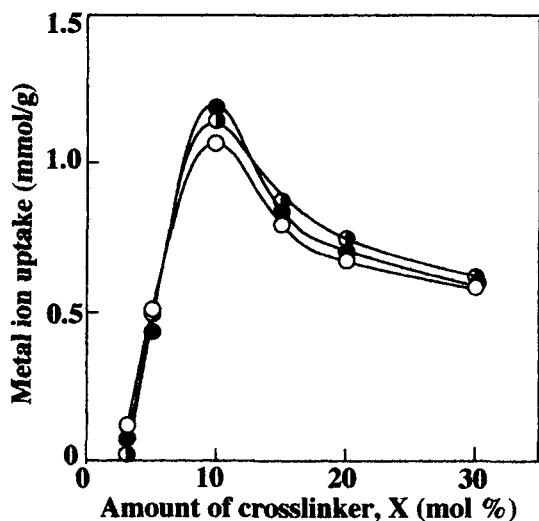
### Chromatographic Separation of La, Nd, and Sm

Into a glass column (inner diameter 1.0 cm, length ca. 80 cm), 50 mL of the wet settled RCSP(10)-100 was packed. After known amounts of the lanthanides were loaded to the column, a hydrochloric acid solution was downflow supplied to the column at a given space velocity. The subsequent procedures were almost the same as those in the breakthrough study. Detailed conditions are described in a later section with the results.

## RESULTS AND DISCUSSION

### Uptake of La, Gd, or Yb by a Series of RSPs and RCSPs

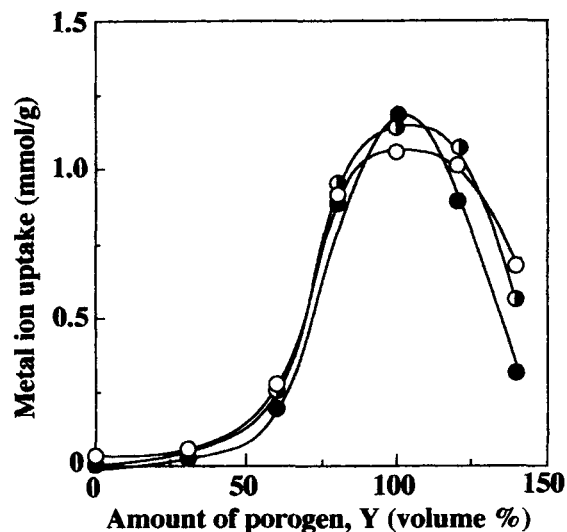
In order to clarify the effect of the crosslinking and the porosity of RSPs and RCSPs on their lanthanide uptake, the uptake of three lanthanides (La, Gd, and Yb) by a series of RSP(X)-Y and RCSP(X)-Y after 24 h shaking was examined. Figure 1 shows the uptake of the lanthanides by the series RSP(X)-100, i.e., the effect of crosslinking. Surprisingly, the



**Figure 1** Effect of crosslinking on uptake of lanthanides with RSP(*X*)-100: (○) La, (◐) Gd, (●) Yb.

lightly crosslinked RSP(3)-100 and RSP(5)-100 cannot efficiently take up the lanthanides in spite of their high contents of the functional group. On the other hand, the highly crosslinked RSPs [RSP(15)-100–RSP(30)-100] can efficiently adsorb the lanthanides, even though their functional group contents are less than those of the lightly crosslinked ones. Thus, the physical pore structures of the resins clearly have significant meanings in the uptake of the lanthanides by the polymer bound phosphinic acid groups. As listed in Table I, the contents of the functional groups in RSP(*X*)-100 decrease with increasing *X*, whereas the reversed tendency can be seen in the dependence of their specific surface areas on *X*. Thus, it seems that the maximum lanthanide uptake at *X* = 10 results from the interaction of the opposing dependencies of these two factors on *X*.

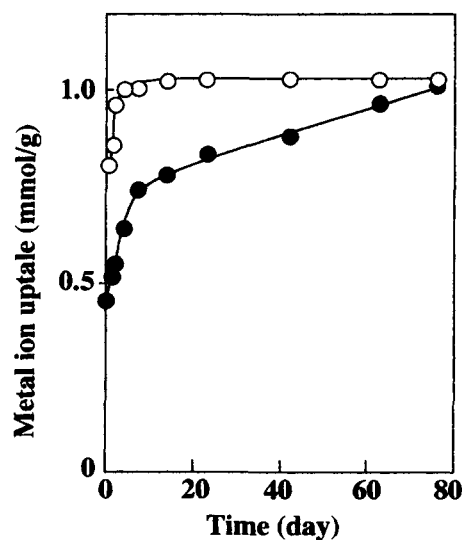
Figure 2 shows the uptake of the three lanthanides with the series RSP(10)-*Y*. As summarized in Table I, the functional group contents of RSP(10)-*Y* are nearly equal except for RSP(10)-0, and the maximum of the specific surface area is observed at *Y* = 100. Thus, it can be said that the lanthanide uptake profile shown in Figure 2 can be closely correlated to that of the specific surface areas of the series RSP(10)-*Y*. However, the uptake of La, Gd, and Yb with RSPs does not always increase with the order La < Gd < Yb. The extreme discrepancy can be seen between RSP(10)-100 and RSP(10)-140. The increasing order of the lanthanide uptake is completely reversed between the two resins. This suggests that the real equilibrium is not always es-



**Figure 2** Effect of porosity on uptake of lanthanides with RSP(10)-*Y*: (○) La, (◐) Gd, (●) Yb.

tablished in the uptake of the lanthanides by RSPs. Indeed, the rate of the uptake of Yb by RSP(10)-140 was extremely slower than that of La, as shown in Figure 3. Clearly, the extremely slow kinetics for the uptake of the heavy lanthanides like Yb is the origin for the anomalous phenomenon mentioned above.

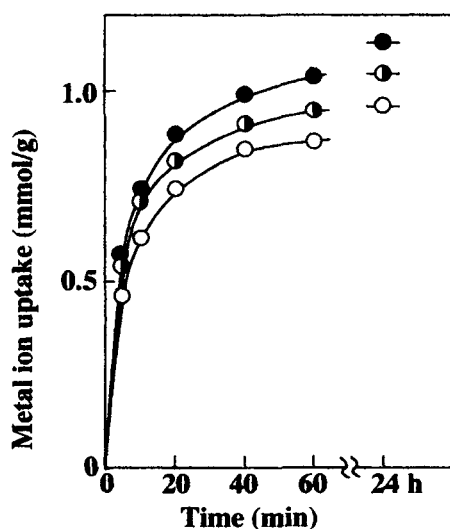
In RSPs, the phosphinic acid groups are directly introduced into phenyl groups of the copolymer matrices (Scheme 1). Consequently, they cannot flexibly change their conformation suitable for coordi-



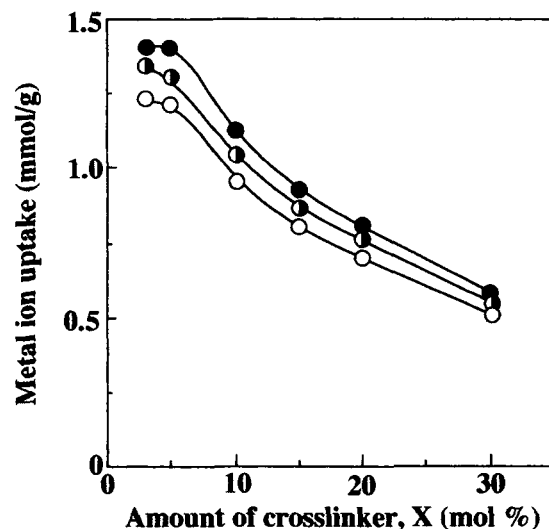
**Figure 3** Time course for uptake of La or Yb with RSP(10)-140 at 30°C: (○) La, (●) Yb.

nation to lanthanide ions unless enough space for their conformational change is provided by the highly porous structures or high swelling. Unfortunately, RSPs cannot highly swell, as shown in Table I. It is then anticipated that the functional groups located on the surfaces of microspheres<sup>15</sup> in RSPs may more rapidly and more efficiently take up lanthanides than those located in the bulk of the microspheres. With increasing the specific surface area, the proportion of the functional groups located on the surfaces of the microspheres will increase. Then, the highly porous RSPs are suitable for the rapid and high uptake of lanthanides. In addition, it seems that the time course of the Yb uptake by lowly porous RSP(10)-140 (Fig. 3) consists of two kinetic paths: the rather rapid and extremely slow ones, which probably correspond to the uptake by the functional groups located on the surfaces of the microspheres, and that by groups located in the bulk of the microspheres.

Opposed to the case of RSPs, RCSPs much more rapidly take up the lanthanides than RSPs, as illustrated in Figure 4; here RCSP(10)-100 exhibits about 90% of the equilibrium uptake at 1 h. Figure 5 shows the lanthanide uptake profile for the resin series RCSP(*X*)-100, i.e., the effect of crosslinking. This profile is closely correlated to their phosphorous contents (cation exchange capacities) but not to their specific surface areas. Although the lightly crosslinked RCSP(3)-100 and RCSP(5)-100 do not have the significant specific surface areas, they can effectively take up the lanthanides, contrary to RSP(3)-100 and RSP(5)-100. This can be ascribed



**Figure 4** Time course for uptake of La, Gd, or Yb with RCSP(10)-100 at 30°C: (○) La, (●) Gd, (●) Yb.



**Figure 5** Effect of crosslinking on uptake of lanthanides with RCSP(*X*)-100: (○) La, (●) Gd, (●) Yb.

to the difference in the swelling between the lightly crosslinked RCSPs and RSPs. As shown in Tables I and II, the lightly crosslinked RCSPs swell much more than the corresponding RSPs. However, too much swelling of the lightly crosslinked RCSPs causes some problems in their practical use, especially in column operations. Then, the effect of the porosity of the moderately crosslinked RCSPs (10 mol % of the crosslinker) was studied. In the series RCSP(10)-*Y* (Table II), the contents of phosphorus of the resins with the physical pore structures (*Y* values of 60–140) are much greater than those of the resins without the porosity (*Y* = 0, 30). This indicates important roles of the porosity in the introduction of the functional groups into the moderately crosslinked precursors RCS(10)-*Y*. Figure 6 shows the lanthanide uptake profile for the series RCSP(10)-*Y*. This profile can be correlated to the functional group contents as well as to the specific surface areas of RCSP(10)-*Y*. Thus, it can be concluded that the highly porous structure of the moderately crosslinked RCSPs is preferable for the high uptake of lanthanides.

In RCSPs, there are two types of the functional groups: phosphinic and methylenephosphonic acid groups (Scheme 1). As shown in Table II, however, the cation exchange capacities of RCSPs are nearly twice their phosphorous contents. This means that the majority are methylenephosphonic acid groups, since phosphonic acid groups are dibasic but phosphinic ones are monobasic. Thus, the majority of the functional groups in RCSPs are linked through methylene groups to the phenyl groups of the resin

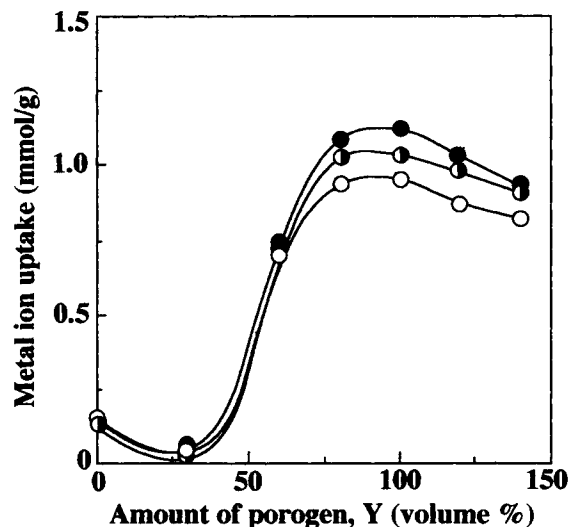


Figure 6 Effect of porosity on uptake of lanthanides with RCSP(10)-Y: (○) La, (○) Gd, (●) Yb.

matrices. This mode of functionalization gives the high freedom for conformational change to the functional groups in their coordination to lanthanide ions. The high freedom of the functional groups in the highly swollen RCSPs or in the highly porous RCSPs leads to the rapid uptake of lanthanides. In addition, the capacities of all RCSPs toward the three lanthanides normally increase with their atomic numbers ( $La < Gd < Yb$ ), different from the case of RSPs.

Referring to the results mentioned above, the moderately crosslinked highly porous RSP(10)-100 and RCSP(10)-100 were used in further studies and employed in the preparation of their respective oxidized derivatives RSPO(10)-100 and RCSPO(10)-

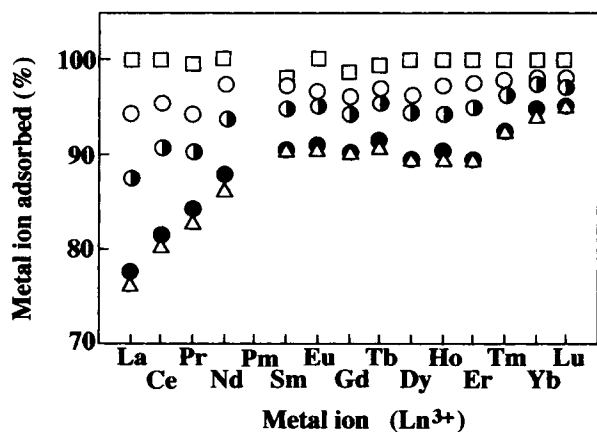


Figure 7 Distribution from 0.1M hydrochloric acid: (□) SP-120, (○) RSP, (●) RSPO, (●) RCSP, (△) RCSPO.

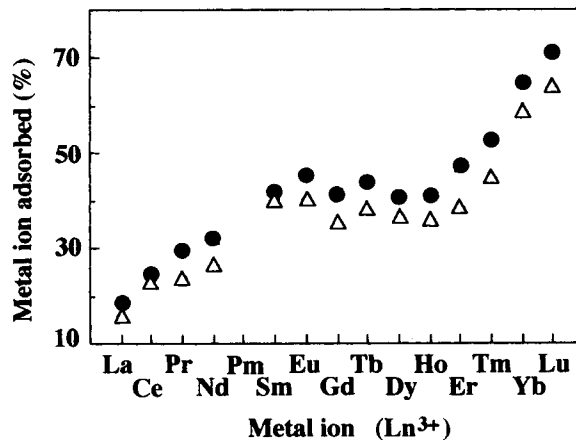


Figure 8 Distribution from 0.3M hydrochloric acid: (●) RCSP, (△) RCSPO.

100 (Table III). Hereafter, these resins are represented as RSP, RSPO, RCSP, and RCSPO by omitting the suffix (10)-100.

#### Distribution Studies

Since distribution coefficients are one of useful indexes for metal ion selectivities of chelating resins, the distribution of all lanthanides except for Pm from 0.1M to 1M hydrochloric acid solutions into RSP, RSPO, RCSP, or RCSPO was studied. Even in the distribution into RSP, no kinetic problem was observed. In this distribution study, the initial

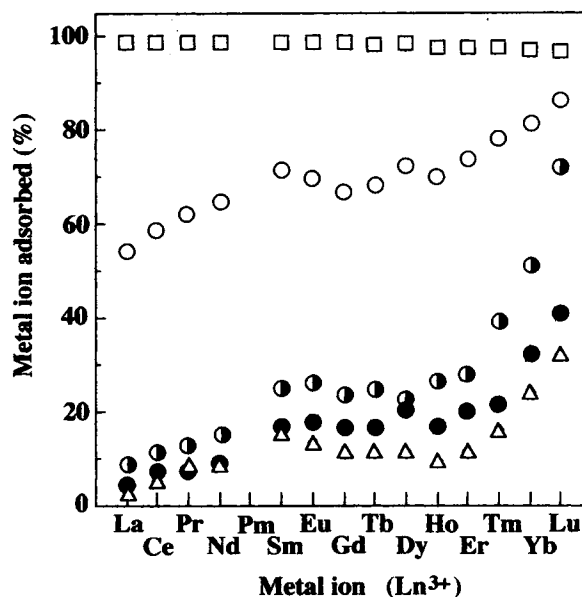
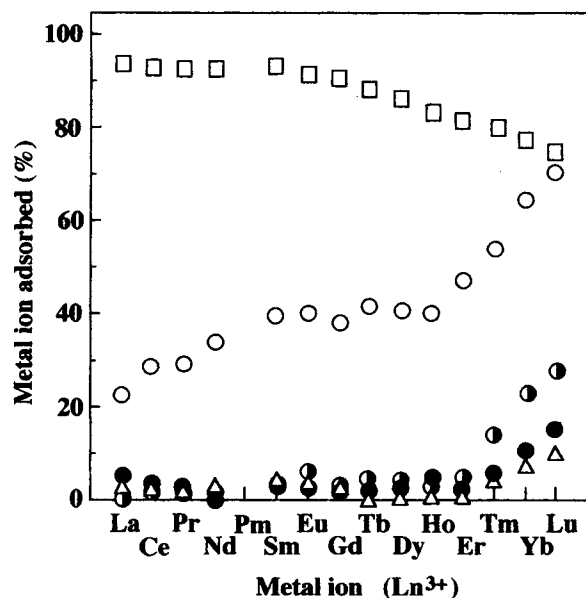


Figure 9 Distribution from 0.5M hydrochloric acid: (□) SP-120, (○) RSP, (●) RSPO, (●) RCSP, (△) RCSPO.



**Figure 10** Distribution from 1M hydrochloric acid: (□) SP-120, (○) RSP, (◐) RSPO, (●) RCSP, (△) RCSPO.

amount of each lanthanide in the aqueous phases (0.0025 mmol) is so small that the lanthanide uptake with RSP may be essentially governed by the rapid kinetic path only.

Figures 7–10 show the results as a function of lanthanide species, indicating that the distribution of each lanthanide from the solution of a given acid-

ity increases in the order  $RCSPO \approx RCSP < RSPO < RSP < SP-120$ . This sequence implies that the phosphinic acid groups bind lanthanides more strongly than the phosphonic acid groups and also that the phosphonic acid groups directly introduced into phenyl groups more strongly take up lanthanides than ones introduced through methylene groups. Thus, the oxidation of RSP into RSPO markedly reduces the distribution of lanthanides. On the other hand, the conversion of RCSP into RCSPO causes a minor change, since the majority of the functional groups in RCSP are already unoxidizable phosphonic acid groups, as mentioned in the preceding section.

As judged from Figures 7–10, the resins based on oxy-acids of phosphorus clearly exhibit lanthanide selectivity patterns quite different from that of the conventional cation exchange resin based on sulfonic acid groups (SP-120). Because of the low basicity of sulfonate groups, trivalent lanthanide ions are strongly distributed into SP-120, overcoming competing distribution with the proton. This means that the elution of the adsorbed lanthanides from SP-120 with mineral acids is difficult to achieve. On the other hand, the basicity of both phosphite and phosphonate is greater than that of sulfonate. Then, the distribution of lanthanides into RSP, RSPO, RCSP, or RCSPO is much more effectively depressed with increasing acidity than the case of SP-120. This means that the lanthanides adsorbed on

**Table IV** Distribution Coefficients at 30°C

Metal Ion	$\log K_D^a$			
	RSP(10)-100 (1)	RSPO(10)-100 (2)	RCSP(10)-100 (3)	RCSPO(10)-100 (3)
La	2.39	1.88	2.24	2.15
Ce	2.56	2.06	2.44	2.34
Pr	2.62	2.10	2.50	2.47
Nd	2.66	2.14	2.56	2.52
Pm	—	—	—	—
Sm	2.78	2.42	2.80	2.76
Eu	2.80	2.46	2.82	2.77
Gd	2.72	2.42	2.76	2.71
Tb	2.79	2.48	2.80	2.72
Dy	2.80	2.52	2.79	2.73
Ho	2.79	2.50	2.78	2.70
Er	2.90	2.65	2.84	2.73
Tm	3.08	2.85	2.97	2.92
Yb	3.23	3.10	3.21	3.18
Lu	3.37	3.23	3.36	3.31

<sup>a</sup> Resin, 40 mg. Aqueous phases, 0.0001M of each lanthanide in HCl solutions: (1) 1M HCl, (2) 0.5M HCl, (3) 0.3M HCl.



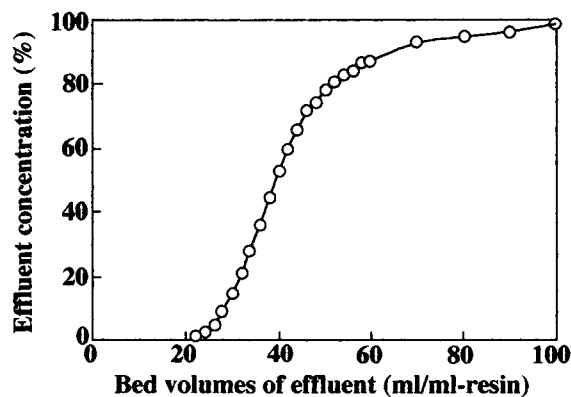
the present chelating resins can be more easily eluted with mineral acids than those adsorbed on SP-120.

Table IV summarizes distribution coefficients. The four kinds of resins present exhibit almost the same selectivity patterns to lanthanides; the distribution coefficients increase with increasing atomic numbers, except for the elements from Sm to Ho. These selectivity patterns can be qualitatively explained by the concept of "the hard and soft acids and bases."<sup>4</sup> Oxygen atoms in oxy-acids of phosphorous can be classified as hard Lewis bases, and the hardness of lanthanide ions (as the Lewis acids) increases with increasing atomic numbers because of lanthanide contraction.<sup>4</sup> Thus, the principle that "the hard base preferentially binds the hard acid"<sup>4</sup> qualitatively explains the lanthanide selectivity sequences observed here.

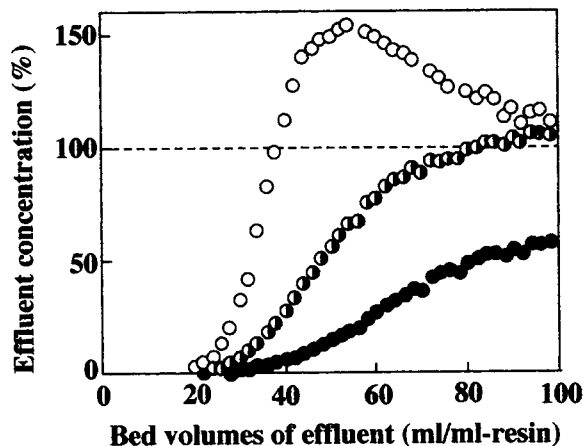
### Breakthrough Behavior of RCSP Column

It is likely that all the presented chelating resins can be applicable to the separation of lanthanides except for those from Sm to Ho. However, it seems that RCSP and RCSP0 are superior to RSP and RSPO, respectively, from the viewpoint of the elution of the adsorbed lanthanides. Due to this advantage as well as the rapid kinetics, RCSP was selected in the column-mode study.

Figure 11 shows a breakthrough curve for La. No La was detected in the column effluent until 21 bed volumes. This gives the breakthrough capacity as high as ca. 0.6 mmol/g resin in spite of the high space velocity of 10 h<sup>-1</sup>. Figure 12 shows the breakthrough curves obtained by feeding the mixed solution of La, Gd, and Yb. Until ca. 20 bed volumes, no leakage of the lanthanides was observed. The



**Figure 11** Breakthrough curve of La. Column: 1 mL of RCSP; loading solution: 0.01M LaCl<sub>3</sub>; flow rate: space velocity 10 h<sup>-1</sup>.



**Figure 12** Breakthrough curves of La, Gd, and Yb. Loading solution: solution containing the three lanthanides at 0.033M each. Other conditions are the same as those in Figure 11: (○) La, (◐) Gd, (●) Yb.

concentrations of La and Gd in the column effluent exceed those in the feeding solution at 38 and 84 bed volumes, respectively. This means that less preferred La or Gd initially adsorbed on the resin is gradually substituted by the most preferred Yb through the mechanism similar to frontal development in the column chromatography.<sup>16</sup>

### Chromatographic Separation of Lanthanide Ions

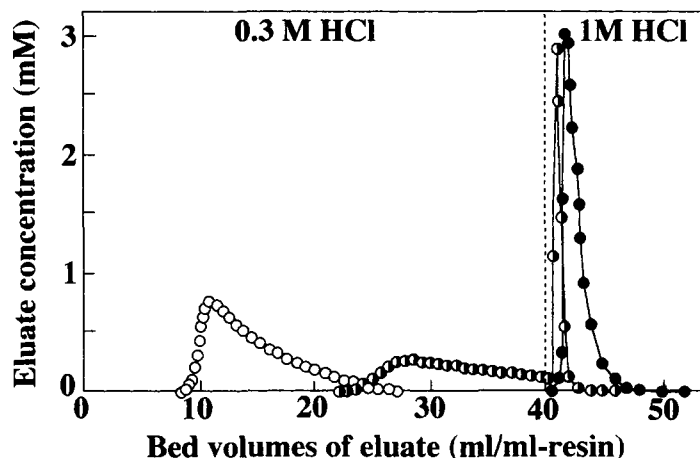
In order to search acids suitable for the elution of lanthanides, the distribution of La, Gd, and Yb from several mineral acid solutions was tested. As summarized in Table V, distribution coefficients of each lanthanide are little affected by the acid species except for phosphoric acid. The rather higher distribution from the phosphoric acid solution can be ascribed to the fact that phosphoric acid is not a strong

**Table V** Distribution Coefficients of La, Gd, and Yb between RCSP<sup>a</sup> and Mineral Acid Solutions<sup>b</sup>

Acid	log $K_D$		
	La	Gd	Yb
HCl (0.3M)	2.2	2.7	3.2
H <sub>2</sub> SO <sub>4</sub> (0.15M)	2.1	2.6	3.1
HNO <sub>3</sub> (0.3M)	2.2	2.7	3.2
HClO <sub>4</sub> (0.3M)	2.2	2.8	3.1
H <sub>3</sub> PO <sub>4</sub> (0.1M)	3.6	3.7	4.0

<sup>a</sup> 40 mg.

<sup>b</sup> 25 mL, concentration of each lanthanide was 0.0001M.



**Figure 13** Elution of lanthanides with hydrochloric acid solution (0.3M or 1M). Column: 50 mL of RCSP; flow rate of eluant: space velocity  $0.6 \text{ h}^{-1}$ ; amounts of metal ions loaded: 0.25 mmol each. (○) La, (◐) Nd, (●) Sm.

acid. These results also indicate that anions from the strong acids affect little the distribution of the lanthanides. Whereas any strong acids in Table V may be usable as an eluting reagent, the chromatographic elution of La, Nd, and Sm with hydrochloric acid solutions was examined as a model case.

Figure 13 shows the elution of the three lanthanides loaded on the RCSP column with 0.3M and 1M hydrochloric acid solutions. In the elution with 40 bed volumes of 0.3M hydrochloric acid, La was eluted quantitatively, but the elution of Sm was incomplete, and Sm was not eluted. On the other hand, the remaining Nd and Sm were rapidly and quantitatively eluted with 1M hydrochloric acid. Then, the effect of the acid concentration was examined, and the results are summarized in Table VI. With increasing acid concentration, elution of the lanthanides is much easier but the separation efficiency

decreases. Then, using 0.5M solution of the acid, the effect of flow rate was examined, and the results are summarized in Table VII. Although the retention volume for each lanthanide is not markedly affected by flow rate, separation efficiency is lowered with increasing flow rate. Consequently, the space velocity of  $0.8 \text{ h}^{-1}$  was selected in the further study, taking into account the separation efficiency as well as the time required. Figure 14 illustrates a chromatogram obtained under the optimized chromatographic conditions. Although tailing of Sm is marked and small overlap of the neighboring peaks is observed, the three lanthanides were successfully separated. Table VIII summarizes the effect of size of the resin and sample size as well. As predicted from the plate theories on column chromatography,<sup>16</sup> the smaller RCSPs and the smaller sample size yielded better separation. Thus, it is expected that even the sep-

**Table VI** Effect of Concentration of Hydrochloric Acid on Chromatographic Separation of La, Nd, and Sm

Concentration of HCl (M)	Flow Rate ( $\text{h}^{-1}$ )	Retention Volume in Bed Volumes (mL/mL Resin)			Overlapping Peak Area (%)		
		La	Nd	Sm	La-Nd	Nd-Sm	La-Sm
0.3	0.6	11.2	28.6	Not eluted	3.0	—	—
0.5	0.8	3.2	6.6	16.0	4.6	2.4	—
1.0	0.8	1.2	1.6	3.0	39.1	27.7	4.7

Column, 50 mL of RCSP. The amount of each lanthanide loaded was 0.25 mmol.

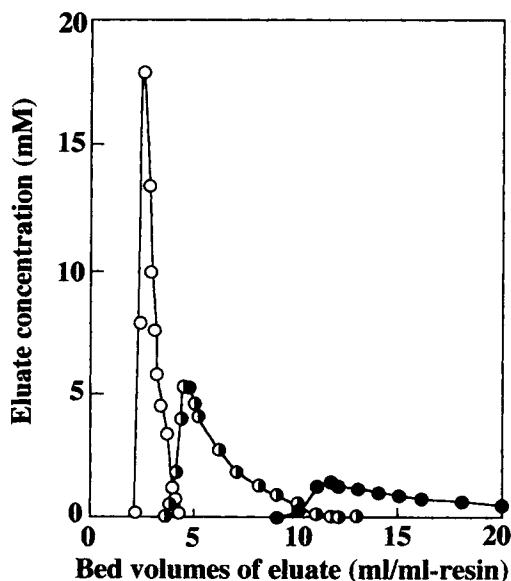
**Table VII** Effect of Flow Rate of Eluant (0.5M HCl) on the Chromatographic Separation of La, Nd, and Sm

Flow Rate (h <sup>-1</sup> )	Retention Volume in Bed Volumes (mL/mL Resin)			Overlapping Peak Area (%)	
	La	Nd	Sm	La-Nd	Nd-Sm
0.4	3.2	6.4	14.8	2.6	1.6
0.6	3.2	6.4	15.4	4.3	2.2
0.8	3.2	6.6	16.0	4.6	2.4
1.0	3.2	6.4	15.6	5.2	11.2
2.0	3.2	7.0	16.0	14.1	15.6

Column, 50 mL of RCSP. The amount of each lanthanide loaded was 0.25 mmol.

aration of neighboring lanthanides, except for those from Sm to Ho, will be accomplished by further improvement of theoretical plate numbers of RCSP columns.

In the industrial separation of lanthanides using columns packed with conventional cation exchange resins, expensive organic complexing reagents such as EDTA should be required.<sup>17</sup> On the other hand,



**Figure 14** Chromatographic separation of La, Nd, and Sm with 0.5M hydrochloric acid solution. Column: 50 mL of RCSP (60–80 mesh); flow rate of eluant: space velocity 0.8 h<sup>-1</sup>; amounts of metal ions loaded: 0.75 mmol of each. (○) La, (◐) Nd, (●) Sm.

**Table VIII** Effect of Particle Size of RCSP and Sample Size on Chromatographic Separation of La, Nd, and Sm

Particle Size of RCSP (mesh)	Sample Size of Each Lanthanide (mmol)	Overlapping Peak Area (%)	
		La-Nd	Nd-Sm
32–60	0.25	4.6	2.2
32–60	0.75	9.0	5.5
60–80	0.25	1.7	0.8
60–80	0.75	4.6	3.6

Column, 50 mL of RCSP. Elution, 0.5M HCl at the space velocity of 0.8 h<sup>-1</sup>.

strong acids like hydrochloric acid can be successfully used as the eluting reagent in the case of RCSP, as illustrated in this work. This is one of the great advantages of RCSP.

## CONCLUSION

In the uptake of lanthanides by the chelating resins containing phosphinic and/or phosphonic acid groups (RSPs and RCSPs), their physical pore structures played important roles. The moderately crosslinked highly porous RSP(10)-100 and RCSP(10)-100 exhibited high capacities for lanthanides. These two resins as well as their oxidation derivatives RSPO(10)-100 and RCSP(10)-100 have similar lanthanide selectivity patterns; the selectivity increases with atomic numbers of lanthanides except for ones from Sm to Ho. Among the four resins, RCSP(10)-100 seems to be most promising, since it takes up lanthanides very rapidly and can be used in the chromatographic separation of lanthanides without use of expensive organic complexing reagents such as EDTA.

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