Preparation of Phosphoric Acid Resins with Large Cation Exchange Capacities from Macroreticular Poly(glycidyl methacrylate-*co*-divinylbenzene) Beads and Their Behavior in Uptake of Metal Ions

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ABSTRACT: In order to prepare phosphoric acid resins (RGPs) with large cation exchange capacities, effects of porosity and cross-linking of the precursory poly(glycidyl methacrylate-*co*-divinylbenzene) beads on their functionalization with phosphoric acid were studied. Two series of precursory copolymers were prepared: one was prepared by changing the amount of divinylbenzene (1–25 mol %) but by fixing that of isobutyl acetate (porogen) at 140 vol % per monomer mixture; the other by changing the amount of the porogen (40–160 vol %) but by fixing that of the cross-linker at 10 mol %. It was clarified that porosity of the precursors plays an important role in the functionalization. Highly porous precursors were functionalized with high efficiency; for example, even the precursors containing 10 mol % of divinylbenzene resulted in RGPs having cation exchange capacities as large as 6–7 meq/g, so long as BET specific surface areas of the precursors were greater than ca. 30 m^2/g. The selectivity study has revealed that RGP exhibits the characteristic metal ion selectivity. Lithium ion was adsorbed in preference to sodium and potassium ions; and so-called hard Lewis acid cations, such as uranyl, ferric, and aluminum ions, are adsorbed even from strongly acidic media (1 < pH < 2). Among common divalent metal ions, in addition, the resin exhibits the highest selectivity toward lead ion. © 1997 John Wiley & Sons, Inc. J Appl Polym Sci **63**: 1327–1334, 1997

Key words: phosphoric acid resins; macroreticular chelating resins; glycidyl methacrylate; hard and soft acids and bases

INTRODUCTION

Among chelating cation exchange resins containing oxy-acid groups of phosphorus, phosphonic acid resins have been studied well,[1–7] and their promising properties in the separation of metal ions have been recently reported.[8–12] On the other hand, studies on phosphoric acid resins are rare.[13–19] Although phosphonic acid resins have

been sometimes called phosphoric acid ones,[20] resins of both types should be strictly differentiated since the acidic sites in the former resins are bound to polymer matrices through carbon-phosphorus cleavages, and those in the latter ones are fixed through carbon-oxygen-phosphorus cleavages (ester bond). In addition, oxidation states of phosphorus are also different between the two types of resins, and those are +5 and +3 for phosphoric and phosphonic acid resins, respectively.

In preparation of phosphoric acid resins, several polymer matrices, such as cellulose,[13,14] poly-(vinyl alcohol)s,[14,16] poly(styrene)s,[15,18,19] and poly(glycidyl methacrylate)s,[17] have been used.
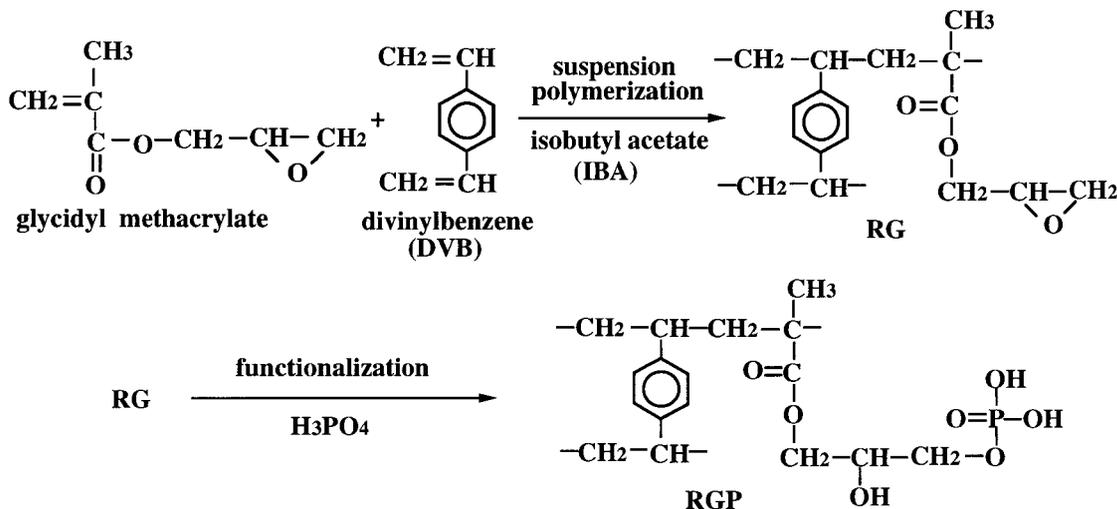
Scheme 1 Preparation of RGP.

EXPERIMENTAL

Among them, of particular interest are cross-linked poly(glycidyl methacrylate) beads (RG), since their functionalization can be simply performed by heating in commercially available phosphoric acid as reported in a previous paper (Scheme 1).[17] In the previous work, however, the efficiency of the functionalization was so low that cation exchange capacities were insufficient from practical viewpoints.[17] Thereafter, efforts were made for the enhancement of the efficiency in the functionalization and improvement of the precursory copolymers as well. Recently, we have succeeded in the enhancement of the efficiency of the functionalization, resulting in large cation exchange capacities.[21] This paper describes the preparation of the improved phosphoric acid resins (RGPs) and their behavior in metal ion uptake.

EXPERIMENTAL

Preparation of Precursory Copolymers (RGs)

Glycidyl methacrylate and divinylbenzene (DVB) were polymerized in the presence of a pertinent porogen by means of suspension polymerization technique. Azobisisobutylonitrile was used as initiator. The procedures for the suspension polymerization were described elsewhere.[22,23] Resulting particles of RG from 60 to 32 mesh were taken by meshing, and the meshed particles were then placed on an inclined steel plate. Only spherical particles rolling down the plate were col-

lected. The spherical beads of RG thus selected were used as precursor.

Functionalization of RG

Precursory RGs were functionalized by heating in commercially available phosphoric acid (85%) on an oil bath. The heating was preliminary conducted using three different reaction vessels: a sealed glass tube (method A), a beaker (method B), and a narrow-necked flask (method C). Among the three methods, method B gave the highest efficiency. This may be ascribable to the fact that water in the phosphoric acid is smoothly eliminated by evaporation during heating, resulting in an increase in the concentration of phosphoric acid. Thus, the functionalization was conducted by the method B. An example of recommended procedures was as follows: RG (5 g) and commercially available phosphoric acid (50 mL) were taken in a 500 mL beaker, and the mixture was heated at 140°C for 2 h under gentle stirring. The resulting RGP was washed with water until the washing was acid-free. After air-drying, the resin was dried *in vacuo*. All RGPs were used in the hydrogen ion form throughout.

Evaluation of Properties of RGs and RGPs

Specific surface areas of RGs and RGPs were measured by means of a BET method using a Shimadzu Flowsorb II 2300 apparatus. Pore volumes and average pore radii were measured by means of a mercury penetration method (Carlo Erba po-

rosimeter Model 1520). Phosphorus contents, cation exchange capacities, salt splitting capacities, and swelling ratios of RGPs were measured according to methods reported elsewhere.[2,17]

Capacities for Metal Ion Uptake

A sample of RGP (0.125 g) and a metal ion solution (50 mL, 0.01M) were taken into a 100 mL Erlenmeyer flask; here, the amount of the loading metal ion (0.50 mmol) is slightly greater than that of the functional groups (ca. 0.44 mmol). After the flask was shaken with a mechanical shaker at 30°C for 24 h, the metal ion concentration in the aqueous phase was determined by means of EDTA titrations. From a decrease in the concentration of the metal ion in the aqueous phase, the metal ion uptake was calculated. The pH of solutions was adjusted with hydrochloric acid (pH < 3), acetic acid, and/or sodium acetate (pH > 3).

Distribution Study

A sample of RGP (40 mg) and a metal ion solution (25 mL, 0.0001M) were taken into a 50 mL Erlenmeyer flask. Here, the amount of the loading metal ion (0.0025 mmol) is much less than that of the functional groups (ca. 0.14 mmol). After the flask was shaken at 30°C for 24 h, the concentration of the metal ion in the supernatant was determined by means of ICP-AES. From a decrease in the metal ion concentration in the aqueous phase, a distribution ratio (D) was calculated according to the following equation:

$$D = \frac{\text{amount of metal ion adsorbed on resin} \, (\text{mmol/g})}{\text{amount of metal ion in aqueous phase} \, (\text{mmol/mL})}$$

The pH of solutions was adjusted with hydrochloric acid.

pH Titration

Samples (0.1 g) of RGP were weighted into a series of Erlenmeyer flasks. To each flask, a solution of a pertinent alkali chloride (LiCl, NaCl, or KCl, 2M, 20 mL) and a given volume of corresponding alkali hydroxide solution (0.1M) were taken. Then, deionized water was added to keep the final volume of the aqueous phase at 40 mL. The flasks were shaken at 30°C until the pH of the aqueous phases became time-independent.

RESULTS AND DISCUSSION

Selection of Porogen in Preparation of Precursor RG

In the previous work,[17] precursors RGs were prepared using 2,2,4-trimethylpentane as porogen. Even though this solvent gave large pore volumes to RGs (0.17–1.24 mL/g), the average pore radii were also large (110–2900 nm), resulting in small specific surface areas (< 5 m^2/g).[23] Then, more pertinent porogens were searched, and it was found that isobutyl acetate (IBA) and 4-methyl-2-pentanone gave high porosity to RG, as shown in Table I. Since IBA gave more reproducible specific surface areas than did 4-methyl-2-pentanone, the former was adopted as porogen in this work. Analyses of porosity by means of a mercury penetration method have clarified that IBA gave smaller average pore radii than did 2,2,4-trimethylpentane, whereas the two solvents gave comparable pore volumes. For example, average pore radii and pore volumes of the RGs prepared by using 140 vol % of IBA and 10 mol % of DVB were 17–29 nm and 0.44–0.73 mL/g, respectively.

Table I   Specific Surface Areas of RG Prepared by Using 10 mol % of DVB and 140 vol %[a] of Porogen

Porogen	Number of Preparation	Averaged Specific Surface Area (m^2/g)	Standard Deviation (m^2/g)
4-Methyl-2-pentanone	11	39.4	7.9 (20)[b]
Isobutyl acetate	14	44.4	3.3 (7.4)

[a] (Volume of porogen/volume of monomer mixture) × 100.
[b] Figures in parentheses are relative standard deviation (%).
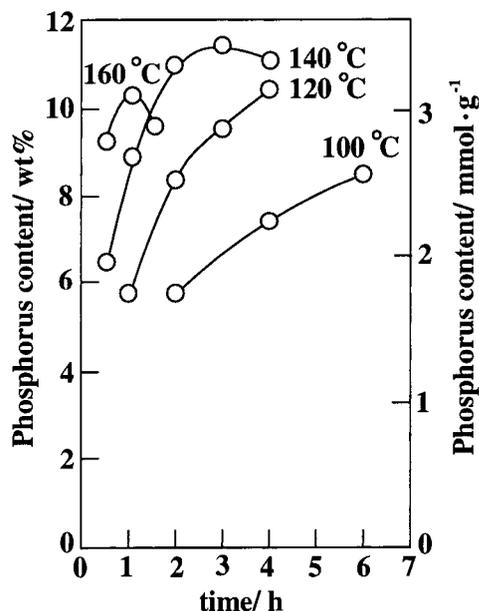
Figure 1 Phosphorus contents of RGP as a function of reaction time or temperature. The precursor RG used here was prepared by using 10 mol % of DVB and 140 vol % of isobutyl acetate.

Optimization of Functionalization Conditions

In the previous work, RG was functionalized with phosphoric acid at 80°C, and the yield of the functionalization was nearly equal to or less than 50% of calculated ones.[17] Then, conditions for the functionalization were optimized by changing reaction temperature and time. Figure 1 shows the results. Although the functionalization rate increases with an increase of temperature up to 140°C, prolonged heating at 140 or 160°C decreases phosphorus contents. This is ascribable to hydrolysis

of ester bonds in RGs, resulting in carboxylic groups during the functionalization. Indeed, infrared (IR) spectral study on these RGPs clearly identified the formation of carboxylic groups, as already observed in the preparation of dithiol resins from RGs.[22] From Figure 1, it can be concluded that optimized conditions are heating at 140°C for 2–3 h. In the further study, then, the functionalization was conducted by heating at 140°C for 2 h.

Properties of RGPs derived from RGs with Different Porosities

In order to clarify the effect of porosity on the functionalization, and on properties of resulting RGPs as well, the series of RGPs with different porosity were derived from the precursors with different porosities. These precursors were prepared by changing the amount of the porogen (IBA) from 40 to 160 volume % per monomer mixture but by fixing that of DVB at 10 mol %. Table II summarizes the results. The precursors prepared by using more than 80 volume % of the porogen were functionalized with high efficiency; in other words, the precursors having specific surface areas of more than ca. 30 m^2/g can be easily functionalized. Indeed, phosphorus contents of RGPs derived from less porous precursors (specific surface areas < 10 m^2/g) are much less than those of the RGPs derived from highly porous ones. Thus, the present work clarified the reason for the low efficiency of the functionalization in the previous work,[17] and the efficiency of the functionalization is drastically improved, not only by optimizing functionalization conditions but also by improving porosity of the precursors.

Table II   Properties of RGPs derived from RGs with Different Porosities

	RG[a]	RGP				
Amount of Porogen (vol %)	Specific Surface Area (m^2/g)	Specific Surface Area (m^2/g)	Phosphorus Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt Splitting Capacity (meq/g)	Swelling Ratio
40	0	0	1.68	3.09	1.38	1.18
60	8.4	0	2.07	3.78	1.62	1.11
80	29.2	13.0	3.44	6.59	2.68	1.57
100	31.8	16.3	3.46	6.48	2.72	1.54
120	43.7	20.8	3.58	6.99	2.84	1.61
140	50.4	24.6	3.61	6.87	2.80	1.82
160	46.9	25.4	3.48	6.66	2.74	1.78

[a] The nominal mol % of divinylbenzene was 10.
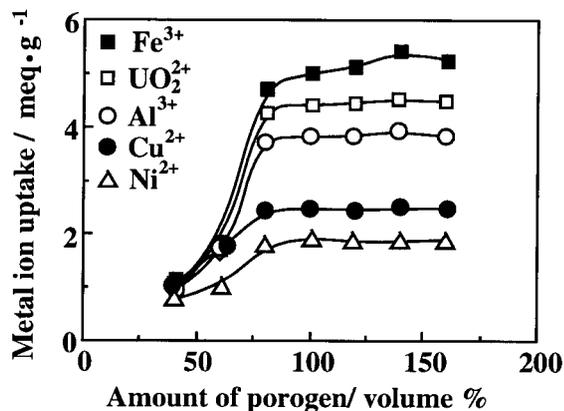
Figure 2 Uptake of metal ions with the RGPs given in Table II (effect of the amount of the porogen on metal ion uptake). Here, the pH of sample solutions was not buffered. Initial pH of solutions is as follows: Fe^{3+}, 2.13; UO_2^{2+}, 3.25; Al^{3+}, 3.60; Cu^{2+}, 4.45; Ni^{2+}, 5.82. The final pH of solutions (from left to right) is as follows:

Fe^{3+} 2.01, 1.91, 1.65, 1.62, 1.61, 1.58, 1.70;
UO_2^{2+} 2.59, 2.40, 1.99, 1.97, 1.96, 1.94, 1.96;
Al^{3+} 2.55, 2.35, 1.98, 1.96, 1.96, 1.93, 1.94;
Cu^{2+} 2.56, 2.45, 2.27, 2.26, 2.26, 2.25, 2.26;
Ni^{2+} 2.69, 2.61, 2.37, 2.36, 2.36, 2.36, 2.35.

In Figure 2, metal ion uptake with this series of RGPs is shown. Capacities for uptake for each metal ion increase up to 80 volume % of the porogen and attain plateau above 80 volume %. As is judged from Table II, specific surface areas and swelling ratios of RGPs derived from RGs prepared by using more than 80 volume % of the porogen are somewhat different each other. However, slight differences in these parameters did not affect the metal ion uptake, and then it seems that the metal ion uptake is essentially governed by the amounts of the functional groups introduced.

Properties of RGPs as a Function of Cross-linking

In order to clarify the effect of cross-linking on the efficiency of the functionalization as well as on properties of resulting RGPs, the series of RGs, which were prepared by changing the amount of DVB from 1 to 25 mol % but by fixing that of IBA (porogen) at 140 volume % per monomeric mixtures, were functionalized. Table III summarizes the results. Specific surface areas of RGPs increase with an increase in cross-linking. On the other hand, the reversed tendency was observed in phosphorus contents and cation exchange capacities; this is mainly ascribed to the fact that the amounts of epoxy groups per unit weight of the precursors decrease with an increase in the amount of the cross-linker. Furthermore, steric hindrance in the functionalization may also increase with an increase in cross-linking.

The cation exchange capacities of lightly cross-linked RGPs (1–5 mol % of DVB) are nearly equal to twice the molar contents of phosphorus since phosphoric acid groups fixed to RGs act as dibasic acid (Scheme 1). However, this is not true for highly cross-linked RGPs (15–25 mol % of DVB); their cation exchange capacities are less than twice the phosphorus contents. This probably suggests that hydroxide ion accessibility into the bead decreases at the higher cross-linking levels, resulting in an apparent decrease in the acid capacity. In addition, we have to point out that the

Table III   Properties of RGPs as a Function of Cross-linking

Amount of DVB (mol %)	RG[a] Specific Surface Area (m²/g)	RGP Specific Surface Area (m²/g)	Phosphorus Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt Splitting Capacity (meq/g)	Swelling Ratio
1	0.6	0	4.11	8.23	3.99	2.86
2.5	5.9	0	4.26	8.57	4.12	3.23
5	16.3	0	4.13	8.20	3.68	2.92
7.5	28.4	9.6	3.78	7.56	3.15	1.88
15	82.7	51.4	3.07	5.72	2.11	1.42
20	114.5	89.7	2.69	5.03	1.79	1.27
25	155.0	129.2	2.30	4.33	1.47	1.16

[a] The amount of IBA was 140 vol %.
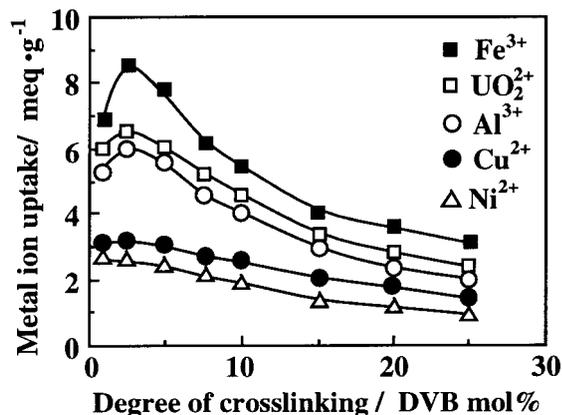
Figure 3 Uptake of metal ions with the RGPs given in Table III (effect of cross-linking on uptake of metal ions). Here, the pH of sample solutions was not buffered. Initial pH of solutions is as follows: Fe^{3+}, 2.13; UO_2^{2+}, 3.25; Al^{3+}, 3.60; Cu^{2+}, 4.45; Ni^{2+}, 5.82. The final pH of solutions (from left to right) is as follows:

Fe^{3+} 1.52, 1.43, 1.46, 1.54, 1.59, 1.69, 1.75, 1.79;
UO_2^{2+} 1.83, 1.79, 1.83, 1.90, 1.94, 2.04, 2.15, 2.23;
Al^{3+} 1.81, 1.75, 1.79, 1.87, 1.93, 2.07, 2.16, 2.23;
Cu^{2+} 2.15, 2.14, 2.16, 2.21, 2.25, 2.34, 2.41, 2.50;
Ni^{2+} 2.20, 2.20, 2.24, 2.30, 2.36, 2.47, 2.57, 2.66.

functionalization of RGs with phosphoric acid accompanies with appreciable reduction of specific surface areas, even though we have no explanation for this phenomenon.

Figure 3 shows uptake of several metal ions with this series of RGPs. The uptake of each metal ion decreases with an increase in the cross-linking. This corresponds to the decrease in the phosphorus contents or cation exchange capacities with an increase in cross-linking. From 14 kinds of RGPs shown in Tables II and III, the RGP(10)-100 derived from the precursor prepared by using 10 mol % of DVB, and 140 volume % of the porogen was selected for use in the metal ion selectivity study, taking into account mechanical strength, cation exchange capacities, and so on. Thus, synthesis of this resin was repeated 10 times, and
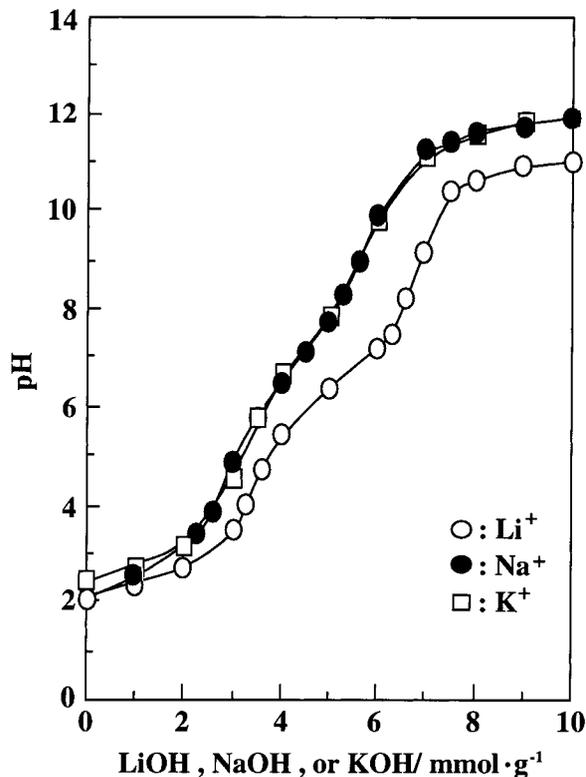
Figure 4 pH titration curves of RGP(10)-100 with LiOH, NaOH, or KOH in the presence of a corresponding alkali chloride ($1M$).

averaged properties of the resulting resins are given in Table IV. So long as freshly prepared precursors were functionalized, the resins with highly reproducible properties were obtained as judged from Table IV. However, the functionalization of the aged RGs stored in dry state for more than several months tended to give slightly low capacities (ca. 6.0 meq/g), even though this slight decrease did not have significant meanings from practical standpoints.

Metal Ion Selectivity of RGP(10)-100

In the previous work, batchwise ion exchange study between Na^+ and Li^+ demonstrated that

Table IV   Properties of RGP (10)-100 Used in the Selectivity Study

Phosphorus Content (mmol/g)	Cation Exchange Capacity (meq/g)	Salt Splitting Capacity (meq/g)	Dry Volume (mL/g)	Wet Volume (mL/g)
3.47 (0.18)[a]	6.87 (0.21)	2.75 (0.07)	1.83 (0.05)	3.26 (0.05)

[a] Figures in parentheses are standard deviations (number of preparation = 10).
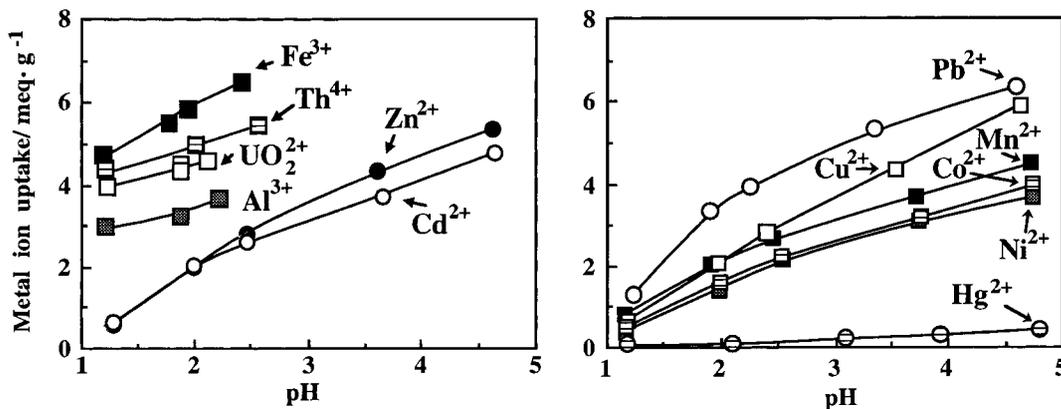
Figure 5 Capacities for metal ion uptake as a function of pH.

RGP prefers Li^+ to Na^+.[17] In order to obtain further evidence on high selectivity of RGP toward Li^+, pH titration study on RGP(10)-100 was conducted. The comparison of three titration curves in Figure 4 clearly indicates that Li^+ is more strongly taken up by this resin, in particular, in the high pH region of pH > 4. Then, it can be concluded that the decreasing order of the selectivity is Li^+ > Na^+ ≈ K^+, and it is noteworthy that this sequence is reversed from that of strong-acid resins containing sulfonic acid groups (Li^+ < Na^+ < K^+).[24] Since Na^+ is not strongly complexed with the functional groups, values of pKa_1 and pKa_2 were calculated by applying the Helfferich's method[24] to the titration data obtained by using NaOH. Calculated values for pKa_1 and pKa_2 are 2.7 and 7.8, respectively, and are not greatly different from thermodynamic values for phosphoric acid (pKa_1 = 2.2; pKa_2 = 7.2).

Figure 5 shows pH profiles of capacities for uptake of various metal ions. These data indicate that RGP(10)-100 exhibits high affinity toward so-called hard Lewis acid cations,[25] such as UO_2^{2+}, Fe^{3+}, Th^{4+} and Al^{3+}, even in the strongly acidic region of pH < 2. Among tested divalent heavy metal ions, the highest affinity was observed for Pb^{2+} and the lowest one for Hg^{2+}, which is a typical soft Lewis acid cation.[25] In addition, RGP(10)-100 exhibits capacities as high as ca. 6 meq/g (3 mmol/g) for Pb^{2+} and Cu^{2+} around pH 5.

Figure 6 shows the relationship between log D and pH. Below pH 1, negative logarithms of hydrochloric acid concentrations are adopted as pH for the sake of simplicity. Least-squares slopes of the plots are summarized in Table V. For the divalent metal ions except for Cd^{2+}, the slopes are nearly equal to +2. This indicates that these cations are adsorbed through ion exchange with proton. The rather steeper slope for Cd^{2+} is probably ascribable to the formation of chloro complexes since it forms the most stable chloro com-
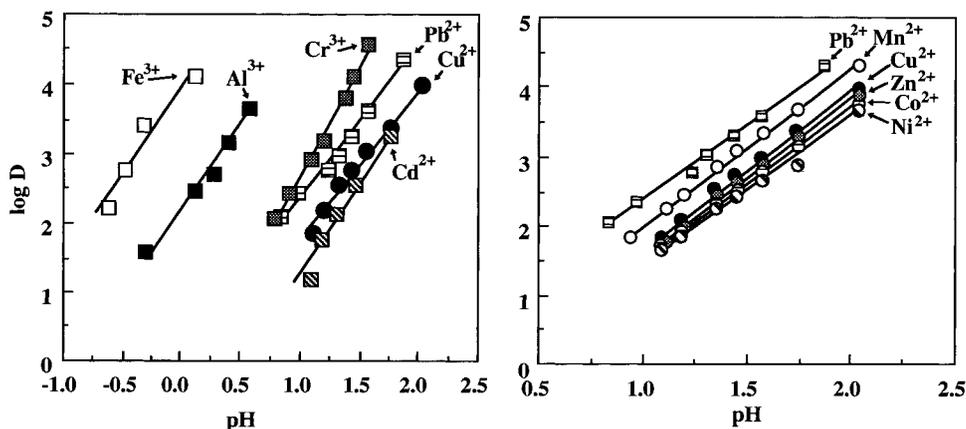
Figure 6 The relationship between log D and pH.

Table V Slopes of Plots of Log D Versus pH

Metal Ion	$\partial \log D/\partial pH$
Al^{3+}	2.40
Cr^{3+}	3.21
Fe^{3+}	2.50
Cd^{2+}	2.64
Co^{2+}	2.11
Cu^{2+}	2.25
Mn^{2+}	2.25
Ni^{2+}	2.03
Pb^{2+}	2.16
Zn^{2+}	2.31

plexes among the tested divalent ions.[26] The slope for Cr^{3+} is nearly equal to +3, suggesting that this is also adsorbed through ion exchange mechanism. In the case of strongly preferred Fe^{3+} and Al^{3+}, on the other hand, slopes are significantly less than their formal charges (+3). This probably means that phosphoryl oxygen atoms contributes to the adsorption of the highly preferred ions as in the case of the resins having phosphonic acid groups.[8] From the results given in Figure 6, it can be concluded that RGP exhibits the following metal ion selectivity sequence below pH 2: $Fe^{3+} \gg Al^{3+} \gg Cr^{3+} > Pb^{2+} > Mn^{2+} > Cu^{2+} > Zn^{2+}$, $Cd^{2+}, Co^{2+}, Ni^{2+}$. As judged from Figures 2, 3, 5, and 6, the metal ion selectivity of RGP is significantly different from that of strong-acid cation exchange resins containing sulfonic acid groups.[24] In particular, we would like to emphasize that RGP exhibits the high selectivity toward so-called hard Lewis acid cations in the concept of hard and soft acids and bases proposed by Pearson.[25] Because of the highest selectivity toward Pb^{2+} among common divalent metal ions, RGP is promising in treatment of wastewater polluted with Pb^{2+}.[27]

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