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METAL ION SELECTIVITY OF MACRORETICULAR CHELATING CATION EXCHANGE RESINS WITH PHOSPHONIC ACID GROUPS ATTACHED TO PHENYL GROUPS OF A STYRENE-DIVINYLBENZENE COPOLYMER MATRIX

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ABSTRACT

To clarify the metal ion selectivity sequence of the phosphonic acid resin named RSPO, in which the functional groups were introduced into phenyl groups of a macroreticular poly(styrene-co-divinylbenzene) matrix, the distribution of 20 kinds of metal ions from 0.0001 mol/L solution of each metal ion onto RSPO was studied in nitric, hydrochloric, sulfuric, and phosphoric acid media. Distribution ratios of divalent metal ions Ba(II), Ca(II), Cd(II), Co(II), Cu(II), Mg(II), Mn(II), Ni(II), Pb(II), Sr(II), and Zn(II) normally decreased with solutions of increased acidity and were not significantly affected by acid species. The clear effect of acid species was observed in the distribution of Fe(III), Mo(VI), and U(VI); although their dis-

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tributions from hydrochloric and sulfuric acid media normally decreased with increasing acidity of solutions, the minimum was observed in their distribution from nitric acid media, indicating that they were distributed onto the resin from approximately 6 mol/L nitric acid through the mechanism similar to solvation extraction of their nitrate complexes with organophosphorous compounds. Phosphoric acid markedly depressed the distribution of Fe(III), Mo(VI), and U(VI) but not the distribution of Al(III), Bi(III), Cr(III), Gd(III), La(III), and Lu(III). The overall metal ion selectivity sequence of RSPO is the order of Mo(VI) ≅ Fe(III) ≅ U(VI) > Bi(III) ≅ Lu(III) > Al(III) ≅ Gd(III) > La(III) > Cr(III) > Pb(II) > Mn(II) ≅ Cd(II) ≅ Cu(II) > Ca(II) ≅ Co(II) ≅ Zn(II) ≅ Ba(II) ≅ Sr(II) > Ni(II) ≅ Mg(II). The metal ion selectivity sequence was also illustrated on the basis of uptake of U(VI), Pb(II), Ca(II), Ba(II), Ni(II) from 0.01 mol/L solutions of each metal ion.

INTRODUCTION

Cross-linked poly(styrene) based phosphonic acid resins have been reported as early as the 1950s (1–6). Unfortunately, their properties had not been studied in detail until Alexandratos et al. (7–11) and Egawa et al. (12,13) studied resins of these kinds in the mid- 1980s. The former group worked on the development of novel bifunctional phosphonic acid resins as well as their metal ion adsorption capabilities. The latter worked on optimization of macropore structures of poly(styrene-co-divinylbenzene) matrices to improve performances of classical phosphonic acid resins and application of the resulting macroreticular resins that have optimized pore structure for the separation of the metal ions, such as U(VI) and lanthanide ions. Related works published through the mid- 1990s were reviewed by Beauvais and Alexandratos (14). Recently, Kabay et al. proposed the use of various phosphonic acid resins in the elimination of Cd(II), Cr(III), and U(VI) from phosphoric acid (15,16). Trochimczuk and Streat also reported preparation, characterization, and metal ion adsorption ability of bifunctional phosphonic acid resins (17–19), and Merdivan, Buchmeiser, and Bonn prepared methylenephosphonic acid resins for the selective enrichment of U(VI) (20). Thus, phosphonic acid resins are expected to be useful for the separation, elimination, and enrichment of heavy metal ions in wide applications, such as the protection of the environment and hydrometallurgy.

In the last decade, we have been studying properties and application of 2 types of macroreticular cross-linked poly(styrene)-based phosphonic acid resins that have optimized pore structures (21–24); one named RSPO has phosphonic acid groups attached to phenyl groups of the copolymer matrix, and the other

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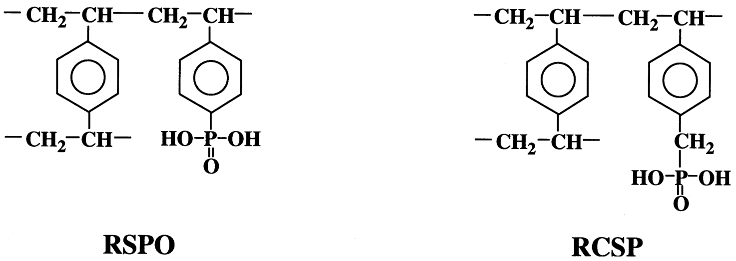

Scheme 1. Structures of RSPO and RCSP.

named RCSP has phosphonic groups fixed through a methylene spacer (Scheme 1). However, detailed metal ion selectivity sequences of phosphonic acid resins for various metal ions have not been fully accumulated, unlike those of sulfonic and carboxylic acid resins. The lack of systematic data on its metal ion selectivity is one of obstacles to expanding the utility of phosphonic acid resins. In a previous work (24), we clarified the metal ion selectivity of RCSP in the nitric acid media. However, no detailed metal ion selectivity of RSPO has been reported. Therefore, in this work, to expand utilities of RSPO, the distribution of 20 kinds of metal ions from nitric, hydrochloric, sulfuric, and phosphoric acid media onto RSPO was investigated to clarify its metal ion selectivity sequence as well as the effect of the 4 mineral acids on the distribution of these metal ions. In addition, the usefulness of the metal ion selectivity sequence determined by the distribution study was discussed on the basis of metal ions uptake from solution at specific metal ion concentration and pH.

EXPERIMENTAL

Materials

The resin RSPO was kindly provided by Mitsui Chemicals Co. It was prepared in a pilot-plant scale according to the method reported by Egawa et al. (12). It was derived from macroreticular styrene-divinylbenzene copolymer beads (degree of cross-linking: 10 nominal mol % of divinylbenzene, 32–60 mesh), which were synthesized by suspension polymerization in the presence of the porogen 2,2,4-trimethylpentane (100 vol % per monomer mixture). RSPO was conditioned in a column according to a conventional method (25), and was finally converted into the hydrogen ion form. The resin RSPO in the hydrogen form was air-dried and dried in vacuum at 40°C for more than 24 hours. RSPO in the hydrogen ion form was used throughout the study. Properties of RSPO in the hydrogen form were evaluated by previously reported methods (12). Its acid capacity, salt-splitting capacity, phosphorous content, and specific surface area were 8.7 mEq/g, 2.4 mEq/g, 4.2 mmol/g, and 42.6 m^2/g, respectively. The acid capacity of RSPO was slightly larger than twice the phosphorous content. This capacity difference is probably the result of a small amount of carboxylic acid groups that form by the oxidation of double bonds in the polymer matrix during the oxidation step of phosphinic acid groups to phosphonic acid ones with 12 mol/L nitric acid (12). Nitrate and chloride salts of appropriate metal ions were used in preparation of test solutions. All chemicals used were of reagent grade.

Distribution Study

Dried RSPO in the hydrogen ion form (0.04 g) and a test solution containing a target metal ion at 0.0001 mol/L (25 mL) were placed in a 50-mL Erlenmeyer flask. Then the flask was shaken with a mechanical shaker for 24 hours at 30°C, and the metal ion concentration in the supernatant was determined by means of inductively coupled plasma atomic emission spectrometry (ICP-AES). Adsorption percentages ($E\%$) and distribution ratios (D) were calculated from the following equations:

$$E\% = \left(\frac{C_o - C_e}{C_o}\right) \times 100$$

$$\begin{aligned} \mathrm{D} &= \frac{\text{amount of metal ion in resin at equilibrium (mmol/g)}}{\text{amount of metal ion in aqueous phase at equilibrium (mmol/mL)}} \\ &= \left(\frac{E\%}{100}\right)\left(\frac{C_o}{C_e}\right)\left(\frac{V}{m}\right) \end{aligned}$$

C_o is the initial concentration of metal ion in solution (mmol/mL); C_e is the equilibrium concentration of metal ion in solution (mmol/mL); V is the volume of solution (mL); and m is the weight of resin (g).

Because precision in the calculation of D decreases drastically as $E\%$ approaches 0 or 100%, values of $E\%$ from 4 to 98% were adopted. In the adjustment of acidity of test solutions, nitric, hydrochloric, sulfuric, or phosphoric acid was used to keep the pH region less than 2.5. The molar ratio of the metal ion to the functional group was fixed at 0.015 in all distribution studies.

Uptake of Metal Ion

Dried RSPO (0.125 g) in the hydrogen ion form and a test solution (50 mL of 0.01 mol/L of a target metal ion) were put into 100-mL Erlenmeyer flasks, and the flasks were shaken with a mechanical shaker for 24 hours at 30°C. The concentration of a metal ion in the supernatant was determined by means of ICP-AES. Uptake of the metal ion was calculated from the decrease in its concentration in the supernatant. The pH of test solutions was adjusted with nitric acid in the pH region below pH 3 and with acetic acid and sodium acetate buffers in the pH region between 3 and 5. The molar ratio of the metal ion to the functional group was fixed at 0.95.

RESULTS AND DISCUSSION

Distribution of Divalent Metal Ions

Figure 1 illustrates the effect of pH on *E*% of Pb(II), Cd(II), and Ni(II) in nitric acid media. Similar sigmoid curves were obtained for *E*% versus pH in the distribution of all divalent metal ions tested. Under the assumption that the distribution of a divalent metal ion onto RSPO proceeds through stoichiometric cation exchange and because the functional group is diprotic (26), we present the following 2 adsorption mechanisms (26):

$$2\mathrm{R{-}P(O)(OH)_2} + \mathrm{M}^{2+} \leftrightarrow \mathrm{(R{-}P(O)(OH)(O))_2M} + 2\mathrm{H}^{+} \qquad K_{21} \qquad (1)$$

$$\mathrm{R{-}P(O)(OH)_2} + \mathrm{M}^{2+} \leftrightarrow \mathrm{(R{-}P(O)(O)_2)M} + 2\mathrm{H}^{+} \qquad K_{22} \qquad (2)$$

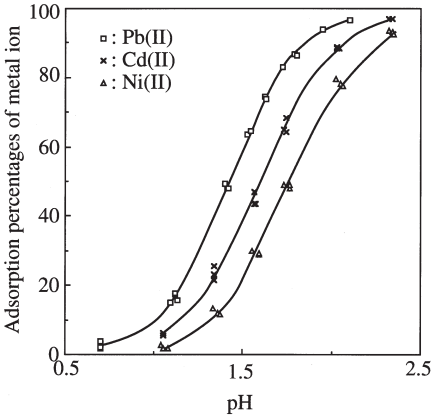

Figure 1. Examples for relationship between adsorption percentages (*E*%) of divalent metal ions and pH (nitric acid media). RSPO: 0.04 g, solution: 0.0001 mol/L of each metal ion (25 mL).

Then, the distribution ratio (D) is expressed as:

$$\begin{aligned} D &= \frac{[(\mathrm{R{-}P(O)(OH)(O)})_2\mathrm{M}] + [(\mathrm{R{-}P(O)(O)_2})\mathrm{M}]}{[\mathrm{M}]} \\ &= \frac{\mathrm{K}_{21}[\mathrm{R{-}P(O)(OH)_2}]^2 + \mathrm{K}_{22}[\mathrm{R{-}P(O)(OH)_2}]}{[\mathrm{H}^+]^2} \end{aligned} \tag{3}$$

Because values of D were measured under such conditions that the molar ratio of the metal ion to the functional group was 0.015 and the acidity of solutions was adjusted only with each mineral acid, the amount of hydrogen ion in the resin phase can be approximated to be constant. Therefore, values of ($\mathrm{K}_{21}[\mathrm{R{-}P(O)(OH)_2}]^2 + \mathrm{K}_{22}[\mathrm{R{-}P(O)(OH)_2}]$) in Eq. (3) can be also regarded as constant, even if the metal ion is quantitatively distributed onto RSPO. Then, the following Eq. (4) holds:

$$\mathrm{Log}\ D = \mathrm{Constant} + 2\ \mathrm{pH} \tag{4}$$

Figure 2 illustrates log D vs. pH plots for Pb(II), Mn(II), and Ni(II) in their distribution from phosphoric acid media, and a linear relationship is observed. Table 1 summarizes the least-square slopes of log D vs. pH plots for the divalent metal ions tested.The correlation coefficients of all plots are greater than 0.99, and the slopes are nearly equal to 2. These results indicate that the distribution proceeds through the stoichiometric cation exchange. Because values of pH at a half-extraction ($\mathrm{pH}_{1/2}$) can be regarded as one of semi-quantitative indexes representing the metal ion selectivity of a given resin, values of $\mathrm{pH}_{1/2}$ were calculated from least square equations of log D vs. pH plots. The values are listed in Table 2. In nitric

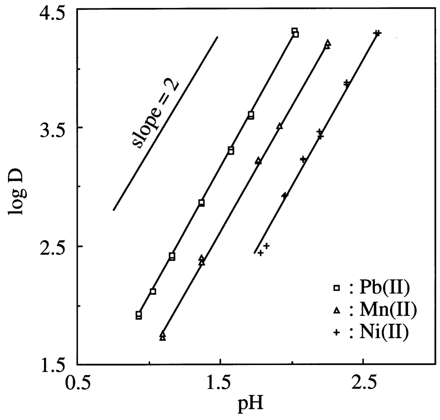

Figure 2. Examples for log D vs. pH plots for divalent metal ions (phosphoric acid media). RSPO: 0.04 g, solution: 0.0001 mol/L of each metal ion (25 mL).

Table 1. Least Square Slopes of log *D* vs. pH Plots for Divalent Metal Ions

	Slope $\left(\frac{\partial \log D}{\partial \mathrm{pH}}\right)$			
Metal	HNO_3	HCl	H_2SO_4	H_3PO_4
Pb(II)	2.23 (0.02)	2.38 (0.04)		2.18 (0.01)
Mn(II)	2.03 (0.03)	1.96 (0.04)	2.13 (0.03)	2.12 (0.02)
Cd(II)	2.10 (0.03)	2.40 (0.03)	2.04 (0.01)	2.10 (0.07)
Cu(II)	1.96 (0.04)	2.04 (0.02)	2.07 (0.03)	2.09 (0.02)
Ca(II)	1.89 (0.04)	2.24 (0.07)	2.09 (0.03)	2.27 (0.03)
Co(II)	1.99 (0.02)	2.04 (0.02)	2.11 (0.02)	1.93 (0.05)
Zn(II)	2.03 (0.04)	2.02 (0.02)	2.05 (0.03)	2.06 (0.05)
Ba(II)	2.09 (0.02)	2.07 (0.03)		1.99 (0.04)
Sr(II)	2.06 (0.02)	2.09 (0.02)		
Ni(II)	2.01 (0.04)	2.06 (0.04)	2.12 (0.02)	2.24 (0.06)
Mg(II)	1.98 (0.02)	2.04 (0.03)	2.05 (0.05)	1.97 (0.02)

Figures in parentheses show standard deviation for least square slope.
Conditions: RSPO 0.04 g, metal ion solution 0.0001 mol/L (25mL).

Table 2. Values of pH at Half Extraction for Divalent Metal Ions

	Half Extraction pH ($pH_{1/2}$)			
Metal	HNO_3	HCl	H_2SO_4	H_3PO_4
Pb(II)	1.43 (0.03)	1.43 (0.05)		1.34 (0.02)
Mn(II)	1.58 (0.04)	1.55 (0.08)	1.65 (0.04)	1.57 (0.03)
Cd(II)	1.61 (0.04)	1.64 (0.05)	1.66 (0.02)	1.57 (0.11)
Cu(II)	1.63 (0.07)	1.53 (0.03)	1.70 (0.05)	1.63 (0.03)
Ca(II)	1.72 (0.07)	1.62 (0.12)	1.74 (0.03)	1.63 (0.04)
Co(II)	1.72 (0.04)	1.71 (0.04)	1.77 (0.04)	1.66 (0.10)
Zn(II)	1.72 (0.07)	1.68 (0.04)	1.70 (0.05)	1.73 (0.10)
Ba(II)	1.73 (0.03)	1.72 (0.04)		1.63 (0.07)
Sr(II)	1.74 (0.03)	1.69 (0.03)		
Ni(II)	1.77 (0.08)	1.74 (0.05)	1.78 (0.02)	1.91 (0.11)
Mg(II)	1.78 (0.04)	1.68 (0.06)	1.77 (0.08)	1.68 (0.04)

Figures in parentheses show error range estimates from standard deviations of both slope and intercept.
Conditions: RSPO 0.04 g, metal ion solution 0.0001 mol/L (25mL).

acid media, values of $pH_{1/2}$ increase in the order of Pb(II) $>$ Mn(II) $\cong$ Cd(II) $\cong$ Cu(II) $>$ Ca(II) $\cong$ Co(II) $\cong$ Zn(II) $\cong$ Ba(II) $\cong$ Sr(II) $>$ Ni(II) $\cong$ Mg(II). This sequence represents the decreasing selectivity order of RSPO to divalent metal ions, indicating that RSPO exhibits the highest selectivity to Pb(II) among those divalent metal ions studied. In the distribution from hydrochloric, sulfuric, and phosphoric acid media, similar selectivity sequences were also observed, whereas the order of $pH_{1/2}$ values for a few divalent metal ions were slightly different among the 4 mineral acids. Although we examined whether or not values of $pH_{1/2}$ can be correlated with stability constants of complexes of these metal ions with Cl^-, NO_3^-, SO_4^{2-}, $H_2PO_4^-$, and HPO_4^{2-} (27,28), no simple correlation was found. This lack of correlation may be due to the small stability constants of divalent metal ions with these inorganic anions (27, 28). However, the values of $pH_{1/2}$ were not significantly affected by the 4 mineral acid species. Naturally, the divalent metal ion selectivity pattern of RSPO is very close to that of methylenephosphonic acid resins (RCSP) (24). Therefore, we concluded that the most outstanding characteristic of the selectivity of the classical phosphonic acid resins RSPO and RCSP to divalent metal ions is their high selectivity to Pb(II) over alkaline earth metal ions. In particular, their high selectivity to Pb(II) over Ba(II) is contrary to that of conventional cation exchange resins that have sulfonic acid groups, which prefer Ba(II) to Pb(II) (29).

As can be estimated from values of $pH_{1/2}$ listed in Table 2, all distribution data for divalent metal ions were evaluated at pH region less than 2.5 as shown Figs. 1 and 2. In this pH region, the exchange reaction (Eq. 1) likely occurs in preference to the reaction depicted by Eq. (2) because pKa_1 and pKa_2 of RSPO are 2.9 and 8.8, respectively (12), and the molar ratio of the metal ion to the functional group is fixed at 0.015 in the distribution study.

Distribution of Trivalent Cations, Mo(VI), and U(VI) from Strong Mineral Acid Media

According to the concept of Helfferich's electroselectivity, cation exchangers generally prefer trivalent cations to divalent ones (25). The smallest value of $pH_{1/2}$ for the divalent metal ions is approximately 1.34 (Table 2), and according to the tenets of electroselectivity, the values of $pH_{1/2}$ for trivalent ions should be less than 1.34. Because liquid junction potentials between sample solutions and an inner filling solution of a reference electrode are not negligibly small (30), the pH measurement with a glass electrode leads to erroneous results in the pH region less than 1. Therefore, results regarding trivalent cations are discussed on the basis of normality of strong mineral acids (Eq/L), and $-\log[H^+]$ is used instead of pH.

Figure 3 shows the dependence of $E\%$ of trivalent metal ions, Mo(VI), and U(VI) on normality of nitric, hydrochloric, and sulfuric acids. Figure 4 shows log D vs. $-\log[H^+]$ plots. Figures 3 and 5 clearly indicate that these metal ions can be

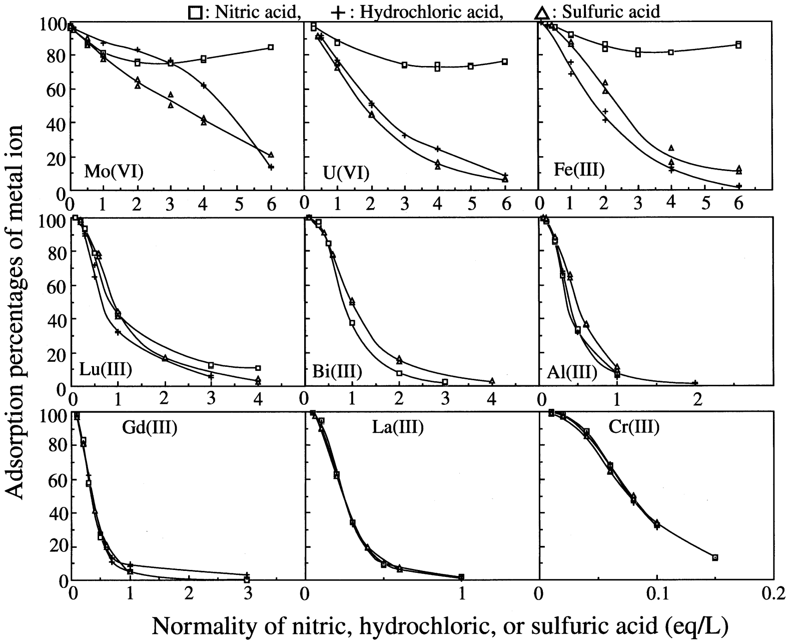

Figure 3. Adsorption percentages of trivalent metal ions, Mo(VI), and U(VI) as a function of normality of strong mineral acids. RSPO: 0.04 g, solution: 0.0001 mol/L of each metal ion (25 mL).

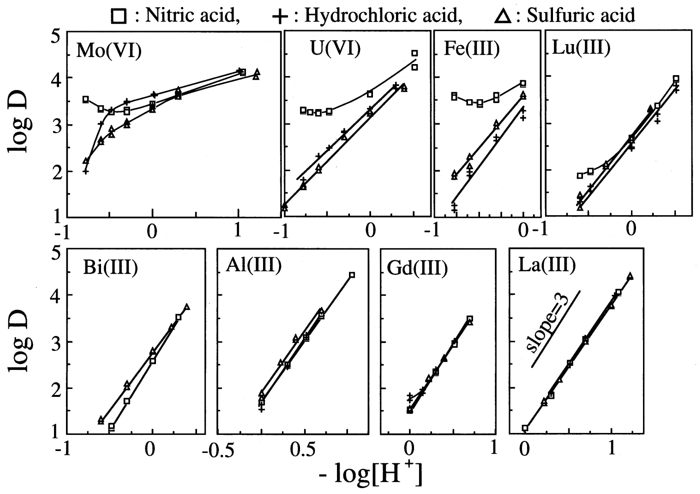

Figure 4. Log D vs. $-\log[H^+]$ plots for trivalent metal ions, Mo(VI), and U(VI). RSPO: 0.04 g, solution: 0.0001 mol/L of each metal ion (25 mL).

classified into 2 groups: One consists of Mo(VI), U(VI), and Fe(III), and the other is made up of Lu(III), Bi(III), Al(III), Gd(III), La(III), and Cr(III). In the distribution of the metal ions belonging to the former group, shapes of log *D* vs. $-\log[\mathrm{H}^+]$ plots depicting the nitric acid media are quite different from those describing behavior in hydrochloric and sulfuric acid media; the minimum of their distribution is observed in the case of nitric acid media, whereas the distribution of these metal ions decreases with increasing concentrations of hydrochloric and sulfuric acids. This minimum implies that their distribution from nitric acid media proceeds through 2 different mechanisms. One is the stoichiometric cation exchange, in which the distribution of a metal ion is depressed by a hydrogen ion, and the other is a mechanism similar to that involved in solvent extraction of Mo(IV), U(VI), and Fe(III) from concentrated nitric acid solutions with organophosphorous compounds, such as tributyl phosphate (TBP) (27,28).

$$\mathrm{M}^{n+}_{aq} + n\mathrm{NO}^-_{3aq} + m\mathrm{TBP}_{org} \leftrightarrow (\mathrm{M(NO_3)}_n\mathrm{TBP}_m)_{org} \qquad (5)$$

In this mechanism, the formation of nitrato-complexes is promoted and the dissociation of phosphonic acid group is depressed with an increase in the nitric acid concentration, resulting in enhancement of the solvation extraction of these nitrato complexes. Because of two opposite adsorption mechanisms in the nitric acid media, the minimum appears in the distribution of Fe(III), Mo(VI) and U(VI). However, Alexandratos et al. did not observe the minimum Fe(III) distribution from nitric acid solutions onto a similar phosphonic acid resin (31). They measured distribution ratios in the presence of sodium nitrate to maintain the nitrate background at 4 mol/L (31), which may account for their results. Slopes for the distribution of U(VI) and Fe(III) from hydrochloric and sulfuric acid media are nearly equal to 2 (Table 3), which is equal to the formal charge of the uranyl ion but not to that of Fe(III). Fe(III) forms stable complexes with chloride and sulfate ions (27,28). This complex formation may be a cause of smaller slopes for Fe(III).

Under the assumption that trivalent metal ions are also distributed by stoichiometric cation exchange, we can render the following 2 possible mechanisms:

$$3\mathrm{R{-}P(O)(OH)_2} + \mathrm{M}^{3+} \leftrightarrow (\mathrm{R{-}P(O)(OH)(O)})_3\mathrm{M} + 3\mathrm{H}^+ \qquad K_{31} \qquad (6)$$

$$2\mathrm{R{-}P(O)(OH)_2} + \mathrm{M}^{3+} \leftrightarrow (\mathrm{R{-}P(O)(O)_2})\mathrm{M}((\mathrm{O})(\mathrm{OH})(\mathrm{O})\mathrm{P{-}R}) + 3\mathrm{H}^+ \qquad K_{32} \qquad (7)$$

$(\mathrm{R{-}P(O)(OH)(O)})_3\mathrm{M}$ and $(\mathrm{R{-}P(O)(O)_2})\mathrm{M}((\mathrm{O})(\mathrm{OH})(\mathrm{O})\mathrm{P{-}R})$ are similar to the complex species of trivalent metal ions adsorbed by iminodiacetic acid resins (32) in which the functional group is diprotic as in the case of RSPO. From Eqs. (6 and 7), we obtained the following relation:

$$\mathrm{Log}\, D = \mathrm{Constant} + 3\mathrm{pH} \qquad (8)$$

The constant is $(K_{31}[\mathrm{R{-}P(O)(OH)_2}]^3 + K_{32}[\mathrm{R{-}P(O)(OH)_2}]^2)$. Table 3 summarizes the least-square slopes of log *D* vs. $-\log[\mathrm{H}^+]$ plots; the plots with correla-

Table 3. Least Square Slopes of log D vs. $-\log[H^+]$ Plots for Trivalent Metal Ions, Mo(VI), and U(VI)

	$\frac{\partial(\log D)}{\partial(-\log[H^+])}$		
Metal	HNO_3	HCl	H_2SO_4
Mo(VI)	d	d	d
Fe(III)	d	2.15 (0.03)	2.10 (0.08)
U(VI)	d	1.78 (0.06)	1.82 (0.06)
Bi(III)	3.09 (0.08)	—	2.34 (0.03)
Lu(III)	2.58 (0.07)	2.58 (0.10)	2.22 (0.08)
Al(III)	2.60 (0.05)	2.96 (0.04)	2.60 (0.13)
Gd(III)	2.65 (0.05)	2.92 (0.08)	2.26 (0.10)
La(III)	2.84 (0.06)	2.82 (0.04)	2.70 (0.03)
Cr(III)	2.86 (0.07)	3.04 (0.05)	3.01 (0.02)

The symbol d means that the correlation coefficient of log *D* vs. pH plots was less than 0.99.

Figures in parentheses show standard deviation of slope.

The pH was used instead of $-\log[H^+]$ because data were collected above pH 1 for Cr(III).

Conditions: RSPO 0.04 g, metal ion solution 0.0001 mol/L (25mL).

tion coefficients greater than 0.99 are regarded as linear. In the case of nitric and hydrochloric acids, slopes for the trivalent ions do not greatly deviate from 3 except for Fe(III), and the slope Cr(III) in sulfuric acid is relatively small. Because of the lowest affinity of RSPO to Cr(III), the pH could be measured by a glass electrode. Plots of log *D* vs. pH for Cr(III) are shown in Fig. 5, and the slope for

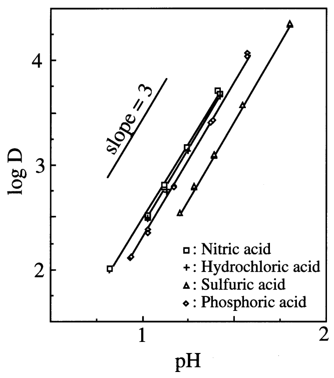

Figure 5. Log *D* vs. pH plots for Cr(III). RSPO: 0.04 g, solution: 0.0001 mol/L of Cr(III) (25 mL).

Table 4. Values of $-\log[H^+]$ at Half Extraction for Trivalent Metal Ions, Mo(VI), and U(VI)

	$-\log[H^+]$ at Half Extraction		
Metal	HNO_3	HCl	H_2SO_4
Mo(VI)	d	d	d
Fe(III)	d	−0.22 (0.06)	−0.36 (0.01)
U(VI)	d	−0.28 (0.01)	−0.20 (0.01)
Bi(III)	0.06 (0.01)	—	0.00 (0.01)
Lu(III)	0.06 (0.01)	0.14 (0.03)	0.03 (0.02)
Al(III)	0.41 (0.02)	0.41 (0.01)	0.34 (0.04)
Gd(III)	0.47 (0.02)	0.46 (0.02)	0.49 (0.05)
La(III)	0.63 (0.03)	0.62 (0.02)	0.63 (0.01)
Cr(III)	1.11 (0.06)	1.14 (0.04)	1.28 (0.02)

The symbol d means that the correlation coefficient of log *D* vs. pH plots was less than 0.99.

Figures in parentheses show error range estimated from standard deviation of both slope and intercept.

The pH was used instead of $-\log[H^+]$ data above pH 1 were collected for Cr(III).

Conditions: RSPO 0.04 g, metal ion solution 0.0001 mol/L (25mL).

Cr(III) coincides well with its formal charge 3 (Table 3). The relatively small slopes for ions in sulfuric acid media may be ascribed to that the activity of ionic species concentrations deviates greater in sulfuric acid media than it does in nitric and hydrochloric acid media (33). In addition, complexes of trivalent cations with sulfate ion are generally more stable than those with monovalent anions (27,28); and complexation may also be one of reasons for the relatively small slopes found for ions in the sulfuric acid media. Although some problems still remain in interpreting the slopes of log *D* vs. $-\log[H^+]$ plots, values of $-\log[H^+]$ at a half extraction ($-\log[H^+]_{1/2}$) give a practical index regarding the affinity of RSPO to these metal ions. Table 4 lists values of $-\log[H^+]_{1/2}$. Data shown in Tables 2 and 4 and Fig. 4 lead to the following overall metal ion selectivity sequences: Mo(VI) $\cong$ Fe(III) $\cong$ U(VI) $>$ Bi(III) $\cong$ Lu(III) $>$ Al(III) $\cong$ Gd(III) $>$ La(III) $>$ Cr(III) $>$ Pb(II) $>$Mn(II) $\cong$ Cd(II) $\cong$ Cu(II) $>$ Ca(II) $\cong$ Co(II) $\cong$ Zn(II) $\cong$ Ba(II) $\cong$ Sr(II) $>$ Ni(II) $\cong$ Mg(II). This order is significantly different from that of conventional cation exchange resins that have sulfonic acid groups (25).

Distribution of Trivalent Cations, Mo(VI), and U(VI) from Phosphoric Acid Media

Some phosphonic acid resins were effective in the elimination of Cd(II), Cr(III), and U(VI) from phosphoric acid (15,16). A commercially available aminomethylphosphonic acid resin, Lewatit OC 1060 (Bayer Chemical Co, Germany), has been used in the elimination of U(VI) from crude phosphoric acid (34). Therefore, the elucidation of RSPO behavior in the distribution of various metal ions from phosphoric acid media is an important endeavor. In the distribution of divalent metal ions, no marked effect of this acid was observed.Therefore, the distribution of trivalent metal ions, Mo(VI), and U(VI) are of interest. Figure 6 shows the dependence of *E%* on the concentration of phosphoric acid. Here, *E* percentages are plotted against molarity (mol/L) of phoshphoric acid because pH or $-\log[H^+]$ in concentration levels of phosphoric acid greater than 1 mol/L is difficult to measure or calculate. The metal ions listed in Fig. 6 are also classified into 2 groups. One consists of Mo(VI), U(VI), and Fe(III), and the other is made up of Lu(III), Gd(III), La(III), and Al(III). The distribution of metal ions in the former group is significantly more depressed by phosphoric acid than they are when in 3 strong mineral acids (Fig. 3). For instance, *E* percentages of Mo(VI), U(VI), and Fe(III) at 4 mol/L of phosphoric acid are much less than those at 4 Eq/L of the 3 strong acids. This depressed distribution of the Mo(VI), U(VI), and Fe(III)metal ions from phosphoric acid media can be ascribed to the specific interaction of phosphoric acid with these metal ions (27,28). On the other hand, *E* percentages of Lu(III), Gd(III), La(III), and Al(III) in phosphoric acid media are much greater than they are in the 3 strong acid ones. For example, *E* percentages of Lu(III) at 2 mol/L phosphoric acid are approximately 60 % (Fig. 6) but those at 2 Eq/L of the 3 strong mineral acids are approximately 20% (Fig. 3). These results mean that the interaction of phosphoric acid with the Lu(III), Gd(III), La(III), and Al(III) is not

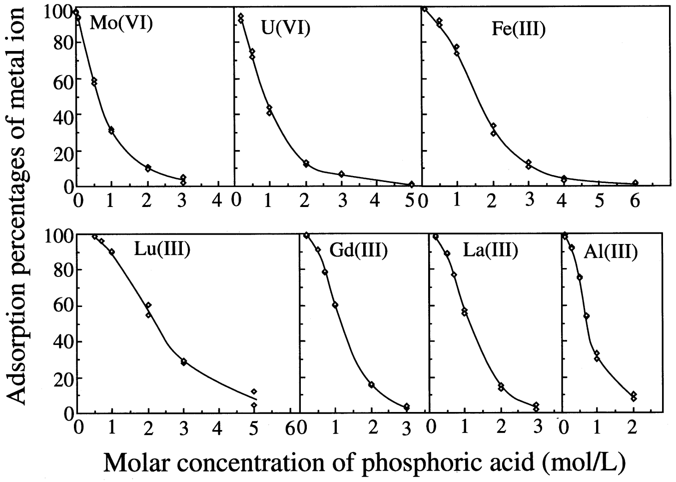

Figure 6. Adsorption percentages of trivalent metal ions, Mo(VI), and U(VI) as a function of molarity of phosphoric acid. RSPO: 0.04 g, solution: 0.0001 mol/L of each metal ion (25 mL).

significant. Therefore, this ion group is more strongly adsorbed by RSPO in phosphoric acid media because of its weak acidity.

Distribution data of Cr(III) were collected less than 1 mol/L of phosphoric acid concentration , so the pH could be measured with a glass electrode. Figure 5 shows log *D* vs. pH plots for the distribution of Cr(III) from 4 kinds of mineral acids solutions. The least-square slope and $\mathrm{pH}_{1/2}$ for Cr(III) distribution from phosphoric acid media are 3.07 (0.03) and 1.17 (0.03), respectively, and these values are nearly equal to those for the Cr(III) in the strong mineral acid media (Tables 3 and 4).

Even though the distribution of Mo(IV) and U(VI) are depressed by phosphoric acid, they are still highly distributed onto RSPO, even at 1 mol/L phosphoric acid, compared with conventional cation exchange resins with sulfonic acid groups. For instance, although *E* percentage of Mo(VI) onto sulfonic acid resin Diaion PK 216 is nearly equal to 0 at pH values of 0 to 4 (35), that of Mo(VI) by RSPO in 1 mol/L phosphoric acid is still 30% as shown in Fig. 6. Thus, RSPO can preferentially take up metal ions with high valencies even from phosphoric acid media. This may result from the high density of phosphonic acid groups in RSPO.

Uptake of Metal Ions at Nearly Equal Molar Ratio of Metal Ion to Functional Group

The metal ion selectivity sequence of RSPO as determined by the distribution study is of particular usefulness. Because the metal ion selectivity sequence was determined from distribution data under limited conditions (pH values were less than 2.5 and the metal ion concentration was fixed at 0.0001 mol/L), uptake of several metal ions was examined to illustrate whether or not the selectivity sequence can predict the order of metal ion uptake by RSPO from an extended pH range and at a relatively high metal ion concentration of 0.01 mol/L. As the first example to show the usefulness of the selectivity sequence, uptake of Pb(II), Ba(II), Ca(II), and Ni(II) was measured at pH values up to approximately 5, and the molar ratio of the metal ion to the functional group was 0.95. The selectivity sequence (Table 2) predicts that RSPO will take up Pb(II) much more than Ba(II), Ca(II), and Ni(II), and the uptake of the latter 3 metal ions will be nearly equal to each other. As shown in Fig. 7, the uptake of Pb(II) at pH 4.5 is as high as approximately 3 mmol/g (6 mEq/g), which is greater than the maximum capacity of any conventional cation-exchange resin with sulfonic acid groups (approximately 4–5 mEq/g) (25), and the uptake of Ba(II), Ca(II), and Ni(II) at pH 4.5 is approximately 1.7 mmol/g (3.4 mEq/g), and the values related to the ions are nearly equal to each other.

The distribution study also clarified that RSPO exhibits the highest selectivity for U(VI), Mo(VI), and Fe(III). The uptake of U(VI) was measured. Because

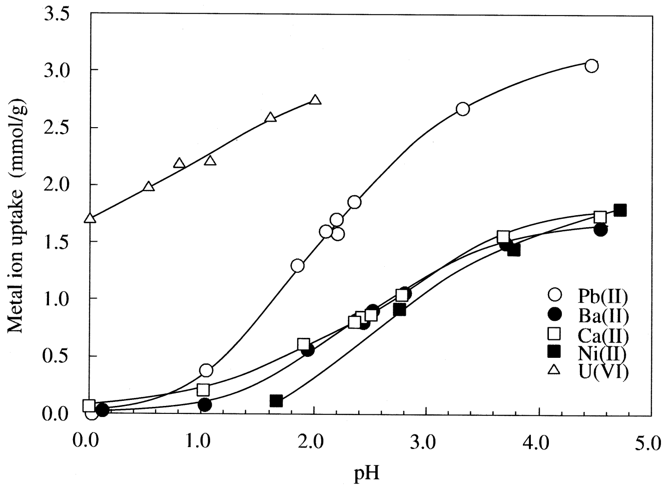

Figure 7. Uptake of several metal ions as a function of pH. RSPO: 0.125 g, solution: 0.01 mol/L of each metal ion (50 mL).

the formation of multinuclear hydrolyzed species of U(VI) has been noted to occur at pH 2 (27,28), the U(VI) uptake at pH from 0 to 1.9 was tested. As shown in Fig. 7, the uptake at pH 1.9 was 2.7 mmol/g. We were surprised that the high 1.7 mmol/g uptake was observed even at pH 0, where RSPO cannot take up even the most preferred divalent metal ion Pb(II). Based on these findings, the decreasing order in uptake of each metal ion from 0.01 mol/L solutions at a given pH is U(VI) $>$ Pb(II) $>$ Ca(II) $\cong$ Ba(II) $\cong$ Ni(II) (Fig. 7); this order correlates to the selectivity sequence determined by the distribution study.

The metal ion selectivity sequence determined in this work is useful for the survey of new applications of RSPO. For instance, the selectivity sequence shows that RSPO exhibits extremely high selectivity to Fe(III) over Zn(II) and Ni(II). Therefore, we have proposed the highly selective elimination of Fe(III) from Fe(III)-contaminated nickel and zinc electroplating baths by means of the RSPO packed column (36). In addition, this selectivity sequence also clearly substantiates the claim that phosphonic acid resins RCSP and RSPO are useful for concentration and separation of U(VI) in acidic eluates (13).

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