

Studies on Selective Adsorption Resins. XXI. Preparation and Properties of Macroreticular Chelating Ion Exchange Resins Containing Phosphoric Acid Groups

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Synopsis

Macroreticular cation exchange resins containing phosphoric acid groups (RGP) were prepared by the reaction of glycidyl methacrylate–divinylbenzene copolymer [or poly(glycidyl methacrylate)] beads (RG) with phosphoric acid or phosphorous oxychloride, and the adsorption behavior of metal ions on the RGP was investigated. The phosphorylation of the polymer beads could be effectively carried out by treatment of the polymer beads with 85% phosphoric acid at 80°C for 3 h. The RGP obtained from glycidyl methacrylate–divinylbenzene (2 mol %) copolymer beads showed high cation exchange capacity, salt splitting capacity, and adsorption capacity for Cu^{2+} , Zn^{2+} , Ni^{2+} , Cd^{2+} , Ca^{2+} , and Ag^+ . On the other hand, the RGP obtained from poly(glycidyl methacrylate) beads had high adsorption capacity for Al^{3+} , Fe^{3+} , and UO_2^{2+} . The RGP prepared by treating the RG with phosphoric acid had a higher selective adsorption for Li^+ than for Na^+ .

INTRODUCTION

We have prepared and studied many kinds of macroreticular chelating resins containing various ligands and have reported that they are more practical than gel type resins for the removal and recovery of heavy metal ions from industrial waste, the recovery of uranium from sea water, etc., because of their high adsorption rate and physical stability.¹⁻⁴ So far cation exchange resins of gel type containing phosphoric acid groups or phosphono groups have been studied.⁵⁻⁷ However, the macroreticular cation exchange resins containing phosphoric acid groups have not been investigated.

This report is concerned with the preparation of macroreticular chelating cation exchange resins having phosphoric acid groups from glycidyl methacrylate–divinylbenzene copolymer beads and their properties.

EXPERIMENTAL

Preparation of Macroreticular Chelating Ion Exchange Resins

The macroreticular glycidyl methacrylate–divinylbenzene (DVB) copolymer [or poly(glycidyl methacrylate)] beads (RG) were synthesized by a suspension polymerization in the presence of 2,2,4-trimethylpentane as diluent.

The RG with the desired diameter was obtained by using a sieve (32–60 mesh). The RG (1 g) was phosphorylated with 85% phosphoric acid (4–10 cm³) or phosphorous oxychloride (4 cm³) at 80°C for 1–3 h in organic solvent (0–10 cm³), which does not react with phosphoric acid. The phosphorylated copolymer beads (RGP) were washed with water until the wash water became neutral and then they were dried.

Measurement of Porosity and Swelling Ratio of the Resins

The specific surface area of the resins was measured on a Yuasa surface area apparatus (BET method). The pore volume and average pore radius were determined on a Carlo-Erba mercury porosimeter (Model 1520). The swelling ratio was calculated by using the following equation:

$$\text{swelling ratio} = \frac{\text{vol wet resin (cm}^3\text{)}}{\text{vol dry resin (cm}^3\text{)}} \quad (1)$$

Measurement of Total Ion Exchange Capacity

In a glass-stoppered 100 cm³ Erlenmeyer flask, 0.25 g of the RGP(H form) was placed, and then 50 cm³ of a 0.1 mol dm⁻³ NaOH–1 mol dm⁻³ NaCl solution were poured in the flask. The mixture was allowed to stand at 25°C for 48 h with occasional shaking. The cation exchange capacity was determined by titrating the concentration of NaOH in the supernatant with a 0.1 mol dm⁻³ HCl solution.

Measurement of Salt Splitting Capacity

The RGP (H form) (0.25 g) was placed in a 100 cm³ Erlenmeyer flask, and 50 cm³ of a 2 mol dm⁻³ NaCl solution were poured into the flask. The mixture was shaken at 30°C for 1 h. The supernatant was poured, by decantation, into a 250 cm³ measuring flask. The above procedure was repeated until the total volume of the supernatant was 250 cm³. The salt splitting capacity was determined by titrating 50 cm³ aliquots of the supernatants with a 0.1 mol dm⁻³ HCl solution.

Determination of pH Titration Curve

In a glass-stoppered 100 cm³ Erlenmeyer flask, 0.5 g of the RGP and 1 mol dm⁻³ KCl solution containing various concentrations of sodium hydroxide were placed. The mixture was shaken at 25°C for 5 days. After that, the pH of the supernatant was measured by Hitachi-Horiba pH meter.

Measurement of Adsorption Capacity for Metal Ions

In a glass-stoppered 100 cm³ Erlenmeyer flask, 0.1 g of the RGP and 50 cm³ of a 0.01 mol dm⁻³ metal ion solution were placed, and the mixture was shaken at 25°C for 96 h. The amount of the metal ion adsorbed on the resins was calculated by the chelatometric or colorimetric determination of metal ion concentration in the supernatant.

Measurement of Selectivity Coefficient (K_{Na}^{Li}) of the RGP

The RGP (Na form) (1.25 meq) was placed in a 100 cm³ Erlenmeyer flask and 25 cm³ of a 0.05 mol dm⁻³ LiCl solution were poured into the flask, and the mixture was shaken at 30°C for 24 h. The Li⁺ and Na⁺ concentration in the supernatant were determined by flame emission spectrophotometry. The selectivity coefficient was calculated by using following equation:

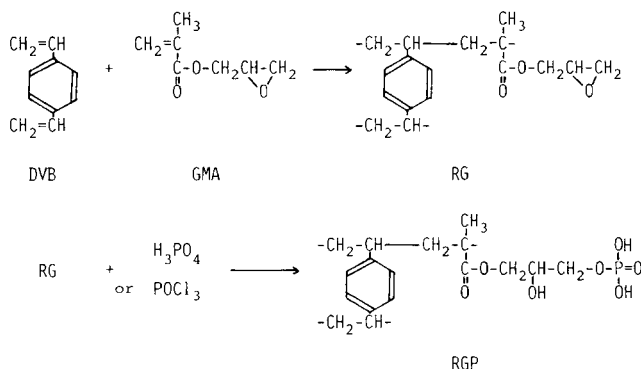
$$K_{Na}^{Li} = \frac{[RLi][Na^+]}{[RNa][Li^+]} \quad (2)$$

where [RLi] and [RNa] represent the amount of Li⁺ and Na⁺ adsorbed on the resin, and [Li⁺] and [Na⁺] represent, respectively, the concentration of Li⁺ and Na⁺ in the solution after equilibration.

RESULTS AND DISCUSSION

Preparation of Macroreticular Chelating Ion Exchange Resins Containing Phosphoric Acid Groups

From preliminary experiments, it was found that the RG with high porosity and physical stability could be prepared by a suspension polymerization in the presence of 50 vol % of 2,2,4-trimethylpentane as diluent. For this reason, all the macroreticular resins used in this research were prepared by a suspension polymerization in the presence of 50 vol % of 2,2,4-trimethylpentane. The macroreticular RGP was prepared as shown in Scheme 1.



Scheme 1 Preparation of resin

In the first place, the RG was phosphorylated with phosphoric acid in various solvents, and the cation exchange capacity of the RGP was measured. The results are shown in Figure 1. The RGP which was prepared by phosphorylation of the RG in benzene or in the absence of solvent had the highest cation exchange capacity (C_t) and salt splitting capacity (C_n). The C_t and C_n of the RGP which was prepared by the phosphorylation in acetone,

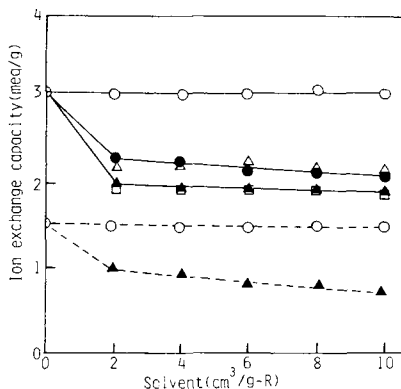


Fig. 1. Phosphorylation of RG with phosphoric acid in various solvents; RG-1 (the number represents mol % of DVB in monomer mixture), 1 g, H_3PO_4 , 4 cm^3 ; 80°C, 3 h. Solvent: (○) benzene; (△) acetone; (●) ethyl methyl ketone; (▲) 1,4-dioxane; (□) water; (—) cation exchange capacity; (- -) salt splitting capacity.

ethyl methyl ketone, 1,4-dioxane, or water are smaller than those of the RGP prepared in benzene or in the absence of solvent. These results suggest that organic solvent or water was not always necessary for the phosphorylation of the RG.

The RG was phosphorylated by varying the amounts of phosphoric acid and the reaction time in the absence of solvent. The phosphorylation of the resins was effectively carried out by treating the RG (1 g) with 4 cm^3 of 85% phosphoric acid at 80°C for 3 h. Both C_i and C_n of the RGP approached constant value at the reaction time above 3 h and C_i was about twice as large as the C_n (Fig. 2).

Next the RG was also phosphorylated with phosphorous oxychloride in 1,4-dioxane at 70°C for 1–5 h (Fig. 3). It was found that the phosphorylation could be easily carried out by treating the RG with phosphorous oxychloride in 1,4-dioxane at 70°C for 1 h and both the C_i and C_n decreased with an

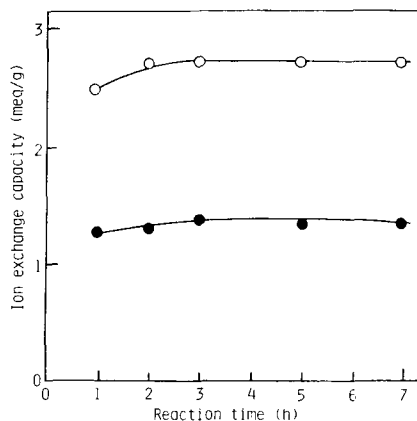


Fig. 2. Effect of reaction time on the phosphorylation of RG; RG-0, 1 g; H_3PO_4 , 4 cm^3 ; benzene, 10 cm^3 ; 80°C: (○) cation exchange capacity; (●) salt splitting capacity.

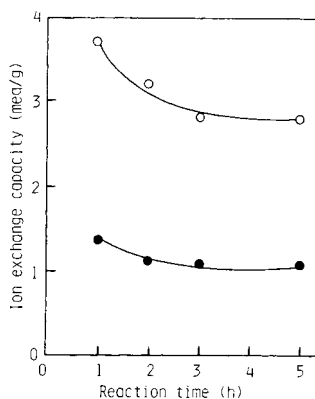


Fig. 3. Phosphorylation of RG with phosphorous oxychloride; RG-0, 1 g; POCl_3 , 5 cm^3 ; 1,4-dioxane, 10 cm^3 ; 70°C: (○) cation exchange capacity; (●) salt splitting capacity.

increase in the reaction time above 1 h. The C_t of the resin was less than twice the C_n . These results are attributed to the occurrence of inter- or intrapolymer bridging via phosphoric acid groups during the phosphorylation. From these results, it is concluded that the phosphorylation with phosphoric acid is a better method than that with phosphorous oxychloride. The RG with various degrees of crosslinking (DVB mol % in monomer mixture) was phosphorylated with phosphoric acid at 80°C for 3 h (Fig. 4). The RGP from RG-2 (the number represents mol % of DVB in monomer mixture) had the maximum C_t and C_n . The C_t and C_n of the RGP prepared from the RG-3–RG-10 decreased with an increase in the amount of DVB. The decrease in the ion exchange capacity is attributed to the decrease in the mol fraction of epoxide groups in the copolymer and to the difficulty of phosphorylation because of low swelling of the RG in phosphoric acid. In spite of higher content of epoxide groups, the RGP prepared from the RG-0 had the lower ion exchange capacity than that of the RGP obtained from the RG-1–RG-3. This is probably due to the differences in the pore structures of the resins. Table I shows the porosities of the RGP. Table I

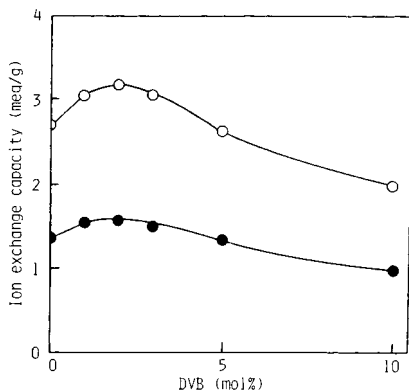


Fig. 4. Effect of crosslinking of RG on the phosphorylation; RG, 1 g; H_3PO_4 , 4 cm^3 ; 80°C, 3 n: (○) cation exchange capacity; (●) salt splitting capacity.

TABLE I
Effect of Crosslinking on the Pore Structure^a

Resin abbreviation	GMA ^b (mol %)	DVB ^c (mol %)	Specific surface area (m ² /g)	Pore volume (cm ³ /g)	Average pore radius (Å)
RGP-0	100	0	0.42	0.28	19,000
RGP-1	99	1	1.15	0.58	17,000
RGP-2	98	2	1.43	0.50	9,400
RGP-3	97	3	1.18	0.60	11,000
RGP-5	95	5	1.43	0.92	17,000
RGP-10	90	10	3.87	0.52	3,600

^a 50 vol % 2,2,4-trimethylpentane per monomer was used as diluent.

^b Glycidyl methacrylate.

^c Divinylbenzene.

also shows that the RGP-0 has lower specific surface areas than other resins and all the RGPs have larger average pore radius than other macroreticular chelating resins reported previously.¹⁻⁴ These results indicate that the phosphorylation rate is not only affected by the content of epoxide groups but also by the porosity of the resins.

pH Titration Curve

In order to study the dissociation behavior of phosphoric acid groups of the resins, the pH titration curve was determined (Fig. 5). From this pH titration curve, two equivalence points can be clearly observed. The first and second equivalence points correspond to the C_n (1.53 meq/g) and C_t (3.08 meq/g) of the resins, respectively. The pK_{a_1} and pK_{a_2} obtained from this pH titration curve are 2.5 and 6.5, respectively. These values agree approximately with those (2.2 and 7.7) of phosphoric acid.

Adsorption of Metal Ions

Effect of crosslinking of the resins on the adsorption of metal ions was studied. The results are shown in Figures 6 and 7. The maximum adsorption

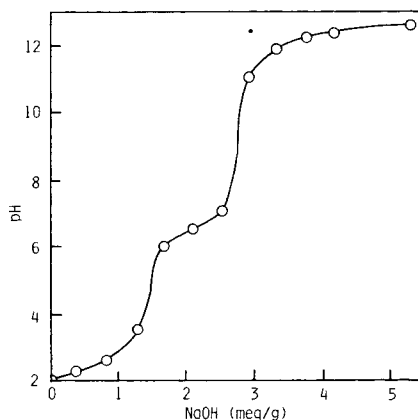


Fig. 5. pH titration curve of RGP prepared by treating the RG with phosphoric acid; RGP-1 ($C_t = 3.08$ meq/g, $C_n = 1.53$ meq/g).

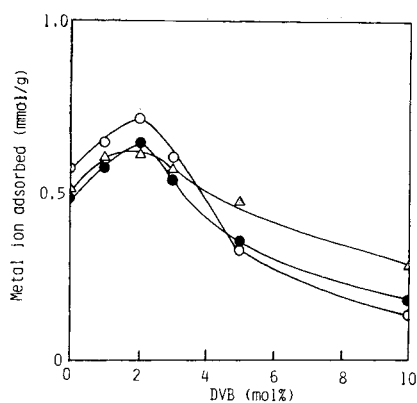


Fig. 6. Effect of crosslinking of RGP on the adsorption of various metal ions; metal ion: (○) Ag⁺; (●) Ca²⁺; (△) Cd²⁺.

Adsorbed metal ion	Initial pH of solution	Final pH
Ag ⁺	5.8	2.8–2.9
Ca ²⁺	5.7	2.7–2.9
Cd ²⁺	5.5	2.6–2.8

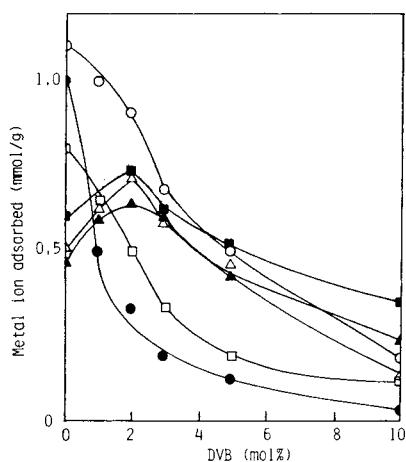


Fig. 7. Effect of crosslinking of RGP on the adsorption of various metal ions; (○) UO₂²⁺; (●) Fe³⁺; (□) Al³⁺; (▲) Cu²⁺; (■) Ni²⁺; (△) Zn²⁺.

Adsorbed metal ion	Initial pH of solution	Final pH
UO ₂ ²⁺	3.2	2.3–3.0
Fe ³⁺	2.3	2.1–2.3
Al ³⁺	3.7	2.4–3.0
Cu ²⁺	4.9	2.6–2.8
Ni ²⁺	5.3	2.7–2.8
Zn ²⁺	5.3	2.6–2.9

TABLE II
Effect of Crosslinking on Swelling Ratio of the Resin

Resin abbreviation	GMA ^a (mol %)	DVB ^b (mol %)	Resin volume (meq/g)		Swelling ratio	Water content (%)
			Dry	Wet		
RGP-0	100	0	2.0	5.5	2.7	70
RGP-1	99	1	2.6	4.6	1.7	63
RGP-2	98	2	2.2	3.2	1.5	51
RGP-3	97	3	2.3	2.9	1.3	47

^a Glycidyl methacrylate.

^b Divinylbenzene.

^c Water content (%) = $100 \times (\text{wt wet resin} - \text{wt dry resin}) / \text{wt wet resin}$.

of Ag^+ , Ca^{2+} , Cd^{2+} , Cu^{2+} , Zn^{2+} , and Ni^{2+} was obtained in the case of the RGP-2. The adsorption of these metal ions depend upon the ion exchange capacity of the resins, whereas in the adsorption of UO_2^{2+} , Fe^{3+} , Al^{3+} , the RGP-0 had the maximum adsorption ability for these metal ions (Fig. 7). To explain these phenomena, the swelling ratio of these resins was measured (Table II). The swelling ratio decreased with an increase in the decrease of crosslinking. Especially the swelling ratio of the RGP-0 was markedly higher than that of other resins. These results indicate that the adsorption of metal ions such as Al^{3+} , Fe^{3+} , and UO_2^{2+} was not only affected by the macropores of the resins but also by the micropores of the wet resins. Figure 7 also shows that the RGP-1 is most effective for the selective adsorption of UO_2^{2+} .

Selective Adsorption of Alkali Metal Ions

The selectivity coefficient ($K_{\text{Na}}^{\text{Li}}$) of the RGP with various degrees of crosslinking was measured. The results are shown in Figure 8. Although the selectivity coefficient of commercial strong acid resins is less than unity,

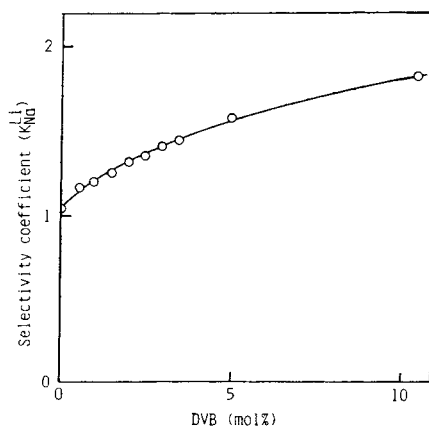


Fig. 8. Effect of crosslinking on the selectivity coefficient ($K_{\text{Na}}^{\text{Li}}$) of RGP.

the K_{Na}^{Li} of the RGP is more than unity. This suggests that the RGP has a higher selectivity for Li^+ than for Na^+ . The selectivity coefficient increases with increasing degree of crosslinking in the range from 0 to 10 mol %.

From the results mentioned above, it is concluded that a RGP with high exchange capacity and adsorption capacity for metal ions can be easily prepared by treating the RG with phosphoric acid at 80°C for 3 h. Such RGP has high adsorption capacity for UO_2^{2+} and higher selective adsorption for Li^+ than for Na^+ .

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