

# Studies of Selective Adsorption Resins. XXV. Preparation of Macroreticular Chelating Resins Containing Aminomethylphosphonic Acid Groups from Methyl Methacrylate / Divinylbenzene Copolymer Beads and Their Adsorption Capacity

HIRONORI MAEDA, *Department of Industrial Chemistry,  
Kumamoto Institute of Technology, Ikeda, Kumamoto 860, Japan,*  
and HIROAKI EGAWA, *Department of Industrial Chemistry,  
Faculty of Engineering, Kumamoto University, Kurokami, Kumamoto  
860, Japan*

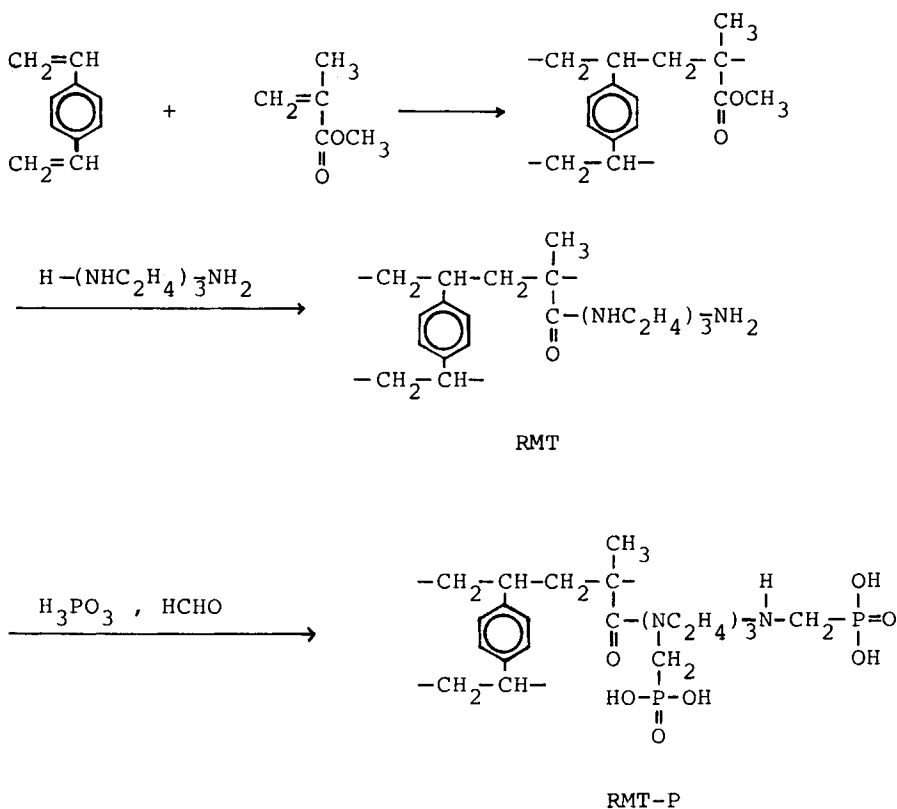
## Synopsis

Macroreticular chelating resins containing aminomethylphosphonic acid groups were prepared by reaction of methyl methacrylate/divinylbenzene copolymer beads with triethylenetetramine, followed by the reaction of the products with phosphorous acid and formaline. The adsorption capacities of this resin for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  were determined at various pH values. The order of chelate stability for the resin was  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ . Copper, nickel, zinc, calcium, and magnesium ions can be eluted with  $1 \text{ mol dm}^{-3}$  hydrochloric acid. The proposed resin appears to be useful for the removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from salt solution.

## INTRODUCTION

Various polymers containing aminomethylphosphonic acid groups have been studied as chelating agents.<sup>1-3</sup> The macroreticular chelating resins are more practical than gel-type resins for the removal and recovery of heavy metal ions from industrial waste solution because of their physical stability and high adsorption rate.<sup>4,5</sup> However, the details of the behavior of the macroreticular chelating resins containing aminomethylphosphonic acid groups have not been investigated.

In this article, the preparation of a macroreticular chelating resin containing aminomethylphosphonic acid groups from methyl methacrylate/divinylbenzene copolymer beads is described and its adsorption capacity for heavy metal ions is discussed. The adsorption of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  on the resin from salt solution was also investigated.



Scheme 1. Preparation of chelating resin.

## EXPERIMENTAL

### Preparation of Macroreticular Chelating Resins

The macroreticular methyl methacrylate/divinylbenzene copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane (TMP) as diluent. Copolymer beads with the desired diameter were selected with a sieve (35–60 mesh). The copolymer beads (1 g) were aminated with triethylenetetramine (5 cm<sup>3</sup>) at 175°C for 7 h. The aminated copolymer beads (RMT) (1 g) were treated with phosphorous acid (2 g) and formaline (3 cm<sup>3</sup>) in the presence of 20% hydrochloric acid (10 cm<sup>3</sup>) as acid catalyst. The resulting resins (RMT-P) were washed with deionized water until the wash water became neutral.

### Measurement of Pore Structure

Resins were dried in a vacuum at 50°C for 8 h. The surface areas of the resins were measured with a Yuasa surface area apparatus (BET method). Pore volumes and average pore radius of the resins were determined on a Carlo-Erba mercury porosimeter (Model 1520).

### Measurement of Adsorption Capacity for Metal Ions

**Batch Method.** In a glass-stoppered Erlenmeyer flask were placed 0.25 g of the resin and 50 cm<sup>3</sup> of buffered metal ion solution (0.01 mol dm<sup>-3</sup>) and mixture was left at room temperature (about 25°C) for 48 h with occasional shaking. The amount of metal ion adsorbed on the resin was calculated from the result of compleximetric titration of the metal ion in the supernatant liquid. The metal ions adsorbed on the resin were then removed by shaking 0.25 g of the resin with 50 cm<sup>3</sup> of 1 mol dm<sup>-3</sup> hydrochloric acid at 30°C for 1 h. The amount of metal ion desorbed was quantified by compleximetric titration.

**Column Method.** A 2 cm<sup>3</sup> sample of the resin (Na Form) was packed in glass column (6 mm $\phi$   $\times$  200 mm). Resin height was about 70 mm. Metal ion solution was passed through the resin bed at a space velocity of 15 h<sup>-1</sup>. The metal content in the effluent was determined by means of the compleximetric titration. Metal ion solutions were prepared from metal chloride of reagent grade.

### Measurement of Phosphor Content

Weighed portions (50 mg) of the resin were decomposed in the Kjeldahl flask with mixed acid. The resulting phosphoric acid was precipitated with ammonium molybdate solution at 60°C, and the phosphor content of the resin was determined by weighing the precipitate.

## RESULTS AND DISCUSSION

### Preparation of the Macroreticular Chelating Resin Containing Aminomethylphosphonic Acid Groups

The macroreticular chelating resins containing aminomethylphosphonic acid groups were prepared by the route in Scheme 1.

The introduction of methylphosphonic acid groups into the RMT was studied under various conditions. The RMT used in this experiment was prepared with methyl methacrylate/divinylbenzene (5 vol%) copolymer beads (TMP 50 vol%/monomer), and its anion exchange capacity was 6.2 mEq/g. The phosphor content of the obtained resins and the adsorption capacity of the resins for Ca<sup>2+</sup> are shown in Figures 1 and 2.

These results indicate that the macroreticular chelating resins containing aminomethylphosphonic acid groups can be prepared easily by treatment the RMT with phosphorous acid and formaline in the presence of acid catalyst at 90°C for 3 h.

The effect of the degree of crosslinking of the resins on the adsorption of calcium ion was investigated by use of the resins with different degrees of crosslinking. Figure 3 shows the Ca<sup>2+</sup> capacity and the phosphor content of the resins in relation to the DVB content.

Although Ca<sup>2+</sup> capacity of the resins decreases with an increase of the degree of crosslinking, the decrease is small over the range of 1–5 vol%. Therefore, the resin with degree of crosslinking of 5 vol% is considered to be suitable for practical use because of its high physical stability.

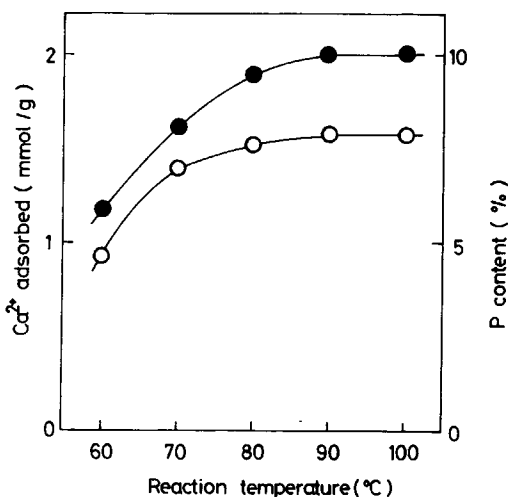


Fig. 1. Effect of reaction temperature on the methylphosphorylation of the RMT; RMT, 1 g;  $\text{H}_3\text{PO}_3$ , 2 g; formaline, 3  $\text{cm}^3$ ; reaction time, 3 h: (○)  $\text{Ca}^{2+}$  adsorbed; (●) P content.

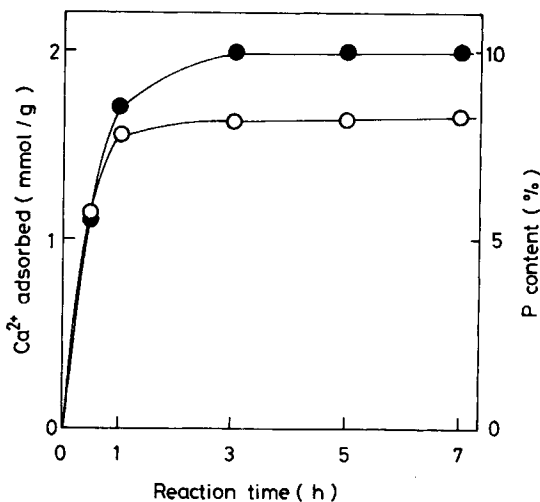


Fig. 2. Effect of reaction time on the methylphosphorylation of the RMT; RMT, 1 g;  $\text{H}_3\text{PO}_3$ , 2 g; formaline, 3  $\text{cm}^3$ ; reaction temperature, 90°C: (○)  $\text{Ca}^{2+}$  adsorbed; (●) P content.

### Effect of Porosity of the Resins on the Phosphor Content and the Adsorption Capacity for $\text{Ca}^{2+}$

The effect of macropore structure (porosity) of the resin on the phosphor content and the adsorption capacity of calcium ion was investigated (Fig. 4). Resins with different porosities were prepared from the methyl methacrylate/divinylbenzene (5 vol%) copolymer beads which were obtained by suspension polymerization with different amount of diluent (TMP) varying from 10% (v/v) to 90% (v/v) relative to the monomer. The pore characteristics (pore volume, specific area, and average pore radius) of the methyl methacrylate/divinylbenzene copolymer beads are shown in Table I.

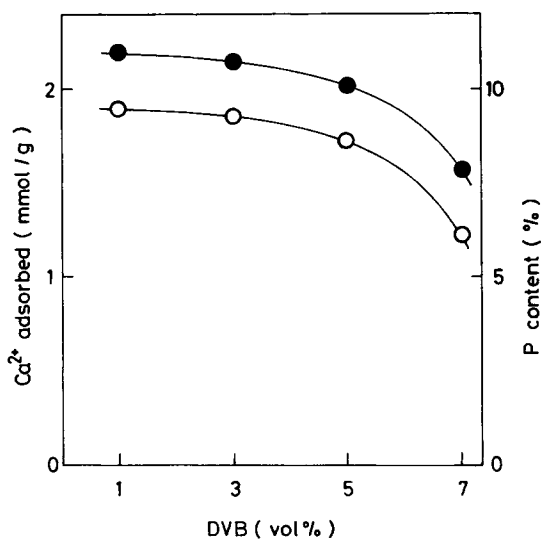


Fig. 3. Effect of cross linking on the P content and the adsorption of Ca<sup>2+</sup>; TMP, 50 vol%: (○) Ca<sup>2+</sup> adsorbed; (●) P content.

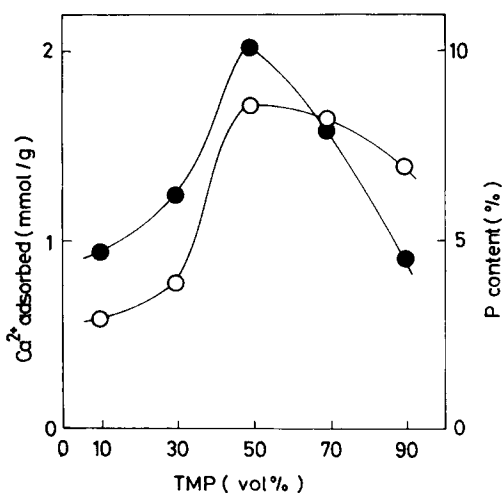


Fig. 4. Effect of porosity on the P content and the adsorption of Ca<sup>2+</sup>; DVB, 5 vol%: (○) Ca<sup>2+</sup> adsorbed; (●) P content.

TABLE I  
Pore Structure of the Macroreticular Copolymer Beads Prepared

No.	DVB <sup>a</sup> (% v/v)	TMP <sup>a</sup> (% v/v)	Pore volume (cm <sup>3</sup> /g)	Specific surface area (m <sup>2</sup> /g)	Average pore radius (nm)
1	5	30	0.23	4.0	41
2	5	50	0.47	8.3	82
3	5	70	0.88	0.8	1580
4	5	90	0.88	0.5	3800

<sup>a</sup>These values represent %(v/v) of DVB in monomer and %(v/v) of 2,2,4-trimethylpentane (TMP) per monomer mixture, used in the synthesis of the resin.

Clearly, the phosphor content of the resin and the adsorption capacity of these resin for  $\text{Ca}^{2+}$  is greatly affected by their porosity. The resin prepared with the methyl methacrylate/divinylbenzene copolymer beads of No. 2 in Table I has the highest phosphor content of 10.05% and provides the highest affinity for  $\text{Ca}^{2+}$ . If three phosphonic acid groups per one unit of triethylenetetramine side chain on the RMT are introduced, it happens that the phosphor content calculated on the basis of the value of anion exchange capacity (6.2 mEq/g) is 10.03%. Therefore, the proposed resins are presumed to have the structure in which three methylphosphonic acid groups are introduced per one triethylenetetramine side chain of the RMT.

### Adsorption Behavior of the Resins for Various Metal Ions

The adsorption capacities of the proposed resin for  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ca}^{2+}$ , and  $\text{Mg}^{2+}$  ions were measured at various pH values with the results given in Figure 5. The resin shows a high affinity for the metal ions studied.

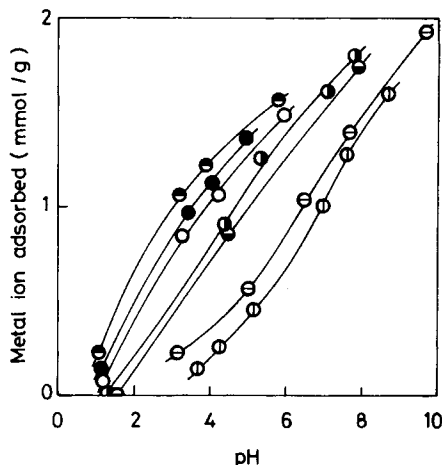


Fig. 5. Effect of pH on the adsorption capacity for various metal ions: (●)  $\text{Cu}^{2+}$ ; (■)  $\text{Pb}^{2+}$ ; (○)  $\text{Zn}^{2+}$ ; (□)  $\text{Ni}^{2+}$ ; (△)  $\text{Co}^{2+}$ ; (◇)  $\text{Ca}^{2+}$ ; (◇)  $\text{Mg}^{2+}$ .

TABLE II  
Elution of Metal Ions Adsorbed on the Proposed Resin

Metal ion	Metal added (mg)	Metal eluted (mg)	Recovery (%)
Mg	9.69	9.64	99.5
Ca	16.48	16.48	100.0
Cu	25.56	25.49	99.7
Ni	20.71	20.65	99.7
Zn	23.77	23.22	97.7
Co	22.09	8.66	39.2
Pb	71.14	25.51	35.9

Adsorption conditions: 50  $\text{cm}^3$  of 0.01  $\text{mol dm}^{-3}$  metal ion solution per 0.25 g of resin, room temperature, 48 h.

Elution conditions: 50  $\text{cm}^3$  of 1  $\text{mol dm}^{-3}$  HCl, 30 °C, 1 h.

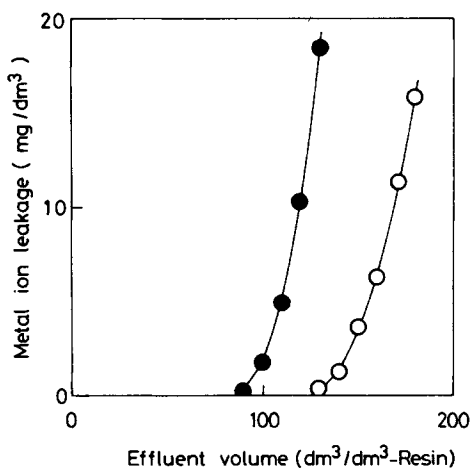


Fig. 6. Breakthrough curves of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ ; resin bed: RMT-P (Na form)  $2 \text{ cm}^3$  ( $6 \text{ mm}\phi \times 70 \text{ mm}$ ), loading solution:  $\text{Ca}^{2+}$  or  $\text{Mg}^{2+}$   $100 \text{ mg dm}^{-3}$ ,  $\text{NaCl}$   $27 \text{ g dm}^{-3}$ , pH 6.6–6.9, flow rate: space velocity (SV)  $15 \text{ h}^{-1}$ ; (○)  $\text{Ca}^{2+}$ ; (●)  $\text{Mg}^{2+}$

The order of affinity is  $\text{Cu}^{2+} > \text{Pb}^{2+} > \text{Zn}^{2+} > \text{Ni}^{2+} > \text{Co}^{2+} > \text{Ca}^{2+} > \text{Mg}^{2+}$ , which is in good accordance with the order of formation constants of introduced ligand, namely, aminomethylphosphonic acid.<sup>6</sup> This resin may be effective material for the removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in the salt solution which is used in soda/chlorine industry, since the resin containing phosphonic acid groups shows a high affinity for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in almost neutral solutions.

Table II shows the recoveries of the metal ions adsorbed on the proposed resin. The metal ions adsorbed on the resin can be eluted easily, except for lead and cobalt ions, by treating with  $1 \text{ mol dm}^{-3}$  hydrochloric acid. It seems that  $\text{Co}^{2+}$  adsorbed on the resin be partially oxidized to form an inert  $\text{Co}^{3+}$  complex.

### Removal of Calcium and Magnesium Ions in Salt solution

The selective adsorption ability of the proposed resin for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in a salt solution was examined under practical column method. Figure 6 shows the breakthrough curves of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$ .

Obviously, the proposed resin has a high affinity for  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  in a salt solution. This fact suggests that the proposed resin should be useful for the removal of  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  from salt solution which is used in soda/chlorine industry. The details of that application are under investigation.

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