# Studies of Selective Adsorption Resins. XXVI. Removal of Calcium and Magnesium Ions in a Salt Solution with Chelating Resin Containing Aminomethylphosphonic Acid Groups

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## Synopsis

Removal of calcium and magnesium ions in a salt solution with the macroreticular chelating resin containing aminomethylphosphonic acid groups was investigated. The resin (RMT-P) exhibited high affinity for calcium and magnesium ions in a salt solution containing 200 g/dm$^3$ of sodium chloride. In the column method, calcium and magnesium ions in a salt solution were preferentially absorbed on the RMT-P, when the salt solution containing 100 mg/dm$^3$ of calcium or magnesium ion was passed through the RMT-P column at a space velocity of 15 h$^{-1}$. The calcium and magnesium ions adsorbed were eluted by allowing 1 mol/dm$^3$ hydrochloric acid to pass through the column. The recycle of adsorption and elution was found to be satisfactory.

## INTRODUCTION

In recent years, ion-exchange membranes technology has been used in soda/chlorine industry. Calcium and magnesium ions in the salt solution used in the industry must be eliminated as much as possible because those ions form insoluble salts on membranes. The application of chelating resins for the removal of calcium and magnesium ions in salt solution has been investigated.[1] In a previous paper, we have reported that a macroreticular chelating resin containing aminomethylphosphonic acid groups shows a high affinity for calcium and magnesium ions in a salt solution.[2] In this article, the selective removal of calcium and magnesium ions from a salt solution by such a resin.

## EXPERIMENTAL

### Preparation of Macroreticular Chelating Resin

The macroreticular methyl methacrylate/divinylbenzene (5 vol %) copolymer beads were synthesized by suspension polymerization in the presence of 2,2,4-trimethylpentane (50 vol %/monomer) as diluent. The macroreticular copolymer beads (35–60 mesh, pore volume 0.47 cm$^3$/g, specific surface area 8.3 m$^2$/g, average pore radius 82 nm, 1 g) were aminated with triethylene-

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tetramine (5 $cm^3$) at 175°C for 7 h. The aminated copolymer beads (1 g) were treated with phosphorous acid (2 g) and formalin (3 $cm^3$) in the presence of 20% hydrochloric acid (10 $cm^3$) as acid catalyst at 90°C for 5 h. The phosphor content of the resin obtained was 10.05%.

### Measurement of Adsorption Capacity for Metal Ions

**Batch Method.** In a glass-stoppered Erlenmeyer flask were placed 0.25 g of the resin (Na form) and 50 $cm^3$ of metal ion solution (0.005 $mol/dm^3$) and the 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.

**Column Method.** A 2 $cm^3$ sample of the resin (Na form) was packed in glass column (6 mm$\phi$ $\times$200 mm). Resin height was about 70 mm. Metal ion solution was passed through the resin bed at a space velocity [volumes ($cm^3$) of loading solution per unit volume ($cm^3$) of resin-hour] of 15 $h^{-1}$. The metal content in the effluent was determined by means of the compleximetric titration or the spectrophotometric procedure based on eriochrome black T.[3] Metal ion solutions were prepared from metal chlorides of reagent grade.

### Measurement of Adsorption Rate

One-half gram of the resin and 225 $cm^3$ of sodium chloride solution were placed in a 300 $cm^3$ three-neck flask. The resins in the flask were degassed under vacuum for 1 min. The mixture was allowed to stand overnight to allow water to permeate into the resins. The flask was set in a fixed temperature bath. After 25 $cm^3$ of calcium chloride solution (100 mg as Ca) was added to the flask with vigorous agitation, 2 $cm^3$ of the aqueous phase was collected with a volumetric pipet at fixed times and the concentration of calcium ion in it was determined.

## RESULTS AND DISCUSSION

### Effect of Sodium Chloride on the Adsorption of Calcium and Magnesium Ions

The effect of sodium chloride on the adsorption of calcium and magnesium ions on the RMT-P was tested. Figures 1 and 2 show the adsorption ability of calcium and magnesium ions on the RMT-P in the presence of sodium chloride, respectively. The value of a commercial cation-exchange resin, Amberlite IRC 50 is also shown for comparison.

Although the adsorption ability of the RMT-P for calcium and magnesium ions gradually decreases with increase in the amount of sodium chloride, the decrease is much smaller than that in the case of commercial cation-exchange resin, Amberlite IRC 50. From these results it is clear that the adsorption ability of the RMT-P for calcium and magnesium ions is hardly affected by the presence of large amounts of sodium chloride at equilibrium of adsorption.

The effect of sodium chloride on the adsorption of calcium ion on the RMT-P was also examined under column operation which is a practical

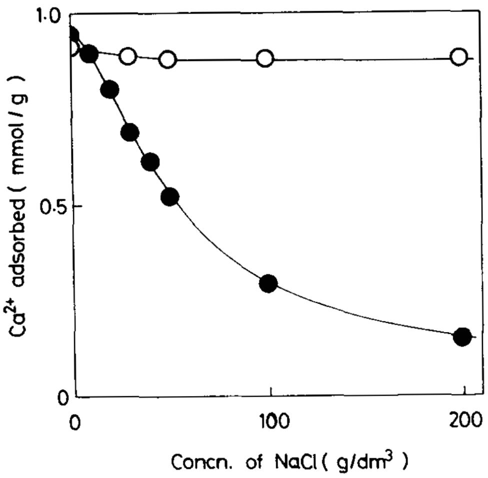

Fig. 1. Effect of NaCl on the adsorption of $Ca^{2+}$; resin: (○) RMT-P; (●) IRC 50.

process for removal of calcium ion from salt solution. Figure 3 shows the breakthrough curves of calcium ion. Calcium ion solution (100 mg/dm$^3$) containing sodium chloride of 10, 30, 50, 100, and 200 g/dm$^3$ was passed through the resin bed at a space velocity of 15 h$^{-1}$, respectively.

In practical column operation, the adsorption ability of calcium ion decreases with increases in the amount of sodium chloride. Although the decrease is larger than that in the case of batch operation, the RMT-P exhibits favorable affinity for calcium ion up to 100 bed volumes when the highly concentrated salt solution (200 g/dm$^3$) was passed through the column. The

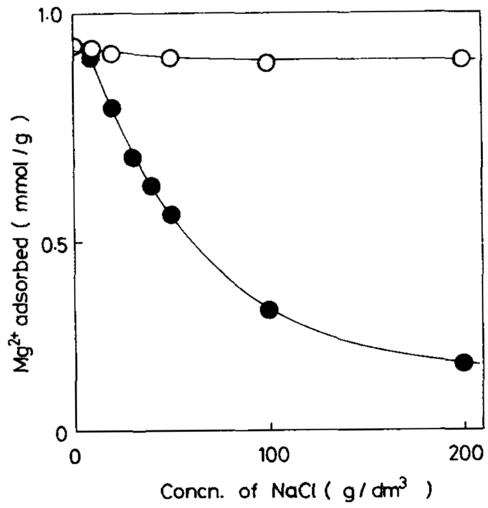

Fig. 2. Effect of NaCl on the adsorption of $Mg^{2+}$; resin: (○) RMT-P; (●) IRC 50.

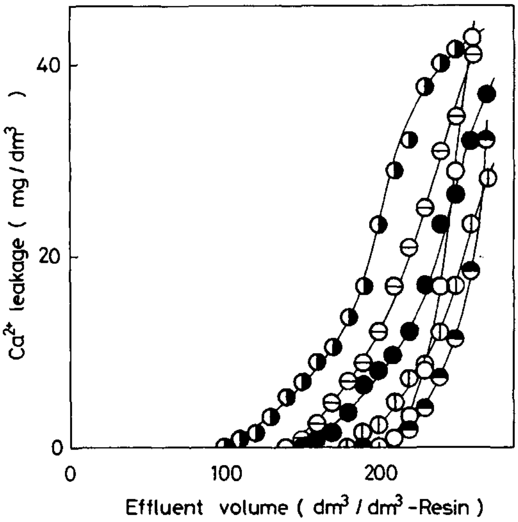

Fig. 3. Breakthrough curves of Ca$^{2+}$; resin bed: RMT-P (Na form), 2 cm$^3$ (6 mmϕ × 70 mm); loading solution: Ca$^{2+}$, 100 mg/dm$^3$; flow rate: space velocity (SV) 15 h$^{-1}$; concentration (g/dm$^3$) of NaCl in the loading solution: (○) 0; (◓) 10; (⦶) 30; (●) 50; (⊖) 100; (◑) 200.

forms of these breakthrough curves suggests that the adsorption band of calcium ion on the RMT-P column expands with increasing amounts of sodium chloride in the loading solution.

Figure 4 shows the initial adsorption rates of calcium ion in salt solution on the RMT-P. The initial adsorption rate of calcium ion on the RMT-P decreases greatly with increasing the amount of sodium chloride in the solution. Therefore, it seems that the adsorption of calcium ion on the RMT-P in the column operation was affected by a coexistence of sodium chloride.

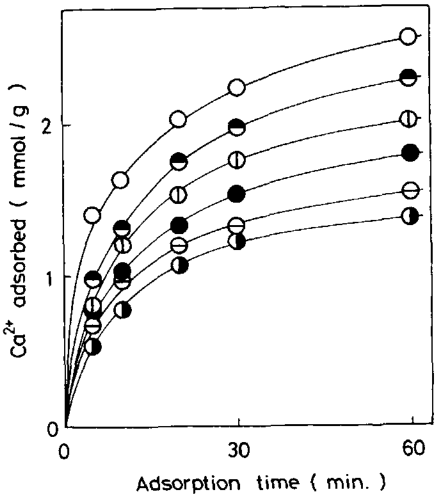

Fig. 4. Adsorption rate of Ca$^{2+}$ on the RMT-P; concentration (g/dm$^3$) of NaCl: (○) 0; (◓) 10; (⦶) 30; (●) 50; (⊖) 100; (◑) 200.

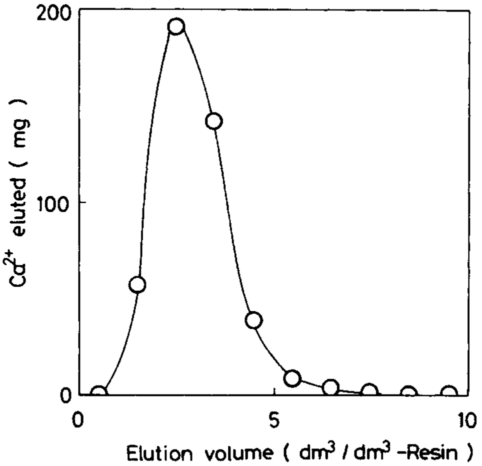

Fig. 5. Elution curve of $Ca^{2+}$; eluent: 1 mol/dm$^3$ HCl; flow rate: SV 7.5 h$^{-1}$.

## Elution of Calcium Ion Adsorbed on the Resin

In order to use repeatedly this resin for removal of calcium ion, it is necessary for calcium ion adsorbed to be eluted easily. The elution of calcium ion adsorbed on the RMT-P was investigated by the column method. Figure 5 shows the elution curve of calcium ion with 1 mol/dm$^3$ of hydrochloric acid. The recovery of calcium ion was 98.8%. Almost complete removal of calcium ion from the resin was achieved by passing 10 bed volumes of 1 mol/dm$^3$ hydrochloric acid through the column at a space velocity of 7.5 h$^{-1}$.

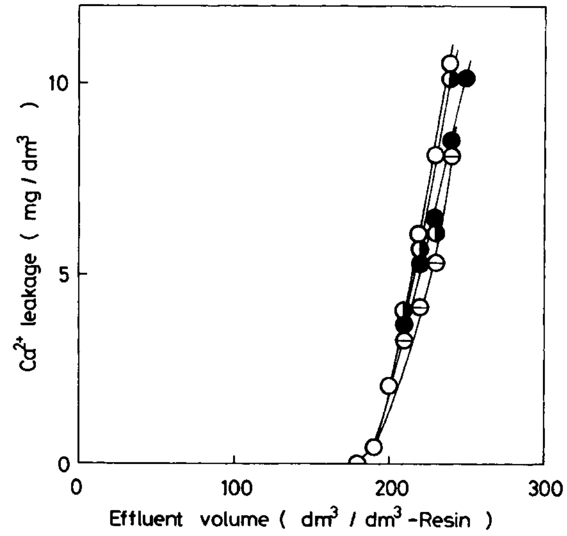

Fig. 6. Recycle test; resin bed: RMT-P (Na form), 2 cm$^3$ (6 mm$\phi$ × 70 mm); loading solution: $Ca^{2+}$, 100 mg/dm$^3$, NaCl, 27 g/dm$^3$; flow rate: SV 15 h$^{-1}$; elution: 1 mol/dm$^3$ HCl, 10 dm$^3$/dm$^3$/resin, SV 7.5 h$^{-1}$; cycle number: (○) 1; (●) 2; (⊖) 3; (◑) 4.

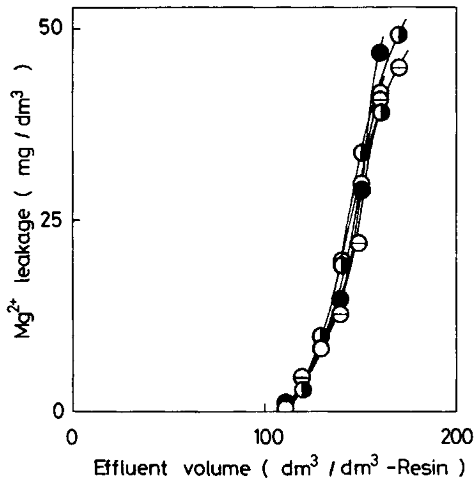

Fig. 7. Recycle test; resin bed; RMT-P (Na form), 2 cm$^3$ (6 mmϕ × 70 mm); loading solution: Mg$^{2+}$, 100 mg/dm$^3$, NaCl, 27 g/dm$^3$; flow rate: SV 15 h$^{-1}$; elution: 1 mol/dm$^3$ HCl, 10 dm$^3$/dm$^3$ resin, SV 7.5 h$^{-1}$, cycle number: (○) 1; (●) 2; (⊖) 3; (◑) 4.

## Recycle Test

Repeated adsorption and elution of calcium and magnesium ions in a salt solution was examined by the column method by using 1 mol/dm$^3$ hydrochloric acid as eluent. Figures 6 and 7 show the breakthrough curves of calcium and magnesium ions for several adsorption-elution cycles. A decrease of adsorption ability of the RMT-P for calcium and magnesium ions was not observed on repeated cycling. From these results, it was found that the recycle of adsorption and elution was satisfactory. It was also shown that, like calcium, magnesium ion adsorbed on the RMT-P was effectively eluted by passing 10 bed volumes of 1 mol/dm$^3$ hydrochloric acid through the column at a space velocity of 7.5 h$^{-1}$. The contraction of volume of the RMT-P in a salt solution was hardly observed, as the resin was a macroreticular type resin.

## Removal of Magnesium Ion in a Salt Solution

Magnesium and calcium ions in salt solution can readily be removed by precipitation with sodium hydroxide and sodium carbonate. However, this procedure leaves in solution residual concentrations of 2–3 mg/dm$^3$. Accordingly, the removal of low concentrations of magnesium ion from a salt solution was tested in a practical column operation. When the solution containing 5 mg/dm$^3$ of magnesium ion and 27 g/dm$^3$ of sodium chloride was passed through the RMT-P column at a space velocity of 15 h$^{-1}$, the magnesium ion concentration in the effluent was less than 0.02 mg/dm$^3$ (determination limit of spectrophotometric procedure) up to 900 bed volumes.

From the results mentioned above, it is clear that the RMT-P containing aminomethylphosphonic acid groups is of practical use for the removal of calcium and magnesium ions in the salt solution used in soda/chlorine industry.

## References

1. M. Hirai, *J. Synthetic Org. Chem. Jpn.*, **42**, 1005 (1984).
2. H. Maeda and H. Egawa, *J. Appl. Polym. Sci.*, **33**, 1275 (1987).
3. J. Fries and H. Gtrost, *Organic Reagents for Trace Analysis*, E. Merk, Darmstadt, 1977, p. 226.

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