

Effects of Modification with Cationic Polymer on the Ion-Exchange Property of Cation-Exchange Resin

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For the change of ion exchange selectivity of cation exchange resin, the gel-type cation exchange resin was modified with cationic polymer, poly(4-vinylpyridine) and polyaniline. On the modified resin with cationic polymer, the ion exchange rate of multivalent cation becomes slower than that of monovalent cation. The ion exchange rate of the modified resin was based on the ionic valency of exchangeable cation with the opposite tendency on a commonly cation exchange resin. It means that the ion exchange of multivalent cation was more inhibited by the modification layer consisting of cationic polymer by the electrostatic repulsive force and sieving effect due to the electric charge density. Furthermore, the modified resin with polyaniline indicates intensive inhibition. From the analysis of ion exchange properties on the modified resin, the modification of cationic polymer has no effect on the ion exchange equilibrium constant. Thus, it is considered that the modification occurs on the ion exchange site at near surface of ion exchange resin beads. This modified resin was used to separate monovalent cation selectively from an aqueous solution of multivalent cations.

Key Words: Ion exchange resin, Selectivity, Modification, Cationic Polymer

1. INTRODUCTION

The separation and concentration of various ions are required in various field. Typically, the ion separation is carried out by the use of ion exchange resin and membrane. The separation process using ion exchange resins is simple and advantageous for the concentration of trace ions from dilute solutions. But, in these methods, the separation of specific ions from mixture solution containing of various ions is difficult. For the improvement of ion exchange selectivity, various modification resins are developed in many researchers. Most of these improvement are grouped into two methods, the modification of chlate compounds onto the anion exchange resin¹⁻⁴ and the introduction of hydrophobic compounds onto the ion exchange resin for the enhancement of hydrophobic interaction.^{5,6}

In previous papers⁷⁻⁹, the selective collection of monovalent ions on an ion exchange resins with Demol N (the polycondensation product of naphthalene sulfate and formaldehyde, made by Kao Chemicals Co. Ltd., Tokyo, Japan), poly(styrenesulfonic acid), and poly(4-vinylpyridine) were reported. On the ion exchange resin modified with polyelectrolyte having electric charge of same polar character as exchangeable ions, the ion exchange rate of multivalent ions become slower than that of monovalent ions. This is explained by the difference of electrostatic repulsion force between exchanged ions and ionic site of the modification layer. Thus, the modification with polyelectrolyte make it

possible to separate specific ions based on the difference of the polar character and ionic valency.

In this work, the modification layer consisting of cationic polymer, polyaniline, was formed on the surface of cation exchange resin by the polymerization onto the resins. And the changes of cation exchange rate on the modified resin prepared in the various conditions were examined.

2. EXPERIMENTAL

2.1 Apparatus

The sample solution was analyzed by the ion chromatography composed of Hitachi model L-6000 pump, Hitachi model L3720 conductivity detector and Hitachi model L5020 column oven with sample injector. The separation column was Shodex IC YK-421 (ϕ 4.6×100 mm, Showa Denko). The analytical signals were recorded and processed with a Hitachi model D-2500 chromatograph integrator.

2.2 Reagents

Gel type cation exchange resin, Amberlite IR120B (Organo Co., Ltd.) in the sodium ion form(0.40-0.53 mm) was used. Poly(4-vinylpyridine) (Aldrich Chemical Co. Inc.) was used to form the modification layer on the surface of the cation exchange resin. The average molecular weight of poly(4-vinylpyridine) polymer is 60,000. All other reagents used were analytical reagent grade and were used without further purification.

Distilled water was prepared by AQUEOUS GS-20 automatic water distillation apparatus (Advantec Toyo Kaisha, Ltd.).

2.3 Modification of cation exchange resin

The cation exchange resin was pretreated with sufficient hydrochloric acid solution (2 mol dm^{-3}). After, pretreated resin was thoroughly washed with water. The ion exchange resin was converted into the hydrogen ion form by the pretreatment, because the peak of another cation was influenced by the peak of sodium ion in the ion chromatography.

The modified resin with poly(4-vinylpyridine) was prepared by the same method as reported in a previous paper.⁹ The modified resin with polyaniline was prepared by the batch method. The pretreated cation exchange resin was immersed into mixture solution 0.3 mol dm^{-3} aniline and 0.2 mol dm^{-3} HCl at 60°C for 5 minutes on a water bath, and was washed with water. After that, the resin exchanged aniline was immersed into 0.1 mol dm^{-3} ammonium peroxodisulfate solution at 60°C for 10 minutes. Then modified resin was filtered and washed with water sufficiently. The modified resin was kept wet condition.

2.4 Ion exchange procedure

Two milliliter of modified resin was introduced into a 300 cm^3 Erlenmeyer flask and several washings were made with distilled water. After that, 100 cm^3 of sample solution was added. This flask was shaken for 40 min at 25°C . Then the concentration of cations in the sample solution was measured using ion chromatography. After that, 100 cm^3 of 0.05 mol dm^{-3} magnesium chloride solution was added into a flask containing of exchanged resin. This flask was shaken for 60 min at 25°C . Released anions were determined using ion chromatography.

The analytical condition of ion chromatography was as follow. Elutriant was aqueous solution containing of 5 mmol dm^{-3} L(+)-tartalic acid, 1 mmol dm^{-3} 2,6-pyridinedicarboxylic acid and 1.5 g dm^{-3} boric acid. Elutriant was flowed at $1 \text{ cm}^3 \text{ min}^{-1}$. The temperature of the column oven was kept at 40°C . Each $10 \mu\text{l}$ of sample solution was injected.

3. RESULTS AND DISCUSSION

3.1 Influence of modification with cationic polymer

The changes of ion exchange rate on the modified cation exchange resin with cationic polymer, poly(4-vinylpyridine) and polyaniline, were measured. For comparison, the ion exchange rate on the bare unmodified resin was measured by the same method. The results for potassium and calcium ions are shown in Fig.1. In every cases, the ion exchange rates are decreased by the modification. Thus, the cation

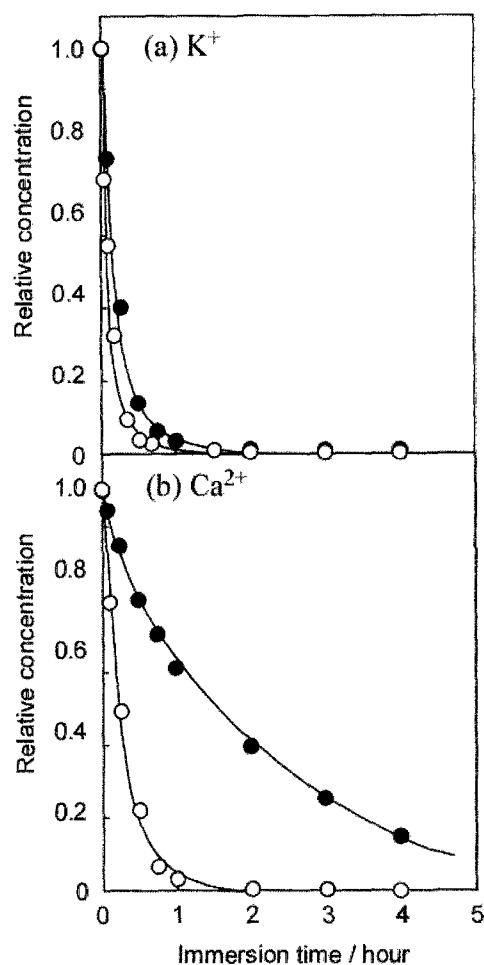


Fig.1 The exchange of modified (●) or unmodified (○) resin in hydrogen ion form and sample solution containing of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ potassium (a) and calcium (b) solution.

exchange reaction was inhibited by cationic modification layer, because of the electrostatic repulsive force between cationic layer and exchangeable cations. It is explainable for the slower ion exchange rate of calcium ion than that of potassium ion. The ion exchange of calcium ion is strongly inhibited by the greater repulsive force due to the high charge number.

Furthermore, on the modified resin with polyaniline, the ion exchange reaction of calcium ion is more restricted than that with poly(4-vinylpyridine).⁹ It is assumed that the modification layer consisting of polyaniline was formed higher density than that of poly(4-vinylpyridine). The polyaniline layer was polymerized in the micropore by the reaction of exchanged aniline monomer and peroxodisulfate ion in the solution. Thus, the synthesized polyaniline can be concentrated in a very dense state into the micropore. Because of the high density cationic layer, the monovalent cation can be exchanged into modified resin preferentially in the solution containing multivalent

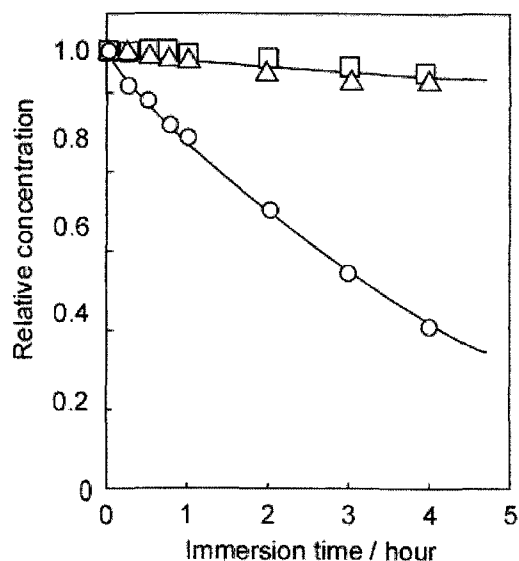


Fig.2 Ion exchange rate on the modified resin with polyaniline prepared in 0.10 (○), 0.15 (Δ), and 0.20 (□) mol dm⁻³ aniline solution. These experiments measured in sample solution containing of 1.0 × 10⁻³ mol dm⁻³ calcium ions.

cations.

3.2 Influences by the modified condition

The influence of the conditions of the modification on the ion exchange rate was investigated. In the modification, the aniline monomer was exchanged into the ion exchange resin initially. The ion exchange rate of the modified resin with various concentration of aniline monomer solution and 0.1 mol dm⁻³ ammonium peroxodisulfate solution and unmodified resin are shown in Fig.2. In this results, the ion exchange of calcium ions was inhibited adequately on the modified resin immersed in the aniline solution above 0.15 mol dm⁻³. Amounts of exchanged aniline monomer in the pre-modified resin may increase with increasing the concentration of the aniline solution. The synthesized polyaniline increased by the use of the aniline solution of high concentration. Thus, the density and/or the thickness of modification layer increased. In this reason, the ion exchange rate decreased with the increasing of the concentration of aniline solution. But the ion exchange rate of potassium ions also decreased by the use of the concentrated solution. Afterward, the suitable aniline concentration of initially immersed solution decided 0.15 mol dm⁻³ in this experiment.

Furthermore, the influence of the concentration of ammonium peroxodisulfate, oxidizing reagent for the polymerization of aniline, on the ion exchange rate was examined. As shown in Fig.3, the ion exchange rate of modified resin decreased with decreasing of the concentration of ammonium peroxodisulfate. It means

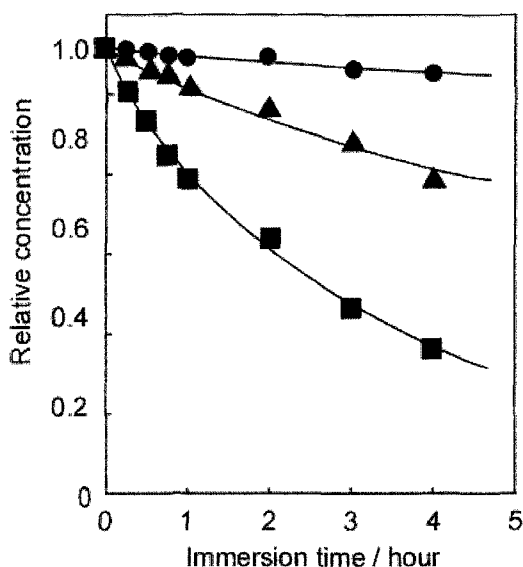
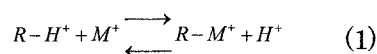


Fig.3 Ion exchange rate on the modified resin with polyaniline prepared in 0.10 (●), 0.15 (▲), and 0.20 (■) mol dm⁻³ ammonium peroxodisulfate solution. These experiments measured in sample solution containing of 1.0 × 10⁻³ mol dm⁻³ calcium ions.

that the relationship between the changes of ion exchange rates and amounts of filled modifier is not simple. In the polymerization process, the precipitation of polyaniline was appeared in the ammonium peroxodisulfate solution. This means that a part of synthesized polyaniline was desorbed from resins. Thus, the density and/or the amounts of polyaniline in the micropore were varied by the rate of polymerization related to the concentration of the oxidized reagents.

3.3 Ion exchange properties of the modified resin

The ion exchange properties of the modified resin was assessed by the similar method described by Kataoka *et al.*¹⁰ According to this method, the cation exchange equilibrium of the resin in hydrogen ion form with other monovalent cations can be described by this equation.



$$K_H^M = \frac{q_M \cdot C_H}{q_H \cdot C_M} \quad (2)$$

$$q_M = Q - \frac{1}{K_H^M} \frac{(C_0 - C_x)q_M}{C_M} \quad (3)$$

where K_H^X is the ion exchange equilibrium constant based on the ion exchange reaction expressed in eq.1, the other variables are corresponding to that describe above. This equation shows that the plot of q_x against $(C_0 - C_x)q_x / C_x$ is a linear relationship with the slope of $-1/K_H^X$ and the intercept of this straight line is ion exchange capacity of resin. For the assessment of ion

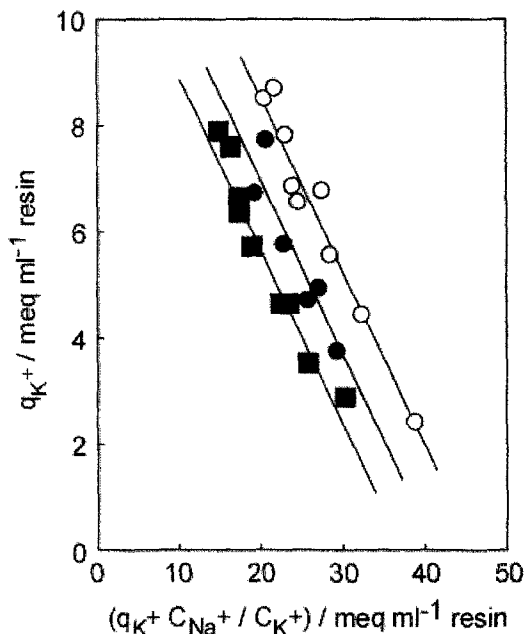


Fig.4 Equilibrium plots for the ion exchange between potassium ion and sodium ion form unmodified (○) resin and modified resin prepared in 0.10 (●) and 0.15 (■) mol dm⁻³ aniline solution.

exchange reaction between a hydrogen ion form resin and an aqueous solution of sodium ion, the relationship of q_K against $(C_0 - C_K)q_K / C_K$ was investigated.

One milliliter of modified resin in sodium ion form was immersed into 100 cm³ sample solution containing of potassium chloride, and shaken for 24 hour at 25°C. The concentration in this sample solution varied from 1.0×10^{-3} to 8.0×10^{-3} mol dm⁻³. After that, the concentrations of the sample solutions were determined by use of ion chromatography. The values of q_K and $(C_0 - C_K)q_K / C_K$ were calculated from their concentration. On the unmodified resin, the same experiment was also carried out.

These results are shown in Fig.4. The plots of q_K against $(C_0 - C_K)q_K / C_K$ obtained from modified and unmodified resin are straight line. In addition, each line is parallel. Thus, the ion exchange equilibrium constant K_K^{Na} of both resins are equal. However, the ion exchange capacity of modified resin is smaller than that of unmodified resin. Namely, the affinity between resin and exchangeable ions were not changed by modification. But the ion exchange capacities decreased, due to the continuous adsorption of polyaniline. The modification layer was formed in the micropore near surface only. It can be confirmed by the observation of cut plane of the modified resin. Thus, the modification with polyaniline influences the ion exchange rate, but does not affected to the ion exchange affinity between resin and exchangeable ions.

By the use of this modified resin, the separation of specific ions due to the difference of ionic valency can be

carried out by the ion exchange reaction for the suitable period. The modified resin with polyaniline was immersed into the mixture solution containing of K⁺ and Ca²⁺, and immersed into NaCl solution for the desorption. In this result, potassium ion was released, but calcium ion was not released into eluting solution. In the elution process, the desorption of adsorbed ion was influenced by the modification layer along with the adsorption process. This modification can be applied to the addition of selectivity due to the difference of ionic valency. It may contribute to the improvement of the ion exchange selectivity.

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