

Ion Exchange Selectivity of Cation Exchange Resin Modified with Cationic Polymer

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In order to change the ion exchange selectivity of cation exchange resin, the surface of gel type cation exchange resin was modified by the adsorption of cationic polymer, poly(4-vinylpyridine). After that modification, the ion exchange rate of divalent cation becomes slower than that of monovalent cation. This observation indicates the presence of cationic polymer layer serves to slow down the rate of cation exchange by the sieving effect and electrostatic repulsive force. Especially, the ion exchange rate of divalent cation was slower than the rate of monovalent cation, due to this electrostatic repulsive force between exchangeable cation and ion exchange groups on modification layer. This ion exchange selectivity of modified resin based on the ionic valency are opposite to that of commonly cation exchange resin. This modified resin was used to separate potassium ions from calcium ions in the aqueous solution.

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

1. INTRODUCTION

Ion exchange resins are widely used in various fields as absorbant of ions. For this usage, it is well accepted that the ion exchange resin is an important material for the separation of ions in aqueous solution because of its high capacity and simplicity. In this method, the multivalent ions become more preferentially incorporated into resin than monovalent ions, since the ion exchange resin has greater affinity to multivalent ion than monovalent ion due to the electrostatic interaction. Thus, the selective collection of specific ions is difficult. There have been various investigations for the improvement of the selective collection of specific ions. Most of these investigations are grouped into two methods. These methods are the modification of chelate compounds on the anion exchange resin for selective collection of metal ions¹⁻³ and introduction of hydrophobic compounds onto the ion exchange resin matrix for selective collection of hydrophobic ions.^{4,5}

The ion exchange membranes are also used in the separation of ions in aqueous solution. But the ion exchange membrane has poor selectivity for specific ions. That is to say, the separation of specific ions with the same charge and polarity by electro dialysis and diffusion dialysis is difficult. It was reported that monovalent cation permselectivity of membrane was improved by the formation of a thin cationic polyelectrolyte layer on the surface of the cation exchange membrane.⁶⁻⁹ This is explained by the difference of electrostatic repulsion force between dialyzed cations and cationic site of the modification layer. Similarly, the modification of a thin

anionic polyelectrolyte layer on the surface of the anion exchange membrane was reported.^{10,11} These studies also based on the electrostatic interactions between dialyzed anions and modification layer.

In this work, the modification layer consisting of cationic polymer, poly(4-vinylpyridine), was formed on the surface of cation exchange resin by the similar method in the case of modified cation exchange membrane. The changes in the rate of ion exchange reaction by use of this modified resin were studied. Further, the modified cation exchange resin was used to separate potassium ion from calcium ion in the aqueous solution.

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 chromato 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.) were used to form the modification layer on the surface of the cation exchange resin. The

average molecular weight of poly(4-vinylpyridine) polymer are 60,000. All other reagents used were analytical grade. Distilled water was prepared by AQUEOUS GS-20 automatic water distillation apparatus (Advantec).

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 distilled water.

Ten milliliter of the cation exchange resin in a hydrogen ion form was introduced into a 200 ml round-bottomed flask and 100 cm^3 of 5 wt% poly(4-vinylpyridine) solution was added. The mixture was stirred for 8 hour at 60°C in a water bath. Then modified resin was filtered and washed with distilled 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 . The amounts of released cations were measured using ion chromatography.

The analytical condition of ion chromatography was as follow. Elutriant was aqueous solution containing of $0.75 \text{ mmol dm}^{-3}$ potassium hydrogen phthalate, 5%(v/v) isopropylalcohol and 2%(v/v) ethyleneglycole. 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 Modification with poly(4-vinylpyridine)

The changes of cation exchange rate by the modification with poly(4-vinylpyridine) was investigated. Two cubic centimeters of the modified or unmodified resins in hydrogen ion form was introduced into 300 cm^3 flask and immersed into a 100 cm^3 of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ chloride salt solution with various cation. Then, flask was shaken at 25°C . The change of the concentration of potassium ion in the solution with immersion time was measured by use of ion chromatography. The similar experiments in the solution containing another cations were carried out by the same method. The ion exchange resin was converted into the hydrogen ion form by the pretreatment, because the peak of another cation was

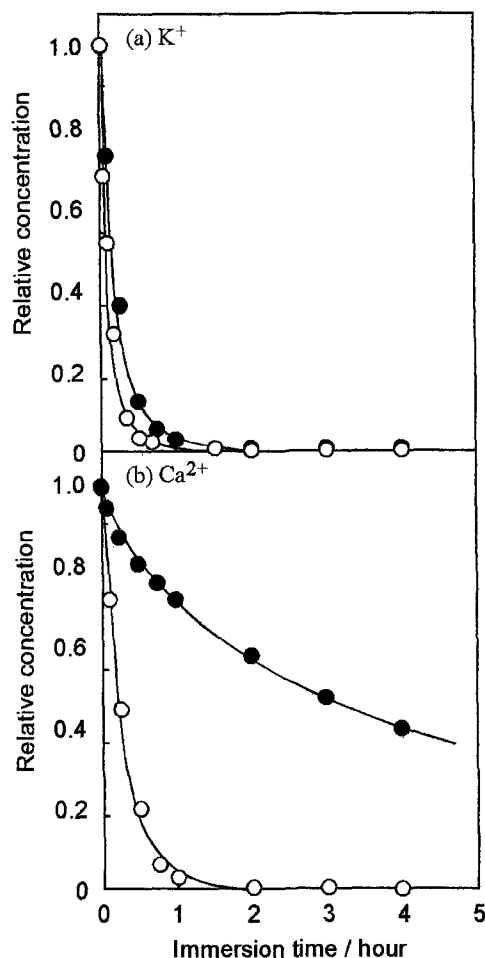


Fig.1 The changes of concentration in the sample solution containing of $1.0 \times 10^{-3} \text{ mol dm}^{-3}$ potassium (a) or calcium (b) ions with the modified (●) or unmodified (○) resin in hydrogen ion form.

influenced by the peak of sodium ion in the ion chromatography. The results for potassium and calcium ions are shown in Fig. 1. In both cases, the ion exchange rates are decreased by the modification. It means that the transfer of exchangeable cation into modified resin was restrained by the electrostatic repulsive force between cationic layer and exchangeable cation. Thus, the ion exchange rate of calcium ions was slower than potassium ions, because of the greater repulsive force due to the high charge number. Therefore, the electric charge density of modification layer is presumed to control the ion exchange rates on the various cations for the separation of specific ions.

3.2 Influences by the modified condition

The influence of the modified conditions on the ion exchange rate was investigated. The modification of ion exchange resin was carried out by the immersion and stirring into a solution containing poly(4-vinylpyridine) at 60°C . The ion exchange rates of the modified resins prepared in the 5wt% and 4wt% of poly(4-vinylpyridine) solution and unmodified resin are shown in Fig.2. The

absorbed amounts of modified resins were 94 and 80 mg cm⁻³ wet resin, respectively. The absorbed amounts are calculated from the changes in concentration of poly(4-vinylpyridine) solution. Thus, these amounts are predicted somewhat greater than actual absorbed amounts, because of evaporation and so on. This absorbed modification layer could not be exchange easily with other cations by the π-electron interaction between pyridine group and benzenoid structure. In this experiments, the rates of ion exchange reaction were decreased with the increase of the absorbed amounts of poly(4-vinylpyridine). The pronounced decrease of ion

exchange rate was shown in the result obtained in the calcium solution. In contrast, the decrease of ion exchange rate obtained in the potassium solution was very small. Consequently, the greater amounts of modification agents led to decrease of ion exchange rates, especially on the multivalent cations. It is consider that the greater amounts of modification agents led to the higher density of cationic sites in the modification layer.

In the modification of resin, the state of modification layer influenced the degree of swelling, changed by the temperature of immersed solution. The influence of the modification temperature on the ion exchange rate was investigated. The ion exchange rates of the modified resins prepared in the 5wt% poly(4-vinylpyridine) solutions at 40, 60 and 90°C and unmodified resin are shown in Fig.3. The amounts of adsorbed cationic polymer on the gel-type ion exchange resin were increased in the higher temperature. It is consider that the micropore on the surface of gel-type resin becomes greater by the swelling as the temperature raised. Thus, as the temperature dropped after the modification, the modified agents introduced into micropore were compressed by the contraction and formed the high electric charge density layer. The high electric charge density led to the slower rate of ion exchange because of greater electrostatic repulsion force between exchangeable cations and cationic site of the modification layer. But the modified resin prepared at higher temperature than 70°C indicates higher rate of ion exchange reaction. In general, the performance of ion exchange resin was degraded by the high temperature, because of the thermal decomposition of ion exchange functional group. However, the capacity of the ion exchange resin was not decreased with the treatments in the hot solution at 90°C for 8hour. Thus, this capacity was not affected by this treatment until 3 times. The increase of the ion exchange rate in the modified resin prepared at 90°C due to the formation of the imperfect modification layer, because of the excessive enlargement of micropore by the swelling. In this paper, the modification of ion exchange resin was carried out in the 5wt% poly(4-vinylpyridine) solution at 60°C.

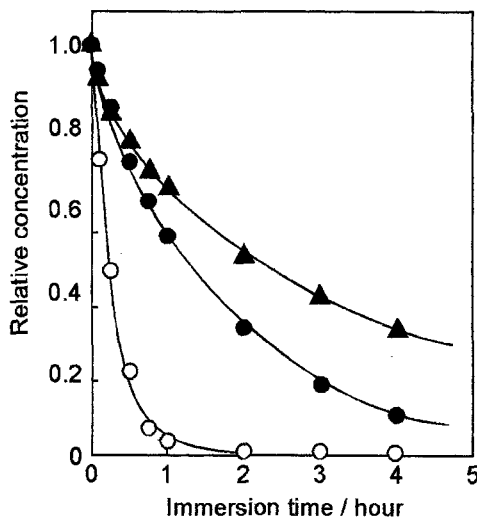


Fig.2 The changes of concentration in 1.0 × 10⁻³ mol dm⁻³ calcium ion solution with the unmodified (○) and modified resin prepared in the 5wt% (●) or 4wt% (▲) poly(4-vinylpyridine) solution.

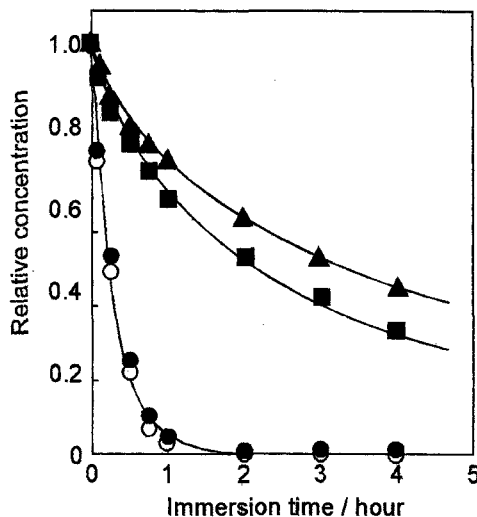
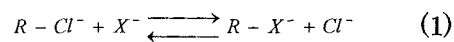


Fig.3 The changes of concentration in 1.0 × 10⁻³ mol dm⁻³ calcium ion solution with the unmodified (○) and modified resin prepared in the 5wt% poly(4-vinylpyridine) solution at 40 (●), 60 (▲), 90°C (■).

3.3 Ion exchange equilibrium

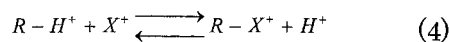
The procedure used for assessing the ion exchange property of the modified resin was similar to that described by Kataoka *et. al.*¹² The following equation has been obtained at the ion exchange equilibrium of the resin in chloride form with other monovalent anions in aqueous solution:



$$K_{Cl}^X = \frac{q_x \cdot C_{Cl}}{q_{Cl} \cdot C_x} \quad (2)$$

$$q_x = Q - \frac{1}{K_{Cl}^X} \frac{(C_0 - C_x)q_x}{C_x} \quad (3)$$

where K_{Cl}^X is the ion exchange equilibrium constant, C and q are the concentrations in aqueous solution and resin respectively, C_0 , the initial concentration and Q , the ion exchange capacity of resin. According to this theory, the cation exchange equilibrium of the resin in hydrogen ion form with other monovalent cations can be described by this equation.



$$K_H^X = \frac{q_x \cdot C_H}{q_H \cdot C_x} \quad (5)$$

$$q_x = Q - \frac{1}{K_H^X} \frac{(C_0 - C_x)q_x}{C_x} \quad (6)$$

where K_H^X is the ion exchange equilibrium constant based on the ion exchange reaction expressed in eq.4, 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 a slope of $-1/K_H^X$ and the intercept of this straight line is ion exchange capacity of resin. For the assessment of ion 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.

Two milliliter of ion exchange resin modified with poly(4-vinylpyridine) in sodium ion form was introduced into a 300 cm³ flask and 100 cm³ of potassium chloride solution was added. The concentration range of sample solutions were from 1.0×10^{-3} to 8.0×10^{-3} mol dm⁻³. The flask was shaken for 24hour at 25°C. 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 experience 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 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. That is to say, the properties of ion exchange were not changed, but the ion exchange capacities were decreased by the modification with poly(4-vinylpyridine). This result is attributed to the cationic polymer, poly(4-vinylpyridine), was absorbed on the surface of resin only and influences the ion exchange rate as the electrostatic repulsion layer.

If the modification agents mainly absorbed onto the surface of resin, this modification layer works in the desorption process. The adsorbed resin, immersed into the 1.0×10^{-3} mol dm⁻³ K⁺ + 1.0×10^{-3} mol dm⁻³ Ca²⁺ solution at 2hour, was immersed into 1.0×10^{-3} mol dm⁻³ NaCl solution for the desorption. In this result, potassium ion was released to the eruate solution, but calcium ion was not detected in eruate. It is consider that the modification layer inhibits desorption of multivalent cations selectively. Thus, this modified resin can apply to the selective separation of monovalent cation from mixture solution containing various charge cations.

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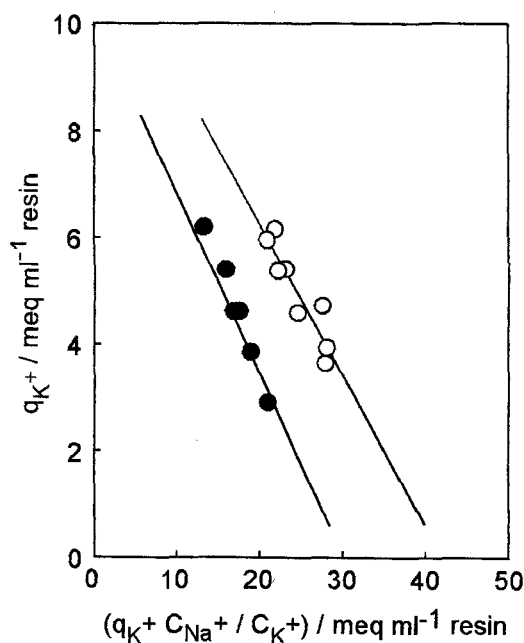


Fig.4 Equilibrium plots for the ion exchange between potassium ion and sodium ion form modified (●) and unmodified (○) resin.