# **Chemical Modification of Anion Exchange Resin**

# Koji Matsusaki, Mitsuru Higa and Nobutaka Endo

Department of Applied Chemistry and Chemical Engineering, Faculty of Engineering, Yamaguchi University, Tokiwadai 2-16-1, Ube City 755-8611, Japan Fax: 81-836-85-9201, e-mail: komatsu@po.cc.yamaguchi-u.ac.jp

In order to change the ion exchange selectivity of anion exchange resin, especially to make the ion exchange of divalent anions more difficult, the surface of gel-type anion exchange resin was modified by the adsorption of an anionic polyelectrolyte: polycondensation product of sodium naphthalene sulfonate and formaldehyde. After the adsorption of the polymer, ion exchange capacity decreased and the rate of ion exchange reaction became slow, though ion exchange equilibrium constants between two anions did not change. Especially, the ion exchange rate of divalent anions was slower than that of the monovalent anions. Using the modified anion exchange resin, separation of nitrate ions from sulfate ions was attempted. The resin was also modified by the adsorption of organic ligand. Using this chelate resin, copper ion was separated and enriched.

Keywords Anion Exchange Resin, Modification, Anionic Polyelectrolyte, Organic Ligand, Separation of Ions.

### **1. INTRODUCTION**

Ion exchange resins are widely used in various fields as a adsorbant of ions. In this case, because anion exchange resins have more affinity to multivalent anions than to monovalent anions, selective collection of monovalent anions on the resin is difficult. Okabayashi et al.<sup>1</sup> reported the selective collection of fluoride ions on an anion exchange resin loaded with alizarin fluorine blue sulfonate.

An ion exchange membrane also has poor selectivity for specific ions. It was reported that monovalent cation permselectivity of the membrane is achieved by the formation of a thin cationic polyelectrolyte layer on the surface of the cation exchange membrane.<sup>2-5</sup> This is based on the difference of electrostatic repulsion force between monovalent cations and the multivalent cations, and the cationic charge on the membrane surface.<sup>6</sup> Similarly, the interactions between the anionic polyelectrolytes and the anion exchange membranes and change in permselectivity between two anions through the resulting membranes were reported.<sup>7,8</sup>

In this work, the formation of a thin anionic polyelectrolyte layer on the surface of anion exchange resin was similarly attempted and the change in the rate of anion exchange reaction by use of this modified resin was studied. The modified resin was used to separate nitrate ion from sulfate ion in the aqueous solution.

The anion exchange resin was also modified by adsorption of organic ligand. This modified resin provided property of chelate resin, and it was used to enrich copper ion in the aqueous solution.

## 2. EXPERIMENTAL

## 2.1 Reagents

Gel-type anion exchange resin, Amberlite IRA-400 (Organo Co., Ltd.) in the chloride form  $(0.40 \sim 0.53 \text{ mm})$ , was used. The polycondensation product of sodium naphthalene sulfonate and formaldehyde (trade name, Demol N, made by Kao Chemicals Co., Ltd.) was used after purification. The molecular weight of this polyelectrolyte offered by the manufacturer is ca. 1000. All other reagents used were of analytical grade.

## 2.2 Modification of anion exchange resin with Demol N

A 10 ml portion of the anion exchange resin in the chloride form was introduced into a 200 ml roundbottomed flask and a 100 ml of 5 g l<sup>-1</sup> Demol N solution was added. The mixture was stirred for 8 hours at 80  $^{\circ}$ C in a water bath. After that, the resin was filtered and washed with pure water. The modified resin was kept wet.

## 2.3 Modification of anion exchange resin with CAS

A 10 ml portion of the anion exchange resin in the chloride form was introduced into a 200 ml roundbottomed flask and a 100 ml of 0.05 mol  $1^{-1}$  Na<sub>2</sub>B<sub>2</sub>O<sub>7</sub> (pH 9.2) and 2000 mg  $1^{-1}$  Chrome Azurol S (CAS) – copper complex (3:1 mol ratio) solution was added. The mixture was stirred for 5 hours at room temperature. After that, the resin was filtered and washed with pure water.

In order to desorb copper ion from the resin, this resin was also introduced to 100 ml of 0.5 mol l<sup>-1</sup> HCl

solution in a 200 ml flask and was stirred for 3 hours. After that, the resin was filtered and washed with pure water.

## 3. RESULTS AND DISCUSSION

3.1 Modification with Demol N

The adsorbed amount of Demol N on the resin at 25 °C was determined. After stirring the mixture of the resin and Demol N solution at 80 °C, we determined the Demol N in a solution at 25 °C by use of UV spectrophotometry at wavelength of 290 nm<sup>9</sup>. The adsorbed amount was 17.2 mg ml<sup>-1</sup> wet resin. This adsorbed polyelectrolyte could not been easily exchanged with other anions. When this modification was carried out at room temperature, however, the adsorbed Demol N was exchanged with other anions. When the modified resin was dried, the resin was broken. Therefore, the modified resin was kept wet.

#### 3.2 Ion exchange equilibrium

As reported by Kataoka et al.<sup>10</sup>, the following equation has been obtained at the ion exchange equilibrium of the resin in the chloride form with other monovalent anions in aqueous solution:

$$R-Cl^{-} + X^{-} \rightleftharpoons R-X^{-} + Cl^{-} \qquad K_{Cl}^{X} = \frac{q_{X}C_{Cl}}{q_{Cl}C_{X}}$$
$$q_{X} = Q - \frac{1}{K_{Cl}^{X}} \frac{(C_{0} - C_{X})q_{X}}{C_{Y}}$$

where  $K_{Cl}^{\chi}$  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. This equation shows that the plot of  $q_{\chi}$  against  $(C_0 - C_{\chi})q_{\chi}/C_{\chi}$  is a linear relationship with a slope of  $-1/K_{Cl}^{\chi}$  and the intercept of this straight line is the ion-exchange capacity of resin. Using a chloride ion form resin and an aqueous solution of nitrate ion, the relationship of  $q_{NO3}$  against  $(C_0 - C_{NO3})q_{NO3}/C_{NO3}$ was investigated.

One ml of the modified resin with Demol N was introduced into a 300 ml Erlenmeyer flask and a 200 ml of sodium nitrate solution with a concentration range of  $2.0 \times 10^{-3}$  to  $1.0 \times 10^{-2}$  mol l<sup>-1</sup> was added. The flask was stoppered and shaken for 24 hours at 25℃. After that, the nitrate ion in the aqueous solution was determined by use of ion chromatography. Using an unmodified resin, the same experiment was also carried out. The results are shown in Fig.1. The plots using the modified resin are straight and each line is parallel to that obtained using the unmodified resin, that is, the  $K_{Cl}^{NO3}$  of both resins are equal. However, the ion exchange capacity of modified resin is smaller than that of unmodified resin. These results show that the



Fig. 1 Equilibrium plots for the ion exchange between chloride-form resin and nitrate ion. Resin: 1.0 ml;
●, modified; ○, unmodified.

characteristics of anion exchange were not changed but the ion exchange capacity was decreased by the modification with polyelectrolyte. That is to say, the Demol N was adsorbed only on the part of the surfaces of resin particles. In the modification of anion exchange membrane with Demol N, the existence of polyelectrolyte only on the surface of membrane was observed by distribution of sulfur which was analyzed by EPMA through a cross-section of membrane<sup>8</sup>.

#### 3.3 Rate of ion-exchange reaction

The change of rate of anion exchange reaction by the modification with polyelectrolyte was investigated. One ml of the modified or unmodified resin in the chloride form was introduced into a 300 ml Erlenmeyer flask and a 100 ml of  $1.0 \times 10^{-3}$  mol l<sup>-1</sup> sodium salt solution with various anions was added. The flask was stoppered and shaken at 25°C. The change of concentration of nitrate ion in the solution with the passage of time was measured by use of ion chromatography. The result for sulfate ion is shown in Fig.2. In this case the rates of ion exchange reaction are decreased by the modification.

On the base of these results for various inorganic anions, the half time of each ion exchange reaction  $(t_{1/2})$  were measured and the ratios of half times obtained by use of the modified resin to those obtained by the unmodified resin were calculated. The results are presented in Table I. They show that the ratios of ion exchange reaction of divalent anions are very much larger than those of monovalent anions and the larger size anion has the slower exchange rate. Such delay of ion exchange rate by the modification is interpreted as the formation of anionic polyelectrolyte layer on the surface of the resin particle. This layer may result in a sieve effect on the ionic size and the electrostatic repulsion force on the charge of anions. Although the size of iodide ion is larger than that of



Fig. 2 The exchange of sulfate ion between chlorideform resin and sodium sulfate (1×10<sup>-3</sup> mol 1<sup>-1</sup>) solution. Resin: 1.0 ml; ●, modified; ○, unmodified.

bromide ion, the ratio of exchange rate of iodide ion was smaller than that of bromide ion. Because the iodide ion has a strong affinity for the resin, the rate of ion exchange may not be so changed. For the perchlorate ion, because of its hydrophobic property<sup>11</sup>, the rate of exchange may also not be changed. In the modification of anion exchange membrane with anionic polyelecrolyte, a similar effect has been observed.<sup>7,8</sup> For the cation exchange resin<sup>12</sup> and the cation exchange membrane<sup>6</sup>, similar effects of large organic cations on the cation exchange were also reported.

### 3.4 Exchange rate of organic anions

The exchange rates of some organic anions by use of the modified resin were similarly investigated under the same conditions as those for inorganic anions. The results obtained were similar to that of inorganic anion and the rates of ion exchange reaction of organic anions were slower than that of inorganic anion. These results also show that the modified resin is useful to collect the inorganic anions in the natural water, because the collection of organic

Table I Rate of anion exchange reaction

	Half-exchange rea			
Anion	Unmodified resin (t <sub>1/2</sub> )	Modified resin $(t_{1/2}^*)$	t <sub>1/2</sub> */t <sub>1/2</sub>	
F <sup>-</sup>	7.7	8.2	1.06	
CI-	8.0	20.8	2.06	
Br	7.8	28.5	3.65	
I-	5.2	9.8	1.88	
NO <sub>3</sub> .	5.8	14.3	2.47	
ClO₄*	13.4	17.8	1.33	
SCN <sup>-</sup>	5.8	14.5	2.50	
$NO_2^-$	5.3	9.2	1.74	
SO4 <sup>2-</sup>	11.9	108.0	9.08	
SO32-	7.2	367.0	60.0	
S <sub>2</sub> O <sub>3</sub> <sup>2-</sup>	5.9	201.0	34.1	

a. Hydroxide-form resin was used.

electrolyte, e.g., humic acid, is able to be suppressed.

The rates of ion exchange reaction of ionic active agents were also decreased by this modification. Therefore, this modification can protect the poisoning<sup>13,14</sup> of anion exchange resin by anionic surface-active agents.

## 3.5 Separation of nitrate ion from sulfate ion

The results given in Table 1 show that the selective collection of monovalent anions is possible by use of the resin modified with Demol N. Therefore, the separation of nitrate ion from sulfate ion was Four ml of the modified resin in the attempted. hydroxide form was introduced into a 1000 ml Erlenmeyer flask and a 1000 ml of mixture solution of  $1.0 \times 10^{-3}$  mol l<sup>-1</sup> sodium nitrate and  $2.0 \times 10^{-2}$  mol l<sup>-1</sup> sodium sulfate was added. The flask was shaken at 25°C. The changes of concentrations of nitrate and sulfate ions in the solution with the passage of time were measured by use of ion chromatography. The results are shown in Fig.3. After shaking for 15 min, the nitrate ion was completely adsorbed. For the sulfate ion, however, about 12 % of its amount was adsorbed. Therefore, after the shaking for 15 min, the resin was filtered and washed with pure water. The desorption of nitrate ion from this resin was attempted. Potassium perchlorate solution was used as an eluent. This resin was introduced into a 300 ml Erlenmeyer flask and 100 ml of  $5.0 \times 10^{-2}$  mol l<sup>-1</sup> potassium perchlorate solution was added, and then the flask was shaken at 25°C. As shown in Fig.4, after the shaking for 60 min, the nitrate ion can be desorbed. If the concentration of sulfate ion in the solution would not interfere with the determination of nitrate ion by ion chromatography, the desorption of sulfate ion from the resin could be permitted.

The separation of nitrate ion from sulfate ion was attempted under the conditions of various concentrations of sulfate. As shown in Table II,



Fig. 3 The adsorption of (○) nitrate and (●) sulfate ions on the modified rsin in the hydroxide-form. Resin: 4.0 ml; [NO<sub>3</sub><sup>-</sup>]<sub>0</sub>: 1.0×10<sup>-3</sup>; [SO<sub>4</sub><sup>2-</sup>]<sub>0</sub>: 2.0×10<sup>-2</sup> mol l<sup>-1</sup>; Sample solution: 1000 ml.



Fig.4 The desorption of  $(\bigcirc)$  nitrate and  $(\bigcirc)$  sulfate ions from the modified resin by perchloric solution. The resin was previously immerged for 15 minutes in the 1000 ml solution of  $1.0 \times 10^{-3}$  mol l<sup>-1</sup> NaNO<sub>3</sub> and 2.0  $\times 10^{-2}$  mol l<sup>-1</sup> Na<sub>2</sub>SO<sub>4</sub>. Resin: 4.0 ml; Eluent: 0.050 mol l<sup>-1</sup> KClO<sub>4</sub> solution.

good separation and enrichment of nitrate ion was obtained.

3.6 Separation and enrichment of copper ion

The modified resin with CAS was applied to separation and enrichment of copper(II) ion in aqueous solution.

Two ml of the modified was introduced into a 300 ml Erlenmeyer flask and a solution of copper(II) was added and the pH was adjusted to 9.2 with  $Na_2B_2O_7$  solution. The flask was shaken for 3 hours at room temperature. After that, the resin was filtered and washed with pure water.

This resin which adsorbed copper ion was introduced to introduced into a 100 ml Erlenmeyer flask and a 10 ml of 0.5 mol  $1^{-1}$  HCl solution was added. The solution was shaken for 5 min. The concentration of desorbed copper into HCl solution was determined by use of graphite furnace atomic absorption spectrometry.

The enrichment ratio was measured by varying the

solution volume of copper. Enrichment of copper by a factor of about 500 was possible. By use of column method, similar results was obtained. The interference with foreign metal ions were little. By use of this enrichment, the trace copper in seawater could be determined. These results show that the enrichment of copper using this modified resin with CAS is optimum to the determination of copper by atomic absorption spectrometry.

#### REFERENCES

[1] Y. Okabayashi, R. Oh, T. Nakagawa, H. Tanaka and M. Chikuma, *Analyst*, **113**, 829 (1988).

[2] T. Sata, R. Izuo, Y. Mizutani and R. Yamane, J. Colloid Interface Sci., 40, 317 (1972).

[3] T. Sata, J. Colloid Interface Sci., 44, 393 (1973).

[4] T. Sata, J. Polym. Sci., Polym. Chem. Ed., 16, 1063 (1978).

[5] T. Sata, K. Takata and Y. Mizutani, J. Appl. Electrochem., 16, 41 (1986).

[6] T. Sata, R. Yamane and Y. Mizutani, J. Polym. Sci., Polym. Chem. Ed., 17, 2071 (1979).

[7] T. Sata and R. Izuo, *Colloid Poly. Sci.*, **256**, 757 (1978).

[8] T. Sata, T. Yamaguchi and K. Matsusaki, J. Membr. Sci., 100, 229 (1995).

[9] K. Hattori and Y. Yano, *Kogyo Kagaku Zasshi*, **66**, 65 (1963).

[10] T. Kataoka, A. Muto, T. Nishiki and N. Kawabata, *Nippon Ionkokan Gakkaishi* (J. Ion Exchange), **5**, 40 (1994).

[11] Y. Marcus, Pure Appl. Chem., 55, 977 (1983).

[12] Y. Tsunoda, R. Ehara, T. Misumi and T. Miwa, Jpn. Patent Appl. Publ. No. 49-3756 (1974).

[13] T. Sata, F. Hanada and Y. Mizutani, J. Membr. Sci., 28, 151 (1986).

[14] H. Small, J. Am. Chem. Soc., 90, 2217 (1968).

Table II Separation and enrichment of nitrate ion

Sample [NO <sub>3</sub> <sup>-</sup> ] <sub>0</sub> / volume / Eluent <sup>a)</sup>		Recovery <sup>b)</sup> ([SO <sub>4</sub> <sup>2-</sup> ] <sub>0</sub> /[NO <sub>3</sub> -] <sub>0</sub> )						
moll <sup>-1</sup>	ml	(C/moll <sup>-1</sup> ,V/ml)	(0)	(20)	(50)	(70)	(100)	(200)
5.0×10 <sup>-5</sup>	1000	KClO <sub>4</sub>	1.00	1.01	1.04	0.92	0.83	
		(0.10,100)				1.02*	1.00*	0.96*
5.0×10 <sup>-5</sup>	1000	HClO <sub>4</sub> (0.20,50)	1.00	1.00				
1.0×10-6	2000	HClO <sub>4</sub> (0.25,40)	1.00	1.04	1.00*	1.03*		

a) C: concentration, V: volume. b) Resin volume: 4.0 ml (\*: 6.0 ml)

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