

Studies of Selective Adsorption Resin. XXIV. Preparation and Properties of Macroreticular Chelating Resins Containing Both Polyethylenepolyamine Side Chains and Mercapto Groups

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Synopsis

The macroreticular chelating resins containing both polyethylenepolyamine side chains and mercapto groups were prepared by the reaction of 2,3-epithiopropyl methacrylate-divinylbenzene macroreticular copolymer beads with polyethylene-polyamine. The adsorption behavior of metal ions on the obtained resins was then investigated. The amination of the macroreticular copolymer beads could effectively be carried out by treatment of the polymer beads with polyethylenepolyamine in organic solvent (benzene, tetrahydrofuran) or in the absence of organic solvent at 80°C or 100°C for 60 min. It was found that the adsorption capacity of the resins for metal ions is not only affected by the ion exchange capacity of the resins but also by the porosity of the resins. Hg^{2+} , Ag^+ , and Cu^{2+} were effectively adsorbed on the resins even at a pH below 3, whereas Co^{2+} , Ni^{2+} , and Cd^{2+} were adsorbed at a pH above 3, Mn^{2+} at a pH above 7, and Ca^{2+} at a pH above 8. These metal ions adsorbed on the resins could easily be eluted with dilute mineral acid solution or dilute mineral acid solution containing thiourea.

INTRODUCTION

We have prepared and studied many kinds of macroreticular chelating resins containing various ligands and have reported that they are more practical than gel-type resins for the removal and recovery of heavy metal ions from industrial waste,¹ and the recovery of uranium from sea water, etc.^{2,3} This is because of the high adsorption rate and physical stability of these resins. So far, chelating resins containing polyethylene-polyamine side chains^{4,5} or mercapto groups^{6,7} have been studied, however, the macroreticular chelating resins containing both polyethylenepolyamine side chains and mercapto groups have not been investigated.

This report is concerned with the preparation of macroreticular chelating resins having both polyethylenepolyamine side chains and mercapto groups from 2,3-epithiopropyl methacrylate(ETMA)-divinylbenzene(DVB) macroreticular copolymer beads and their properties.

EXPERIMENTAL

Preparation of Macroreticular Chelating Resins

The ETMA-DVB macroreticular copolymer beads(RE) were synthesized by a suspension polymerization in the presence of 2,2,4-trimethylpentane (TMP) as diluent.^{5,7,8} The RE with desired diameter was obtained by using a sieve (32–60 mesh). The RE (1 g) was aminated with polyethylenepolyamine (5–25 cm³) in organic solvent or in the absence of organic solvent at the desired temperature for a desired time. The aminated copolymer beads were washed with 1 mol dm⁻³ HCl solution and allowed to stand in it overnight. Then the resins were washed with 1 mol dm⁻³ NaOH solution and immersed in it overnight. The resins were then washed with water until the wash water became neutral and then they were dried.

Measurement of Porosity and Swelling Ratio of the Resin

The specific surface area of the resins was measured on a Yuasa surface area apparatus (BET method). The pore volume and average pore radius were determined on a Carlo-Erba mercury porosimeter (Model 1520). The swelling ratio was calculated by the following equation:

$$\text{Swelling ratio} = \frac{\text{Volume of wet resin}(\text{cm}^3)}{\text{Volume of dry resin}(\text{cm}^3)} \quad (1)$$

Measurement of Anion Exchange Capacity

In a glass-stoppered 100 cm³ Erlenmeyer flask, 0.5 g of the aminated resin(OH form) was placed, and then 50 cm³ of a 0.2 mol dm⁻³ HCl–1 mol dm⁻³ KCl solution were placed in the flask. The mixture was allowed to stand at room temperature for 48 h with occasional shaking. The anion exchange capacity was determined by titrating the concentration of HCl in the supernatant with a 0.2 mol dm⁻³ NaOH solution.

Measurement of Adsorption Capacity for Metal Ions

In a glass-stoppered 100 cm³ Erlenmeyer flask, 0.125 g of the aminated resins and 50 cm³ of a 0.01 mol dm⁻³ metal ion solution were placed and the mixture was shaken at room temperature for 96 h. The amount of the metal ion adsorbed on the resins was calculated by the chelatometric determination of metal ion concentration in the supernatant.

Elution of Metal Adsorbed on the Resins

The elution of metal adsorbed on the resin was carried out by a batch method as follows: The resin(0.125 g) with adsorbed metal ions was placed in a 100 cm³ Erlenmeyer flask and then 50 cm³ eluent was added to it. The flask was shaken at 25°C for 1 h and the supernatant filtered with a glass filter. The metal ion concentration in the supernatant(eluate) was determined by Inductively Coupled Argon Plasma Atomic Emission Spectrophotometer(Nippon Jarrel-Ash ICAP-575).

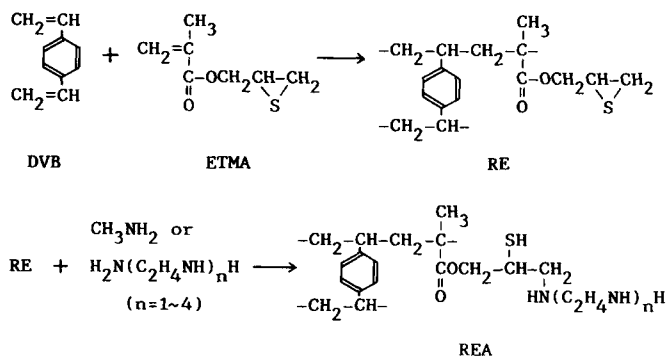
RESULTS AND DISCUSSION

Preparation of Macroreticular Chelating Resins Containing Amino and Mercapto Groups

The macroreticular chelating resins containing amino and mercapto groups were prepared by the route in Scheme 1.

First the RE were prepared by varying the amount of TMP at constant amount of DVB or by varying the amount of DVB at constant volume of TMP in a suspension polymerization. The pore characteristics (specific surface area, pore volume, and average pore radius) of those copolymer beads are shown in Table I. In the case of the RE obtained by varying the amount of TMP (from 30 vol% to 90 vol%) at constant amount (5.5 mol%) of DVB, the copolymer bead, RE-5.5-50 (the former and latter number represent mol% of DVB in monomer mixture and vol% of TMP per monomer mixture, respectively), has the highest specific surface area. In the case of the RE obtained by varying the amount of DVB (from 3.3 mol% to 9.5 mol%) in the presence of constant volume (50 vol%) of TMP, it was indicated that the specific surface area increased and the average pore radius decreased with an increase in the amount of DVB. The copolymer bead, RE-5.5-50 was aminated with methyl amine or various polyethylenepolyamines at 100°C for 1 h.

The anion exchange capacity and the adsorption capacity for Hg^{2+} and Ag^+ of the resins obtained were measured. The results are shown in Table II. The resin (RET) obtained by amination with triethylenetetramine (TTA) had the maximum anion exchange capacity and adsorption capacity for Hg^{2+} and Ag^+ . For this reason, TTA was mainly used for the preparation of the aminated resins. The RET was prepared under various conditions and the properties of the resins obtained were shown in Figure 1. It was found that the amination of RE could be carried out smoothly at 80 or 100°C. The anion exchange capacity increased with an increase in the reaction temperature and it became a constant value at the reaction time above 60 min at each temperature. The adsorption capacity of the RET for Hg^{2+} increased with an increase in the reaction temperature, whereas the adsorption capacity for Ag^+ decreased with an increase in the reaction temperature. These results indicate that the adsorption capacity for Hg^{2+}



Scheme 1 Preparation of resin

TABLE I
 Pore Structure of RE

DVB (mol%) ^a	TMP (vol%) ^a	Specific surface area (m ² /g)	Pore volume (ml/g)	Average pore radius (Å)
5.5	30	2.9	0.28	770
5.5	50	9.1	0.70	620
5.5	60	4.5	1.11	1560
5.5	70	1.5	1.15	4250
5.5	90	1.8	1.65	10300
3.3	50	3.9	0.73	1180
5.5	50	9.1	0.70	620
7.5	50	15.6	0.92	700
9.5	50	32.9	1.05	320

^a These values represent mol% of DVB in monomer and vol% of 2,2,4-trimethylpentane (TMP) per monomer mixture, used in the synthesis of RE. Mol% of DVB was calculated from the composition of commercial DVB (DVB 57%, ethylvinyl benzene 40%).

of the RET was proportional to the anion exchange capacity of the resins and that for Ag⁺ was not proportional to the anion exchange capacity. These results are attributed to the fact that Hg²⁺ has higher affinity for N atom than for S atom. The reason why the adsorption of Ag⁺ decreased with increasing temperature is not clear at present.

The amination of the RE was carried out in benzene or tetrahydrofuran with various concentrations of TTA. Figure 2 shows the anion exchange capacity and the adsorption capacity for Hg²⁺ and Ag⁺ of the RET obtained by the amination with TTA in benzene at 80°C for 1 h. The RET obtained by the amination with TTA(20–60 vol%) in benzene exhibited the high anion exchange capacity and the adsorption capacity for Hg²⁺ and Ag⁺. The same results were obtained in the case of the RET obtained by the amination with TTA in tetrahydrofuran. The amination of the resins was also carried out in the presence of the various amounts of TTA to constant amount of the RE. Figure 3 shows the anion exchange capacity and the adsorption capacity for Hg²⁺ and Ag⁺ of the RET obtained by varying the mole ratio of TTA per episulfide group of the RE. From the results it was

 TABLE II
 Anion Exchange Capacity (C_A) and Adsorption Capacity of Metal Ion of the Resins with Both Mercapto and Various Amino Groups

Amine used ^a	C _A (mEq/g)	Metal ion adsorbed ^b	
		Hg ²⁺ (mmol/g)	Ag ⁺ (mmol/g)
CH ₃ NH ₂	1.98	1.92	1.41
H ₂ N(C ₂ H ₄ NH)H	3.22	2.41	1.75
H ₂ N(C ₂ H ₄ NH) ₂ H	4.16	2.73	1.75
H ₂ N(C ₂ H ₄ NH) ₃ H	5.01	2.97	2.04
H ₂ N(C ₂ H ₄ NH) ₄ H	4.74	2.87	1.93

^a CH₃NH₂ (40% aqueous solution) and 100% polyethylenepolyamine were used for the amination of RE; RE-5.5-50, lg; Amine, 5 cm³; 100°C, 1h.

^b Loading: 0.01 mol dm⁻³ solution, 4 mmol/g resin; Room temp., 96 h.

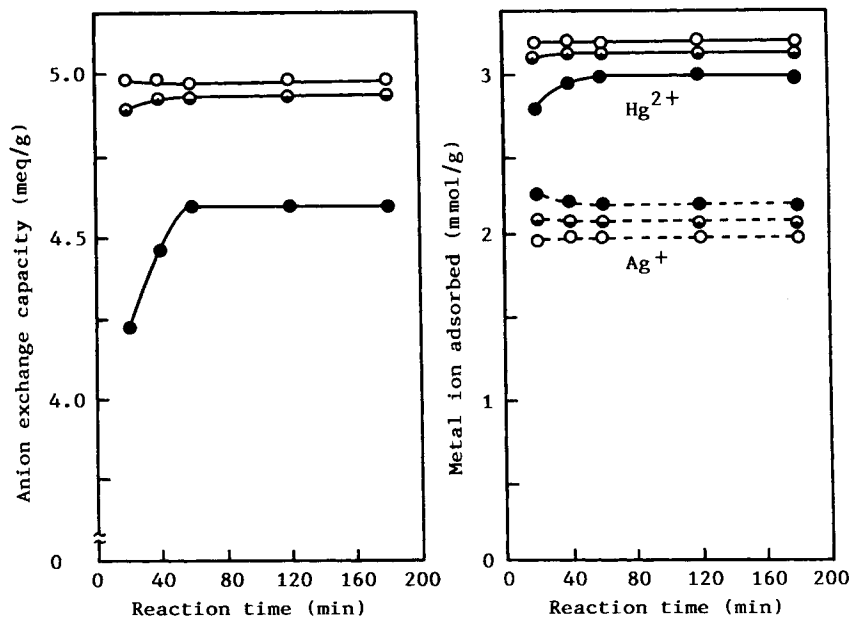


Fig. 1. Effect of reaction temperature and time on the reaction of RE with TTA; RE-5.5-50, lg; TTA (100%), 5 cm³; 80°C, 3 h. Reaction temperature: (●) 60°C; (○) 80°C; (○) 100°C.

found that addition of one mole of TTA per episulfide group was enough to obtain the resins with high anion exchange capacity.

Table III shows the properties of the RET obtained by the reaction of RE having various pore structures (indicated in Table I) with TTA. All the RET

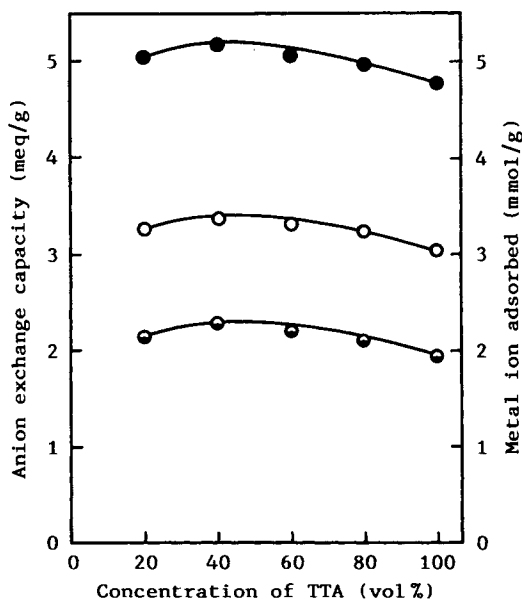


Fig. 2. Effect of concentration of TTA in benzene on the amination of RE; RE-5.5-50, lg; TTA benzene solution, 5 cm³; 80°C, 1h. (●) Anion exchange capacity; (○) Hg²⁺ adsorbed; (○) Ag⁺ adsorbed.

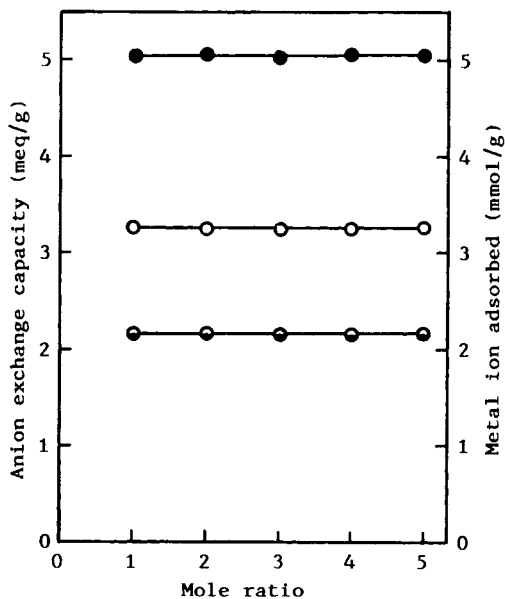


Fig. 3. Effect of mol ratio of TTA per episulfide group of RE on the amination; RE-5.5-50, 1g; TTA (20%) benzene solution, 5–25 cm³; 80°C, 1 h. (●) Anion exchange capacity; (○) Hg²⁺ adsorbed; (○) Ag⁺ adsorbed.

has anion exchange capacity of 4.2–5.1 mEq/g. Of all of them, the RET-5.5-50(resins 2 and 7) have the highest anion exchange capacity. It was suggested that the degree of amination is affected by the porosity and the degree of crosslinking of RE. The swelling ratio decreased slightly with an increase in the amount of TMP and DVB in a suspension polymerization.

Effect of Porosity and Crosslinking of the Resins on the Adsorption of Metal Ions

Figures 4A and 4B show the adsorption capacity for Hg²⁺ and Ag⁺ in relation to the diluent (TMP) volume and the DVB content used in the synthesis of these resins(shown in Table III), respectively. As shown in

TABLE III
Properties of RET

RET ^a		N content (%)	C _A (mEq/g)	Dry volume (ml/g)	Wet volume (ml/g)	Swelling ratio
No.	Symbol					
1	5.5–30 ^b	6.8	4.2	1.6	2.2	1.38
2	5.5–50	7.9	5.1	2.2	2.8	1.27
3	5.5–60	7.8	5.0	2.3	2.9	1.26
4	5.5–70	7.8	4.9	2.4	3.0	1.25
5	5.5–90	7.7	4.7	2.8	3.2	1.14
6	3.3–50	8.0	5.0	2.1	3.0	1.43
7	5.5–50	7.8	5.1	2.2	2.9	1.32
8	7.5–50	7.6	4.6	2.4	3.1	1.29
9	9.5–50	6.4	4.3	2.5	3.0	1.20

^a Amination conditions : RE, 1g; TTA (40 vol%) benzene solution, 5 cm³ ; 80°C, 1h.

^b The former and latter number represent the mol% of DVB in monomer and vol% of TMP per monomer mixture, used in the synthesis of RE respectively.

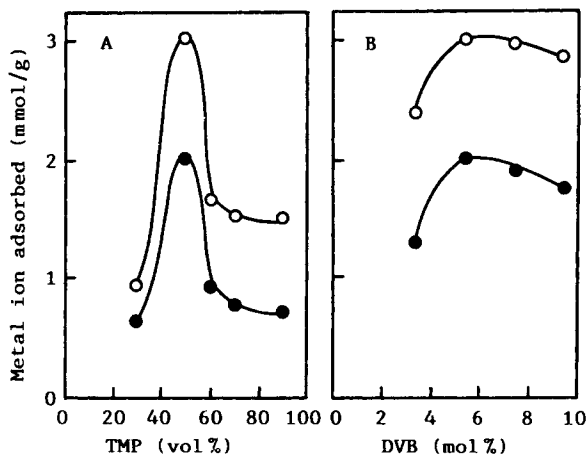


Fig. 4. Effect of porosity and crosslinking of RET on the adsorption of metal ions; A: DVB 5.5 mol%, B: TMP 50 vol%. (○) Hg^{2+} ; (●) Ag^{+} .

Figures 4A and 4B, the resins 2,7,8, and 9 had a high affinity for metal ions, whereas the resins, 1,3,4,5, and 6 had a poor affinity for metal ions. Clearly, the adsorption capacity for metal ions is not only effected by ion exchange capacity of the resins but also by the porosity of the resins. The chelating resin, RET-5.5-50, which was prepared from the RE synthesized by using 5.5 mol% of DVB in the presence of 50 vol% of TMP had the highest adsorption capacity for metal ions.

Effect of pH on the Adsorption of Metal Ions

The effect of pH on the adsorption of various metal ions with the RET-5.5-50 was studied by a batch method. Buffer solutions containing various metal ions were used to set the pH of the equilibrating solutions. At pH 1 and 2, hydrochloric acid (or nitric acid for Hg^{2+} and Ag^{+})-sodium acetate buffers were used. In the pH range 3-6, acetic acid-sodium acetate buffers were employed. At pH range 7-11, ammonium acetate-ammonium hydroxide buffers were used. The results are shown in Figure 5. Hg^{2+} , Ag^{+} , and Cu^{2+} were effectively adsorbed on the resins even at a pH below 3,

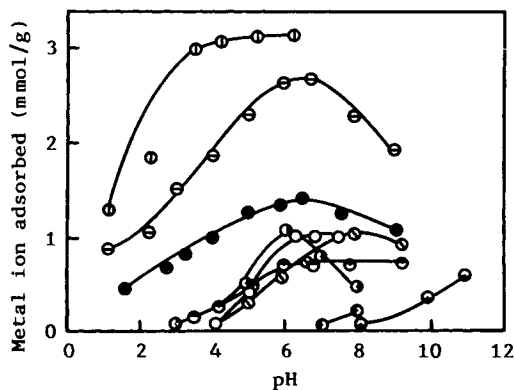


Fig. 5. Effect of pH on the adsorption of various metal ions; Metal ion: (○) Hg^{2+} ; (○) Ag^{+} ; (●) Cu^{2+} ; (○) Cd^{2+} ; (○) Zn^{2+} ; (○) Co^{2+} ; (○) Ni^{2+} ; (○) Mn^{2+} ; (○) Ca^{2+} .

TABLE IV
Elution of Metal Adsorbed on the RET with Mineral Acid Solution

Eluent (Eq dm ⁻³)	Elution (%)						
	Cu			Hg		Ag	
	HCl	H ₂ SO ₄	HNO ₃	HCl	HNO ₃	HCl	HNO ₃
0.5	76.1	78.5	84.3			0.2	3.7
1.0	76.7	79.1	86.5	22.0	39.3	0.9	16.5
2.0	76.7	78.0	90.5	29.5	43.4	1.8	30.9
6.0	78.2	69.6	100.0	41.8	48.8	16.1	54.7

Elution conditions : resin, 0.125~0.150 g; eluent, 50 cm³; shaking at 25°C for 1 h.

whereas Co²⁺, Ni²⁺, and Cd²⁺ were adsorbed at a pH above 3, Mn²⁺ at a pH above 7, and Ca²⁺ at a pH above 8. In the higher pH range, Ag⁺, Cu²⁺, Cd²⁺, Zn²⁺, Co²⁺, Ni²⁺, and so on form stable ammonia complexes with ammonium ions in buffer solutions. The decrease in adsorption of Ag⁺, Cu²⁺, and Cd²⁺ at the higher pH range is due to the formation of stable metal-ammonia complexes in the buffer solutions. These results suggest the effective separation of metal ions can be carried out by varying the pH of the loading solution and the pH of eluent.

The Elution of Metal Ions from the Resins

Figure 5 also shows that the elution of Co²⁺, Ni²⁺, Zn²⁺, Cd²⁺, Mn²⁺, and Ca²⁺ adsorbed on the resins could be easily carried out with 1–0.5 mol dm⁻³ mineral acid. Therefore, the elution of Cu²⁺, Hg²⁺, and Ag⁺ was investigated by a batch method. As shown in Table IV, Cu²⁺ adsorbed on the resins could be eluted with 1–2 mol dm⁻³ mineral acid, especially with nitric acid. The elution of Hg²⁺ and Ag⁺ with mineral acid was unsatisfactory. It was found in the previous paper that Hg²⁺ and Ag⁺ adsorbed on the macroporous resins containing mercapto groups can be eluted with hydrochloric acid solution containing thiourea.⁷ For this reason, the elution of Hg²⁺ and Ag⁺ with hydrochloric acid solution containing thiourea was carried out (Table V). Almost 100% of Ag⁺ and 63–65% of Hg²⁺ adsorbed on the resins could be eluted with 0.1 mol dm⁻³ hydrochloric acid containing 3–5% (w/v) thiourea.

TABLE V
Elution of Metal Adsorbed on the RET with 0.1 mol dm⁻³ HCl Containing Thiourea

CS(NH ₂) ₂ in 0.1 mol dm ⁻³ HCl (w/v %)	Elution (%)	
	Hg	Ag
0.5	46.1	81.4
1.0	61.0	86.4
2.0	61.5	98.2
3.0	63.2	100.0
5.0	65.4	100.0

Elution conditions : resin, 0.125~0.150 g; eluent, 50 cm³; shaking at 25°C for 1 h.

From the results described above it was found that the resins containing polyethylenepolyamine side chains and mercapto groups can effectively be used for the recovery and removal of metal ions.

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