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Preparation and Properties of Chelating Resins containing 8-Hydroxyquinoline

Atsushi Sugii, Naotake Ogawa, and Masayuki Hisamitsu

Faculty of Pharmaceutical Sciences, Kumamoto University[1]

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Two macroreticular polystyrene resins containing 8-hydroxyquinoline (oxine) groups were prepared. Resin I with oxine group attached to polystyrene *via* thioureido linkage was prepared by treating aminopolystyrene with 8-hydroxy-5-quinolyl isothiocyanate in a mixed solution of triethylamine and dioxane. Resin II was prepared by the reaction of chloromethylpolystyrene with zinc-oxine chelate in nitrobenzene. Resin I was highly selective for Hg(II) and Cu(II), but resin II was selective only for Hg(II) in the pH range below 5.

Keywords——chelating resins containing oxine; macroreticular resin; 8-hydroxy-5-quinolyl isothiocyanate; adsorption of metal ions; recovery of Cu(II) and Hg(II)

Since Erlenmeyer and Dahn[2] first reported separation of metal ions on the columns of powdered 8-hydroxyquinoline(oxine), some attempts to prepare the polymer containing oxine groups as the functional group have been proposed. The oxine polymers reported can be substantially classified into following three groups: (A) Cross-linked polystyrene resins with oxine group attached to a styrene *via* azo linkage,[3–5] (B) condensation resins[5–9] represented by resorcinol-formaldehyde-oxine resin, and (C) poly(5-vinyl-oxine) resin.[10] Instead of the cross-linked polystyrene, silica gel and porous glass beads have also been used as starting materials[11,12] in the case of (A). These oxine polymers have advantages and disadvantages, but the most important characteristic is their selectivity for metal ions based on complexation of the oxine group.

In this paper, two macroreticular (MR) polystyrene resins containing oxine group, whose structures are distinct from the types mentioned above, are proposed and their properties for adsorption of metal ions are described. The new resins are chemically and mechanically stable and showed a high selectivity for Hg(II) and Cu(II).

Results and Discussion

Synthesis of Resins

The resins containing oxine as the functional group were synthesized by the pathway illustrated in Chart 1. MR type styrene-divinylbenzene (DVB) copolymer (7.5% DVB) was used for the starting material because its chemical reactivity is higher than that of the gel

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type copolymer with the same degree of cross-linking. Vernon and Eccles[5] have also pointed out the usefulness of MR type oxine resin made from oxine and Amberlite XAD 2.

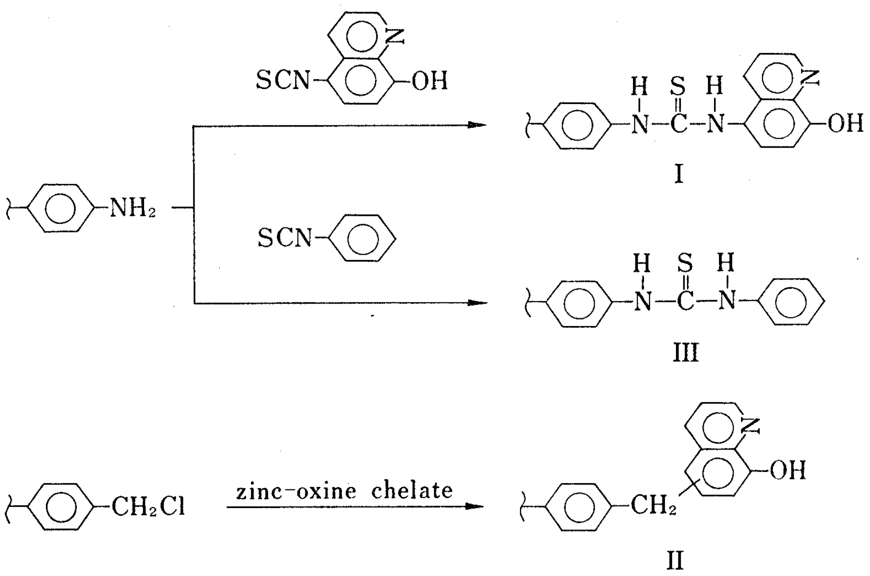

Chart 1

Resin I with an oxine group attached to polystyrene *via* thioureido linkage was prepared by the reaction of aminopolystyrene and 8-hydroxy-5-quinolyl isothiocyanate in a mixed solution of triethylamine and dioxane. From the analytical value of sulfur, the portion of the oxine groups introduced on the resin is presumed to be about 70% of the amino group units on the aminopolystyrene. The IR spectrum of this resin suggests that it has the proposed structure.

The preparation of other type of oxine resin whose oxine group is bonded to polystyrene *via* a methylene linkage was designed to obtain a more chemically stable resin. When oxine was treated with chloromethylresin in the presence of aluminium chloride, only a small amount of the desired product was formed. Resin II was obtained by the reaction of chloromethylresin and zinc-oxine chelate in nitrobenzene. From the hydrogen-sodium exchange capacity, it was assumed that oxine groups responsible for complexation were introduced in about 60% of chloromethyl group units on the starting resin. Resin III containing only thioureido group was also prepared for the use as control experiment.

Stability of Resins

Resins I to III treated with 0.01—5 M HCl and NaOH solutions for 2—7 days at room temperature showed no significant changes in their infrared (IR) spectra. In addition, no disintegration of the resin beads was observed during shaking in the above solutions. When resin I was treated with acidic solutions at pH below 1, the solutions became pale yellow and ultraviolet (UV) spectra of the solutions were identical with that of authentic 8-hydroxy-5-quinolyl isothiocyanate. However, the decomposition in acidic solutions was negligibly small. Resin III containing thioureido group showed a similar behavior and phenyl isothiocyanate was detected. On the other hand, resin II containing no thioureido linkage was quite stable even in acidic solutions.

Adsorption of Metal Ions

The adsorption behavior of seven metal ions on each resin was examined by a batch operation. The rate of adsorption was determined for Hg(II) and Cu(II). Fig. 1 summarizes the experimental results; it can be seen that main portion of the metal ions is adsorbed within the first 6 hr.

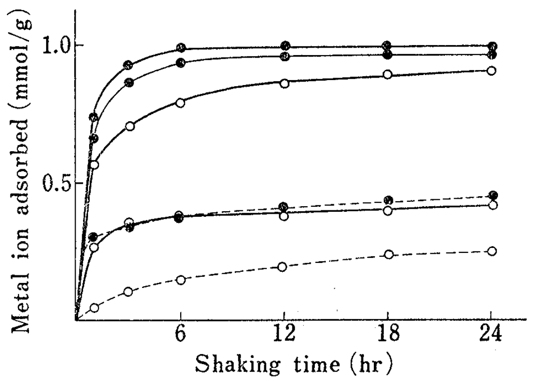

Fig. 1. Effect of Shaking Time on Adsorption of Cu(II) and Hg(II)

—○— Cu(II), —●— Hg(II),
——— resin I, ------ resin II, ——— resin III.
pH 3.0, metal ion, 0.01 M, 10 ml; resin, 100 mg.

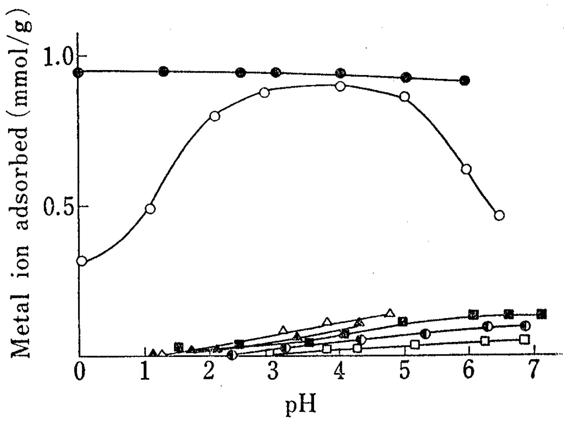

Fig. 2. pH-Dependence of Adsorption of Metal Ions on Resin I

—△— Al(III), —▲— Fe(III), —□— Co(II),
—■— Ni(II), —○— Cu(II), —◐— Zn(II),
—●— Hg(II).
Metal ion, 0.01 M, 10 ml; resin, 100 mg; shaking time, 24 hr.

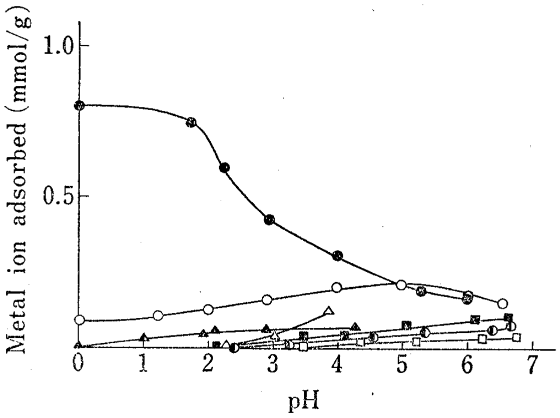

Fig. 3. pH-Dependence of Adsorption of Metal Ions on Resin II

Condition and symbols are the same as those in Fig. 2.

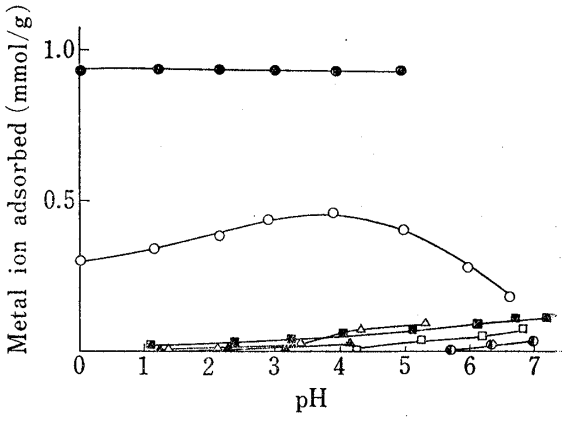

Fig. 4. pH-Dependence of Adsorption of Metal Ions on Resin III

Condition and symbols are the same as those in Fig. 2.

The equilibrium adsorption of metal ions at different pH is presented in Figs. 2—4. The adsorption of Hg(II) on resin I is independent of pH over the pH range of 0—6. Resin III containing thioureido group also showed a similar adsorption behavior. It is suspected that the adsorption of Hg(II) on I is mainly due to complexation with the thioureido group in the acidic region. On the other hand, resin II adsorbed considerable amount of Hg(II) in strong acidic solutions (pH 0—2), but the adsorption decreased with increasing of pH above 3. Over the lower pH range, adsorption of Hg(II) on resin II is appreciable due to

Table I. Adsorption of Hg(II) from Different Acid Solutions

Acid 0.1 M	Hg(II) used	Hg(II) adsorbed (mmol/g)		
		Resin I	Resin II	Resin III
HCl	$HgCl_2$	3.62	1.22	3.22
HNO_3	$Hg(NO_3)_2$	2.70	0.98	1.17

Resin, 100 mg; concentration of Hg(II) solution, 0.05 M; total volume, 10 ml; shaking time, 24 hr.

anion exchange of chloro-complex ions of Hg(II), $HgCl_3^-$ and $HgCl_4^{2-}$, while it is assumed that Hg(II) is adsorbed by complexation with the oxine group at pH higher than 3. This is obvious from the fact that the adsorption of Hg(II) in HNO_3 is lower than that in HCl at the same concentration. Table I shows the adsorption of Hg(II) from different acid solutions.

Adsorption of Hg(II) was further examined by using various concentrations of Hg(II). The data in Table II show that the adsorption of Hg(II) by the resins increases with increasing concentration of Hg(II) but, when the concentration of Hg(II) is 0.3 M or above, adsorption of the metal becomes almost constant in each resin. In the case of higher concentration of Hg(II), each resin adsorbs Hg(II) in fairly large quantities, more than the amount expected from the H–Na exchange capacity. Physical sorption of $HgCl_2$ must be considered for this behavior; Hg(II) may exist mainly in the form of $HgCl_2$ which dissociates incompletely in solutions.

TABLE II. Effect of Concentration on Adsorption of Hg(II) in Hydrochloric Acid Solution

Concentration of Hg(II) (M)	Hg(II) adsorbed (mmol/g)		
	Resin I	Resin II	Resin III
0.01	1.01	0.75	1.00
0.05	3.54	1.28	3.39
0.1	6.36	2.19	5.37
0.2	7.08	2.92	5.78
0.3	8.20	3.66	5.73
0.5	8.11	3.65	5.62

Concentration of HCl, 0.1 M; $HgCl_2$ solution, 10 ml; resin, 100 mg; shaking time, 24 hr.

Although Cu(II) shows affinity for resins I and III, even in strong acidic solutions (pH <2), this can be explained by complexation with thioureido group. In the case of I, the decreased adsorption of Cu(II) in a buffer solution of pH above 5 may be explained on the basis of competition between complexation with ammonia in the solution and chelation with oxine and thioureido groups on the resins.

The adsorption of other metal ions such as Al(III), Co(II), Fe(III), Ni(II), and Zn(II) with the resins increased with increasing pH, but the adsorption capacities were lower than those expected from their nitrogen or sulfur content. This is explained on the basis of a steric interaction due to the polymer structure of the resins.

Recovery experiments of Hg(II) and Cu(II) from the resins were carried out by a batch operation, and experimental result is shown in Table III. Recovery of Hg(II) from each resin was attained by using 10% thiourea solution in 1 M HCl. On the other hand, Cu(II)

TABLE III. Recovery of Hg(II) and Cu(II) from the Resins

Resin[a]	Recovery (%)					
	Hg(II)			Cu(II)		
	1 M HCl	5 M HCl	10% Tu[b]	1 M HCl	5 M HCl	10% Tu[b]
I	5.1	10.2	98.2	33.7	63.7	100
II	32.3	60.6	100	100	100	100
III	5.5	11.6	97.0	0	0	100

a) Resins were shaken with Hg(II) or Cu(II) at optimal conditions shown in Figs. 2—4, and 100 mg each of the resin that adsorbed metal ions were used.
b) 10% thiourea solution in 1 M HCl
acid solutions, 10 ml; shaking time, 24 hr.

was recovered from II with 1 M HCl. The quantitative recovery of Cu(II) from each resin was achieved only by treatment with a thiourea solution. In general, desorption of metal ions adsorbed on the oxine group is easier than that of the thioureido group. The contribution of thioureido group to the complexation of Hg(II) in I is larger than that of oxine group.

It is concluded that resin I has higher selectivity and capacity for Hg(II) but is rather unstable in strong acidic media. On the other hand, resin II shows a similar adsorption behavior for metal ions and is more stable even in acidic media, but its capacity is lower than that of I.

Experimental

IR spectra were measured as KBr disks on a JASCO DS-701G spectrophotometer. The stock metal ion solutions used in this experiment were prepared by dissolving reagent grade nitrates or chlorides in water or acidic solutions which were approximately 0.1—0.5 M and were then standardized by titration with ethylenediaminetetraacetic acid. $AcONH_4$–HCl system[7] was used as the buffer solutions.

H–Na exchange capacity of the resins was determined by shaking 0.1 g of each dry resin with 1 N MeONa for 24 hr and titrating the excess alkali back to pH 3.7 (Alizarin S). In recovery experiment of Hg(II), ^{203}Hg was used as the tracer. Particle size between 35 and 60 mesh obtained from dry sieving was used in adsorption studies of metal ions.

8-Hydroxy-5-quinolyl Isothiocyanate——Ammonium 8-hydroxy-5-quinolyl dithiocarbamate, mp 170—172° (dec.), was prepared from 5-amino-8-hydroxyquinoline dihydrochloride and CS_2 in NH_4OH solution by the usual way. This dithiocabamate (27 g) was allowed to react with ethyl chlorocarbonate (22 g) in 250 ml of dry benzene, a method for preparation of 4-hydroxyphenyl isothiocyanate[13] being applied. Recrystallization from benzene gave pale yellow needles (5.6 g), mp 137—138°. *Anal.* Calcd. for $C_{10}H_6N_2OS$: C, 59.4; H, 3.0; N, 13.9. Found: C, 59.3; H, 2.9; N, 13.8. IR ν_{max}^{KBr} cm^{-1}: 3020 (OH), 2150 (NCS).

Resin I——Cross-linked aminopolystyrene was prepared by the reduction (Sn and HCl) of MR type nitropolystyrene (N, 8.0%, 7.5% DVB) according to the method described by Parrish,[3] and the structure was confirmed by its IR spectrum. *Anal.* Found: N, 9.4. Acid exchange capacity: 6.6 meq/g. The aminopolystyrene (30 g) was allowed to react with 8-hydroxy-5-quinolyl isothiocyanate (60 g) in a mixed solution of 65 ml of dioxane and 35 ml of Et_3N at 50—60° for 6 hr with stirring. After the resulting resin was separated from the reaction mixture by filtration, the resin product was washed successively with MeOH and H_2O, and dried at room temperature in a vacuum desiccator. A brown resin was obtained. *Anal.* Found: N, 10.8, S, 7.7. H–Na exchange capacity: 3.6 meq/g.

Resin II——Thirty grams of MR type chloromethylpolystyrene (Cl, 19.0%, 7.5% DVB) was allowed to react with anhydrous zinc-oxine chelate (63 g) in 225 ml of nitrobenzene at 150—160° for 6 hr. The reaction mixture was filtered and the solid was washed successively with 10% HCl, H_2O and 4% NaOH, then washed with a large amount of H_2O until the washings became neutral. Then the resin was washed with $(CH_3)_2CO$ to remove organic impurities and dried at room temperature in vacuum desiccator. A brown resin was obtained. *Anal.* Found: N, 3.7, Cl, 1.0. Salt splitting capacity: 0.07 meq/g. H–Na exchange capacity: 2.4 meq/g.

Resin III——The aminopolystyrene (30 g) was allowed to react with phenyl isothiocyanate (40 g) in a similar manner as for resin I. *Anal.* Found: N, 9.80, S. 10.5. H–Na exchange capacity: 3.3 meq/g.

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