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Preparation and Chelation Properties of Polystyrene–Divinylbenzene Copolymer Resins Containing Pyridylamines, Salicylamine, and 2-Thenylamine

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Bidentate and tridentate ligands, 2-pyridylmethylamine, *N*-[2-(2-pyridyl)ethyl]ethylenediamine, salicylamine, and 2-thenylamine are incorporated into polystyrene–2%-divinylbenzene copolymer beads. These chelating resins are evaluated for their chelation capacity toward transition metal ions (Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}) at various pH. The chelating resins containing pyridine derivatives show a high capacity and selectivity. The selectivity of the resins for the metal ions is in the order, $Cu^{2+} \gg Ni^{2+} > Co^{2+} \geq Zn^{2+}$ which is in accord with the order of the formation constants of the introduced ligands. Separation of a metal ion mixture (Cu^{2+}, Ni^{2+}, Zn^{2+}) into its components is undertaken by a column containing the chelating resin derived from *N*-[2-(2-pyridyl)ethyl]ethylenediamine. The present resins can also be used for the elimination of trace amount of harmful heavy metal ions such as Hg^{2+} and $CrO_4{}^{2-}$.

Much attention has been drawn to the chelating polymers having the function to recover metal ions from mine tailings[1] and to eliminate trace amount of harmful metal ions from industrial effluents.[2] A large number of chelating polymers have been developed,[3] and some of them are commercially available.[4] Polystyrene–divinylbenzene copolymer is an extensively used matrix for chelating polymers because it is readily available and sufficiently durable. For the chelating polymers used in an aqueous solution, it is essential to introduce a hydrophilic character into the hydrophobic polymer matrix. Multidentate polyamines are such ligands and many polyamine-type chelating polymers based on polystyrene–divinylbenzene copolymer have been synthesized.[5] However, the introduction of multidentate polyamine tends to be accompanied by intra- and inter-strand bridging reactions which create an ambigous structure around the ligand moiety and steric restrictions for the chelate formation.[5a]

In the present work, bidentate and tridentate amines containing an aromatic side arm (Fig. 1) are introduced into insoluble polymer beads by reaction with chloromethylated polystyrene–2%-divinylbenzene copolymer. The ligands must preferentially be linked to the polymer by *N*-alkylation of the primary amine and not from the aromatic ring side. Thus, the undesirable bridging reactions can be greatly diminished. We also took into consideration Pearson's "hard and soft acid and base" concept[6] for the design of the ligands.

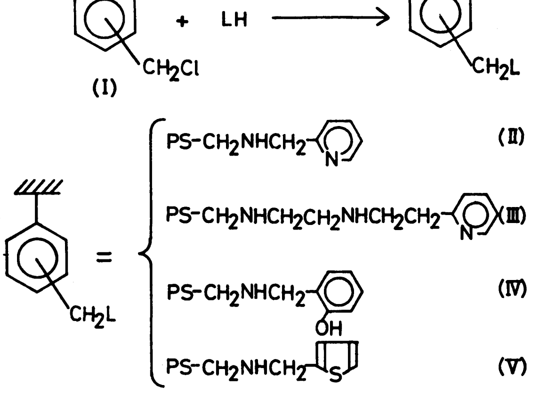

Fig. 1. Proposed structures of polymer chelating resins.

This paper deals with the preparation of the chelating resins, the examination of their capacity and selectivity toward some transition metal ions. Applications for the separation of mixed metal ions into their components and the elimination of harmful metal ions (Hg^{2+}, $CrO_4{}^{2-}$) using these resins are also investigated.

Experimental

General Procedures. All the melting and boiling points are uncorrected. The pH from 3.0 to 7.0 was adjusted with acetate buffer and below pH 3.0 with hydrochloric acid. Infrared spectra were recorded with a Hitachi 285 grating infrared spectrophotometer. ^1H NMR spectra were measured with a JEOL FX-100 spectrometer in chloroform-*d* with TMS as the internal standard. Metal ion concentration was determined with a Shimadzu atomic absorption/frame photometer Model AA-610S. Hg^{2+} was analyzed as follows: Solution containing Hg^{2+} was extracted with dithizone–chloroform solution and the solvent was evaporated on a porcelain boat. The dried sample was heated and the evaporized Hg was analyzed with an atomic absorption photometer.

Ligands. 2-Pyridylmethylamine was supplied from Aldrich Chemical Co. and purified by distillation before use. *N*-[2-(2-Pyridyl)ethyl]ethylenediamine, and salicylamine were prepared according to the method described in the literature.[7,8] 2-Thenylamine was prepared by a method similar to that for 2-pyridylmethylamine[9] using thiophene-2-aldehyde instead of pyridine-2-aldehyde. This method gave a better yield than the published one.[10] All the ligands were purified by distillation or recrystallization and identified by ^1H NMR.

Chloromethylated Polystyrene. Polystyrene-2%-divinylbenzene copolymer beads (200—400 mesh, Kanto Chemical Co.) were chloromethylated with chloromethyl methyl ether and tin(IV) chloride according to a published method.[11] The chloromethylated resin was thoroughly extracted with dioxane and dried *in vacuo* at 50 °C.

Preparation of Polymer Chelating Resins. The present ligands were incorporated into polystyrene beads using the following procedure.

TABLE 1. ANALYTICAL DATA AND CAPACITY OF LIGANDS INCORPORATED IN POLYSTYRENE

Resin	Analytical data (%) Cl	N	Ligand capacity mequiv. g^{-1} a)	Conversion % b)
I	20.82	—	5.86	86.0
II	1.29	8.03	2.87	69.4
III	3.07	9.51	2.26	67.7
IV	8.44	3.20	2.29	58.7
V	0.70	4.07	2.91	71.8

a) Calculated from the actual chlorine content (I), and nitrogen content (II, III, IV, and V).[1b] Ligand capacity (mequiv. g^{-1}) $= \frac{\% \mathrm{N}}{14n} \times 10$, where % N = % nitrogen in product, and n = number of nitrogen atoms in the ligand. b) Based on the ratio of the actual ligand content to the theoretical value calculated from the total displacement of chlorine by the ligand.[1b] % Conversion $= \frac{\% \mathrm{N}}{14n} \times \frac{(L-35.5)\%\mathrm{Cl}/100+35.5}{\%\mathrm{Cl}/100}$, where % Cl = % chlorine in the original chloromethylated polystyrene, L = ligand molecular weight minus 1.

A mixture of chlorolmethylated polystyrene beads (17.3 g, 0.1 mol) and ligand (0.4 mol) in dioxane (250 cm^3) was refluxed for 48 h with stirring. The resin was filtered off, washed first with water, and then with dioxane and transfered into a Soxhlet extractor. After extraction with dioxane for 48 h, the resin was collected, washed thoroughly with diethyl ether and dried *in vacuo* at 50 °C. The dried resins thus obtained were pale yellow or slightly brown. The analytical results (Cl, N) are summerized in Table 1.

Determination of Capacity for Metal Ion Uptake. Complexation capacities of the resins were determined as a function of pH by treating with buffered solution of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. Experiments were typically undertaken as follows.

One gram of dry resin was added to 100 cm^3 of buffered metal ion solution (0.2 mol/dm^3). After 20 h stirring at room temperature, the resin was loaded on a glass column (ϕ 1.0 cm × 20 cm) and washed with water. The chelated ion was stripped from the resin by elution with 2 M hydrochloric acid.† The eluate was collected in a volumetric flask and finally diluted to the mark with water. The amount of matal ion in the eluate was determined with and atomic absorption spectrometer. In most cases the resins can be regenerated by treating successively with 0.2 M hydrochloric acid, 0.2 M ammonia, and water. No significant change in capacity was detected after several times recycling the resins except for the treatment with Co^{2+}.

Chromatographic Separation of Metal Ion Mixture. One milliliter of metal salt mixture ($NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 2H_2O$; 1 g of each salt was dissolved in 100 cm^3 of water) was poured onto a column (ϕ1.0 cm × 13 cm) containing resin III in Table 1 (5.0 g, dry weight) which was treated with 0.1 M acetate buffer (pH 5.5) in advance. The adsorbed band was eluted at a rate of 0.27 cm^3 min^{-1} with the desired eluent: 0.1 M acetate buffer (pH 5.2) for Zn^{2+}; 0.1 M acetic acid for Ni^{2+}; and 0.5 M hydrochloric acid for Cu^{2+}. The eluate was fractionated into 4 cm^3 portions and the amount of metal ion was determined.

Elimination of Harmful Metal Ions. *Hg^{2+}*: One hundred millgram of dry resin was stirred with a buffered solution (50 cm^3) containing Hg^{2+} (1×10^{-3} g dm^{-3}) at various pH. The resin was removed by filtration after an appropriate time, and the residual Hg^{2+} in the filtrate was analyzed. The time-course of the Hg^{2+} uptake was followed by occasional extraction of samples from the mother liquor without removing the resin. The effect of ionic strength on the elimination of Hg^{2+} was examined using sodium chloride as a co-existing salt.

Cr(VI) (CrO_4^{2-}): The procedure of the elimination experiment was essentially the same as that for Hg^{2+} except that the initial concentration of Cr(VI) was 2.0×10^{-2} g dm^{-3}.

Results and Discussion

Preparation of Polymer Chelating Resins. Polystyrene–divinylbenzene copolymer is a convenient substrate for studies of polymer-support ligands because it is readily available and chemically durable. It has been pointed out that the increase in the degree of cross-linking brings about an increase in steric hindrances due to the bulky benzene nuclei, but the reduction of the cross-linking diminishes the mechanical strength of the polymer particles.[2b,5b] The polystyrene–2%-divinylbenzene beads which were used in the present study are low in divinylbenzene content, but have mechanical strength sufficient for the usual experiments. Four-fold excess of ligand to the chloromethylated polystyrene was used throughout this work, since the reaction conversion did not improve on addition of a further amount of ligand. A part of the ligand is quenched as the acid acceptor. The capacity of the incorporated ligand and the reaction conversion derived from the analytical data are summerized in Table 1. The reaction conversion was in the range of 60 to 70% with respect to the available chloromethyl groups. Although the structure of the chloromethylated polystyrene remains ambigous,[12] the ligand must be linked to the polymer matrix by the reaction of the chloromethyl group with the nucleophilic amine. The chlorine contents of the resins II and V are relatively lower than those expected from the reaction conversions. This must be due to the intra- and inter-strand bridging reactions with further alkylation of the hetero atoms. A rough estimation based on the elemental analysis of the resins II and V revealed that 65—70% of the introduced ligands have the structure depicted in Fig. 1. The undesirable side reactions are not significant for the resins III and IV and more than 80% of the ligands incorporated take up a non-bridged structure.

Complexation Capacity of Chelating Resins with Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+}. The capacity of the polymer chelating resins were evaluated for the uptake of Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} as a function of pH. The maximum

TABLE 2. MAXIMUM CHELATION CAPACITY OF POLYMER RESINS FOR TRANSITION METAL IONS

Resin	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+} (mequiv. g^{-1})
II	0.64	0.98	2.02	1.19
III	0.29	0.77	1.61	0.98
IV	0.01	0.00	0.17	0.08
V	0.03	0.00	0.05	0.10

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† 1 M = 1 mol dm^{-3}.

capacity of the present resins are given in Table 2. The resins containing pyridine derivatives (II, III) reveal high capacities comparable to those of commercial resins[13] for the uptake of the ions. However, resins IV and V which contain relatively "softer" ligating atoms than nitrogen show little or no affinity towards these metal ions. Such a result is in accord with the fact that metal chelates of salicylamine with Cu^{2+}, Ni^{2+}, and Zn^{2+} were not formed in methanol.[14] All the chelating resins revealed a reproducible capacity on repeated adsorption and desorption cycling for most of the metal ions except for III with Co^{2+}. When Co^{2+} was adsorbed on resin III, a considerable amount of the metal ion was strongly retained on the resin, so that it could not be stripped off even by treatment with conc. hydrochloric acid. This is presumably because Co^{2+} is partially oxidized on the resin giving an inert Co^{3+} complex.

The chelating capacity *vs.* pH curves for the resins II and III are given in Figs. 2 and 3, respectively. Copper(II) was most strongly retained on these resins giving a characteristic blue color and the chelation capacity is larger than for other ions. Nickel(II) ion was retained at lower pH region than Co^{2+} and Zn^{2+}. Considerable overlapping of curves is seen for the Co^{2+} and Zn^{2+} indicating that the difference in affinity of the two ions is very small. The pH dependence curves clearly imply that the order of affinity for the resins II and III is $Cu^{2+} \gg Ni^{2+} > Co^{2+} \geq Zn^{2+}$, which is in good accordance with the order of formation constants of introduced ligands, *i.e.*, 2-pyridylmethylamine[15] and *N*-[2-(2-pyridyl)ethyl]ethylenediamine.[7] This observation prompted us to separate a metal ion mixture into its components by column chromatography. A solution containing Cu^{2+}, Ni^{2+}, and Zn^{2+} was adsorbed on a column loaded with resin III and the adsorbed band was eluted with a solution of decreasing pH. Figure 4 shows the elution curve in which the three metal ion components are well separated. This order is in agreement with the results of Storch and Manecke.[16]

Elimination of Harmful Metal Ions. *Hg^{2+}*: Elimination of trace amount of Hg^{2+} was examined under batch process using these chelating resins. Figure 5 shows the plot of residual Hg^{2+} against the pH of the solution. All the resins examined are found to be effective for the removal of nearly 99% of the initial Hg^{2+} at their optimum conditions. Resins II and III can adsorb the ion over a relatively wide pH range, while resins IV and V are effective below pH 3.0 and 2.0, respectively. It is noted that the latter two resins remove Hg^{2+} nearly quantitatively in spite of their low affinity towards the first transition metal ions. This selectivity may be understood by considering that Hg^{2+} is a "soft" acid which prefers to associate with "soft" ligand atoms.[6] Hence the resins IV and V can be used for the selective elimination of Hg^{2+} in the presence of "hard" metal ions. The time-course of Hg^{2+} uptake by the resins IV and V was followed by extraction of samples from the mother solution at appropriate

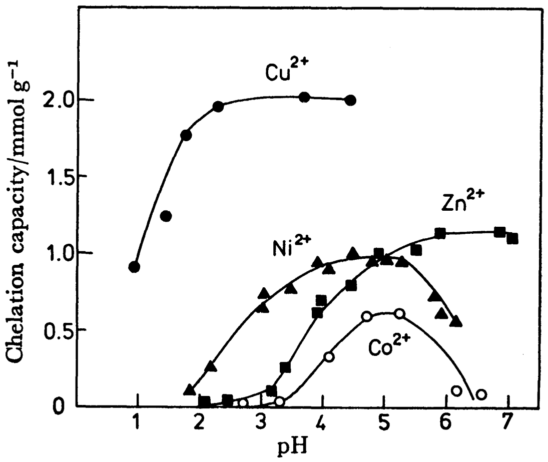

Fig. 2. Chelation capacity of resin II as a function of pH.
-●-: Cu^{2+}, -▲-: Ni^{2+}, -■-: Zn^{2+}, -○-: Co^{2+}.

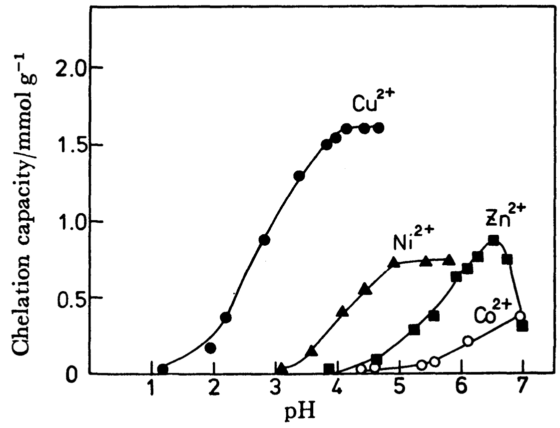

Fig. 3. Chelation capacity of resin III as a function of pH.
-●-: Cu^{2+}, -▲-: Ni^{2+}, -■-: Zn^{2+}, -○-: Co^{2+}.

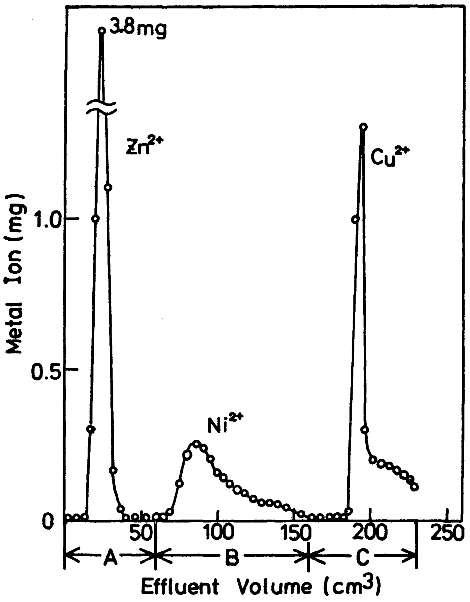

Fig. 4. Chromatographic separation of a three-components metal ion mixture.
A: 0.1 M acetate buffer(pH 5.2), B: 0.1 M acetic acid (pH 3.02), C: 0.5 M HCl.

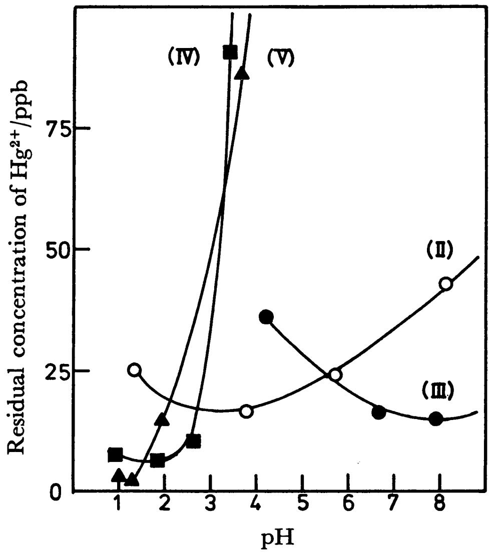

Fig. 5. Elimination of Hg^{2+} by resin II, III, IV, and V.
Conditions: amount of resin; 100 mg in 50 cm^3, concentration of Hg^{2+}; 1×10^{-3} g dm^{-3}, treating time; 15 h.

intervals. In both cases, the rapid decrease in Hg^{2+} concentration was observed and the equilibrium was attained after *ca.* 1 h. The effect of sodium chloride on the removal of Hg^{2+} was also examined for these resins. The activities of both resins do not change significantly in the presence of 0.1 M NaCl and only slightly decreases when the concentration reached 1 M. Thus these resins would be promising materials for the removal of Hg^{2+} in an effluent from soda/chlorine industry in which high concentrations of NaCl are encountered.

CrO_4^{2-}: The removal of CrO_4^{2-} was examined under batch-wise process. Resins II, III, and IV can remove CrO_4^{2-} nearly quantitatively at pH ranging 3 to 6, while the resin V reveals little affinity towards this ion. Thus it seems that "hard" ligating atoms are preferable to "soft" ones towards CrO_4^{2-}. The rate of adsorption of CrO_4^{2-} was examined at the optimum pH of each resin. Resins II and III which contain pyridine derivatives adsorbed 99% of CrO_4^{2-} in less than 10 min and the equilibrium was attained within 30 min, whereas resin IV required *ca.* 3 h for equilibriation. In all cases, CrO_4^{2-} was captured very strongly on the resin and hence quantitative recovery of the ion from the resin was difficult. Resin–CrO_4^{2-} complexes turned dark brown on standing in an aqueous solution for several hours due to oxidation of the ligand moiety. Thus the reduction in activity of the resins is inevitable on repeated cycling. Decrease in activity of the resins was also observed when sodium sulfate (>0.1 M) co-existed in the solution. This may suggest that the resins act as anion exchanger in some extent rather than a chelating agent. The details of the structure of the resin–CrO_4^{2-} complexes are under investigation.

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