

Synthesis and Metal Binding Properties of Poly(hydroxamic acid) Resins from Poly(ethyl acrylate-co-divinylbenzene) Beads

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SYNOPSIS

Poly(hydroxamic acid) resins from crosslinked poly(ethyl acrylate)s were prepared and their metal binding properties were investigated. The metal binding capacities of this type resin for metal ions were determined at specific pH. In the acidic region, the chelating resin showed high adsorption capacity for copper, iron, vanadium, and uranium. Metal adsorption capacities varied according to polymerization condition, i.e. crosslinking ratio and degree of dilution. Equilibration rates of the chelating resins were investigated to evaluate their use as materials for chromatographic separation. Selectivity for various metals was also observed from the mixed metal solution. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

Chelating resins have received considerable attention in some fields, such as removal of trace metal ions, because of their high selective adsorption capacity for metal ions.

Among many chelating ligands, hydroxamic acids are known for their chelation ability with heavy metals. Various synthetic methods have been reported to prepare a chelating resin containing pendant hydroxamic acid groups. For example, Kern and Schulz¹ reported that a reaction of poly(methyl acrylate) with hydroxylamine in benzene resulted in the formation of a polymer with 80% acryl hydroxamic acid, 14% acrylic acid, and 6% methyl acrylate, which formed the red-brown iron(III) complex. Several chelating resins with hydroxamic acid groups were prepared from Amberlite IRC-50 by conversion of carboxylic acid groups to acid chloride² or to an ester³ followed by treatment with hydroxylamine. Polyacrylonitrile,⁴⁻⁶ poly(acrylic acid),⁷ and polyacrylamide⁸ are other starting materials for

the preparation of poly(hydroxamic acid) resins. Vernon and Eccles⁹⁻¹⁴ studied chelating ion exchange resins containing hydroxamic acid groups extensively, preparing various hydroxamic acid polymers via various synthetic routes.

Acrylic polymer beads crosslinked with divinylbenzene (DVB) were prepared from various combinations of monomers with diluent,^{15,16} but few contain ethyl acrylate (EA).¹⁷

In this study, porous crosslinked poly(ethyl acrylate) (PEA) beads were prepared by suspension polymerization in the presence of diluent. The resulting polymers were treated with hydroxylamine to obtain poly(hydroxamic acid) resin via a simple one-step reaction. Various metal binding properties of the resulting poly(hydroxamic acid) such as binding capacity, adsorption rate, and selectivity were observed. Effects of polymerization conditions such as crosslinking ratio and degree of dilution on the metal binding capacities were investigated.

EXPERIMENTAL

Materials and Reagents

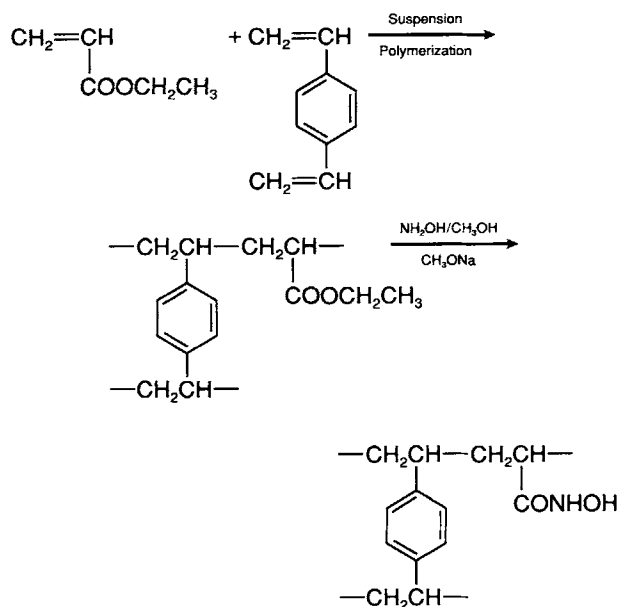
EA was washed twice with aqueous 5% sodium hydroxide solution to remove inhibitors, then with

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Scheme 1 Synthesis of poly(hydroxamic acid) resin.

distilled water several times. After washing, it was dried over calcium chloride for 24 h. DVB used as a crosslinking agent was a 55% mixture with ethylvinylbenzene and was used as received.

The other chemicals, sodium sulfate, calcium carbonate, gelatine, 2,2,4-trimethyl pentane (TMP), hydroxylamine hydrochloride, sodium methoxide, metal ion standard solutions, uranyl nitrate hexahydrate, solvents, and other reagents of GR grade were used without further purification.

Preparation of Poly(hydroxamic acid) Resin

Suspension Polymerization of Poly(ethyl acrylate-co-divinylbenzene)

Poly(EA-co-DVB) was prepared by the suspension polymerization technique in the presence of TMP as a diluent.^{18,19} Distilled water, sodium sulfate, calcium carbonate, and 2% aqueous gelatine solution were placed in a 1-L three-necked flask equipped with reflux condenser, mechanical stirrer, and thermometer. Benzoyl peroxide, EA, and DVB monomer mixture, and an appropriate amount of TMP used as a diluent were added into the flask with stirring.

After the suspension copolymerization, the resulting copolymer was filtered and washed with 1N hydrochloric acid solution, distilled water, and methanol. Finally it was extracted with acetone in a Soxhlet apparatus for 24 h, air dried, and dried in a vacuum oven at 40°C for 24 h.

Preparation of Chelating Resin

Hydroxylamine hydrochloride was used to convert these resins into poly(hydroxamic acid) resins. After the reaction, the copolymer was filtered and washed with methanol, 1N hydrochloric acid solution, methanol, deionized water, and methanol. Then it was extracted in a Soxhlet apparatus with acetone for 24 h, air dried, and dried in a vacuum oven at 40°C for 24 h.

Alkali Treatment

The prepared chelating resin (1 g) was treated with 100 mL of 0.1 M sodium hydroxide solution at room temperature for 24 h. The resulting resin was washed

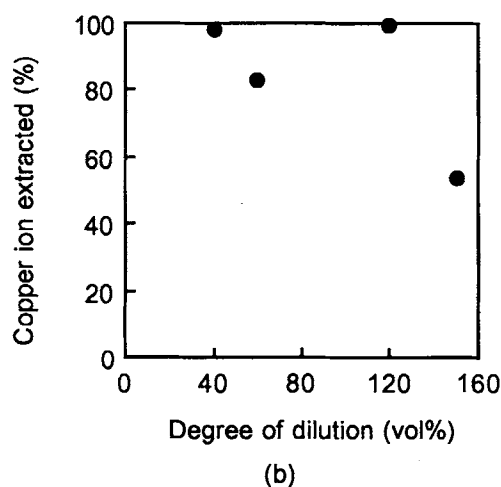
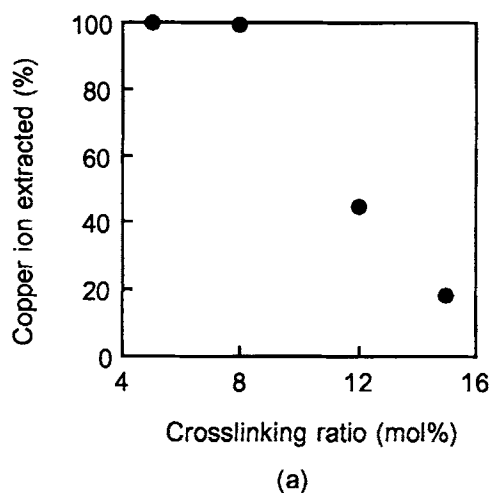


Figure 1 Effects of crosslinking ratio and degree of dilution on copper adsorption capacity of poly(hydroxamic acid) resins. Resin, 0.10 g/100 ppm, 20 mL copper solution (pH 4): (a) dilution 120 vol %; (b) crosslinking 8 mol %.

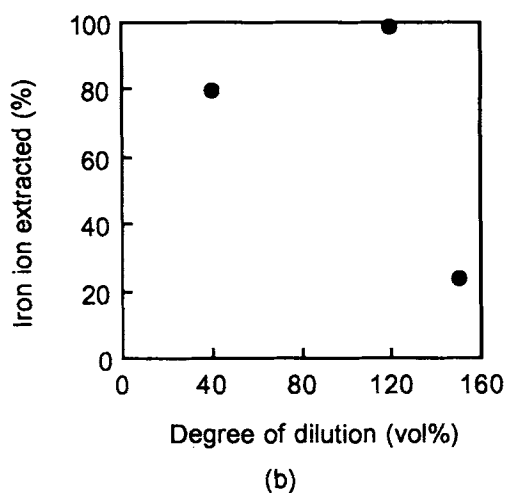
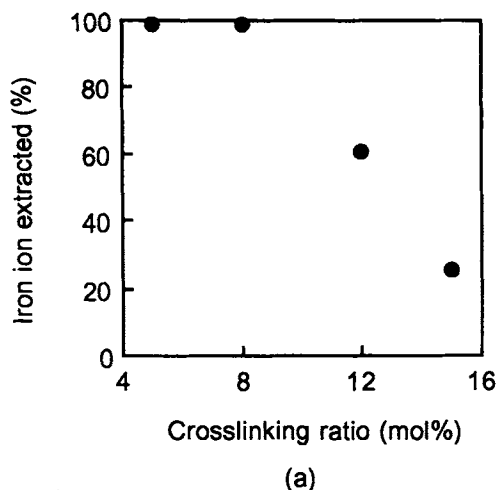


Figure 2 Effects of crosslinking ratio and degree of dilution on iron adsorption capacity of poly(hydroxamic acid) resins. Resin, 0.10 g/100 ppm, 20 mL iron solution (pH 2.5): (a) dilution 120 vol %; (b) crosslinking 8 mol %.

with deionized water until the washing water became neutral, air dried, and dried in a vacuum oven at 40°C for 24 h.

Metal Binding Capacity

Preparation of Metal Solution

The commercially available 1000-ppm metal ion standard solution (except for uranium) was diluted to 100 ppm with deionized distilled water followed by an adjustment to the desired pH with sodium hydroxide or hydrochloric acid solution.

The appropriate quantities of uranyl nitrate were dissolved in 0.1M nitric acid solution to obtain 1000-

ppm standard solution. The solution was also diluted to 100 ppm with deionized distilled water followed by adjustment of pH by the same method as described above.

The metal solutions used in this experiment were copper, iron, mercury, vanadium, and uranium.

Metal Binding Capacity (Batch Extraction)

The capacity of the resin for each metal ion was determined by the batch method. Resin samples (0.10 g) were equilibrated with 20 mL of 100-ppm metal ion solutions for 24 h in clean glass ampoules. After equilibration, the amount of metal ion still in solution was determined with an atomic absorption

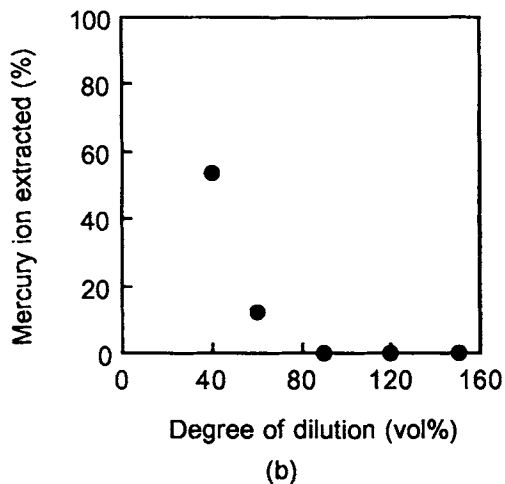
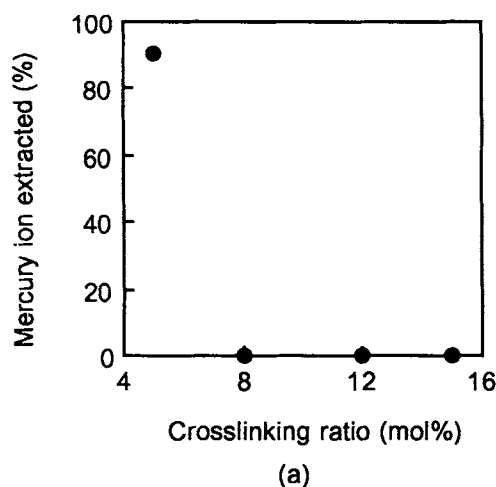


Figure 3 Effects of crosslinking ratio and degree of dilution on mercury adsorption capacity of poly(hydroxamic acid) resins. Resin, 0.10 g/100 ppm, 20 mL mercury solution (pH 3): (a) dilution 120 vol %; (b) crosslinking 8 mol %.

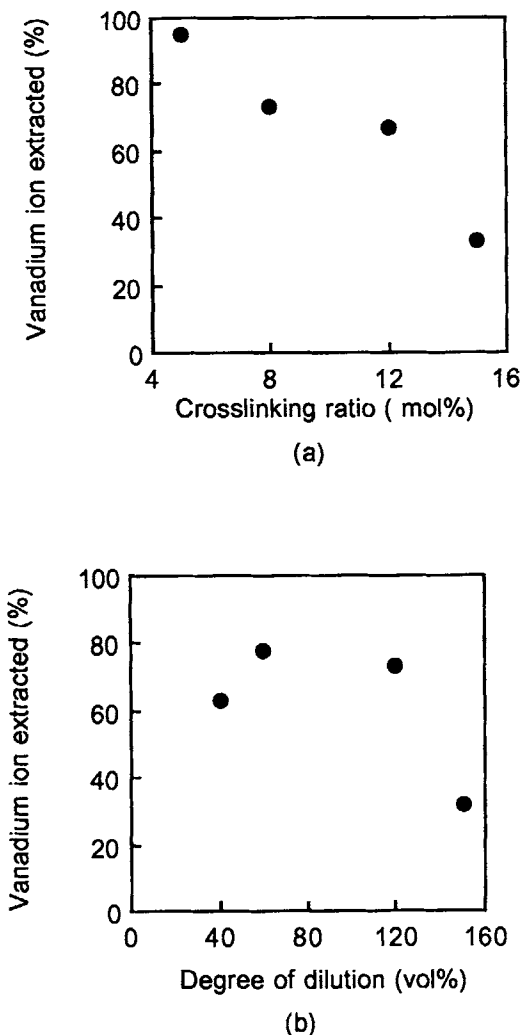


Figure 4 Effects of crosslinking ratio and degree of dilution on vanadium adsorption capacity of poly(hydroxamic acid) resins. Resin, 0.10 g/100 ppm, 20 mL vanadium solution (pH 3): (a) dilution 120 vol %; (b) crosslinking 8 mol %.

spectrophotometer (AAS, GBC 904AA). An inductively coupled plasma spectrometer (ICP, Shimadzu ICPQ-1000) was used to determine the amount of metal ions such as vanadium, mercury, and uranium remaining in the solution. Prior to equilibration, samples were adjusted to suitable pH as follows: Cu^{2+} , pH 4.0; Fe^{3+} , pH 2.5; Hg^{2+} , pH 3.0; V^{5+} , pH 3.0; UO_2^{2+} , pH 3.0.

Resin-Metal Kinetics

Batch studies were carried out to determine the kinetics of the metal ion uptake by the resin. Resin samples (0.20 g) were placed in 50-mL glass ampoules; 40 mL of 100-ppm metal ion solutions were

added to each ampoule. Shaking was begun immediately upon addition of the test solutions to the resin samples. At regular time intervals, a 0.50-mL aliquot was removed from the test solution with a syringe and the concentration of metal ion remaining in the solution was determined by AAS or ICP.

Selectivity

The selectivity of the resin for various metals was determined by a competitive batch method. Resin samples (0.10 g) were equilibrated for 24 h with 20 mL of metal ion solution containing 100 ppm each of a specific metal ion pair, except for the mercury ion which was 180 ppm.

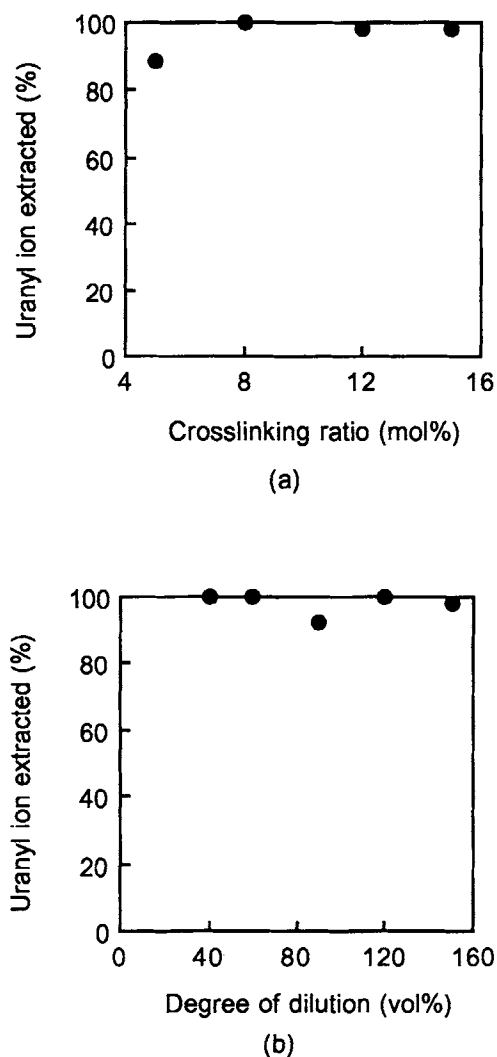


Figure 5 Effects of crosslinking ratio and degree of dilution on uranium adsorption capacity of poly(hydroxamic acid) resins. Resin, 0.10 g/100 ppm, 20 mL uranium solution (pH 3): (a) dilution 120 vol %; (b) crosslinking 8 mol %.

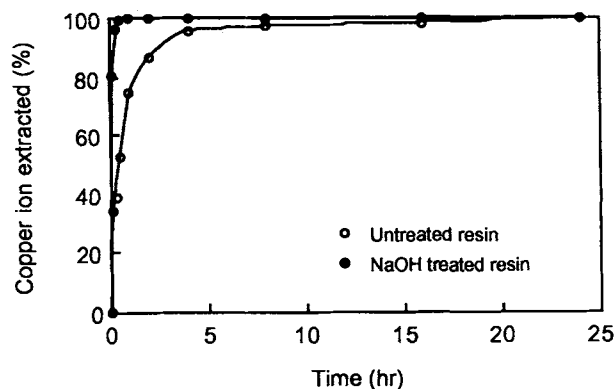


Figure 6 Copper ion adsorption rate of poly(hydroxamic acid) resin. Resin, 0.20 g/100 ppm, 40 mL solution (pH 4); crosslinking 8 mol %, dilution 120 vol %.

Selectivity studies were carried out at the following pHs:

Pair	Cu	Fe	Co	Ni	V
Fe	2.0	—	—	—	—
Co	4.5	2.5	—	—	—
Ni	4.2	2.5	4.5	—	—
V	4.2	2.0	4.3	4.5	—
Hg	4.6	2.5	4.5	4.5	4.5

These pH values applied in these selective studies were established for two reasons: the metal should not be precipitated under the test condition; the pH should not affect the selective binding in mixed metal solution.

AAS and ICP were used for the determination of the uncomplexed metal ion concentrations.

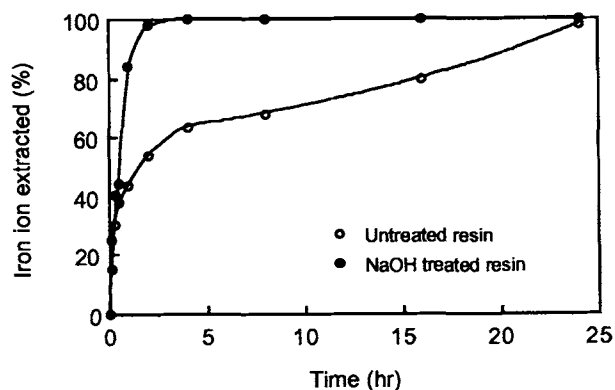


Figure 7 Iron ion adsorption rate of poly(hydroxamic acid) resin. Resin; 0.20 g/100 ppm, 40-mL solution (pH 2.5); crosslinking 8 mol %, dilution 120 vol %.

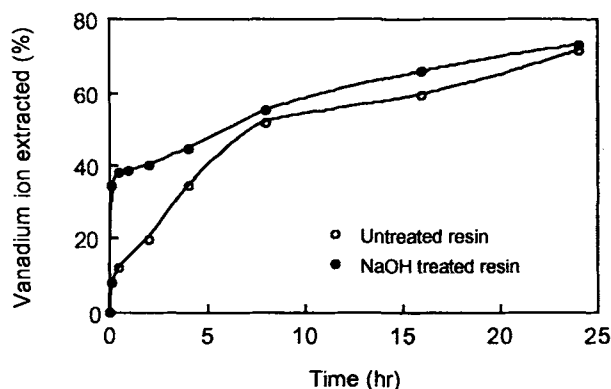


Figure 8 Vanadium ion adsorption rate of poly(hydroxamic acid) resin. Resin, 0.20 g/100 ppm, 40-mL solution (pH 3); crosslinking 8 mol %, dilution 120 vol %.

RESULTS AND DISCUSSION

Preparation of Poly(hydroxamic acid) Resin

The chelating resins with hydroxamic acid groups were prepared by the method in Scheme 1. Although DVB is a kind of hydrophobic crosslinker, it has been used most frequently in polymer supports. Hydroxamic acid polymers were prepared by the reaction of crosslinked PEA beads with a methanolic solution of hydroxylamine.¹⁸ More details on the identification and characterization of poly(hydroxamic acid) resins from crosslinked PEAs have been published elsewhere.¹⁹ It is difficult to measure the content of DVB in the copolymer. Thus, in general, the crosslinking ratio means the DVB concentration fed into the polymerization system in the field of polymer supports. The measurement of apparent densities of the copolymer could be an indirect method to obtain information for crosslinking ratio.

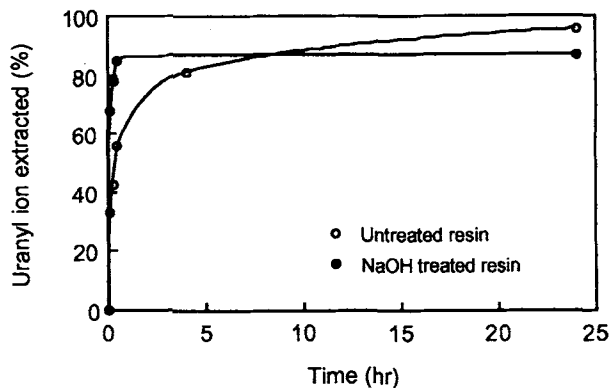


Figure 9 Uranyl ion adsorption rate of poly(hydroxamic acid) resin. Resin, 0.20 g/100 ppm, 40-mL solution (pH 3); crosslinking 8 mol %, dilution 120 vol %.

Table I Competitive Uptake of Metal Pairs by Poly(hydroxamic acid) Resin

Metal Pair	Alone (mmol/g)	Mixed (mmol/g)	Relative Difference (%)
Cu/Fe	0.26/0.08	0.04/0.28	-85/+350
Cu/Co	0.26/0.07	0.27/0	+104/*
Cu/Ni	0.26/0.11	0.25/0	-4/*
Cu/V	0.26/0.31	0.29/0.33	+112/+106
Cu/Hg	0.26/0	0.25/0.06	-4/*
Fe/Co	0.08/0.07	0.13/0.01	+163/-86
Fe/Ni	0.08/0.11	0.09/0	+113/*
Fe/V	0.08/0.31	0.33/0.16	+413/-48
Fe/Hg	0.08/0	0.16/0.07	+200/*
Co/Ni	0.07/0.11	0.05/0.06	-29/-45
Co/V	0.07/0.31	0.03/0.29	-57/-6
Co/Hg	0.07/0	0.09/0.06	+129/*
Ni/V	0.11/0.31	0.01/0.25	-91/-19
Ni/Hg	0.11/0	0.08/0.04	-27/*
V/Hg	0.31/0	0.28/0.02	-10/*

Resin prepared from crosslinked poly(ethyl acrylate) with crosslinking 8 mol % and dilution 120 vol %.

Adsorption Behavior for Various Metal Ions

The bead turns to a characteristic color according to the metal solution, with the color deepening as the metal ion is consumed after the addition of metal solution to the polymer. Batch extraction experiments were used to compare the complexing ability of the hydroxamic acid resins. Figure 1 shows the dependence of copper ion extraction on the degree of dilution and crosslinking ratio of the resin at pH 4. Higher DVB content results in a decrease in the copper ion adsorption capacity of the resin. As is readily evident, higher DVB content in the resin matrix gives a more compact and rigid crosslinked structure to the resin. Also hydrophobic DVB limits the diffusion of metal ions into the resin.

Total adsorption capacity of Cu^{2+} , Fe^{3+} , Hg^{2+} , V^{5+} , and UO_2^{2+} at pH 4, 2.5, 3.0, 3.0, and 3.0, respectively, are shown in Figures 1-5. The resins show high adsorption capacity for copper, iron, vanadium, and uranyl ions. Proper polymerization conditions, i.e. the degree of dilution and crosslinking ratio, should be chosen in order to extract mercury ion. But in general the metal binding capacity decreased when more DVB was used, at the same hydroxamic acid group content.¹⁹ The metal capacity is lower in each case than the hydroxamic acid capacity as deduced from the nitrogen content of the resin. This difference is because two or more hydroxamic acid groups can combine with one metal. The remaining

difference may be due to steric factors that limit the approach of metal to some of the hydroxamic acid groups.

The kinetics of the resin-metal interaction are of considerable importance if the resin is to be used in a dynamic system such as a packed column and a flowing stream.²⁰ If complexation is not sufficiently rapid for certain metals, then their concentration on a packed column is unlikely owing to the short contact time between the resin and the solution. In those cases a batch extraction with a large excess of resin should be conducted over an extended period.

At pH 4 the uptake of Cu^{2+} at a concentration of 100 ppm reaches a value of 50 and 95% extracted after 25 min and 3 h equilibration, respectively, as shown in Figure 6. Fe^{3+} is somewhat slower, requiring 1.5 h to reach the 50% extracted level and 16 h to the 80% extracted level, as shown in Figure 7. But by alkali treatment the adsorption rate was remarkably enhanced such that only 5 min were needed to extract the Cu^{2+} ion to a value of 80% and 1 h for the Fe^{3+} ion. Adsorption of vanadium and uranyl ions by the hydroxamic acid resin at pH 3 for various shaking periods are given in Figures 8 and 9, respectively. The time taken by the resin to occupy 50% of its total adsorption, $t_{1/2}$, was 4 h for vanadium and 30 min for uranium. But only 5 min were needed to attain 50% extraction by alkali treatment of the resin. This large increase in rate can be attributed to the formation of a favorable

Table II Competitive Uptake of Metal Pairs by Poly(hydroxamic acid) Resin

Metal Pair	Alone (mmol/g)	Mixed (mmol/g)	Relative Difference (%)
Cu/Fe	0.27/0.10	0.01/0.10	-96/0
Cu/Co	0.27/0.06	0.29/0.06	+107/0
Cu/Ni	0.27/0.11	0.25/0	-7/*
Cu/V	0.27/0.16	0.22/0.05	-19/-69
Cu/Hg	0.27/0	0.26/0.11	-4/*
Fe/Co	0.18/0.06	0.32/0.06	+178/0
Fe/Ni	0.18/0.11	0.23/0.07	+128/36
Fe/V	0.18/0.16	0.16/0	-11/*
Fe/Hg	0.18/0	0.18/0.03	0/*
Co/Ni	0.06/0.11	0.13/0.23	+217/+209
Co/V	0.06/0.16	0.08/0	+133/*
Co/Hg	0.06/0	0.27/0.10	+450/*
Ni/V	0.11/0.16	0.09/0	-18/*
Ni/Hg	0.11/0	0.20/0.09	+182/*
V/Hg	0.16/0	0.28/0.02	+175/*

Resin prepared from crosslinked poly(ethyl acrylate) with crosslinking 15 mol % and dilution 40 vol %.

pore structure (micropore) based on extensive swelling²¹ and increase in the resin hydrophilicity due to the alkaline hydrolysis of esters in the resin by alkali treatment. The faster rate of extraction facilitates the chromatographic separations. Shah and Devi²² observed that $t_{1/2}$ is inversely proportional to the metal ion concentration.

Results of a competitive batch uptake study, which was carried out to determine if certain metals would enhance or inhibit the uptake of other metals, are shown in Tables I and II. Cu^{2+} is preferentially complexed over Co^{2+} and Ni^{2+} . Similarly, Fe^{3+} is preferentially complexed over Cu^{2+} , Co^{2+} , Ni^{2+} , V^{5+} , and Hg^{2+} and V^{5+} over Ni^{2+} , Co^{2+} , and Hg^{2+} . Because the metal ions are initially at the same concentration and both are in excess of the resin, a competition will exist between the metal pairs for the available active sites on the resin. The effects of the crosslinking ratio on the metal ion selectivity were great when vanadium was in the metal pair (Table II). Unlike the result of 8 mol % crosslinking, Cu^{2+} , Co^{2+} , or Ni^{2+} are selectively adsorbed over V^{5+} by the resin crosslinked with 15 mol % DVB. Therefore it is more reasonable to think that the vanadium ion is more sensitive to the resin matrix than the other ions, especially the crosslinking ratio.

CONCLUSIONS

Chelating resins containing hydroxamic acid ligand were prepared by suspension polymerization of poly(EA-co-DVB) followed by subsequent reaction with hydroxylamine. Their metal binding properties were investigated. The poly(hydroxamic acid) showed good adsorption capacity for copper, iron, vanadium, and uranium ions. Alkali treatment of the chelating resins aided adsorption of metals, which was thought to be due to new ligands or micropores. This type of resin had a particular selectivity for specific metal ions.

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