Synthesis and Characterization of Hydroxamic Acid Resin of Poly(4-Vinyl-2'-carboxybenzophenone)

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SYNOPSIS

The synthesis and characterization of poly(hydroxamic acid) ion-exchange resin from a poly(carboxylic acid) resin is described and its exchange properties for Cu(II), Ni(II), and Fe(III) are studied. The metal polychelates are investigated by magnetic measurements, diffuse reflectance spectroscopy, and infrared spectroscopy. © 1994 John Wiley & Sons, Inc.

INTRODUCTION

Hydroxamic acids are known to form chelate complexes of a high stability with a wide range of metal ions. A variety of techniques for the production of polymeric hydroxamic acids have been proposed. N-benzoyl-N-phenylhydroxylamine (BPHA) has found many applications in analysis since its preparation by Bamberger[1] and the first exploratory work by Shome.[2] An excellent account of the preparation and widespread analytical uses of BPHA and its analogs has been given by Majumdar.[3] Cornaz et al.[4,5] and Patrie et al.[6] briefly described the preparation and chelating properties of ion-exchangers containing the hydroxamic acid moiety and noted a high selectivity for iron(III). Chelating ion-exchangers containing the N-carbonyl phenylhydroxylamine functional group have been synthesized and their exchange behavior toward copper(II), cobalt(II), iron(III), vanadium(V), and uranium(VI) have been investigated by Vernon and Eccles.[7] In the present communication, the synthesis and characterization of hydroxamic acid resin of poly(4-vinyl-2'-carboxybenzophenone) are described.

EXPERIMENTAL

Preparation of the Resin

Electrophilic substitution[8] of polystyrene (0.5 g) with phthalic anhydride (1.0 g) was carried out by the Freidel-Crafts reaction to prepare poly(4-vinyl-2'-carboxybenzophenone) from which a poly(hydroxamic acid) resin was prepared via an ester. Esterification was carried out by refluxing it with an excess of ethanol (20 mL) to which concentrated sulfuric acid (2 mL) was added as a catalyst. The ester was then filtered, washed with water, and dried. The ester (1.0 g) was placed in a flask and methanol (20 mL) was added. To this, 1.0 g of hydroxylammonium chloride (~ 50% excess for 2 : 1 proportion) and potassium hydroxide (1.0 g) was added and the mixture was stirred at room temperature for 24 h. The product was filtered, washed with water and methanol, and dried at 60–70°C:
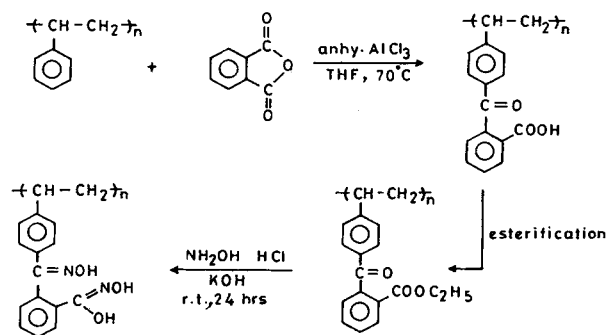
Sodium-exchange Capacity and Degree of Functionalization

A sample of the resin (0.5 g) was equilibrated with 25.0 mL of $\sim$ 0.5 M sodium bicarbonate solution for 24 h and it was filtered and washed thoroughly with water. The total filtrate was acidified with 50 mL of $\sim$ 0.5 M hydrochloric acid, boiled to expel carbon dioxide, and back-titrated with $\sim$ 0.5 M sodium hydroxide solution. Similarly, a blank titration was carried out.

Water Regain

A 1.0 g sample of the resin was soaked in water for 48 h and filtered under slightly reduced pressure, the filtration being continued for some time after the disappearance of surface water. The resin was pressed lightly between filter papers to remove surface moisture, then transferred rapidly to a watch-glass and weighed.

Ion-exchange Studies on the Resin

For the ion-exchange studies, $\sim$ 1.0 mg/mL metal ion solutions were used in all the experiments. Aliquots of 25.0 mL of this solution were taken and the pH was varied using dilute acetic acid after the removal of mineral acid with sodium carbonate. The resin, 0.5 g, was added to each and equilibrated for 24 h. The adsorbed metal ions were eluted with $\sim$ 2.0 M hydrochloric acid and determined complexometrically.

The effect of the presence of different electrolytes, viz., NaCl, Na_2SO_4, $NaNO_3$, and $NaClO_4$, on the adsorption of Cu^{2+}, Ni^{2+}, and Fe^{3+} was studied. The resin samples (0.1 g) were suspended in the electrolytes of different concentrations for preconditioning for 24 h and then added to the respective concentrations of electrolytes mixed with metal-ion solutions, after adjusting the required pH. After 24 h, the resin was filtered and washed with water and the adsorbed metal ions were determined complexometrically after eluting with $\sim$ 2.0 M hydrochloric acid.

To 25.0 mL aliquots of the metal-ion solutions, different amounts of resin were added after adding the appropriate electrolyte and adjusting the optimum pH. After 24 h, the adsorbed metal ions were determined.

After mixing 25.0 mL aliquots of metal ions with appropriate electrolytes and adjusting to the re-

quired pH value, the amount of resin required for the maximum adsorption was added to each and the adsorption was studied at different time intervals up to 24 h.

The effect of the presence of Cd(II) ions on the adsorption of Cu(II) ions was studied by adjusting the suitable pH, electrolyte, amount of resin, and the time of equilibration. Cu(II)—Fe(III) as well as Ni(II)—Fe(III) separations were carried out under optimum conditions.

Magnetic susceptibility measurements of copper and nickel polychelates of the resin were carried out on the Gouy balance at 300 K and corrected for the diamagnetic correction of the resin in hydrogen form. The metal–resin complexes were studied by diffuse reflectance spectroscopy using Spekol-10 with an R-40 reflectance accessory. All spectra were examined undiluted using magnesium oxide as a reference. Infrared spectra of the resin and the resin polychelates synthesized in the present work were scanned on a Shimadzu FTIR spectrophotometer, Model 4200, as KBr pellets.

RESULTS AND DISCUSSION

Figure 1 represents the mmol g^{-1} of the metal ions adsorbed at different pH. Figure 2 shows the effect of electrolytes on the adsorption of Cu(II), Ni(II), and Fe(III). The amount of Cu(II) taken up is maximum in the presence of 0.5 M Na_2SO_4; that of
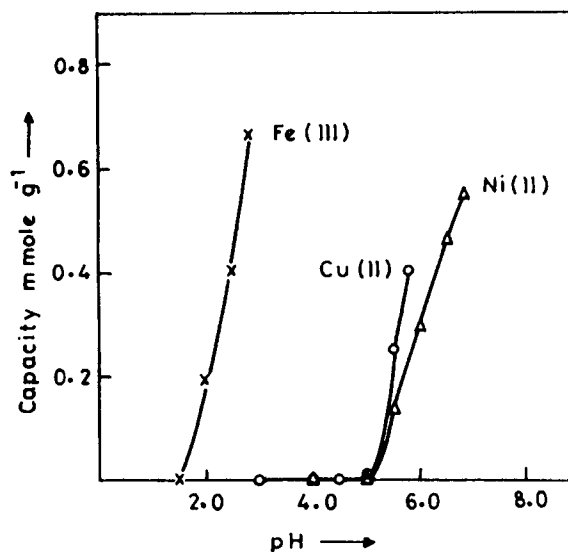

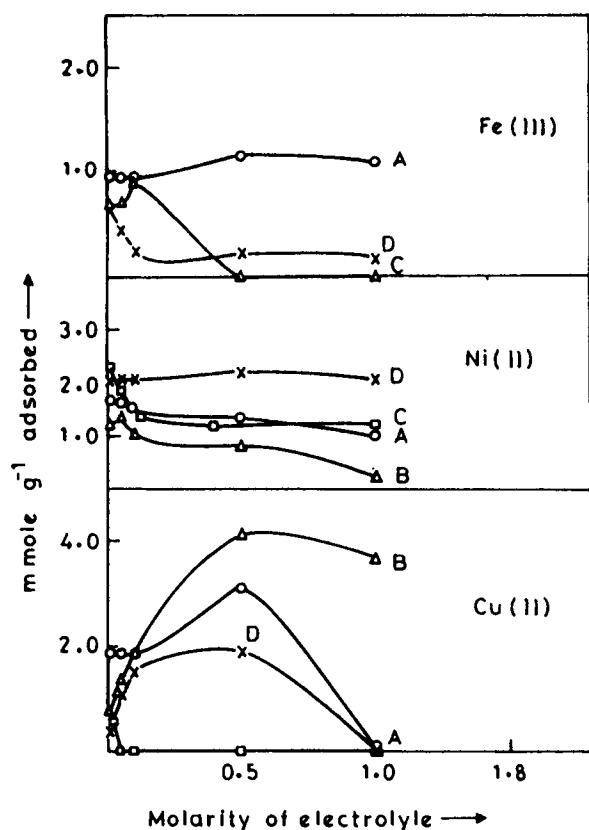**Figure 1**   Capacity vs. pH curves for metal ions.

Figure 2 mmol g^{-1} of metal ions adsorbed vs. molarity of electrolyte: (A) NaCl; (B) Na$_2$SO$_4$; (C) NaNO$_3$; (D) NaClO$_4$.
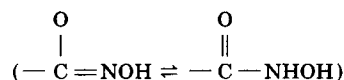
Ni(II), in the presence of 0.01M NaNO$_3$; whereas that of Fe(III), in the presence of 0.5M NaCl. The amount of resin required for the maximum adsorption of Cu(II) is $\geqslant$ 0.6 g for 26.75 mg of Cu(II). The amount required for Ni(II) is $\geqslant$ 0.9 g for 25.25 mg, and for Fe(III), $\geqslant$ 0.5 g for 26.75 mg. The time required for the maximum adsorption is 3 h for Cu(II), 18 h for Ni(II), and 4 h for Fe(III). Table I summarizes the salient features of the resin.

The resin has a remarkably high capacity for Cu(II), for which the equilibration rate is very fast ($t_{1/2} \sim$ 18 min) with 8 mM Cu(II) solution. The selective adsorption and estimation of iron(III) from its mixture with copper(II) and nickel(II) can be achieved via control of the pH. The equilibration rate $t_{1/2}$ for Ni(II) and Fe(III) is 2 h 18 min and 18 min, respectively. Desorption of the adsorbed metals is very rapid with 2M hydrochloric acid and the resin has a high chemical stability so that it can be recycled for even more than 20 cycles without significant loss of metal-ion capacities.

Study of Polychelates

The magnetic measurements show that the magnetic susceptibility of Cu(II) polychelate is 1.66 B.M. The diffuse reflectance spectral measurements of Cu(II) polychelate show a band at 15.15 kK and another at 21.28 kK. Whereas the higher-energy band is due to a charge-transfer transition, the lower-energy band is due to a d-d transition. Its position and structure indicate a planar stereochemistry around Cu(II) for which this band would correspond to the $^2B_{1g} \rightarrow {}^2E_g$ transition. The magnetic susceptibility of the Ni(II) polychelate is 2.69 B.M. The spectrum of Ni(II) polychelate shows bands at 15.38, 16.13, and 16.95 kK with contribution from d-d transitions, whereas bands at > 21.00 kK most probably originate from charge-transfer transitions. The spectrum of Fe(III) polychelate shows bands at 22.73 and 24.39 kK having contributions from charge-transfer transitions. In addition, a band is observed at 14.50 kK. These bands are in the region reported by Vernon and Eccles[9] for 3 : 1-type Fe(III) polychelates of hydroxamic acid resins. The magnetic and diffuse reflectance spectral data suggest that the oximic N atom as well as hydroxamic N atom participate in bonding to metal ions, in addition to the unreacted —COOH groups. Blue-colored copper(II) polychelate has Cu(II) present in the four-coordinate geometry, whereas green-colored nickel(II) polychelate of the resin appears to achieve a pseudo-octahedral environment around Ni(II).

The infrared spectrum of the resin in the Fourier transform mode shows a broad and strong band at 3460 cm^{-1} that can be attributed to ν OH and NH stretching of the

$$\begin{array}{ccc} & \text{O} & & \text{O} \\ & | & & \| \\ (- & \text{C} = \text{NOH} & \rightleftharpoons & - \text{C} - \text{NHOH}) \end{array}$$

group. The C═O of the hydroxamic group (which may be considered as N-hydroxyamide) is expected

Table I   Resin Features

Water regain	0.04 g g^{-1}
Sodium–hydrogen exchange capacity	3.2 mmol g^{-1}
Copper capacity at pH 6.0	
(in the presence of 0.5M Na$_2$SO$_4$)	4.12 mmol g^{-1}
Nickel capacity at pH 6.8	
(in the presence of 0.01M NaNO$_3$)	2.30 mmol g^{-1}
Iron (III) capacity at pH 2.7	
(in the presence of 0.5M NaCl)	1.24 mmol g^{-1}

to give a band at 1700–1650 cm^{-1} (the amide I band of secondary amides). This is found at 1650 cm^{-1}. The weak absorption band at $\sim$ 1675 cm^{-1} is probably due to ν C$=$O (unreacted aryl keto group). The hydroxamic acid group also gives an absorption band at $\sim$ 1550 cm^{-1} (the amide II) band. The spectrum reveals a medium intensity band at 1516 cm^{-1} that may be assigned to this absorption. The medium intensity band at 1383 cm^{-1} is assigned to OH deformation vibration, whereas a weak band at 1277 cm^{-1} is attributed to δ C$=$O vibration of a keto aryl group. The ν N$-$O (symmetric) vibration of oximic group is found at 907 cm^{-1}. The characteristic band of the 1,2-disubstituted phenyl ring is at 754 cm^{-1}. The spectra of polychelates of Cu(II), Ni(II), and Fe(III) with the resin show very weak absorption in the ν OH region, indicating the participation of the hydroxamic O atom in binding to metal ions. The ν N$-$O absorption is found at higher energy than in the spectrum of the resin, suggesting the bonding of Fe(III) through the oximic nitrogen atom.

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