

Synthesis and Characterization of Oxime Resin of Poly(4-vinyl, 2'-carboxybenzophenone) and Its Metal Polychelates

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SYNOPSIS

The synthesis and characterization of oxime resin of poly(4-vinyl, 2'-carboxybenzophenone) is described and its exchange properties for Cu(II), Ni(II), and Co(II) are studied. The metal polychelates are investigated by magnetic measurements, diffuse reflectance spectroscopy, and infrared spectroscopy. © 1995 John Wiley & Sons, Inc.

INTRODUCTION

We have recently reported¹ the synthesis and chelating ion-exchange properties of a hydroxamic acid resin derived from modified polystyrene. In this communication the synthesis and characterization of an oxime resin of poly(4-vinyl, 2'-carboxybenzophenone) and its metal chelates are described.

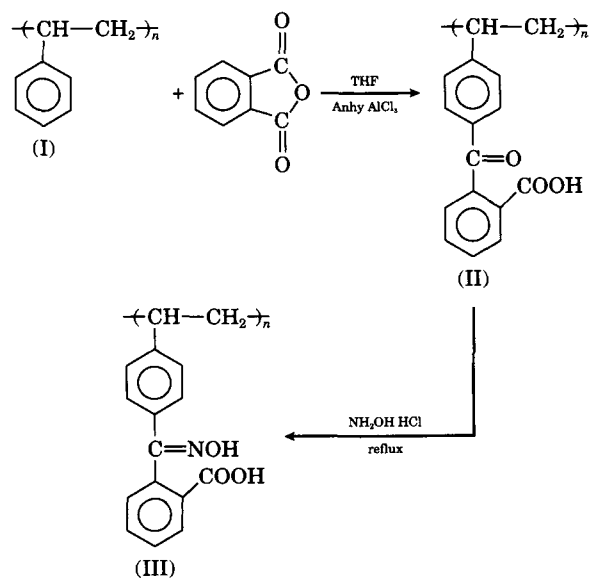
EXPERIMENTAL

Synthesis of Oxime Resin

Details of synthesis of poly(4-vinyl, 2'-carboxybenzophenone) (II) were as reported earlier^{1,2} from which the oxime resin was obtained by refluxing 10 g of (II) with hydroxylammonium chloride (10 g) in dioxane (100 mL) and ethanol (80 mL) for 24 h.³ The product (III) was filtered and washed thoroughly with water and finally with methanol and dried at 60–70°C.

Found: C, 69.57%; H, 5.28%; N, 3.89%. Calc: C, 68.59%; H, 5.64%; N, 4.08%.

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Sodium-exchange capacity and degree of functionalization as well as water regain of the resin were studied. Exchange of Cu^{2+} , Ni^{2+} , and Co^{2+} was evaluated under different conditions of pH, electrolytes, time of equilibration, and amount of resin. Effect of presence of Ni^{2+} , Co^{2+} , and Zn^{2+} on the adsorption of Cu^{2+} was investigated. Cobalt-copper and cobalt-nickel separations were studied under the optimum conditions for the maximum adsorption of Co^{2+} . Magnetic susceptibilities, diffuse reflectance spectra, as well as infrared spectra were measured for the characterization of the metal polychelates.

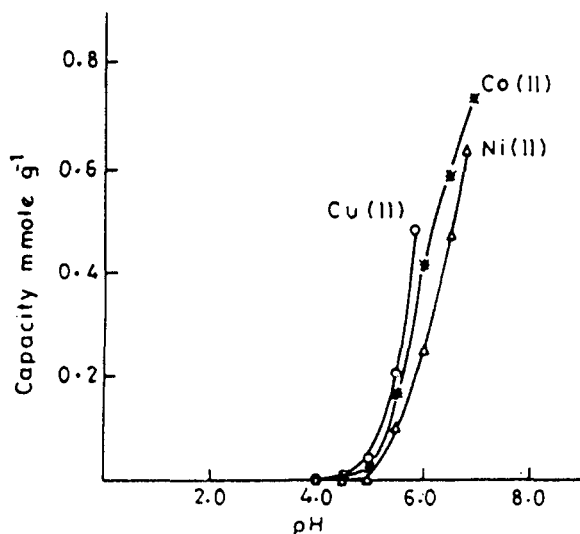


Figure 1 Capacity vs. pH curves for metal ions.

RESULTS AND DISCUSSION

Figure 1 shows the mmol g^{-1} of the metal ions adsorbed at different pH values. Figure 2 shows the effect of different electrolytes on the uptake of Cu^{2+} , Ni^{2+} , and Co^{2+} . The amount of Cu^{2+} taken up is maximum in the presence of $0.5M Na_2SO_4$ but is negligible in the presence of $NaNO_3$. Adsorption of Ni^{2+} is maximum in the presence of $0.01M NaNO_3$ as well as $0.1M NaClO_4$, and that of Co^{2+} is maximum in the presence of $1M NaClO_4$. The amounts of resin required for the maximum adsorption of Cu^{2+} , Ni^{2+} , and Co^{2+} are ≥ 0.9 , ≥ 0.2 , and ≥ 0.2 g for 25 mg of Cu^{2+} , Ni^{2+} , and Co^{2+} , respectively. The time required for the maximum adsorption of Cu^{2+} , Ni^{2+} , and Co^{2+} is 2, 16, and 8 h, respectively. Table I summarizes the salient features of the resin.

Analytical studies reveal high capacities for Cu^{2+} and Co^{2+} . The time for 50% adsorption ($t_{1/2}$) for the resin (equilibration rate) for the sorption of Cu^{2+} is very short (~ 18 min). Stripping of the adsorbed metal ions is achieved readily by elution with $\sim 2M$ HCl. The resin possesses a high chemical stability; even more than 20 adsorption-regeneration cycles do not result in significant decrease in metal ion capacities. The separation studies on cobalt-copper mixtures show that copper is adsorbed on the resin, and cobalt remains in the solution even though the conditions favorable for cobalt are adjusted, the separation being achieved via selective adsorption of copper. In case of cobalt-nickel mixtures, when the amounts are in the ratio of $\geq 3 : 1$, separation is achieved via selective adsorption of Co^{2+} ions.

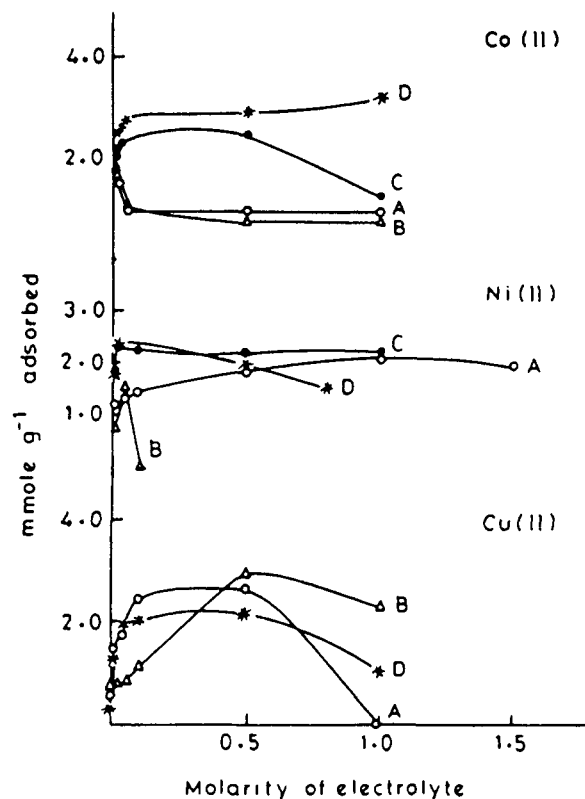


Figure 2 mmol g^{-1} of metal ions adsorbed vs. molarity of electrolyte. (A) NaCl, (B) Na_2SO_4 , (C) $NaNO_3$, and (D) $NaClO_4$.

Study of Metal Polychelates

The magnetic moment of resin-Cu polychelate is 1.58 BM, somewhat less than that expected for Cu^{2+} complexes with one unpaired electron. Cu^{2+} probably has a planar 4-coordinate environment in the chelate though it does not rule out a distorted octahedral environment. The magnetic moment of resin-Ni polychelate is 2.90 BM, i.e., in the range expected for an octahedral Ni^{2+} complex. Ni^{2+} probably

Table I Salient Features of Oxime Resin of Poly(4-vinyl,2'-carboxybenzophenone)

Degree of functionalization	77%
Water regain	$0.18 g g^{-1}$
Total sodium-hydrogen exchange capacity using $NaHCO_3$ ($-COOH + \rightleftharpoons NOH$)	$6.3 mmol g^{-1}$
Cu^{2+} capacity at pH 6.0 ($0.5M Na_2SO_4$)	$2.96 mmol g^{-1}$
Ni^{2+} capacity at pH 6.8 ($0.01M NaNO_3$)	$2.38 mmol g^{-1}$
Co^{2+} capacity at pH 6.9 ($1.0M NaClO_4$)	$3.14 mmol g^{-1}$

achieves an octahedral environment by binding to two additional ligand atoms. Though the present polychelate of Co^{2+} shows a moment of 3.96 BM, much lower than that of an octahedral Co^{2+} complex, its dark pink color is more indicative of a distorted octahedral coordination environment around Co^{2+} .

Infrared (IR) spectrum of the oxime resin shows νOH at $\sim 3350\text{ cm}^{-1}$ as a broad band. The polystyrene band at 1600 cm^{-1} obscures $-\text{COOH}$ absorption. $\nu\text{C}=\text{N}$ (oximic) is found at 1580 cm^{-1} . δOH (oximic) is at 1370 cm^{-1} while oximic $\nu\text{N}-\text{O}$ (sym) is at 905 cm^{-1} . The characteristic band of a 1,2-disubstituted phenyl ring is located at 750 cm^{-1} . Spectra of Cu^{2+} , Ni^{2+} , and Co^{2+} polychelates show the νOH at $\sim 3400\text{--}3500\text{ cm}^{-1}$. $\nu\text{C}=\text{N}$ and $\nu\text{N}-\text{O}$ are found to be shifted to lower and higher energy, respectively. Participation of the oximic nitrogen atoms in bonding to metal ions is indicated in the polychelates, in addition to the involvement of $-\text{COOH}$.

The diffuse reflectance spectrum of Cu^{2+} polychelate shows bands at $\sim 15.00\text{ kK}$ and 15.65 kK , probably due to a split $d-d$ band while another $d-d$ band (with structure) is split into components at 16.15, 16.65, and 17.20 kK. These two bands may be assigned to the ${}^2B_{1g} \rightarrow {}^2A_{1g}$ and ${}^2B_{1g} \rightarrow {}^2E_g$ transitions of a planar, 4-coordinate Cu^{2+} chelate.

Charge-transfer bands are observed at higher energies. Ni^{2+} polychelate reveals a band at 14.92 kK having contribution from a $d-d$ transition. A split $d-d$ band is observed with components at 16.13, 16.66, and 17.24 kK. The spectrum is indicative of a distorted octahedral local symmetry around Ni^{2+} . Charge-transfer bands are at $> 21\text{ kK}$. The spectrum of Co^{2+} polychelate is dominated by a broad band at $\sim 19\text{ kK}$, typical of octahedral Co^{2+} compounds. While major contribution to this band is from the highest energy $d-d$ transition, ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$, there is some contribution from the transition, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$, lying close to the former as is often observed in octahedral Co^{2+} complexes due to the proximity of the ${}^4T_{1g}(P)$ and ${}^4A_{2g}$ energy levels.

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