

Chelating Resins. III. Synthesis, Characterization, and Capacity Studies of Formaldehyde-Condensed Phenolic Schiff Bases Derived from 1,2-Diamines and Hydroxy Benzaldehydes

S. SAMAL,^{1,*} R. R. DAS,² D. SAHOO,¹ S. ACHARYA,¹ R. L. PANDA,¹ and R. C. ROUT¹

¹Department of Chemistry, Ravenshaw College, Cuttack 753 003, India; ²Department of Chemistry, S. B. Women's College, Cuttack 753 008, India

SYNOPSIS

Schiff bases of hydroxy benzaldehydes with aliphatic and aromatic 1,2-diamines were resinified in HCHO in alkaline media. These resins were found to form complexes readily with Cu(II), Co(II), and Ni(II). The materials were characterized by infrared, ¹H-NMR, UV-visible (UV-vis) spectral studies, and thermogravimetric analyses. The phenolic oxygen and the azomethene nitrogen were the ligating sites, one or more lattice positions in polychelates being occupied by water molecules. ¹H-NMR provided evidence for bridging methylene and terminal methylol groups. The UV-vis spectra showed weak absorptions in the d—d transition range. Capacity studies of the resins indicated metal loadings up to 70% at room temperature in an appropriate pH of the salt solutions. The effects of contact time, particle size of the sorbents, resin quantity, and pH on the adsorption characteristics were studied. In the pH range 3–8, the resins derived from the structurally rigid Schiff bases exhibited higher capacity for the metal ions than the resins derived from structurally flexible Schiff bases. Kinetic parameters computed from the thermogravimetric data indicated the resins to be more stable than the corresponding polychelates. © 1996 John Wiley & Sons, Inc.

INTRODUCTION

Chelate-forming polymeric ligands have been extensively studied by several authors and many reviews are available in the field.^{1,2} These resins have been used for preconcentration and separation of trace elements from sea water and their analytical use in conjunction with atomic absorption spectroscopy has been well established.^{3,4} The selective behavior of these resins is based on the stability of the metal complexes at appropriate pH values. Such polymers also formed stable complexes with several metal ions. Using these materials, the complete removal of several metal ions from dilute aqueous solutions has been reported.⁵

In recent reports, different hydroxy functionalized polyazomethenes have been modified by complexation using Cu(II) ions and the percentage of Cu(II) introduced into the polymeric chain is determined by inductively coupled plasma atomic emission spectroscopy.⁶ The synthesis and characterization of linear Ce(IV) Schiff base coordination polymers exhibiting high thermal stability and high glass transition temperature have been reported.⁷ Suitable chelating resins for chemical and biomedical applications with high capacity and selectivity toward Fe(III) combined with a good stability and reusability without loss in chelating capacity have been reported.⁸ Polymer-supported Mo and V catalysts were also employed for epoxidation of alkenes by alkyl hydroperoxides.⁹ Several heavy metal ions such as Hg(I), Cu(II), and Pb(II) were extracted using thiol chelating resins¹⁰ and chelating resins supporting dithiocarbamate and methyl thiourea

* To whom correspondence should be addressed.

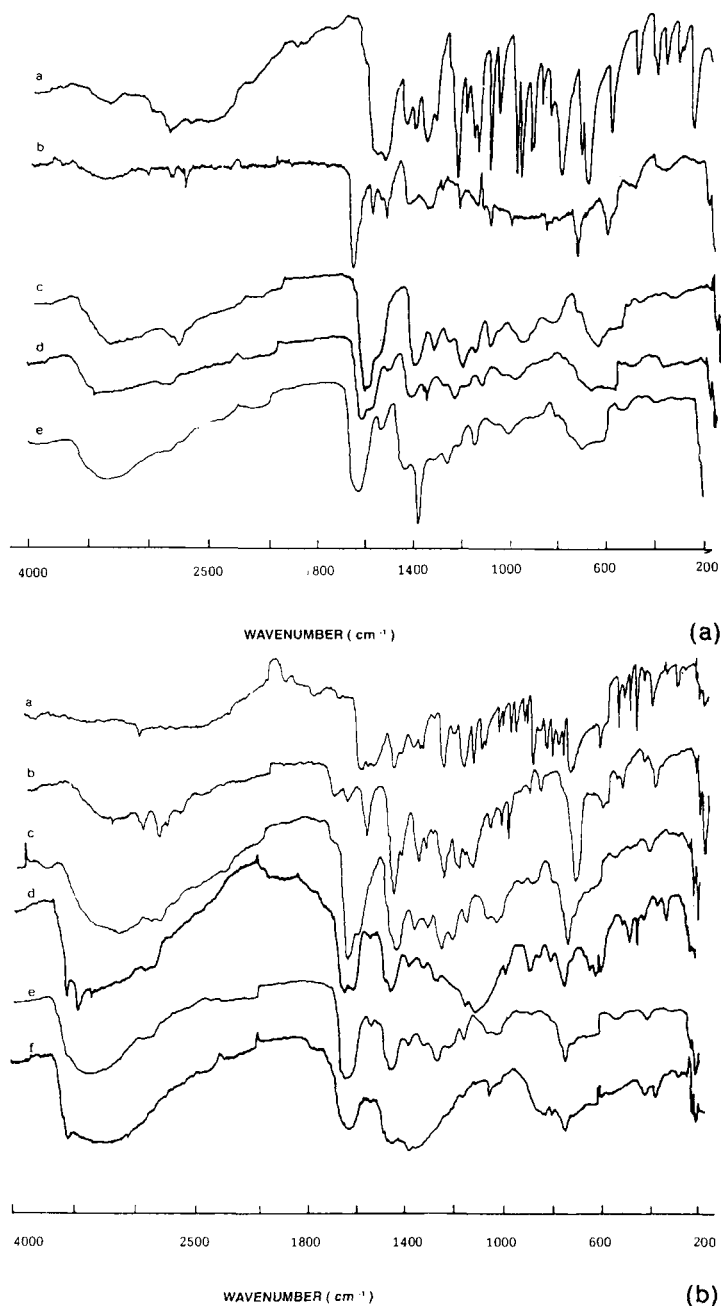


Figure 1 A: IR spectra of (a) *o*-HBED, (b) *o*-HB-HCHO, (c) *o*-HBED-HCHO, (d) *o*-HBED-HCHO-Cu(II), (e) *o*-HBED-HCHO-Ni(II); B: IR spectra of (a) *o*-HB-*o*-PD, (b) *o*-PD-HCHO, (c) *o*-HB-*o*-PD-HCHO, (d) *o*-HB-*o*-PD-HCHO-Cu(II), (e) *o*-HB-*o*-PD-HCHO-Co(II), (f) *o*-HB-*o*-PD-HCHO-Ni(II).

groups.¹¹ The behavior of macroreticular chelating resins containing phosphinic and phosphonic acid groups was studied in the absorption of trivalent lanthanides such as La(III), Nd(III), Sm(III), Gd(III), and Yb(III).¹²

Chelating ligands containing aromatic amino and phenolic functions enter into condensation reactions readily with formaldehyde and furfur-

aldehyde. Schiff bases synthesized by condensing phenolic carbonyls with amines are known to form a number of metal complexes depending upon the nature of coordination sites. When such ligands are condensed with formaldehyde or furfuraldehyde, the corresponding resins would be expected to form polymeric metal complexes under suitable conditions and could be employed for

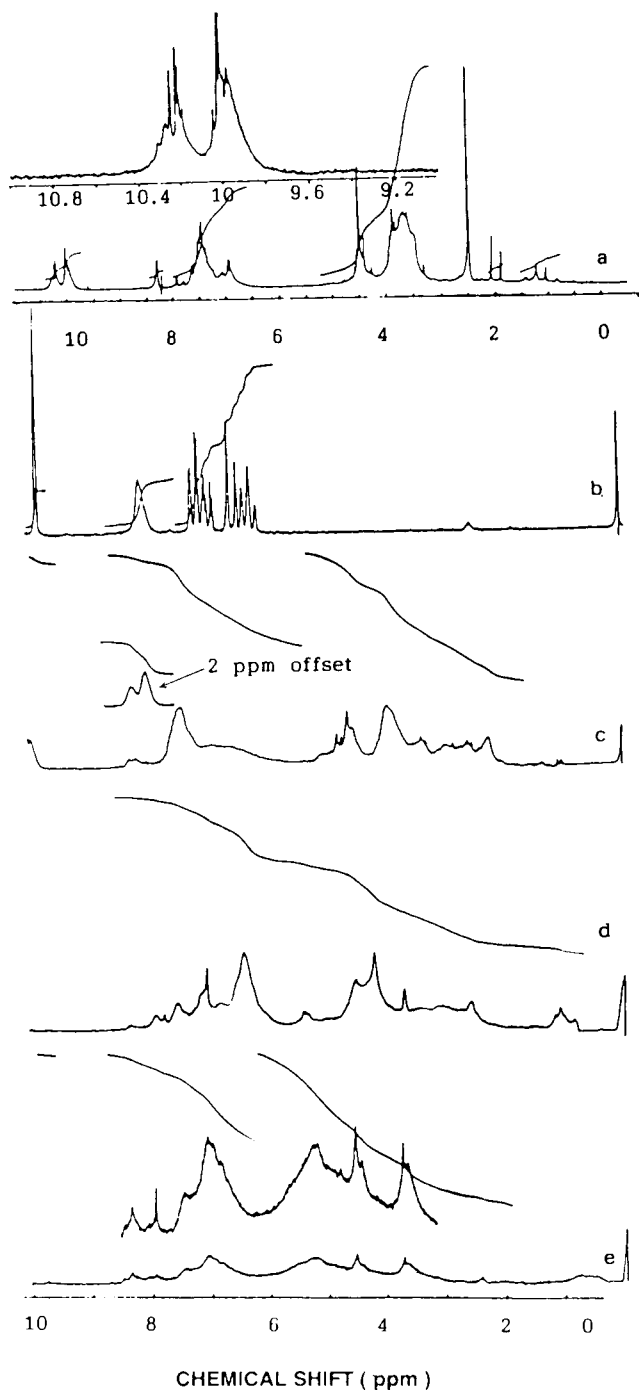


Figure 2 $^1\text{H-NMR}$ spectra (400 MHz) of (a) *o*-HB-HCHO and $^1\text{H NMR}$ spectra (90 MHz) of (b) *o*-HB-HCHO, (c) *o*-PD-HCHO, (d) *o*-HBED-HCHO, (e) *o*-HB-*o*-PD-HCHO.

extraction of metal ions from dilute aqueous solutions.

In this paper we report the synthesis and characterization of chelating resins prepared by condensing phenolic Schiff bases having multiple ligating sites with formaldehyde. The resins were chosen

to provide molecular arrangements that would lead to flexible or rigid structures with identical coordination sites. The capacity of such resins toward Cu(II) and Ni(II) ions in aqueous media was correlated to the structural features of the resins. The Schiff bases, the resins, and the polychelates were characterized by spectral studies and thermogravimetric analysis (TGA).

The Schiff bases from ethylene diamine-salicylaldehyde and *o*-phenylene diamine-salicylaldehyde resinified by condensing with HCHO in alkaline media were selected for the present study. The spectral data of Cu(II), Co(II), and Ni(II) polychelates were analyzed to ascertain the coordination sites. The TGA of the resins and the polychelates were carried out and the thermal stability order was evaluated using several kinetic models. The metal uptake behavior of the resins under noncompetitive conditions was followed spectrophotometrically.

EXPERIMENTAL

The Schiff bases of aliphatic and aromatic diamines with hydroxy benzaldehydes were synthesized following standard procedure. For detailed study, the Schiff bases of *o*-phenylene diamine-salicylaldehyde (*o*-HB-*o*-PD) and ethylene diamine-salicylaldehyde (*o*-HBED) were selected. To prepare the resin, 1 gm of Schiff base was suspended in 25 mL distilled water and about 10–15 drops of 2M NaOH were added; the mixture was warmed to 50–60°C for 5 min, and formaldehyde (37% vol/vol) in the molar ratio 1 : 2 was added; the mixture was then refluxed in oil bath at 120–130°C for 1–2 h. The insoluble resin was filtered and washed in distilled water followed by petroleum ether, and dried at 70°C. To 100 mg of the resin (100 mesh) suspended in dry alcohol, ethanolic solution of the metal salt (0.15M M^{2+}/L) was added followed by 2 drops of N/50 KOH in water, and the mixture was stirred at 45–50°C for 1 h. The polymeric complex so formed was filtered, washed in hot ethanol followed by petroleum ether, and dried *in vacuo* at 70°C. Metal salt solutions of 0.08M M^{2+}/L were used for metal uptake experiments. Studies were conducted either in the natural pH of the solutions or in a desired pH adjusted by adding dilute NaOH or HCl. The aqueous solution of salt (10 mL) was treated with 100 mg of resin and agitated over a magnetic stirrer at 30–40°C for a period varying from 5 min to 1 h. The metal-loaded resin was filtered and thoroughly washed with water, and the metal ion in the filtrate and the washings was determined spectrophotometrically.¹³

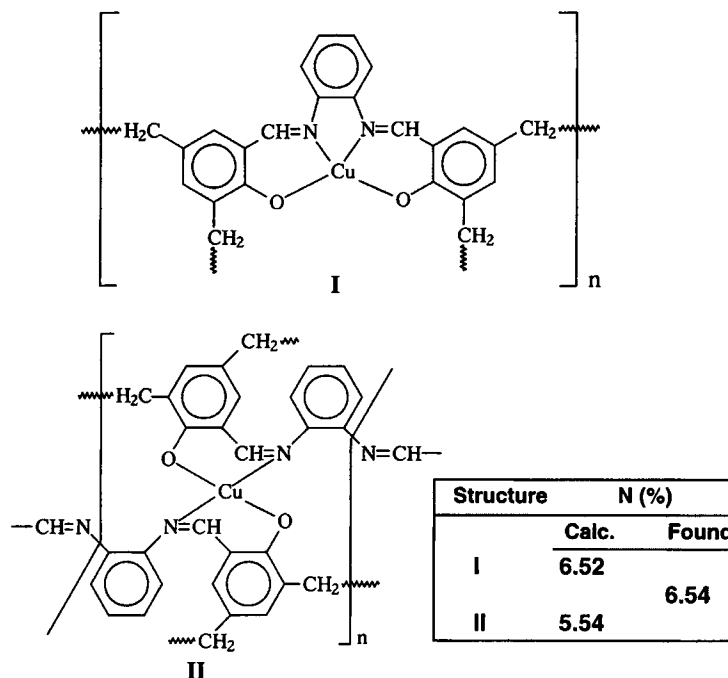


Figure 3 Intrachain (I) and interchain (II) structures for the Cu(II) polychelate of the resin *o*-HB-*o*-PD-HCHO.

CHARACTERIZATION

The infrared (IR) spectra were recorded on a Perkin-Elmer Model 881/557 in KBr phase. The $^1\text{H-NMR}$ spectra were recorded in dimethyl sulfoxide (DMSO) d_6 solution at 90 MHz or 400 MHz on a Fourier transform nuclear magnetic resonance (FTNMR) instrument. Elemental analyses were performed on a Carlo-Erba 1108 elemental analyzer. The electronic spectra of the samples were recorded on a Hitachi UV-Vis spectrophotometer using CHCl_3 as the solvent. The TGA were performed on a Du Pont thermogravimetry analyzer at a heating rate of $10^\circ\text{C}/\text{min}$ under nitrogen atmosphere. The intrinsic viscosity, $[\eta]$, of the resin was determined by viscometry using an Ubbelohde viscometer. The average molecular weight of the resin soluble in tetrahydrofuran (THF) was determined by gel permeation chromatography (GPC) on a Millipore instrument.

RESULTS AND DISCUSSION

Resins were soluble in DMSO; fully or partially soluble in THF, dimethylformamide, dioxane, CHCl_3 , and CCl_4 ; but sparingly soluble in methanol and ethanol. The polychelates were partially soluble in

most of these solvents. The intrinsic viscosity, $[\eta]$, of the resins determined in DMSO solvent at 30°C varied between 0.14 and 0.21 dL/g. The resin *o*-HBED-HCHO was fully soluble in THF with $\bar{M}_n = 81$, $\bar{M}_w = 369$, $\bar{M}_z = 1293$, and $\bar{M}_{z+1} = 2428$, and polydispersity was 4.574. The GPC of the resin *o*-HB-*o*-PD-HCHO could not be run because it was not completely soluble in THF.

IR Spectra

The IR spectra of the Schiff bases, the resins *o*-HBED-HCHO, *o*-HB-*o*-PD-HCHO, and the corresponding polychelates along with the resins of salicylaldehyde-formaldehyde (*o*-HB-HCHO) and *o*-phenylene diamine-formaldehyde (*o*-PD-HCHO) were examined to demonstrate comparative features (Fig. 1).

The IR spectra of the salicylaldehyde-HCHO resin (*o*-HB-HCHO) showed a strong carbonyl peak which vanished in the Schiff base *o*-HBED. The phenolic Schiff base on condensation with HCHO formed the resin *o*-HBED-HCHO, the IR spectra of which lacked the sharp absorptions seen in the Schiff base. The azomethine ($\text{C}=\text{N}$) stretch appeared as a strong broad band mixed up with the $\text{C}=\text{C}$ ring stretch. The Cu(II) polychelate *o*-

Table I Energy of Activation from Thermogravimetric Data

Samples	Models →	Activation Energy (kcal)		
		CR	VK	BR
<i>o</i> -HBED-HCHO		11.512	5.742	6.556
<i>o</i> -HBED-HCHO-Cu(II)		3.679	1.964	2.666
<i>o</i> -HB- <i>o</i> -PD-HCHO		3.514	3.054	2.619
<i>o</i> -HB- <i>o</i> -PD-HCHO-Cu(II)		3.211	2.118	2.430

CR, Coats & Redfern; VK, Van Krevelen; BR, Broido.

HBED-HCHO-Cu(II) showed features almost identical to its resin with the relevant absorption bands for C=C and Ph—O not registering a significant shift on coordination to the metal ion. The C=N absorption decreased by 10 cm^{-1} and the C—H band appeared to weaken. The Cu—O and Cu—N were not observed. The Ni(II) polychelate of the resin showed some distinct features. The O—H band at 3380 cm^{-1} was broad, indicating the presence of either coordinating or lattice water. A strong absorption band at 1380 cm^{-1} could be linked to N—O stretch of a free NO_3^- ion¹⁴ resulting from $\text{Ni}(\text{NO}_3)_2$ used as the Ni(II) salt in synthesizing the polychelate. The C=N stretch decreased by 30 cm^{-1} while the Ph—O absorption remained unaffected.

The *o*-phenylene diamine-HCHO resin (*o*-PD-HCHO) showed N—H stretch at 3320 cm^{-1} . The Schiff base *o*-HB-*o*-PD and its resin showed complete absence of N—H and C=O stretch. The formation of the axomethine function C=N broadened the sharp N—H band observed at 1600 cm^{-1} in *o*-PD-HCHO overlapping the C=C ring stretch. Much of the complex features of the Schiff base vanished in the IR spectrum of the resin *o*-HB-*o*-PD-HCHO, C=N stretch shifting to 1650 cm^{-1} and the C=C ring stretch appearing as a shoulder at 1610 cm^{-1} . The Cu(II) polychelate showed prominent O—H stretch at 3490 cm^{-1} along with the Cu—O band at 610 cm^{-1} and Cu—N at 460 cm^{-1} . The C=N and Ph—O absorptions did not show any noticeable shift, which might be due to the low Cu(II) content. Similar observations were recorded by some authors,⁶ though others have reported lowering of axomethine absorption by 10 cm^{-1} and Ph—O to decrease by 20 cm^{-1} .⁷

In addition to the three fundamental modes of O—H absorption, the appearance of absorption bands at 980, 880, and 795 cm^{-1} indicates the presence of coordinating water molecules¹⁴ in the Cu(II) polychelate. The Ni(II) polychelate of the resin showed

the presence of lattice water. The C=N stretch appeared to shift by 30 cm^{-1} to the low frequency region as compared with the resin. The Ni—O stretch was not registered and the Ni—N stretch at 415 cm^{-1} was weak. The IR features of the Co(II) polychelate were very similar to those of the resin.

The observations indicated that all the coordination sites might not be involved in the complexation process. A number of coordinating sites might not be accessible because of the rigid network of the resins resulting in any noticeable shift of C=C and Ph—O bands.

UV-vis Spectra

The UV-vis spectra of the resins showed multiple peaks within up to 400 nm (*o*-HBED-HCHO: λ_{max} 260 nm, 338 nm; *o*-HB-*o*-PD-HCHO: λ_{max} 258 nm, 336 nm); no absorptions were noticed in the visible region. The polychelates, on the other hand, being less soluble than the resins in chloroform, showed a relatively less intense absorption in the UV region, λ_{max} shifting to 346 and 386 nm in the case of Cu(II) polychelate of the resins *o*-HBED-HCHO and *o*-HB-*o*-PD-HCHO, respectively. Beyond 400 nm, very broad and weak absorptions were noticed in the polychelates and the λ_{max} values were not well defined. This could be because of the poor solubility of the polychelate in the chosen solvent. The weak absorptions in the visible range result from d—d transition, which indicates that the possible ligand environment might have resulted from very low molecular weight resins forming a soluble fraction of the polychelate; also, some of the soluble resin fractions might have a very low metal content. In the absence of well-defined absorptions in the visible region, no attempt was made to interpret the results as regards the ligand environment of the metal ions in the polymer matrix.

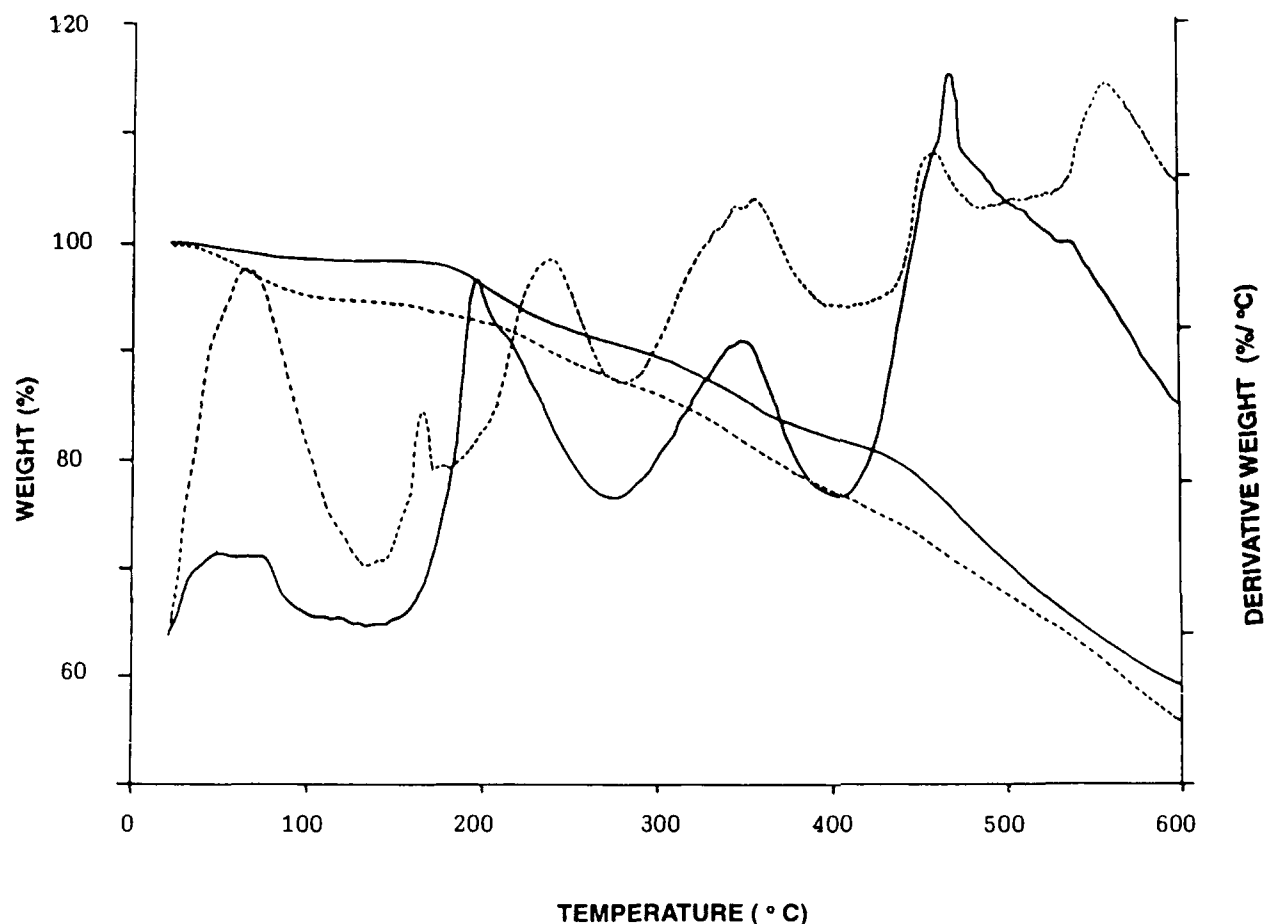


Figure 4 Thermogram of (—) *o*-HBED-HCHO and (-----) *o*-HBED-HCHO-Cu(II); heating rate 10°C/min in N₂ atmosphere.

¹H-NMR Spectra

The ¹H-NMR spectra for *o*-HB-HCHO, *o*-HBED-HCHO, *o*-PD-HCHO, and *o*-HB-*o*-PD-HCHO are shown in Figure 2. The 90 MHz spectra of *o*-HB-HCHO presented a complex pattern between 7.2 and 7.6 ppm arising out of ring proton coupling. The —CHO proton appeared at 10.4 ppm as a sharp singlet. The 400 MHz FT ¹H-NMR spectrum of this resin showed the methylene proton at 3.9 ppm (Ar—CH₂—Ar) along with the methylene group connected to hydrogen-bonded OH (Ar—CH₂—OH) registered at 4.5 ppm occurring as terminal functions in the resins.¹⁵ In addition, the aldehydic proton peak was seen to split into a doublet between 9.8 and 10.4 ppm. The resins of the corresponding ethylene diamine Schiff base, *o*-HBED-HCHO, registered aldimine proton at 9.9 to 10.2 ppm. Intense peaks at 3.92 and 4.6 ppm were linked to methylene group bridging —CH₂— or terminal methylol functions. The resin *o*-PD-HCHO showed a complex pattern for the ring protons between 6 and 8 ppm. The methylene protons were registered at δ

3.65 and 4.18 as bridging and end methylol groups, respectively. The corresponding salicylaldehyde Schiff base resin *o*-HB-*o*-PD-HCHO did not register the aldimine proton. The polychelates of the resins showed distinctive features to be completely masked with peak broadening resulting in any worthwhile assignments possible. The features could result from poor solubility of the polychelates in DMSO.

Reaction Scheme

Reactivity of the resins of Schiff bases with metal ions through coordination of the axomethine nitrogen and phenolic oxygen would be governed by the molecular geometry, i.e., rigidity or flexibility of the backbone and nucleophilicity of the atoms involved in coordination. Oriol and colleagues⁶ from EPR studies of Cu(II) polychelates derived from Schiff bases, observed interchain (repeating units as bidentate ligands) or intrachain (repeating units as tetradentate ligands) coordination. While the ethylene diamine-based Schiff base polymers were em-

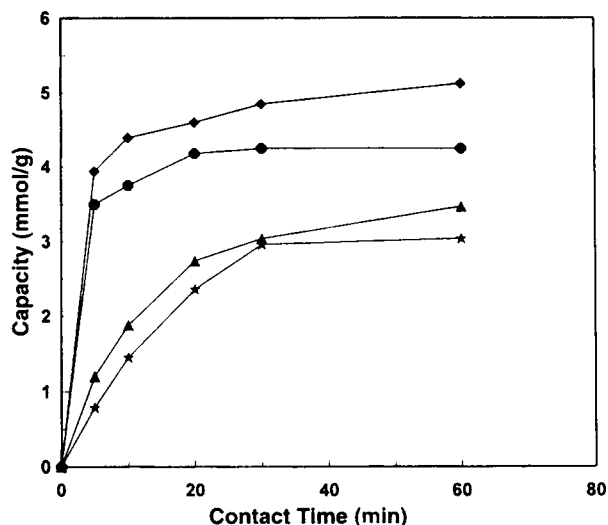


Figure 5 Effect of contact time on capacity of the resins: Size 100 mesh, $[M(II)]-0.08M$; temp. $30^{\circ}C$; natural pH; capacity of *o*-HB-*o*-PD-HCHO for (◆) Cu(II) and (▲) Ni(II); capacity of *o*-HBED-HCHO for (●) Cu(II) and (★) Ni(II).

employing tetradentate repeating units, the *p*-phenylene diamine-based Schiff bases resulted in interchain coordination. Elemental analyses (N%) of the polychelates conform to intrachain structure (I) (Fig. 3) rather than to interchain structure (II), contrary to what was observed by Oriel and co-workers for the Schiff base derived from *p*-phenylene diamine, the relative position of the amino groups being a determining factor. The Schiff base from *o*-phenylene diamine provides a more stereochemically favorable tetradentate coordination in the intrachain arrangement. Identical observations were obtained with a Schiff base derived from *o*-phenylene diamine, the N and O atoms exhibiting intramolecular coordination to Co(II).¹⁶

Thermogravimetric Analysis

The TGA data are furnished in Table I, and Figure 4 shows the general nature of the thermograms of the resins and the polychelates. The relative thermal stability of the materials was assessed by comparing the weight loss in the temperature range $130-600^{\circ}C$. The first stage of decomposition was the desorption of water molecules. Thus within $130^{\circ}C$ the resins and the polychelates lost about 6% of weight. Beyond $130^{\circ}C$ the materials were observed to lose weight passing through several decomposition stages. In the case of *o*-HBED-HCHO resin, the first stage of decomposition started at $145^{\circ}C$, whereas for the Cu(II) polychelate it was $185^{\circ}C$, the temperatures of maximum rate of weight loss being 195 and $240^{\circ}C$, respectively. In the case of *o*-

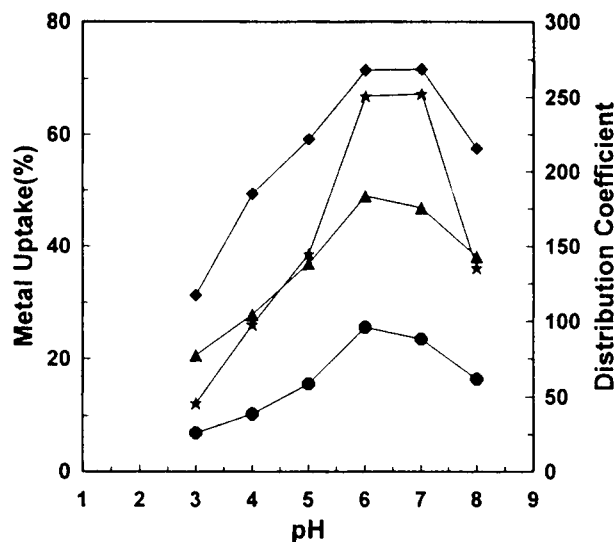


Figure 6 Effect of pH on the distribution coefficient K_D^* ; resin: *o*-HB-*o*-PD-HCHO; size: 100 mesh, $[M(II)]-0.08M$; contact time: 10 min; temp. $30^{\circ}C$; (★) Cu(II), (●) Ni(II), at metal uptake (%) (◆) Cu(II), (▲) Ni(II).

$$*K_D = \frac{\text{mmol of metal on the sorbent}}{\text{mmol of metal in solution}}$$

$$\times \frac{\text{Volume of solution (mL/g)}}{\text{gm of resin}} \text{ (mL/g)}$$

HB-*o*-PD-HCHO, the major decomposition stage started at $399^{\circ}C$ whereas the polychelate began decomposing at $321^{\circ}C$.

The relative thermal stability was evaluated comparing the activation energy computed by regression analysis of the TGA data and by employing different kinetic models (Coats & Redfern, Van Krevelen, and

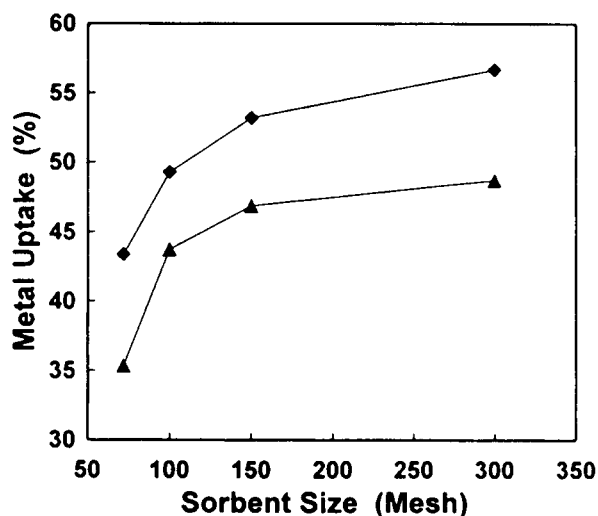


Figure 7 Effect sorbent size: Resin- 100 mg; contact time - 5 min, $[Cu(II)]-0.08M$; pH- 4.5; temp. - $30^{\circ}C$ (◆) *o*-HB-*o*-PD-HCHO, (▲) *o*-HBED-HCHO.

Broido).¹⁷⁻¹⁹ The computed activation energy data for the different models indicated the resins to be more stable than the polychelates. The resins presumably became more crosslinked on heating, whereas the structural arrangement of the polychelates with the coordinating sites already linked to the metal ions in an intrachain arrangement did not allow crosslinking. Also, the polychelates contained adsorbed water and water coordinated to the metal ions which were lost, resulting in higher weight loss in the initial stages of decomposition.

Metal Uptake Behavior of the Resins

The resins *o*-HBED-HCHO and *o*-HB-*o*-PD-HCHO were treated with Cu(II) and Ni(II) salt solutions in aqueous media. The percentage of metal uptake under noncompetitive conditions at natural pH of the solution was followed spectrophotometrically. The effects of contact time, particle size of the sorbents, and pH on the adsorption characteristics were studied using the batch method. The saturation time for metal uptake of the resins obtained by plotting the percentage of metal uptake with time keeping the initial metal concentration constant (Fig. 5) was found to be 10 and 30 min for Cu(II) and Ni(II), respectively, at the natural pH of the solutions.

The variation of contact time showed a maximum capacity of 3.94 mmol/g for *o*-HB-*o*-PD-HCHO resin toward Cu(II) at 10 min and 3.04 mol/g toward Ni(II) at 30 min for resins of 100 mesh, the capacity slightly increasing with time. Comparatively, the *o*-HBED-HCHO resin showed a lower capacity toward the metal ions under similar experimental conditions.

The capacity of the resins was significantly affected with the variation of pH; the percentage of the metal uptake and the distribution coefficient K_d (Fig. 6) went on increasing to about pH 6 and thereafter a decreasing trend was noticed. Decreasing pH not only affected the capacity of the resins and K_d , but the equilibrium time also increased. The size of the resin particles also affected the capacity of the resins (Fig. 7). For Cu(II) the capacity increased from 3.47 mmol/g at 5 min contact time to 4.53 mmol/g for the resin *o*-HB-*o*-PD-HCHO, the sorbent particle size varying between 72 and 300 mesh.

The instrument facility provided by the Regional Sophisticated Instrumentation Centres at Central Drug Research Institute, Lucknow, and the Indian Institute of Technology, Mumbai, is gratefully acknowledged.

REFERENCES

1. E. Blasius and B. Brozio, in *Chelates in Analytical Chemistry*, Vol. 1, H. A. Flaschaka and A. J. Barnard, Jr., Eds., Marcel Dekker, New York, 1967, p. 49.
2. C. Kantipuly, S. Katragadda, A. Chow, and H. D. Gesser, *Talanta*, **37**, 491 (1990).
3. G. Schmuckler, *Talanta*, **12**, 281 (1965).
4. J. P. Riley and D. Taylor, *Anal. Chim. Acta*, **40**, 479 (1968).
5. G. Schmuckler, *Talanta*, **10**, 745 (1963).
6. L. Oriel, P. J. Alonso, J. I. Martineoz, M. Pinol, and J. L. Serrano, *Macromolecules*, **27**, 1869 (1994).
7. H. Chen, J. A. Cronin, and R. D. Archer, *Macromolecules*, **27**, 2174 (1994).
8. M. Feng, L. Van Der Does, and A. Bantjes, *J. Appl. Polym. Sci.*, **52**, 21 (1994).
9. R. T. Stamenova, C. B. Tsvetanov, K. G. Vassilev, S. K. Tanielyan, and S. K. Ivanov, *J. Appl. Polym. Sci.*, **42**, 807 (1991).
10. A. Lezzi, S. Cobianco, and A. Rogger, *J. Polym. Sci., Polym. Chem. Ed.*, **32**, 1817 (1994).
11. A. Lezzi and S. Cobianco, *J. Appl. Polym. Sci.*, **54**, 889 (1994).
12. H. Egawa, K. Yamabe, and A. Jyo, *J. Appl. Polym. Sci.*, **52**, 1153 (1994).
13. J. Bassett, R. C. Denney, G. H. Jeffery, and J. Mendham, *Vogel's Textbook of Quantitative Analysis*, Fourth ed., Longman, England, 1978, pp. 156 and 748.
14. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, 1962, pp. 94 and 156.
15. R. M. Silverstein, G. C. Bassler, and T. C. Morrill, *Spectrometric Identification of Organic Compounds*, Fourth ed., John Wiley & Sons, New York, 1980, p. 224.
16. F. A. Cotton and G. Wilkinson, *Advanced Inorganic Chemistry*, Fifth Ed., John Wiley & Sons, New York, 1988, p. 638.
17. A. W. Coats and J. P. Redfern, *J. Polym. Sci., Polym. Lett. Ed.*, **3**, 921 (1965).
18. D. W. Van Krevelen, C. Van Heerden, and F. J. Humfjens, *Fuel*, **30**, 253 (1951).
19. A. Broido, *J. Polym. Sci., Polym. Lett. Ed.*, **A-2**, **7**, 1761 (1969).

Received September 11, 1995

Accepted April 22, 1996