

This article was downloaded by:

On: 24 January 2011

Access details: *Access Details: Free Access*

Publisher *Taylor & Francis*

Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Macromolecular Science, Part A

Publication details, including instructions for authors and subscription information:

<http://www.informaworld.com/smpp/title~content=t713597274>

Ion-Exchange Study of Poly[(2,4-dihydroxy benzophenone) Propylene] Resin and its Polychelates: Synthesis, Characterization

J. D. Joshi^a; N. B. Patel^b; S. D. Patel^b

^a Department of Chemistry, Sardar Patel University, Gujarat, India ^b J & J Science College Nadiad, Gujarat, India

To cite this Article Joshi, J. D. , Patel, N. B. and Patel, S. D.(2006) 'Ion-Exchange Study of Poly[(2,4-dihydroxy benzophenone) Propylene] Resin and its Polychelates: Synthesis, Characterization', *Journal of Macromolecular Science, Part A*, 43: 8, 1167 – 1178

To link to this Article: DOI: 10.1080/10601320600735173

URL: <http://dx.doi.org/10.1080/10601320600735173>

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: <http://www.informaworld.com/terms-and-conditions-of-access.pdf>

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

Ion-Exchange Study of Poly[(2,4-dihydroxy benzophenone) Propylene] Resin and its Polychelates: Synthesis, Characterization

J. D. JOSHI,¹ N. B. PATEL,² AND S. D. PATEL²

¹Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, Gujarat, India

²J & J Science College Nadiad, Gujarat, India

The polymeric ligand poly[(2,4-dihydroxy benzophenone) propylene] H(DHBP-PD) forms 1:2 metal-ligand complexes with Cu(II), Ni(II), Co(II) and Zn(II). The polymeric ligand and its polychelates were characterized on the basis of elemental analyses, magnetic susceptibilities, IR-spectroscopy, UV-visible spectra, NMR, thermogravimetric analyses. The molecular weight of resin was determined using number average molecular weight (\bar{M}_n) by Vapor Pressure Osmometry (VPO) method. The stereochemistry, in case of the Cu(II) polychelate, is square-planar, tetrahedral for Zn(II) and octahedral for Ni(II) and Co(II). The stereochemistry in each chelate is proposed on the basis of magnetic susceptibilities and electronic spectra. IR spectra shows that the bidentate ligand coordinates through the oxygen atom of the carbonyl group and the oxygen atom of the phenolic group with replacement of hydrogen by metal ions. All the chelates are paramagnetic in nature except the Zn(II) chelate which is diamagnetic. The ion-exchange study of the prepared resin was checked by batch equilibration method at varying electrolyte concentration, pH and time with selected metal ions such as Cu(II), Ni(II), Fe(III) and UO_2^{2+} (VI).

Keywords resin, polychelates, transition metals, thermal study, ion exchange

Introduction

Chelating polymers have attracted more interest, due to their applications in waste water treatment, metal recovery from diluted solutions, as protective coatings on metal surfaces or as a priming layer, coating on paper, fiber and fabrics, selective binding of enzymes (1, 2). The study of polymeric ligands and their metal complexes is very useful in metal separation, as a catalyst and in bio-inorganic chemistry (3, 4). Several coordination polymers have been prepared from aromatic and aliphatic polymers containing pendant functional groups which act as a chelating group in binding polyvalent metal ions (5). The reaction of trimethylolpropane, triacrylates with benzophenone as an initiator (6) in UV acrylic coating displays excellent curing speed. In the present communication, an attempt has been made to synthesize the resin poly[(2,4-dihydroxy benzophenone)

Received January 2005; Accepted February 2006.

Address correspondence to J. D. Joshi, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar 388 120, Gujarat, India. E-mail: jdjoshi314@gmail.com

propylene] to study its ion-exchange property. Also, its polychelates with Cu(II), Ni(II), Co(II) and Zn(II) metals were synthesized and characterized by various spectral methods. The synthesized resin shows good ion-exchange capacity towards the studied metal ions.

Experimental

Synthesis of Resin

All chemicals used were of AR grade. To a well-stirred and ice-cooled mixture of 2,4-dihydroxy benzophenone (DHBP, Aldrich) (8.56 gm, 0.04 mole) and 1,3-propane diol (Aldrich, PD) (2.88 ml, 0.04 mole), polyphosphoric acid (Lancaster) (PPA) (20 gm) was added slowly with stirring as a catalyst. The reaction mixture was left at room temperature for half an hour and heated on an oil bath at 120°C for 9 h. The reaction mixture was then cooled, poured on crushed ice, and left overnight. A reddish brown solid was separated out. It was collected by filtration and washed with cold water and methanol to remove unreacted acid and monomer. The polymer was reddish brown in color, m.p. >270°C, yield 3.45 gm (38.40%). The reaction is shown in Figure 1.

Synthesis of Polychelates

All polychelates were synthesized by following the similar method. The Cu(II), Ni(II), Co(II) and Zn(II) acetates of (Merck), AR grade, were used in the preparation of the polychelates.

The dried resin (0.01 mole) was dissolved in DMSO (50 mL). The metal acetate (0.005 mole) was also dissolved in DMSO (25 mL). The hot and clear solution of the metal acetate was added with constant stirring to the hot and clear solution of the ligand. A reddish brown colored product separated out immediately. The suspension was digested on a water bath at 90°C for 2 h and then filtered. The solid was washed with hot DMSO to remove unreacted metal acetate. Finally, the product was washed with acetone and dried at 60°C for 24 h. The yield of each polychelate was between 66 and 77%.

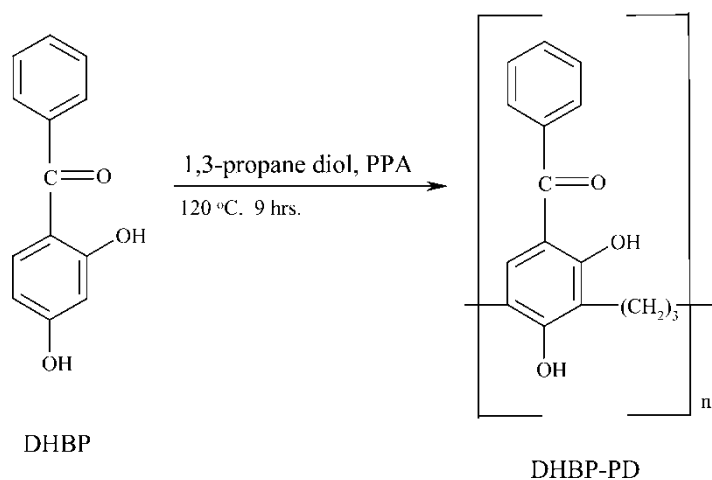


Figure 1. Reaction for the preparation of resin.

Analytical Procedures

The carbon and hydrogen were analyzed with a Coleman C, H, N analyzer (Table 1). The metal content was determined with standard Na₂EDTA after decomposing the polychelates with a mixture of concentrated hydrochloric acid, sulfuric acid and perchloric acid in a 5:2:3 mL ratio, respectively. Magnetic susceptibilities were measured by the Gouy method at 25°C. The IR spectra of the samples in KBr pellets were recorded on a model 938 Perkin-Elmer Spectrophotometer. Thermal measurements were performed using a Du Pont thermal analyzer at 10°C min⁻¹ heating rate. ¹H-NMR spectra were determined in DMSO-d₆ with FT-NMR spectrophotometer using TMS as an internal reference. The Number Average Molecular Weight (\bar{M}_n) of polymeric ligand (resin) sample was measured with a Knauer Germany (VPO) using DMF as solvent at 90°C and polystyrene (PS) as a calibrant.

Results and Discussion

Infrared Spectra

The broad band appearing in the range 3350–3600 cm⁻¹ is due to -O-H stretching. The -O-H group originates from the phenolic hydroxyl group and water absorbed by resins. The major contribution to this particular band comes from the absorbed water. The band due to -O-H stretching is less broad in the IR spectra of the polymer, which suggests the absence of absorbed water. Hence, this band would have been largely due to the presence of hydroxyl groups. The strong band of -C=O around 1630–1640 cm⁻¹ and a weak band of -O-H at 2720–2750 cm⁻¹ indicate an intramolecular hydrogen bond. The band in the range of 1235 ± 15 cm⁻¹ is attributed to -O-H in plane bending. The bands observed around the 1380–1510 cm⁻¹ region are attributed to -C=C- stretching (aromatic) vibrations. The band in the 2925 cm⁻¹ region is attributed to the -CH₂- group. The band in the 1000–1190 cm⁻¹ region is attributed to -C-H in plane bending. In the spectra of each of the resins, a band observed around 900 ± 10 cm⁻¹ is due to the isolated hydrogen on the phenolic moiety repeating unit of the polymer chain. The band around 900 cm⁻¹ may be attributed to the 1,2,3,4,5-penta substituted phenyl ring, having only one isolated H atom. The medium intensity band at 855 ± 10 cm⁻¹ shows the 1,2,4,5-tetra substituted phenyl ring, having two H is on the phenyl ring. The strong bands observed around the 1250 ± 15 cm⁻¹ region is attributed to the Ph-O-CH₃ ether linkage. The presence of a band around 890 ± 10 cm⁻¹ suggests that the linkage in the resin chain occurs through 3 and 5 positions on the monomer. The important IR frequencies of the polymeric ligand and its polychelates are shown in Table 2. The -C=O stretching frequency in the resin is observed around 1630–1640 cm⁻¹, appearing at a lower frequency of 20 to 30 cm⁻¹ in all of the polychelates, which suggests -C=O → M coordination (7). In the polychelates the band observed around 460 cm⁻¹ indicates the M-O bond. It suggests that phenolic and carbonyl groups are involved in bond formation with metal ion.

Vapor Pressure Osmometry

The number average molecular weight (\bar{M}_n) of the polymeric ligand (resin) sample was estimated by Vapor Pressure Osmometry (8) (Table 3). The dilute solutions, 2.21, 4.42, 6.63 and 8.84 g.kg⁻¹ of polymer samples were prepared in DMF to determine \bar{M}_n .

Table 1
Analytical data and some physical properties of the polymeric ligand and its polychelates

| Compound | Color | Formula weight of repeating unit | Analysis (%) found (calculated) | | | μ_{eff} (B.M.) | D.P. ^b °C |
|--|---------------|----------------------------------|------------------------------------|------------------|----------------|---------------------------|----------------------|
| | | | M | C | H | | |
| (DHBP-PD) _n [C ₁₆ H ₁₄ O ₃] | Reddish brown | 254 | — | 75.59 (75.69) | 5.51 (5.44) | — | >280 |
| [Cu(DHBP-PD) ₂] _n [C ₃₂ H ₂₆ O ₆ Cu] _n | Reddish brown | 570 | 11.14 (11.02) | 66.36 (66.48) | 4.56 (4.52) | 1.91 | >300 |
| [Ni(DHBP-PD) ₂ (H ₂ O) ₂] _n [C ₃₂ H ₃₀ O ₈ Ni] _n | Reddish brown | 601 | 9.76 (9.88) | 63.38 (63.31) | 4.99 (5.08) | 2.88 | >350 |
| [Co(DHBP-PD) ₂ (H ₂ O) ₂] _n [C ₃₂ H ₃₀ O ₈ Co] _n | Reddish brown | 601 | 9.81 (9.99) | 63.89 (63.72) | 4.99 (4.82) | 4.53 | >350 |
| [Zn(DHBP-PD) ₂] _n [C ₃₂ H ₂₆ O ₆ Ni] _n | Reddish brown | 571 | 11.47 (11.41) | 67.25 (67.21) | 4.55 (4.58) | Diamagnetic | >350 |

DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].
b = decomposition point

Table 2
Infrared spectra of the polymeric ligand and its polychelates (cm^{-1})^a

| Compound | ν (O-H) | ν (-CH ₂) bridge | ν (C=O) chelate | ν (C=C) aromatic | ν (Ar-OR) ether linkage | Penta substituted- Ph ring | ν (M-OH) |
|--|-------------|-------------------------------------|------------------------|-------------------------|--------------------------------|-------------------------------|--------------|
| (DHBP-PD) _n | 3350–3600 b | 2925 w | 1640 s | 1510 m | 1250 m | 900 m | — |
| [Cu(DHBP-PD) ₂] _n | 3350–3600 b | 2930 w | 1635 s | 1495 m | 1265 m | 885 m | 460 w |
| [Ni(DHBP-PD) ₂ (H ₂ O) ₂] _n | 3350–3600 b | 2935 w | 1630 s | 1490 m | 1255 m | 910 m | 460 w |
| [Co(DHBP-PD) ₂ (H ₂ O) ₂] _n | 3350–3600 b | 2920 w | 1640 s | 1500 m | 1265 m | 915 m | 465 w |
| [Zn(DHBP-PD) ₂] _n | 3350–3600 b | 2925 w | 1630 s | 1500 m | 1250 m | 905 m | 465 w |

^ab = broad, m = medium, s = strong, w = weak; DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].

Table 3
Molecular weight determination of resin by vapor pressure osmometry method

| Resin | Concentration (g kg ⁻¹) | Milli volts | Slope of plot | $\bar{M}_n = K/\text{slope}$ (g mol ⁻¹) |
|------------------------|--|----------------|------------------|--|
| (DHBP-PD) _n | 2.21 | 20 | 10.14 | 1134 |
| | 4.42 | 43 | | |
| | 6.63 | 67 | | |
| | 8.84 | 81 | | |

Polystyrene $K = 1.15 \times 10^4$; DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].

The VPO experiment was carried out for each concentration and the corresponding bridge output reading in millivolts was noted.

The plot of (millivolts) vs (concentration) was drawn. With the help of the slope and the VPO constant K , the \bar{M}_n value of the polymer was calculated and found, $\bar{M}_n = 1134 \text{ g mole}^{-1}$.

Thermogravimetric Analyses

Thermogravimetric analyses (TGA) data of the resin and polychelates are presented in Table 4. This data reveals that, the rate of decomposition of the polychelate is higher than that of the parent resin, indicating that there may be strong intramolecular hydrogen bonding in the polymer. The absence of such hydrogen bonding in the polychelate favors the reduction in thermal stability of polychelates compared to the parent resin (9). It seems that metal ions accelerate the decomposition of the polychelates. The thermal stability of the ligand and metal chelates is in the order: ligand > polychelates. The presence of water molecules considered as water of coordination. According to Nikolaev et al. (10) water eliminated above 150°C may be due to coordination of the metal ion in the case of Ni(II) and Co(II), which is supported by cumulative % weight loss and thermal data presented in Table 5.

Electronic Spectra and Magnetic Measurements

The electronic spectra of Cu(II) complex shows two bands at 17,265 and 23,480 cm⁻¹ with magnetic moment 1.91 B.M. The first band can be assigned to ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transition and second broad band is due to charge transfer from ligand to metal ion, which clearly indicates the square-planer geometry for Cu(II) polychelate. The position of bands at 9,786, 15,843 and 22,356 cm⁻¹ in Ni(II) polychelate indicates the distorted octahedral geometry with magnetic moment 2.88 B.M. (11–13). The three bands are assigned to the transitions ${}^3A_{2g} \rightarrow {}^3T_{2g}$, ${}^3A_{2g} \rightarrow {}^3T_{1g}$, and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P) for Ni(II) polychelate. While Co(II) polychelate shows two bands at 8,794 and 19,897 cm⁻¹, the first band corresponds to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and second band corresponds to ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) with magnetic moment value at 4.53 B.M. indicates the octahedral geometry. The Zn(II) polychelate is diamagnetic as expected and has tetrahedral geometry. From the above study, the proposed geometry of polychelates is as shown in Figure 2.

Table 4
Cumulative weight loss data of the polymeric ligand and its polychelates at various temperatures (°C)

| Compound | 100 | 150 | 200 | 250 | 300 | 350 | 400 | 450 | 500 | 550 | 600 |
|--|------|------|------|-------|-------|-------|-------|-------|-------|-------|-------|
| (DHBP-PD) _n | — | — | — | 0.98 | 3.12 | 12.15 | 20.71 | 33.22 | 51.77 | 70.15 | 79.51 |
| [Cu(DHBP-PD) ₂] _n | — | — | 6.09 | 20.24 | 34.21 | 44.68 | 54.71 | 65.61 | 72.71 | 75.19 | 74.51 |
| [Ni(DHBP-PD) ₂ (H ₂ O) ₂] _n | 4.83 | 4.99 | 9.80 | 12.34 | 25.02 | 36.58 | 48.01 | 60.03 | 73.11 | 75.61 | 75.98 |
| [Co(DHBP-PD) ₂ (H ₂ O) ₂] _n | 4.58 | 4.60 | 7.80 | 8.42 | 19.31 | 30.41 | 42.89 | 56.04 | 68.89 | 70.71 | 70.76 |
| [Zn(DHBP-PD) ₂] _n | — | — | 1.31 | 5.12 | 13.94 | 21.36 | 31.36 | 40.56 | 51.82 | 63.22 | 63.22 |

DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].

Table 5
Water content at 25°C and cumulative weight loss data of the polychelates
at 100, 150 and 200°C

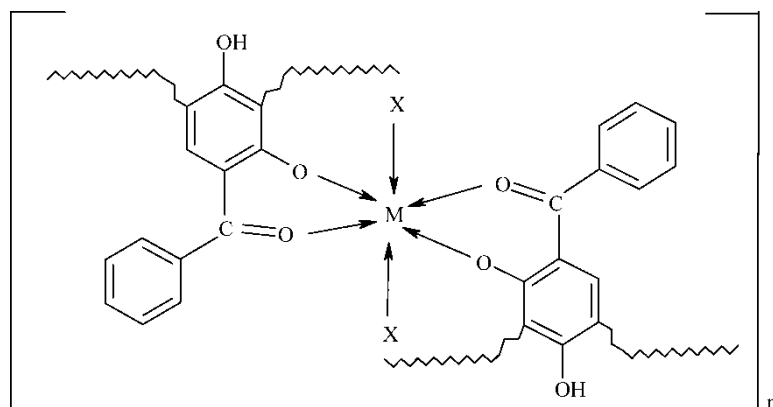
| Compound | Found | | | | | | | |
|--|--------------------------|------|-------|------|-------|------|-------|------|
| | H ₂ O at 25°C | | 100°C | | 150°C | | 200°C | |
| | (g) | (%) | (g) | (%) | (g) | (%) | (g) | (%) |
| [Ni(DHBP-PD) ₂ (H ₂ O) ₂] _n | 36.00 | 5.07 | 34.29 | 4.83 | 35.42 | 4.99 | 69.58 | 9.80 |
| [Co(DHBP-PD) ₂ (H ₂ O) ₂] _n | 36.00 | 5.04 | 32.70 | 4.58 | 32.34 | 4.60 | 55.69 | 7.80 |

DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].

¹H-NMR Spectra

The ¹H-NMR spectrum of 2,4-dihydroxy benzophenone (DHBP), poly [2,4-dihydroxy benzophenone] H(DHBP-PD) and polychelates (M-DHBP-PD) are presented in Table 6.

DHBP shows signals at $\delta = 12.3$ and $6.8-7.8$ ppm are due to -OH groups (*ortho* and *para*) to (Ar-C=O) and aromatic ring protons, respectively (14). H(DHBP-PD) shows signals at $\delta = 12.2$ and $6.85-8.7$ ppm are due to -OH groups (*ortho* and *para*) to (Ar-C=O) and aromatic ring protons, respectively. The broad signal at $\delta = 1.2-2.5$ ppm appears, due to the presence of (Ar-C=O-Ar-CH₂-CH₂-CH₂) protons. In all the polychelates, the signal of the -OH group completely disappeared, indicating that the bond formation takes place through the -OH *ortho* to (Ar-C=O). Also, aromatic protons were shifted downfield by 0.15–1.30 ppm in the NMR spectra of the polychelates due to the deshielding effect of the metal ion on the ligand proton.



Where, M = Cu(II), Ni(II), Co(II) and Zn(II).

X = H₂O for Ni(II) and Co(II).

Figure 2. Proposed geometry of the polymeric chelate.

Table 6
¹H-NMR data of the polymeric ligand and its polychelates (δ , ppm)

| Ligand/polychelates | δ (ppm) | | |
|--|----------------|------------------|---------------------------------|
| | -OH | Aromatic protons | (CH ₂) ₃ |
| DHBP-PD | 12.3 | 6.8–7.8 | — |
| (DHBP-PD) _n | 12.2 | 6.85–8.7 | 1.2–2.5 |
| [Cu(DHBP-PD) ₂] _n | 12.1 | 6.85–8.7 | 1.2–2.5 |
| [Ni(DHBP-PD) ₂ (H ₂ O) ₂] _n | — | 6.95–8.6 | 1.2–2.5 |
| [Co(DHBP-PD) ₂ (H ₂ O) ₂] _n | — | 6.95–8.6 | 1.2–2.5 |
| [Zn(DHBP-PD) ₂] _n | — | 6.95–8.6 | 1.2–2.5 |

DHBP-PD = poly[(2,4-dihydroxy benzophenone) propylene].

Ion-Exchange Study

The purified resin sample DHBP-PD was finally powdered to pass a 300 mesh screen and used in all experiments for ion-exchange study.

The batch equilibration method was used. The details of the procedure for selectivity of the Cu(II), Ni(II), Fe(III) and UO₂²⁺(VI) metal ions by the resin, is similar as reported earlier (15).

The selectivity of resin DHBP-PD towards Cu(II), Ni(II), Fe(III) and UO₂²⁺(VI) metal ions, is to study the influence of various factors such as, influence of an electrolyte on uptake of metal ion, effect of pH of the medium on metal binding capacity, evaluation of the rate of metal uptake and evaluation of distribution ratio (K_D) of metal ions over the wide range of pH. The results are shown in the Tables 7–10.

Influence of an Electrolyte on Uptake of Metal Ion

The influence of Cl⁻, NO₃⁻ and SO₄²⁻ at various concentrations on the equilibrium state of the metal-resin interaction has been studied. The results are presented in Table 7. It reveals that the amount of metal ion taken up by the resin is increasing with an increase in concentration of NO₃⁻ and Cl⁻ and decreasing with an increase in concentration of SO₄²⁻. This may be due to the sulphate form rather strong chelates with metal, while nitrate and chloride might form weak chelates. Therefore, the influence of NO₃⁻ and Cl⁻ is less on the position of metal chelates at equilibrium state than does SO₄²⁻.

Effect of pH of the Medium on Metal Binding Capacity

The results of selected metals uptake have been presented in Table 8. The rate of metal ion uptake depends on the nature of metal ion. The study was restricted up to maximum pH = 6, due to hydrolysis of metal ion at higher pH. The formation of metal hydroxide interfere with the ion-exchange process. It is found that the relative amount of metal adsorbed by the resin increases with increasing pH of the medium.

Evaluation of the Rate of Metal Uptake

To determine the time required to reach the state of equilibrium under given experimental conditions, a series of experiments have been carried out, in which the metal taken up by

Table 7
Effect of electrolyte concentration on metal ion adsorption capacity of
DHBP-PD resin

| Metal ion | Electrolyte concentration (Mol. lit ⁻¹) | Metal ion uptake (meq g ⁻¹) in presence of electrolyte | | |
|-------------------------------|---|---|-------------------|---------------------------------|
| | | NaCl | NaNO ₃ | Na ₂ SO ₄ |
| Cu ²⁺ | 0.05 | 0.26 | 0.35 | 0.35 |
| | 0.10 | 0.31 | 0.39 | 0.33 |
| | 0.50 | 0.60 | 0.57 | 0.15 |
| | 1.00 | 0.66 | 0.62 | 0.13 |
| Ni ²⁺ | 0.05 | 0.18 | 0.37 | 0.30 |
| | 0.10 | 0.24 | 0.40 | 0.27 |
| | 0.50 | 0.45 | 0.56 | 0.12 |
| | 1.00 | 0.50 | 0.59 | 0.09 |
| Fe ³⁺ | 0.05 | 0.23 | 0.35 | 0.37 |
| | 0.10 | 0.28 | 0.38 | 0.33 |
| | 0.50 | 0.46 | 0.53 | 0.21 |
| | 1.00 | 0.53 | 0.55 | 0.19 |
| UO ₂ ²⁺ | 0.05 | 0.52 | 0.38 | 0.19 |
| | 0.10 | 0.59 | 0.45 | 0.17 |
| | 0.50 | 0.73 | 0.76 | 0.09 |
| | 1.00 | 0.77 | 0.84 | 0.07 |

Resin, DHBP-PD = 50 mgs; Mt(NO₃)₂ = 2 mL, 0.1 M; Volume of electrolyte solution, 40 mL; Time, 24 h; Temperature = 30°C; pH of the medium, 4.5 for Cu²⁺, Ni²⁺, 4.0 for UO₂²⁺ and 2.5 for Fe³⁺.

the chelating resin was estimated from time to time. It is assumed that at 25°C and under given conditions, the state of equilibrium is established in 24 h. The rate of metal uptake is expressed as percentage of the attainment at state of equilibrium (Table 9). If “X” mg of metal ions were adsorbed, after 1 h and “Y” mg of metal ions were adsorbed at

Table 8
Effect of pH of the medium on metal ion binding capacity with
DHBP-PD resin

| Metal ion | Metal ion uptake (meq g ⁻¹) | | | | |
|-------------------------------|---|------|------|------|------|
| | pH of the medium | | | | |
| | 3.0 | 3.5 | 4.0 | 4.5 | 5.0 |
| Cu ²⁺ | 0.51 | 0.54 | 0.62 | 0.64 | 0.70 |
| Ni ²⁺ | 0.52 | 0.57 | 0.59 | 0.66 | 0.71 |
| Fe ³⁺ | 0.43 | 0.49 | 0.55 | 0.68 | 0.76 |
| UO ₂ ²⁺ | 0.70 | 0.76 | 0.84 | 0.92 | 1.01 |

Resin, DHBP-PD = 50 mgs; M (NO₃)₂ = 2 mL, 0.1 M; Volume of electrolyte solution, 40 mL; Time, 24 h; Temperature = 30°C.

Table 9
Rate of metal ion uptake by resins as function of time

| Time in hours | Metal ion uptake (meq.g ⁻¹) | | | |
|---------------|---|------------------|------------------|-------------------------------|
| | pH of the medium (3.0–5.0) | | | |
| | Cu ²⁺ | Ni ²⁺ | Fe ³⁺ | UO ₂ ²⁺ |
| 1.0 | 37.25 | 26.79 | 48.93 | 53.21 |
| 2.0 | 48.13 | 34.75 | 59.08 | 64.06 |
| 3.0 | 60.28 | 46.19 | 71.42 | 76.01 |
| 4.0 | 71.86 | 58.21 | 80.39 | 85.71 |
| 5.0 | 80.03 | 71.92 | 88.90 | 93.29 |
| 6.0 | 87.41 | 79.93 | 94.26 | — |
| 7.0 | 93.28 | 88.23 | — | — |

Resin, DHBP-PD = 50 mgs; M (NO₃)₂ = 2 mL, 0.1 M; Volume of electrolyte solution, 40 mL; Time, 24 h; Temperature = 30°C. Assuming 100% equilibrium is established after 24 h.

equilibrium, i.e., after 24 h, $X \times 100/Y$ would be the measure of percentage of equilibrium attained after one hour. It may be noted that the rate of Cu(II) is more during the first 2 h and, after 2 h, it becomes slow, while for other metal ions, adsorption of the respective metal ions become rapid almost after 3 h and a state of equilibrium is attained after 24 h for all metal ions.

Evaluation of Distribution Ratio (K_D) of Metal Ions Over the Wide Range of pH

The distribution of each of the metal ions [Cu(II), Ni(II), Fe(III) and UO₂²⁺(VI)] between the resin phase (solid) and aqueous phase (liquid) is estimated at the appropriate pH, using a 1.0 M NaNO₃ solution. The experiments were carried out from 3 to 5 pH. The amount of the metal ion which remained in the aqueous phase was estimated. The original metal ion concentration is known, and the metal ion adsorbed by the resin was estimated. The results

Table 10
Distribution ratio of ions adsorbed by the resin (DHBP-PD) and remain in the solution at equilibrium

| Metal ions | Distribution ratio (K_D) | | | | |
|-------------------------------|------------------------------|--------|--------|--------|--------|
| | pH of the medium | | | | |
| | 1.0 | 2.0 | 3.0 | 4.0 | 5.0 |
| Cu ²⁺ | — | — | 170.87 | 231.65 | 398.54 |
| Ni ²⁺ | — | — | 90.12 | 187.33 | 310.68 |
| Fe ³⁺ | 22.34 | 214.84 | — | — | — |
| UO ₂ ²⁺ | 64.89 | 300.45 | 489.32 | — | — |

Resin, DHBP-PD = 50 mgs; M (NO₃)₂ = 2 mL, 0.1 M; Volume of electrolyte solution, 40 mL; Time, 24 h; Temperature = 30°C.

were shown in Table 10. The distribution ratio ' K_D ' has been calculated from the following equation.

$$K_D = \frac{\text{Amount of metal adsorbed on resin}}{\text{Amount of metal in solution}} \times \frac{\text{Volume of solution}}{\text{Weight of resin}}$$

The effect of pH on the amount of metal ions distributed between two phases can be explained by the results shown in Table 10. It can be seen that the distribution ratio increases for Cu(II), Ni(II), Fe(III) and UO_2^{2+} (VI) metal ions as the pH of the medium increases. Also the value of distribution ratio for given pH depends upon the nature of the polymeric ligand (resin).

Conclusions

From elemental analyses, IR, thermogravimetric analyses, UV-visible spectra, $^1\text{H-NMR}$ spectra, magnetic properties and Vapor Pressure Osmometry the proposed geometry of the polychelate is as shown in Figure 2. The resin has good binding capacity for the Cu(II) compared to Ni(II), Fe(III) and UO_2^{2+} (VI) at various conditions employed for the ion exchange study. The results revealed that the resin can be used as an ion exchanger.

Acknowledgements

The author thanks the Head, Department of Chemistry, Sardar Patel University, Vallabh Vidyanagar, for providing laboratory facilities.

References

1. Geckeler, K.E. and Rongnong, Z. (1994) *Chem. Abstr.*, 121: 10302f.
2. Purohit, R. and Devi, S. (1992) *Analyst*, 117 (7): 1175.
3. Warshawsky, A. (1998) *Polymeric Ligands in Hydrometallurgy. In Synthesis and Separation Using Functional Polymers*; Wiley: New York, 327.
4. Alelah, A. and Moet, A. (1990) *Functionalized Polymers and Applications*; Chapman Hall: London, 93.
5. Diab, M.A., El-Sonbati, A.Z., and Ghoniem, M.M. (1989) *Acta Polymerica*, 40: 545.
6. Braun, D., Richter, E., Rabie, S.T., and Yassin, A.A. (1999) *Angew. Makromol. Chem.*, 271: 93–100.
7. Yadawe, M.S. and Patil, S.A. (1992) *J. Ind. Chem. Soc.*, 69 (10): 674–675.
8. Silverstein, R.M. and Webster, F.X. (1998) *Spectrometric Identification of Organic Compounds*, 6th Ed.; John Wiley & Sons, Inc.: New York.
9. Eliassi, A. and Modarress, H. (2001) *Euro. Poly. J.*, 37: 1487–1492.
10. Nikolaev, V.A., Logvinenko, L.T., and Myachina, L.T. (1969) *Thermal Analysis*; Academic Press: New York, 779.
11. Patel, A.K., Patel, V.M., and Joshi, J.D. (1999) *Synth. React. Inorg. Met.-Org. Chem.*, 29 (2): 193–203.
12. Joshi, J.D., Sharma, S.S., Patel, J.N., and Vora, J.J. (2003) *Asian. J. Chem.*, 15 (1): 349–352.
13. Kriza, A., Reiss, A., Florea, S., and Carproin, T. (2000) *J. Ind. Chem. Soc.*, 77: 207–208.
14. Sekera, M. (2000) *Synth. React. Inorg. Met.-Org. Chem.*, 30 (2): 191–204.
15. Andrzej, W.T. (1998) *Euro. Poly. J.*, 34 (11): 1657–1662.