

Chelating and ion exchange properties of poly{N-(4-acetyl-3-hydroxyphenyl)maleimide}

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Poly{N-(4-acetyl-3-hydroxyphenyl)maleimide} (PAHPM) and its polychelates with Cu(II), Ni(II), Co(II), dioxouranium(II), Mn(II) and Zn(II) have been prepared and analyzed by elemental analysis, diffuse reflectance spectra, magnetic moments, thermal properties and infrared spectra. The polymer, PAHPM, is found to show selective chelating and ion-exchange properties for certain metal ions.

We have earlier reported the preparation of N-(4-acetyl-3-hydroxyphenyl)maleimide and its homo and co-polymers¹. In continuation of our work on N-phenyl maleimide based cation exchanger, we report herein the ion exchange and complexation properties of the homopolymer.

Experimental

The polymer, poly{N-(4-acetyl-3-hydroxyphenyl)maleimide} (PAHPM), was prepared and characterized as reported earlier¹ by free radical polymerization of the monomer using AIBN as the initiator. $[\bar{M}_n = 4.4 \times 10^3 \text{ g mol}^{-1}$; $[\eta] = 0.11 \text{ dl g}^{-1}$ at 30°C; softening range = 310–320°C].

Preparation of metal chelates

Ni(II) chelate

The polymer solution was prepared by dissolving PAHPM (4.62 g, 0.02 mol) in 150 ml DMF. A solution of nickel(II) nitrate (3.2 g, 0.011 mol) in DMF (70 ml) was added dropwise to the polymer solution with constant stirring. The pH was maintained at 6.5 for total precipitation of the metal chelate. The precipitate was digested on a water bath at 75°C for 3 hr, filtered, washed with hot DMF, distilled water and finally with ethanol and dried at 60°C.

The Cu(II), Co(II), UO₂(II), Zn(II) and Mn(II) polychelates were prepared similarly.

Analysis and physical measurements

The polychelate was first decomposed using a

mixture of conc. H₂SO₄ + conc. HNO₃ + HClO₄ + NaClO₄ (2:15:15:1) and then dissolved in water. The diluted solution was then titrated against EDTA².

The C, H and N elemental analysis was carried out using CHNO-rapid analyser (Heracus, Germany). IR spectra were recorded on a Perkin-Elmer 983 spectrophotometer. Diffuse reflectance spectra were scanned on a Beckman DK-2A ratio recording spectrophotometer. Magnetic susceptibility was determined at room temperature by the Gouy method using HgCo(SCN)₄ as the calibrant.

Ion-exchange properties

An air dried PAHPM sample was ground to 100-mesh size and allowed to swell under the conditions of study before the actual metal sorption experiment by batch equilibrium method³ was carried out.

Ion-exchange experiments were performed to study the effect of type and concentration of an electrolyte in the media on sorption of metal ions, rate of metal ion sorption, distribution of metal ion at different pH values, and, the effect of metal ion concentration on the sorption. In each case the calculations were carried out as discussed earlier⁴.

Results and discussion

The polymer, PAHPM, is soluble in solvents like DMF, THF, DMSO and partially soluble in aq. NaOH. All the poly-chelates studied were intensely coloured solids and the elemental analyses (Table 1) show 1:2 metal to ligand ratio for bivalent metal ions. It was however, not possible to determine the molecular weight of these polychelates as they were insoluble in the common organic solvents. Chelation can take place in two ways: through binding of the chelating groups of the same polymer chain (intra) and through bridging between two chains (inter) (see Fig. 1). If only intra binding takes place, the polychelates may have solubility in some solvents. The insolubility of the polychelates suggests that the binding is predominantly intermolecular.

IR spectra of the polymer and polychelates show a broad band at 3300-3620 cm⁻¹ due to -OH stretching vibration⁵. The strong band at 2720 cm⁻¹ in the polymer due to ν-OH (intramolecular H-bonding) is absent in the case of

Table 1—Elemental analysis and magnetic moment data of polymer and its polychelates

Polymer/ polychelate	Colour	Yield	% Found (Calc.)				μ_{eff} (B.M.)	Mol. wt. of repeating unit (g)
			M	C	H	N		
PAHPM=L	Light pink	83	—	61.21 (62.33)	4.19 (3.93)	5.91 (6.06)	—	231.21
Cu(L) ₂	Light green	88	12.17 (12.09)	53.63 (55.01)	3.10 (3.08)	5.26 (5.34)	1.83	523.96
Ni(L) ₂	Greenish blue	86	10.42 (10.54)	50.75 (51.73)	3.89 (3.98)	4.89 (5.03)	3.42	555.13
Co(L) ₂	Brown	84	11.25 (11.31)	51.72 (51.71)	3.99 (3.98)	5.25 (5.37)	4.93	519.36
UO ₂ (L) ₂	Light brown	89	35.16 (36.26)	39.81 (39.34)	2.45 (2.47)	3.75 (3.64)	diamagnetic	766.49
Zn(L) ₂	Pale yellow	67	12.19 (12.39)	53.84 (54.82)	3.17 (3.07)	5.34 (5.33)	diamagnetic	525.80
Mn(L) ₂	Brown	78	9.78 (9.93)	52.38 (52.09)	4.01 (4.01)	4.99 (5.06)	5.42	551.36

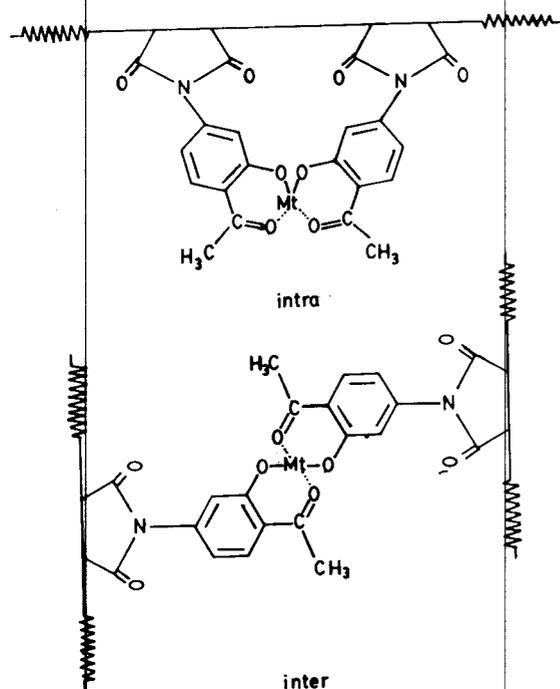


Fig. 1—Tentative structure of the polychelate.

the polychelates. This is indicative of replacement of the hydrogen atom of phenolic group by the metal ion⁶. Further, the strong band due to $\nu_{\text{C=O}}$ is shifted to lower frequency by 10-20 cm^{-1} in polychelates indicating coordination of the metal ion through an oxygen of ketone group⁷. The bands at ~ 450 and 560 cm^{-1} have been observed only in the spectra of polychelates. These can be assigned to O-M and C-O-M vibrational modes respectively⁸.

The diffuse reflectance spectra of the polychelates were studied between 28500 and 7700 cm^{-1} . Cu(II) polychelate exhibits two bands, at ~ 15350 and 24690 cm^{-1} , indicating square planar geometry⁹. The former may be assigned to ${}^2E_{1g} \rightarrow {}^2E_g$ transition and the latter to a symmetry forbidden ligand \rightarrow metal charge transfer band¹⁰. Ni(II) polychelate shows two absorption bands at 9320 and 16528 cm^{-1} due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions, respectively, for octahedral environment around Ni(II)¹¹. In Co(II) polychelate, the broad band around 16975 cm^{-1} is assigned to ${}^4A_2 \rightarrow {}^4T_1(P)$ transition, indicating a tetrahedral geometry^{12,13}. Mn(II) polychelate shows three unresolved bands at 18480, 21500 and $23600\text{-}24300 \text{ cm}^{-1}$, which may be assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}({}^4G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}({}^4G)$ and ${}^6A_{1g} \rightarrow {}^4E_g({}^4A_{1g}({}^4G))$ transitions, respectively, for octahedral environment around Mn(II) ion¹⁴.

Since the spectra of the polychelates of dioxouranium(VI), Zn(II) are not very well resolved, no attempt has been made to analyse them.

Magnetic moment values (Table 1) suggest a square planar configuration for Cu(II)¹⁵, octahedral for Ni(II)¹⁶ and Mn(II)¹⁷, and tetrahedral for Co(II)¹⁸ polychelates. As expected Zn(II) and dioxouranium(VI) polychelates are diamagnetic.

The polymer, PAHPM, is a weak cation exchanger, but because of good chelating properties, binds the cation strongly. In the presence of NaNO_3 as an electrolyte the order of the rate of metal ion uptake is: Fe^{3+} , $\text{Pb}^{2+} > \text{Cu}^{2+}$, $\text{Ni}^{2+} > \text{Zn}^{2+}$, Ca^{2+} , Mg^{2+} . It is observed that Cu^{2+} , Ni^{2+} , Ca^{2+} and Mg^{2+} uptake increases with increasing concentration of NaNO_3 as well

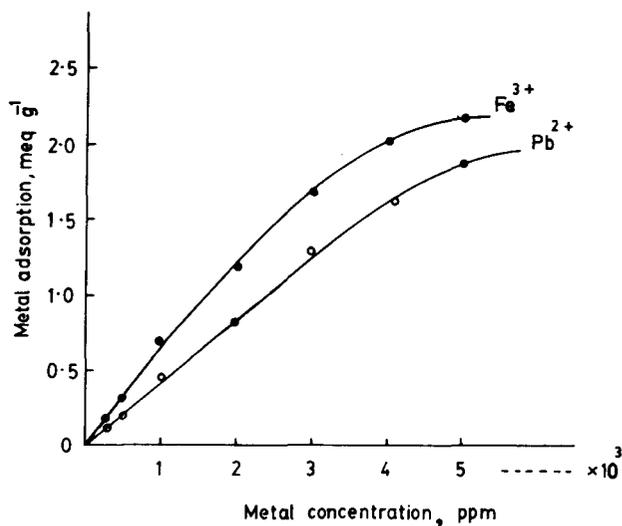


Fig. 2—Effect of metal ion concentration on the adsorption of metal ion by PAHPM.

as NaCl. However adsorption of only Cu^{2+} and Pb^{2+} increases with increase in concentration of Na_2SO_4 .

The pH of the medium has a strong effect on sorption of the metal ions. The amount of metal ion taken up by the resin increases with increase in pH of the medium. Distribution ratio, D , of the metal ions shows very high selectivity for Fe^{3+} , Cu^{2+} and Ni^{2+} over the other metal ions investigated. This is useful in selecting the optimum pH for a preferred uptake of a particular ion from the mixture. For example, separation of Fe^{3+} from a $\text{Fe}^{3+}/\text{Zn}^{2+}$ mixture could be carried out at pH 2.5 and that of Cu^{2+} from $\text{Cu}^{2+}/\text{Zn}^{2+}$ mixture at pH 5.

Figure 2 shows the effect of metal ion concentration on the amount of metal adsorbed. Fe^{3+} is adsorbed to a higher extent than Pb^{2+} at each stage. This further confirms that the ion-exchange

depends on the nature of the metal ion and its stability constant with a particular ligand¹⁹.

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