

Poly(1,3-[2-methoxy-4-hydroxy-5-acetylphenylene]butylene) (HMAP-BG) as a polymeric ligand

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Abstract. Poly(1,3[2-methoxy-4-hydroxy-5-acetylphenylene]butylene) was prepared by Friedel–Craft polycondensation of 2-hydroxy, 4-methoxyacetophenone and 1,4-butane-diol in presence of polyphosphoric acid catalyst. The polymer samples were characterized by IR spectra, TGA and their M_n determined by nonaqueous titration. Viscosity measurements in DMSO showed that solutions exhibited normal behaviour.

Polymers were complexed with Cu(II), Ni(II), Mn(II), Co(II) and Zn(II) and characterized. Chelation and ion exchange properties were also studied by employing the batch equilibrium method.

Keywords. Poly(1,3-[2-methoxy-4-hydroxy-5-acetylphenylene]butylene); polymeric ligand.

1. Introduction

Polymers prepared by condensation of salicylic acid and formaldehyde have been the subject of extensive investigation (DeGeiso *et al* 1962). The ion-exchange properties of polymers prepared by condensation of resacetophenone with formaldehyde (Parmar *et al* 1981) and 2-hydroxy, 4-methoxyacetophenone and formaldehyde also have been reported (Parmar *et al* 1983). The polymer prepared by condensation of 2-hydroxy, 4-methoxyacetophenone and 1,4-butane diol may prove to be a more useful polymeric ligand because of the large separation of the 2-hydroxy, 4-methoxyacetophenone units in two successive repeating units. We report here the polymeric complexes derived from the interaction of the above ligand with Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) metal ions. All polymeric complexes were characterized by physico-chemical methods. Thermal properties of polymeric complexes were compared with the parent copolymer viz. the ligand. The batch equilibration developed by DeGeiso *et al* (1962) and Gregor *et al* (1952) was adopted for the study of the chelating and ion-exchange properties. This involved the study of the influence of the different electrolytes on the metal ion uptake by the polymer sample, the estimation of the time required to reach the state of equilibrium under given experimental conditions, and the measurements of the distribution ratio of different metal ions between the polymer phase and the solution phase over a wide pH range.

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2. Experimental

2.1 Materials

Monomer (2-hydroxy, 4-methoxyacetophenone) was prepared by known methods (Dey 1935) (m.p. 52°C). 1,4-butane diol (Merck) and DMSO were used after distillation. Pyridine (AR grade) was purified by refluxing it over sodium hydroxide pellets and then distilling with careful exclusion of moisture.

2.2 Synthetic outlines

Polyphosphoric acid (40 g) was added with constant stirring to a well-mixed and ice-cooled mixture of 2-hydroxy, 4-methoxyacetophenone (4.98 g, 0.03 mol) and 1,4-butane diol (2.7 ml, 0.03 mol). The reaction mixture was left at room temperature for half an hour and refluxed at 100°C for 11 h using an oil bath. After cooling, the reaction mixture was poured on crushed ice (400 g) with vigorous shaking and allowed to stand overnight. The separated product was filtered, washed with large amounts of cold water to remove unreacted diol and polyphosphoric acid catalyst. The air dried sample was Soxhlet-extracted with methanol to remove unreacted 2-hydroxy, 4-methoxyacetophenone. Finally it was washed with acetone and dried at 60°C for 24 h (yield 92%). The product was yellowish brown in colour and is designated HMAP-BG.

The general method for the preparation of polychelates is given below. Appropriate metal acetates were used in the synthesis. 0.01 moles of polymer were dissolved in 30 ml of DMSO and 0.05 mol of appropriate metal acetate was also dissolved in DMSO. The hot and clear solution of metal acetate was added with continuous shaking to the hot solution of polymer. A yellowish brown product was digested on a water bath for 1 h and filtered. The filtered product was washed with hot DMSO followed by hot water to remove trace excess of metal acetates. At the end the product was washed with acetone and dried at 60°C for 24 h.

2.3 Physical measurements

Average molecular weight (\bar{M}_n) was estimated by non-aqueous conductometric titration in pyridine against standard sodium methoxide. Viscosities of polymer solution (3% W/V) in DMSO were determined at 35°C using an Ubbelohde viscometer. Polymer samples were placed in selected solvents and tested at room temperature by visual inspection. Elemental analyses of polymer and polychelates were done using a Coleman C-H-N analyzer. The metal contents of polymeric complexes were estimated after decomposing them with a mixture of sulphuric acid, hydrochloric acid, perchloric acid and sodium perchlorate, and using EDTA titrimetric methods. IR spectra of the polymer and its polychelates were recorded using a Perkin-Elmer-983 Spectrophotometer with KBr pellets. Thermogravimetric analyses (TGA) of polymers and coordination polymers were performed with a Du Pont thermal analyser at a heating rate of 10°C/min. Electronic spectra of polychelates were recorded on a DK 2A spectrophotometer and magnetic measurements were carried out with semimicro Sartorius Gouy balance at room temperature. The purified sample HMAP-BG was finely powdered to pass through a 300-mesh screen and used in all experiments carried out in the ion-exchange study.

2.4 Metal uptake determinations

The cation uptake studies in the presence of electrolytes were carried out as below. The polymer (25 mg) was suspended in an electrolyte solution (40 ml) of known concentration and the pH adjusted as required using 0.1 M HCl or 0.1 M NaOH. The suspension was stirred for 24 h at 25°C, a solution of the concerned metal ion (2 ml, 0.1 M) added and the mixture stirred at 25°C for 24 h and filtered. The solid was washed with distilled water. The filtrate and the washings were combined and the concentration of the metal determined by titration with EDTA. A blank experiment was carried out without adding the polymer and the metal ion concentration of the solution similarly determined. The amount of the metal ion taken up by the polymer in the presence of a given electrolyte was then known by difference.

3. Results and discussion

The polymeric sample was yellowish brown in colour, and was insoluble in common organic solvents like MEK, THF, DMF, acetone, methanol, ethanol, CHCl_3 , CCl_4 but soluble in DMSO and formic acid.

Molecular weight (\bar{M}_n) was estimated by non-aqueous conductometric titration. The specific conductance was plotted against milliequivalents of sodium methoxide required for neutralization of 100 g of the polymer. There were many breaks in the plots. From this plot, the first and last breaks were noted. The average degree of polymerization of the polymer can be calculated (Mitra and Chatterjee 1964; Chatterjee 1964) using the formula: last break/first break = \overline{DP} , and the average-number molecular mass (\bar{M}_n) could be obtained by multiplying \overline{DP} by the formula weight. Thus values of \bar{M}_n ($\overline{DP} \times 200$ g/mol) are listed in table 1.

Viscometric measurements were carried out at four different concentrations ranging from 3 to 1.61%. Polymer solution showed normal behaviour. Intrinsic viscosity was determined by known equations (Kraemer 1938; Huggin 1942). The values of $[\eta]$ obtained from the both relations are in good agreement. The observations are satisfactory because the values of K_1 (Huggins constant) and K_2 (Kraemer's constant) follow the condition: $K_1 + K_2 = 0.5$ in all cases (Maron and Reznik 1969).

Table 2 shows important IR absorption bands. All polymer samples gave rise to almost identical IR spectra (figure 1). The polycondensation reaction of 2-hydroxy, 4-methoxyacetophenone with butylene glycol in presence of PPA is an electrophilic substitution reaction on benzene ring. Here the preferred attack of butylene glycol would be at positions 3 and 5 as they are ortho with respect to the electron-releasing

Table 1. Viscosity data and molecular weight data of copolymer.

Copolymer	$[\eta] \times 10^2$ <i>a</i>	dL/g <i>b</i>	Huggin's constant K_1	Kraemer's constant K_2	$K_1 + K_2$	Conductometric titration	
						\overline{DP}	\bar{M}_n
HMAP-BG	6.84	6.83	0.555	-0.038	0.517	12.00	2643

*Values of $[\eta]$ are derived from Huggin's equation

^bValues of $[\eta]$ are derived from Kraemer's equation

Table 2. IR spectral data of ligand (copolymer) and its polychelates.

HMAP-BG	Cu(II) chelate	Ni(II) chelate	Co(II) chelate	Mn(II) chelate	Zn(II) chelate	Probable assignment
3360(<i>sb</i>)	3360	3360(<i>br</i>)	3360(<i>br</i>)	3360(<i>br</i>)	3360(<i>sb</i>)	–OH stretching
2890(<i>mbr</i>)	2890(<i>mbr</i>)	2890(<i>mbr</i>)	2890(<i>mbr</i>)	2890(<i>mbr</i>)	2890(<i>mbr</i>)	ν as –CH ₂ – stretching
2750(<i>mbr</i>)	—	—	—	—	—	OH intramolecular H bonded
1625(<i>vs</i>)	1615(<i>s</i>)	1610(<i>s</i>)	1610(<i>s</i>)	1610(<i>s</i>)	1610(<i>s</i>)	$\nu_{C=O}$ stretching
1425(<i>m</i>)	1425(<i>m</i>)	1425(<i>m</i>)	1425(<i>m</i>)	1425(<i>m</i>)	1425(<i>m</i>)	–CH ₂ – scissoring
1265(<i>s</i>)	1260(<i>s</i>)	1260(<i>s</i>)	1260(<i>s</i>)	1265(<i>s</i>)	1260(<i>s</i>)	δ OH deformation or in- plane bending or as C=O stretching
830(<i>s</i>)	840(<i>s</i>)	840(<i>s</i>)	845(<i>s</i>)	840(<i>s</i>)	840(<i>s</i>)	2 adjacent H atoms of phenyl ring
805(<i>s</i>)	805(<i>s</i>)	805(<i>m</i>)	805(<i>m</i>)	805(<i>m</i>)	805(<i>m</i>)	phenyl ring
865(<i>m</i>)	865(<i>m</i>)	865(<i>m</i>)	865(<i>m</i>)	865(<i>m</i>)	860(<i>m</i>)	1, 2, 4, 5-tetra or penta- substituted phenyl ring
910(<i>m</i>)	910(<i>m</i>)	910(<i>m</i>)	960(<i>m</i>)	960(<i>w</i>)	960(<i>m</i>)	

v = very, *s* = share, *m* = medium, *br* = broad

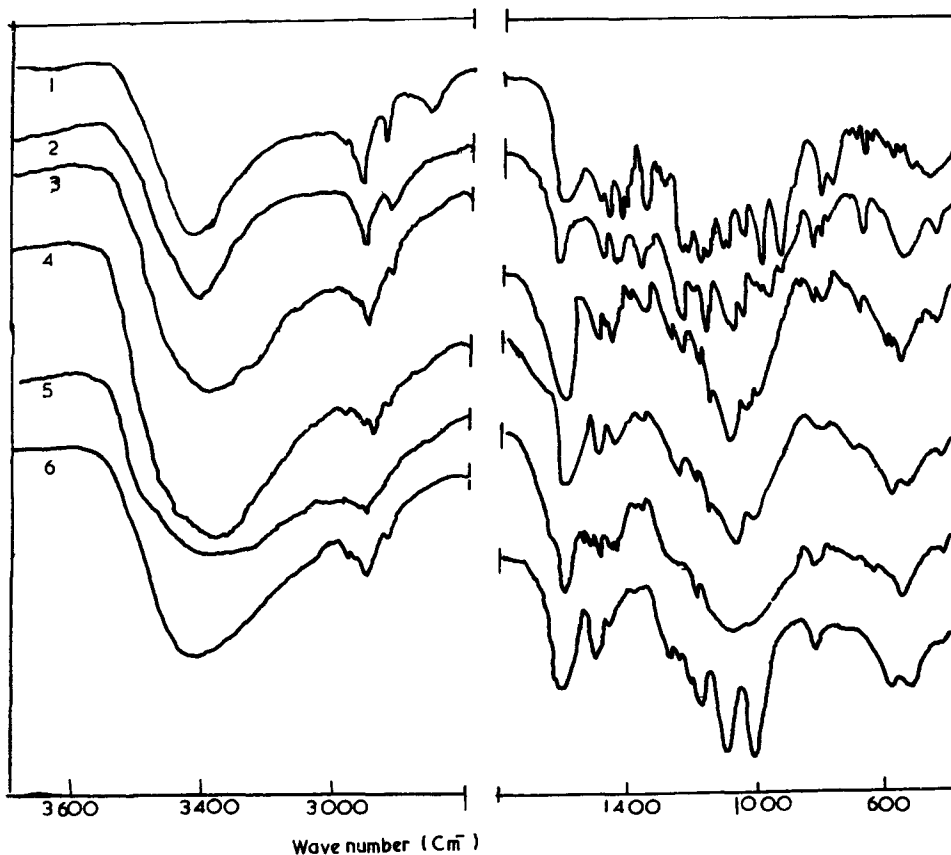
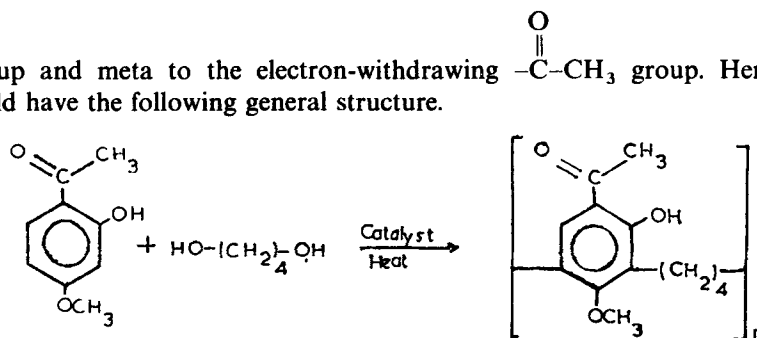
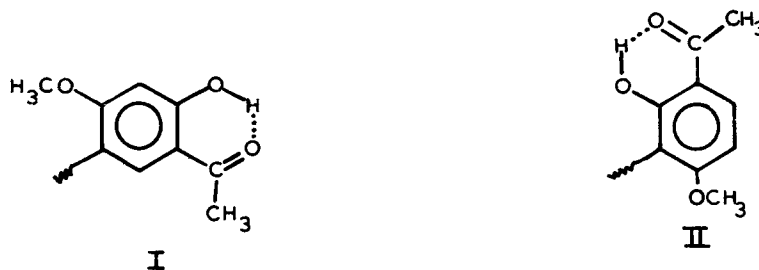


Figure 1. IR spectra of ligand (HMAP-BG) and its polychelates: (1) HMAP-BG; (2) Cu-chelate; (3) Zn-chelate; (4) Ni-chelate; (5) Co-chelate; (6) Mn-chelate.

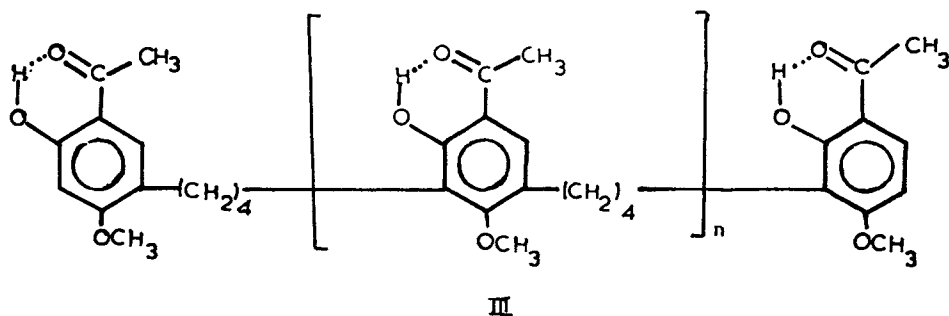
-OH group and meta to the electron-withdrawing -C(=O)CH_3 group. Hence the resin would have the following general structure.



A strong band ($\nu_{\text{C=O}}$) at $1,630\text{ cm}^{-1}$ and a weak band around $2,750\text{ cm}^{-1}$ indicate an intramolecular hydrogen bonding (Makanishi 1964). The inflection around $2,895\text{ cm}^{-1}$ can be assigned to C-H stretching of the butylene bridge of the polymeric chain (Patel and Patel 1981). Accordingly each phenyl ring (except the end groups of the chain) would be 1, 2, 3, 4, 5-pentasubstituted and contain only one isolated H-atom. The end group would have either structure I (para substitution) or structure II (ortho substitution). However, structure I is more favourable as para substitution to phenolic OH is preferred to such ortho substitution in polymer reaction. The data given in table 2 strongly suggest that both possible types of end groups (I and II) may be



present in the polymer chain. From the IR and analytical data the following structure is suggested for the polymer.



The polymer sample undergoes thermal decomposition in a single step. The observed trend reveals that thermal stability increases with increase in the amount of catalyst used in reaction as well as when the reaction period is increased, as indicated in table 3.

Table 3. TGA data of copolymers and polychelates.

Compound	% weight loss at temperature °C												
	100	150	200	250	300	350	400	450	500	550	600	650	700
HMAP-BG	—	—	1.10	5.09	11.10	17.25	22.29	30.01	38.52	47.01	57.93	65.71	70.00
[CuL ₂] _n	1.0	4.5	20.01	37.51	49.12	55.29	60.00	60.00	60.00	60.00	60.00	60.00	60.00
[NiL ₂ X ₂] _n	—	0.5	8.49	19.51	31.73	39.53	46.58	53.71	58.10	62.99	65.55	67.13	68.03
[CoL ₂ X ₂] _n	—	0.7	5.11	11.03	16.00	25.19	33.51	41.79	50.00	56.53	61.51	62.00	62.00
[MnL ₂ X ₂] _n	—	—	5.31	12.54	20.00	31.15	40.53	47.36	53.19	58.11	62.57	65.04	65.04
[ZnL ₂] _n	—	—	1.5	5.51	11.58	20.01	27.58	36.51	45.00	44.03	55.15	55.15	55.15

where L = HMAP-BG. X = H₂O.

4. Characterization of polychelates

All polychelates were yellowish brown in colour and were insoluble in water and common organic solvents. Hence, it was not possible to characterize them by conventional methods. The analytical data presented in table 4 clearly indicate that all polychelates confirm to the simple formula [ML₂]_n.

The magnetic moment values and observed bands in electronic spectra and their assignments are presented in tables 4 and 5, respectively.

The magnetic moment of the Cu(II) chelate is 1.85 BM (Mahapatra and Ram Rao 1972) and two bands were observed at 16,260 and 24,691 cm⁻¹ in its electronic spectrum. We suggest a square planar geometry for the Cu(II) chelate. Ni(II) polychelate exhibits a magnetic moment of 3.12 BM (Cotton and Wilkinson 1979) which is in the expected range for Ni(II) in an octahedral coordination sphere. The number and position of the *d-d* transition bands in the Ni(II) chelate and their assignments suggest octahedral geometry. According to weak field approximation the energy of the first transition band (ν_1) corresponds to 10Dq. The ligand field parameters have been calculated (Koning 1971) and are presented in table 5. The

Table 4. Elemental analyses data and magnetic susceptibility of polychelates.

Compound	Mol. wt. of repeating unit	Colour	Elemental analyses (%)			μ_{eff} (BM)
			C	H	M	
[CuL ₂] _n	502	Yellowish brown	62.50 (62.47)	5.99 (6.02)	12.60 (12.55)	1.80
[NiL ₂ X ₂] _n	533	Yellowish brown	58.61 (58.66)	6.40 (6.42)	10.87 (11.00)	3.12
[CoL ₂ X ₂] _n	533	Yellowish brown	58.60 (58.54)	6.50 (6.42)	11.00 (11.04)	5.04
[MnL ₂ X ₂] _n	529	Yellowish brown	62.00 (61.97)	6.02 (6.00)	12.90 (12.97)	6.09
[ZnL ₂] _n	504	Yellowish brwon	62.40 (62.32)	5.98 (6.00)	12.80 (12.97)	Diamagnetic

where L = HMAP-BG, X = H₂O and values shown in parenthesis are calculated on the basis of empirical formula.

Table 5. Electronic spectral data of polychelate.

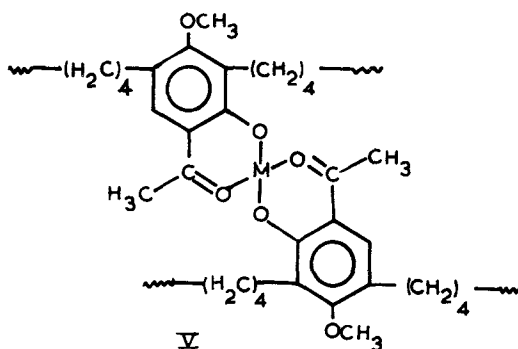
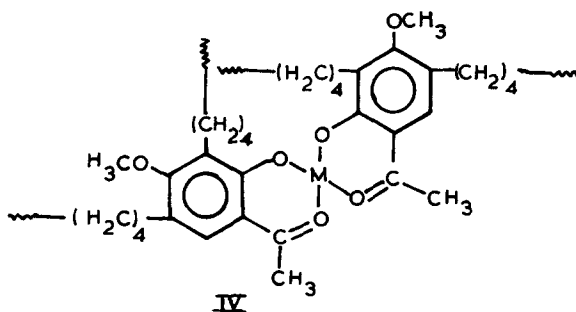
Compound	Observed transition (cm ⁻¹)	Assignment	Calculated transition (cm ⁻¹)	Calculated ligand field parameters
[CuL ₂] _n	16,260	² B _{1g} → ² A _{1g}	—	—
	24,691	Charge transfer	—	—
[NiL ₂ X ₂] _n	9,852	³ A _{2g} → ³ T _{2g} (F)	9,852	D _q = 985.2, B = 748.46 = 0.683v ₂ /v ₁ = 1.66
	16,393	³ A _{2g} → ³ T _{1g}	15,638	
	24,390	³ A _{2g} → ³ T _{1g} (P)	25,144	
[CoL ₂ X ₂] _n	8,333	⁴ T _{1g} → ⁴ T _{2g} (F)	9,659	D _q = 1095.17, B = 926.38 = 0.827v ₂ /v ₁ = 2.13
	—	⁴ T _{1g} → ⁴ A _{2g} (F)	20,611	
	19,610	⁴ T _{1g} → ⁴ A _{1g} (P)	22,263	
[MnL ₂ X ₂] _n	16,120	⁶ A _{1g} → ⁴ T _{1g} (⁴ G)	—	—
	19,047	⁶ A _{1g} → ⁴ T _{2g} (⁴ G)	—	—
	22,727	⁶ A _{1g} → ⁴ E _g , ⁴ E _{1g} (⁴ G)	—	—

Co(II) chelate showed a magnetic moment of 5.04 BM and two bands were observed in its electronic spectrum (Figgis and Lewis 1967). Ligand field parameters 10Dq, B value (926.38) and β value (0.827) were calculated (Koning 1971) and also used to deduce the position of v₂ band in the chelate, the v₂/v₁ value was found to be 2.13. The magnetic moment value, positions of bands in electronic spectra and v₂/v₁ value (Jorgensen 1956) correspond to an octahedral geometry for Co(II). Mn(II) chelate showed a magnetic moment of 6.09 BM which satisfactorily lies in the range for high-spin octahedral complexes (Chandra and Sharma 1982). Three weak bands were observed at 16,120, 19,407 and 22,727 cm⁻¹ which are the expected position for Mn(II) in octahedral geometry. As expected, the Zn(II) polychelate was found to be diamagnetic and we suggest tetrahedral geometry.

The important IR bands and their assignments are listed in table 2. The band at 3350–3580 cm⁻¹ is due to the –OH stretching vibrations. The band at 2750 cm⁻¹ is absent in chelates suggesting deprotonation of the phenolic –OH group by metal ions. The band appearing at 1570–1600 cm⁻¹ is attributed to ν_{C=O} stretching vibrations. This band is observed at lower frequencies in the case of chelates compared to the usual position suggesting coordination of metal ions through the oxygen of carbonyl group. The other band due to –OCH₃ group and substitution pattern were found to be similar in polychelates and polymer.

The IR studies, elemental analyses and solubility data of polychelates suggest that chelation might have occurred between two chelating groups from different polymeric chains as shown in structures IV and V. Thus metal ion is the bridging unit between donor sites of two different polymeric chains.

TGA data of polychelates are given in table 3. The study of these data reveals that polychelates are less stable than the parent polymeric ligand (Voges *et al* 1971). The stability order was found to be: polymeric ligand > Zn > Co > Mn > Ni > Cu. This order matches with that reported for coordination polymers (Bottei and Fangmann 1964). The lowest stability of the Cu(II) chelate may be attributed to catalytic oxidative effect of Cu(II) (Winslow and Manning 1964).



5. Ion-exchange properties

To ascertain the selectivity of the polymer (HMAP-BG) for the selected metal ions, we have studied the influence of various electrolyte on the selectivity of metal ions, the rate of metal uptake, and the distribution of the metal ions between the polymer and solution containing metal ions.

To find out which electrolyte system has maximum uptake, the influence of chlorate, nitrate, chloride and sulphate ions on the position of the equilibrium was examined at various concentrations. From the data given in table 6, it appears that the amount of each metal ion taken up by HMAP-BG increases with the increasing concentration of ClO_4^- , NO_3^- and Cl^- , while it decreases with increasing concentration of SO_4^{2-} . This may be explained in terms of stability constants of the chelates with this polymer. Sulphate might form rather strong chelates with Fe(III), Ni(II), $\text{UO}_2(\text{II})$ and Cu(II), while perchlorate, nitrate and chloride might form weak chelates and therefore might not be expected to influence the position of the Fe(III), Ni(II), $\text{UO}_2(\text{II})$ or Cu(II) chelate equilibrium as much as sulphate. A similar trend has been also observed by others (Patel and Patel 1979).

Table 7 shows the dependence of the rate on the nature of metal ion. The shortest time to reach the equilibrium is about 5 h for Cu(II), Ni(II) and Fe(III) and 6 h for $\text{UO}_2(\text{II})$ ions.

The rate of metal ion uptake follows the order $\text{Fe(III)} > \text{Cu(II)} > \text{Ni(II)} > \text{UO}_2(\text{II})$.

Table 8 shows the effect of pH on the amount of metal ions distributed between two phases. The perusal of results reveals that the relative amount of metal ions taken up by the polymer increase with increasing pH of the medium. This study is restricted

Table 6. Application of effect of different electrolytes in uptake of several metal ions $Mt(NO_3)_2 = 0.1 \text{ mol/l}^a$.

Metal ion	Electrolyte Mol/l	pH	Uptake of ions (mmol \times 10) in the presence of			
			NaCl	NaNO ₃	NaClO ₃	Na ₂ SO ₄
Cu ⁺²	0.01	4.5	0.10	0.22	0.07	0.21
	0.05		0.15	0.24	0.09	0.19
	0.10		0.20	0.30	0.13	0.16
	0.50		0.26	0.32	0.18	0.12
	1.00		0.30	0.39	0.22	0.09
Ni ⁺²	0.01	4.5	0.09	0.17	0.11	0.25
	0.05		0.11	0.20	0.13	0.23
	0.10		0.13	0.23	0.18	0.19
	0.50		0.16	0.24	0.21	0.14
	1.00		0.21	0.26	0.23	0.10
UO ₂ ⁺²	0.01	4.00	0.21	0.25	0.28	0.34
	0.05		0.25	0.27	0.30	0.31
	0.10		0.28	0.31	0.34	0.25
	0.50		0.36	0.33	0.37	0.21
	1.00		0.40	0.40	0.43	0.17
Fe ⁺³	0.01	2.5	0.09	0.12	0.06	0.21
	0.05		0.15	0.16	0.12	0.17
	0.50		0.17	0.21	0.16	0.15
	0.50		0.22	0.27	0.20	0.12
	1.00		0.26	0.32	0.24	0.08

^aVolume of electrolyte: 40 ml, volume of metal ion solution = 0.1 mol/l, 2 ml; 24 h, temperature = room temperature.

Table 7. Metal ion uptake as a function of time^a.

Metal ion	Percentage of metal uptake at different time (h)							
	0.5	1.0	2.0	3.0	4.0	5.0	6.0	7.0
Cu ⁺²	31.48	44.18	58.94	67.61	77.16	82.20	90.17	97.99
Ni ⁺²	11.73	25.38	51.59	61.09	76.97	85.30	90.97	95.23
UO ₂ ⁺²	26.53	28.97	41.83	56.19	70.09	81.38	87.69	94.98
Fe ⁺³	21.70	41.98	55.23	69.17	76.16	86.70	96.97	—

^aMt(NO₃)₂ = 0.1 mol/l; volume = 2 ml; NaNO₃ = 1 mol/l; volume 44 ml; pH 2.5 for Fe⁺³; 4.0 UO₂⁺²; and 4.5 for Cu⁺², Ni⁺²

up to a pH of 5, in order to prevent metal hydrolysis at higher pH. In case of Fe(III), the change in pH from 1 to 2.5, the distribution ratio *D*, changes by a factor of 19.26 whereas change in pH from 2.5 to 5.0, the distribution ratio *D*, changes by a factor of 4.21 and 5.1 for Cu(II) and Ni(II) respectively. Similarly when pH changes from 1 to 4 the values of distribution ratios of divalent metal ions measured in the pH range 2.5 to 4.0 were found to be UO₂(II) > Cu(II) > Ni(II) which match with that reported (Irving and Williams 1963). The results of this study are helpful in the

Table 8. Distribution ratio D^* of different metal ions as a function of pH.

Metal ion	Distribution ratio of the metal ion at different pH						
	1.0	1.5	2.0	2.5	3.0	4.0	5.0
Cu(II)	—	—	—	73:30	147:66	180:60	308:53
Ni(II)	—	—	—	45:57	77:79	125:07	235:85
UO ₂ (II)	35:95	121:91	180:18	350:35	392:89	427:45	—
Fe(III)	14:94	82:92	151:03	287:84	—	—	—

$$*D = \frac{\text{m mol of metal on the copolymer}}{\text{m mol of metal in the solution}} \times \frac{\text{volume of solution}}{\text{weight of resin}}$$

Mt(NO₃)₂ = 0.1 mol/l, volume: 2 ml; NaNO₃ = mol/l, volume: 40 ml; 24 h; room temperature.

selecting the optimum pH for selective uptake for particular metal ion from mixtures of different ions.

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