

Synthesis and characterization of 2, 4-dihydroxy-benzaldehydeoxime-formaldehyde polymers and their application as ion-exchangers

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Abstract. Polymers were prepared by the condensation of 2, 4-dihydroxybenzaldehydeoxime (2, 4-DBO) and formaldehyde (F) in the presence of oxalic acid as catalyst with varying molar ratios of reacting monomers. Polymers were characterized by their IR spectra, elemental analyses, TGA and \bar{M}_n as determined by vapour pressure osmometry as well as by non-aqueous conductometric titrations. Viscosity measurements of the solutions of polymer samples were carried out in dimethylformamide. Chelation ion-exchange properties have also been studied employing the batch equilibration method. This method involved the measurement of distribution of a given metal between the polymer sample and a solution containing metal ions. The study was carried out over a wide pH range and in media of various ionic strengths. The polymer showed a higher selectivity for UO_2^{2+} and Fe^{3+} ions than for Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} ions.

Keywords. Chelation ion exchange; batch equilibration; distribution ratio.

1. Introduction

8-Hydroxyquinoline, salicylic acid and 4-amino-2-hydroxybenzoic acid were condensed with formaldehyde in acidic medium to obtain ion-exchange resins (Aristov and Kostantinov 1961; DeGeiso *et al* 1962; Patel *et al* 1981). Similarly, Salicylaldehydeoxime was condensed with *o*-hydroxybenzyl alcohol and 2, 6-dimethyl-4-methylphenol (Guivetchi 1969) and resacetophenoneoxime condensed with formaldehyde using oxalic acid as catalyst (Parmar *et al* 1982) to obtain ion-exchange resins. As 2,4-dihydroxybenzaldehydeoxime is a chelating agent it is obvious that polymers prepared from 2,4-dihydroxybenzaldehydeoxime are also the subject of extensive investigations for their chelation properties.

We report in this paper the systematic study of the selectivity and capacity of 2,4-dihydroxybenzaldehydeoxime (2,4-DBO)-formaldehyde (F) polymers (2,4-DBO-F) in ion-exchange reactions.

2. Experimental

2.1 Materials

All chemicals used were of analytical grade. DMF was used after distillation. Pyridine and methanol were purified by conventional chemical methods.

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2.2 Synthesis of monomer

2,4-Dihydroxybenzaldehyde (m.p. 132°C) was prepared in our laboratory (Mangoni 1958). 2,4-Dihydroxybenzaldehydeoxime (m.p. 195°C) was prepared by condensing 2,4-Dihydroxybenzaldehyde with hydroxylamine in 70% ethanol.

2.3 Preparation of 2,4-dihydroxybenzaldehydeoxime-formaldehyde polymers

2,4-DBO (15.3 gm, 0.1 mol) and oxalic acid (1% w/w) dissolved in water were heated on a water-bath for 1 h and then polymerized with 37% formaldehyde (8.1 ml, 0.1 mol). The contents were refluxed with good stirring at 85–87°C for 6 h on a water-bath. The solid yellow product obtained was filtered, washed with large amounts of boiling water and dried. Dried polymer was Soxhlet-extracted with solvent ether to remove unreacted 2,4-DBO. Polymer was purified by reprecipitation from DMF with water and dried at 60°C. Polymer did not melt upto 250°C. It is soluble in DMF, acetone, THF and aq. NaOH. Different polymer samples were prepared employing different molar-ratios of formaldehyde. The samples and reaction details are given in table 1.

2.4 Measurements

The carbon, hydrogen, nitrogen analyses were made on the Coleman C-H and N Analyzer. The number average molecular weights (M_n) of the polymers was determined by non-aqueous conductometric titration and by a Hewlett Packard Vapour Pressure Osmometer using DMF as a solvent and benzil as a calibrant at 71°C. The intrinsic viscosities of the polymers were measured in DMF at 35°C using an Ubbelohde viscometer. The TG curves were recorded on Du Pont Thermal Analyzer-951 in air at a heating rate of 10°C min⁻¹. IR spectra in KBr disks were recorded on a Perkin-Elmer-983 spectrophotometer.

2.5 Ion-exchanging properties

The purified polymer sample 2,4-DBO-F-1 was finely powdered to pass a 300-mesh screen and used in all experiments carried out in the ion-exchange study. We have adopted the batch-equilibration method (Gregor *et al* 1952). The details of the

Table 1. Synthesis and analytical data of polymers

Polymers	Reactants			Colour	Yield, %	C ^a (wt %)	H ^a (wt %)	N ^a (wt %)
	2,4-DBO (mol)	37% Formalde- hyde (mol)	Oxalic acid (w/w)					
2,4-DBO-F-I	0.1	0.1	1%	Yellow	65	58.10	4.22	8.46
2,4-DBO-F-II	0.1	0.2	1%	Yellow	61	58.15	4.32	8.50
2,4-DBO-F-III	0.1	0.3	1%	Yellow	59	59.20	4.28	8.52
2,4-DBO-F-IV	0.1	0.4	1%	Yellow	54	58.70	4.30	8.38

^aRepeat unit: empirical formula – C₈H₇O₃N; molecular weight-165; elemental analysis, calculated-C 58.18%, H 4.24%, N 8.48%

procedure for different types of studies in the selectivity of various metal ions by the above polymer are similar to those reported earlier from this laboratory (Patel and Patel 1979).

3. Results and discussion

3.1 Molecular weight determination

The number average molecular weights (\bar{M}_n) of all polymer samples were determined by non-aqueous conductometric titration in pyridine against sodium methoxide (NaOMe) in pyridine and \bar{M}_n values of the polymer samples were calculated following known methods (Chatterjee 1970; Chatterjee and Agrawal 1971). \bar{M}_n of the 2,4-DBO-F polymers were also determined by vapour pressure osmometry (VPO) in DMF at 71°C. The values are presented in table 2. The values obtained by both methods are in good agreement. Polymers synthesised from equimolar proportion of 2,4-DBO and F have comparatively higher molecular weights in the series. The use of formaldehyde in more than stoichiometric proportions gave low molecular weight polymers.

3.2 Viscosity measurements

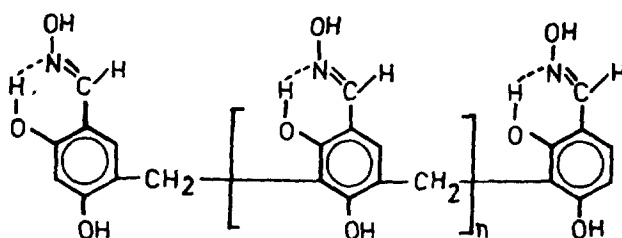
The viscometric measurements in DMF were obtained and plots of reduced viscosity vs. concentration (4.00 to 2.15 g.dl⁻¹) were made for each set of data. The intrinsic viscosity, $[\eta]$ was determined from the corresponding linear plots (table 2). It has been observed that polymer having higher \bar{M}_n in the series indicated higher intrinsic viscosity.

3.3 IR spectra

All the polymers give rise to nearly similar spectra. The strong C = N stretch at 1615 cm⁻¹ and a weak band around 2720 cm⁻¹ indicate an intramolecular H-bond (Nakanishi 1964). The vibrational absorption bands at 2930, 1460 and 735 cm⁻¹ suggest the presence of methylene bridges in the polymers (Gupta and Malik 1969; Nakanishi 1964). An N–O stretch is observed at 960 cm⁻¹. From infrared spectral and analytical data, the following structure for the polymer is suggested.

Table 2. Molecular weight determination, viscometric and TG data of polymers

Polymers	M_n		Intrinsic viscosity [η] × 10 ² (dl/g)	% weight loss at temperature °C					Activation energy (E) (kcal/mol) for	
	By VPO	By conducto- metric titration		100	200	300	400	500	First step	Second step
2,4-DBO-F-I	3154	3145	6.55	0	3	31	70	83	18.63	4.62
2,4-DBO-F-II	2387	2475	5.90	0	3	28	56	93	3.14	6.19
2,4-DBO-F-III	2093	2145	5.10	0	4	31	67	95	11.92	8.86
2,4-DBO-F-IV	1891	1958	4.37	0	3	20	76	97	8.69	11.76



3.4 Thermogravimetric analysis

All the polymers are thermally stable upto 200°C and undergo thermal degradation in two steps. The first step of decomposition starts from 200°C and appears to terminate around 350°C where the rate of decomposition becomes slower. Decomposition becomes rapid after 350°C and is completed at 500°C where 83 to 97% weight loss is observed. Polymer prepared using equimolar proportion of reactants is thermally more stable. The Broido method was applied to the TG data to determine the energy of activation (Broido 1969).

3.5 Effect of electrolytes on metal uptake

We examined the influence of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} ions at various concentrations on the position of the equilibrium of metal-polymer interaction. Perusal of data given in table 3 reveals that the amount of Cu^{2+} , Ni^{2+} , UO_2^{2+} , and Fe^{3+} ions taken up by 2,4-DBO-F-1 polymer sample increases with increasing concentration of ClO_4^- , NO_3^- , and Cl^- and decreases with increasing concentration of SO_4^{2-} whereas uptake of Co^{2+} and Mn^{2+} by the above polymer increases with decreasing concentration of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} . This may be explained in terms of stability constants of complexes which Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} ions form with these ligands (Bjerrum *et al* 1958; Cotton and Wilkinson 1972; Davadov and Plate 1975). Sulphate might form rather strong chelates with Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} while perchlorate, nitrate and chloride might form weak chelates and therefore might not be expected to influence the position of the Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} and Mn^{2+} chelate equilibrium to the extent expected for the sulphate.

3.6 Evaluation of the rate of metal uptake

The rate of metal adsorption of 2,4-DBO-F-1 was determined to evaluate the shortest period of time for which equilibration could be carried out while operating as close to equilibrium conditions as possible. Table 4 shows the dependence of the rate of metal ion uptake on the nature of the metal. Fe^{3+} and UO_2^{2+} ions required slightly more than three hours for the establishment of equilibrium. Cu^{2+} and Ni^{2+} ions required about six hours for equilibrium. In experiments with solution containing UO_2^{2+} and Fe^{3+} ions more than 75% of equilibrium was established in the first hour. Mn^{2+} and Co^{2+} ions required almost 7 h for equilibrium. The rate of metal ion uptake follows the order UO_2^{2+} , Fe^{3+} > Cu^{2+} , Ni^{2+} > Co^{2+} , Mn^{2+} .

3.7 Distribution ratio of metal ions at different pH levels

The effect of pH on the amount of metal ion distributed between two phases can be explained by the results shown in table 5. The results indicate that the relative

Table 3. Evaluation of the effect of different electrolytes in the uptake of metal ions $[M^{n+}(\text{NO}_3)_n] = 0.1 \text{ mol l}^{-1a}$.

Metal ion	Electrolyte (mol/l)	pH	mmol $\times 10$ of metal ion uptake in the presence of			
			NaClO ₄	NaCl	NaNO ₃	Na ₂ SO ₄
Cu ²⁺	0.01	5.5	0.19	0.33	0.22	0.35
	0.05		0.22	0.34	0.33	0.32
	0.10		0.27	0.36	0.38	0.29
	0.50		0.37	0.39	0.43	0.28
	1.00		0.60	0.50	0.45	0.26
Ni ²⁺	0.01	5.5	0.12	0.10	0.24	0.32
	0.05		0.18	0.19	0.26	0.29
	0.10		0.22	0.22	0.29	0.25
	0.50		0.30	0.24	0.30	0.24
	1.00		0.50	0.25	0.31	0.21
Co ²⁺	0.01	5.5	0.38	0.36	0.29	0.25
	0.05		0.35	0.30	0.24	0.23
	0.10		0.32	0.28	0.21	0.21
	0.50		0.30	0.27	0.19	0.20
	1.00		0.29	0.25	0.18	0.18
Mn ²⁺	0.01	5.5	0.27	0.25	0.26	0.35
	0.05		0.24	0.21	0.23	0.32
	0.10		0.21	0.18	0.21	0.28
	0.50		0.19	0.17	0.16	0.23
	1.00		0.16	0.15	0.14	0.17
UO ₂ ²⁺	0.01	4.0	0.54	0.22	0.46	0.40
	0.05		0.55	0.24	0.48	0.38
	0.10		0.75	0.25	0.66	0.36
	0.50		0.77	0.39	0.72	0.35
	1.00		0.80	0.45	0.75	0.33
Fe ³⁺	0.01	2.75	0.12	0.09	0.40	0.26
	0.05		0.27	0.13	0.45	0.24
	0.10		0.29	0.16	0.46	0.23
	0.50		0.35	0.26	0.47	0.15
	1.00		0.38	0.33	0.52	0.05

^aVolume of electrolyte solution: 25 ml, volume of 0.1 mol l⁻¹ metal ion solution: 2 ml; time: 24 h; temp: 28°C.

amounts of metal ions taken up by the polymer increase with increasing pH of the medium. The study was carried up to a definite pH value for the particular metal ion to prevent hydrolysis of metal ions at higher pH. UO₂²⁺ ion is taken up more selectively than any other metal ion under study. Cu²⁺ and Ni²⁺ ions are taken up by polymer in preference to Co²⁺ and Mn²⁺ ions. The lower distribution ratio of Fe³⁺ compared to UO₂²⁺ may be attributed to steric hindrance. Co²⁺ and Mn²⁺ ions have low distribution ratios in the range of pH 4 to 6. This can be attributed to the low stability constants i.e. weak ligand stabilization energies of the metal complexes (Cotton and Wilkinson 1972; Davadov and Plate 1975). The

Table 4. Comparison of the rates of metal (M^{n+}) ion uptake^a.

Metal ion	Percentage of metal ion uptake ^b at different times (h)							
	0.5	1	2	3	4	5	6	7
Cu ²⁺	40.5	53.0	66.8	72.0	79.5	89.0	100.0	—
Ni ²⁺	42.0	49.0	53.5	64.0	72.8	86.5	99.0	99.0
Co ²⁺	25.0	36.0	50.0	58.0	69.0	79.0	88.0	100.0
Mn ²⁺	29.0	42.0	51.0	61.0	66.5	80.5	89.0	99.5
UO ₂ ²⁺	61.0	82.0	89.0	98.4	99.0	—	—	—
Fe ³⁺	55.4	78.0	90.0	97.2	99.5	—	—	—

^a[$M^{n+}(\text{NO}_3)_n$] = 0.1 mol l⁻¹; volume: 2 ml; NaNO₃ = 1 mol l⁻¹; volume: 25 ml; pH: 3.0; temp: 28°C.

^b $\frac{\text{mmoles of metal ion adsorbed} \times 100}{\text{mmoles of metal ion adsorbed at equilibrium}}$

Table 5. Distribution ratios D^a of different metal ions as a function of the pH.

Metal ion	Distribution ratio of the metal ions at different pH values.						
	1.5	2.0	2.5	3.0	4.0	5.0	6.0
Cu ²⁺	—	—	19.9	40.70	66.00	229.00	290.32
Ni ²⁺	—	—	57.50	74.10	92.60	137.00	183.45
Co ²⁺	—	—	28.00	48.80	62.20	79.00	98.90
Mn ²⁺	—	—	—	16.50	49.80	67.80	75.27
UO ₂ ²⁺	52.50	115.80	180.00	305.00	454.54	—	—
Fe ³⁺	66.90	201.90	351.35	—	—	—	—

^a $D = \frac{\text{mmoles of metal ion taken up by 1 gm of polymer}}{\text{mmoles of metal ion present in 1 ml of solution}}$

$M^{n+} (\text{NO}_3)_n = 0.1 \text{ mol l}^{-1}$; volume: 2ml; NaNO₃ = 1 mol l⁻¹; volume: 25 ml; temp: 28°C; time: 24 h (equilibrium state).

possible order of selectivity of a cation exchange resin for divalent metal ions would be Pd > Cu > Ni > Co > Zn > Cd > Fe > Mn > Mg (Irving and Williams 1956). In the present study the observed order of distribution ratios of divalent ions measured in the range of 3 to 6 pH was found to be UO₂²⁺ > Cu²⁺ > Ni²⁺ > Co²⁺ > Mn²⁺. The results of this study are helpful in selecting the optimum pH for a selective uptake of a metal ion from a mixture of different ions. For example, the results suggest the optimum pH value 2.5 for the separation of Cu²⁺ and Fe³⁺ ions, at which the distribution ratio D for Cu²⁺ is 19.9 and that of Fe³⁺ is 351.35.

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