

Synthesis and characterization of 2-hydroxy-4-methoxyacetophenone-urea-formaldehyde resins and their ion-exchange properties

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Abstract. Resins were prepared by condensing 2-hydroxy-4-methoxyacetophenone (2-H-4-MAc) with urea and formaldehyde in the presence of 2 M HCl/2 M H₂SO₄ catalyst with varying molar ratios of reacting monomers. The resin samples were characterized by elemental analyses and IR spectral studies. M_n was determined by vapour pressure osmometry and non-aqueous conductometric titration in pyridine. Viscosity measurements of the resin samples were carried out in dimethylformamide. Chelation ion-exchange properties of 1:1 resin for selected metal ions have also been studied employing the batch-equilibration method. This method involved the measurement of distribution of a given metal between a resin sample and a solution containing metal ions. The study was carried out over a wide pH range and in media of differing ionic strengths.

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

1. Introduction

2,4-dihydroxyacetophenone (resacetophenone) has been used extensively as an analytical reagent in the determination of metal ions due to its chelating property (Gandhi and Desai 1968; Graddon and Mockler 1968; Manku *et al* 1971). Copolycondensation products of resacetophenone and resorcinol with formaldehyde in alkaline media were prepared and their chelation ion-exchange properties studied (Pennington and Williams 1959). Chelating ion-exchange resins prepared by copolycondensation of 8-hydroxyquinoline or phenol derivatives like *O*-aminophenols, β -resorcylic acid or resorcinol with formaldehyde have been reported (Pennington and Williams 1959; Aristov and Kostantinov 1961). The salicylic acid/*p*-chloro-(bromo)-formaldehyde resins have been reported as showing a chelation ion-exchange capacity (DeGeiso *et al* 1962; Patel *et al* 1982; Patel and Patel 1983). The salicylic acid-urea-formaldehyde resins show a chelation ion-exchange capacity (Joshi and Patel 1982). Resins were also synthesized by the condensation of salicylic acid/*p*-hydroxybenzoic acid and thiourea with trioxane in presence of 2 M HCl as catalyst and their ion-exchange capacity studied (Manavalan and Patel 1983, 1984). 2-hydroxy-4-methoxyacetophenone has been condensed with formaldehyde using oxalic acid as catalyst to obtain ion-exchange resins (Parmar *et al* 1981). These studies inspired us to prepare and characterise 2-hydroxy-4-methoxyacetophenone-urea-

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formaldehyde resins (2-H-4-MAcUF) and study their selectivity and capacity for ion-exchange reactions.

2. Experimental

Analytical reagent grade pyridine, methanol and dimethylformamide (DMF) were used after purification. The monomer 2-H-4-MAc was prepared by the method reported in the literature (Dey 1935).

For the preparation of the resin, a mixture of 2-H-4-MAc (8.3 g, 0.05 mol); urea (1.5 g, 0.025 mol) and formaldehyde (0.075 mol) in the presence of 2 M HCl/2 M H₂SO₄ was heated at 100 ± 1°C for 4 h on an oil-bath. The white coloured resin that separated out was washed with hot water and finally with acetone to remove unreacted 2-H-4-MAc-F resin. The resin was purified by the method reported earlier (Joshi and Patel 1982). It is soluble in DMF and aq. NaOH. Different resin samples were prepared using different ratios of 2-H-4-MAc, urea and formaldehyde. Details of samples and reactions are given in table 1.

Carbon and hydrogen analyses were done on the Coleman C-H Analyzer. Nitrogen was estimated by the Kjeldahl method. The number average molecular weights (\bar{M}_n) of all resin samples were determined by non-aqueous conductometric titration in pyridine against sodium methoxide (NaOMe) in pyridine and \bar{M}_n values of the resin samples were calculated following known methods (Chatterjee 1970; Chatterjee and Agrawal 1971). \bar{M}_n of the 2-H-4-MAcUF resins were also determined by vapour pressure osmometry (VPO) in DMF at 71°C. The values are presented in

Table 1. Characterization of resins.

Resins	Reactants				Colour	Yield %	Elemental analysis (wt.%)		
	2-H-4-MAc (mol)	Urea (mol)	Formaldehyde (mol)	Catalyst (2 M)			C	H	N
2-H-4-MAcUF-I	0.05	0.05	0.1	HCl	White	62	58.10 (57.60)*	5.54 (5.60)	11.05 (11.20)
2-H-4-MAcUF-II	0.075	0.05	0.125	HCl	White	56	60.98 (61.98)	5.65 (5.95)	7.82 (7.93)
2-H-4-MAcUF-III	0.05	0.025	0.075	HCl	White	53	63.12 (63.29)	5.76 (5.93)	6.07 (6.15)
2-H-4-MAcUF-IV	0.0625	0.025	0.0875	HCl	White	45	60.28 (61.68)	5.68 (5.61)	6.32 (6.54)
2-H-4-MAcUF-V	0.05	0.05	0.1	H ₂ SO ₄	White	48	59.02 (60.27)	5.41 (5.47)	8.13 (8.27)
2-H-4-MAcUF-VI	0.075	0.05	0.125	H ₂ SO ₄	White	46	61.21 (63.37)	5.39 (5.61)	4.41 (4.62)
2-H-4-MAcUF-VII	0.05	0.025	0.075	H ₂ SO ₄	White	42	62.83 (64.29)	5.52 (5.61)	3.53 (3.57)
2-H-4-MAcUF-VIII	0.0625	0.025	0.0875	H ₂ SO ₄	White	47	62.18 (63.88)	4.48 (5.61)	4.01 (4.03)

* Calculated values are given in parentheses

Table 2. Molecular weight determination, viscometric data and IR frequencies of resins.

Resins	\bar{M}_n		Intrinsic viscosity [η] $\times 10^2$ (dl/g)	Huggins constant K_1	Kraemer constant K'_1	$K_1 + K'_1$	Important IR frequencies	
	By conductometric titration	By VPO					Wave- number	Assignment
2-H-4-MAcUF-I	3000	2989	2.625	2.4666	-1.8930	0.5736	3100-3600 (<i>mbr</i>)*	-OH stretching (chelated)
2-H-4-MAcUF-II	2850	2804	2.262	2.5454	-1.9766	0.5688	2820(<i>m</i>) 2720(<i>w</i>)	-CH ₂ stretching Intramolecular H bonding
2-H-4-MAcUF-III	2730	2698	2.437	2.7226	-2.1388	0.5838	1625(<i>s</i>)	ν C=O
2-H-4-MAcUF-IV	2568	2526	1.212	8.6892	-8.1708	0.5184	1490(<i>m</i>) 1450(<i>m</i>) 1425(<i>m</i>) 1415(<i>w</i>)	-C=C-stretching (aromatic vibration)
2-H-4-MAcUF-V	2347	2314	1.437	6.5364	-5.9862	0.5502	1285(<i>m</i>)	-OH in-plane bending
2-H-4-MAcUF-VI	1757	1712	1.762	4.9679	-4.4216	0.5460	1195(<i>m</i>) 1110(<i>m</i>) 1085(<i>m</i>)	-C-H in-plane bending
2-H-4-MAcUF-VII	1936	1902	1.100	12.3750	-11.8010	0.5740	910(<i>m</i>)	Isolated H on phenol ring or pentasubstituted phenyl ring
2-H-4-MAcUF-VIII	2065	2004	1.900	3.1712	-2.5941	0.5768	860(<i>m</i>)	1,2,4,5-tetra- substituted phenyl ring
							715(<i>m</i>)	-CH ₂ rocking.

* *m* = medium; *br* = broad; *w* = weak; *s* = strong

table 2. The values obtained by both methods are in good agreement. The viscometric measurements (table 2) were carried out in DMF at 35°C.

The ion-exchange study of the purified resin sample 2-H-4-MAcUF-I (200 mesh) adopting batch-equilibration methods (Gregor *et al* 1952) was carried out using the procedures described earlier (Patel and Patel 1979).

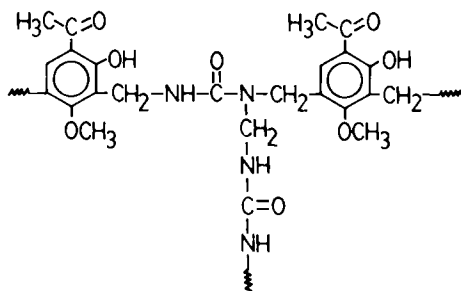
3. Results and discussion

3.1 \bar{M}_n , viscosity and IR spectra

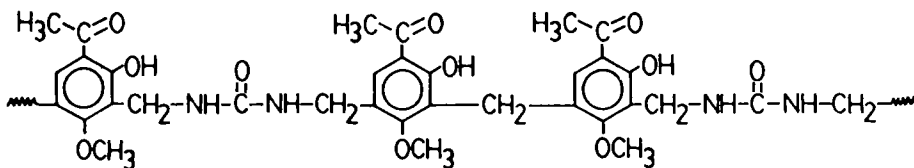
From table 2, it is seen that the resins synthesised from equimolar proportion of the reactants have comparatively higher values of \bar{M}_n .

Plots of reduced viscosity vs. concentration (2.0 to 0.93 g dl⁻¹) were made for each set of data (table 2). The intrinsic viscosity $[\eta]$ was determined from the corresponding linear plots. The values K_1 and K'_1 calculated satisfy the relation $K_1 + K'_1 = 0.5$ (Huggin 1942).

Major IR frequencies of the resin samples are given in table 2. All the resins give rise to nearly similar spectrums. The strong band at $\nu_{C=O}$ (~ 1625 cm⁻¹) and a weak band at ν_{OH} (~ 2720 cm⁻¹) indicate an intramolecular H-bond (Nakanishi 1964). The vibrational absorption bands at 2820 cm⁻¹ and 715 cm⁻¹ suggest the presence of methylene bridges in the resins (Nakanishi 1964; Gupta and Malik 1969). The phenolic OH in-plane bending is observed at 1285 cm⁻¹. Bands appearing in the region 1050–1200 cm⁻¹ are attributed to C–H in-plane bending (Dyer 1971). From infrared spectral and analytical data, the following structures (I and II) of the resin may be suggested (Chatterjee 1970; DeGeiso *et al* 1962; Patel and Patel 1982; Slonim and Alekseyeva 1977).



(I)



(II)

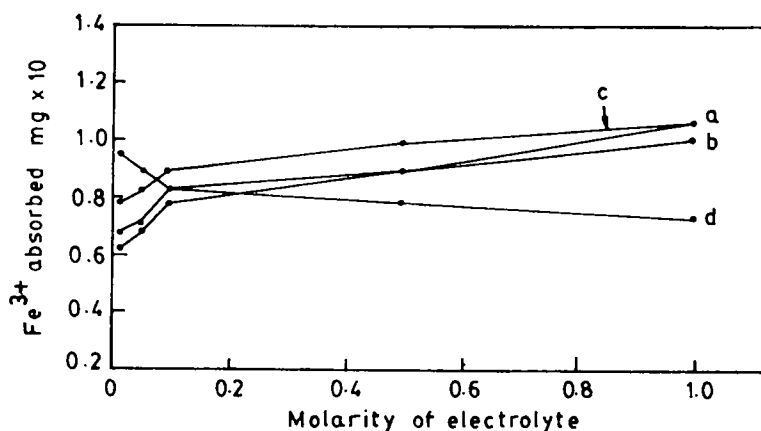


Figure 1. Effect of electrolyte on the metal uptake by 2-H-4-MAcUF-I resin: (a) ClO_4^- ; (b) Cl^- ; (c) NO_3^- ; (d) SO_4^{2-} .

3.2 Effect of electrolytes on metal uptake

The effect of different electrolytes on the uptake of several metal ions by the 2-H-4-MAcUF-I resin is given in figure 1. Examination of data reveals that the amount of Cu^{2+} , Ni^{2+} , Fe^{3+} and UO_2^{2+} taken up by the resin increases with increasing concentrations of ClO_4^- , NO_3^- and Cl^- and decreases with increasing concentrations of SO_4^{2-} whereas the uptake of Co^{2+} , Zn^{2+} and Mn^{2+} by the above resin increases with decreasing concentrations of ClO_4^- , NO_3^- , Cl^- and SO_4^{2-} . This may be explained in terms of the stability constants of the complexes which Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Mn^{2+} ion form with these ligands (Bjerrum *et al* 1958; Cotton and Wilkinson 1972; Davydova and Plate 1975). Sulphate ions may form rather strong chelates with Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Mn^{2+} while perchlorate, nitrate and chloride ions might form weak chelates and therefore may not influence the position of the Fe^{3+} , UO_2^{2+} , Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} and Mn^{2+} chelate equilibrium to the extent expected for sulphate ions.

3.3 Evaluation of the rate of metal uptake

The rate of metal adsorption by 2-H-4-MAcUF-I 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. Figure 2 shows the dependence of the rate of metal ion uptake on the nature of the metal. Examination of the results with the resin 2-H-4-MAcUF-I indicates that Fe^{3+} and UO_2^{2+} ions require slightly more than three hours for the establishment of equilibrium, whereas Cu^{2+} and Ni^{2+} ions require about six hours. In experiments with solutions containing UO_2^{2+} and Fe^{3+} ions, about 60% equilibrium was established after 1 h. Mn^{2+} , Zn^{2+} and Co^{2+} ions required almost the same time, 7 h to reach equilibrium. The experiments reveal that the rate of metal ion uptake follows the order:



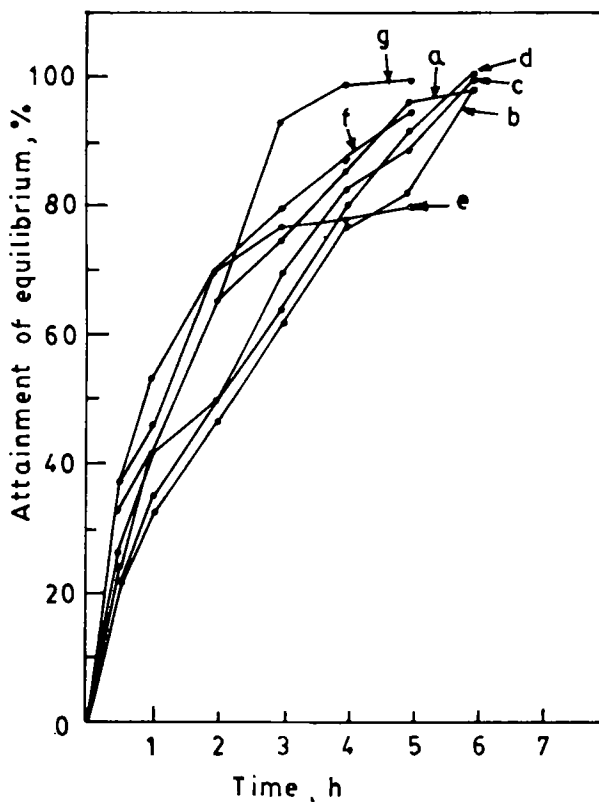
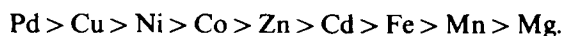


Figure 2. Rate of metal uptake by 2-H-4-MAcUF-I resin: (a) Cu(II); (b) Ni(II); (c) Co(II); (d) Zn(II); (e) Mn(II); (f) Fe(III); (g) $\text{UO}_2(\text{II})$.

3.4 Distribution ratio of metal ions at different pH levels

The study was carried out only up to pH 6 in order to prevent hydrolysis of the metal ions at a higher pH (figure 3). In the case of Fe^{3+} and UO_2^{2+} the highest value of the working pH range was 2.5. The UO_2^{2+} ion is taken up more selectively than any other metal ion under study. The lower distribution ratio of Fe^{3+} compared to that of UO_2^{2+} may be attributed to steric hindrance imposed by the polymer matrix which inhibits the completion of the $\text{Fe}^{\text{III}} d^2 sp^3$ hybrid with trimers of 2-H-4-MAcUF-I as opposed to the formation of the chelate of Fe^{III} with monomeric 2-H-4-MAc. UO_2^{2+} only needs dimers of 2-H-4-MAcUF-I for completion of its coordination requirement which is easily accomplished (DeGeiso *et al* 1962). Cu^{2+} and Ni^{2+} ions are taken up by resin in preference to Co^{2+} , Mn^{2+} and Zn^{2+} ions. Co^{2+} , Mn^{2+} and Zn^{2+} have low distribution ratios in the pH range 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; Davydova and Plate 1975). The possible order of preference of a cation exchange resin for divalent metal ions is (Irving and Williams 1956),



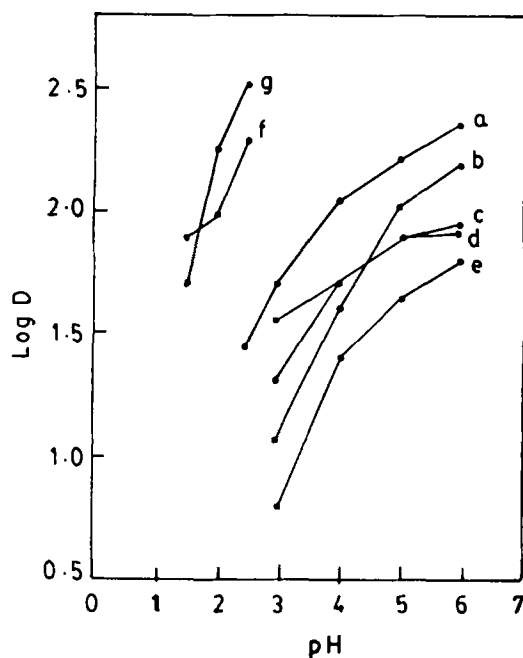
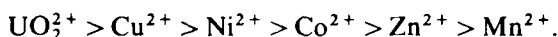


Figure 3. Distribution ratio of metal ions between aqueous solution and 2-H-4-MAcUF-1 resin at different pH values: (a) Cu(II); (b) Ni(II); (c) Co(II); (d) Zn(II); (e) Mn(II); (f) Fe(III); (g) $\text{UO}_2(\text{II})$.

In the present study, the observed order of distribution ratios of divalent ions, measured in the pH range 3 to 6 was found to be



Thus the results of this study are helpful in selecting the optimum pH for the selective uptake of a metal ion from a mixture of different ions. For example, the results suggest the optimum pH value of 2.5 for the separation of Cu^{2+} and Fe^{3+} ions, at which the distribution ratio D for Cu^{2+} is 28 and that of Fe^{3+} is 194. In order to assess the potentialities of separation of metal ions such as Fe^{3+} and UO_2^{2+} from other metal ions various combinations of metal solutions prepared were: (i) Fe^{3+} and Cu^{2+} , (ii) Fe^{3+} and Ni^{2+} , (iii) Fe^{3+} and Co^{2+} , (iv) Fe^{3+} and Zn^{2+} , (v) UO_2^{2+} and Cu^{2+} , (vi) UO_2^{2+} and Ni^{2+} , (vii) UO_2^{2+} and Co^{2+} , and (viii) UO_2^{2+} and Zn^{2+} . The solutions for separation were prepared by mixing 1 ml of a 1 M solution of either Fe^{3+} or UO_2^{2+} and 1 ml of a 1 M solution of Cu^{2+} , Ni^{2+} , Co^{2+} or Zn^{2+} ion. Selective uptake of the metal ion was studied by adjusting optimum pH values at 2.5 and 4.5. In the mixture the distribution ratio of Fe^{3+} was found to be 166 (table 3) which is slightly lower than the value 194 found when Fe^{3+} alone was studied. Similarly, in the mixture the distribution ratio of UO_2^{2+} was found to be 308 which is slightly lower than the value of 339 found when UO_2^{2+} alone was studied. The lowering of the distribution ratio may be due to the interference of the other metal ions present. However, decrease in the distribution ratio is smaller and hence efficient separation can be achieved.

Table 3. Separation of metal ion.

Mixture of metal ions	Distribution ratio of Fe ³⁺ at pH 2.5	Distribution ratio at UO ₂ ²⁺ at pH 2.5	Distribution ratio of M ²⁺ at pH 4.5*
Fe ³⁺ + Cu ²⁺	166.00		135.71
Fe ³⁺ + Ni ²⁺	159.14		89.42
Fe ³⁺ + Co ²⁺	151.83		64.28
Fe ³⁺ + Zn ²⁺	146.24		52.39
UO ₂ ²⁺ + Cu ²⁺		308.00	140.49
UO ₂ ²⁺ + Ni ²⁺		302.00	90.32
UO ₂ ²⁺ + Co ²⁺		299.93	63.76
UO ₂ ²⁺ + Zn ²⁺		293.18	54.61

* M²⁺ – metal ions such as Cu²⁺, Ni²⁺, Co²⁺ and Zn²⁺

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