

Synthetic Resins. XIII. Synthesis and Characterization of the Resins Derived from Quinacetophenone/Substituted Benzoic Acid/Furfuraldehyde

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SYNOPSIS

Some resins have been synthesized by reacting quinacetophenone with substituted benzoic acids and furfuraldehyde in the presence of basic catalysts. The resins have been characterized by IR spectra of the characteristic groups. The number average molecular weights of the resins have been evaluated by the conductance method. The solubility and viscosity behaviors of the resin copolymers have been determined. Cu^{+2} , Ni^{+2} , Co^{+2} , Mn^{+2} , and Mg^{+2} chelates have been prepared. The resins were shown to be selective ion-exchange resins for certain metal ions. A batch equilibrium method was used for studying the selectivity of the metal ions. The thermal behavior of the resins has been determined and the values of energy of activation of the resins were computed by using the Freeman-Anderson and Broido methods. The biological assays of some of the resin copolymers were found to be highly sensitive.

INTRODUCTION

In recent years, much attention has been focused on synthetic resins derived from hydroxy aromatic compounds because of their use as ligating reagents, ion exchangers, thermal stabilizers, and antibacterial and antifungal reagents.¹⁻¹⁸ *o*-Hydroxyacetophenones and *o*-hydroxybenzophenones have been reacted with formaldehyde for the preparation of several heat and light stabilizing reagents.¹⁹ Chelating ion-exchange resins have been prepared by condensing resacetophenone with formaldehyde in the presence of basic catalysts.²⁰ Sykora and Dubsy²¹ have prepared some cation exchange resins by condensing resacetophenone-anthranilic acid-formaldehyde in the presence of sodium hydroxide as catalyst. Parmar et al.^{22,23} have synthesized resacetophenone formaldehyde resins in acidic medium and studied their properties.

A survey of the literature reveals that resins have not been synthesized by using quinacetophenone (2,5-dihydroxyacetophenone) and furfuraldehyde.

In the present investigation, a number of resin copolymers have been synthesized by reacting quinacetophenone-substituted benzoic acid-furfural using sodium hydroxide as the catalyst.

These resins have been synthesized to compare the thermal, fungicidal, and bacteriocidal properties of the resin copolymers prepared by using resacetophenone (2,4-dihydroxyacetophenone). The comparison of the properties will be published in forthcoming publications. The polychelates of the resin copolymers with some metal ions like Cu^{+2} , Ni^{+2} , Co^{+2} , Zn^{+2} , Mg^{+2} , and Mn^{+2} have been synthesized. The resins have been characterized by using infrared spectroscopy, solubility behavior, etc. The thermal stability, ion-exchange properties, density, molecular weight, and bacteriocidal properties of the resins have been evaluated.

EXPERIMENTAL

Resin Synthesis

A mixture of 2,5-dihydroxyacetophenone (quinacetophenone, 0.2 mol), substituted benzoic acid (0.1 mol), and furfuraldehyde (0.1 mol) was refluxed at

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Table I Physicochemical Study of Resins Prepared from 2,5-Dihydroxy Acetophenone-Substituted Benzoic Acid-Furfural

Sample No.	Comonomer	Decomposition Temp (°C)	% Yield	Density	Solubility Parameter (δ) Ranges in Solvents	Solubility Parameter (δ) by Diff. Methods		\overline{M}_n
						Small	Hoy	
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	<i>o</i> -Hydroxybenzoic acid ^a	> 300	46	2.61	24.8°	24.89	24.81	—
2	<i>p</i> -Hydroxybenzoic acid ^b	> 300	49	2.41	18.6–24.8	21.87	21.42	1278
3	<i>o</i> -Hydroxybenzoic acid ^c	> 300	54	2.46	18.6–29.7	24.93	24.10	1145
4	<i>p</i> -Hydroxybenzoic acid ^a	> 300	52	2.42	21.7°	21.78	21.69	1110
5	<i>o</i> -Hydroxybenzoic acid ^c	> 300	57	2.37	21.9–24.8	22.95	22.38	1026
6	<i>p</i> -Hydroxybenzoic acid ^c	310	51	0.926	20.3–24.6	22.49	21.93	—
7	<i>o</i> -Hydroxybenzoic acid ^d	> 300	66	1.39	18.6–24.8	21.76	21.19	—
8	<i>p</i> -Hydroxybenzoic acid ^d	280	62	1.47	21.9–29.7	24.14	23.46	1350
9	<i>o</i> -Aminobenzoic acid ^a	> 300	58	0.886	18.6–29.7	24.67	23.85	—
10	<i>p</i> -Aminobenzoic acid ^a	> 300	62	0.831	20.9–29.7	25.38	24.84	—
11	<i>o</i> -Aminobenzoic acid ^b	> 300	56	.011	18.6–29.7	24.73	23.94	—
12	<i>p</i> -Aminobenzoic acid ^b	> 300	59	.907	18.6–29.7	24.54	24.03	—
13	<i>o</i> -Aminobenzoic acid ^c	220	64	.917	20.9–24.8	23.14	22.65	—
14	<i>p</i> -Aminobenzoic acid ^c	240	60	.994	21.9–29.7	25.87	25.63	—
15	<i>o</i> -Aminobenzoic acid ^d	> 300	63	.976	24.8°	21.83	21.51	—
16	<i>p</i> -Aminobenzoic acid ^d	> 300	59	.981	—	—	—	—
17	<i>o</i> -Chlorobenzoic acid ^a	290	41	1.39	18.6–29.7	24.32	24.09	—
18	<i>p</i> -Chlorobenzoic acid ^a	300	60	1.26	18.6–24.6	21.70	21.56	—
19	<i>o</i> -Chlorobenzoic acid ^b	> 300	52	1.27	—	—	—	—
20	<i>p</i> -Chlorobenzoic acid ^b	> 300	55	1.38	—	—	—	—
21	<i>o</i> -Chlorobenzoic acid ^c	310	63	1.56	—	—	—	—
22	<i>p</i> -Chlorobenzoic acid ^c	300	59	1.61	24.6°	23.85	23.35	—
23	<i>o</i> -Chlorobenzoic acid ^d	315	66	1.73	21.9–24.6	23.26	23.08	—
24	<i>p</i> -Chlorobenzoic acid ^d	> 300	68	1.87	21.9°	21.95	21.82	—

Catalyst used: ^asodium hydroxide; ^bpotassium hydroxide; ^ctriethyl amino; ^dpyridine.
^e swells.

120°C for 7–8 h in the presence of 40% NaOH (5 mL) with periodic shaking. After completion of the reaction, the contents were extracted with ice cold water, filtered, and washed repeatedly with hot water to remove the unreacted materials. The residue was dried in vacuum.

Some of the resins were also prepared using the catalyst, pyridine (95%, 5 mL), KOH (40%), and triethyl amine (5 mL) by the above method. The physicochemical properties of the resins are shown in Table I.

Chelate Synthesis

Method I

The resin copolymer was dissolved in a mixture of DMF–methanol (1 : 1) and the pH of the solution

was maintained at 7.5. To this solution, metal nitrate solution was added dropwise with constant stirring. The precipitated metal chelates were filtered, washed repeatedly, dried in vacuum, and collected.

Method II

The resin copolymer was dissolved in a mixture of DMF–methanol (1 : 1) and to this the metal acetate solution was added dropwise, with constant stirring, followed by the addition of sodium acetate solution. The entire solution was refluxed for 3 h. The product was cooled and washed repeatedly, dried in vacuum, and collected.

The density and inherent viscosity of the resins were determined by means of a pycnometer and Ubbelohde viscometer, respectively, in benzene and acetone at 30°C. The infrared (IR) spectra were re-

corded on a Shimadzu (Japan) spectrophotometer on KBr pellets. The thermogravimetric analysis (TGA) was made on a Hungarian MDM Darivatograph of the Pauliu-Erdey system at a heating rate of 10°C/min in air.

A digital Systronics (India) conductance bridge was used for conductometric titrations. The titration vessel was stirred with magnetic stirrer which was switched off during each measurement. The titrations were performed at room temperature with a 2–3 min wait after each addition of titrate to obtain an equilibrium reading. Approximately, 0.05 g of the copolymer was taken. Propyl alcohol was used as the medium of titration and tetra(methyl-ammonium hydroxide) was used as the titrant base. The reproducibility of each titration has been checked and found to be within $\pm 1-2\%$.

Resins numbering 1–6 (Table VIII) were used for studying the bacteriological properties. The following bacteria were used.

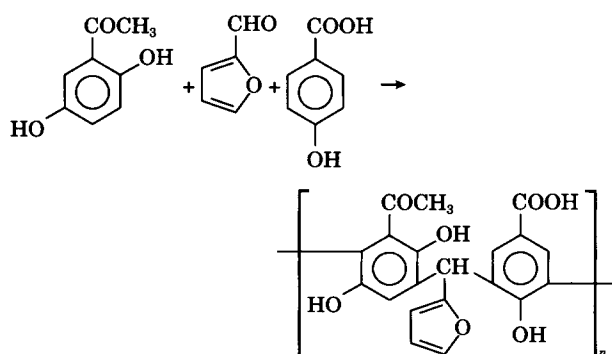
- (i) *Escharichia coli* (*E. coli*)
- (ii) Nonlactose formenter (Nlf)
- (iii) *Klebsila pneumoniae* (Kleb)
- (iv) *Pseudomonas aeruginosa* (Pseu)
- (v) *Streptococcus visidius* (Stv.)
- (vi) *Staphylococcus spidermis* (Staph)

The bacteria cultures were grown in a nutrient bottle and 3 h young cultures were used for the test.

RESULTS AND DISCUSSION

Infrared Studies

The polycondensation reaction of quinacetophenone with furfuraldehyde and *p*-hydroxy benzoic acid may be represented as follows:



The IR spectra of some of the resin copolymers have been taken. The structure of the repeat unit of the above resin was identified from IR spectra of the copolymer.

The bands in the region (3300–3400 cm^{-1}) suggest the presence of OH group (intermolecular hydrogen bonding). The peaks at 1725 and 1690 cm^{-1} are as-

signed to the $\text{C}=\text{O}$ stretching of the $\text{C}=\text{O}-\text{CH}_3$ group which is considerably reduced due to the presence of hydrogen bonding. A peak at 1575 cm^{-1} may be attributed to the carboxylate anionic stretching.

Molecular Weight Determination

Figure 1 shows the conductometric titration curve of the resins prepared from (a) quinacetophenone-furfural-*o*-hydroxybenzoic acid, (b) quinacetophenone-furfural-*p*-hydroxybenzoic acid, and (c) quinacetophenone-furfural-*o*-aminobenzoic acid against tetramethylammonium hydroxide as the titrant base. Examination of the conductometric titration curves reveals that there are several breaks in the plot of specific conductance against millimoles of the titrant base added per 100 g copolymer. The titration curve as shown in Figure 1 comprises a decrease in conductance followed by a step by step increase and then decrease, and, after neutralization, a continued straight line is noted. The calculation of \bar{M}_n (number average molecular weight) values

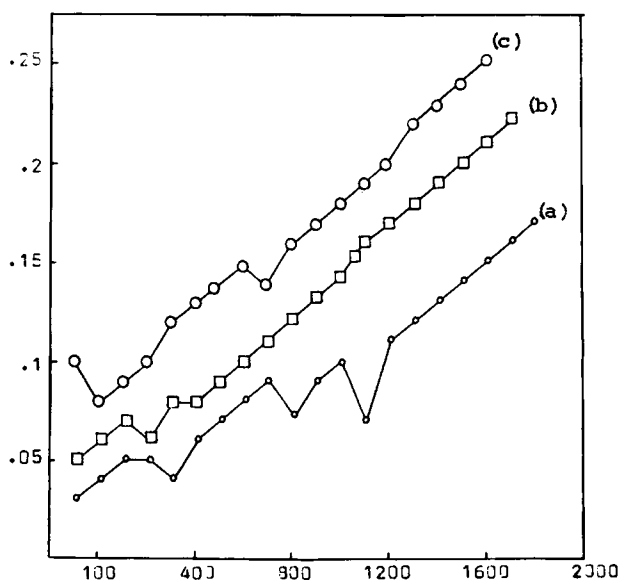


Figure 1 Conductometric titration curve of the resin: (a) quinacetophenone-furfural-*o*-hydroxybenzoic acid; (b) quinacetophenone-furfural-*p*-hydroxybenzoic acid; (c) quinacetophenone-furfural-*o*-aminobenzoic acid.

was based on the method of Chatterjee et al.²⁴⁻²⁶ The first break corresponds to the neutralization of the more acidic phenolic hydroxy group of all the repeating units. Further, the second break in the plot represents the stage at which both types of phenolic hydroxyl group of all types of repeat units are neutralized. On this basis, the average degree of polymerization (\overline{DP}) is represented by the equation:

$$\overline{DP} = \frac{(\text{Total mg base required for complete neutralization})/2}{\text{mg base for the smallest interval}}$$

The smallest interval between successive breaks in the titration curve is 300. The degree of polymerization can be obtained by dividing the total amount of base added to neutralize all the hydroxyl groups in the chain by the amount added during the shortest interval. The average degree of polymerization of the resins can therefore be calculated. The product of average degree of polymerization and the formula weight of the repeat units provides the average molecular weight of the polymer. The number-average molecular weight of the resin copolymer prepared by condensing quinacetophenone-furfuraldehyde and benzoic acid is calculated and furnished in Table I.

Solubility Behavior

Nearly 0.02 g resin copolymer was placed in 2 mL of different solvents such as benzene, acetone, carbon tetrachloride, dimethyl sulfoxide, and tetrahydrofuran, etc. and allowed to stand for about 2 weeks.²⁷ The solubility parameter ranges of the resins in different solvents are furnished in Table I.

Most of the resin copolymers were found to be insoluble in the solvents. However, they were found to swell considerably. This fact may be attributed to higher molecular weight of the resin copolymers. The solubility parameter (δ) values are computed from the solubility parameter (δ) vs. hydrogen bonding index (ν) for different solvents as shown in Figure 2.

The solubility parameter has also been computed from Small's group contribution method using the molar attraction constant (G) values reported by Small²⁸ and Hoy^{29,30} using the relationship

$$\delta = \rho G/M$$

where $\sum G$ is the sum of group molar attraction constant, M is the molecular weight of the repeat unit, and ρ is the density of the resin copolymer.

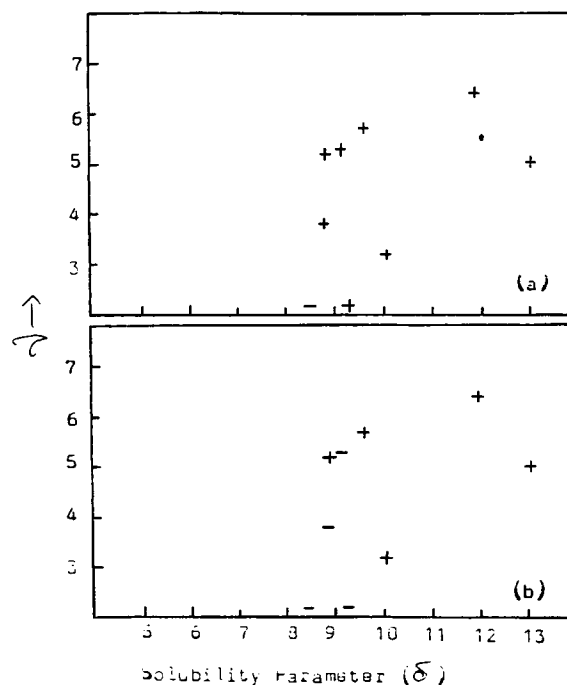


Figure 2 Solubility map of the resin: (a) quinacetophenone-furfural-*p*-chlorobenzoic acid; (b) quinacetophenone-furfural-*o*-aminobenzoic acid.

The values obtained are furnished in Table I for comparison. It can be seen that the values obtained by Small's method are slightly higher than those of Hoy's values. However, this discrepancy in the second decimal is considered negligible.

Further, as seen from Table II, the solubility of the chelates is comparatively lower than their precursor resins and in some cases they are almost insoluble.

Viscosity Behavior

Intrinsic viscosity was computed by using the Huggins³¹ and Kramer³² equation. The Martin³³ equation was used to check the authenticity of the Huggins and Kramer equation. The values are presented in Table III:

$$\frac{\eta_{sp}}{C} = (\eta) + k_H + (\eta)C^2 \quad \text{due to Huggins}$$

$$\frac{\ln \eta_{rel}}{C} = (\eta) - k_K(\eta)C^2 \quad \text{due to Kramer}$$

$$\frac{\ln \eta_{sp}}{C} = \ln(\eta) + k_M(\eta)_c \quad \text{due to Martin}$$

The intrinsic viscosity value of the resins obtained from Huggins-Kramer and Martin equations as

Table II Physicochemical Study of Chelates Prepared from 2,5-Dihydroxy Acetophenone Resins

Sample No.	Comonomer	Metal Ion Used	Decomposition Temp	% Yield	Density	Solubility Parameter (δ) Ranges in Solvents	Solubility Parameter (δ) by Diff. Methods	
							Small	Hoy
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1	<i>o</i> -Chlorobenzoic acid	Chromium	290	55	0.728	—	—	—
2	—do—	Manganese	> 300	60	0.819	21.5–24.8	22.82	22.40
3	—do—	Zinc	300	45	0.953	—	—	—
4	—do—	Nickel	290	65	0.871	—	—	—
5	—do—	Cobalt	> 300	48	0.762	24.6 ^a	24.72	24.38
6	—do—	Magnesium	> 300	44	0.923	—	—	—
7	—do—	Copper	> 300	46	0.841	20.9–24.8	22.53	21.87
8	<i>p</i> -Chlorobenzoic acid	Chromium	280	56	1.231	—	—	—
9	—do—	Manganese	> 300	40	1.005	24.8–29.7	27.30	26.82
10	—do—	Zinc	> 300	46	1.2	—	—	—
11	—do—	Nickel	300	52	1.156	—	—	—
12	—do—	Cobalt	290	61	1.123	—	—	—
13	<i>p</i> -Chlorobenzoic acid	Magnesium	> 300	55	0.978	28.7 ^a	28.9	28.14
14	—do—	Copper	> 300	49	1.456	—	—	—
15	<i>p</i> -Aminobenzoic acid	Chromium	310	62	1.386	—	—	—
16	—do—	Manganese	> 300	64	1.237	—	—	—
17	—do—	Zinc	> 300	48	1.431	21.9 ^a	22.04	21.75
18	—do—	Nickel	260	56	1.235	—	—	—
19	—do—	Cobalt	> 300	62	0.970	18.6–20.9	19.64	19.31
20	—do—	Magnesium	290	58	1.105	—	—	—
21	—do—	Copper	> 300	51	1.121	—	—	—

shown in Table III vary in the second decimal but that can be attributed to the mode of calculation.

The $k_H + k_K$ value is 0.489 for the quinacetophenone-*p*-hydroxy benzoic acid-furfural resins, 0.491 for quinacetophenone-*p*-amino benzoic-furfural resins, and 0.501 for quinacetophenone-*p*-chloro benzoic acid-furfural resins. These are in good agreement with theoretical values of 0.5 as reported by Maron and Reznik.³⁴

Ion-Exchange Properties

The influence of various electrolytes in the selectivity of ions, rate of metal uptake, and distribution

ratio (D) between the copolymer and solution containing the metal ions have been investigated. A large number of metal ions have been used in the present investigation for this study.

Effect of Electrolyte on the Metal Uptake

The effect of different electrolytes such as chloride, sulfate, nitrate, and perchlorate ions at various concentrations on uptake of several metal ions by the resin copolymer is furnished in Table IV. The results indicate that the amount of Cu^{+2} , Zn^{+2} , Mn^{+2} , Mg^{+2} , Co^{+2} , and Ni^{+2} taken up by the resin (as noted in Table IV) increases with increase in con-

Table III Viscometric Data of 2,5-Dihydroxy Acetophenone Resins

Sample No.	Name of Copolymer	Huggin-Krammerea	Martinea	R_H	R_K	Constants	
		η_{H-K}	η_M			$R_H + R_K$	R_M
1	<i>p</i> -Hydroxybenzoic acid-furfural	2.45	2.490	0.323	0.166	0.489	2.581
2	<i>p</i> -Aminobenzoic acid-furfural	2.05	2.21	0.324	0.167	0.491	2.623
3	<i>p</i> -Chlorobenzoic acid-furfural	1.87	1.88	0.305	0.196	0.501	3.074

Table IV Evaluation of the Effect of Different Electrolytes in Uptake of Several Metal Ions^a

Sample No.	Metal Ion	Electrolyte (mol/L)	pH	Weight (mmol) of Metal Ion Uptake in the Presence of					
				NaCl	NaNO ₃	KCl	KNO ₃	No ₂ So ₄	KClO ₄
(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(10)
	Co ⁺²	0.01	6	2.09	2.57	2.11	1.81	1.56	1.71
		0.05		2.22	2.80	2.31	2.00	1.25	1.88
		0.1		2.46	2.91	2.61	2.25	1.11	2.00
		0.5		2.75	3.10	2.72	2.47	0.91	2.12
	Mn ⁺²	0.01	9.5	2.28	2.00	2.75	2.2	1.44	2.61
		0.05		2.47	2.33	2.94	2.47	1.39	2.94
		0.1		2.75	2.47	3.27	2.75	1.15	3.19
		0.5		2.94	2.47	3.46	2.94	0.98	3.46
	Zn ⁺²	0.01	6	2.27	2.36	2.1	2.1	2.14	1.02
		0.05		2.44	2.6	2.1	2.43	1.96	1.11
		0.1		2.57	2.8	2.38	2.43	1.85	1.26
		0.5		2.59	2.92	2.60	2.66	1.50	1.35
	Mg ⁺²	0.01	9.5	0.42	0.44	1.11	1.17	1.92	1.88
		0.05		0.63	0.57	1.29	1.32	1.74	2.25
		0.1		0.69	0.48	1.41	1.35	1.52	3.06
		0.5		0.87	0.66	1.47	1.8	1.32	3.31
	Cu ⁺²	0.01	10	2.4	1.9	1.90	2.15	1.80	1.87
		0.05		1.73	2.15	2.21	2.43	1.50	2.00
		0.1		1.90	2.26	2.38	2.71	1.30	2.25
		0.5		2.01	2.38	2.60	3.14	1.11	2.42
	Ni ⁺²	0.01	10	2.42	2.66	1.25	1.39	1.73	2.32
		0.05		2.66	2.86	1.44	1.50	1.66	2.54
		0.1		2.86	3.02	1.73	1.87	1.46	2.8
		0.5		2.97	3.21	1.80	2.25	1.30	2.96

^a Volume of electrolyte solution = 25 mL, time 24 h; volume of metal ion soluble = 2 mL, room temperature. [(NO₃)₂] = 0.1 mol L⁻¹.

centration of electrolyte but a decreasing trend is noticed in case of sulfate ions. The increasing trend may be explained in the light of the stability con-

stants of these complexes.³⁵⁻³⁷ Sulfate ion might form rather strong chelates with the above metal ions while the other ions under investigation form

Table V Comparison of Rates of Metal Ion Uptake in Different Times^a

Metal Ion	% of Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
Cu ⁺²	15.5	27.5	37.5	43	58.5	69	80	97
Zn ⁺²	24.2	31	44	59.5	66	73	78	83
Mn ⁺²	30	32	41	55	61	69	76	80
Co ⁺²	25.5	33	45	53	54	68	85	94
Mg ⁺²	22.5	29.5	40.5	47	52	64	71	74
Ni ⁺²	18	26	35.5	48.5	60	65	74	85

^a (mmol metal ion adsorbed × 100)/(mmol metal ion adsorbed at equilibrium), [(NO₃)₂] = 0.1 mol/L, volume = 2 mL, NaNO₃ = 1 mol/L, volume = 25 mL, pH = 6, room temperature.

Table VI Distribution Ratio D^a of Different Metal Ions as a Function of pH

Sample No.	Metal Ion	pH				
		2	3	4	6	8
1	Cu ⁺²	6.06	9.72	22.51	67.83	81.24
2	Zn ⁺²	9.19	31.09	53.7	72.50	79.76
3	Mn ⁺²	7.52	28.56	56.24	70.74	91.84
4	Co ⁺²	12.44	20.26	51.38	86.60	101.4
5	Mg ⁺²	4.64	10.64	48.82	66.00	82.00
6	Ni ⁺²	11.23	16.25	25.51	64	80.2

$$^a D = \frac{\text{mmol metal ion on the copolymer}}{\text{mmol metal ion in solution}} \times \frac{\text{volume solution}}{\text{weight copolymer}}$$

[(NO₃)] = 0.1 mol/L, volume = 2 mL, NaNO₃ = 1 mol/L, volume = 25 mL, time = 24 h, room temperature.

weak chelates and, therefore, might not be expected to influence the position of the metal chelates equilibrium to the extent expected for the sulphate ion.

Rate of Metal Uptake

In Table V, the dependence of the rate of metal ion uptake on the nature of metal ion is shown. The rate of metal adsorption was studied to ascertain the shortest period of time for which the equilibrium could be established. Results indicate that these ions require different time periods for their equilibrium. The rate of metal uptake follows the order:

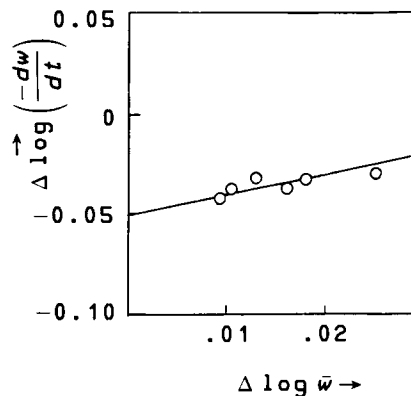
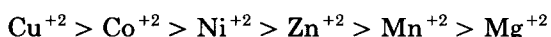


Figure 3 Typical Freeman-Anderson plot of the resin: quinacetophenone-furfural-*p*-aminobenzoic acid.

Distribution Ratio of Metal Ion at Different pH

The effect of pH on the amount of metal ion distribution is shown in Table VI. From the results, it is evident that the relative amount of metal ions taken up by the copolymer increases with increasing pH value of the medium. This investigation was carried out up to a definite pH value, i.e., up to pH 6 for the particular metal ions to prevent hydrolysis of metal ion at higher pH.

Further, it is evident that Co⁺², Mn⁺², and Cu⁺² ions are taken up more selectively by the copolymer than Zn⁺² and Mn⁺² ions. The low distribution ratio of Mn⁺² and Zn⁺² ions may be explained by considering the stability constants, i.e., weak ligand stabilization of metal complexes.³⁵⁻³⁷ The observed order of the distribution ratio of divalent metal ions

Table VII Thermal Data of the 2,5-Dihydroxy Acetophenone Resins

Sample No.	Name of Polymer	Decomposition Percentage at Different Temp										E^* by Diff. Methods ^a				
		100	200	300	400	500	600	700	800	900	Broido	F-A	CR	OI	t_g	
1	Quinoacetophenone-furfural- <i>o</i> -hydroxybenzoic acid	5.9	10.00	15	29.00	34.00	54	62	74	—	13.78	13.82	35	30.4	215	
2	Quinoacetophenone-furfural- <i>p</i> -hydroxybenzoic acid	4.1	8.6	19	32.00	42	56	64	79	—	12.25	12.41	21	65.2	265	
3	Quinoacetophenone-furfural- <i>o</i> -chlorobenzoic acid	4.8	9.5	13	35.00	41	58	62	70	—	5.35	5.55	30	43.8	280	
4	Quinoacetophenone-furfural- <i>p</i> -chlorobenzoic acid	7.2	12	17	23.5	38	55	66	71	79	17.6	17.72	32	41.00	320	
5	Quinoacetophenone-furfural- <i>p</i> -aminobenzoic acid	6.7	14	15	27	39	62	68	73	—	16.62	16.83	29	32	340	

^a E^* = activation energy.

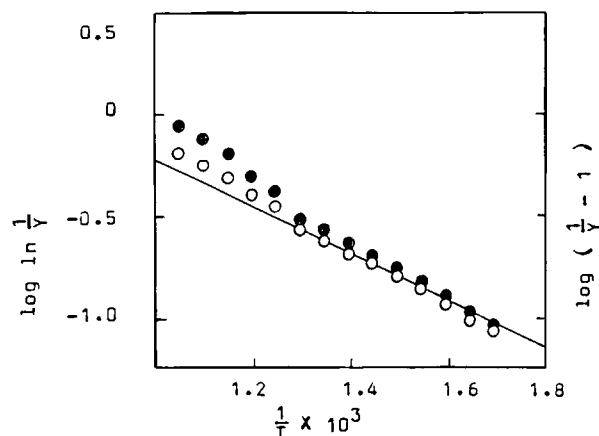


Figure 4 Typical Broido plot of the resin: quinoacetophenone-furfural-*o*-chlorobenzoic acid.

in the pH range of 2–6 is same as reported by Irving and Williams.³⁸ The results of this study are helpful in selecting the optimum pH for a selective uptake of metal ion from a mixture of different ions.

Thermal Behavior

The TG thermograms of the resin copolymer from quinoacetophenone, substituted benzoic acid, and furfuraldehyde in presence of different catalysts are shown in Table VII. The degradation of these resins follows a complex process. The initial weight losses up to 200°C are due to the removal of water. The 50% weight loss of all the resins occurs at about 600°C. Almost all the resins show 100% decomposition beyond 900°C. This indicates that the resins have very high decomposition temperature. The resins prepared from quinoacetophenone-furfural-

dehyde-*p*-chlorobenzoic acid decompose at higher temperature than the other four resins studied. The char residue, oxygen index, and glass transition temperature of the resins have been calculated by the following equation³⁹:

$$\text{OI} + 100 = 17.5 + 4 \text{ CR}$$

where OI = oxygen index and CR = char residue, and are furnished in Table VII.

In order to determine the mechanism of decomposition, kinetic parameters have been evaluated using the Freeman and Anderson⁴⁰ and the Broido⁴¹ methods. The former method involves the evaluation of quantities $\log(-dw/dt)$ and $\log \bar{W}$ corresponding to a constant difference in $1/T$ as shown below. According to

$$\log\left(-\frac{dw}{dt}\right) = n \Delta \log \bar{W} - \frac{E^*}{2.303R} \Delta \frac{1}{T}$$

The slope of the plot of $\Delta \log(-dw/dt)$ vs. $\Delta \log \bar{W}$ gives n , the order of reaction, and the intercept gives E^* , the energy of activation.

The Broido method is based on the equation,

$$\log\left(\ln \frac{1}{Y}\right) = \frac{E^*}{2.303R} \frac{1}{T} + K$$

The energies of activation of the polymers calculated by using the Freeman-Anderson (Fig. 3) and Broido (Fig. 4) methods are furnished in Table VII.

Biological Assays

The biological assay was carried out by a modified method of Carraher et al.⁴² The organism from the

Table VIII Bacteriological Results of Copolymers^a

Sample No.	Name of Polymer	<i>E. coli</i>	Nif	Kleb	Pseu	Stv.	Staph.
1	Quinoacetophenone-furfural- <i>p</i> -hydroxybenzoic acid	HS	HS	MS	MS	HS	HS
2	Quinoacetophenone-furfural- <i>o</i> -hydroxybenzoic acid	HS	MS	WS	WS	MS	HS
3	Quinoacetophenone-furfural- <i>o</i> -aminobenzoic acid	WS	WS	MS	MS	WS	MS
4	Quinoacetophenone-furfural- <i>p</i> -aminobenzoic acid	WS	WS	WS	MS	MS	WS
5	Quinoacetophenone-furfural- <i>o</i> -chlorobenzoic acid	MS	HS	HS	MS	WS	MS
6	Quinoacetophenone-furfural- <i>p</i> -chlorobenzoic acid	MS	HS	WS	MS	MS	MS

^a HS = highly sensitive; WS = weakly sensitive; MS = moderately sensitive; NS = not sensitive.

culture sensitivity disc was taken and dipped into the test tube containing the broth solution. The tube was put inside an incubator for 2–3 hours at a temperature of 37°C. Then the broth solution was spread over the Agar plate and the excess of the solution was decanted. The resin was dissolved in DMS and was applied to the discs at different places on the Agar plate. The plate was kept inside the incubator overnight and the bacterial inhibition was noted. The results are furnished in Table VIII.

A perusal of the results indicate that most of the resins are highly sensitive to the bacteria studied. Out of the six resin copolymers studied in the present investigation, the resin copolymer prepared from quinacetophenone–furfural–*p*-hydroxybenzoic acid is highly sensitive to most of the bacteria. Further work in this area is under progress.

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