Synthetic Resins. XII. Synthesis and Characterization of the Resins Derived from Resacetophenone–Substituted Benzoic Acids–Furfural

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SYNOPSIS

A number of resin copolymers have been synthesized by condensing resacetophenone with substituted benzoic acids and furfural in the presence of some base as catalyst. The resins have been characterized by IR spectra of the characteristic groups. The number-average molecular weights of the resins have been determined by the conductance method. The solubility and viscosity behavior of the resins have been determined. Cu^{2+}, Ni^{2+}, Co^{2+}, Mn^{2+}, Zn^{2+}, and Mg^{2+} chelates have been prepared. The resins were shown to be selective ion exchangers for certain metal ions. The batch equilibrium method was used to study the selectivity of the metal ions. The thermal behavior of the resins has been determined. The values of energy of activation of the degradation of the resins were computed by using the Freeman-Anderson and Broido methods. The biological assays of some of the resins have been evaluated, and some of them were found to be highly sensitive to the bacteria studied.

INTRODUCTION

Synthetic resins derived from hydroxy aromatic compounds have attracted the attention of many research workers in the recent years because of their versatile use as ligating agents, ion exchangers, thermal stable compounds, and antibacterial and antifungal activities.[1-18] Hydroxy acetophenones such as o-hydroxy acetophenone and some of its derivatives and o-hydroxy benzophenone have been condensed with formaldehyde in the presence of acid catalysts for the preparation of several heat and light stabilizing resins.[19] Pennigton and Williams[20] have prepared chelating ion-exchange resins by condensing resacetophenone with formaldehyde in the presence of sodium hydroxide as the catalyst. These resins were used in chromatographic separation of Cu^{2+}, Ni^{2+}, and Co^{2+} ions. Sykora and Dubsky[21] have reported the preparation of cation exchange resins by condensing resacetophenone–anthranillic acid–formaldehyde in presence of sodium hydroxide as catalyst. Parmar et al.[22,23] have synthesized res-acetophenone–formaldehyde resins in acidic medium and studied their chelation ion-exchange properties. A survey of the literature reveals that no systematic studies have been undertaken using furfural as the condensing agent. The introduction of a furan ring into the polymeric chain might enhance their thermal and other properties.

In the present investigation a number of resin copolymers have been synthesized by condensing resacetophenone–substituted benzoic acid–furfural using sodium hydroxide as the catalyst. The polychelate of the resin copolymers with some metal ions like Cu^{2+}, Ni^{2+}, Co^{2+}, Zn^{2+}, Mg^{2+}, and Mn^{2+} have been prepared. The resins have been characterized by using infrared spectra, solubility behavior, etc. The thermal stability, ion-exchange properties, density, molecular weight, and the bacteriocidal properties of the resins have been evaluated, and many interesting results have been obtained.

EXPERIMENTAL

Resin Synthesis

A mixture of 2,4-dihydroxy acetophenone (0.2 mol) (resacetophenone), substituted benzoic acid (0.1

mol), and furfural (0.1 mol) was refluxed at 120°C for 7–8 h in the presence of 40% NaOH (5 mL) with periodic shaking. After the 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 then dried at vacuum.

Some of the resins were also prepared using the catalyst, pyridine (95%, 5 mL), KOH (40%), and triethylamine (5 mL) by adopting the above method.

The physico-chemical properties of the resins are furnished 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 then filtered and washed repeatedly. It was then dried at vacuum and collected.

Method II

The resin copolymers were 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, filtered, and washed repeatedly, dried at vacuum and collected.

The density and intrinsic viscosity of the resins were determined by means of a pycnometer and Ubbelohde viscometer, respectively, in benzene and

Table I   Physico-Chemical Study of Resins Prepared from 2,4-Dihydroxy Acetophenone–Substituted Benzoic Acid–Furfural

Solution	Comonomer[a]	Decomposition Temp. (°C)	% Yield	Density	Solubility Parameter Ranges in Solvents	Solubility Parameter (δ) by Different Methods		$\overline{M}_n$
						Small	Hoy	
1	2	3	4	5	6	7	8	9
1	o-Hydroxy benzoic acid (1)	>300	62	0.327	—	—	—	—
2	p-Hydroxy benzoic acid (1)	>300	64	0.722	—	—	—	—
3	o-Hydroxy benzoic acid (2)	>300	49	0.528	20.9–24.8	22.85	21.93	1207
4	p-Hydroxy benzoic acid (2)	290	41	0.686	18.6–24.6	21.75	21.08	934
5	o-Hydroxy benzoic acid (3)	⩾300	54	1.1	20.3	20.41	20.29	1028
6	p-Hydroxy benzoic acid (3)	310	58	2.61	18.6–29.7	24.41	23.82	990
7	o-Hydroxy benzoic acid (4)	285	59	1.47	21.5–29.7	25.73	24.76	1169
8	p-Hydroxy benzoic acid (4)	270	66	0.726	—	—	—	—
9	o-Amino benzoic acid (1)	>300	65	2.52	19.2–24.8	22.59	21.89	—
10	p-Amino benzoic acid (1)	>300	49	0.417	20.3–29.7	25.64	25.12	—
11	o-Amino benzoic acid (2)	>300	64	0.881	19.2–24.7	22.62	21.82	—
12	p-Amino benzoic acid (2)	>300	48	0.968	24.6	26.71	24.52	—
13	o-Amino benzoic acid (3)	>300	68	0.271	24.8–29.7	26.72	26.14	—
14	p-Amino benzoic acid (3)	300	41	0.562	18.8–29.7	24.54	23.82	—
15	o-Amino benzoic acid (4)	310	44	0.610	20.3–21.9	20.95	20.32	—
16	p-Amino benzoic acid (4)	>300	66	0.738	18.2–20.3	19.95	19.46	—
17	o-Chloro benzoic acid (1)	295	55	0.735	19.2–24.7	22.75	22.21	—
18	p-Chloro benzoic acid (1)	290	58	0.824	20.3–24.6	22.94	22.15	—
19	o-Chloro benzoic acid (2)	>300	60	1.26	18.2–24.8	21.72	21.48	—
20	p-Chloro benzoic acid (2)	>300	64	1.48	21.5–29.7	26.23	25.89	—
21	o-Chloro benzoic acid (3)	>300	61	1.20	20.9–24.6	22.15	21.94	—
22	p-Chloro benzoic acid (3)	>300	49	2.05	21.5–24.8	23.24	22.89	—
23	o-Chloro benzoic acid (4)	280	51	2.21	19.2–24.7	21.5	21.24	—
24	p-Chloro benzoic acid (4)	>300	54	1.23	18.6–29.7	24.3	23.75	

[a] Numbers in parentheses indicate catalyst used: (1) sodium hydroxide, (2) potassium hydroxide, (3) triethyl amine, and (4) pyridine.

acetone at 30°C. The infrared (IR) spectra were recorded on a Shimadzu (Japan) spectrophotometer on KBr pellets. The thermogravimetric analysis (TGA) were made on a Hungarian MOM Derivatograph of the Pauliu-Erdey system at a heating rate of 10°C/min in air.

A digital Systronics conductance bridge was used for conductometric titrations. The titration vessel was stirred with a magnetic stirrer that was switched off during each measurement. The titrations were performed at room temperature and 2–3 min was used after each addition of titrant to obtain equilibrium reading. Approximately 0.05 g of the copolymer was taken. Propyl alcohol was used as the medium of titration and tetramethylammonium hydroxide was used as the titrant base. The reproducibility of each titration curve has been checked and found to be within ±1–2%.

The compounds numbering 1, 2, 3, 4, 5, 6 (Table VIII) were used for studying the bacteriocidal properties. The following bacteria were used.

1. *Escharichia coli* (*E. coli*).
2. *Nonlactose fermentor* (Nlf)
3. *Klebsila pneumoniae* (Kleb)
4. *Pseudomonas aeruginosa* (Pseudo)
5. *Streptococcus viridius* (Stv)
6. *Staphylococcus epidermis* (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 resacetophenone with furfural and p-hydroxy benzoic acid may be represented as follows:
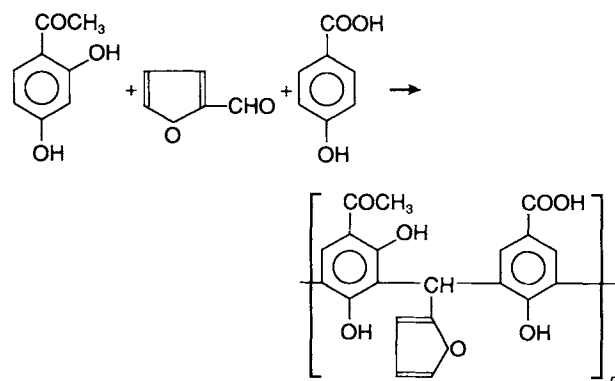
The IR spectra of some of the resin copolymers have been taken. The structure of the repeat unit of this resin was identified from IR spectra of the polymer.

The bands in the region (3300–3400 cm^{-1}) suggest the presence of an OH group (intermolecular hydrogen bonding). The peaks at 1275 cm^{-1} and 1690 cm^{-1} are assigned to the $-\overset{\overset{\text{O}}{\|}}{\text{C}}-$ stretching of the $-\overset{\overset{\text{O}}{\|}}{\text{C}}-CH_3$ group, which are considerably reduced due to the presence of hydrogen bonding. Bands appearing in the 1005–1160 cm^{-1} region are attributed to C–H in-plane bending. The bands in the 1460–1600 cm^{-1} region are attributed to C$=$C stretching (aromatic vibrations). The band around 855 cm^{-1} is due to 1,2,3,4-tetra-substituted phenyl ring. Bands appearing in a the range of 960, 915, and 860 cm^{-1} suggest the presence of furan ring.

Molecular Weight Determination

Figure 1 shows the conductometric titration curve of the resin prepared from resacetophenone–furfural–o-hydroxy benzoic acid against tetramethyl ammonium hydroxide as the titrant base. The examination of the conductometric titration curves
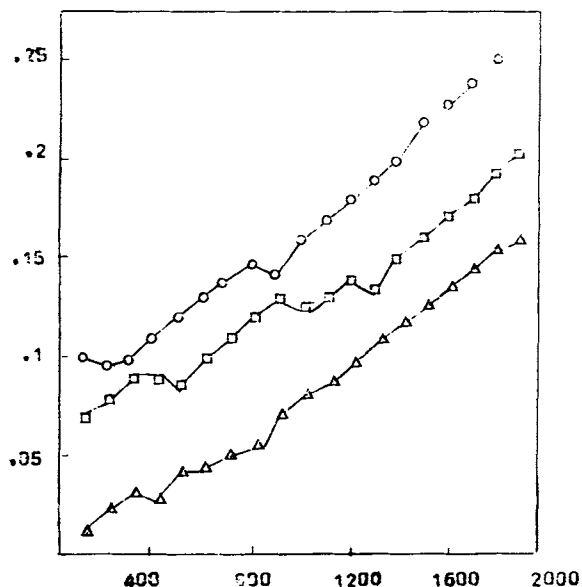

Figure 1 Conductometric titration curve of (a) resacetephenone–furfural–p-hydroxy benzoic acid; (b) resacetephenone–furfural–o-hydroxy benzoic acid; (c) resacetephenone–furfural–p-amino benzoic acid.

revealed that there were several breaks in the plot of specific conductance against millimoles of titrant base added per 100 g of the copolymer. The titration curve as shown in Figure 1 comprises the decrease in conductance followed by step-by-step increase and then decrease and after the neutralization a continued straight line is marked. The calculation of $\bar{M}_n$ (number-average molecular weight) values were based on the method of Chatterjee et al.[24-26] The first break corresponds to the neutralization of a more acidic phenolic hydroxyl group of all the repeating units. Further, the break in the plot beyond which continuous increase in the observed values represents the stage for which both the type 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

$$\overline{DP} = \frac{\text{Total meq. of base required for complete neutralization}/2}{\text{meq. of base for the smallest interval}}$$

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 resin thus can be calculated. The product of the 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 resacetophenone–furfural and benzoic acid has been calculated by employing this method.

Solubility Behavior

Nearly 0.02 g of the resin copolymer was placed in 2 mL of different solvents and allowed to stand for about 2 weeks.[27] The solubility parameter range of the resins in different solvents are furnished in Table I.

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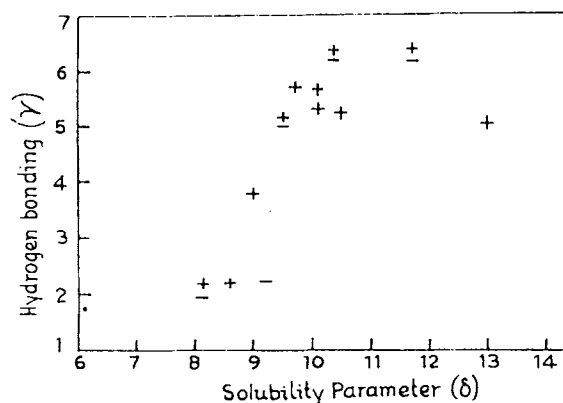

Figure 2 Solubility map of the resin resacetophenone-furfural-p-aminobenzoic acid.

The solubility parameter has also been computed from Small's group contribution method using the molar attraction constant (G) values reported by Small[28] and Hoy[29,30] using the following relationship:

$$\delta = \rho\left(\frac{\Sigma G}{M}\right)$$

where ΣG 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 polymer.

The values obtained are furnished in Table I for comparison. It can be seen that the values obtained by using Small's method were a little higher than those obtained by Hoy's method. However, this little discrepancy in the second decimal can be very well neglected.

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

Viscosity Behavior

Intrinsic viscosity was computed by using the Huggins[31] and Krammer[32] equations. The Martin[33] equation was also used to check the authenticity of the Huggins and Krammer equations. The values are presented in Table III.

$$\frac{\eta_{sp}}{C} = [\eta] + \kappa_H + [\eta]^2 C \quad \text{due to Huggins}$$

$$\ln\frac{\eta_{rel}}{C} = [\eta] - \kappa_K[\eta]^2 C \quad \text{due to Krammer}$$

$$\ln\frac{\eta_{sp}}{C} = \ln[\eta] + \kappa_M[\eta] C \quad \text{due to Martin}$$

Table II Physico-Chemical Study of Chelates Prepared from 2,4-Dihydroxy Acetophenone Resins

Solution	Comonomer	Metal Ion Used	Decomposition Temp. (°C)	% Yield	Density	Solubility Parameter Ranges in Solvents	Solubility Parameter (δ) by Different Methods	
							Small	Hoy
1	o-Chloro benzoic acid	Chromium	240	66	0.441	19.2–24.6	21.98	21.42
2	-do-	Manganese	290	72	0.726	18.2–24.8	22.76	22.15
3	-do-	Zinc	>300	64	0.611	21.9[a]	22.12	21.85
4	-do-	Nickel	280	52	0.399	20.9–29.7	25.64	24.97
5	-do-	Cobalt	>300	59	1.76	24.8–29.7	27.25	26.76
6	-do-	Magnesium	>300	44	1.52	20.3–24.6	22.54	22.13
7	-do-	Copper	260	58	1.61	24.8[a]	24.94	24.08
8	p-Chloro benzoic acid	Chromium	250	56	1.92	21.9–29.7	25.95	25.43
9	-do-	Manganese	>300	67	2.686	19.2[a]	19.31	18.84
10	-do-	Zinc	>300	60	2.05	20.3–24.8	22.51	22.64
11	-do-	Nickel	295	58	3.14	17.5–20.3	19.6	19.47
12	-do-	Cobalt	300	42	1.694	24.8–29.7	27.56	27.05
13	-do-	Magnesium	>300	64	2.276	18.6–29.7	24.93	24.10
14	-do-	Copper	>300	69	2.441	20.3–24.6	22.49	21.93
15	p-Amino benzoic acid	Chromium	240	48	1.265	21.9–29.7	24.14	23.46
16	-do-	Manganese	300	65	1.271	24.8[a]	21.83	21.51
17	-do-	Zinc	>300	55	2.356	20.9–29.7	25.38	24.84
18	-do-	Nickel	270	60	2.45	21.9–29.7	25.87	25.63
19	-do-	Cobalt	>300	61	3.07	—	—	—
20	-do-	Magnesium	>300	61	1.82	21.9–24.6	23.26	23.08
21	-do-	Copper	260	64	1.51	20.9–24.8	22.53	21.87

[a] Swells.

The intrinsic viscosity values of the resin copolymers obtained from Huggins–Krammer and Martin equations as shown in Table III vary in the second decimal, which can be attributed to the mode of calculation.

The $\kappa_H + \kappa_K$ value is 0.479 for the resacetophenone-p-hydroxybenzoic acid furfural resins, 0.483 for resacetophenone-p-amino benzoic acid–furfural resins, and 0.499 for resacetophenone-p-chlorobenzoic acid–furfural resin is 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 ion 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 in various con-

Table III Viscometric Data of the 2,4-Dihydroxy Acetophenone Resins

Solution	Name of Comonomer	Huggin–Krammer Eq. [η_{H-K}]	Martin Eq. [η_M]	Constants			
				K_H	K_K	$K_H + K_K$	K_M
1.	p-Hydroxy benzoic acid	2.87	2.92	0.337	0.142	0.479	3.012
2.	p-Amino benzoic acid	3.12	3.314	0.267	0.216	0.483	1.865
3.	o-Chloro benzoic acid	2.34	2.42	0.295	0.204	0.499	2.524

centrations in the uptake of several metal ions by the resin copolymer is furnished in Table IV. The perusal of 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 the concentration of electrolyte but a decreasing trend is noticed in case of sulfate ions. The increasing trend may be explained in light of the stability constants of these complexes.[35-37] Sulfate ion might form rather strong chelates with the above metal ions while the other ions under investigation form weak chelates and therefore may not be expected to influence the position of the metal chelates equilibrium to the extent expected for the sulfate ion.

Rate of Metal Uptake

In Table V the dependence of the rate of metal ion uptake on the nature of metal ion has been furnished. The rate of metal absorption was studied to

ascertain the shortest period of time for which the equilibrium could be established. The perusal of the results indicate that these ions require different time periods for their equilibrium. The rate of metal uptake follows the order $Cu^{2+} > Co^{2+} > Ni^{2+} > Zn^{2+} > Mn^{2+} > Mg^{2+}$.

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 result 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 ion 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

Table IV Evaluation of the Effect of Different Electrolytes in Uptake of Several Metal Ions[a] [$Mt(NO_3)_2$ = 0.1 mol/L]

Solution	Metal Ion	Electrolyte (mol/L)	pH	Weight in mmol of Metal in Uptake in Presence of					
				NaCl	NaNO$_3$	KCl	KNO$_3$	Na$_2$SO$_4$	KClO$_4$
1	2	3	4	5	6	7	8	9	10
1	Co^{2+}	0.01	6	2.17	1.88	2.04	2.75	1.18	1.93
		0.05		2.80	2.25	2.22	2.91	1.08	2.06
		0.1		3.10	3.06	2.46	3.06	1.00	2.22
		0.5		3.20	3.31	2.62	3.12	0.824	2.44
2	Mn^{2+}	0.01	9.5	2.09	2.61	1.26	2.66	1.91	1.86
		0.05		2.33	2.94	1.32	2.86	1.76	1.98
		0.10		2.53	3.19	1.41	3.13	1.56	2.14
		0.50		2.66	3.46	1.47	3.27	1.36	2.32
3	Zn^{2+}	0.01	6	1.79	1.71	2.53	2.65	1.72	2.14
		0.05		2.33	1.88	2.71	2.86	1.45	2.36
		0.10		2.62	2.00	2.92	3.05	1.39	2.65
		0.50		2.89	2.12	2.97	3.20	1.15	2.89
4	Mg^{2+}	0.01	9.5	1.26	1.02	0.936	0.78	1.80	1.71
		0.05		1.32	1.11	1.05	0.90	1.66	1.89
		0.10		1.41	1.26	1.20	0.91	1.30	1.96
		0.50		1.47	1.35	1.32	1.17	1.13	2.04
5	Cu^{2+}	0.01	10	1.28	1.87	2.03	2.23	1.90	1.58
		0.05		2.21	2.00	2.40	2.06	1.73	1.71
		0.10		2.43	2.25	2.85	2.68	1.40	1.86
		0.50		2.60	2.42	2.95	2.95	1.38	2.02
6	Ni^{2+}	0.01	10	1.17	2.32	2.31	2.42	1.25	2.22
		0.05		1.51	2.54	2.55	2.61	1.20	2.43
		0.10		1.70	2.80	2.72	2.72	1.13	2.56
		0.50		2.22	2.96	2.97	2.91	1.10	2.68

[a] Volume of electrolyte solution, 25 mL; time, 24 h. Volume of metal ion soluble, 2 mL, room temperature.

Table V   Comparison of Rates of Metal Ion Uptake in Different Time

Metal ion	% of Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
Cu^{2+}	17.2	21.4	36.00	45.00	51.00	73.00	84.00	96.00
Zn^{2+}	21.6	24.8	35.70	41.00	49.20	62.00	75.00	86.00
Mn^{2+}	32.0	37.0	42.00	48.50	54.00	69.50	78.30	82.00
Co^{2+}	26.2	42.5	49.00	56.50	63.00	71.20	80.50	93.00
Mg^{2+}	14.0	28.5	33.00	39.40	48.00	55.50	66.50	77.30
Ni^{2+}	23.0	39.4	48.60	56.50	68.30	76.50	82.00	87.00

$$\frac{\text{mmol of metal ion adsorbed} \times 100}{\text{mmol of metal ion adsorbed at equation}}$$

$Mt(NO_3)_2$ = 0.1 mol/L; volume = 2 mL.
$NaNO_3$ − 1 mol/L; volume = 25 mL.
pH = 6; room temperature.

of Mn^{2+} and Zn^{2+} ions may be attributed 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 in the pH range of 2 to 6 is the 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 resins were prepared with a view to study their thermal behavior. The thermograms of the resin copolymer from resacetophenone, substituted benzoic acid, and furfuraldehyde in the presence of different catalysts are shown in Table VII. The degradation of resins follows a complex process. The initial weight loss up to 200°C is due to the removal of water. The 50% weight loss of all the resins occur at about 600°C. Almost all the resins show 100% decomposition beyond 900°C. This indicates that the resins can withstand very high temperature for their decomposition. The resins prepared from resacetophenone–furfural–p-chloro benzoic acid decomposes at higher temperatures than the other three resins studied. The char residue, oxygen index, and glass transition temperature of the resins have also been calculated and are furnished in Table VII. A comparison of the decomposition temperature of the resins prepared from resacetophenone–substituted benzoic acid–furfural was made with the resins prepared by using formaldehyde.[39] It was observed that the resins prepared by using furfural decomposes at higher temperature than the resins prepared by using formaldehyde.

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

Solution	Metal Ion	pH				
		2	3	4	6	8
1	Cu^{2+}	6.22	7.02	11.76	34.21	85.31
2	Zn^{2+}	5.91	15.68	19.01	49.8	79.03
3	Mn^{2+}	9.19	13.09	51.05	72.14	96.81
4	Co^{2+}	9.80	11.35	43.56	81.21	103.50
5	Mg^{2+}	7.52	9.8	18.12	41.00	84.00
6	Ni^{2+}	11.11	17.25	20.51	65.00	81.50

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

$Mt(NO_3)_2$ = 0.1 mol/L; volume = 2 mL; $NaNO_3$ = 1 mol/L.
Volume = 25 mL, time = 24 h; room temperature.

Table VII Thermal Data of the 2,4-Dihydroxy Acetophenone Resins

Solution	Name of Comonomer	Decomposition Percentage at Different Temps.									E^a by Different Methods		C.R.	O.I.	t_s
		100	200	300	400	500	600	700	800	900	Brodio	F–A			
1	Resacetophenone-o-hydroxy benzoic acid–furfuraldehyde	5.4	9.3	17	23	39	52	63	75	—	14.57	14.70	41	27.2	225
2	Resacetophenone-p-hydroxy benzoic acid–furfuraldehyde	3.2	7.0	12	28	35	56	68	78	—	12.10	12.35	14	68.7	275
3	Resacetophenone-p-chloro benzoic acid–furfuraldehyde	4.5	8.8	15	26	37	50	66	69	—	5.25	5.60	21	42.5	275
4	Resacetophenone-p-chloro benzoic acid–furfuraldehyde	6.7	10	14	22.5	34	55	62	67	75	15.30	15.55	32	39.0	340

^{a} E = activation energy.

In order to determine the mechanism of decomposition, the kinetic parameters have been evaluated using the Freeman and Anderson[40] and Broido[41] methods (Fig. 3). The former method involves the evaluations of quantities $\Delta \log(-dW/dt)$ and $\Delta \log \bar{W}$ corresponding to a constant difference in $1/T$ according to

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

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

The Broido method (Fig. 4) was based on the equation

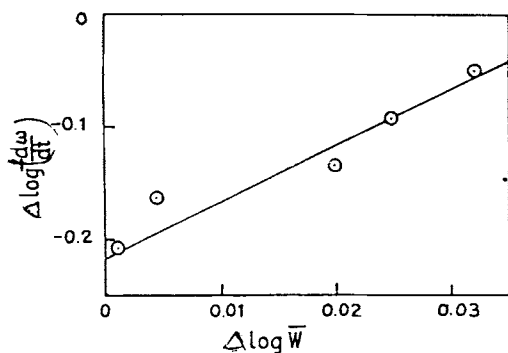$$\log\left(\ln \frac{1}{Y}\right) = \left(\frac{E^*}{2.303R}\right)\frac{1}{T} + K$$

The energy of activation of the resin polymers calculated by using the Freeman–Anderson and Brodio 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 culture sensitivity disk was taken and was dipped into the test tube containing broath solution. The tube was put inside an incubator for 2–3 h at a temperature of 37°C. The broath solution was spreaded over the agar plate and the excess of solution was decanted out. The resin was dissolved in DMSO and was applied to the disks, which were fixed at different places of the agar plate. The plate was kept inside the incubator overnight and the bacterial inhibition was observed. The results are furnished in Table VIII.
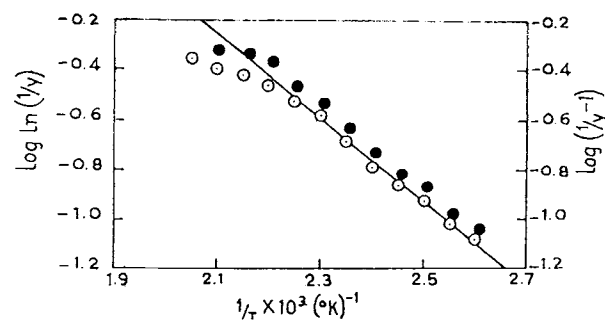

Figure 3 Typical Freeman–Anderson plot of the resin resacetophenone–furfural–o-chloro benzoic acid.

Figure 4 Typical Broido plot of the resin resacetophenone–furfural–o-amino benzoic acid.

Table VIII Bacteriological Results of Copolymers[a]

Solution	Name of Comonomer	*E. coli*	Nlf	Kleb	Pseu	Stv	Staph
1	Resacetophenone–furfural–o-hydroxy benzoic acid	HS	HS	MS	HS	HS	MS
2	Resacetophenone–furfural–p-hydroxy benzoic acid	MS	MS	WS	NS	NS	MS
3	Resacetophenone–furfural–o-amino benzoic acid	WS	MS	WS	NS	NS	WS
4	Resacetophenone–furfural–p-amino benzoic acid	WS	MS	WS	WS	NS	WS
5	Resacetophenone–furfural–p-chloro benzoic acid	HS	HS	HS	MS	HS	MS
6	Resacetophenone–furfural–o-chloro benzoic acid	HS	HS	MS	WS	NS	MS

[a] HS = highly sensitive, WS = weakly sensitive, MS = moderately sensitive, and NS = not sensitive.

A perusal of the results indicate that most of the resins are highly sensitive to the bacteria studied. Out of the seven resin copolymers studied in the present investigation, the resin copolymer prepared from resacetophenone–furfural–o-hydroxy benzoic acid is highly sensitive to most of the bacteria. Further work in those arena is under progress.

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