

# Synthetic Resins. XX. Chelation Ion Exchange Properties of Resins Derived From Semicarbazone of 2-Hydroxy Acetophenone-Substituted Benzoic Acid-Formaldehyde

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## SYNOPSIS

A number of resins have been synthesized by reacting orthohydroxy acetophenone-semicarbazone with substituted benzoic acid and formaldehyde in the presence of some acid and basic catalyst. The physicochemical properties of the resins have been reported. The ion exchange properties of the resins have been investigated. Influence of electrolytes on the metal uptake of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$  has been studied. The distribution of metal ions at different pH has also been reported. © 1992 John Wiley & Sons, Inc.

## INTRODUCTION

Synthetic resins derived from hydroxy and amino aromatic compounds have attracted the attention of many researchers because of their versatile use as ion exchangers,<sup>1,2</sup> photographic binders,<sup>3</sup> thermal stabilisers, etc.<sup>4-7</sup> We reported the synthesis and characterisation of resins derived from a large number of hydroxy and amino acetophenones-formaldehyde condensates.<sup>8-15</sup> This communication presents the chelation ion exchange properties of resin copolymers derived from the semicarbazone derivatives of 2-hydroxy acetophenone-substituted benzoic acids-formaldehyde resins.

## EXPERIMENTAL

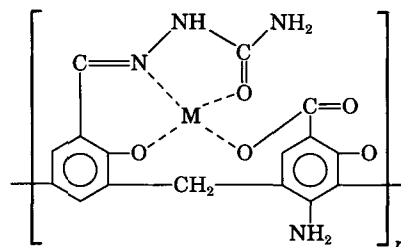
### Preparation of Resins

#### Method

The copolymers were prepared by refluxing a mixture of semicarbazone of 2-hydroxy acetophenone (0.025 mol), substituted benzoic acid (0.025 mol), and formaldehyde (0.1 mol) in a round-bottom flask in the presence of acid (2*N*) and alkali (40% w/v)

as catalysts at 120°C for 6–8 h. Sulphuric acid, hydrochloric acid, and succinic acid were used as the acid catalysts, whereas sodium hydroxide and potassium hydroxide were used as the basic catalysts. During the course of the reaction a periodical shaking was needed to ensure thorough mixing. After completion of the reaction, the contents were collected with ice-cold water. The product was filtered and washed repeatedly to drive out the unreacted materials.

A typical polymer structure for metal ion chelation is presented below.



The physicochemical properties of the resins are shown in Table I.

## ION EXCHANGE STUDY

Resins were ground in a pebble mill, dry sieved to obtain a 40/60 mesh range fraction, then placed in

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**Table I Physicochemical Properties of Resins Prepared From Semicarbazone of 2-Hydroxy Acetophenone and Substituted Benzoic Acid (in Presence of Formaldehyde)**

Serial (No.)	Name of the Comonomer	Catalyst	Time of Heating (h)	Decomposition Temperature (°C)	Colour/Structure	Solubility	Solubility Parameter Ranges in Solvents That are Hydrogen Bonded <sup>a</sup>		
							Weak	Moderate	Strong
1	<i>o</i> -Hydroxy benzoic acid	HCl	8	300	Black/cry.	DMF	18.0-20.5	20.3-24.8	—
2	<i>o</i> -Hydroxy benzoic acid	H <sub>2</sub> SO <sub>4</sub>	8	300	Black/cry.	DMF	19.2-20.5 <sup>b</sup>	19.2-24.8	21.7-21.9
3	<i>o</i> -Hydroxy benzoic acid	Succinic acid	8	280	Brown/amor.	DMF	—	19.2-24.8	21.9-24.8
4	<i>o</i> -Hydroxy benzoic acid	NaOH	6	190	Brown/amor.	DMF	—	24.6-24.8	20.7-29.7
5	<i>o</i> -Hydroxy benzoic acid	KOH	6	180	Yellow/amor.	DMF	—	19.2-24.8	—
6	<i>p</i> -Hydroxy benzoic acid	HCl	8	280	Brown/cry.	DMF	19.2-20.5 <sup>b</sup>	18.6-24.8	20.7-29.7
7	<i>p</i> -Hydroxy benzoic acid	H <sub>2</sub> SO <sub>4</sub>	8	300	Black/cry.	DMF	—	19.2-24.8	21.9-24.8
8	<i>p</i> -Hydroxy benzoic acid	Succinic acid	10	280	Chocolate/cry.	DMF	—	18.6-24.8	20.7-24.8
9	<i>p</i> -Hydroxy benzoic acid	NaOH	6	220	Yellowish brown/ amor.	Acetone	—	18.6-20.3	20.7-24.8
10	<i>p</i> -Hydroxy benzoic acid	KOH	6	180	Reddish brown/ amor.	DMF	17.6-20.5 <sup>b</sup>	18.6-24.8	20.7-24.8
11	<i>o</i> -Amino benzoic acid	HCl	8	280	Black/cry.	DMF	—	24.6-24.8	20.7-29.7
12	<i>o</i> -Amino benzoic acid	H <sub>2</sub> SO <sub>4</sub>	8	300	Red/cry.	DMF	—	19.2-24.8	—
13	<i>o</i> -Amino benzoic acid	Succinic acid	10	300	Brown/cry.	Nitro benzene	19.0-19.4 <sup>b</sup>	24.6-24.8 <sup>b</sup>	21.7-21.9
14	<i>o</i> -Amino benzoic acid	NaOH	6	220	Brown/amor.	Pyridine	19.2-20.5 <sup>b</sup>	18.6-24.8	21.7-29.7
15	<i>o</i> -Amino benzoic acid	KOH	8	250	Yellow/amor.	Pyridine	19.2-20.5 <sup>b</sup>	18.6-24.8	21.7-29.7
16	<i>p</i> -Amino benzoic acid	HCl	8	300	Black/cry.	DMSO	—	19.2-24.8	21.9-24.8
17	<i>p</i> -Amino benzoic acid	H <sub>2</sub> SO <sub>4</sub>	10	300	Brown/cry.	DMSO	—	19.2-24.8	21.9-24.8
18	<i>p</i> -Amino benzoic acid	Succinic acid	9	280	Grey/cry.	DMF	—	19.2-24.8	—
19	<i>p</i> -Amino benzoic acid	NaOH	5	180	Brown/cry.	DMF	—	24.6-24.8	20.7-29.7
20	<i>p</i> -Amino benzoic acid	KOH	6	210	Yellow/cry.	Toluene	—	18.6-24.8	18.6-24.8
21	<i>o</i> -Chloro benzoic acid	HCl	7	280	Black/cry.	DMF	—	18.6-24.8	20.7-24.8
22	<i>o</i> -Chloro benzoic acid	H <sub>2</sub> SO <sub>4</sub>	8	300	Brown/cry.	DMF	17.6-20.5 <sup>b</sup>	18.6-24.8	20.7-24.8
23	<i>o</i> -Chloro benzoic acid	Succinic acid	8	300	Chocolate/amor.	Pyridine	19.2-20.5 <sup>b</sup>	18.6-24.8	21.7-29.7
24	<i>o</i> -Chloro benzoic acid	NaOH	6	210	Yellowish brown/ amor.	Acetone	—	18.6-20.3	20.7-24.8
25	<i>o</i> -Chloro benzoic acid	KOH	5	200	Brown/amor.	Acetone	—	18.6-20.3	20.7-21.8
26	<i>p</i> -Chloro benzoic acid	HCl	7	280	Brown/cry.	DMSO	—	19.2-24.8	21.9-24.8
27	<i>p</i> -Chloro benzoic acid	H <sub>2</sub> SO <sub>4</sub>	8	290	Black/cry.	DMF	—	18.6-24.8	20.7-24.8
28	<i>p</i> -Chloro benzoic acid	Succinic acid	10	280	Grey/amor.	DMF	—	18.6-24.8	20.7-24.8
29	<i>p</i> -Chloro benzoic acid	NaOH	5	180	Yellow/cry.	Toluene	—	18.6-24.8	18.6-24.8
30	<i>p</i> -Chloro benzoic acid	KOH	5	200	Brown/cry.	Pyridine	19.2-20.5 <sup>b</sup>	18.6-24.8	21.7-29.7

Cry, crystalline; amor, amorphous.

<sup>a</sup>  $(J/m^3)^{1/2} \times 10^{-3}$ .

<sup>b</sup> Swelling parameter.

a glass column and backwashed with demineralised water to remove extraneous chemicals. The resins were converted to their hydrogen forms by passing a large excess of 5*N* HCl through the beds. After about 16 h, the converted exchangers were washed with a minimum of distilled water, air dried, and stored.

The resins were screened taking into consideration their exchange capacity. A typical resin [semi-carbazone of 2-OH acetophenone, *p*-amino benzoic acid (HCHO)] is reported here to provide a detailed study of the kinetics of the exchange process. Electrolytes like NaCl, NaNO<sub>3</sub>, Na<sub>2</sub>SO<sub>4</sub>, NaClO<sub>4</sub>, etc. were taken at varying molar concentrations with variation of pH. The percentage of attainment of equilibrium with time was also studied.

#### Determination of Metal Uptake in the Presence of Various Electrolytes

The sample polymer (25 mg) was suspended in the electrolyte solution of known concentrations. The

pH of the solution was adjusted. To this suspension, 1 ml 0.1*M* solution of the metal ion under study was added and the pH was adjusted. The mixture was stirred for 24 h at room temperature, followed by filtration. The filtrate and washings were collected and estimated for metal ion uptake by titration against standard EDTA. A blank experiment was also carried out in the above manner without adding the polymer sample. The amount of the metal ion taken up by the polymer in the presence of the given electrolyte of known concentration results from the difference between the blank reading and the reading in the actual experiment. This experiment was repeated in the presence of several electrolytes and the results are furnished in Table II.

#### Evaluation of the Rate of Metal Uptake

To estimate the time required to reach the state of equilibrium under the given experimental conditions, a series of experiments of the type described above were carried out in which the metal ion taken

**Table II** Evaluation of the Effect of Different Electrolytes in Uptake of Several Metal Ions, Me(NO<sub>3</sub>)<sub>2</sub> (0.1 mol/L)

Metal Ion	Electrolytes (mol/L)	pH	Weight (mmol) of Metal Ion Uptake in the Presence of					
			NaCl	KCl	NaNO <sub>3</sub>	KNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	KClO <sub>4</sub>
Cu <sup>2+</sup>	0.01	10	0.021	0.020	0.029	0.028	0.126	0.032
	0.05		0.050	0.052	0.068	0.072	0.102	0.071
	0.1		0.072	0.082	0.100	0.102	0.076	0.079
	0.5		0.088	0.105	0.109	0.111	0.062	0.091
Co <sup>2+</sup>	0.01	6	0.032	0.021	0.020	0.081	0.171	0.012
	0.05		0.061	0.042	0.051	0.052	0.138	0.032
	0.1		0.105	0.088	0.092	0.098	0.129	0.062
	0.5		0.141	0.138	0.132	0.136	0.080	0.132
Ni <sup>2+</sup>	0.01	10	0.020	0.024	0.021	0.022	0.172	0.024
	0.05		0.058	0.058	0.062	0.071	0.122	0.062
	0.1		0.079	0.081	0.098	0.108	0.104	0.072
	0.5		0.098	0.096	0.148	0.154	0.076	0.098
Zn <sup>2+</sup>	0.01	6	0.026	0.032	0.018	0.020	0.148	0.022
	0.05		0.051	0.062	0.071	0.068	0.106	0.052
	0.1		0.082	0.102	0.102	0.108	0.061	0.071
	0.5		0.122	0.144	0.152	0.152	0.040	0.112
Mg <sup>2+</sup>	0.01	10	0.028	0.032	0.020	0.022	0.138	0.022
	0.05		0.052	0.061	0.052	0.051	0.098	0.061
	0.1		0.092	0.110	0.092	0.092	0.056	0.108
	0.5		0.141	0.142	0.140	0.136	0.038	0.146
Mn <sup>2+</sup>	0.01	10	0.022	0.026	0.032	0.028	0.182	0.028
	0.05		0.052	0.044	0.072	0.052	0.138	0.042
	0.1		0.076	0.078	0.108	0.078	0.098	0.078
	0.5		0.118	0.124	0.126	0.126	0.062	0.128

up by the chelating resin was estimated from time to time at 25°C in the presence of 25 ml 1M NaNO<sub>3</sub> solution. It is assumed that, under the given experimental conditions, the state of equilibrium is established within 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ions taken up after a certain time related to that in the state of equilibrium (Table II) using the following equation:

$$\frac{\text{Amount of metal ion absorbed in mmol} \times 100}{\text{Amount of metal ion absorbed at equilibrium in mmol}} = \text{Percentage of the attainment of the state of equilibrium}$$

### Evaluation of Distribution of Metal Ions at Different pH

The distribution of each of the six metal ions, i.e., Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup>, between the polymer and aqueous phases was estimated at 25°C and in the presence of a 1M NaNO<sub>3</sub> solution. The experiments were carried out at pH 2-8. The distribution ratio, *D*, is defined by the following relation:

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

The results are furnished in Table III.

## RESULTS AND DISCUSSION

### Influence of Electrolyte on the Metal Uptake

The influence of electrolytes such as Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, SO<sub>4</sub><sup>2-</sup>, and ClO<sub>4</sub><sup>-</sup> at various concentrations on the

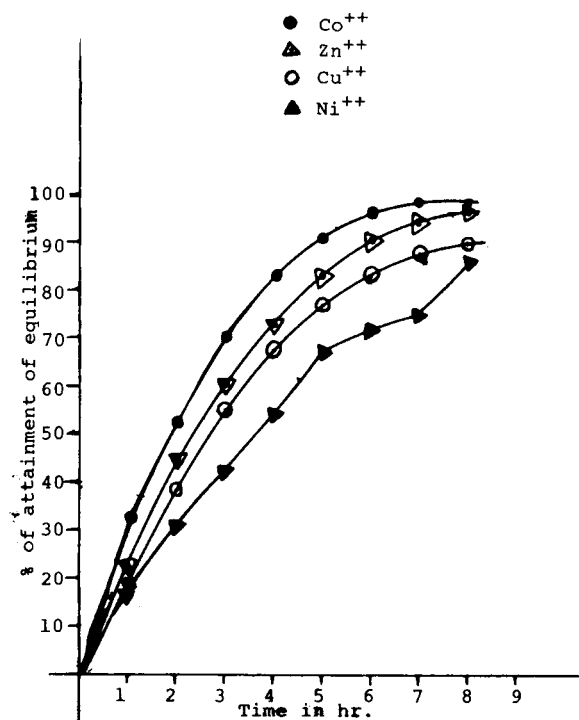


Figure 1 Rates of metal uptake of the resin at pH 6 for 0.1M solution metal nitrate.

position of the equilibrium of metal polymer interaction has been investigated. Perusal of the results (Table II) reveal that the amount of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> taken by most of the copolymers decreases with the increase of the concentration of SO<sub>4</sub><sup>2-</sup> ion. But, the amount of uptake of all the metal ions increases with increase in the concentration of Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> ions. This may be explained in terms of the stability constants of the complexes of Cu<sup>2+</sup>, Ni<sup>2+</sup>, Co<sup>2+</sup>, Zn<sup>2+</sup>, Mn<sup>2+</sup>, and Mg<sup>2+</sup> ions with ligands. Sulphates might be forming strong chelates with the above metal ions,

Table III Comparison of Rates of Metal Ion Uptake at Different Times

Metal Ion	% Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
Cu <sup>2+</sup>	18	39	55	68	77	84	88	90
Co <sup>2+</sup>	32	52	70	83	91	95	98	
Ni <sup>2+</sup>	17	30	42	54	68	72	75	86
Mg <sup>2+</sup>	21	31	37	51	62	85	94	97
Mn <sup>2+</sup>	30	52	71	82	90	92	95	98
Zn <sup>2+</sup>	22	44	60	72	84	90	94	97

Related to the amount of metal ions in the state of equilibrium (100%). Temperature = room temperature. Me(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L; NaNO<sub>3</sub> = 1 mol/L; pH = 6 for Co<sup>2+</sup> and Zn<sup>2+</sup>, 10 for Mg<sup>2+</sup>, Mn<sup>2+</sup>, Zn<sup>2+</sup>, and Cu<sup>2+</sup>.

**Table IV** Distribution Ratio  $D^*$  of Different Metal Ions as a Function of pH

Sl. No.	Metal Ion	Distribution Ratio of the Metal Ions at Different pH				
		2	3	4	6	8
1	Cu <sup>2+</sup>	6.18	9.20	22.40	65.82	81.2
2	Co <sup>2+</sup>	11.20	12.2	19.5	28.8	40.2
3	Ni <sup>2+</sup>	12.23	16.98	25.54	66.70	80.20
4	Mg <sup>2+</sup>	35.2	60.50	96.0	110.2	180.5
5	Mn <sup>2+</sup>	8.42	22.5	52.3	71.2	88.5
6	Zn <sup>2+</sup>	20.2	35.4	47.1	62.1	95.8

Time = 24 h, Temperature = room temperature (equilibrium state).

$D^*$  = mmol of metal ion in the copolymer/mmol of metal ion in the solution  $\times$  volume of solution/weight of copolymer.

Me(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L, vol = 2 mL; NaNO<sub>3</sub> = 1 mol/L, vol = 25 mL.

whereas the other mentioned ions form weak chelates with the same metal ions. These results indicate that in the case of Cu<sup>2+</sup>, Co<sup>2+</sup>, Ni<sup>2+</sup>, Mn<sup>2+</sup>, Mg<sup>2+</sup>, and Zn<sup>2+</sup> chelates equilibrium is not influenced highly by NO<sub>3</sub><sup>-</sup>, Cl<sup>-</sup>, and ClO<sub>4</sub><sup>-</sup> ions whereas it is influenced by SO<sub>4</sub><sup>2-</sup> ions.

### Rate of Metal Uptake

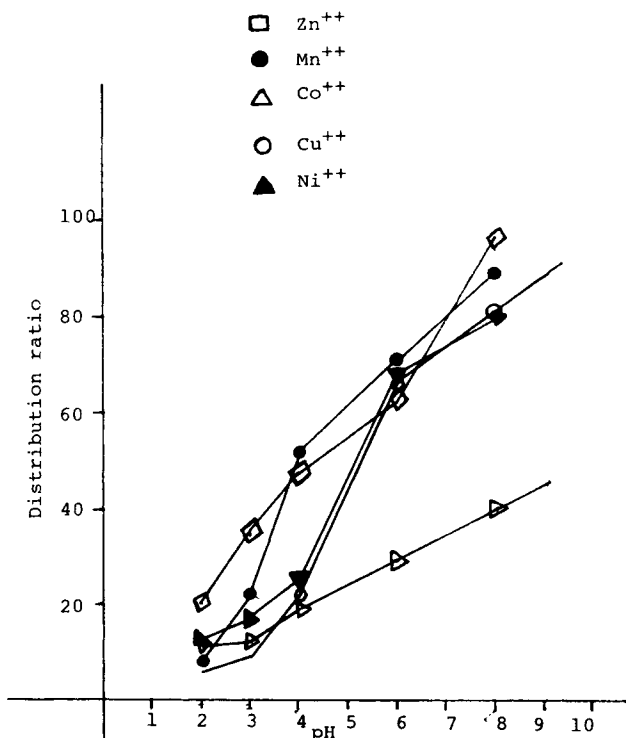
Table III shows the dependence of the rate of metal ion uptake upon the nature of the metal ion. The

rates of metal adsorption of the resins were determined to find the shortest time period for which equilibrium could be carried out while operating as close to equilibrium conditions as possible. The rate of metal uptake is represented in Figure 1.

### Distribution of the Metal Ion at Different pH

The effect of pH on the amount of metal ion distribution between the two phases has been studied and the results are furnished in Table IV and Figure 2. Perusal of the results indicates that the relative amount of metal ion taken up by the copolymer increases steadily with increase of the pH of the medium. The investigation was carried up to a definite pH value for a particular metal ion to prevent the hydrolysis of metal ions at higher pH. Between pH 2-4, Cu<sup>2+</sup>, Co<sup>2+</sup>, and Ni<sup>2+</sup> ions have low distribution ratio whereas Zn<sup>2+</sup> and Mn<sup>2+</sup> ions have low distribution ratio at pH 2 only. This could be attributed to the low stability constant.

The results of this study are helpful in selecting the optimum pH for a selective uptake for a metal ion from mixture of different ions.



**Figure 2** Distribution ratio of metal nitrate at different pH.

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