

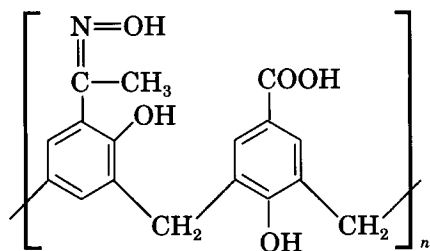
# Synthetic Resins. XXI. Ion-Exchange Properties of the Resins Derived from Oximes of 2-Hydroxy Acetophenone-Substituted Benzoic Acid-Formaldehyde

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## INTRODUCTION

A large number of synthetic resins derived from hydroxy and amino aromatic compounds have attracted the attention of many research workers because of their versatile uses as ion exchangers, photographic binders, thermal stabilizers, etc. We have reported the synthesis and characterization of the resins derived from a large number of hydroxy and amino acetophenones-formaldehyde.<sup>1-7</sup> A large number of chelates have been reported using oximes of the aromatic ketones. A survey of the literature reveals that chelates have not been prepared from the synthetic resins derived from the oximes of the hydroxy acetophenones. This communication presents the ion exchange properties of the resin copolymers derived from oxime derivative of 2-hydroxy acetophenone-substituted benzoic acid-formaldehyde resins. The plausible structure of the resin synthesized by condensing oxime derivative of 2-hydroxy acetophenone with formaldehyde and *p*-hydroxy benzoic acid as the comonomer is represented below.



## RESULTS AND DISCUSSION

### Influence of Electrolytes on the Metal Uptake

The influence of the electrolytes such as  $\text{Cl}^-$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ , and  $\text{ClO}_4^-$  at various concentrations on the position of the equilibrium of metal polymer in-

teractions has been investigated. Perusal of the results reveals that the amount of  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Mn}^{2+}$  taken up by most copolymers decreases with the increase of the concentration of  $\text{SO}_4^{2-}$  ion. But the amount of uptake of all the metal ions increases with increase in the concentration of  $\text{Cl}^-$ ,  $\text{NO}_3^-$  and  $\text{ClO}_4^-$  ions. This may be explained in terms of the stability constants of the complexes with  $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Mg}^{2+}$  ions with these ligands. Sulfate anions may have strong interactions with the above metal ions, whereas the other mentioned anions might have weak interactions with the same metal ions. Hence, in case of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Zn}^{2+}$ , since the interaction is very low the equilibrium is not influenced highly by  $\text{NO}_3^-$ ,  $\text{Cl}^-$  and  $\text{ClO}_4^-$  ions whereas it is influenced by  $\text{SO}_4^{2-}$  ions.

### Rate of Metal Uptake

The dependence of the rate of metal ion uptake on the nature of the metal is shown in Table I. The rates of metal absorption of the resins were deter-

**Table I** Composition of Rates of Metal Ion Uptake at Different Times

Metal Ion	% of Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
$\text{Mg}^{2+}$	38	57	75	88	97	100	—	—
$\text{Cu}^{2+}$	19	40	56	65	73	81	87	95
$\text{Mn}^{2+}$	33	53	71	84	92	95	99	—
$\text{Zn}^{2+}$	16	31	43	55	68	74	76	85
$\text{Ni}^{2+}$	22	32	38	52	63	86	95	98
$\text{Co}^{2+}$	31	53	72	83	91	93	96	99

$\text{Me}(\text{NO}_3)_2 = 0.1 \text{ mol/L}$ .

$\text{NaNO}_3 = 1 \text{ mol/L}$ .

pH = 6 for  $\text{Co}^{2+}$  and  $\text{Zn}^{2+}$ .

pH = 10 for  $\text{Mg}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ .

Temperature—room temperature Relative to the amount of metal ions in the state of equilibrium (100%).

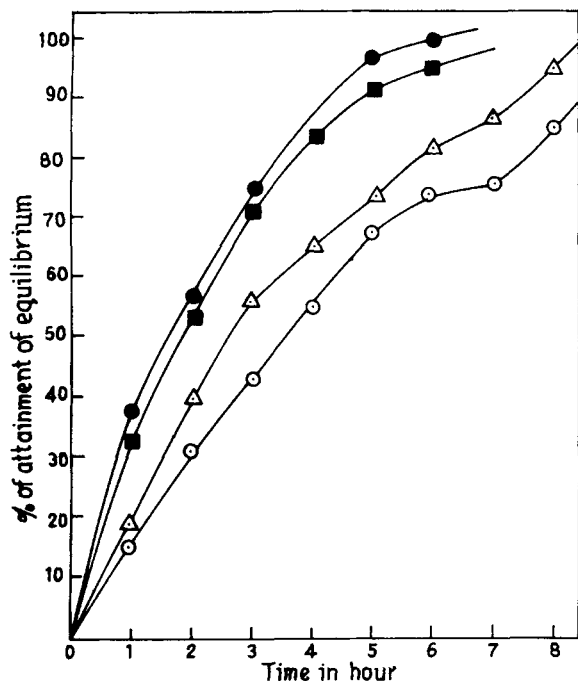


Figure 1 Rates of metal uptake of the resin at pH 6 for 0.1 M solution of metal nitrate. (●): Mg<sup>2+</sup>, (■): Mn<sup>2+</sup>, (△): Cu<sup>2+</sup>, (○): Zn<sup>2+</sup>.

mined in order to establish the shortest time period possible to reach equilibrium. The rate of metal uptake of Mg<sup>2+</sup>, Mn<sup>2+</sup>, Cu<sup>2+</sup>, and Zn<sup>2+</sup> is represented in Figure 1.

**Distribution of the Metal Ion at Different pH**

The effect of pH on metal ion distribution between the two phases has been studied and the results are furnished in Table II. The perusal of the result in-

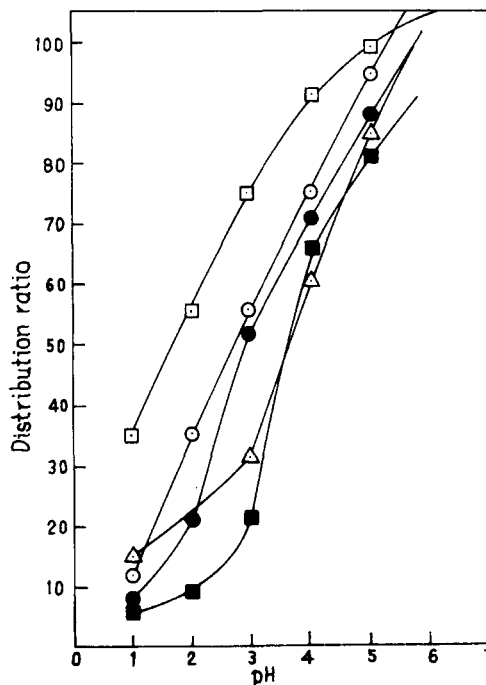


Figure 2 Distribution ratio of metal nitrate at different pH. (□): Mg<sup>2+</sup>, (○): Zn<sup>2+</sup>, (△): Mn<sup>2+</sup>, (●): Ni<sup>2+</sup>, (■): Cu<sup>2+</sup>.

dicates that, the relative amount of the metal ion taken up by the copolymer increases steadily with the increase of the pH of the medium (Fig. 2). The investigation was carried out up to a definite pH value for a particular metal ion to prevent the hydrolysis of metal ions at higher pH. Cu<sup>2+</sup> and Ni<sup>2+</sup> ions have a low distribution ratio between pH 2 and pH 4, whereas Zn<sup>2+</sup>, Mg<sup>2+</sup>, and Mn<sup>2+</sup> ions have a low distribution ratio only at pH 2. This could be attributed to the low stability constant of these ions.

Table II Distribution Ratio D\* of Different Metal Ions As a Function of pH

Serial No.	Metal Ion	Distribution Ratio D* of Different Metal Ions at Different pH				
		1	2	3	4	5
1	Mg <sup>2+</sup>	35.2	55.1	75.0	—	—
2	Cu <sup>2+</sup>	6.18	9.20	22.40	65.82	81.2
3	Mn <sup>2+</sup>	9.0	22.5	52.3	71.2	88.5
4	Zn <sup>2+</sup>	12.2	35.4	56.3	75.1	95.0
5	Ni <sup>2+</sup>	15.3	20.1	27.3	61.0	85.1
6	Co <sup>2+</sup>	11.20	12.2	19.5	28.8	40.2

$$D^* = \frac{M \text{ mol of metal ion in the copolymer}}{M \text{ mol of metal ion in the solution}} \times \frac{\text{Volume of solution}}{\text{Wt of copolymer}}$$

Me(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L, Volume = 2 mL.  
 NaNO<sub>3</sub> = 1 mol/L, Volume = 25 mL.  
 Time = 24 h Room temperature (equilibrium state).

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

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