

## NOTES

# Synthetic Resins. XIX. Chelation Ion Exchange Properties of 2,4-Dinitrophenyl Hydrazone of Quinacetophenone-Formaldehyde Resin

### INTRODUCTION

Synthetic resins have attracted the attention of many researchers<sup>1-5</sup> because of their versatile use as ion exchangers, photographic binders, and high-temperature-resistant polymers. During the last decade, we have reported the synthesis and characterization of a large number of resins derived from some hydroxy and amino acetophenones.<sup>6-13</sup> In recent years our emphasis has been the use of the derivatives of the hydroxy acetophenones for the preparation of resin copolymers to explore their ion-exchange properties.

In the present investigation, we have used the 2,4-dinitrophenyl hydrazone derivative of quinacetophenone to prepare some resin copolymers to be used as ion exchangers. Because the 2,4-dinitrophenyl hydrazone unit contains two nitrogen atoms in the unit it is expected that the ligating behavior of these resins will be more pronounced in comparison to other resins.

### EXPERIMENTAL

#### Preparation of the Resin

**Method I.** A mixture of 2,4-dinitrophenyl hydrazone of quinacetophenone, substituted benzoic acid or substituted phenols (0.0025 mol) and formaldehyde (0.1 mol) were refluxed at 110°C for 8 to 10 h in the presence of 2 mL of 2*N* HCl. After completion of the reaction, the contents were extracted with ice cold water, filtered, and washed repeatedly with hot water to remove unreacted materials. The residue was then dried in vacuum. Properties of the resins prepared by this method are described in Table I.

**Method II.** The copolymer sample was prepared by condensing 2,4-dinitrophenyl hydrazone of quinacetophenone (0.005 mol) with substituted benzoic acid or substituted phenol and formaldehyde (0.1 mol) in a round-bottom flask in the presence of NaOH (40%) as the catalyst. The reaction mixture was heated at 120°C for 8–10 h. 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.

#### Characterization of Resin

A typical formaldehyde condensate of 2,4-dinitrophenyl hydrazone of quinacetophenone–hydroquinone may be attributed to the structure shown in Figure 1.

This was confirmed by the characteristic infrared (IR) bands (Fig. 2, Perkin-Elmer 781 Spectrophotometer, KBr pellets).

The polymer shows characteristic IR bands near 1600, 3300, and 1400  $\text{cm}^{-1}$  for C=N stretching, intramolecular hydrogen-bonded N—H stretching and hydrogen-bonded, N—H bending (scissoring) vibration of secondary amines. Bands between 1350 and 1300  $\text{cm}^{-1}$  for secondary and tertiary aromatic amines and those near 1150 and 1420  $\text{cm}^{-1}$  for C—O stretching and O—H bending vibration of phenol were observed. Absorption was near 1000 and 1465  $\text{cm}^{-1}$  for coupling of C—O and C—C stretching vibrations and for C—H bending vibration of methylene group, respectively.

The ion-exchange study, determination of metal uptake in the presence of various electrolytes, evaluation of the rate of metal uptake, and evaluation of distribution of metal ions at different pH were carried out as per our previous communication.<sup>7</sup>

### RESULTS AND DISCUSSIONS

#### Influence of Electrolytes on the Metal Uptake

The influence of such electrolytes 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 interactions have been investigated. Perusal of the results furnished in Table II 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 the copolymer (QAP 2,4-DNP-HQ-F) sample decreases with the increase of the concentration of  $\text{SO}_4^{2-}$  and  $\text{ClO}_4^-$  ions. This may be explained in terms of the stability constant of complexes with  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Mg}^{2+}$  ions formed with these ligands.<sup>14-16</sup> Sulphate and perchlorate may form strong

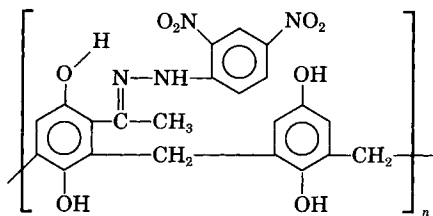


Figure 1 Structure of repeat unit of resin.

chelates with the above metal ions whereas other of these ions may form weak chelates with the same metal ions. The influence of different concentrations of electrolytes on  $\text{Cu}^{2+}$  ion uptake is shown in Figure 3.

#### Rate of Metal Uptake

Table III shows the dependence of the rate of metal ion uptake on the nature of the metal. The rates of metal adsorption by the resins were measured to determine the shortest time period in which equilibrium could be attained while operating as close to equilibrium conditions as possible.  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ , and  $\text{Ni}^{2+}$  require almost 8 hours for the establishment of equilibrium whereas  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ , and  $\text{Mg}^{2+}$  require more than 8 hours.

The rate of metal uptake follows the order:  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Ni}^{2+} > \text{Zn}^{2+}$ ,  $\text{Mg}^{2+}$ , and  $\text{Co}^{2+}$  (Fig. 4).

#### 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

Table I Preparation of Resins Derived from Quinacacethophenone 2,4-Dinitrophenyl Hydrazone

Sl. No.	Comonomer	Catalyst	Heating Time (h)
1.	Hydroquinone	HCl	8
2.	Acetyl salicylic acid	NaOH	12
3.	Hydroxyacetophenone	HCl	8
4.	<i>m</i> -Amino acetophenone	HCl	10
5.	<i>p</i> -Chloroacetophenone	HCl	8
6.	<i>o</i> -Chloro aniline	HCl	10
7.	<i>p</i> -Hydroxybenzoic acid	HCl	10
8.	Resorcinol	NaOH	8
9.	$\alpha$ -Naphthol	NaOH	8
10.	<i>p</i> -Cresol	NaOH	10
11.	<i>p</i> -Nitrophenol	NaOH	11
12.	8-Hydroxyquinoline	NaOH	8

are listed in the Table IV. The results indicate that the relative amount of the metal ion taken up by the copolymer increases steadily with increasing pH of the medium. Since at higher pH there is the possibility of hydrolysis, the investigation was carried out up to a definite pH value for the particular metal ion.  $\text{Mn}^{2+}$  and  $\text{Mg}^{2+}$  ions are taken up more selectively than  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Zn}^{2+}$  ions.  $\text{Ni}^{2+}$  and  $\text{Zn}^{2+}$  ions have a low distribution ratio between pH 2 and 6. This could be attributed to the low stability constant (i.e., weak ligand stabilization energy of the metal complexes).<sup>17,18</sup> The observed order of metal ion distribution is  $\text{Mg}^{2+} > \text{Mn}^{2+} > \text{Cu}^{2+} > \text{Zn}^{2+} > \text{Co}^{2+}$  and  $\text{Ni}^{2+}$

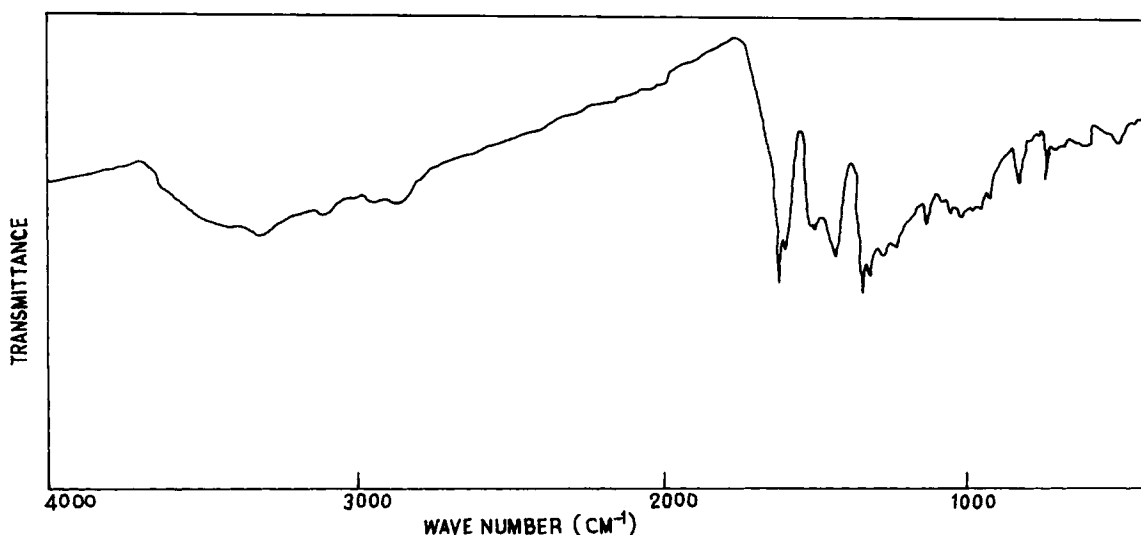


Figure 2 Plot of wave number versus % transmittance.

**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	pH	Weight (mmol) of Metal Ion Uptake in Presence of				
			NaCl	KCl	NaNO <sub>3</sub>	Na <sub>2</sub> SO <sub>4</sub>	KClO <sub>4</sub>
Cu <sup>2+</sup>	0.01	10	0.047	0.037	0.022	0.081	0.093
	0.05		0.063	0.045	0.037	0.070	0.085
	0.10		0.079	0.056	0.048	0.062	0.073
	0.50		0.086	0.071	0.062	0.049	0.060
Co <sup>2+</sup>	0.01	6	0.033	0.042	0.021	0.078	0.087
	0.05		0.044	0.055	0.036	0.067	0.076
	0.10		0.056	0.067	0.044	0.058	0.066
	0.50		0.071	0.079	0.057	0.047	0.055
Ni <sup>2+</sup>	0.01	10	0.039	0.039	0.043	0.085	0.086
	0.05		0.051	0.048	0.056	0.072	0.076
	0.10		0.062	0.056	0.067	0.063	0.065
	0.50		0.071	0.068	0.079	0.052	0.056
Zn <sup>2+</sup>	0.01	6	0.036	0.041	0.031	0.069	0.083
	0.05		0.045	0.053	0.043	0.056	0.071
	0.10		0.057	0.061	0.057	0.047	0.063
	0.50		0.066	0.069	0.063	0.031	0.045
Mn <sup>2+</sup>	0.01	10	0.021	0.028	0.020	0.061	0.077
	0.05		0.033	0.036	0.033	0.052	0.068
	0.10		0.045	0.044	0.047	0.044	0.060
	0.50		0.058	0.056	0.055	0.036	0.054
Mg <sup>2+</sup>	0.01	10	0.034	0.038	0.042	0.064	0.076
	0.05		0.041	0.047	0.053	0.053	0.066
	0.10		0.053	0.057	0.062	0.044	0.055
	0.50		0.061	0.068	0.072	0.033	0.047

Resin studied: Me = metal; volume of electrolyte solution = 25 mL; volume of metal ion solution = 2 mL; time: 24 h; temperature: room temperature.

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

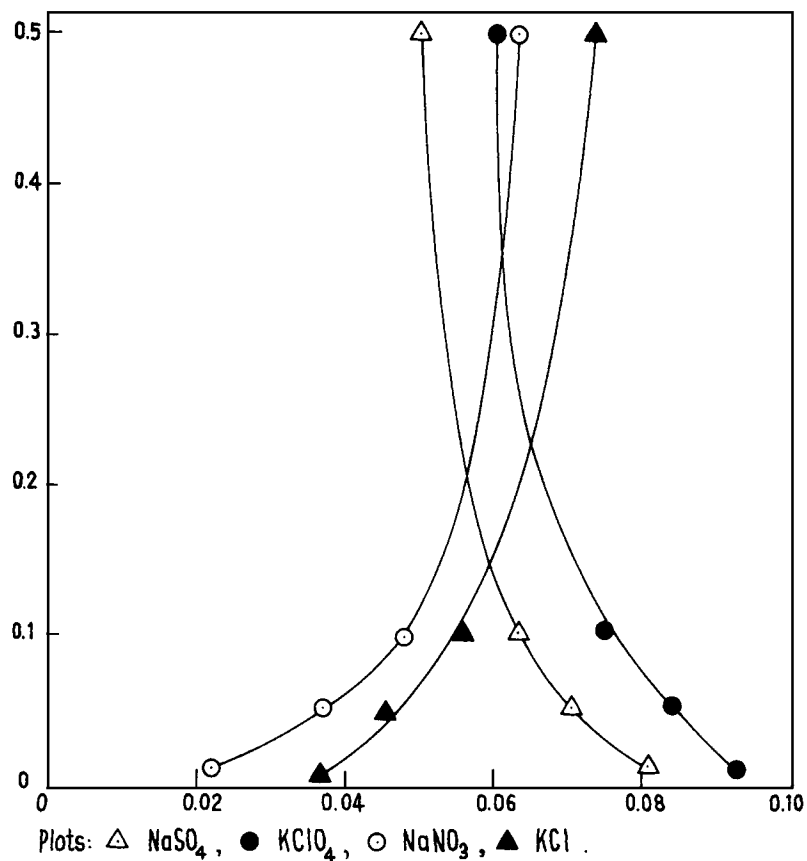
Metal Ion	% Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
Cu <sup>2+</sup>	13.5	27.5	40.0	50.0	59.5	72.0	90.0	95.0
Zn <sup>2+</sup>	20.0	38.0	52.5	62.0	70.0	74.5	78.0	83.5
Mn <sup>2+</sup>	26.0	42.5	57.0	66.5	74.0	79.0	83.5	98.5
Co <sup>2+</sup>	34.0	50.0	64.0	73.0	78.5	82.0	85.5	87.0
Mg <sup>2+</sup>	15.0	32.0	45.0	56.0	65.0	70.0	80.0	85.0
Ni <sup>2+</sup>	22.0	35.0	44.0	55.0	66.0	80.0	85.0	90.0

[Me(NO<sub>3</sub>)<sub>2</sub>] = 0.1 mol/L; Volume = 2 mL.

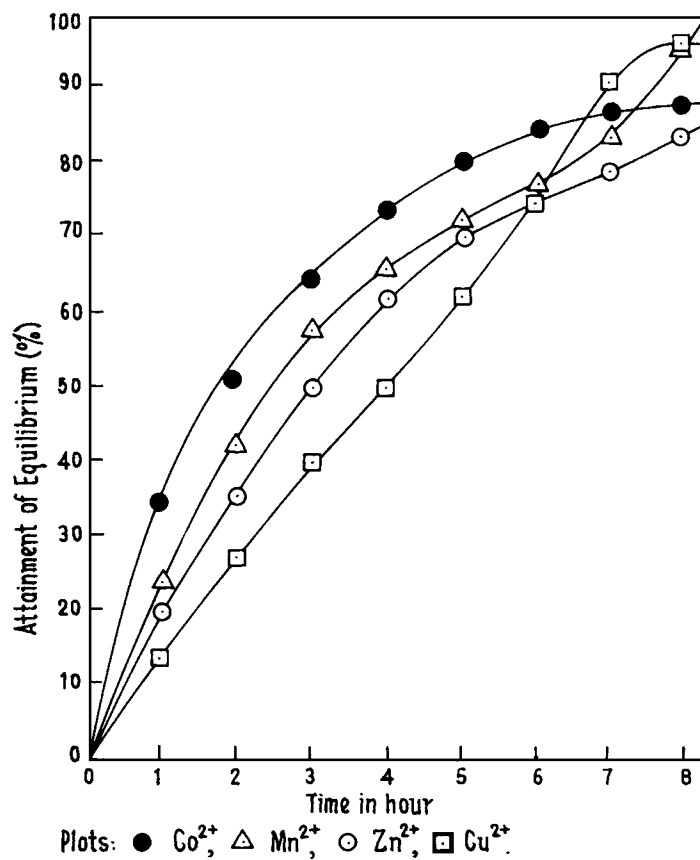
NaNO<sub>3</sub> = 1 mol/L; Volume = 25 mL.

pH = 6; Temp. = room temperature.

Related to the amount of metal ions in the state of equilibrium (100%).



**Figure 3** Plot of the effect of basic electrolyte on the adsorption of  $\text{Cu}^{2+}$  by QA-2,4-DNPH-HQ-F resin.



**Figure 4** Plot of (%) attainment of equilibrium versus time.

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

Metal Ion	pH				
	2	4	6	7	8
Cu <sup>2+</sup>	39.0	49.5	71.0	75.0	89.58
Co <sup>2+</sup>	22.0	37.53	65.0	73.0	83.0
Ni <sup>2+</sup>	22.0	31.55	61.56	75.0	83.0
Mn <sup>2+</sup>	32.0	44.0	73.0	82.0	94.0
Mg <sup>2+</sup>	21.0	45.0	70.0	78.0	95.0
Zn <sup>2+</sup>	24.0	31.0	55.0	69.0	84.0

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

Me(NO<sub>3</sub>)<sub>2</sub> = 0.1 mol/L; Volume = 2 mL.

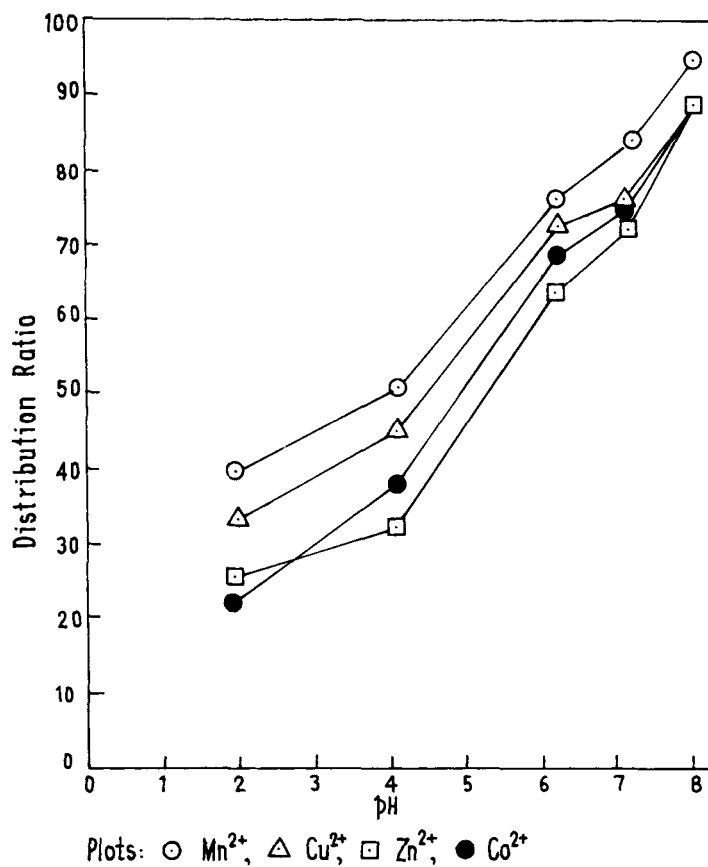
NaNO<sub>3</sub> = 1 mol/L; Volume = 25 mL.

Time = 24 h; Temp. = room temperature (equilibrium state).

(Fig. 5). The results of this study are helpful in selecting the optimum pH for selective uptake of a metal ion from a mixture of different ions.

Comparing the rate of metal uptake and the distribution of metal ions at different pH, it is observed that the resin prepared from 2,4-dinitrophenyl hydrazone of quin-

acetophenone-formaldehyde is a more efficient ligating reagent than quinacetophenone-formaldehyde resin. This is because of the presence of two donor nitrogen atoms in the proximity of the hydroxyl group of the acetophenone moiety which can donate electrons to the metal ions for a complex formation.

**Figure 5** Plot of distribution ratio versus pH.

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