

Synthetic Resins. XIV. Chelation Ion Exchange Properties of 2,4-Dinitro Phenylhydrazone of 2-Hydroxy Acetophenone-Formaldehyde Resin

Much research is being directed towards the preparation of polymeric chains which are propagated because of the formation of metallic chelates, so that also synthetic resins derived from hydroxy and amino compounds have attracted the attention of many research workers because of their versatile use as ion exchangers, photographic binders, thermal stabilizers, etc. Pennington and Williams¹ prepared a chelating ion-exchange resin by condensing resacetophenone with formaldehyde in the presence of NaOH as catalyst. Sykora and Dubsky² have prepared a selective ion exchange resin by reacting a condensation product of resacetophenone and anthranilic acid with formaldehyde. Parmar et al.³ have synthesized resacetophenone formaldehyde resin in acidic medium and studied their chelation ion exchange properties. Recently Nayak and coworkers⁴⁻⁹ have reported the synthesis and characterization of some resin polymers derived from a large number of hydroxy and amino acetophenones. A survey of the literature reveals that the systematic studies have been carried out for the ligating and ion-exchange properties of the resins derived from 2,4-dinitrophenyl hydrazone derivatives of 2-hydroxy acetophenone. This communication represents the chelation ion-exchange properties of 2,4-dinitrophenyl hydrazone of 2-hydroxy acetophenone-*o*-hydroxy benzoic acid-formaldehyde resin.

PREPARATION OF THE RESIN

A mixture of 2,4-dinitrophenyl hydrazone of 2-hydroxy acetophenone, substituted benzoic acid or substituted phenols (0.0025 mol), and formaldehyde (0.1 mol) were refluxed at 110°C for 8–10 h in presence of 2 mL of 2*N* HCl. After the completion of the reaction contents were extracted with ice cold water, filtered, and washed repeatedly with hot water to remove the unreacted materials. The residue was then dried in vacuum. The method of studying ion-exchange properties have been presented in our previous communication.⁴⁻⁹

RESULTS AND DISCUSSION

Influence of Electrolytes on the Metal Uptake

The influence of the electrolytes such as Cl^- , NO_3^- , SO_4^{2-} , and ClO_4^- at various concentrations on the position of the equilibrium of metal polymers interaction have been investigated. The results have been furnished in Table I. The perusal of the results indicates that the amount of Cu^{2+} , Mn^{2+} , Zn^{2+} , Mg^{2+} , CO^{2+} , and Ni^{2+} are

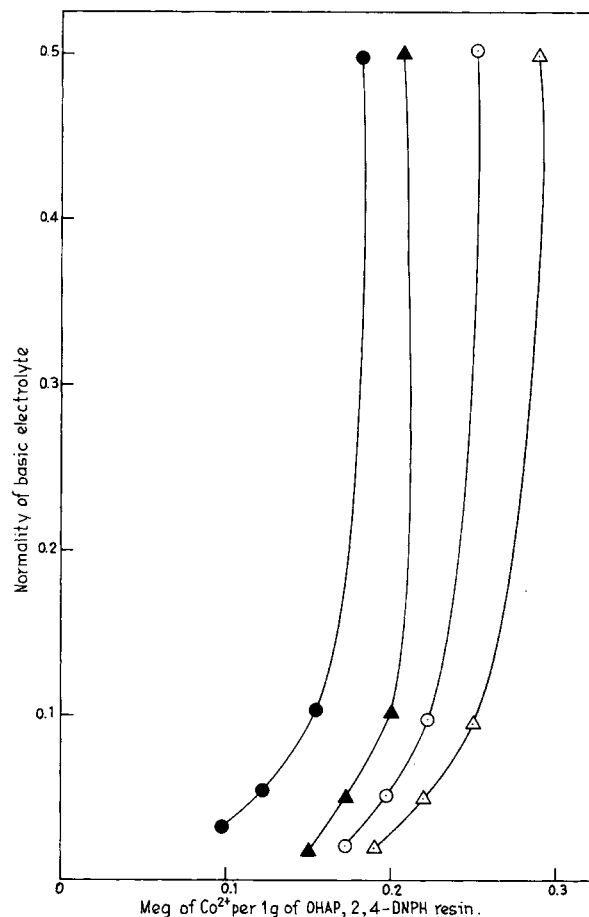


Figure 1 A plot of the effect of basic electrolyte on the absorption of Co^{2+} of OHAP 2,4-DNPH resin: (Δ) NaCl; (\circ) NaClO_4 ; (\blacktriangle) Na_2SO_4 ; (\bullet) NaNO_3 .

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

Metal Ion	Electrolytes (mol/L)	pH	Weight (mmol) of Metal Ion Uptake in Presence of			
			NaCl	NaNO ₃	Na ₂ SO ₄	KClO ₄
Cu ⁺²	0.01	10	0.117	0.102	0.231	0.072
	0.05		0.124	0.144	0.282	0.112
	0.1		0.143	0.153	0.317	0.156
	0.5		0.178	0.176	0.345	0.192
Co ²⁺	0.01	6	0.172	0.079	0.141	0.184
	0.05		0.196	0.112	0.156	0.201
	0.1		0.234	0.136	0.194	0.234
	0.5		0.293	0.158	0.204	0.255
Ni ⁺²	0.01	10	0.168	0.126	0.071	0.164
	0.05		0.192	0.139	0.154	0.179
	0.1		0.206	0.162	0.179	0.187
	0.5		0.225	0.189	0.193	0.194
Mg ⁺²	0.01	10	0.085	0.105	0.095	0.124
	0.05		0.096	0.130	0.108	0.138
	0.1		0.116	0.151	0.122	0.146
	0.5		0.135	0.164	0.152	0.174
Zn ⁺²	0.01	6	0.139	0.048	0.188	0.184
	0.05		0.154	0.093	0.215	0.216
	0.1		0.174	0.125	0.243	0.230
	0.5		0.198	0.140	0.281	0.276
Mn ⁺²	0.01	10	0.112	0.109	0.125	0.147
	0.05		0.158	0.126	0.141	0.168
	0.1		0.174	0.142	0.175	0.173
	0.5		0.196	0.158	0.210	0.205

^a Resin studies: 2-HAP, 2,4-DNPH-OHBA = Formaldehyde: Me = metal; [Mt(NO₃)₂] = 0.1 mol/L; volume of electrolyte solution 25 mL; volume of metal ion solution 2 mL; time 24 h; temperature, room temperature.

taken up by the copolymer (2,4-dinitrophenyl hydrazone of 2-hydroxy acetophenone-2-hydroxy benzoic acid-formaldehyde, 2-HAP 2,4-DNPH-OHBA-F) sample in-

Table II Comparison of Rates of Metal Ion Uptake in Different Time^a

Metal Ion	% of Metal Ion Uptake at Different Time (h)							
	1	2	3	4	5	6	7	8
Cu ⁺²	20	48	70	82	85	88	94	95
Co ²⁺	38	61	74	82	86	90	97	—
Ni ⁺²	27	61	72	77	84	88	96	—
Mg ⁺²	15	33	48	60	72	83	88	95
Mn ⁺²	24	43	64	73	80	85	91	96
Zn ⁺²	16	38	51	58	64	71	79	84

^a [Me(NO₃)₂] = 0.1 mol/L; volume 2 mL, [NaNO₃] = 1 mol/L; volume 25 mL; temp 25°C. Related to the amount of metal ions in the state of equilibrium (100%).

creases with the increase of the concentration of Cl⁻, NO₃⁻, SO₄⁻², and ClO₄⁻ ions. This may be explained in terms of the stability constants of the complexes with Cu²⁺, Ni²⁺, Co²⁺, Zn²⁺, Mn²⁺, and Mg²⁺ ions with ligands. This indicates that the above anions form strong chelates with the metal ions. The effect of Co²⁺ with different electrolyte was shown in Figure 1.

Rate of Metal Uptake

The rate of metal adsorption was determined to find out the shortest time period for which equilibrium could be carried out while operating as close to equilibrium condition as possible. Table II shows the dependence of the rate of metal ion uptake on the nature of the metal. The perusal of the results indicate that Co²⁺ and Ni²⁺ ions require about 7 h for equilibrium whereas Cu²⁺, Mg²⁺, and Mn²⁺ ions require about 8 h for equilibrium. The rate of metal uptake follows the order Co²⁺, Ni²⁺ > Cu²⁺, Mg²⁺, Mn²⁺ > Zn²⁺, which is shown in Figure 2.

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

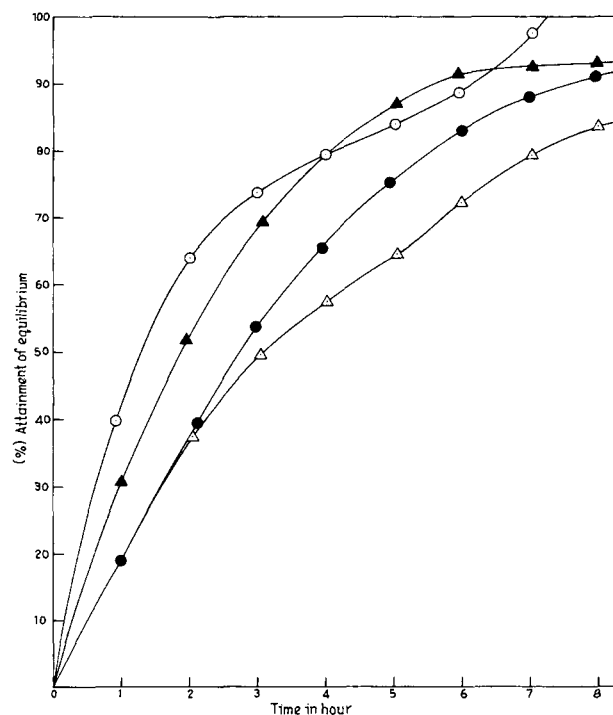
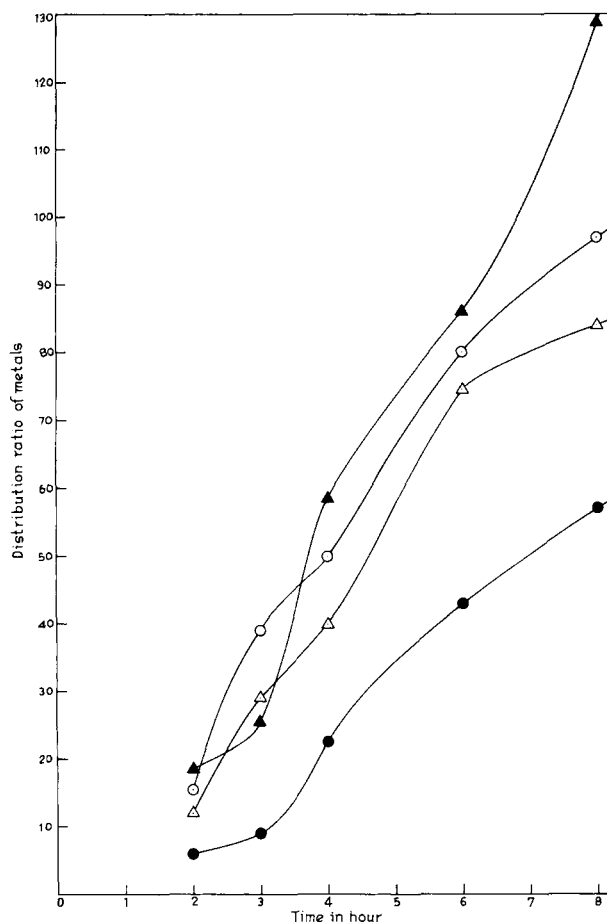
Metal Ion	Distribution Ratio of the Metal Ions at Different pH				
	2	3	4	6	8
Cu ²⁺	17.6	24.4	56.8	85.6	126.7
Co ²⁺	14.5	19.8	25.4	36.9	42.2
Ni ²⁺	12.7	26.4	39.2	74.5	102.6
Mn ²⁺	6.12	8.74	22.51	43.7	62.8
Mg ²⁺	7.42	21.0	47.6	52.63	77.4
Zn ²⁺	15.47	39.9	51.6	75.6	84.2

$$^a D^* = \frac{\text{mmol metal on the copolymer}}{\text{mmol metal in the solution}} \times \frac{\text{vol solution}}{\text{wt copolymer}}$$

Me(NO₃)₂ 0.1 mol/L; volume 2 mL; NaNO₃ 1 mol/L; volume 40 mL; time 24 h; equilibrium state; temp 25°C.

Distribution of the Metal Ion at Different pH

The effect of pH on the amount of metal ions distribution between the two phases has been studied. The perusal of the results shown in Table III indicates that the relative amount of the metal ion taken up by the copolymer increases with the increase of pH of the medium. The in-


Figure 2 Rate of metal uptake: (○) Co²⁺; (▲) Cu²⁺; (●) Mg²⁺; (△) Zn²⁺.

Figure 3 A plot of distribution ratio: (●) Mn²⁺; (○) Ni²⁺; (▲) Cu²⁺; (△) Zn²⁺.

vestigation was carried out up to a definite pH value for the particular metal ion to prevent the hydrolysis of metal ions at higher pH. Cu²⁺ and Ni²⁺ ions are taken up more selectively by the copolymer than Co²⁺, Mn²⁺ and Zn²⁺, Mg²⁺, and Mn²⁺ ions have low distribution ratio between pH 2 and pH 4. This could be attributed to the low stability constants, i.e., weak ligand stabilization energy of the metal complexes.^{10,11} The observed order of metal ion distributions is Cu²⁺ > Ni²⁺ > Zn²⁺ > Mg²⁺ > Mn²⁺ > Co²⁺, which is shown in Figure 3. The observed order of distribution ratios of divalent metal ions measured in the range of pH from 2 to 8 are similar to that of the distribution predicted by Irving and Williams.¹⁰ Hence this study is very much useful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different ions.

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D. K. RATH
P. L. NAYAK
S. LENKA

Department of Chemistry
Ravenshaw College
Cuttack-753 003
Orissa, India

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