

Synthetic Resins. XXXVI. Synthesis, Characterization, and Study of Chelation Ion-Exchange Properties of Quinol–Crotonaldehyde Resin

INTRODUCTION

During the last two decades the polymerization of a large number of unsaturated aldehydes^{1,2} has been extensively investigated. The polycondensation of phenol with formaldehyde has also been studied.³ Not much work has been done on polycondensation of substituted aromatic compounds with unsaturated aldehyde. In the last few years extensive use has been made of ¹H-NMR spectroscopy for studying phenol–urea and melamine–formaldehyde resins. Most articles have been published^{4–8} on phenol–formaldehyde resins. Much research is being directed toward the preparation of polymeric chains, which are propagated because of the formation of metallic chelates. Most of the workers in the field of polymeric chelates were primarily interested in the synthesis of chelating resins. Gregor et al.⁹ and Pennington and Williams¹⁰ used the batch equilibrium method to determine selectivity and capacity of chelating polymers with solutions of metal ions containing a buffer of high capacity. Pennington and William¹¹ prepared a chelation ion-exchange resin by condensing resacetophenone with formaldehyde in the presence of NaOH as a catalyst. Sykora and Dubsy¹² prepared a selective ion-exchange resin by reacting a condensation product of resacetophenone and anthranilic acid with formaldehyde. Parmar et al.¹³ synthesized resacetophenone formaldehyde resin in an acidic medium and studied their chelation ion-exchange properties. Lenka et al.^{14–17} studied the ion-exchange properties of a large number of resins synthesized by condensing aromatic-substituted compound with formaldehyde. Majda Zigon et al.^{18,19} synthesized resorcinol–cinnamaldehyde–crotonaldehyde resins in different mediums and characterized their properties.

The work described in the present communication deals with the systematic study of the selectivity and capacity of quinol–crotonaldehyde resins.

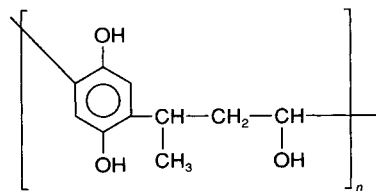
EXPERIMENTAL

A mixture of quinol (0.02 mol) and crotonaldehyde (0.02 mol) was taken in a glass vessel along with 2 mL of acetone. Then 2 mL of concentrated hydrochloric acid was added dropwise to the reaction mixture. The glass vessel was

then equipped with a condenser, a magnetic stirrer, and a water bath. The contents were refluxed at 50–60°C for 5 h. During the heating process the mixture was shaken periodically. After completion of the reaction, the mixture was poured into ice-cold water. The solid obtained was filtered, followed by repeated washing with hot distilled water and finally dried in vacuum. The same procedure was adopted for preparing resins in NaOH medium by heating for 8 h, and IR and ¹H-NMR spectra were studied at R.S.I.C., C.D.R.I., Lucknow.

CHARACTERIZATION OF RESINS

A typical crotonaldehyde condensate of quinol may attribute the repeat unit of this type,



which was confirmed by the characteristic IR bands and illustrated in Figure 1.

Further, its ¹H-NMR spectra was done in a Perkin-Elmer R-32 at R.S.I.C., C.D.R.I. Lucknow, and the possible types of couplings observed are shown in Figure 2. From the value of chemical shift and types of coupling, the plausible repeat unit of the resin was also predicated.

ION-EXCHANGE STUDY

Resins were ground in a pebble mill, dry sieved to obtain a 40/60 mesh range fraction, and then placed in a glass column and back washed with demineralized water to remove extraneous chemicals. The resins were converted to their hydrogen forms by passing a large excess of 5N 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. The kinetics of the exchange process of a typical resin (quinol–crotonaldehyde) was studied in detail. Electrolytes such as NaCl, NaNO₃, KCl,

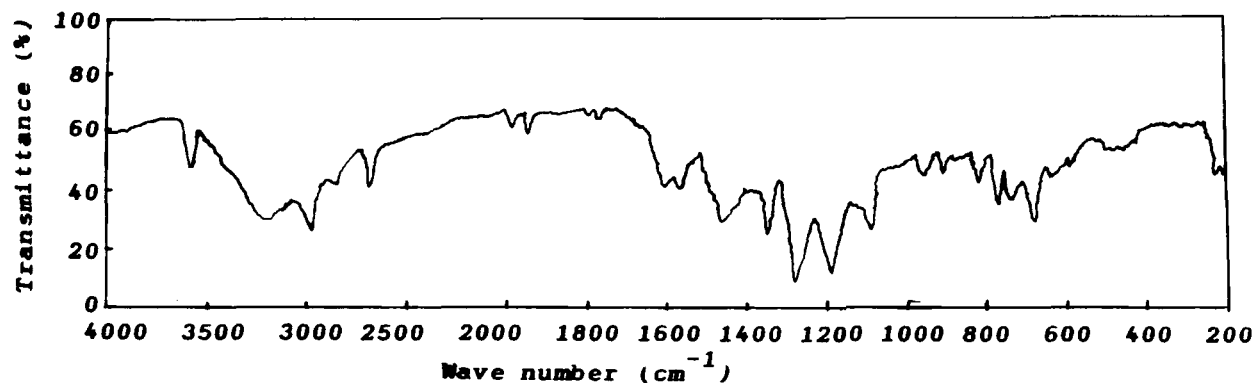


Figure 1 Infrared spectra of quinol-crotonaldehyde resin.

Na_2SO_4 , and NaClO_4 were taken at varying molar concentrations with variations of pH. The percentage (%) of attainment of equilibrium with time was also studied.

Determination of Metal Uptake in the Presence of Various Electrolytes

The resin samples (25 mg each) were suspended in the electrolyte solution (0.25 mL) of known concentration. The pH of the solution was adjusted to the required value by using either 0.1 M HCl or 0.1 M NaOH. The suspension was stirred for a period of 24 h at 25°C. To this suspension, 2 mL of 0.1 M solution of the metal ion under study was added and the pH was adjusted. The mixture was stirred at 25°C for 24 h and then filtered. The solid was washed. The filtrate and washings were collected and estimated for metal ion uptake by titrating against standard EDTA. A blank was also estimated for the metal ion content. The amount of metal ion taken up by the polymer in the presence of a given electrolyte of known concentration is a result of the difference between the blank reading and the reading in the actual experiment. This experiment was

repeated in the presence of several electrolytes. The results with five different metal ions are reported in Table I.

Evaluation of the Rate of Metal Uptake

In order to estimate the time required to reach the state of equilibrium under given experimental conditions, a series of experiments of the type discussed above was carried out in which the metal ion taken up by the chelating resins was estimated periodically at 25°C in the presence of 25 mL of 1 M NaNO_3 solution. It is assumed that, under the given conditions, the state of equilibrium is established in 24 h. The rate of metal uptake is expressed as percentage of the amount of metal ion taken up after a certain time, related to that in the state of equilibrium (Table II) using the following equation:

Percent of attainment of the state of equilibrium

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

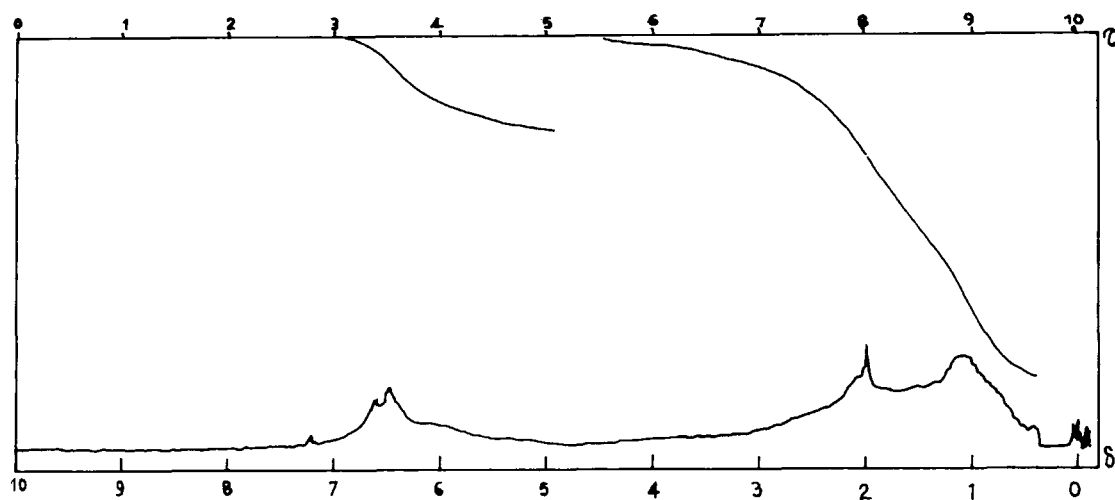


Figure 2 $^1\text{H-NMR}$ spectra of quinol-crotonaldehyde.

Table I Effect of Different Electrolytes on the Uptake of Several Metal Ions for Quinol-Crotonaldehyde Resin^a

Metal (1)	Concentration of Electrolyte (mol/L) (2)	pH (3)	Milimoles of Metal Absorbed per Gram of Dry Resin in Presence of				
			NaCl (4)	NaNO ₃ (5)	KCl (6)	Na ₂ SO ₄ (7)	NaClO ₄ (8)
Mg ²⁺	0.01	10	0.168	0.189	0.152	0.136	0.157
	0.05		0.178	0.168	0.164	0.152	0.168
	0.1		0.194	0.152	0.171	0.157	0.171
	0.5		0.198	0.142	0.184	0.165	0.176
Co ²⁺	0.01	6	0.165	0.193	0.173	0.151	0.182
	0.05		0.144	0.179	0.163	0.158	0.176
	0.1		0.132	0.158	0.152	0.172	0.162
	0.5		0.124	0.144	0.138	0.177	0.155
Fe ²⁺	0.01	10	0.180	0.136	0.177	0.119	0.153
	0.05		0.153	0.131	0.168	0.117	0.164
	0.1		0.141	0.126	0.152	0.112	0.172
	0.5		0.131	0.117	0.146	0.102	0.179
Cu ²⁺	0.01	10	0.116	0.189	0.108	0.174	0.126
	0.05		0.112	0.181	0.102	0.167	0.133
	0.1		0.101	0.167	0.191	0.163	0.149
	0.5		0.090	0.156	0.084	0.156	0.162
Cd ²⁺	0.01	10	0.074	0.109	0.078	0.103	0.114
	0.05		0.067	0.106	0.069	0.112	0.108
	0.1		0.064	0.093	0.058	0.148	0.096
	0.5		0.061	0.087	0.053	0.170	0.088

^a Mt (NO₃) = 0.1 mol/L; volume = 2 mL; volume of electrolyte = 25 mL; temperature = room temperature.

Evaluation of Distribution of Metal Ions at Different pH

The distribution of each of the metal ions, Cu²⁺, Co²⁺, Mg²⁺, Fe²⁺, and Cd²⁺ between the polymeric ligand and the aqueous phase, was estimated at 25°C in the presence of 1 M NaNO₃ solution at different pH values of 3, 4, 4.5, 5, 6, 8, and 10. From the known starting concentration and the amount of metal in solution after each equilibrium, the distribution ratio of the metal between the solution and the resin was calculated according to

$$K_D = \frac{\text{mmol of metal ion on the copolymer}}{\text{mmol of metal ion in solution}} \times \frac{\text{vol. of solution}}{\text{wt. of copolymer}}$$

where K_D is the distribution constant.

The results are shown in Table III.

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

Metal Ion	pH	% of Metal Ion Uptake at Different Times (h)						
		2	4	6	8	10	12	24
Mg ²⁺	10	42	55	77	84	87	93	—
Co ²⁺	6	24	48	68	72	84	92	—
Cu ²⁺	10	32	60	74	90	96	—	—
Fe ²⁺	10	51	75	86	89	98	—	—
Cd ²⁺	10	31	43	56	69	75	89	—

^a Me(NO₃) = 0.1 mol/L; volume = 2 mL; NaNO₃ = 0.5 mol/L, volume = 2 mL; temperature = room temperature, related to the amount of metal ion in the state of equilibrium (100%).

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

Metal Ion	Distribution Ratio						
	3	4	4.5	5	6	8	10
Mg ²⁺	49.4	68.7	92.8	104.3	136.8	139.1	158.5
Co ²⁺	65.3	139.1	197.8	249.7	363.2	505.26	576.8
Cu ²⁺	38.4	72.8	96.2	144.7	272.2	292.3	297.78
Fe ²⁺	43.6	82.8	115.78	167.3	224.2	236.5	258.3
Cd ²⁺	53.2	72.5	89.6	161.7	193.1	298.4	368.8

^a $D^* = \frac{\text{mmol of metal ion in the copolymer}}{\text{mmol of metal ion in the solution}} \times \frac{\text{vol. of solution}}{\text{wt. of copolymer}}$; Me(NO₃) = 0.1 mol/L; volume = 2 mL; NaNO₃ = 1 mol/L; volume = 40 cm³; time = 24 h; temp. = room temperature.

RESULTS AND DISCUSSION

Influence of Electrolytes on the Metal Uptake

The influence of the electrolytes such as Cl⁻, NO₃⁻; SO₄⁻, and ClO₄⁻ of various concentrations on the position of the equilibrium of metal-polymer interaction have been investigated. Perusal of data given in Table I reveals that the amount of Fe²⁺ and Cu²⁺ and Cd²⁺ ions taken up by quinol-crotonaldehyde copolymer samples decreases with increasing concentration of Cl⁻, NO₃⁻, and SO₄⁻ and increases with increasing concentration of Cl⁻, NO₃⁻, and SO₄⁻ and increases with increasing concentration of ClO₄⁻, whereas uptake of Co²⁺ and Cd²⁺ ions by the copolymer decreases with increasing concentration of Cl⁻, NO₃⁻ and ClO₄⁻ and increases with increasing concentration of SO₄⁻. But in the case of the Mg²⁺ metal ion, the amount of uptake decreases with increasing concentration of NO₃⁻ and increases with increasing concentration of Cl⁻, SO₄⁻, and ClO₄⁻.

Rate of Metal Uptake

The rate of metal adsorption was determined to indicate the shortest time period for which equilibrium could be carried out while operating as close to the equilibrium condition as possible. Table II shows the dependence of the rate of metal ion uptake on the nature of the metal. The results indicate that Cu²⁺ and Fe²⁺ ions require 10 h for equilibrium, whereas the Mg²⁺, Co²⁺, and Cd²⁺ ions require about 12 h for equilibrium. The rate of metal uptake follows the order Fe²⁺ > Cu²⁺ > Mg²⁺, Co²⁺ > Cd²⁺.

Distribution of the Metal Ion at Different pH

Table III represents the effect of pH on the distribution ratios of the metal ions between an aqueous solution and resin. The data indicates that the relative amount of the

metal ion taken up by the copolymer increases with the increase in pH of the medium. 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. Cu²⁺ and Cd²⁺ ions have low distribution ratios between pH 3 and pH 4.5. This could be attributed to the low stability constants, that is, the weak ligand stabilization energy of the metal complexes.²⁰ Co²⁺ ions are taken up more selectively than any other metal ions under study. The observed order of metal ion distribution is Co²⁺, Cd²⁺, Cu²⁺, Fe²⁺, and Mg²⁺. The observed order of distribution ratios of divalent metal ions, measured in the range of pH 3–10, are similar to that of the distribution predicated by Irving and Williams.²¹ Hence, this study is useful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different ion.

The chelating behavior of some of the resins prepared has been compared with the chelating behavior of some model chelating compounds. It has been found that some of the polymers have chelating properties comparable to the model compounds. Further investigation on this topic is in progress and will be published in the future.

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