

Synthetic Resins. XVIII. Chelation Ion Exchange Properties of 2,4-Dinitrophenylhydrazone of 4-Hydroxy Acetophenone–Formaldehyde Resins

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SYNOPSIS

A large number of copolymers were synthesized by condensing 2,4-dinitrophenyl hydrazone of 4-hydroxy acetophenone (4 HA 2,4 DNPH) with substituted benzoic acids/phenols and formaldehyde in the presence of NaOH or HCl as catalyst. The resins were characterized by IR spectra. The decomposition temperature, solubility parameter, and viscosity of the polymers have been determined. The ion-exchange properties have been studied using the batch equilibrium method. The measurement of the distribution of a given metal ion between an aqueous solution and the resins has been performed. The investigation was carried out over a wide range of pH and varying the ionic strength of the medium. © 1992 John Wiley & Sons, Inc.

INTRODUCTION

Much research is being directed towards the preparation of polymeric chains, which are propagated because of the formation of metallic chelates. During the last four decades, interest in the chemistry of coordination compounds has increased substantially because of the compound biological interest. Most of the workers in the field of polymeric chelates were primarily interested in the synthesis of chelating resins. Gregor et al.¹ and Pennington and Williams² 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 Williams³ prepared a chelation ion-exchange resin by condensing resacetophenone with formaldehyde in the presence of NaOH as a catalyst. Sykora and Dubsy⁴ have prepared a selective ion exchange resin by reacting a condensation product of resacetophenone and anthranilic acid with formaldehyde. Parmar et al.⁵ have synthesized resacetophenone formaldehyde resin in an acidic medium and have studied their chelation ion exchange properties. Patel⁶ reported the prep-

aration and chelating properties of polychalkones derived from 8-hydroxy quinoline-5 aldehyde. Patel and Patel⁷ studied the synthetic study of ion-exchange properties and ligating behavior of res-propiophenone–formaldehyde copolymers.

The work described in the present communication deals with the systematic study of the selectivity and capacity of 2,4-dinitrophenyl hydrazones of 4-hydroxy acetophenone, acetyl salicylic acid–formaldehyde resin.

EXPERIMENTAL

Preparation of the Resins

Method I

A mixture of 2,4-dinitrophenyl hydrazones of 4-hydroxy acetophenone, 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 2N HCl. After the completion of the reaction, the contents were extracted with ice-cold water and were filtered and washed repeatedly with hot water to remove the unreacted materials. The residue was then dried in vacuum. The resins prepared by the above method are furnished in Table I.

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Table I Physico-Chemical Properties of Resins Derived from 4-Hydroxyacetophenone 2,4-Dinitrophenylhydrazone

Sl. No.	Comonomer	Catalyst	Heating Time (h)	D.T.	Color	Solubility	Solubility Parameter (δ) Ranges in Solvents that are Hydrogen Bonded (J/m^3) $\frac{1}{2} \times 10^8$		
							Weak	Moderate	Strong
1	O-Hydroxy Benzoic Acid	HCl	8	210	Deep Brown ^c	DMF, DMSO	—	18.6–24.8	21.9–24.8
2	P-Hydroxy Benzoic Acid	HCl	8	170	Brown ^c	DMF	—	19.2–24.8	21.9–24.8
3	O-Amino Benzoic Acid	HCl	10	> 300	Brown ^c	Pyridine	—	18.6–24.8 ^b	21.9–24.8
4	P-Amino Benzoic Acid	HCl	8	230	Chocolate ^c	DMSO	—	19.2–24.8	21.9–24.8
5	Acetylsalicylic Acid	HCl	8	> 300	Reddish Gray ^c	DMF	—	19.2–24.8	20.7–24.8
6	α -Naphthol	HCl	8	> 300	Brown ^c	Acetone	17.6–21.5	18.6–24.8	18.6–29.7
7	β -Naphthol	HCl	8	260	Yellowish Brown ^a	Pyridine	18.8–20.5 ^b	19.2–20.3 ^b	18.6–21.9 ^b
8	Resorcinol	HCl	10	170	Black ^a	DMSO	—	18.6–24.8	21.9–24.8
9	P-Hydroxy Benzoic Acid	NaOH	6	220	Grayish Black ^a	DMF	—	24.6–24.8	21.9–25.8
10	M-Toluic Acid	NaOH	10	> 300	Brown ^c	Acetone	—	18.6–24.8 ^b	18.6–21.9 ^b
11	O-Toluic Acid	NaOH	10	250	Brown ^c	THF	—	19.2–24.8	18.6–25.8
12	P-Chloroniline	NaOH	6	240	Black ^a	Pyridine	18.8–20.5	19.2–20.3	18.6–21.9
13	P-Amino Benzoic Acid	NaOH	10	> 300	Orange ^a	Methanol	18.2–20.5	19.2–24.8 ^b	18.6–29.7 ^b
14	Phenolphthalein	NaOH	6	> 300	Yellow ^c	Nitrobenzene	19.0–19.4	18.6–24.8 ^b	—
15	M-Aminoaceto-Phenone	NaOH	8	260	Grayish Yellow ^c	DMF	—	19.2–24.8	20.7–24.8

^a Amorphous.

^b Swelling parameter.

^c Crystalline.

Method II

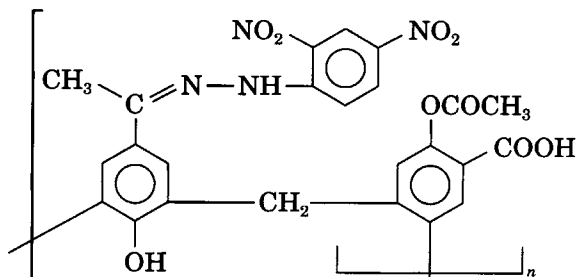
The copolymer sample was prepared by condensing 2,4-dinitrophenyl hydrazone of 4-hydroxy acetophenone (0.005 mol) with substituted benzoic acid or substituted phenols and formaldehyde (0.1 mol) in a round bottom flask in the presence of NaOH (40%) as the catalyst. The reaction mixture was heated at 100°C for 8–10 h. After the completion of the reaction, the contents were extracted with ice-cold water, were filtered, and washed repeatedly with hot water to remove the unreacted materials. The resins prepared by the above method are listed in Table I.

Characterization of Resins

The resins were characterized by dilute solution viscometry, using an ubbelohde suspended level viscometer. The measurements were carried out with 0.5% (w/v) solution in dimethylsulfoxide, dimethyl formamide, and acetone at 30°C.

The solubility characteristics were studied by placing (0.01 g) of resin in 2 mL of various solvents and allowing the solutions to stand for 2 weeks. The solvent effect was judged in terms of swelling or dissolution. The solubility parameter of each was then computed.

A typical formaldehyde condensate of 2,4-dinitrophenyl hydrazone of 4-OH acetophenone, acetyl salicylic acid may attribute the structure of this type, which was confirmed by the characteristic IR bands (Fig. 1).



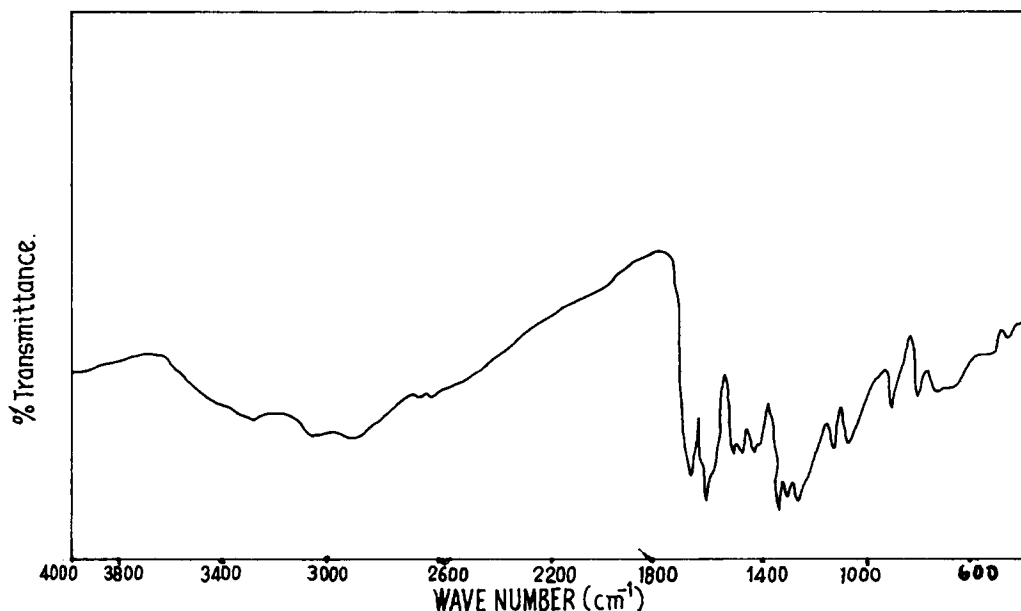


Figure 1 IR spectra of 4 HAP 2,4-DNPH-ASA-F resin.

The structure of the repeat unit of this resin was identified from IR spectra (Perkin-Elmer 781 spectrophotometer, KBr Pellets). The polymer shows characteristic IR bands (Fig. 1) near 1600, 3300, and 1650 cm^{-1} , for C=N stretching, N—H stretching, and N—H bending (scissoring) vibrations of secondary amines, respectively. Bands near 1350 and 1300 cm^{-1} are for secondary and tertiary amines. Bands near 1150, 1420, and near 1465 cm^{-1} are for C—O stretching (phenol), O—H bending (phenol), and C—H bending of methylene group. Bands near 1575 and 1700 cm^{-1} are for carboxylate anionic stretching and C=O stretching due to the



Ion Exchange Study

Resins were ground in a pebblesmill, dry-sieved to obtain a 40/60 mesh range fraction, and then were 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 5 N HCl through the beds. After about 16 h, the converted exchangers were washed with a minimum of distilled water, were air dried, and were stored.

The resins were screened taking into consideration their exchange capacity. The kinetics of the

exchange process of a typical resin (2,4-dinitrophenyl hydrazone of 4-OH acetophenone, acetyl salicylic acid, HCHO) was studied in detail. Electrolytes, such as NaCl, NaNO_3 , 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 was filtered. The solid was washed. 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 same manner without adding the polymer sample. The 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 re-

Table II Evaluation of the Effect of Different Electrolytes in Uptake of Several Metal Ions, Me (NO₃)₂ 0.1 mol/L

Metal Ion	Electrolytes mol/L	pH	Weight in M mol of Metal Ion Uptake				
			NaCl	KCl	NaNO ₃	Na ₂ SO ₄	KClO ₄
Cu ²⁺	0.01	10	0.080	0.088	0.093	0.037	0.017
Cu ²⁺	0.05	10	0.073	0.078	0.076	0.056	0.034
Cu ²⁺	0.10	10	0.064	0.071	0.052	0.079	0.057
Cu ²⁺	0.50	10	0.057	0.064	0.039	0.096	0.083
Co ²⁺	0.01	6	0.128	0.099	0.106	0.031	0.043
Co ²⁺	0.05	6	0.115	0.093	0.099	0.056	0.063
Co ²⁺	0.10	6	0.097	0.086	0.090	0.067	0.079
Co ²⁺	0.50	6	0.071	0.084	0.086	0.091	0.097
Ni ²⁺	0.01	10	0.089	0.094	0.079	0.031	0.033
Ni ²⁺	0.05	10	0.081	0.076	0.051	0.054	0.042
Ni ²⁺	0.10	10	0.074	0.062	0.037	0.074	0.056
Ni ²⁺	0.50	10	0.051	0.047	0.022	0.099	0.080
Zn ²⁺	0.01	10	0.067	0.061	0.083	0.015	0.023
Zn ²⁺	0.05	10	0.061	0.054	0.072	0.043	0.047
Zn ²⁺	0.10	10	0.053	0.046	0.065	0.054	0.058
Zn ²⁺	0.50	10	0.027	0.017	0.039	0.065	0.066
Mn ²⁺	0.01	10	0.077	0.027	0.059	0.058	0.061
Mn ²⁺	0.05	10	0.069	0.025	0.053	0.065	0.068
Mn ²⁺	0.10	10	0.053	0.023	0.049	0.079	0.086
Mn ²⁺	0.50	10	0.028	0.018	0.043	0.093	0.095
Mg ²⁺	0.01	10	0.030	0.059	0.071	0.036	0.023
Mg ²⁺	0.05	10	0.027	0.053	0.065	0.047	0.029
Mg ²⁺	0.10	10	0.025	0.047	0.058	0.054	0.037
Mg ²⁺	0.50	10	0.021	0.026	0.038	0.082	0.061

Resin studied: 4-OH acetophenone 2,4-dinitrophenylhydrazon-acetylsalicylic acid-formaldehyde-HCl (4 HAP 2,4 DNP-ASA-F).

Volume of electrolyte solution: 25 mL.

Volume of metal ion solution: 2 mL.

Time: 24 h; Temp.: Room temperature.

peated in the presence of several electrolytes. The results with six different metal ions are reported in Table II.

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 described 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 NaNO₃ 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 III) using the following equation.

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

Metal Ion	% of Metal Ion Uptake at Different Times (h)							
	1	2	3	4	5	6	7	8
Cu ²⁺	21	43	57	65	73	78	85	94
CO ²⁺	24	53	72	84	93	97	98	100
Ni ²⁺	18	35	50	61	76	88	95	—
Mg ²⁺	6	20	37	51	68	87	95	98
Mn ²⁺	46	65	77	85	90	93	95	97
Zn ²⁺	35	55	71	79	85	89	92	97

Me (NO₃)₂ = 0.1 mol/L, Volume = 2 mL; NaNO₃ = 1 mol/L. Volume = 40 mL. pH = 6 for CO²⁺ and Zn²⁺; pH = 10 for Ni²⁺, Mn²⁺ and Mg²⁺.

Temp. = Room temperature; Related to the amount of metal ion in the state of equilibrium (100%).

$$\frac{\text{Amount of metal ion absorbed in m mol}}{\text{Amount of metal ion absorbed at equilibrium in m mole}} \times 100$$

Percentage of attainment
= of the state of equilibrium

Evaluation of Distribution of Metal Ions at Different pH

The distribution of each of the metal ions, Cu^{2+} , Co^{2+} , Ni^{2+} , Zn^{2+} , Mg^{2+} , Mn^{2+} , between the polymeric ligand and the aqueous phase, was estimated at 25°C in the presence of 1 M NaNO_3 solution at different pH values of 2, 3, 4, 6, and 8. 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:

$$K_D = \frac{\text{m mol of metal ion on the copolymer}}{\text{m mol of metal ion in solution}} \times \frac{\text{volume of solution}}{\text{weight of Copolymer}}$$

The results are shown in Table IV.

RESULTS AND DISCUSSION

Influence of Electrolytes on the Metal Uptake

The influence of the electrolyte, such as Cl^- , NO_3^- , SO_4^{2-} , and ClO_4^- at various concentrations, on the

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

Metal Ion	Distribution Ratio of Metal Ions at Different pH				
	2	3	4	6	8
Cu^{2+}	35.3	39.8	48.8	53.6	72.5
CO^{2+}	11.7	14.3	19.9	29.4	40.6
Ni^{2+}	8.4	10.3	42.8	114.4	163.1
Mn^{2+}	6.2	8.4	24.5	40	73.6
Mg^{2+}	37.4	62.7	102.0	128.4	237.6
Zn^{2+}	13.6	37.8	53.1	67.5	96.2

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

$\text{Me}(\text{NO}_3)_2 = 0.1 \text{ mol/L}$; Volume = 2 mL; $\text{NaNO}_3 = 1 \text{ mol/L}$; Volume = 40cc.

Time = 24 h; Temp.: Room temperature.

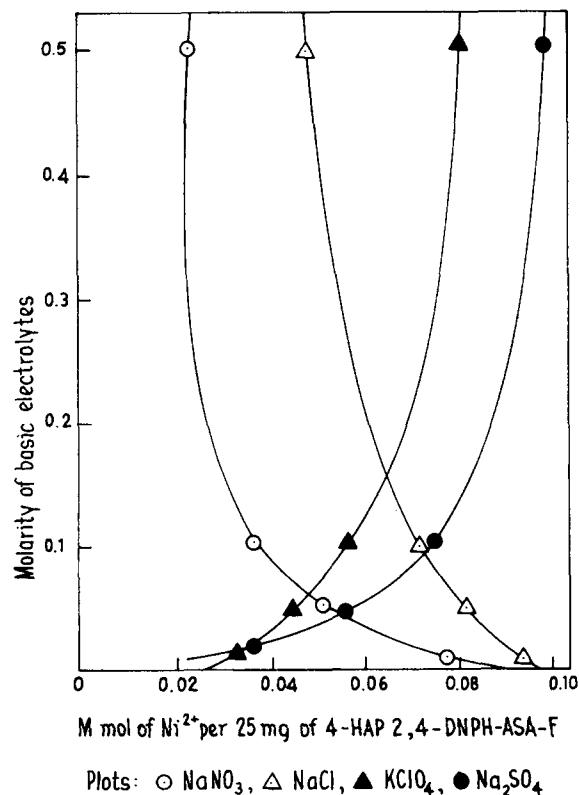


Figure 2 A plot of the effect of basic electrolyte on the adsorption of Ni^{2+} by 4-HAP 2,4-DNPH-ASA-F resin.

position of the equilibrium of metal polymer interaction, have been investigated. The results are shown in Table II. The result reveals that the amount of Cu^{2+} , Ni^{2+} , Co^{2+} , Zn^{2+} , Mg^{2+} , and Mn^{2+} that is taken up by the copolymer (4-HAP 2,4-DNPH-ASA-F) sample decreases with the increase of the concentration of the SO_4^{2-} and ClO_4^- ions. The amount of uptake ion, however, increases with increasing concentration of Cl^- , NO_3^- ion, which is shown in Figure 2.

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 III shows the dependence of the rate of metal ion uptake on the nature of the metal. The results indicate that Ni^{2+} ions require 7 h for equilibrium, whereas Cu^{2+} , Co^{2+} , Mg^{2+} , Mn^{2+} , and Zn^{2+} ions require about 8 h for equilibrium. The rate of metal uptake follows the order $\text{Ni}^{2+} < \text{Cu}^{2+} < \text{Mn}^{2+}, \text{Zn}^{2+} < \text{Mg}^{2+} < \text{Co}^{2+}$, which is shown in Figure 3.

Distribution of the Metal Ion at Different pH

Table IV represents the effect of pH on the distribution ratios of the metal ions between an aqueous solution and 4-HAP, 2,4-DNPH-ASA-F 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 (Fig. 4). 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. Ni^{2+} , Mn^{2+} , and Co^{2+} ions have low distribution ratios between pH 2 and pH 4. This could be attributed to the low stability constants, that is, the weak ligand stabilization energy of the metal complexes 8, 9. The observed order of metal ion distribution is Mg^{2+} , Ni^{2+} , Zn^{2+} , Mn^{2+} , Cu^{2+} , and Co^{2+} . The observed order of distribution ratios of divalent metal ions, measured in the range of pH 2 to 8, are similar to that of the distribution predicted by Irving and Williams.⁸ Hence, this study is useful in selecting the optimum pH for a selective uptake of a particular metal ion from a mixture of different ions.

The chelating behavior of some of the resins prepared has been compared with the chelating behavior of some model chelating compounds. It has been

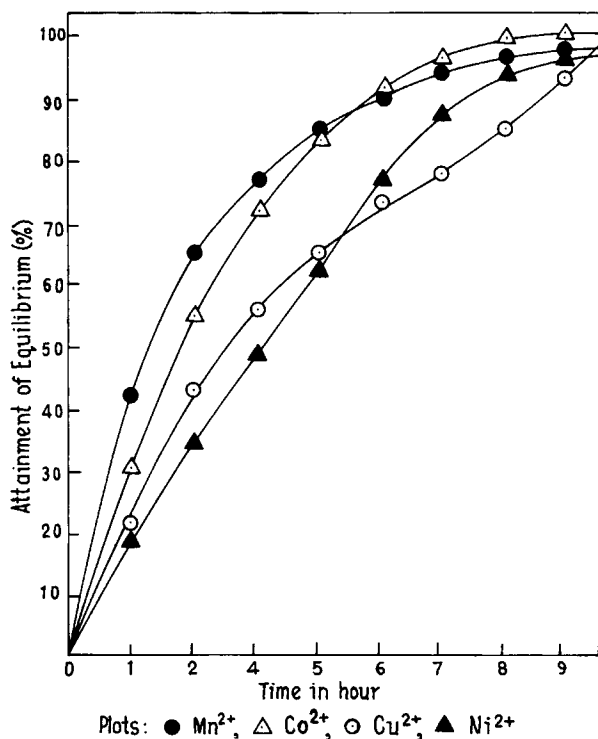


Figure 3 Rates of metal uptake of 4-HAP 2,4-DNPH-ASA-F resin at pH 6 for 0.1 M solutions of Mn^{2+} , CO^{2+} , Cu^{2+} , and Ni^{2+} nitrates.

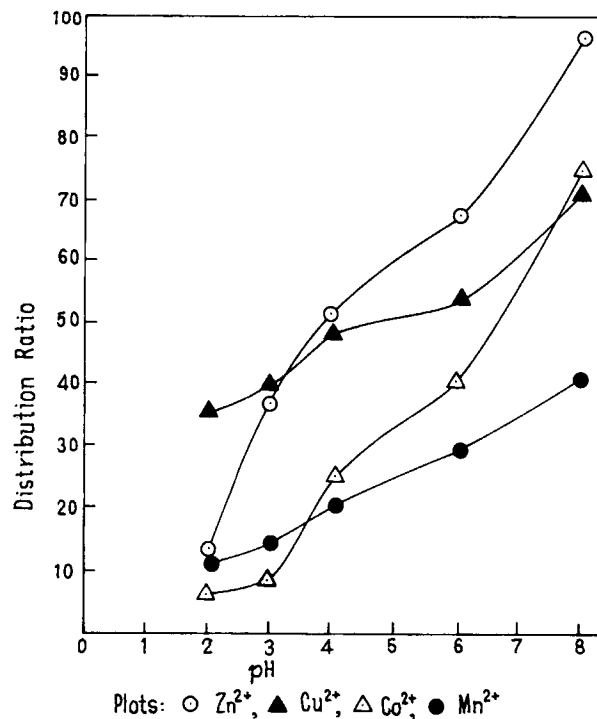


Figure 4 Distribution ratio of CO^{2+} , Mn^{2+} , Zn^{2+} , and Cu^{2+} nitrates at different pH.

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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