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SYNTHETIC RESINS. XXXV. CHELATION ION EXCHANGE PROPERTIES OF 2,4-DINITROPHENYL HYDRAZONE OF RESACETOPHENONE-FURFURAL RESIN

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A number of resin copolymers were synthesised by condensing 2,4-dinitrophenyl hydrazone of resacetophenone with furfural and substituted hydroxy aromatic compounds in the presence of some acids and bases as catalyst. The physicochemical properties of the resins have been reported. The ion exchange properties have studied by using a batch equilibrium method. The distribution of a number of metal ions between an aqueous solution and the resin have been measured. A wide range of pH and variable ionic strengths have been investigated.

INTRODUCTION :

Recently, the synthesis and characterisation of polymer-metal chelates has attracted the attention of many researchers because of their versatile uses[1]. Kurimera and coworkers[2] have reported a series of pendant type polymer-metal complexes having a uniform structure by the substituted reaction between a polymer ligand and a metal ion such as Co(III) and Cr(III). Dingman et.al[3]. studied the adsorption of metal ions on (polyethyl enimine) cross-linked with toluene diisocyanate and reported that the amount of metal ions adsorbed decreases with increase in the degree of cross-linking. Nayak and co-workers[4-14] have extensively studied the chelation ion-exchange properties of a large number of resin copolymers. This communication presents the results of the chelation ion-exchange properties of some resin co-polymers derived from 2,4-dinitrophenyl hydrazone derivatives of resacetophenone-furfural-resorcinol.

EXPERIMENTAL :

Preparation of the resins

A mixture of 2,4-dinitrophenyl hydrazone of resacetophenone (RA-2,4-DNPH) (0.05 mol), substituted benzoic acid or substituted phenols (0.05 mol) and furfural (0.01 mol) were refluxed at 110°-120°C for 8-10 h. in the presence of 2ml of 2N HCl or 40% NaOH. After the completion of the reaction, the contents were extracted with ice cold water and were filtered and washed repeatedly with hot water. The residue was then dried in vacuum. The resins prepared are listed in Table-I.

The metal uptake by different ions (Table-2), the study of the distribution ratio and the distribution of the metal ions at different pH were studied by our previous methods.[4-14]

RESULTS OF DISCUSSION

Influence of electrolytes on the metal uptake :

The influence of the electrolytes such as Cl^-, NO_3^-, SO_4^{-2} at various concentrations on the position of the equilibrium of metal-polymer interaction have been investigated. The results are shown in Table-2. The results reveal that the amount of Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2}, Mn^{+2}, Mg^{+2} taken up by the copolymer prepared from 2,4-dinitrophenylhydrazone of resacetophenone-resorcinol-furfural increases with an increase in the concentration of Cl^-, NO_3^- ions, but the uptake of the metal ions decreases with increasing the concentration of sulphate ions as shown in fig.1. This may be explained by considering the stability constants of the complexes of Cu^{+2}, Ni^{+2}, Co^{+2}, Zn^{+2} Mn^{+2}, Mg^{+2} ions which are formed with these ligands.[15-17] Sulphate ions may be forming strong chelates with the above metal ions, whereas the other ions are forming weak celates.

TABLE-I

Synthesis and analytical data of copolymers

Sl.No.	Copolymers[c]	Yield(%)	Colour
1.	RA 2,4-DNPH[a]+Resorcinol	63	Brown
2.	RA 2,4-DNPH[a]+Bisphenol-A	60	Black
3.	RA 2,4-DNPH[a]+Phenolphthalein	55	Brown
4.	RA 2,4-DNPH[b]+ α-naphthol	55	Black
5.	RA 2,4-DNPH[b]+ β-naphthol	55	Black
6.	RA 2,4-DNPH[b]+0-Toluic acid	60	Black
7.	RA 2,4-DNPH[a]+4-OH Benzoic acid	60	Black
8.	RA 2,4-DNPH[a]+4-Cl Benzoic acid	58	Black
9.	RA 2,4-DNPH[b]+2-NH_2-Benzoic acid	55	Black
10.	RA 2,4-DNPH[a]+2-OH-Acetophenone	60	Brown

[c] All the copolymers are soluble in DMSO,DMF, Acetone and their decomposition termperatures are more than 300°C.

RA 2,4-DNPH-Resacetophenone, 2,4-dinitrophenyl-hydrazone (2.5×10^{-3} Mol/litre)

a - Conc HCl, b - 40% NaOH.

Rate of metal uptake

Table-3 shows the dependence of the rate of metal ion uptake on the nature of the metal. The rates of metal absorption of the resins were determined to find out the shortest time period in which equilibrium could be attained, while operating as close to the equilibrium conditions as

TABLE-2

Evaluation of the effect of different electrolytes in uptake of several metal ions $Me(NO_3)_2$=0.1 mol/L for RA2,4DNPH-resorcinol furfural resin.

Metal ion	Electrolytes mol/L	pH	Weight in m.mol of metal ion uptakein presence of				
			NaCl	KCl	$NaNO_3$	KNO_3	Na_2SO_4
Cu^{+2}	0.01	10	0.065	0.071	0.079	0.082	0.162
	0.05		0.091	0.088	0.099	0.121	0.112
	0.1		0.121	0.095	0.130	0.140	0.094
	0.5		0.145	0.159	0.157	0.149	0.081
Zn^{+2}	0.01	6	0.057	0.061	0.035	0.035	0.093
	0.05		0.069	0.077	0.048	0.046	0.074
	0.1		0.072	0.079	0.052	0.053	0.063
	0.5		0.077	0.092	0.063	0.081	0.058
Mn^{+2}	0.01	10	0.023	0.035	0.028	0.026	0.178
	0.05		0.053	0.052	0.065	0.055	0.135
	0.1		0.073	0.089	0.105	0.074	0.094
	0.5		0.109	0.121	0.131	0.119	0.065
Cu^{+2}	0.01	6	0.051	0.059	0.042	0.060	0.153
	0.05		0.059	0.077	0.055	0.065	0.139
	0.1		0.075	0.081	0.061	0.076	0.129
	0.5		0.092	0.090	0.073	0.081	0.074
Mg^{+2}	0.01	10	0.024	0.036	0.070	0.039	0.061
	0.05		0.029	0.050	0.081	0.051	0.049
	0.1		0.031	0.062	0.095	0.059	0.025
	0.5		0.035	0.071	0.105	0.089	0.023
Ni^{+2}	0.01	10	0.024	0.031	0.028	0.020	0.175
	0.05		0.050	0.054	0.065	0.063	0.128
	0.1		0.081	0.083	0.098	0.110	0.103
	0.5		0.098	0.121	0.185	0.155	0.064

Volume of electrolyte solution : 25 ml.
Volume of metal ion solution : 2 ml.
Time : 24 h Temperature : room temperature.

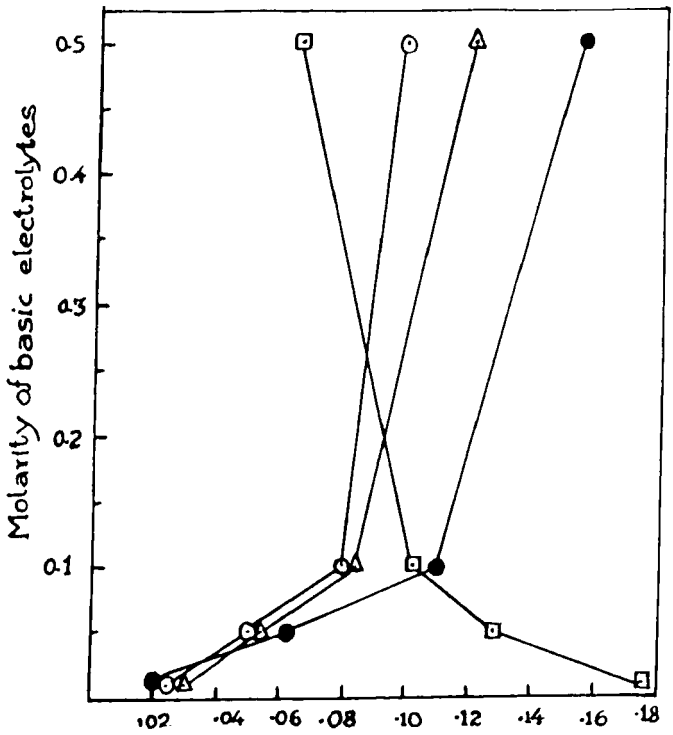

Fig.1 Plots : ⊙ NaCl ▲ KCl ● KNO_3 ⊡ Na_2SO_4

possible. Cu^{+2},Co^{+2}, Mn^{+2}required almost 8h for the establishment of equilibrium, where as Zn^{+2}, Mg^{+2}, Ni^{+2}, required more than 8h. The rate of metal uptake follows the order Mn^{+2}> Cu^{+2}> Co^{+2}> Ni^{+2}> Zn^{+2}> Mg^{+2}.

$Me(NO_3)_2$ - 0.1 mol/l, Volume - 2 ml

$NaNO_3$ - 1 mol/l, Volume - 25 ml.

pH-6, Temperature - room temperature

TABLE-3

Comparison of rates of metal-ion uptake at different times.

Metal ion	Percentage of metal ion uptake at different times (h)							
	1	2	3	4	5	6	7	8
Cu^{+2}	26	37	53	64	71	81	89	96
Zn^{+2}	23	30	46	58	66	75	81	85
Mn^{+2}	32	59	75	87	94	97	98	98
Co^{+2}	25	36	47	54	57	78	88	95
Mg^{+2}	24	31	41	48	54	66	70	75
Ni^{+2}	24	26	38	49	63	76	84	87

TABLE-4

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}	5.35	9.28	22.90	69.01	80.70
Zn^{+2}	10.50	31.85	50.90	70.96	80.92
Mn^{+2}	8.49	26.82	54.75	72.10	92.80
Co^{+2}	11.65	21.59	51.90	86.15	99.85
Mg^{+2}	4.30	10.75	49.59	67.53	79.90
Ni^{+2}	12.82	16.90	26.73	65.40	82.20

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

$Me(NO_3)_2$ = 0.1 mol/l, Volume - 2 ml.

$NaNO_3$ - 1 mol/l, Volume - 25 ml.

Time - 24 h, Temperature - room temperature.

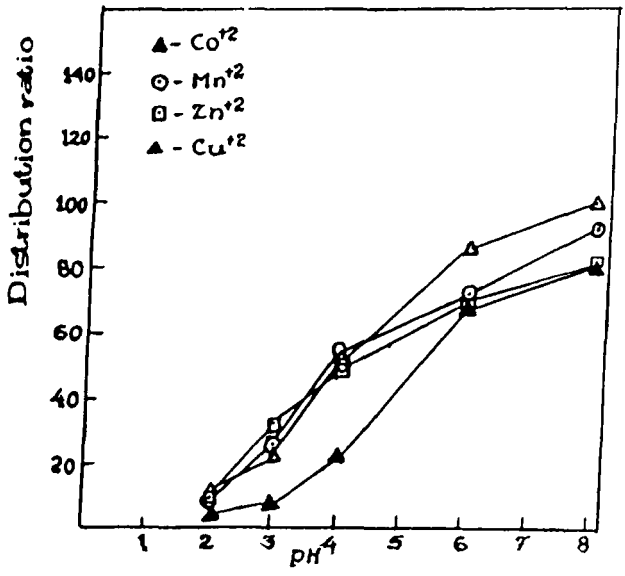

Fig.2 Distribution ratio of Co^{+2} Mn^{+2} Zn^{+2} & Cu^{+2} nitrate at different PH

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

Distribution of the metal ions at different pH.

Table-4 shows the effect of pH on the distribution ratios of metal ion between an aqueous solution and RA,2,4DNPH-resorcinol-furfural resin.

The results indicate that the relative amount of the metal ion taken up by the copolymer increases steadily with the increase of the pH of the medium since at higher pH values there is the possibility of hydrolysis, the investigation was carried out upto a definite pH value for the particular metal-ion. Co^{+2} and Mn^{+2} ions are taken up more selectively

than Cu^{+2}, Ni^{+2}, Zn^{+2}, and Mg^{+2} ions. Cu^{+2} and Ni^{+2} ions have low distribution ratio between pH 2 and 4, where as Co^{+2}, Zn^{+2}, Mn^{+2} and Mg^{+2} ions have a low distribution ratio at pH 2 and pH 3. This could be attributed to the low stability constant i.e. weak ligand stabilisation energy of the metal complexes[18,19]. The observed order of metal ion distributed is $Co^{+2} > Mn^{+2} > Ni^{+2} > Zn^{+2} > Mg^{+2} > Cu^{+2}$.(Fig.2)

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

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