CHAPTER-V

V . Phenol - Furfural - Hexamine Type Chelating Amphoteric Ion Exchange Resin

EXPERIMENTAL

V - (a) Synthesis of Chelating Amphoteric ion-exchange resin:

A chelating amphoteric ion exchange resin was synthesised from salicylic acid, furfural and hexamine according to the following procedure:

Hexamine (0.01 mole) and salicylic acid (0.0125 mole) were dissolved in 150 ml of ca. 2 N HCl and the reaction mixture was refluxed on sandbath for 1 hour. Furfural (0.09 mole) was added in fractions within 30 minutes. The reaction mixture was further refluxed on sandbath for 1 hour during which the mixture gelled to a soft mass. The gel was separated from the reaction vessel and cured in an oven at about 80°C for 30-32 hours.

The black resin was made free from unreacted acid and amine by washing with the distilled water, conditioned by treating alternately with 0.1 N NaOH and 0.1 N HCl solutions, and converted into H- and OH-forms as usual. The air dried resin was crushed to the size -60 + 100 mesh and stored in polyethylene bottles.

V - (b) Moisture content of resin:

Moisture content of the resin (H-and OH-forms) was determined as described in I-(b). The values are presented in Table-H-66(A).

V - (c) Density of resin:

(i) True density (d_{res}), (ii) Apparent (column) density (d_{col}) and (iii) void volume fraction of the resin (H-form and OH-form) were determined as described in I-(c) (i); (ii) and (iii).

The values of d_{res} and d_{col} and void volume fraction of the resin (H-form and OH-form) are presented in Table-H-66(A).

V - (d) (i) Total ion exchange capacity and (ii) Concentration of ionogenic groups:

Total ion exchange capacity, concentration of ionogenic groups and volume capacity (H-form and OH-form) of the resin were determined as described in I-(d)(i) and (ii) respectively and the results are reported in Table - H-66(A).

V - (e) Metal (Cu) exchange capacity:

Copper exchange capacity of resin (H-form) was determined by following the procedure as described in I - (e) and the result is reported in Table-H-66(A).

V - (f) Rate of exchange:

Rate of exchange of the resin (H-form and OH-form) was determined as described in I-(f).

The values of the capacities of the resin were plotted against time and shown in Fig. 37(A) and presented in Table-H-67.

V - (g) pH-titration and apparent pK_a and pK_b values:

pH titration study was carried out and apparent pK_a and pK_b values were calculated according to the procedures described in I-(g).

A pH titration curve is presented in Fig. 37 (B) while the apparent pK_a and pK_b values for the resin are presented in Table - H-66(A).

V - (h) Thermal stability:

Thermal stability of the resin (H - , Li- , Na- , K- , OH - and Cl-forms) was determined as described in I-(h). The results are presented in Table-H-68.

V - (i) Oxidation resistance test:

Oxidation resistance test of the resin in free acid and free base form was carried out as described in I-(j). The results are reported in Table-H-66(A).

V - (j) Sorption behaviour of some bivalent metal cations on cationic form (NH_4^+ - form) of the amphoteric resin from ammonium acetate - dimethylformamide media:

A sorption study was carried out following the procedure as described in I-(l) and the results of K_d values are presented in Table-H-69.

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RESULTS AND DISCUSSION

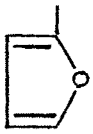
General:

In recent years, attempts have been made to obtain resins by polycondensation of phenolic derivative (chelating agent) with furfural. Dimitric et al (149) reported a synthèsis of Novolac type ion exchange resins from furfural and phenol. Muslimov Kh I et al (150) reported a synthesis of electron-exchange polymers from furfural and pyrogallol. Askarov M A (151, 152) and Isveshko G S (153) reported the synthesis of cation exchange resins based on products of the polycondensation of furfural and salicylic acid or p-hydroxybenzoic acid. Askarov et al (154, 155) and Isveshko (156) reported the synthesis of ion exchange resins from furfural - salicylic acid, furfural-p-toluene sulfonic acid and furfural-hydroformamide polyethylene polyamine and studied radiation resistance and thermal stability. Biswas and Packirisamy (157) synthesized cation exchange resin from Tetrahydrofuran and furfural and characterized by its total and salt spliting capacities, thermal behaviour and pH-metric titration.

We have synthesized a chelating amphoteric ion exchange resin from salicylic acid, furfural and hexamine. The condensate is insoluble in benzene and methanol in which individual components are miscible or soluble. Therefore the resin appears to be a condensate product of salicylic acid with polyfurfural, particularly because furfural is very susceptible to polymerization.

General characteristics and structure:

The chelating ion exchanger synthesised is fairly porous in nature with average physical stability and good chemical resistance to 3N acids and alkalis and it is black in colour.

In the present work, the polymer was obtained by polycondensation under mild reaction and curing conditions, cross-linking is possible by the formation of - CH -  linkages although on the basis of analytical data [Table-H-66(B)] and other physico-chemical studies, it can be suggested that salicylic acid gets condensed with hexamine in molar ratio of 2 : 1. The most likely structure is presented in Fig. I-S-49.

The moisture content of the resin suggests high degree of cross-linking in the resin. The difference in the moisture content of cationic as well as anionic form and the difference in the density of the cationic and anionic form is small and hence the resin can stand recycling to a good degree. The values of void volume fraction reveal a fairly porous nature of this ion exchanger.

The ratio CEC_{obs} / CEC_{cal} is 1.41 ($\sim$ 3/2) indicating that the cation exchange capacity is slightly higher than the expected which may be attributed to the contribution of weakly acidic - COOH group, while the ratio AEC_{obs} / AEC_{cal} is 0.955 ($\sim$ 1). For this resin, the total ion exchange capacity is directly related to the concentration of ionogenic groups.

The results of the rate of ion exchange of the resin are reported in Table-H-67 and presented in Fig.37(A). It is seen that the rate of anion exchange is fast which may be attributed to the diffusion of ions inside the matrix. An eighty per cent of the total anion exchange capacity is realized within 25 minutes as against 540 minutes for cation exchange capacity. The shape of the curve, with a rapid exchange in the initial stage followed by slowing down, may be attributed to the porous nature of the matrix (158).

The pH titration curve [Fig. 37-(B)] is a characteristic of a weakly acidic and weakly basic monofunctional ion exchanger.

The results of thermal stability of this amphoteric resin (in H-, Li- , Na- , K- , OH - and Cl- forms) at various temperature are reported in Table-H-68. No change in the capacity of any of the above forms of the resin is found upto 100°C. But all the forms exhibit an increase in the capacity when heated to above 120°C. This may be due to,

(i) destruction of some of the - CH - bridges between aromatic ring and - N - , creating more gaps in the matrix, thereby facilitating the acess to more phenolic groups, and

(ii) removal of the decomposition products which had neutralized the ionogenic groups.

On oxidative degradation, the cationic form of the resin exhibits an increase in percentage water content by 1.36% as against 8.93% exhibited by anionic form inferrring that the anionic form is more susceptible to oxidation from the cationic form.

The results of the sorption study of this resin (NH_4^+-form) are reported in Table-H-69.

From the data, it is quite obvious that, the sorption of the metal ions decreases with the increasing concentration of NH_4OAc [Concentration (V/V) of DMF being constant]. The decrease in K_d values with the increase in the concentration of NH_4OAc may be attributed to the formation of complex species of a small positive charge or neutral species. It is well known that the metal ion forms a complex with acetate ion and the sorption behaviour depends on the nature of the complex formed. Eusebius et al (143) reported that if the charge on the complex is positive, zero or negative then the sorption would be poor. In this study, with the increase in the concentration of NH_4OAc, acetate ion removes the co-ordinated water molecules leading to the formation of complex species with a small positive charge, and consequently K_d value is decreased. On further increasing the concentration of NH_4OAc, it is likely that neutral species may be formed. This may further decrease the K_d value.

Earlier workers (144,145) have reported that if the concentration of NH_4OAc is high,, the most likely species in the resin phase would be $[M^{II}(OAc)^+]$. We believe that the function of the DMF is to assist the formation of acetate complexes by influencing the dielectric constant of the media. Ca (II) has slightly higher K_d values as compared to the other metal cations. This may be due to higher affinity of ammonium ion towards Ca(II) as against towards the resin. The absorption capacities of various metal ions at different molar concentrations are relatively close suggesting that the chromatographic separation of these cations would not be efficient in the molar concentration range. This resin does not appear to differentiate significantly between the various divalient metal cations under investigation.

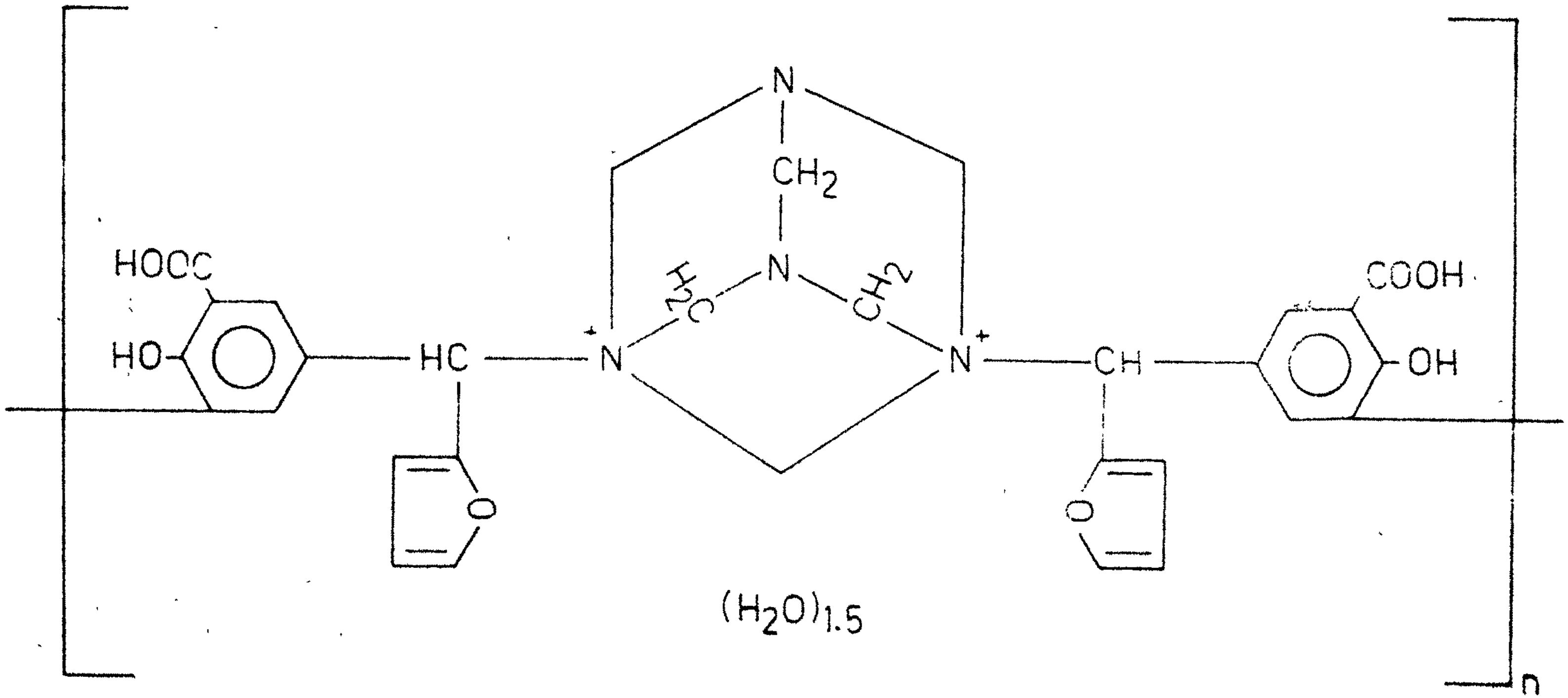


FIG-I-S-49

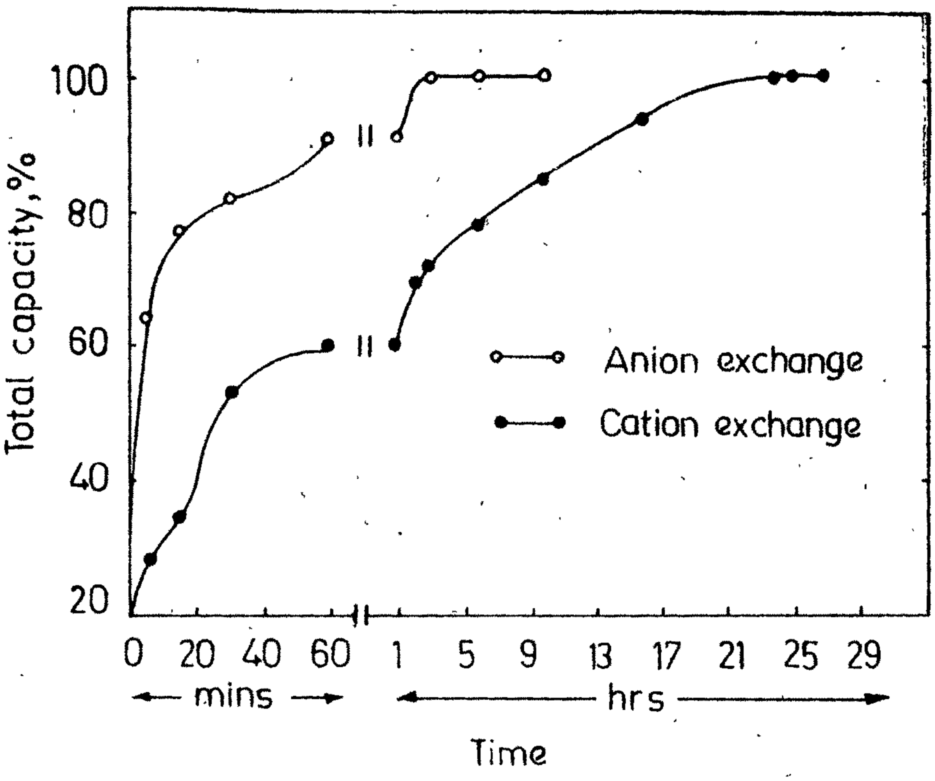


FIG-37(A)

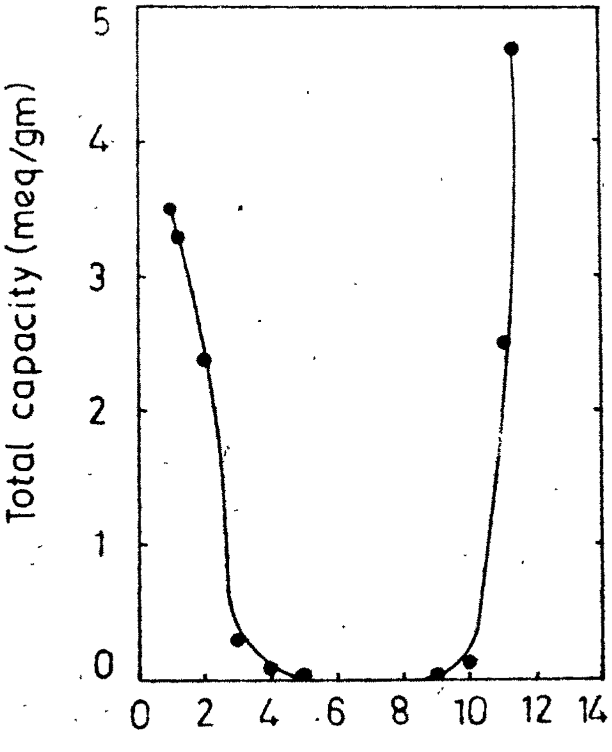


FIG-37(B)

TABLE - H-66(A)

Characteristics of the Amphoteric resin

	Characteristics	Resin in	
		H-form	OH-form
1	Moisture content, %	15.110	11.720
2	True density (d_{res}), g/cc	1.424	1.445
3	Apparent density (d_{col}), g/ml	0.373	0.293
4	d_{col} / d_{res}	0.262	0.202
5	Void volume fraction ($1 - d_{col} / d_{res}$)	0.738	0.798
6	Total capacity (meq/gm)	4.712	3.183
7	Concentration of ionogenic groups, Cr, (meq / cm^3)	5.700	4.060
8	Volume capacity, Q, (g.meq/l)	1.493	0.820
9.	Copper exchange capacity (meq/gm)	3.410	
10	pK values	pK_a=10.67	pK_b = 2.63
11.	Isoionic point value	—— 6.65 ——	
12.	Moisture content(%) after oxidative degradation	16.470	20.650

TABLE-H-66(B)

Analysis, Formula etc. of Amphoteric resin

Resin	Formula	Calculated			Observed		
		% C	% H	% N	%C	%H	%N
HSF	$(C_{30} H_{31} O_{9.5} N_4)_n$	60.10	5.17	9.35	60.17	5.47	9.30

TABLE - H - 67

Rate of exchange of Amphoteric resin

Time in mins/hrs.	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
5 mins	2.037	1.319
15 mins	2.451	1.649
30 mins	2.610	2.497
60 mins	2.865	2.827
2 hrs	-	3.298
3 hrs	3.183	3.393
6 hrs	3.183	3.675
10 hrs	3.183	4.005
16 hrs	-	4.429
24 hrs	-	4.712
25 hrs	-	4.712
27 hrs	-	4.712

TABLE - H - 68

Thermal stability of Amphoteric resin

Temp °C	Total capacity (meq/g) of absolutely dry resin as determined after heating						Total capacity (meq/g) of absolutely dry resin as determined after regeneration					
	H-Form	OH-form	Li-form	Na-form	K-form	Cl-form	H-form	OH-form	Li-form	Na-form	K-form	Cl-form
100°	4.712	3.183	2.100	2.280	2.130	4.300	4.712	3.183	2.120	2.307	2.260	4.318
120°	4.804	3.361	2.090	2.520	2.370	4.930	4.860	3.400	2.740	2.620	2.450	5.020
140°	5.080	4.129	2.750	2.550	2.720	5.140	5.153	4.260	2.804	2.678	2.840	5.230

Original capacity (meq/g)
of absolutely dry resin
determined at room temp. (30±1 °C)

H-form = 4.712
OH-form = 3.183
Li-form = 2.689
Na-form = 2.297
K-form = 2.140
Cl-form = 4.389

TABLE - H - 69

Values of distribution coefficients (K_d) in NH_4OAc - DMF media (29 ± 1°C)

Cation	Distribution Coefficient		
	A*	B*	C*
Ca (II)	27.11	26.99	18.82
Mg(II)	16.16	10.99	04.90
Co (II)	15.84	14.14	10.57
Ni (II)	15.39	11.86	07.24
Cu (II)	16.31	15.94	14.88
Zn (II)	20.60	19.01	07.84

* [Molar concentrations of NH_4OAc viz., A = 0.02 M ; B = 0.25 M ; C = 1.0 M]