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Synthesis and Physico-chemical Studies of Some New Amphoteric Ion Exchangers

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A few new amphoteric ion exchangers have been synthesized by condensing salicylic acid, hydroquinone, 3-hydroxy-2-naphthoic acid, anthranilic acid, pyrocatechol, 8-hydroxyquinoline, β-resorcylic acid and gallic acid with acetaldehyde employing thiourea as a cross-linking agent. Total capacity, moisture content, *p*H titration curves, rate of exchange, oxidative degradation and thermal stability of these resins have been determined.

Ion exchange resins show selectivity in their absorption of various metallic cations and possess high absorption capacity[1,2]. These resins may be used in chromatographic separations of certain metals and in the recovery and removal of traces of certain metallic ions from high concentration of other electrolytes[1,3].

Hojo *et al.*[4] reported a chelating ion-exchange resin synthesised from gallic acid, phenol and formaldehyde. Gregor *et al.*[5] reported a chelating ion-exchanger obtained from anthranilic acid, resorcinol and formaldehyde. Matsumura and Komiya[6], Rabeck and Zielinaki[7] and Davies *et al.*[8] reported salicylic acid and formaldehyde polymers. Kapadia and Dalal[9] reported ion exchange resins derived from acetaldehyde and salicylic acid, 3-hydroxy-2-naphthoic acid, anthranilic acid, pyrocatechol, 8-hydroxyquinoline, resacetophenone, β-resorcylic acid and gallic acid.

In this paper, we report the synthesis of new amphoteric resins using thiourea as the cross-linking agent. Employing thiourea, it was possible to obtain cross-linked product having both anionic and cationic groups in the polymer matrix, giving resins with amphoteric character.

Experimental Procedure

General method of preparation of resins—Thiourea (TU 0.03 mole) and various phenolic derivatives (0.03 mole) such as salicylic acid (SA), hydroquinone (HY), 3-hydroxy-2-naphthoic acid (3H), anthranilic acid (AN), pyrocatechol (PY). 8-hydroxyquinoline (8H), β-resorcylic acid (β-R) and gallic acid (GA), were dissolved in requisite quantity of 5% NaOH solution. To the resultant reaction mixture, 0.3 mole acetaldehyde (AC) was added; the solution turned reddish yellow or dark red. The above mixture resulted in a firm gel when refluxed on a water bath for 45-50 min. The gel was normally cured further for 9 hr at about 90°C, washed thoroughly with 0.1 *N* HCl, 0.1 *N* NaOH and finally with distilled water, and crushed to the size −20+40 or −60+100 mesh as needed.

The normal procedure to synthesize amphoteric resin is to introduce ionogenic groups after polymerization. In the synthesis of resins reported in this investigation, the active groups of the monomer (salicylic acid, hydroquinone, 3-hydroxy-2-naphthoic acid, anthranilic acid, pyrocatechol, 8-hydroxyquinoline, β-resorcylic acid and gallic acid) were neutralized before polymerization. So even after polymerization it is expected that the active groups are not decomposed. As carboxylic groups normally get decomposed above 100°C, the resins were cured below 90°C.

All the chemicals used were of AR grade. Doubly distilled CO_2-free water was used throughout. An Elico *p*H-meter (model CL-44) was used for *p*H measurements. The moisture content and total exchange capacity of the resins (Table 1) were determined by the method reported in literature[10].

Oxidation resistance test—The oxidation resistance study was carried out according to the method described by Dorfner[11].

Table 1—Total Capacity and Moisture Content

Resins	Moisture, %		Total capacity meq/g	
	H-form	OH-form	CEC	AEC
TU(SA)AC	2.29	3.58	2.389	1.269
TU(HY)AC	1.43	1.31	2.423	1.208
TU(3H)AC	4.16	1.09	2.312	1.367
TU(AN)AC	2.91	2.32	2.282	1.749
TU(PY)AC	7.87	0.07	2.484	1.475
TU(8H)AC	3.26	1.57	2.549	1.264
TU(β-R)AC	2.15	1.12	2.688	1.060
TU(GA)AC	0.29	0.40	2.391	1.601

Exactly 0.5 g of the desired form of the amphoteric resin was treated with 10-20 ml of 6% (wt/vol.) hydrogen peroxide solution at 45°C for 72-95 hr. Then the resin was quantitatively taken out from the flask and subjected to the moisture content determination as usual. The results are reported in Table 2.

*p*H *Titration curves*—The *p*H titration study was carried out according to the method described by Kunin[12].

A portion of the desired form of the resin (0.5 g) (−20+40 mesh) was accurately weighed into stoppered bottles. For the anion exchanger 0.1034 N HCl in 1 N NaCl and for the cation exchanger 0.09902 N NaOH in 1 N NaCl and 1 N NaCl solutions were added in different proportions to make up the volume to 50 ml and to give solutions of varying *p*H in the range 1.5-7.0 and 7.0-11.3 respectively. The resin was equilibrated with the mixture for 48 hr at 30°C and then the residual acidity or basicity and corresponding *p*H were determined. The values of the capacities of the resin were plotted against the *p*H of the solution (Fig. 1).

Thermal stability—About 0.5 g of the desired form of the amphoteric resin of known capacity (−60+100 mesh) was heated in an electrical oven at a predetermined temperature for 8 hr. The capacity of the portion of the heated sample was determined by directly equilibrating with the standard acid or alkali solution. Another portion of the heated resin was properly regenerated with a regenerant and the capacity determined. The experiment was repeated by heating the resin to different temperatures in the range 40-80°C and the results are reported in Tables 3 and 4.

Rate of exchange—For the rate of exchange study, the free acid forms of the amphoteric ion exchangers (0.5 g, accurately weighed were allowed to come in equilibrium individually with 100 ml of 0.1 N NaOH in 1 N NaCl solution for different intervals of time with intermittent stirring. Similarly, for the free base forms, 0.1 N HCl in 1 N NaCl solution was used. The solutions were decanted at definite predetermined intervals and a portion was titrated against the standard acid and standard alkali solution for cation exchanger and anion exchanger respectively and from that the % capacity realized at different intervals was calculated. The results are presented in Figs 2 and 3.

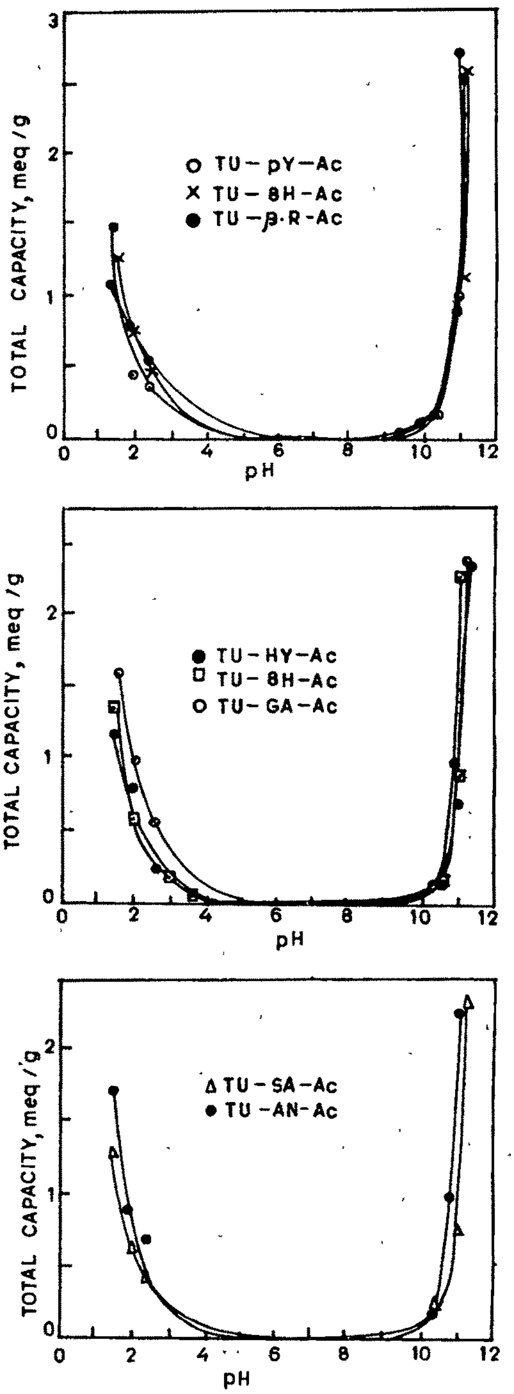

Fig. 1—*p*H Titration curves

Results and Discussion

It is seen from Table 1 that the capacities of these resins are indicative of weakly basic anion exchangers and weakly acidic cation exchangers. Data on moisture content are indicative of high degree of cross-linking in these resins.

Data on oxidative degradation reveal that amphoteric ion exchangers as anion exchangers are more susceptible to oxidative degradation than amphoteric ion exchangers as cation exchangers. As cation exchangers, the following order was observed for their stability on oxidative degradation:

TU(PY)AC > TU(3H)AC > TU(SA)AC > TU(AN)AC
> TU(8H)AC > TU(β-R)AC > TU(HY)AC
> TU(GA)AC,

Table 2—Data on Oxidation Resistance

Resins	Ion exchanger as cation exchanger			Ion exchanger as anion exchanger		
	Untreated exchanger	H_2O_2 treated exchanger	% Increase in water content	Untreated exchanger	H_2O_2 treated exchanger	% Increase in water content
TU(SA)AC	2.29	4.24	1.95	3.58	11.61	8.03
TU(HY)AC	1.43	5.44	4.01	1.31	9.21	7.90
TU(3H)AC	4.16	5.07	0.91	1.09	9.47	8.38
TU(AN)AC	2.91	5.24	2.33	2.32	6.74	4.42
TU(PY)AC	7.87	9.45	0.58	0.07	9.56	9.49
TU(8H)AC	3.26	6.15	2.89	1.57	7.63	6.06
TU(β-R)AC	2.15	6.09	3.94	1.12	11.13	10.01
TU(GA)AC	0.29	9.00	8.71	0.40	8.41	8.01

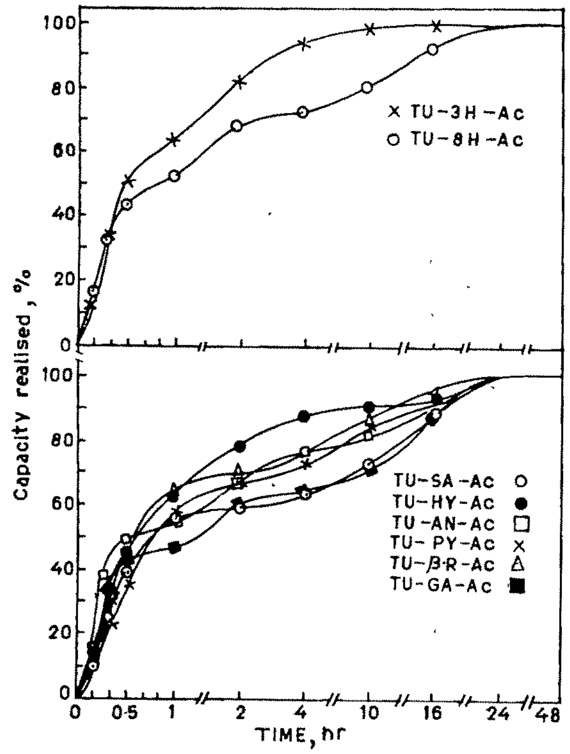

Fig. 2—Rate of exchange for cation exchangers

while as anion exchangers, the order for the stability was

TU(AN)AC > TU(8H)AC > TU(HY)AC
> TU(GA)AC > TU(SA)AC > TU(3H)AC
> TU(PY)AC > TU(β-R)AC.

The above order of stability can be explained on the basis of % increase in water content (Table 2). A resin exhibiting the lowest % increase in water content is the most resistant to oxidation.

These resins can be used as anion exchangers as well as cation exchangers depending upon the pH of the solution. In the pH range 1-7, ion exchangers behave as anion exchangers and the curves over this range (Fig. 1)

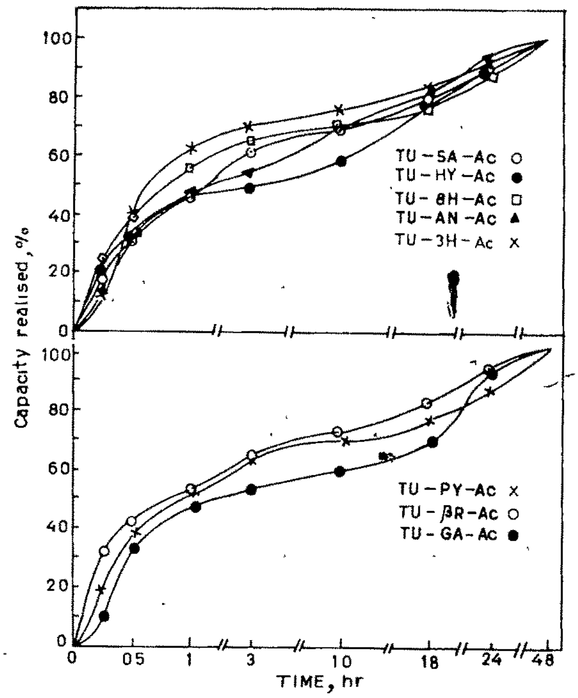

Fig. 3—Rate of exchange for anion exchangers

are characteristic of weakly basic resins. pH titration curves of these resins are quite comparable with those of commercially available weakly basic anion exchanger resins[13]. It was not possible to carry out the pH titrations below pH 1.3 and above pH 11.3 due to lack of facilities.

Thermal stability study of amphoteric ion exchangers reveals that the amphoteric ion exchangers as anion exchangers are stable up to 40°C. However, as cation exchangers, they are stable up to 60°C above which they get decomposed and exhibit lower exchange capacity. This could be probably due to the decomposition of carboxylic group above this temperature.

For the thermal stability study, the resins were converted into their sodium and potassium forms and

Table 3—Thermal Stability of the Amphoteric Ion Exchangers as Cation Exchangers

Resins	Original capacity (meq/g) of absolutely dry resin	Loss in capacity of absolutely dry resin determined after heating at 80°C %			Loss in capacity of absolutely dry resin determined after regeneration, %		
		H-form	Na-form	K-form	H-form	Na-form	K-form
TU(SA)AC	2.389	25.58	2.33	13.44	39.31	21.17	37.09
TU(HY)AC	2.423	38.18	11.14	22.25	66.98	29.05	13.52
TU(3H)AC	2.312	48.88	9.92	13.05	88.15	26.24	22.51
TU(AN)AC	2.282	32.30	15.16	19.53	38.43	19.22	16.57
TU(PY)AC	2.484	26.09	42.82	39.37	31.72	9.87	15.09
TU(8H)AC	2.549	26.44	4.15	35.98	31.93	24.30	0.90
TU(β-R)AC	2.688	46.28	10.19	12.58	51.56	24.72	17.40
TU(GA)AC	2.391	29.74	44.46	19.56	33.88	7.89	14.57

Table 4—Thermal stability of the Amphoteric Ion Exchangers as Anion Exchangers

Resins	Original capacity (meq/g) of absolutely dry resin	Loss in capacity of absolutely dry resin determined after heating at 80°C, %		Loss in capacity of absolutely dry resin determined after regeneration, %	
		OH-form	Salt form	OH-form	Salt form
TU(SA)AC	1.269	59.81	8.22	53.27	17.70
TU(HY)AC	1.208	55.71	26.26	51.98	25.30
TU(3H)AC	1.367	85.51	34.27	43.52	14.19
TU(AN)AC	1.749	79.13	20.89	77.24	7.42
TU(PY)AC	1.475	38.17	36.20	35.25	2.47
TU(8H)AC	1.264	58.39	34.38	54.03	12.67
TU(β-R)AC	1.060	35.85	33.85	32.90	26.90
TU(GA)AC	1.601	30.02	14.91	28.29	13.17

studied along with the free acid or base forms. The data on thermal stability (Tables 3 and 4) suggest the following order of stability:

Na-form > K-form > H-form.

The salt form is more stable than the free acid or base form. The results are consistent with the earlier observation[14].

Fig. 2 show the rate of exchange of the resins as cation exchangers with 0.1 *N* NaOH and 1 *N* NaCl solution. It is seen that (a) complete exchange occurs in 24 hr for all the resins under investigation, (b) more than 50% of the total capacity is realized in about 1 hr; and (c) as the rate of exchange is very fast, continuous stirring is essential.

The rate of exchange for the cation exchangers is in the order,

TU(3H)AC > TU(β-R)AC > TU(HY)AC
> TU(8H)AC > TU(PY)AC > TU(AN)AC
> TU(SA)AC > TU(GA)AC.

Fig. 3 show the rate of exchange of the resins as anion exchangers with 0.1 *N* HCl in 1 *N* NaCl solution. It is seen that (a) complete exchange occurs in 48 hr for all the resins under investigation; and (b) more than 50% of the total capacity is realized in about 3 hr.

The rate of exchange for the anion exchangers is in the order:

TU(AN)AC > TU(β-R)AC > TU(GA)AC
> TU(3H)AC > TU(HY)AC > TU(SA)AC
> TU(8H)AC > TU(PY)AC.

All the resins are stable towards 3 *N* alkali and 6 *N* acid solutions and show a colour change when converted from hydrogen form to salt form.

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Synthesis & Evaluation of a New Chelating Amphoteric Ion Exchanger

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An amphoteric chelating ion exchange resin has been synthesized by condensing salicylic acid with furfural employing hexamine as a cross-linking agent The total ion exchange-capacity, moisture content, density, rate of exchange, *p*H-titration behaviour, oxidative degradation, thermal stability and absorption specificity towards certain metal cations have been investigated

In continuation of our work on synthesis and physicochemical studies of some new amphoteric ion exchangers[1], we now report the synthesis of amphoteric resin from furfural, salicylic acid and hexamine.

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 hr. Furfural (0.09 mole) was added in fractions within 30 min. The reaction mixture was further refluxed on sandbath for 1 hr 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 hr. The black resin was made free from unreacted acid and amine by washing with 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. Total exchange capacity, moisture content, density, rate of exchange, *p*H titration curve, oxidative degradation, thermal stability and K_d values for some metal cations were determined by the methods described in the literature[2-6].

The cation exchange capacity is slightly higher than expected (Table 1). This may be attributed to the contribution of the weakly acidic −COOH group. The moisture content of the resin suggests high degree of cross-linking. The difference in the moisture content and the density of the resin in H− and OH− forms is small and the resin can stand recycling to a good degree. The most likely structure for the resin is (I). The rate of exchange is very high for the anionic form (Fig. 1). This may be due to diffusion of ions inside the matrices. 80% of the total anion exchange capacity is realized within 25 min as against 9 hr 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 matrices[7].

The *p*H-titration curve in Fig 2 is characteristic of weakly acidic and weakly basic monofunctional exchanger. Oxidative degradation of the amphoteric resin as cation exchanger exhibits an increase in water content by 1.36% as against 8.93% for the anionic form. This suggests that the anionic form is more susceptible to oxidation than the cationic form. Cationic and anionic forms of the resin showed 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 fascilitating the acess to more phenolic groups; and (ii) removal of the decomposition products which had neutralized the ionogenic groups. No change in the total capacity for all forms (H−, OH−, Li−, Na−, K− and Cl− forms) of the resin is observed up to 100°C. From the Table 2, it is

Table 1—Characteristics of the Amphoteric Resin

Total capacity meq/g		Moisture		Analytical data			True density g/cc		Column density g/ml	
AEC	CEC	H-form	OH-form	C%	H%	N%	H-form	OH-form	H-form	OH-form
3.183	4.712	15.11	11.72	60.3 (cal)	4.86 (cal)	9.38 (cal)	1.424	1.445	0.373	0.293
3.334 (cal)				60.17 (F)	5.47 (F)	9.30 (F)				

(cal) = calculated, (F) = found

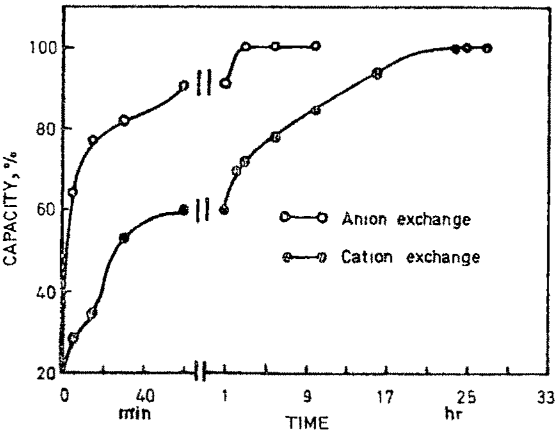

Fig 1—Plot of capacity vs time

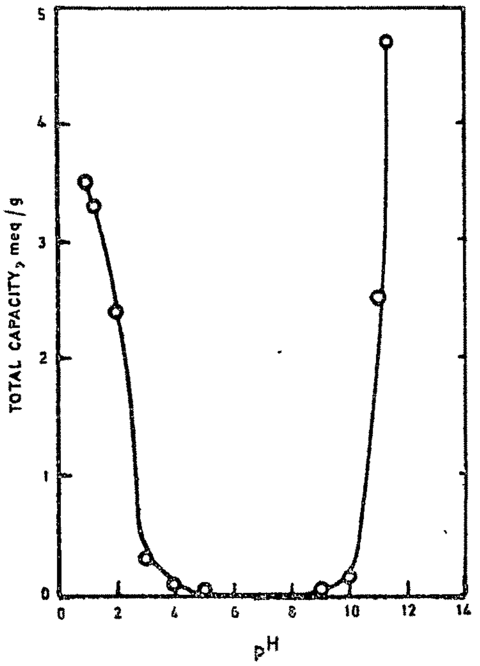

Fig 2—Plot of total capacity vs *p*H

seen that sorption of the metal ions decreases with the increase in the concentration of NH_4OAc (concentration of DMF being constant). The decrease in K_d values with 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.*[8] 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 coordinated 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 will be formed. This may further decrease the K_d value. Earlier workers[9,10] 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 with other metal ions 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 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 divalent metal ions under investigation.

Table 2—Values of Distribution Coefficients in NH_4OAc-4% DMF (29 ± 1°C)

Cation	Distribution coefficient		
	A	B	C
Ca(II)	27 11	26 99	18 82
Mg(II)	16 16	10 99	4.90
Zn(II)	20 60	19 01	7.84
Cu(II)	16.31	15 94	14.88
Co(II)	15 84	14 44	10 57
Ni(II)	15 39	11 86	7 24

[Molar concentrations of NH_4OAc A = 0.02*M*, B = 0.25*M*, C = 1 0*M*]

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