CHAPTER-IV

IV Phenol - Acetaldehyde - Thiourea Type Chelating Amphoteric Ion Exchange Resins

EXPERIMENTAL

IV (a) Synthesis of Chelating Amphoteric ion-exchange resins:

Phenolic derivatives such as salicylic acid, hydroquinone, 3-hydroxy-2-naphthoic acid, anthranilic acid, pyrocatechol, 8-hydroxyquinoline, β-resorcylic acid and gallic acid (0.03 mole) were taken along with thiourea (0.03 mole) in a 500 ml round bottom three necked flask fitted with a stirrer, a thermometer and a condenser and were dissolved in a requisite quantity of 5% NaOH solution. To the resultant reactant mixture, acetaldehyde (0.3 mole) was added giving a reddish yellow or a dark red solution. The above mixture resulted in a firm gel when refluxed on a water bath for 45 - 50 minutes. The resulted gel was normally cured further for 9 hours more at 90°C. The resulting hard mass was then crushed to -20 + 40 or - 60 + 100 BSS mesh size as needed. The resins were conditioned by alternate treatment with 0.1 N NaOH and 0.1 N HCl solutions. After several alternate regeneration cycles, the resins were dried in an oven below 90°C to remove the surface moisture. All these resins are non-melting and insoluble in water.

IV (b) <u>Moisture content of resins</u>:

Moisture content of these resins (H^+ form and OH^- form) was determined as described in I - (b).

The values of % moisture content of these resins (H^+ form and OH^- form) are presented in Table - TU - 54.

IV (c) <u>Density of resins</u>:

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

The values of d_{res} and d_{col} of these resins H^+ form and OH^- form) are presented in Table-TU - 55

The values of void volume fraction of these resins (H^+ form and OH^- form) are presented in Table - TU - 56.

IV (d) (i) Total ion exchange capacity and (ii) concentration of ionogenic groups:

Total ion exchange capacity (H^+ form and OH^- form) was determined as described in I - (d)-(i).

Concentration of ionogenic groups and volume capacity of these resins (H^+ form and OH^- form) were determined as described in I - (d)-(ii).

The values of total ion exchange capacity, concentration of ionogenic groups and volume capacity of these resins as cation exchanger as well as anion exchanger are presented in Table-TU - 57 and Table - TU - 58 respectively.

IV (e) Metal (Cu) exchange capacity:

Metal (Cu) exchange capacity of these resins (H^+ form) was determined by following the procedure described in I - (e) and the values are presented in Table - TU - 57.

IV - (f) Rate of exchange:

Rate of exchange of these resins (H^+ form and (OH^- form) were determined as described in I - (f).

The values of the capacities of these resins were plotted against time and shown in Figs. 28 to 33 and presented in Table - TU - 59.

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

pH titration studies and apparent pK_a and pK_b values of these resins were determined as described in I - (g).

The values of the capacities of the resin were plotted against the pH of the solution and shown in Figs. 34 to 36.

The apparent pK_a and pK_b values for these resins are presented in Table - TU - 60.

IV - (h) Thermal stability:

Thermal stability of these resins as cation exchanger in free acid form and in salt form such as sodium form was determined as described in I - (h). The results are presented in Table - TU - 61.

Thermal stability of these resins as anion exchanger in free base form and in salt form such as chloride form was determined as described in I - (h). The results are presented in Table - TU - 62.

IV - (i) Oxidation resistance test:

Oxidation resistance test of these resins in free acid and free base form was carried out as described in I - (j). The results are presented in Table - TU - 63 and Table - TU - 64 respectively.

IV - (j) Infra-red spectra of resins:

The infra-red spectra of resins were studied on a Perkin Elmer Model No. 297 Infracord spectrophotometer by the potassium bromide disc technique using a blank potassium bromide disc in the reference beam.

The probable assignment of the peaks in the infra-red spectra is presented in Table-TU-65.

IV Phenol - Acetaldehyde - Thiourea Type Chelating Amphoteric Ion Exchange Resins

RESULTS AND DISCUSSION

General:

In recent years, attempts have been made to obtain resins by polycondensation of phenol derivative (chelating agent) with formaldehyde. Topp (71), De Geiso et al (72), Komiya et al (73), Rabeck et al (74), Davies et al (75) etc have reported salicylic acid - formaldehyde condensation resins. Anthranilic acid - formaldehyde condensation resins have been studied by Gregor (53) and gallic acid - formaldehyde resin by Hojo (77). Resins from naphthaquinone/anthraquinone derivatives and formaldehyde have been studied by Soloway (78), Manecke (79), Izoret (80) etc. Resins from phenol derivatives and acetaldehyde have been synthesised and studied for their physico-chemical properties by Kapadia and Dalal (147).

We have synthesised chelating amphoteric ion exchangers from the various phenolic derivatives, acetaldehyde and thiourea. The phenolic derivatives employed for synthesising the resins possess the following structural features.

(i) one phenolic group and one carboxylic group in ortho position on a phenyl ring,

(ii) two phenolic groups in ortho or meta position on a phenyl ring,

(iii) one phenolic group and one carboxylic group in ortho position on a naphthalene ring,

(iv) one amino group and one carboxylic group on a phenyl ring,

(v) one phenolic group and one ring nitrogen,

(vi) two phenolic groups in meta position and one carboxylic group in ortho position on a phenyl ring and,

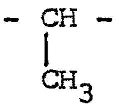
(vii) three phenolic groups and one carboxylic group on a phenyl ring.

Gelling and Curing:

In phenol-Acetaldehyde-Thiourea series under investigation, gelling time and curing period for all the resins are same, inferring that the gelling time and curing period are directly related to phenolic compounds' functionality only.

General Characteristics and Structures:

The chelating exchangers, in general, are fairly porous in nature with average physical stability and good chemical resistance to 3 N acids and alkalis and show a change of colour when converted from hydrogen or hydroxyl form to sodium or chloride form respectively.

In the present investigation, the polymers were obtained by the polycondensation under mild reaction and curing conditions, cross linking is possible by the formation of  $-\underset{\displaystyle CH_3}{\underset{|}{CH}}-$ linkages although these could be formed only at position 4 and 6 relative to hydroxyl group, since one of these positions ortho and para to the hydroxyl group was blocked by a carboxyl group or other group as shown in the probable structures in Figs. I-S-43 to I-S-48.

On the basis of analytical data and other physico-chemical studies, we may have some generalisations, viz.,

(i) 8-hydroxyquinoline gets condensed with thiourea in the molar ratio 2 : 1,

(ii) 3-hydroxy-2-naphthoic acid and pyrocatechol get condensed with thiourea in the molar ratio 3 : 1 and,

(iii) salicylic acid, hydroquinone and anthranilic acid get condensed with thiourea in the molar ratio 4 : 1.

Moisture retention % :

Percentage moisture of the resins are presented in Table - TU-54. The percentage moisture of the resins in H-form varies between 0.29 and 7.80 and that for resins in OH-form varies from 0.07 and 3.58. Thus these resins have very low range of percentage moisture. This may be attributed to high degree of crosslinking. We observed with few exceptions that, for these amphoteric resins, the moisture content of the resins in OH-form is lower than that of the resins in H-form. Further, we suggest that since the difference in the moisture content of the resins in H - and OH - forms is small, these resins under investigation can stand recycling to a good degree.

Density of resins:

(i) True density (d_{res}):

The results of true density (d_{res}) are presented in Table - TU-55. It is seen that the values of true density (d_{res}) are ranging from 1.10 to 1.30 gm/cm^3 for H-form of resins and from 1.01 to 1.26 gm/cm^3 for OH-form of resins.

(ii) Apparent (column) density (d_{col}) :

The results of column density (d_{col}) are presented in Table - TU-55. The values of apparent or column density vary between 0.40 and 0.52 gm/ml for the resins in H-form and between 0.41 and 0.50 gm/ml for the resins in OH-form.

We observe in general, that with the exception [TU(HQ) AC], for the amphoteric resins under study the true density (d_{res}) of the resins in OH-form is lower than that of the resin in H-form by 0.043 to 0.280. Further, we observe that since the difference in true density of the resin in H-form and OH-form is small, the resins under study can stand recycling to a good degree.

Void volume fraction:

The results of the void volume fraction are presented in Table - TU - 56. It is observed that the values of the void volume fraction vary between 0.54 and 0.67 for the resins in H-form and between 0.51 and 0.63 for the resins in OH-form. The values of the void volume fraction suggest fairly good porous nature of the resins.

Ion exchange capacity:

Chelating exchangers containing free phenolic or carboxylic groups are weak. The results of total cation exchange capacity as well as anion exchange capacity observed can be compared with the calculated ones as presented in Table - TU - 57 and Table - TU - 58.

In general, two ranges exist,

(i) value of CEC_{obs} / CEC_{cal} and AEC_{obs} / AEC_{cal} is approximately close to 1,

(ii) value of CEC_{obs} / CEC_{cal} and AEC_{obs} / AEC_{cal} is close to 3/2.

Concentration of ionogenic groups:

The data regarding the concentration of ionogenic groups are presented in Table - TU - 57 and Table - TU-58 for H-form and OH-form of these amphoteric resins respectively. With few exceptions, total ion exchange capacity is found to be related to the concentration of ionogenic groups. Higher the ion exchange capacity, greater the concentration of ionogenic groups.

Metal (Cu) exchange capacity:

Results of copper ion exchange capacity of these amphoteric resins (H-form) are presented in Table - TU-57. It is observed that the copper exchange capacity of the resins varies between 0.721 and 1.661 meq/gm.

The decreasing order for the copper ion exchange capacity of these resins is,

TU(BR)AC > TU(HQ)AC > TU(GA)AC >
TU(8-OH)AC > TU(PY)AC > TU(SA)AC >
TU(3-OH)AC > TU(AN)AC.

Rate of exchange:

Figs. 28 to 33 show the rate of cation exchange as well as anion exchange of the amphoteric resins.

A perusal of the trends of the rate of exchange for amphoteric resins as cation exchanger and an anion exchanger infers that the rate is fairly good.

In the case of amphoteric resins as cation exchanger, it is observed that,

(i) complete exchange occurs in 24 hours,

(ii) more than 50% of the total capacity is realized in about one hour.

Since the rate of exchange is comparatively slow, the intermittent shaking procedure is adopted. All the amphoteric resins investigated as cation exchanger show the rapid rates of exchange in the beginning followed by the slower rates of exchange, which may be due to surface exchange and exchange in the interior due to diffusion.

(iii) The rate of exchange for these resins are in the decreasing order as follows:

TU(3-OH)AC > TU(BR)AC > TU(HQ)AC >
TU(8-OH)AC > TU(PY)AC > TU(AN)AC >
TU(SA)AC > TU(GA)AC.

In case of amphoteric resins as anion exchanger, it is observed that,

(i) complete exchange occurs in 48 hours,

(ii) more than 50% of the total capacity is realized in about three hours,

(iii) the rate of exchange for these resins are in the decreasing order as follows:

TU(AN)AC > TU(BR)AC > TU(GA)AC >
TU(3-OH)AC > TU(HQ)AC > TU(SA)AC >
TU(8-OH)AC > TU(PY)AC.

It is observed that the rate of exchange of amphoteric resins as cation exchanger is faster than that of anion exchanger.

pH titrations:

The pH titration curves for the amphoteric resins are presented in Figs 34 to 36.

These resins exhibit low values of cation and anion exchange capacities over the pH range 1 - 12. It is evident from the Figs. 34 to 36 that the resins are capable of exchanging anions or cations over the pH range 1 - 12 and amphoteric in nature. These resins can be used as anion exchanger as well as cation exchanger, depending upon the pH of the solution.

In the pH range 1 - 7, the resins acted as anion exchanger (Figs. 34 - 36) and curves over this range are characteristic of weakly basic resin and may be compared with the curves of commercially available weakly basic anion exchange resins. The cation exchange behaviour of these resins are similar to that of weak acid resin.

Apparent pK_a and pK_b values:

The apparent pK_a and pK_b values calculated from the pH titration curves and using the equations (9) and (14) as described earlier on pages 66, 68 are presented in Table - TU - 60.

It is observed that the values of pK_a obtained for overall cation exchange process in general for various ion exchangers studied vary between 10.933 and 11.062 which is slightly higher than that of phenolic hydroxyl group and that of pK_b obtained for overall anion exchange process for these resins are lying between 2.22 and 2.78 which is a characteristic of bases of weak strength.

The values are in decreasing order as,

for pK_a: TU(SA)AC > TU(8-OH)AC > TU(3-OH)AC > TU(GA)AC > TU(BR)AC > TU(HQ)AC > TU(PY)AC > TU(AN)AC

for pK_b: TU(BR)AC > TU(GA)AC > TU(AN)AC >
TU(8-OH)AC > TU(HQ)AC > TU(SA)AC >
TU(3-OH)AC > TU(PY)AC.

Isoionic point:

The values of isoionic point (i_p) are presented in Table - TU - 60. The values vary in the range of 6.587 to 6.873.

The values are in the decreasing order as,

TU(BR)AC > TU(GA)AC > TU(8-OH)AC >
TU(AN)AC > TU(SA)AC > TU(HQ)AC >
TU(3-OH)AC > TU(PY)AC.

Thermal stability:

The results of thermal stability, at different temperature, of amphoteric resins as cation exchanger in free acid form and in salt form such as sodium and potassium forms are presented in Table - TU - 61 and as anion exchanger in free base form and in salt form such as chloride form are presented in Table - TU - 62.

It is seen that,

(i) no change in total capacity for the amphoteric resins as anion exchanger is observed upto 40°C.

Hence, we suggest that these resins could be safely used as anion exchanger upto temperature 40°C,

(ii) the amphoteric resins as cation exchanger are stable upto 80°C. Hence, we suggest that these resins could be safely used as cation exchanger upto 80°C. Above this temperature, they show decrease in capacity when heated resins were regenerated and tested could be due to the decomposition of carboxylic group above this temperature as reported by Vasilyer (158). In conformity with the observation of Hall et al (142), the results reveal that the salt forms are more stable than the free acid or free base forms. The data on thermal stability (Table - TU - 61) and Table - TU - 62) suggest the following order of stability.

Na - form > K - form > H - form

and

Cl - form > OH-form

Oxidation resistance:

Results of oxidation resistance test of different amphoteric exchangers as cation exchanger are presented in Table- TU - 63 and as anion exchanger are presented in Table - TU - 64. Amphoteric resin [TU(PY)AC] as cation exchanger exhibits the lower increase in % water content and thus is the most resistant to oxidation. Amphoteric resin [TU(AN)AC] as anion exchanger the lowest in exhibits the lowest increase in % water content and thus is the most resistant to oxidation.

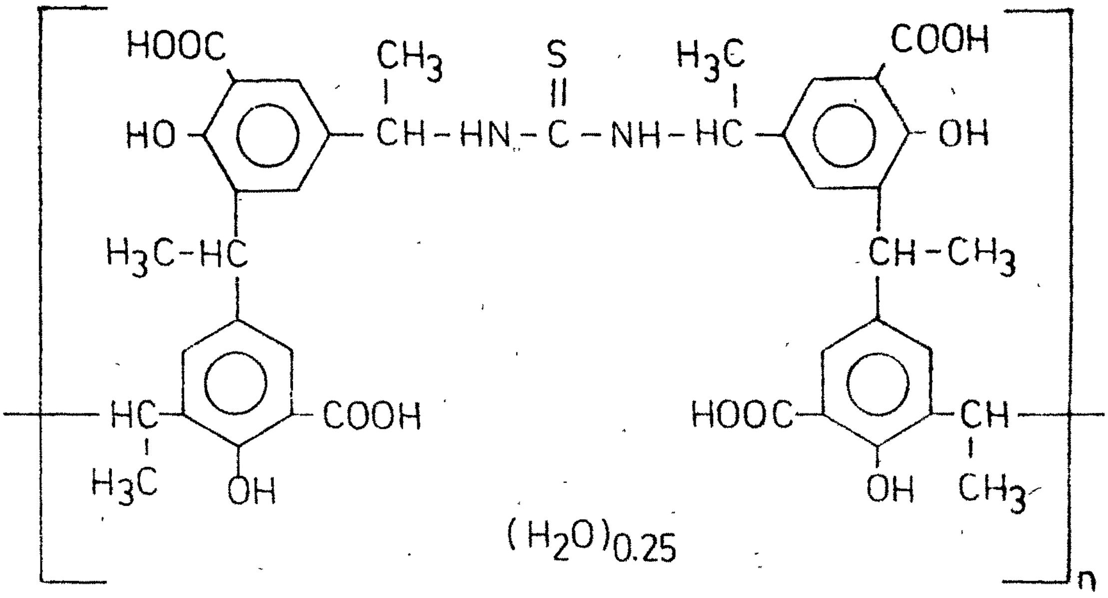
We observed that the oxidative degradation for amphoteric resins as anion exchanger showed greater increase in % water content than the amphoteric resins as cation exchanger. Hence, we suggest that anionic form is more susceptible to oxidation than the cationic form.

Amphoteric resins as cation exchanger show the following decreasing order for their stability on oxidative degradation as,

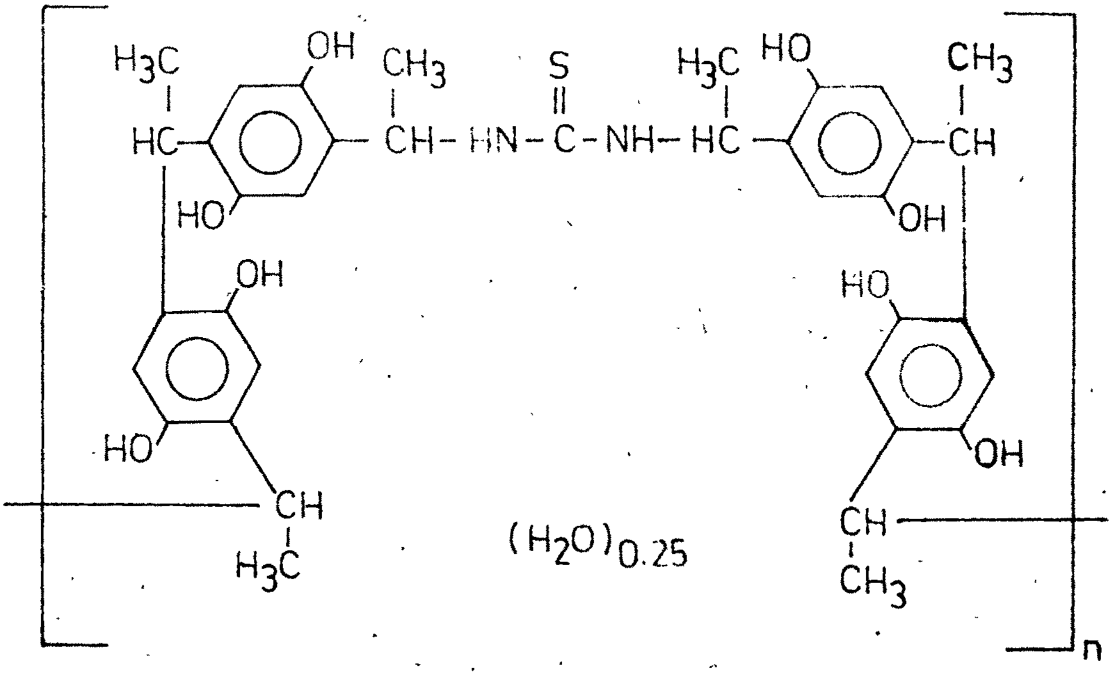
TU(PY)AC > TU(3-OH)AC > TU(SA)AC >
TU(AN)AC > TU(8-OH)AC > TU(BR)AC >
TU(HQ)AC > TU(GA)AC.

Amphoteric resins as anion exchanger show the following decreasing order for their stability on oxidative degradation as,

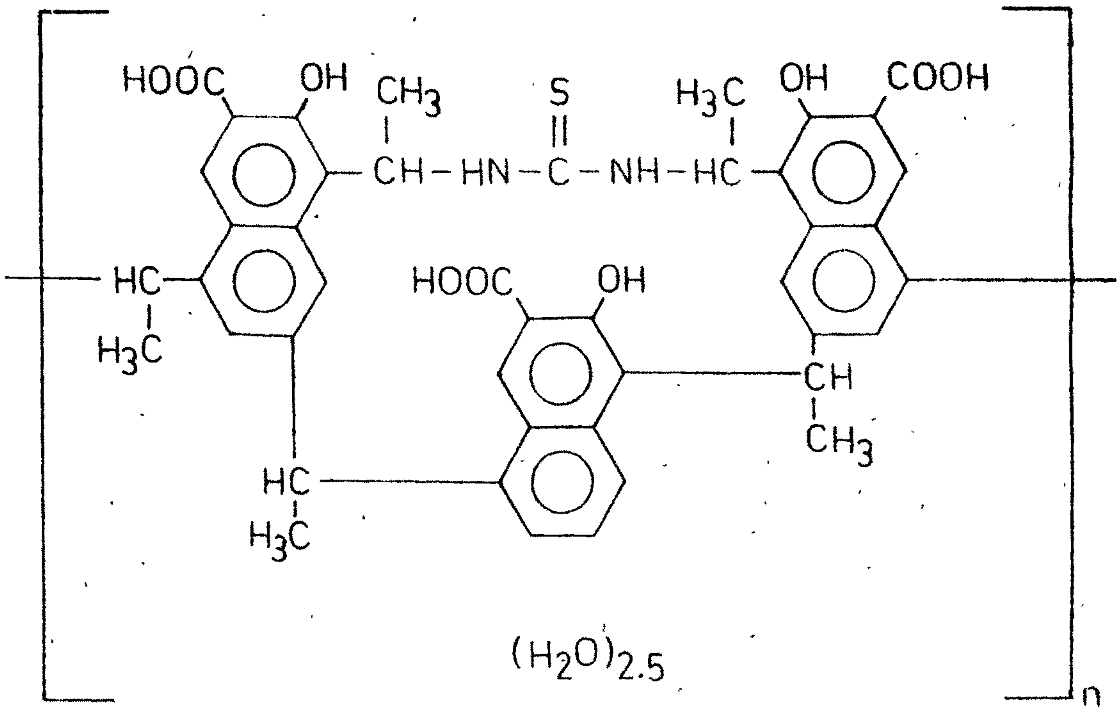
TU(AN)AC > TU(8-OH)AC > TU(HQ)AC >
TU(GA)AC > TU(SA)AC > TU(3-OH)AC >
TU(PY)AC > TU(BR)AC.



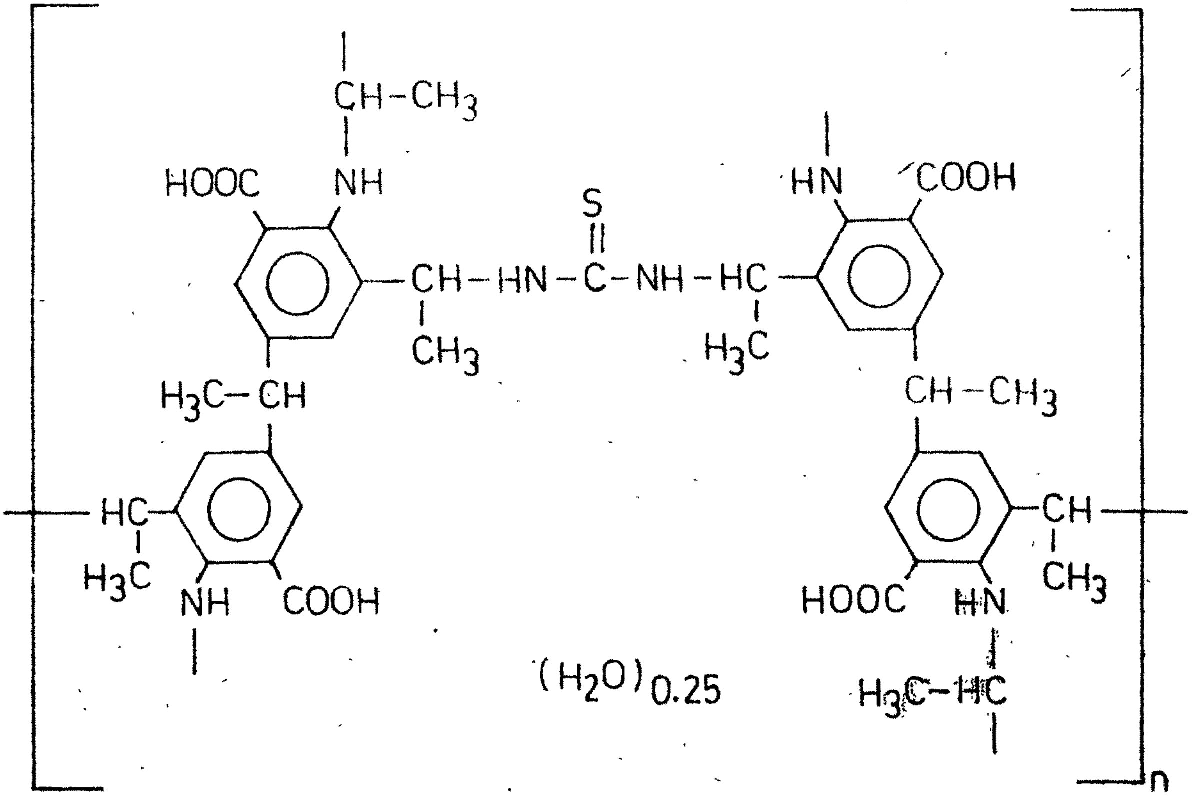
TU(SA)AC (I-S-43)



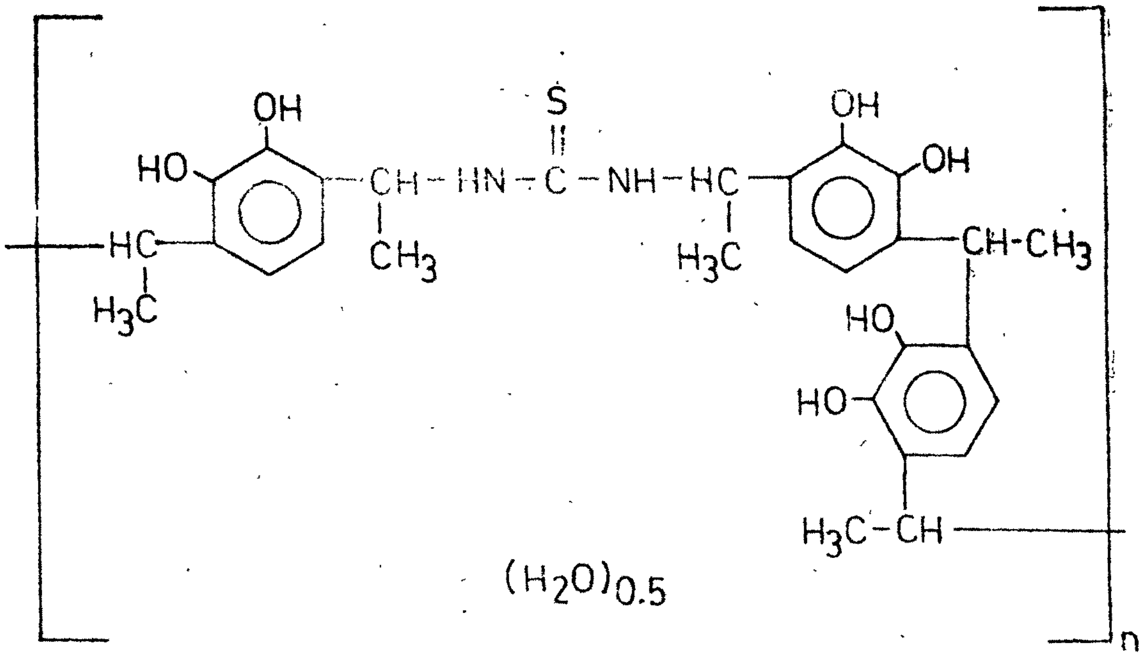
TU(HQ)AC (I-S-44)



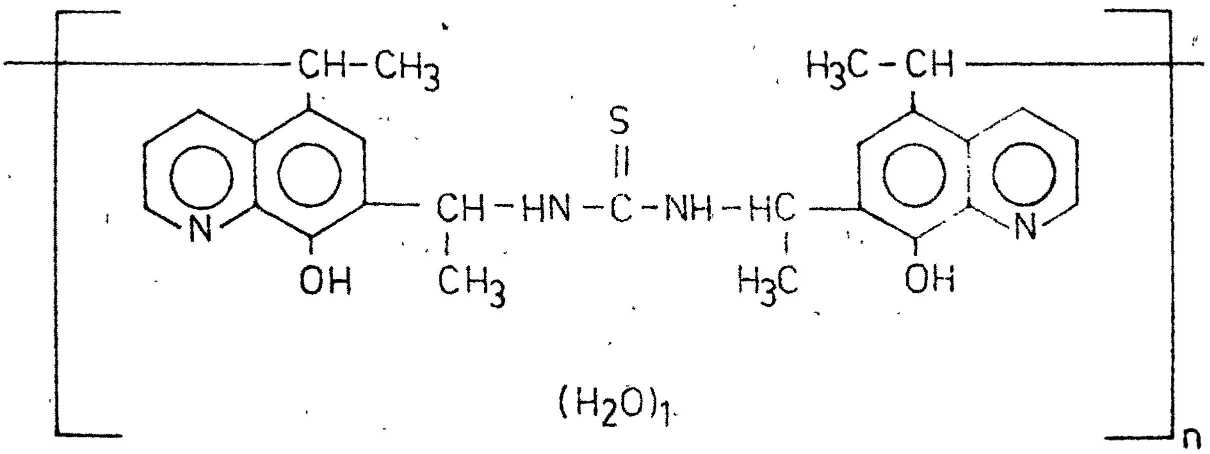
TU(3-OH)AC (I-S-45)



TU(AN)AC (I-S-46)



TU(PY)AC (I-S-47)



TU(8-OH)AC (I-S-48)

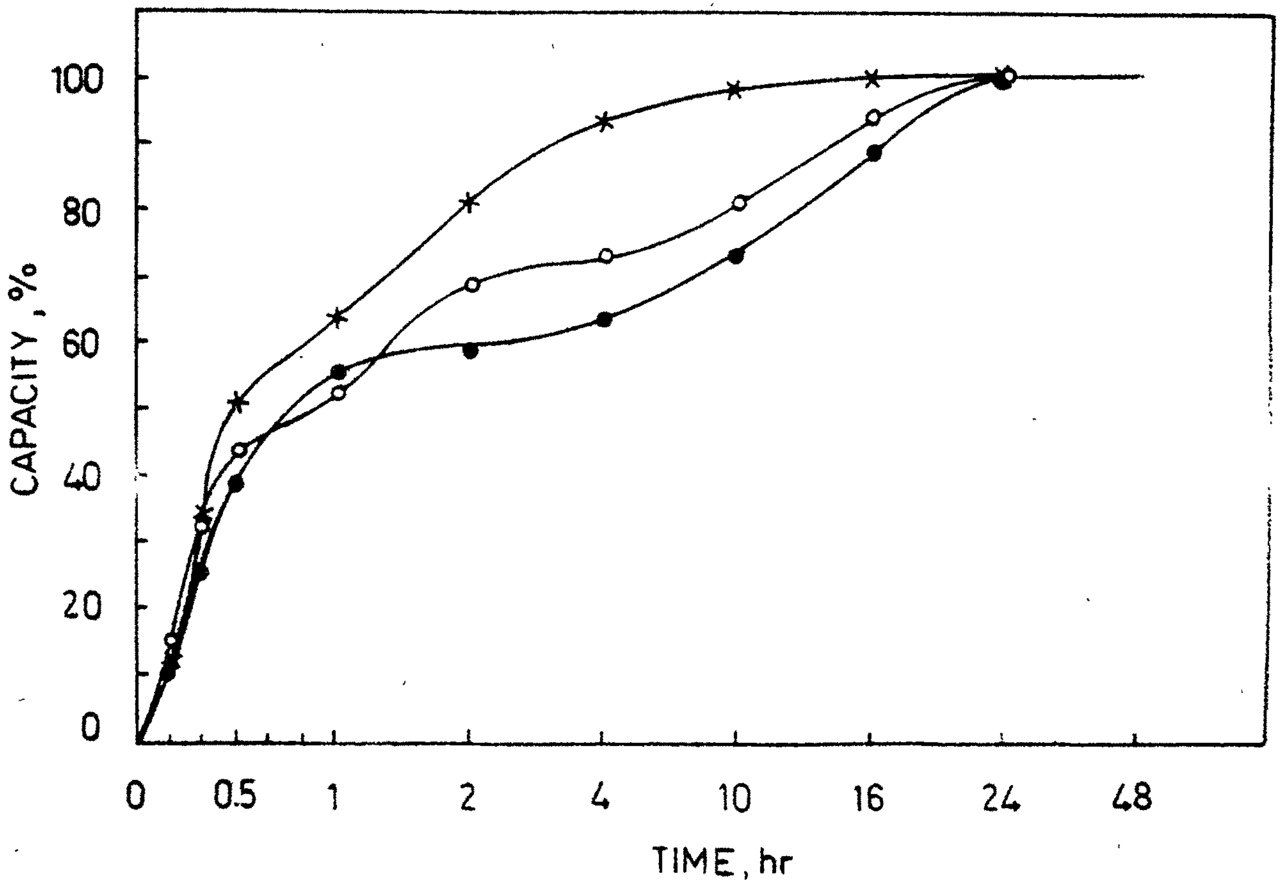


FIG 28 – RATE OF CATION EXCHANGE OF TU(3-OH)AC [×—×], TU(8-OH)AC [○—○] AND TU(SA)AC [●—●] RESINS

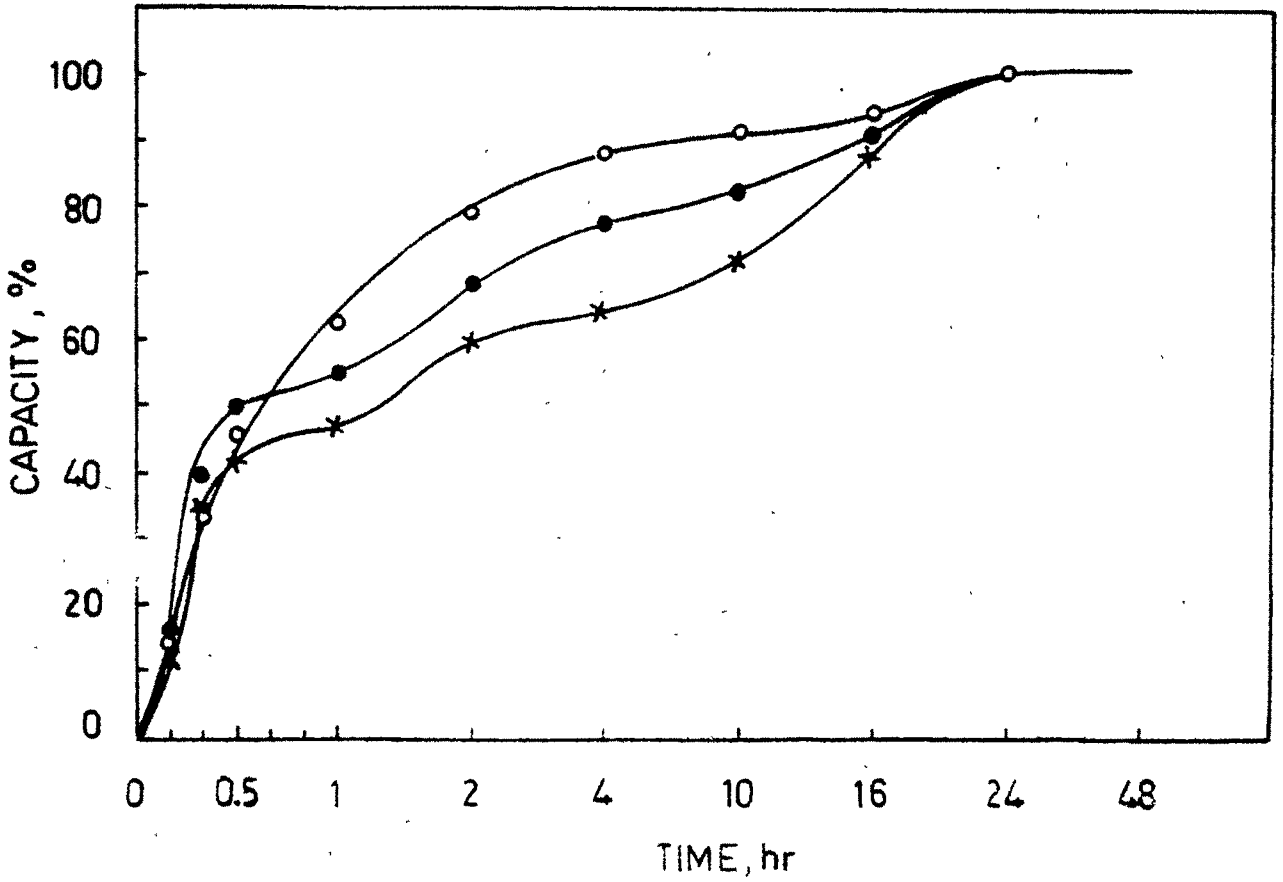


FIG 29 - RATE OF CATION EXCHANGE OF TU(HQ)AC [○—○], TU(AN)AC [●—●] AND TU(GA)AC [×—×] RESINS

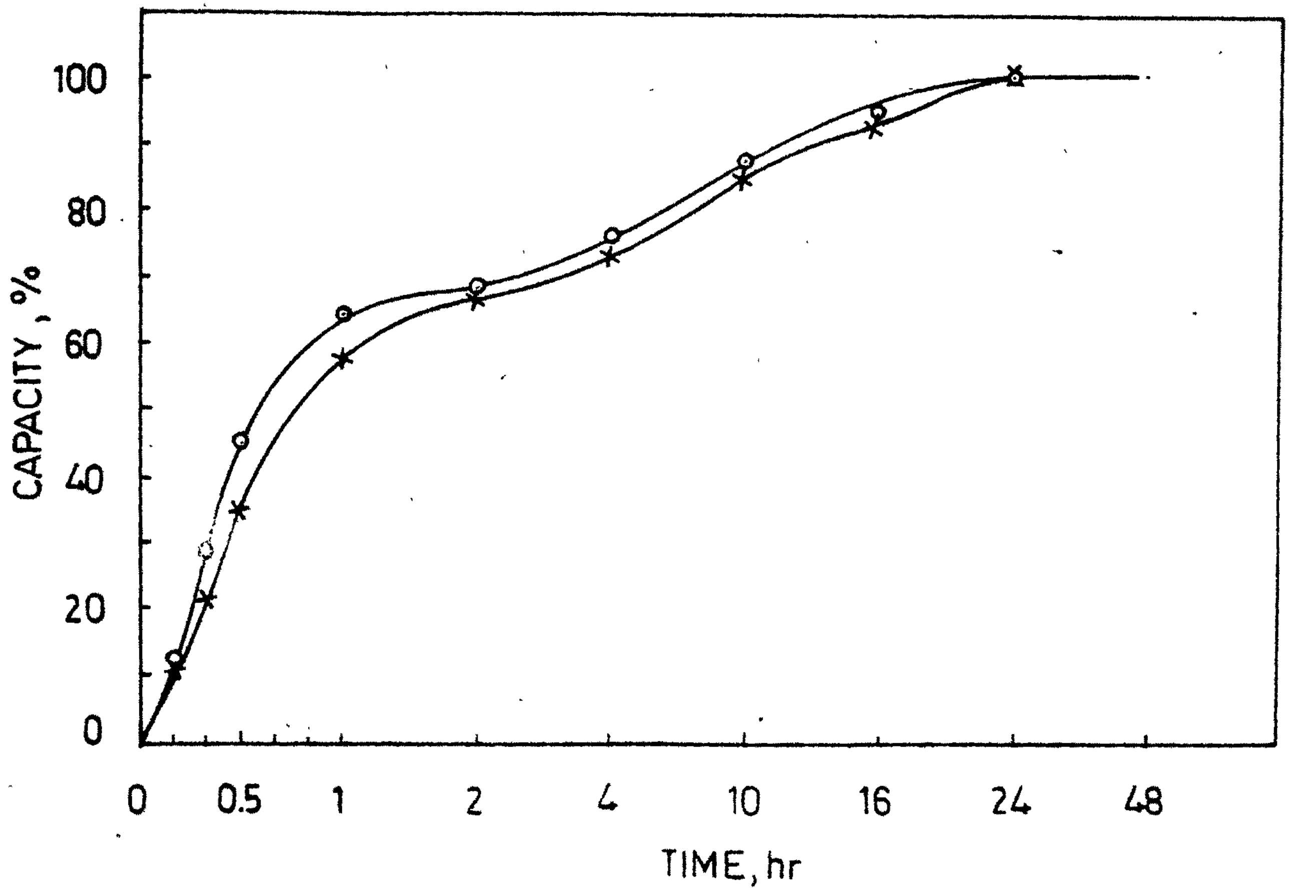


FIG 30 – RATE OF CATION EXCHANGE OF TU(BR)AC [o—o] AND TU(PY)AC [x—x] RESINS

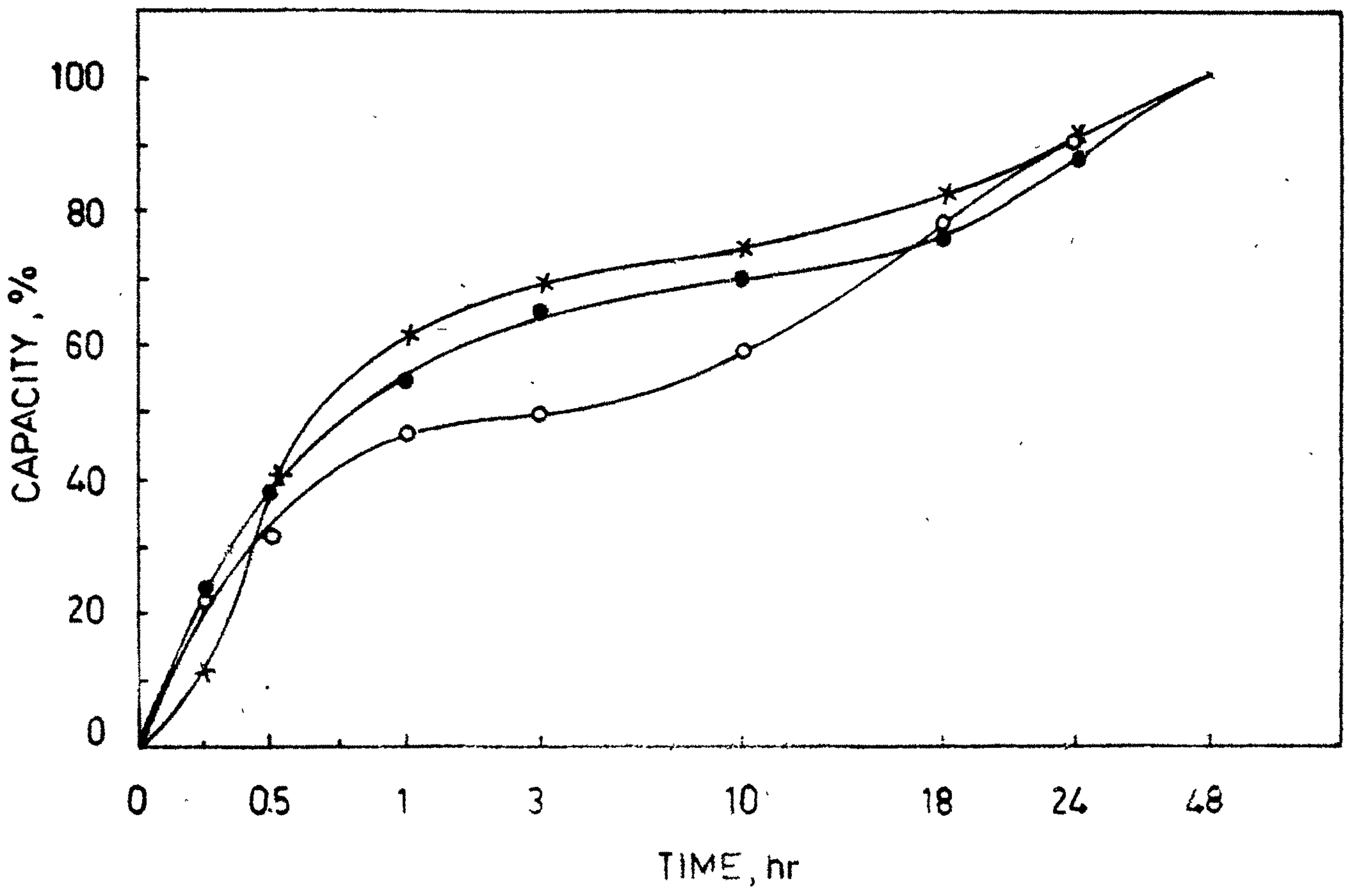


FIG 31 – RATE OF ANION EXCHANGE OF TU(3-OH)AC [x—x], TU(8-OH)AC [●—●] AND TU(HQ)AC [○—○] RESINS

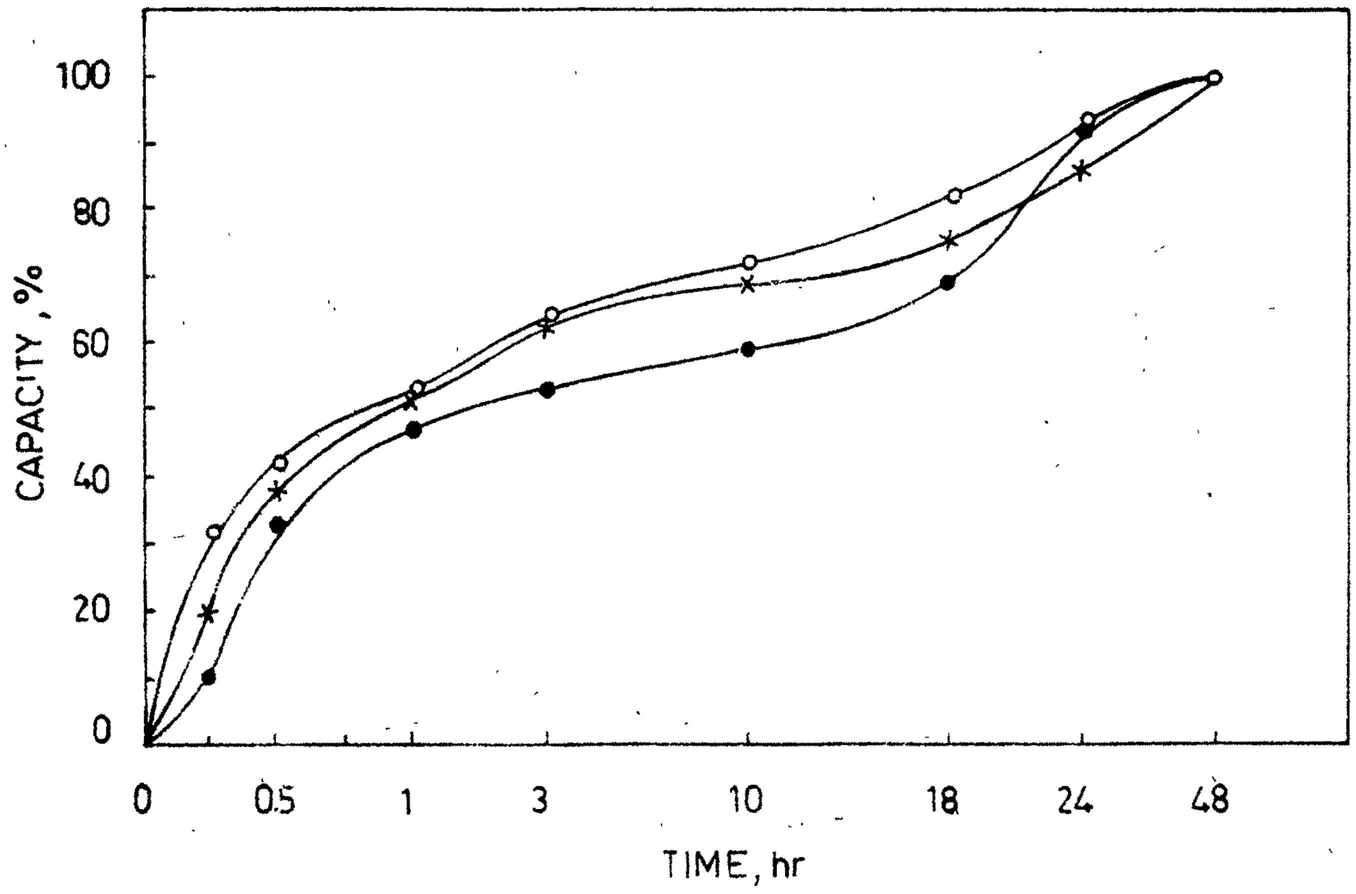


FIG 32 - RATE OF ANION EXCHANGE OF TU(BR)AC [○—○], TU(PY)AC [×—×] AND TU(GA)AC [●—●] RESINS

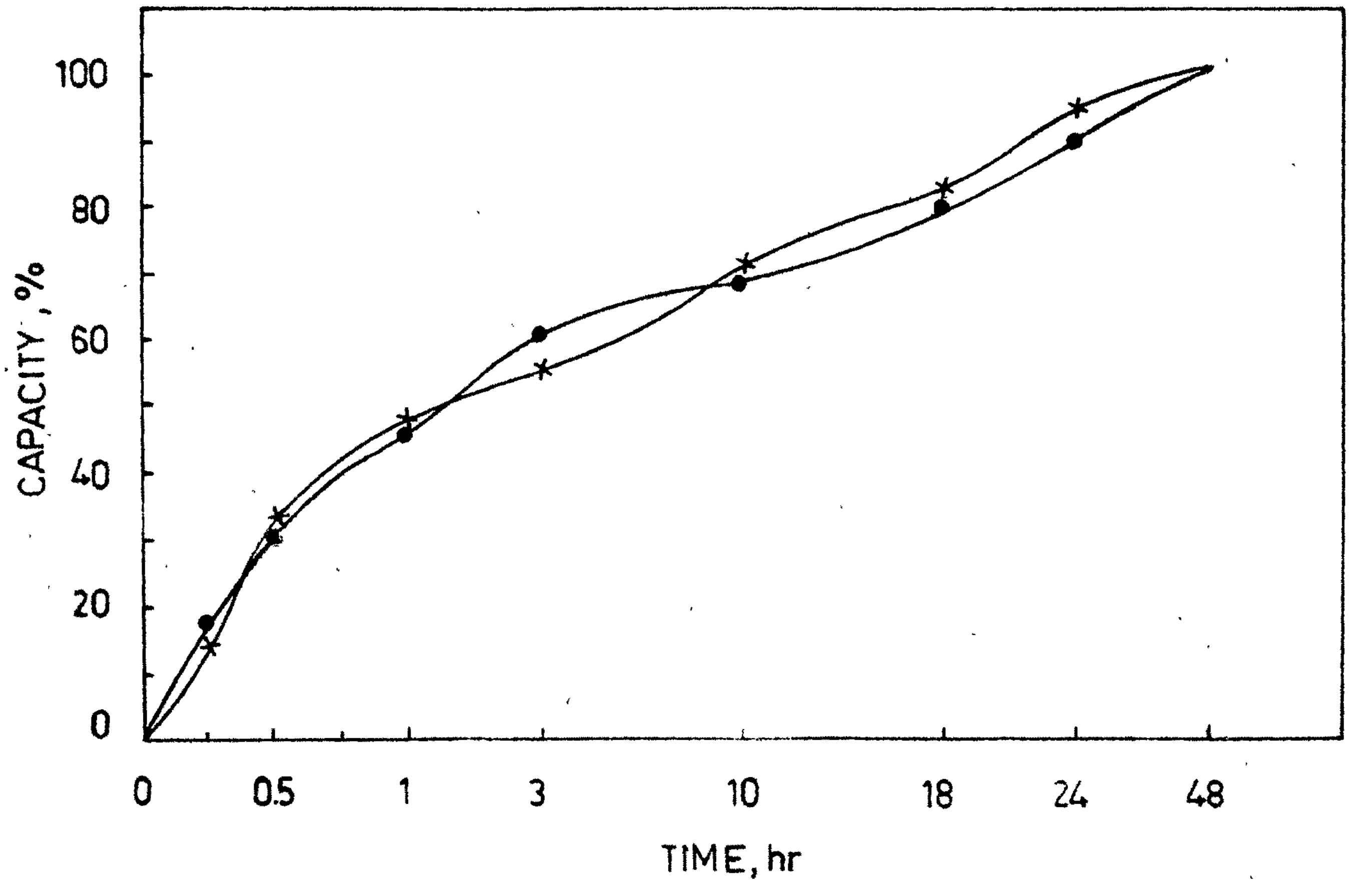


FIG 33 - RATE OF ANION EXCHANGE OF TU(AN)AC [×—×] AND TU(SA)AC [●—●] RESINS

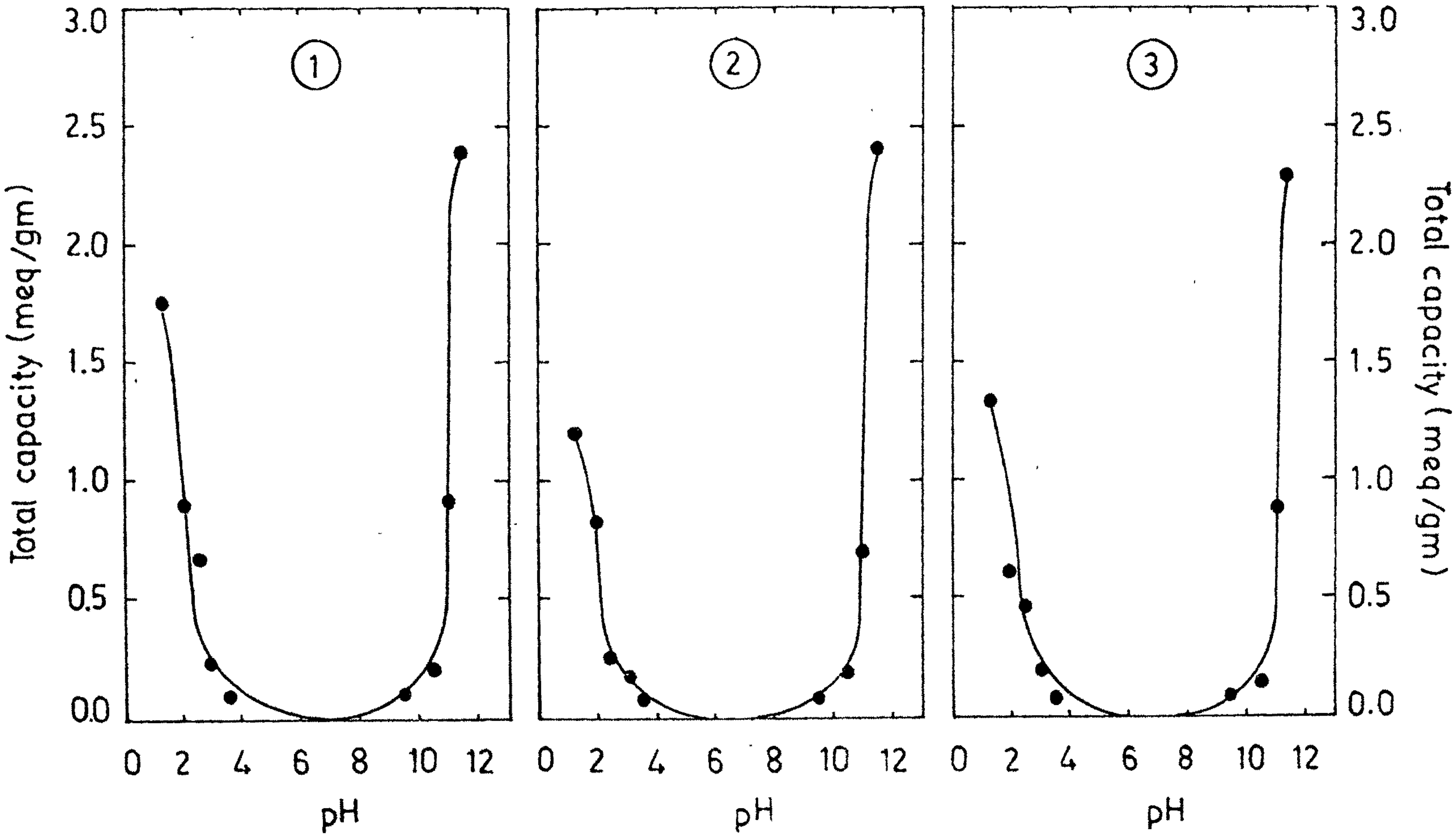


FIG 34 – P^H - TITRATION CURVES OF ① TU(SA)AC ② TU(HQ)AC ③ TU(3-OH)AC RESINS

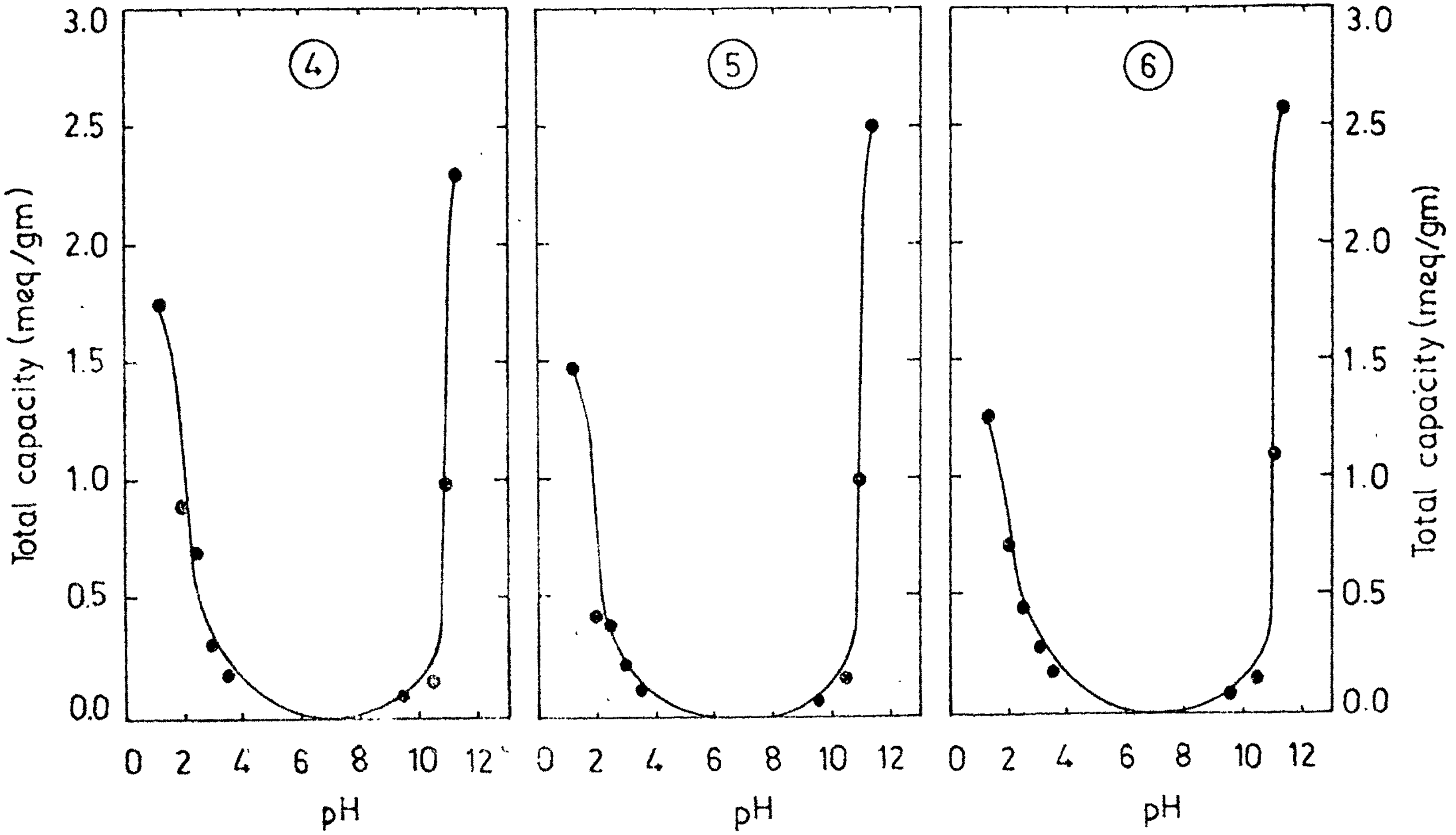


FIG 35 – pH-TITRATION CURVES OF ④ TU(AN)AC ⑤ TU(PY)AC ⑥ TU(8-OH)AC RESINS

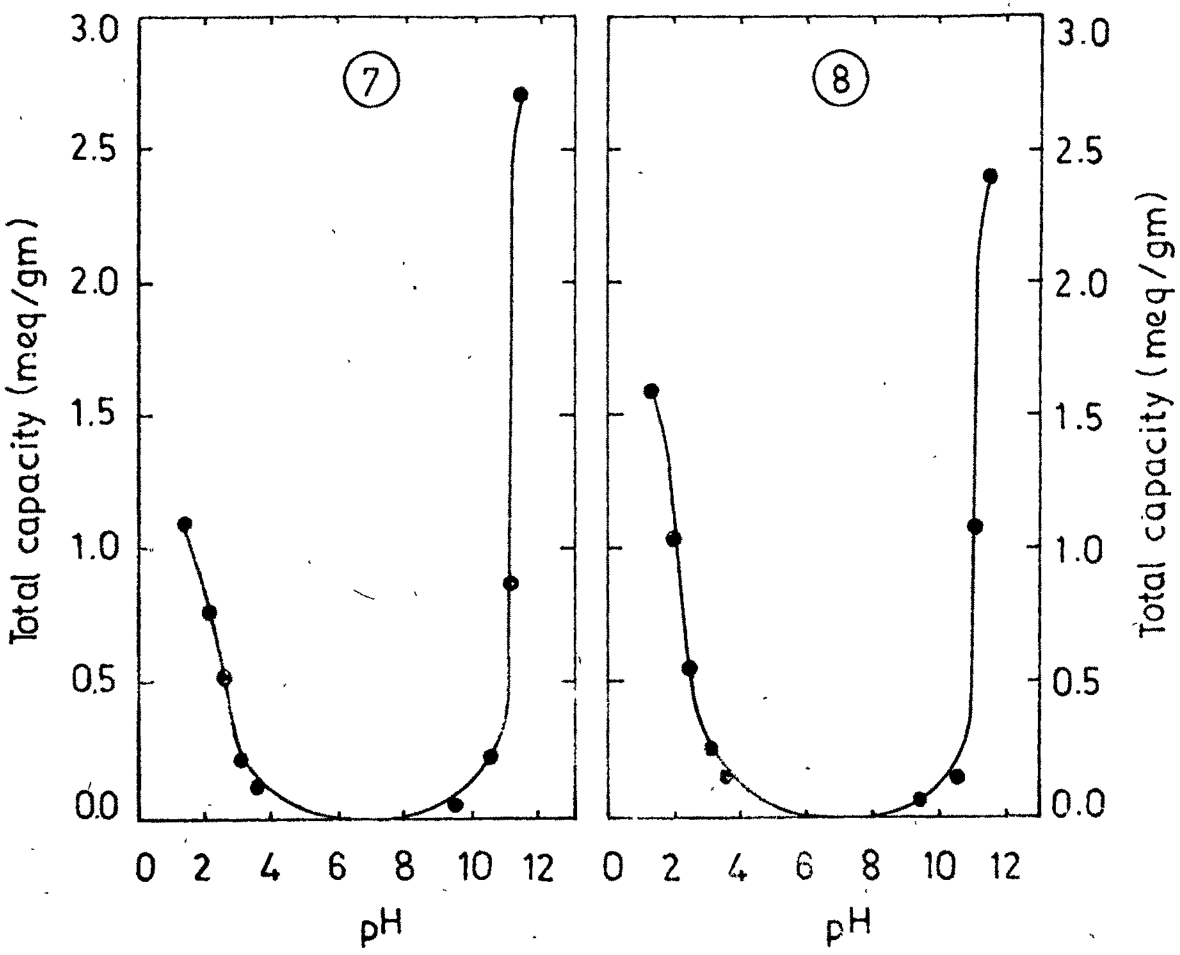


FIG 36 – pH-TITRATION CURVES OF ⑦ TU(BR)AC ⑧ TU(GA)AC RESINS

TABLE - TU - 52

Abbreviation

No.	Resin	Abbreviation
1	Acetaldehyde - Salicylic acid - Thiourea	TU(SA)AC
2	Acetaldehyde - Hydroquinone - Thiourea	TU(HQ)AC
3	Acetaldehyde - 3-hydroxy-2-naphthoic acid - Thiourea	TU(3-OH)AC
4	Acetaldehyde - Anthranilic acid - Thiourea	TU(AN)AC
5	Acetaldehyde - Pyrocatechol - Thiourea	TU(PY)AC
6	Acetaldehyde - 8-hydroxyquinoline - Thiourea	TU(8-OH)AC
7	Acetaldehyde - β-resorcylic acid - Thiourea	TU(BR)AC
8	Acetaldehyde - Gallic acid - Thiourea	TU(GA)AC

TABLE - TU - 53

Analyses, Formulae etc. of Amphoteric resins

No.	Resin	Formula	Analysis					
			Calculated			Observed		
			% C	% H	% N	% C	% H	% N
1.	TU(SA)AC	$(C_{41} H_{42.5} O_{12.25} N_2S)_n$	62.24	5.376	3.542	61.90	5.320	3.450
2	TU(HQ)AC	$(C_{37} H_{42.5} O_{8.25} N_2S)_n$	65.44	6.264	4.127	64.87	6.610	3.850
3	TU(3-OH)AC	$(C_{44} H_{43} O_{11.5} N_2S)_n$	64.78	5.276	3.435	65.13	5.102	3.120
4	TU(AN)AC	$(C_{45} H_{50.5} O_{8.25} N_6S)_n$	64.40	6.023	10.020	64.09	6.270	9.850
5	TU(PY)AC	$(C_{29} H_{35} O_{6.5} N_2S)_n$	63.62	6.398	5.120	63.87	6.570	4.920
6	TU(8-OH)AC	$(C_{27} H_{30} O_3 N_4S)_n$	66.12	6.122	11.430	65.71	6.470	11.050
7	TU(BR)AC	-	-	-	-	-	-	-
8	TU(GA)AC	-	-	-	-	-	-	-

TABLE - TU - 54

% Moisture content of Amphoteric resins

No.	Resin	% Moisture	
		H^+ form	OH^- form
1	TU(SA)AC	2.29	3.58
2	TU(HQ)AC	1.43	1.31
3	TU(3-OH)AC	4.16	1.09
4	TU(AN)AC	2.91	2.32
5	TU(PY)AC	7.87	0.07
6	TU(8-OH)AC	3.26	1.57
7	TU(BR)AC	2.15	1.12
8	TU(GA)AC	0.29	0.40

TABLE - TU - 55

Density of resins

No.	Resin	Resin in H^+ form		Resin in OH^- form	
		true density (d_{res}) (gm/cm^3)	apparent (column) density (d_{col}) (gm/ml)	true density (d_{res}) (gm/cm^3)	apparent (column) density (d_{col}) (gm/ml)
1	TU(SA)AC	1.220	0.420	1.049	0.410
2	TU(HQ)AC	1.106	0.405	1.130	0.460
3	TU(3-OH)AC	1.180	0.460	1.090	0.470
4	TU(AN)AC	1.210	0.400	1.150	0.425
5	TU(PY)AC	1.127	0.520	1.020	0.500
6	TU(8-OH)AC	1.303	0.430	1.260	0.480
7	TU(BR)AC	1.228	0.440	1.109	0.488
8	TU(GA)AC	1.290	0.490	1.010	0.430

TABLE - TU - 56

Void volume fraction of resins

No.	Resin	Resin in H^+ form		Resin in OH^- form	
		d_{col}/d_{res}	Void volume fraction $(1 - d_{col}/d_{res})$	d_{col}/d_{res}	Void volume fraction $(1 - d_{col}/d_{res})$
1	TU(SA)AC	0.375	0.625	0.390	0.610
2	TU(HQ)AC	0.382	0.618	0.407	0.593
3	TU(3-OH)AC	0.390	0.610	0.430	0.570
4	TU(AN)AC	0.330	0.670	0.370	0.630
5	TU(PY)AC	0.460	0.540	0.490	0.510
6	TU(8-OH)AC	0.330	0.670	0.381	0.619
7	TU(BR)AC	0.358	0.642	0.440	0.560
8	TU(GA)AC	0.380	0.620	0.425	0.575

TABLE - TU - 57

Capacity and concentration of ionogenic groups of Amphoteric resins as cation exchanger

No.	Resin	Total capacity CEC_{obs} (meq/gm)	Total capacity CEC_{cal} (meq/gm)	$\frac{CEC_{obs}}{CEC_{cal}}$	Concentration of ionogenic groups, Cr (meq/cm^3)	Volume capacity Q (gm. eq/1)	Cu-exchange capacity (me q/gm)
1	TU(SA)AC	2.389	2.530	0.944	2.610	0.978	1.151
2	TU(HQ)AC	2.423	1.474	1.644	2.530	0.967	1.547
3	TU(3-OH)AC	2.312	2.454	0.942	2.612	1.010	0.756
4	TU(AN)AC	2.282	1.192	1.910	2.670	0.880	0.721
5	TU(PY)AC	2.484	1.828	1.359	2.570	1.180	1.330
6	TU(8-OH)AC	2.549	2.041	1.249	3.210	1.060	1.473
7	TU(BR)AC	2.688	-	-	3.470	1.240	1.661
8	TU(GA)AC	2.391	-	-	3.070	1.170	1.528

TABLE - TU - 58

Capacity and concentration of ionogenic groups of Amphoteric resins as anion exchanger

No.	Resin	Total capacity AEC_{obs} (meq/gm)	Total capacity AEC_{cal} (meq/gm)	$\frac{AEC_{obs}}{AEC_{cal}}$	Concentration of ionogenic groups, Cr (meq/cm^3)	Volume capacity Q (gm.eq/1)
1	TU(SA)AC	1.269	1.265	1.003	1.283	0.500
2	TU(HQ)AC	1.208	1.474	0.820	1.347	0.550
3	TU(3-OH)AC	1.367	1.227	0.897	1.474	0.630
4	TU(AN)AC	1.749	1.192	1.467	1.964	0.727
5	TU(PY)AC	1.475	1.828	0.807	1.503	0.737
6	TU(8-OH)AC	1.264	2.041	0.620	1.567	0.597
7	TU(BR)AC	1.060	-	-	1.162	0.511
8	TU(GA)AC	1.601	-	-	1.610	0.680

TABLE - TU - 59

Rate of exchange of resins

No.	Resin	Time in mins/hrs	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1	TU(SA)AC	10 mins.	0.2405	-
		15 mins.	-	0.2320
		20 mins.	0.5900	-
		30 mins.	0.9210	0.3900
		1 hr.	1.3300	0.5810
		2 hrs.	1.4020	-
		3 hrs.	-	0.7800
		4 hrs.	1.5350	-
		10 hrs.	1.7470	0.8720
		16 hrs.	2.1320	-
		18 hrs.	-	1.0150
		24 hrs.	2.3890	1.1390
		48 hrs.	2.3890	1.2690
2	TU(HQ)AC	10 mins.	0.3650	-
		15 mins.	-	0.2670
		20 mins.	0.8260	-
		30 mins.	1.1160	0.3810
		1 hr.	1.5220	0.5670
		2 hrs.	1.9280	-
		3 hrs.	-	0.5980
		4 hrs.	2.1310	-
		10 hrs.	2.2050	0.7160
		16 hrs.	2.2780	-
		18 hrs.	-	0.9420
		24 hrs.	2.4230	1.0900
		48 hrs.	2.4230	1.2080

(TABLE - TU - 59 contd........)

No.	Resin	Time in mins/hrs	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
3	TU(3-OH)AC	10 mins.	0.2940	-
		15 mins.	-	0.1140
		20 mins.	0.7580	-
		30 mins.	1.2520	0.5600
		1 hr.	1.5640	0.8460
		2 hrs.	1.9820	-
		3 hrs.	-	0.9470
		4 hrs.	2.1900	-
		10 hrs.	2.2190	1.0250
		16 hrs.	2.2770	-
		18 hrs.	-	1.1400
		24 hrs.	2.3120	1.2560
		48 hrs.	2.3120	1.3670
4	TU(AN)AC	10 mins.	0.2510	-
		15 mins.	-	0.2410
		20 mins.	0.8900	-
		30 mins.	1.1330	0.5730
		1 hr.	1.2360	0.8130
		2 hrs.	1.5440	-
		3 hrs.	-	0.9580
		4 hrs.	1.7450	-
		10 hrs.	1.8510	1.2420
		16 hrs.	2.0540	-
		18 hrs.	-	1.4340
		24 hrs.	2.2820	1.6600
		48 hrs.	2.2820	1.7490

(TABLE -TU - 59 contd.......)

No.	Resin	Time in mins/hrs	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
5	TU(PY)AC	10 mins.	0.3000	-
		15 mins.	-	0.2900
		20 mins.	0.5220	-
		30 mins.	0.8690	0.5620
		1 hr.	1.4210	0.7540
		2 hrs.	1.6460	-
		3 hrs.	-	0.9390
		4 hrs.	1.8170	-
		10 hrs.	2.0910	1.0190
		16 hrs.	2.2880	-
		18 hrs.	-	1.1210
		24 hrs.	2.4840	1.2730
		48 hrs.	2.4840	1.4750
6	TU(8-OH)AC	10 mins.	0.4100	-
		15 mins.	-	0.3020
		20 mins.	0.8430	-
		30 mins.	1.1380	0.4890
		1 hr.	1.3480	0.6830
		2 hrs.	1.7580	-
		3 hrs.	-	0.8220
		4 hrs.	1.8620	-
		10 hrs.	2.0880	0.8900
		16 hrs.	2.3830	-
		18 hrs.	-	0.9630
		24 hrs.	2.5490	1.1130
		48 hrs.	2.5490	1.2640

(TABLE - TU - 59 contd.....)

No.	Resin	Time in mins/hrs	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
7	TU(BR)AC	10 mins.	0.3550	-
		15 mins.	-	0.3420
		20 mins.	0.7800	-
		30 mins.	1.2260	0.4450
		1 hr.	1.7370	0.5620
		2 hrs.	1.8390	-
		3 hrs.	-	0.6840
		4 hrs.	2.0430	-
		10 hrs.	2.3490	0.7640
		16 hrs.	2.5330	-.
		18 hrs.	-	0.8650
		24 hrs.	2.6880	0.9900
		48 hrs.	2.6880	1.0600
8	TU(GA)AC	10 mins.	0.3000	-
		15 mins.	-	0.1530
		20 mins.	0.6930	-
		30 mins.	0.9800	0.6200
		1 hr.	1.0990	0.7440
		2 hrs.	1.4300	-
		3 hrs.	-	0.8500
		4 hrs.	1.5320	-
		10 hrs.	1.7050	0.9390
		16 hrs.	2.0850	-
		18 hrs.	-	1.1060
		24 hrs.	2.3910	1.4820
		48 hrs.	2.3910	1.6010

TABLE - TU - 60

Apparent pK_a and pK_b values and Isoionic point of resins

No.	Resin	Apparent pK_a values	Apparent pK_b values	Isoionic point
1	TU(SA)AC	11.062	2.363	6.712
2	TU(HQ)AC	10.957	2.442	6.699
3	TU(3-OH)AC	10.978	2.295	6.636
4	TU(AN)AC	10.933	2.503	6.718
5	TU(PY)AC	10.946	2.228	6.587
6	TU(8-OH)AC	10.985	2.461	6.723
7	TU(BR)AC	10.962	2.785	6.873
8	TU(GA)AC	10.965	2.614	6.789

TABLE - TU - 61

Thermal Stability of Amphoteric resins as cation exchanger

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Loss in capacity of absolutely dry resin as determined after heating,%			Loss in capacity of absolutely dry resin as determined after regeneration,%		
			H-form	Na-form	K-form	H-form	Na-form	K-form
40°	TU(SA)AC	2.389	NIL	NIL	NIL	NIL	NIL	NIL
	TU(HQ)AC	2.423	NIL	NIL	NIL	NIL	NIL	NIL
	TU(3-OH)AC	2.312	NIL	NIL	NIL	NIL	NIL	NIL
	TU(AN)AC	2.282	NIL	NIL	NIL	NIL	NIL	NIL
	TU(PY)AC	2.484	NIL	NIL	NIL	NIL	NIL	NIL
	TU(8-OH)AC	2.549	NIL	NIL	NIL	NIL	NIL	NIL
	TU(BR)AC	2.688	NIL	NIL	NIL	NIL	NIL	NIL
	TU(GA)AC	2.391	NIL	NIL	NIL	NIL	NIL	NIL

(TABLE - TU - 61 contd......)

Temp. °C	Resin	Original capacity (meq/mg) of absolutely dry resin	Loss in capacity of absolutely dry resin as determined after heating,%			Loss in capacity of absolutely dry resin as determined after regeneration,%		
			H-form	Na-form	K-form	H-form	Na-form	K-form
60°	TU(SA)AC	2.389	NIL	NIL	NIL	NIL	NIL	NIL
	TU(HQ)AC	2.423	NIL	NIL	NIL	NIL	NIL	NIL
	TU(3-OH)AC	2.312	NIL	NIL	NIL	NIL	NIL	NIL
	TU(AN)AC	2.282	NIL	NIL	NIL	NIL	NIL	NIL
	TU(PY)AC	2.484	NIL	NIL	NIL	NIL	NIL	NIL
	TU(8-OH)AC	2.549	NIL	NIL	NIL	NIL	NIL	NIL
	TU(BR)AC	2.688	NIL	NIL	NIL	NIL	NIL	NIL
	TU(GA)AC	2.391	NIL	NIL	NIL	NIL	NIL	NIL

(TABLE - TU - 61 contd......)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Loss in capacity of absolutely dry resin as determined after heating,%			Loss in capacity of absolutely dry resin as determined after regeneration,%		
			H-form	Na-form	K-form	H-form	Na-form	K-form
80°C	TU(SA) AC	2.389	25.58	2.33	13.44	39.31	21.17	37.09
	TU(HQ) AC	2.423	38.18	11.14	22.25	66.98	29.05	13.52
	TU(3-OH) 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(8-OH) AC	2.549	26.44	4.15	35.98	31.93	24.30	0.90
	TU(BR) 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 - TU - 62

Thermal Stability of Amphoteric resins as anion exchanger

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Loss in capacity of absolutely dry resin as determined after heating,%		Loss in capacity of absolutely dry resin as determined after regeneration,%	
			OH - form	Cl - form	OH - form	Cl- form
40°	TU(SA) AC	1.269	NIL	NIL	NIL	NIL
	TU(HQ) AC	1.208	NIL	NIL	NIL	NIL
	TU(3-OH) AC	1.367	NIL	NIL	NIL	NIL
	TU(AN) AC	1.749	NIL	NIL	NIL	NIL
	TU(PY) AC	1.475	NIL	NIL	NIL	NIL
	TU(8-OH) AC	1.264	NIL	NIL	NIL	NIL
	TU(BR) AC	1.060	NIL	NIL	NIL	NIL
	TU(GA) AC	1.601	NIL	NIL	NIL	NIL

(TABLE - TU - 62 contd......)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Loss in capacity of absolutely dry resin as determined after heating,%		Loss in capacity of absolutely dry resin as determined after regeneration,%	
			OH - form	Cl - form	OH - form	Cl - form
60^o	TU(SA) AC	1.269	59.81	8.22	53.27	17.70
	TU(HQ) AC	1.208	55.71	26.26	51.98	25.30
	TU(3-OH) 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(8-OH) AC	1.264	58.39	34.38	54.03	12.67
	TU(BR) AC	1.060	35.85	33.85	32.90	26.90
	TU(GA) AC	1.601	30.02	14.91	28.29	13.17

TABLE - TU - 63

Oxidation resistance of Amphoteric resins as cation exchanger

No.	Resin	% Moisture		Increase in % water content
		Untreated exchanger	H_2O_2 treated exchanger	
1	TU(SA)AC	2.29	4.24	1.95
2	TU(HQ)AC	1.43	5.44	4.01
3	TU(3-OH)AC	4.16	5.07	0.91
4	TU(AN)AC	2.91	5.24	2.33
5	TU(PY)AC	7.87	9.45	0.58
6	TU(8-OH)AC	3.26	6.15	2.89
7	TU(BR)AC	2.15	6.09	3.94
8	TU(GA)AC	0.29	9.00	8.71

TABLE - TU - 64

Oxidation resistance of Amphoteric resins as anion exchanger

No.	Resin	% Moisture		Increase in % water content
		Untreated exchanger	H_2O_2 treated exchanger	
1	TU(SA)AC	3.58	11.61	8.03
2	TU(HQ)AC	1.31	9.21	7.90
3	TU(3-OH)AC	1.09	9.47	8.38
4	TU(AN)AC	2.32	6.74	4.42
5	TU(PY)AC	0.07	9.56	9.49
6	TU(8-OH)AC	1.57	7.63	6.06
7	TU(BR)AC	1.12	11.13	10.01
8	TU(GA)AC	0.40	8.41	8.01

TABLE-TU-65

Major peaks observed in the infrared spectra of resins

No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
1	TU(SA)AC	3500-3300	broad	O-H stretching absorption
		2980, 2930	sharp & weak	C-H aliphatic, stretching
		1680-1640	medium	-C -NH-, amide linkage.
		1380	sharp	C-H bending, $-\overset{|}{\underset{|}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration
2	TU(HQ)AC	3500-3300	broad	O-H stretching, absorption
		2980,2940	sharp & weak	C-H aliphatic stretching
		1670-1650	medium	-C -NH-, amide linkage
		1380	sharp	C-H bending, $-\overset{|}{\underset{|}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration

Table-TU-65 contd.....

No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
3	TU(3-OH)AC	3500-3300	broad	O-H stretching, absorption
		2980, 2940	sharp & weak	C-H aliphatic, stretching
		1680-1660	medium	-CS-NH-, amide linkage
		1380	sharp	C-H bending, $-\overset{|}{\underset{|}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration
4	TU(AN)AC	3500-3300	broad	O-H stretching, absorption
		2970,2930	sharp & weak	C-H aliphatic stretching
		1680-1660	medium	-CS-NH-, amide linkage
		1380	sharp	C-H bending, $-\overset{|}{\underset{|}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration
5	TU(PY)AC	3500-3300	broad	O-H stretching, absorption
		2980,2940	sharp & weak	C-H aliphatic stretching
		1680-1650	medium	amide linkage, (-CS-NH-)
		1380	sharp	C-H bending $-\overset{|}{\underset{|}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration

Table-TU-65 contd......

No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
6	TU(8-OH)AC	3500-3300	broad	O-H stretching absorption
		2970,2930	sharp & weak	C-H aliphatic, stretching
		1670-1660	medium	-CS-NH-, amide linkage
		1380	sharp	C-H bending $-\overset{\vert}{\underset{\vert}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration
7	TU(BR)AC	3500-3300	broad	O-H stretching absorption
		2980,2940	sharp & weak	C-H aliphatic, stretching
		1670-1650	medium	-CS-NH-,amide linkage
		1380	sharp	C-H bending, $-\overset{\vert}{\underset{\vert}{C}}-CH_3$
		1120-1050	weak & broad	C=S stretching vibration
8	TU(GA)AC	3500-3500	broad	O-H stretching absorption
		2970, 2930	sharp & weak	C-H aliphatic, stretching
		1670-1600	medium	-CS-NH-,amide linkage
		1380-1370	sharp	C-H bending, $-\overset{\vert}{\underset{\vert}{C}}-CH_3$
		1110-1050	weak & broad	C=S stretching vibration