CHELATING POLYMERS

B : CROSS-LINKED POLYMERIC NETWORKS AS ION EXCHANGE RESINS

VI INTRODUCTION

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There has been considerable activity in the field of chelating ion exchange polymers in recent years. Studies on ion exchangers and organic/inorganic ligands led scientists to develope ion exchange polymers possessing chelating properties. In analytical as well as in preparative inorganic chemistry, there exists considerable need for chelating polymers which combine the ease of operation of the conventional ion exchangers and specificity/selectivity of the ligands. The research schools which contributed considerably towards the preparation and understanding of the nature and behaviour of such chelating polymers are those of Bayer[1], Blasius[2], Gregor[3], Hering[4], Kennedy[5], Manecke[6], Schmuckler[7], De Geiso[8],etc. Such polymers can find use in column chromatography, thin layer chromatography, ligand exchange chromatography,membrane formation, desalination, waste water treatment,etc.

Ion exchangers may be specific in terms of functional groups introduced in them through specific ligands. Because of its specificity, an ion exchanger can sorb (exchange) one ionic species to the exclusion of others under broad range of conditions. This is examplified below :

Skogseid[9] subjected polystyrene to nitration, reduction, condensation with picryl chloride and further nitration, and obtained an ion exchanger having structure (VI-S-1).

Dipicrylamine (VI-S-2) is a specific precipitating agent of potassium, and the above ion exchanger (VI-S-1) shows an excellent specific uptake of potassium ions.

Specific ion exchangers include the entire group of chelating resins whose specificity is based on the chelate or complex forming functional groups. The best known commercial type (VI-S-3) is the iminodiacetate ion exchanger (Dowex A-1), in which iminodiacetate groups are attached to the styrene matrix, and which can fix polyvalent ions with a high affinity by the formation of heterocyclic metal chelate complexes (VI-S-4).

A series of specific, chelate forming ion exchangers has been prepared and studied mainly in the field of analysis.

Many compounds which form chelates with metal cations have been incorporated into resin structure by polycondensation with phenols and aldehydes. Examples are anthranillic acid[10,11] (VI-S-5).

o-Amino phenol[10,12] (VI-S-6), anthranilic acid diacetic acid[13] (VI-S-7), m-phenylene diglycine[10] (VI-S-8) and m-phenylene diaminotetraacetic acid[13] (VI-S-9).

When chelating agents are introduced into styrene-type resins, ion exchangers are mechanically and chemically more stable than the condensation polymers. Various methods of preparing resins with iminodiacetic acid group are developed[14]. In their complexing tendency these resins are similar to ethylenediamine tetra acetic acid (E.D.T.A.) (VI-S-10). Hydroxamic acid groups have been introduced into a resin with carboxylic acid groups[15,16]. These resins are specific for Fe^{3+} ions. Resins with mercapto groups prefer Hg^{2+} ions [17,18]. Mercapto groups have also been introduced into polyamide resin such as nylon[17].

A resin with chromotropic acid group prefering Ti^{4+} has been made[19]. Agents such as β-naphthol have been introduced by coupling with diazotised resins[3,20]. Resins containing chlorophyll and haemin derivatives form extremely strong chelates with ions such as Fe^{3+} [21,22].

Gregor, Taifor and Backer[23] investigated various ion exchangers exhibiting chelating properties towards the transition elements. The most promising resin found by these investigators was prepared from m-phenylenediglycine, o-aminophenol and formaldehyde. When compared with ordinary carboxylic or amine resin, these resins showed selectivities for transition elements that could not be accounted for by simple ion exchange processes.

A resin containing a beta diketone group and exhibiting a very high selectivity for copper has been synthesized by Mc Burney[24].

Kennedy and co-workers[5] found that polymerised and insolubilised phosphonates (VI-S-11) were selective for uranyl, ferric, cobalt and lithium salts in non-aqueous solvents such as ketones and primary alcohols. These polymeric adsorbents exhibit little or no ion exchange capacity in the usual sense, however the iron, uranyl, cobalt and lithium salts are adsorbed by these resins as Werner Coordination Complexes and these may be eluted with acetone-water solution or dimethyl formamide.

The possible industrial applications of some of these and related products are in such diverse fields as (1) hydrometallurgy (2) desalination (3) waste-water treatment (4) permselective membrane (5) ion exclusion (6) catalyst (7) recovery and purification of biochemicals, etc.

Hydrometallurgy :

The application of ion exchange technology in hydrometallurgical practice includes winning, purification and concentration of metals from aqueous solutions, regardless of their origin. Thus, it deals with the winning of metals from solutions obtained by ore treatment as well as with the recovery of metals from hydrometallurgical effluents. However, even though considerable data are available on metal ions and ion exchangers, the commercial processes of metal winning and refining by ion exchange have remained limited to just a few.

Desalination :

For a longtime, water treatment was the sole application of ion exchangers in technology; it is still the most important one today.

Waste water treatment : (Decontamination) :

Ion exchange processes are employed for waste effluent treatment and share many characteristics with conventional water treatment; nevertheless, waste effluent treatment deserves a separate consideration because of two other aspects, i.e., it is performed because its components are too valuable or because they are too toxic or too dangerous in other ways.

Decontamination of radioactive effluents is the field of application for ion exchangers which has assumed a firm position in radiation chemistry.

Because of the increasing cost of industrial water, another object in the search for suitable waste water treatment processes is that the effluent be purified to the point where it can be reused for the same process.

According to Schtanikow[25], virus-contaminated water can also be purified by ion exchangers.

Ion exclusion :

The ion exclusion method serves for the separation of ionized substance from non-ionized or weakly ionized substance when both are present in aqueous solution. It is important for the components that are to be separated to be inert with respect to the exchanger material.

Ion exclusion has proved to be a method for the chromatographic deionization or atleast removal of the major fraction of ionic components from organic products with the simple technique of ion exchange.

Ion Exchange Catalyst :

Ion exchangers are used as catalysts. The catalytic activity is present in the counter ions. Cation exchangers in the H-form and anion exchangers in the OH-form catalyse processes which are accelerated by acids and alkalis respectively. The resin network serves solely as a catalyst support.

Ion exchange resins show a particular affinity for acid and base catalysis in organic reactions, since they can be easily transformed into the H-form or OH-form and their porocity and swelling offer a sufficiently large active surface, so that even large organic molecules can penetrate the interior of the resin.

Present work :

Osborn[26] writes on chelating resins : Recently much interest has been aroused in analytical circles by the so-called chelating resins.... Despite the promise of these resins, very little has been done so far towards a real investigation of the problem.... Opinion is much divided at the present moment amongst ion exchange researchers as to the future of this type of resin, but the author feels that research along these lines may well be fruitful.

Kunin[27], while discussing the future of the ion exchange, writes : Ion exchangers of high specificity have intrigued many investigators. Although the commercial development of such materials has not come to pass, notable strides have been made.

He also suggests that there is still much work to be done by way of.... introducing new and different functional groups which may have special affinity for certain ions.

We considered that there is a wide scope for the investigations on chelating polymers as ion exchange resins, and that amphoteric character can be introduced by using amines/amides in the polymerisation process.

Our earlier attempts of cross-linking the linear polymers obtained in Part A of these investigations were not much successful. Hence we concentrated our efforts on preparing cross-linked polymers from monomers and studying their properties.

We planned the work as follows :

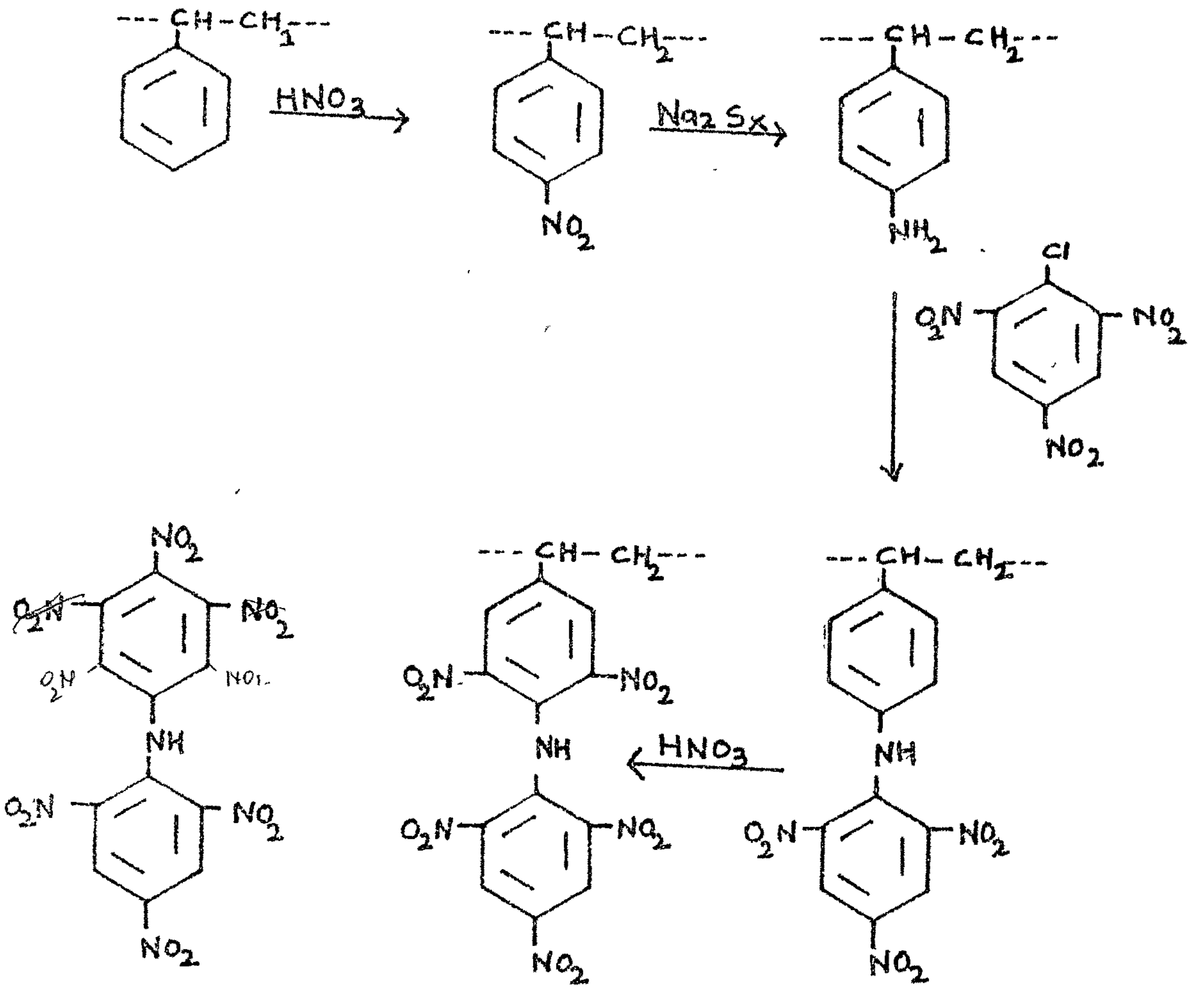
(i) preparation of amphoteric chelating and related polymeric resins from substituted phenol, melamine and formaldehyde by polycondensation reaction;

(ii) study of the ion exchange characteristics of these resins, particularly cation exchange, anion exchange and copper ion exchange;

(iii) preparation of chelating and related polymeric resins from substituted phenol, urea and formaldehyde and study of their ion exchange characteristics;

(iv) preparation of chelating and related polymeric resins from substituted phenol, aromatic/heterocyclic amine and formaldehyde and study of their ion exchange characeteristics.

Experiments carried out and results obtained are presented and discussed in the following pages.



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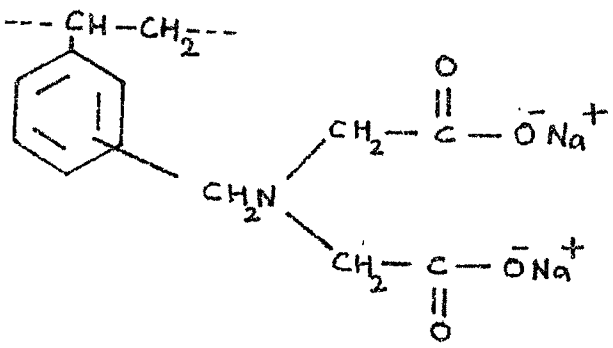

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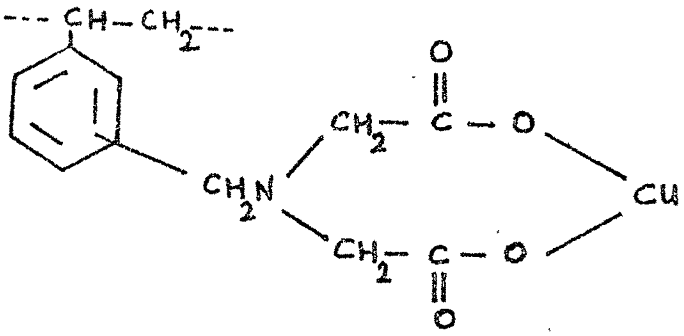

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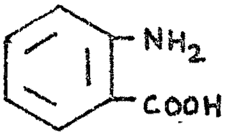

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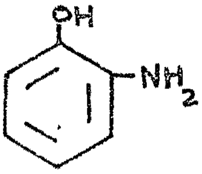

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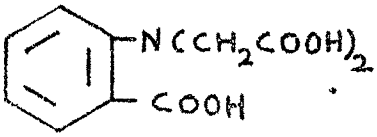

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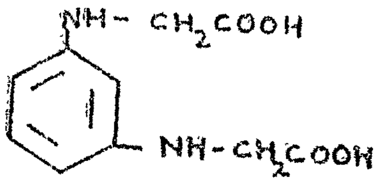

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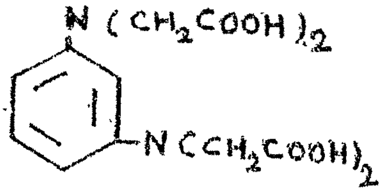

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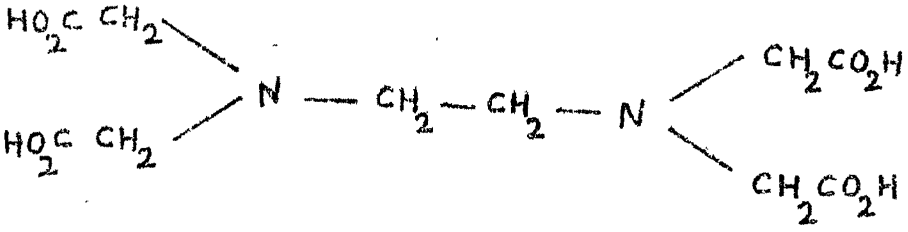

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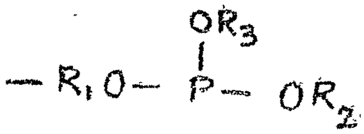

$$-R_1O-\overset{\overset{OR_3}{|}}{P}-OR_2$$

(VI-S-11)

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VII EXPERIMENTAL

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VII. EXPERIMENTAL

VII (a). Synthesis of chelating polymers using melamine :

Melamine and formaldehyde were taken in a 250 ml. round bottom three-necked flask fitted with a stirrer, a thermometer and a condenser. The contents of the flask were warmed on a water-bath to about 70°C with stirring till all the melamine dissolved. The phenol derivative (salicylic acid, sulpho salicylic acid, beta-resorcilic acid, amino salicylic acid, 3-hydroxy-2-naphthoic acid, hydroquinone, catechol, resorcinol, pyrogallol, or salicylaldehyde) dissolved in requisite quantity of sodium hydroxide was added to this mixture. The reaction mixture was heated at 90°C under reflux until the reaction mixture gelled to a soft mass. The gel was removed from the reaction vessel and cured in an oven at about 90°C.[28] The resulting hard mass was crushed and particles having

35-60 and 60-100 BSS mesh size were collected and used in subsequent investigations. Data regarding molar proportions of the phenol derivative, melamine and formaldehyde used and the conditions observed are given in Table VII- T-1.

(In the case of 8-hydroxyquinoline, it was dissolved in requisite quantity of hydrochloric acid instead of sodium hydroxide)*.

All these resins are non-melting and insoluble in water(they swell in water). They were analysed for C, H and N. Their colour, analysis and probable formula are given in Table VII- T-2.

VII (b). Moisture content of resins :

Moisture content of the resin was determined by drying an exactly weighed sample (H form or OH form) of the resin in an oven at 110 - 115°C for 24 hours[29] and reweighing it after cooling it in a desiccator. The calculation is :

$$\frac{\text{Wt. of oven dried resin} \times 100}{\text{Wt. of resin before drying}} = \%\ \text{Solid}$$

$$100 - \%\ \text{Solid} = \%\ \text{Moisture.}$$

VII (c). Total cation exchange capacity :

Approximately 10 gms. of the resin were weighed and taken in the funnel and converted into H form with one litre one normal hydrochloric acid. The resin was filtered, washed to neutrality with distilled water and dried in air.[30]

About one gm. (exactly weighed) sample of the resin, prepared as above, was taken in dry 250 ml. Erlenmeyer flask. A similar sample was used to determine the moisture content as suggested earlier. To the sample in the Erlenmeyer flask, were added 200 ml. of standardized 0.1N sodium hydroxide in 1.0 N sodium chloride solution. The mixture was kept for 24 hours. 50 ml. aliquots of the supernatant liquid were titrated with standard 0.1N acid[28]. The total cation exchange capacity is calculated as follows:

$$\frac{(200 \times \text{N.NaOH}) - 4(\text{ml. acid} \times \text{N.acid})}{\text{Sample weight} \times \frac{(\%\ \text{Solid})}{(100)}} =$$

$$\frac{\text{Milliequivalents of cation exchange}}{\text{gms. of dry H - form resin}} = \text{CEC}\ .$$

VII (d) <u>Total anion exchange capacity</u> :

Approximately 10 gms. of resin were weighed and taken in the funnel and converted to OH form with one litre one normal sodium hydroxide. The resin was filtered and washed to neutrality with distilled water and dried in air[30].

About one gm. (exactly weighed) sample of the resin, prepared as above, was taken in a dry 250 ml. Erlenmeyer flask. A similar sample was used to determine the moisture content as suggested earlier. To the sample in the Erlenmeyer flask, were added 200 ml. of standardized 0.1N hydrochloric acid in 1.0 N sodium chloride solution. The mixture was kept for 24 hours. 50 ml. aliquots of the supernatant liquid were titrated with standard 0.1N alkali[30]. The total anion exchange capacity is calculated as follows :

$$\frac{(200 \times N.HCl) - 4(\text{ml. alkali} \times N.\text{alkali})}{\text{sample weight} \times \left(\frac{\%\ \text{Solid}}{100}\right)} =$$

$$\frac{\text{Milliequivalents of anion exchanged}}{\text{gms. of dry OH - form resin}} = \text{AEC}$$

The values of % moisture and ion exchange capacity (CEC and AEC) are presented in Table VII- T-3.

VII (e). pH Titration :

Approximately 0.5 gm. (exactly weighed) samples of the resin (H - form or OH - form) were taken in different 150 ml. dry conical flasks. Different solutions were prepared by diluting different quantities of 0.1N acid (or 0.1N alkali) in 1.0 N sodium chloride to the calculated volume with 1.0N sodium chloride solution. 100 ml. of such a solution was added to a flask containing the resin (alkali solution to H - form resin and acid solution to OH - form resin). The flasks were shaken at intervals and pH of the solution was measured until constant pH values were attained (usually 24 to 48 hours were required). The pH of the solution was then exactly measured using pH meter. Then after 25 ml. aliquots of the supernatant liquid were titrated with standard 0.1N acid or alkali as required.[30]

The values of equilibrium pH of the solution and ion exchange capacity realised for meqs of alkali or acid taken per gram of the dry resin are presented in Tables VII- T-4 and VII- T-5.

VII (f) Rate of Exchange :

(i) Cation Exchange :

The resin was converted to the H-form as suggested earlier. The H-form of the resin (0.5 gm.) was equilibrated with 100 ml. 0.1N sodium hydroxide in 1.0 N sodium chloride solution for different periods of time. Different mixtures were kept for different periods of time, at the end of which the solution were decanted, and aliquots were titrated against standard acid and from this, the cation exchange capacity realised at different time intervals was calculated.

(ii) Anion Exchange :

The resin was converted to the OH-form as suggested earlier. The OH-form of the resin (0.5 gm.) was equilibrated with 100 ml. 0.1N hydrochloric acid in 1.0 N sodium chloride solution for different periods of time. Different mixtures were kept for different periods of time, at the end of which the solutions were decanted, and aliquots were titrated against standard alkali and from this, the anion ion exchange capacity realised at different time intervals was calculated.

The values of the ion exchange capacity realised at different intervals of time are presented in Table VII T-6.

VII (g) Metal (Cu) Exchange capacity :

About 1 gm. (exactly weighed) H-form of the resin was taken in dry 250 ml. Erlenmeyer flask. To the sample in Erlenmeyer flask were added 200 ml. of standardized 0.05N copper acetate in 5% sodium acetate solution.

The mixture was kept for 24 hours, 50 ml. aliquots of the supernatant liquid were titrated with standard 0.05N sodium thiosulphate solution. The copper exchange capacity is calculated as follows :

$$\frac{(\ 200 \times \text{N.Copper(II)}\ ) - 4(\text{ml.Na-thiosulphate} \times \text{N.Na-thiosulphate}}{\text{Sample weight} \times \left(\frac{\%\ \text{Solid}}{100}\right)}$$

$$= \frac{\text{Milliequivalents of Cu-exchange}}{\text{gms. of dry H - form resin}} = \text{Exchange capacity (Cu ion)}$$

The results are presented in Table VII- T-7.

VII (h). Copper Titration :

Approximately 0.5 gm. (exactly weighed) samples of the resin (H-form) were taken in different 150 ml. dry conical flasks. The addition of solutions is made to each flask according to the scheme shown in Table VII- T-8. The mixture was kept for 24 hours. 25 ml. aliquots of the supernatant liquid were titrated with standard 0.05N sodium thiosulphate.

The values of exchange capacity (copper ion) realised per gram of the dry resin are presented in Table VII- T-9.

VII (i). Synthesis of chelating polymers using urea/thiourea :

Urea (thiourea) and formaldehyde were taken in 250 ml. round bottom flask fitted with a condenser. The contents of the flask were warmed on water-bath till all urea (thiourea) dissolved. The phenol derivative (salicylic-acid, sulpho salicylic acid, resorcinol, catechol, hydroquinone or salicylaldehyde) dissolved in requisite quantity of sodium hydroxide was added to this mixture. The reaction mixture was heated on sand-bath under reflux until the reaction mixture gelled to a soft mass. The gel was removed from the reaction vessel and cured in an oven at about 90°C. The resulting hard mass was crushed and particles having 35 to 60 and 60 to 100 BSS mesh size were collected and used for subsequent measurements. Data regarding molar proportions of the phenol derivative, urea (or thiourea) and formaldehyde used and the conditions observed are given in Table VII- T-10.

All these resins are non-melting and insoluble in water (they swell in water). They were analysed for C, H, and N. Their colour, analysis and probable formula are given in Table VII- T-11.

VII (j). Moisture content, total cation exchange capacity and total anion exchange capacity :

1. Moisture content of these resins was determined as described in VII (b).

2. Total cation exchange capacity of these resins was

determined as described in VII (c).

3. Total anion exchange capacity of these resins was determined as described in VII (d).

The values of % moisture and ion exchange capacity (CEC and AEC) are presented in Table VII- T-12.

VII (k). pH Titration, rates of ion exchange and exchange capacity (Copper ion) :

1. pH titration of these resins was determined as described in VII (e).

2. Rates of cation and anion exchange (CEC and AEC) of these resins were determined as described in VII (f).

3. Metal (Cu) exchange capacity of these resins was determined as described in VII (g).

The results of these determinations are presented in tables VII- T-13, VII- T-14 and VII- T-15.

VII (l). Synthesis of chelating polymers using amino pyridine/p-phenylenediamine :

The phenol derivative (salicylic acid, hydroquinone or catechol) and formaldehyde were taken in 250 ml. round bottom flask fitted with a condenser. The contents of the flask were warmed on sand-bath till all the phenol derivative dissolved. Amino pyridine (or p-phenylenediamine) dissolved in requisite quantity of hydrochloric acid was added to this mixture. The reaction mixture was heated on sand-bath under reflux until the reaction mixture gelled to a soft mass. The gel was removed from the reaction vessel and cured in an oven at about 90°C. The resulting hard mass was crushed and particles having 35 to 60 and 60 to 100 BSS mesh size were collected and used for subsequent measurements. Data regarding molar proportion of the phenol derivative, amino pyridine (or p-phenylenediamine) and formaldehyde used and the conditions observed are given in Table VII- T-16.

All these resins are non-melting and insoluble in water (they swell in water). They were analysed for C, H and N. Their colour, analysis and probable formula are given in Table VII- T-17.

VII (m). Moisture content, total cation exchange capacity and total anion exchange capacity :

1. Moisture content of thse resins was determined as described in VII (b).
2. Total cation exchange capacity of these resins was determined as described in VII (c).
3. Total anion exchange capacity of these resins was determined as described in VII (d).

The values of % moisture and ion exchange capacity (CEC and AEC) are presented in Table VII- T-18.

VII (n). pH Titration, rates of ion exchange and exchange capacity (Copper ion) :

1. pH Titration of these resins was determined as described in VII (e).
2. Rate of exchange (CEC and AEC) of these resins was determined as described in VII (f).

3. Exchange capacity (Copper ion) of these resins was determined as described in VII (g).

The results of these determinations are presented in tables VII- T-19, VII- T-20 and VII- T-21.

VII (o). **Copper titration** :

Copper titration of two resins (QUF and CPPF) was carried out as described in VII (h). The results of these determinations are presented in Table VII- T-22.

Table VII- T-1

Amounts of reactants used, periods of gelation and curing.

Formaldehyde (37%) = 30 ml.
Melamine = 4.2 gm.

NO. 1.	Resin 2.	Phenol derivative (amount in gm. or ml.) 3.	Gelling period (in hours) 4.	Curing period (in hours) 5
1.	SAMF	Salicylic acid (4.6 gm.)	1	12
2.	SSAMF	Sulpho salicylic acid (8.5 gm.)	6	12
3.	RAMF	beta-Resorcilic acid (5.1 gm.)	5	8
4.	NAMF	3-Hydroxy-2-naphthoic acid (6.2 gm.)	3	8

Table VII- T-1 (cont.)

1.	2.	3.	4.	5.
5.	ASAMF	5-Amino salicylic acid (5.1 gm)	6	12
6.	RMF	Resorcinol (3.7 gm)	1/2	10
7.	CMF	Catechol (4.0 gm)	1	8
8.	QMF	Hydroquinone (4.0 gm)	1	8

Table VII- T-1 (cont.)

1.	2.	3.	4.	5.
9.	GMF	Pyrogallol (4.2 gm)	2	8
10.	SMF	Salicylaldehyde (7.0 ml)	16	20
11.	OQMF	8-Hydroxyquinoline (4.7 gm)	1*	10

Table VII- T-2

Analysis, formula, etc. of resins

NO.	Resin	Colour	Formula	Analysis					
				Require			Found		
				% C	% H	% N	% C	% H	% N
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
1.	SAMF	Pink	$(C_{20}H_{38}N_{12}O_{13})_n$	36.7	5.8	25.6	37.01	5.49	25.17
2.	SSAMF	White	$(C_{19}H_{32}N_{12}O_{13}S)_n$	34.1	4.8	25.2	34.30	5.09	25.89
3.	RAMF	Red	$(C_{15}H_{18}N_{6}O_{7})_n$	45.7	4.5	21.2	45.30	4.85	21.81

Table VII- T-2 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
4.	NAMF	Pink	$(C_{20}H_{32}N_{12}O_{9})_n$	41.1	5.5	28.7	41.52	4.99	27.81
5.	ASAMF	Red	$(C_{19}H_{31}O_{8}N_{13})_n$	40.1	5.4	31.9	41.13	5.34	31.70
6.	RMF	Red	$(C_{23}H_{28}N_{6}O_{9})_n$	52.1	5.3	15.9	52.14	5.61	16.13
7.	CMF	Black	$(C_{22}H_{30}N_{6}O_{10})_n$	48.8	5.5	15.5	48.39	5.37	15.02

Table VII- T-2 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
8.	QMF	Black	$(C_{19}H_{28}N_6O_9)_n$	47.1	5.7	17.3	47.52	5.06	18.90
9.	GMF	Pink	$(C_{13}H_{19}N_6O_7)_n$	42.1	5.1	22.7	41.64	4.82	22.80
10.	SMF	Yellow	$(C_{11}H_{16}N_6O_4)_n$	44.6	5.4	28.3	44.07	5.79	27.70
11.	OQMF	Yellow	$(C_{14}H_{18}N_7O_{3.5})_n$	49.4	5.3	28.8	49.26	4.93	28.50

Table VII- T-3

% Moisture and Ion-exchange capacity of resins

NO.	Resin	% Moisture		Total capacity (meq/gm)	
		Resin in H-form	Resin in OH-form	CEC	AEC
1.	2.	3.	4.	5.	6.
1.	SAMF	12.0	14.3	3.20	5.10
2.	SSAMF	13.3	15.3	3.34	4.26
3.	RAMF	19.2	15.5	3.81	3.97
4.	NAMF	12.7	10.0	2.59	3.95

Table VII T-3 (cont.)

1.	2.	3.	4.	5.	6.
5.	ASAMF	15.6	11.4	2.42	5.76
6.	RMF	23.0	15.0	4.22	3.01
7.	CMF	20.5	15.0	4.45	2.94
8.	QMF	15.8	11.9	4.24	2.77

Table VII- T-3 (cont.)

1.	2.	3.	4.	5.	6.
9.	GMF	20.3	15.1	3.51	4.38
10.	SMF	15.8	16.1	3.54	4.40
11.	OQMF	15.6	11.5	2.81	5.80

Table VII- T-4

pH Titration

NO.	Resin	meq alkali taken/gm. dry resin	Equilibrium pH	Cation exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAMF	0.00	7.0	0.00
		1.43	9.6	0.74
		2.98	10.8	1.52
		15.30	11.6	3.20
2.	SSAMF	0.00	6.0	0.00
		3.64	10.5	2.16
		5.04	11.6	2.54
		12.90	12.2	2.75

Table VII- T-4 (cont.)

1.	2.	3.	4.	5.
3.	RAMF	0.00	5.8	0.00
		1.39	9.2	1.26
		3.03	10.9	1.90
4.	NAMF	0.00	5.5	0.00
		1.28	10.0	1.04
		2.33	10.8	1.35

Table VII-T-4 (cont.)

1.	2.	3.	4.	5.
5.	ASAMF	0.00	5.4	0.00
		1.22	10.4	0.85
		2.36	10.8	1.24
6.	RMF	0.00	6.0	0.00
		1.06	9.8	0.99
		2.65	11.0	1.83
		5.32	11.8	2.60
		15.02	12.4	3.76

Table VII- T-4 (cont.)

1.	2.	3.	4.	5.
7.	CMF	0.00	5.5	0.00
		1.25	9.6	1.13
		2.36	10.5	1.81
8.	QMF	0.00	5.2	0.00
		1.40	9.6	1.20
		2.03	10.3	1.46

Table VII- T-4 (cont.)

1.	2.	3.	4.	5.
9.	GMF	0.00	5.4	0.00
		1.65	8.0	1.35
		2.60	9.6	2.12
10.	OQMF	0.00	6.0	0.00
		1.20	11.0	0.97
		2.38	11.7	1.61
		4.77	12.2	1.91
		7.20	12.8	2.20

Table VII- T-5

pH Titration

NO.	Resin	meq acid taken/gm. dry resin	Equilibrium pH	Anion exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAMF	0.00	6.8	0.00
		1.29	4.0	1.12
		2.76	2.6	2.53
		5.65	1.8	3.58
2.	SSAMF	0.00	6.2	0.00
		1.44	4.0	1.33
		2.95	2.8	2.52
		5.93	1.6	3.72
		17.61	1.0	4.20

Table VII- T-5 (cont.)

1.	2.	3.	4.	5.
3.	RAMF	0.00	5.6	0.00
		1.38	2.6	1.29
		2.68	1.6	2.31
4.	NAMF	0.00	5.8	0.00
		1.33	2.4	1.24
		2.66	1.4	2.12
5.	ASAMF	0.00	5.8	0.00
		1.38	2.8	1.29
		3.40	1.4	2.84

Table VII- T-5 (cont.)

1.	2.	3.	4.	5.
6.	RMF	0.00	5.8	0.00
		1.56	3.0	1.56
		2.58	2.1	2.09
		4.66	1.4	2.49
		7.81	1.2	2.57
7.	CMF	0.00	5.6	0.00
		1.36	2.5	1.27
		2.81	1.5	2.24

Table VII- T-5 (cont.)

1.	2.	3.	4.	5.
8.	QMF	0.00	5.4	0.00
		1.22	2.7	1.14
		2.33	1.6	1.95
9.	GMF	0.00	5.5	0.00
		1.69	2.9	1.57
		3.40	1.6	2.70
10.	OQMF	0.00	5.8	0.00
		1.06	3.2	0.99
		2.80	2.4	2.41
		4.23	1.7	3.41
		7.09	1.3	4.19
		11.56	1.0	4.66

Table VII- T-6
Rate studies

NO.	Resin	Time (in hours)	Cation Exchange capacity realised (meq/gm.)	Anion Exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAMF	1/6	0.32	0.51
		1	1.12	1.27
		2	1.28	1.78
		24	3.20	5.10
2.	SSAMF	1	2.84	3.00
		2	3.15	3.45
		24	3.34	4.26

Table VII- T-6 (cont.)

1.	2.	3.	4.	5.
3.	RAMF	1/6	0.83	2.07
		1	1.30	2.61
		2	2.04	2.95
		24	3.81	3.97
4.	NAMF	1/6	0.51	0.63
		1	0.99	1.48
		2	1.53	–
		24	2.59	3.95
5.	ASAMF	1/6	0.72	1.14
		1	1.46	2.30
		24	2.42	5.76

Table VII- T-6 (cont.)

1.	2.	3.	4.	5.
6.	RMF	1	1.77	2.33
		2	2.30	2.72
		24	4.22	3.31
7.	CMF	1/6	1.20	2.13
		1	1.71	2.50
		2	2.65	2.71
		24	4.45	2.94
8.	QMF	1/6	1.55	2.01
		1	1.79	2.29
		2	2.64	2.52
		24	4.24	2.77

Table VII- T-6 (cont.)

1.	2.	3.	4.	5.
9.	GMF	1/6	2.47	3.31
		1	2.87	3.73
		2	3.11	–
		24	3.51	4.38
10.	OQMF	1	1.29	2.01
		2	1.54	2.82
		5	–	3.33
		24	2.81	5.80

Table VII T-7

Copper Exchange Capacity

NO.	Resin	Exchange capacity (copper ion) (in meq/gm.)
1.	SAMF	1.12
2.	SSAMF	1.20
3.	RAMF	1.49
4.	NAMF	1.26
5.	ASAMF	1.07
6.	RMF	1.75
7.	CMF	1.33
8.	QMF	1.45
9.	GMF	1.76
10.	SMF	1.07
11.	OQMF	1.73

Table VII- T-8

Flask NO.	ml. of water	ml. of 0.05N Cu(II) in 5% sodium acetate solution.
1.	95	5
2.	90	10
3.	80	20
4.	70	30
5.	50	50

Table VII. T-9

Copper Titration

NO.	Resin	meq copper(II) taken/gm of dry resin	Exchange capacity realised (copper ion) (in meq/gm)
1.	2.	3.	4.
1.	RAMF	0.79	0.55
		2.19	1.05
2.	NAMF	0.93	0.74
		2.70	1.05
		5.80	1.24

Table VII- T-9 (cont.)

1.	2.	3.	4.
3.	RMF	0.46	0.41
		0.92	0.78
		1.52	1.14
		2.62	1.45
		4.11	1.68
4.	CMF	0.95	0.57
		2.44	0.90
5.	GMF	1.07	0.90
		3.08	1.61
		5.02	1.64

Table VII- T-10(a).

Amounts of reactants used, periods of gelation and curing..

Formaldehyde (37%) = 30 ml.
Urea = 6.0 gm.

NO. 1.	Resin 2.	Phenol derivative (amount in gm$\overset{\text{or}}{/}$ml.) 3.	Gelling period (in hours) 4.	Curing period (in hours) 5.
1.	SAUF	Salicylic acid (4.6 gm.)	6	12
2.	QUF	Hydroquinone (4.0 gm.)	1/2	10
3.	CUF	Catechol (4.0 gm.)	1	10
4.	RUF	Resorcinol (3.7 gm.)	10	12
5.	SUF	Salicylaldehyde (7.0 ml.)	6	12

Table VII T-10(b).

Amount of reactants used, periods of gelation and curing.

Formaldehyde (37%) = 30 ml.

Thiourea = 7.5 gm.

1.	2.	3.	4.	5.
6.	RTF	Resorcinol (3.7 gm.)	9	10
7.	CTF	Catechol (3.7 gm.)	9	12
8.	QTF	Hydroquinone (3.7 gm.)	9	12
9.	STF	Salicylaldehyde (7.0 ml.)	6	10
10.	OQTF	8-Hydroxyquinoline (4.7 gm.)	8	10

Table VII- T-11

Analysis, formula, etc. of resins

NO.	Resin	Colour	Formula	Analysis					
				Required			Found		
				%C	%H	%N	%C	%H	%N
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
1.	SAUF	Pink	$(C_9H_{12}N_2O_5)_n$	47.0	5.2	12.2	45.44	5.42	13.29
2.	QUF	Black	$(C_{18}H_{28}N_2O_{11})_n$	48.0	6.2	6.2	48.66	5.11	6.45
3.	CUF	Black	$(C_{11}H_{16}N_2O_6)_n$	48.8	6.6	10.4	49.56	5.46	9.90
4.	RUF	Pink	$(C_9H_{14}N_2O_5)_n$	46.9	6.0	12.2	46.80	5.67	13.04
5.	SUF	Red	$(C_{19}H_{22}N_2O_8)_n$	55.5	5.8	6.8	56.08	5.65	6.80

Table VII- T-11 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
6.	OQTF	Pink	$(C_{23}H_{32}N_4O_9S)_n$	51.1	5.9	10.4	52.0	4.60	10.45
7.	RTF	Pink	$(C_{20}H_{34}N_2O_{13}S)_n$	44.4	6.3	5.2	43.10	5.05	5.05
8.	QTF	Brown	$(C_{24}H_{32}N_2O_{11}S)_n$	51.8	5.7	5.0	50.53	5.14	4.84
9.	CTF	Black	$(C_{24}H_{32}N_2O_{11}S)_n$	51.8	5.7	5.0	49.95	4.98	4.22
10.	STF	Yellow	$(C_9H_{11}N_2O_{2.5}S)_n$	49.1	5.0	12.7	49.50	5.41	12.98

Table VII- T-12.

% Moisture and Ion-exchange capacity of resin

NO.	Resin	% Moisture		Total capacity (meq/gm)	
		Resin in H-form	Resin in OH-form	CEC	AEC
1.	2.	3.	4.	5.	6.
1.	SAUF	13.1	12.1	3.90	2.88
2.	QUF	13.9	14.3	4.32	1.45
3.	CUF	13.8	12.1	4.25	1.24
4.	RUF	14.8	11.0	3.39	1.86

Table VII- T-12 (cont.)

1.	2.	3.	4.	5.	6.
5.	SUF	14.8	13.2	4.50	1.95
6.	CTF	16.8		2.80	
7.	RTF	11.0	12.2	2.84	1.70
8.	QTF	18.6		2.70	

Table VII- T-13 (a)

pH Titration

NO.	Resin	meq alkali taken/gm. dry resin	Equilibrium pH	Cation exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAUF	0.00	5.2	0.00
		8.52	12.2	3.06
		17.41	12.5	3.50
		26.23	12.7	3.70
		34.19	12.8	3.82
2.	QUF	0.00	5.0	0.00
		0.97	8.9	0.88
		2.74	10.0	2.11

Table VII- T-13 (a) (cont.)

1.	2.	3.	4.	5.
3.	CUF	0.00	5.1	0.00
		1.14	9.0	0.94
		2.78	10.2	2.20
4.	RUF	0.00	4.8	0.00
		1.30	9.2	1.20
		2.99	11.0	1.91
		5.65	11.8	2.22

Table VII- T-13 (a) (cont.)

1.	2.	3.	4.	5.
5.	SUF	0.00	5.6	0.00
		1.31	8.5	1.19
		2.86	10.6	2.19
		5.07	11.5	3.02
		7.80	11.8	3.82
6.	RTF	0.00	4.8	0.00
		1.30	10.4	1.06
		2.00	11.1	1.46
		4.63	11.6	2.03
		6.28	12.2	2.23
		11.77	12.4	2.45

Table VII- T-13 (b)

NO.	Resin	meq acid taken/gm. dry resin	Equilibrium pH	Anion exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAUF	0.00	5.3	0.00
		1.48	2.8	1.37
		2.78	1.8	1.84
		5.74	1.4	2.10
		8.58	1.0	2.18
2.	QUF	0.00	5.2	0.00
		1.51	1.4	1.00
		2.88	0.9	2.10

Table VII- T-13 (b) (cont.)

1.	2.	3.	4.	5.
3.	CUF	0.00	5.1	0.00
		1.70	1.2	1.12
		3.22	0.8	2.32
4.	RUF	0.00	5.0	0.00
		1.38	1.8	1.18
		2.80	1.0	1.76

Table VII- T-13 (b) (cont.)

1.	2.	3.	4.	5.
5.	SUF	0.00	5.4	0.00
		1.43	1.9	1.24
		2.77	1.0	1.84
6.	RTF	0.00	4.9	0.00
		1.32	1.6	1.10
		2.78	1.0	1.72

Table VII- T-14.

Rate studies

NO.	Resin	Time (in hours)	Cation exchange capacity realised (meq/gm.)	Anion exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	SAUF	1	3.54	2.62
		2	3.84	2.78
		5	3.91	2.88
		24	3.91	2.88
2.	QUF	1/6	1.20	1.44
		1	2.67	1.63
		2	3.04	1.63
		24	4.32	1.63

Table VII- T-14 (cont.)

1.	2.	3.	4.	5.
3.	CUF	1/6	1.10	1.12
		1	2.56	1.40
		2	2.98	1.40
		24	4.25	1.40
4.	RUF	1	2.37	1.20
		2	2.59	1.89
		5	2.80	1.89
		24	3.39	1.89

Table VII- T-14 (cont.)

1.	2.	3.	4.	5.
5.	SUF	1/6	[illegible]	1.26
		1	2.54	1.95
		2	2.90	1.95
		5	3.48	1.95
		24	4.50	1.95
6.	RTF	1	2.44	1.18
		2	2.59	1.82
		5	2.84	1.82
		24	2.84	1.82

Table VII- T-15.

Copper exchange capacity

NO.	Resin	Exchange capacity (copper ion) (in meq/gm.)
1.	SAUF	1.51
2.	QUF	2.68
3.	CUF	2.54
4.	RUF	2.20
5.	SUF	0.85
6.	CTF	0.58
7.	RTF	1.80
8.	QTF	0.85

Table VII- T-16.

Amounts of reactants used, periods of gelation and curing.

Formaldehyde (37%) = 30 ml.
Amino-pyridine = 3.2 gm.

NO.	Resin	Phenol derivative (in gms.)	Gelling period (in hours)	Curing period (in hours)
1.	2.	3.	4.	5.
1.	SAAPF	Salicylic acid (4.6 gm.)	20	20
2.	QAPF	Hydroquinone (3.7 gm.)	13	15
3.	CAPF	Catechol (3.7 gm.)	18	15

Table VII- T-16 (cont.)

Amounts of reactants used, periods of gelation and curing.

Formaldehyde = 30 ml.

p-Phenylene diamine == 3.6 gm.

1.	2.	3.	4.	5.
1.	QPPF	Hydroquinone (3.7 gm.)	12	20
2.	CPPF	Catechol (3.7 gm.)	12	20

Table VII- T-17

Analysis, formula, etc. of resins.

NO.	Resin	Colour	Formula	Analysis					
				Required			Found		
				% C	% H	% N	% C	% H	% N
1.	SAAPF	Pink	$(C_{25}H_{26}N_2O_{10})_n$	58.8	5.1	5.5	59.89	5.33	5.85
2.	QAPF	Black	$(C_{20}H_{24}N_2O_7)_n$	60.0	6.0	7.0	59.20	5.22	7.01
3.	CAPF	Black	$(C_{23}H_{27}N_2O_{8.5})_n$	58.7	5.7	5.9	56.72	5.39	5.84
4.	QPPF	Black	$(C_{28}H_{33}N_2O_{9.5})_n$	61.1	6.0	5.1	60.17	6.09	5.38
5.	CPPF	Black	$(C_{28}H_{33}N_2O_{7.5})_n$	61.1	6.0	5.1	60.77	5.96	4.94

Table VII- T-18

% Moisture and Ion-exchange capacity of resin.

NO.	Resin	% Moisture		Total capacity (meq/gm)	
		Resin in H-form	Resin in OH-form	CEC	AEC
1.	2.	3.	4.	5.	6.
1.	SAAPF	13.9	-	4.68	-
2.	QAPF	11.8	4	4.47	-

Table VII- T-18(cont.)

1.	2.	3.	4.	5.	6.
3.	CAPF	12.2	-	4.22	-
4.	QPPF	15.4	12.7	4.70	3.42
5.	CPPF	11.0	10.8	4.97	3.02

Table VII- T-19 (a)

pH Titration

NO.	Resin	Meq alkali taken/gm dry resin	Equilibrium pH	Cation exchange capacity realised (meq/gm.)
1.	2.	3.	4.	5.
1.	QPPF	0.00	5.8	0.00
		1.18	9.4	1.22
		2.40	10.6	2.23
		4.48	11.6	3.18
2.	CPPF	0.00	6.0	0.00
		1.12	9.6	1.18
		2.47	10.9	2.36
		5.02	11.8	3.24
		7.56	12.0	4.62

Table VII- T-19 (b)

NO.	Resin	meq acid taken/gm. dry resin	Equilibrium pH	Anion exchange capacity realised (meq/gm.)
1.	QPPF	0.00	5.6	0.00
		1.28	2.8	1.18
		2.36	1.6	1.98
2.	CPPF	0.00	5.8	0.00
		1.42	2.4	1.29
		2.92	1.4	2.28

Table VII- T-20

Rate studies

NO.	Resin	Time (in hours)	Cation Exchange capacity (meq/gm.)	Anion Exchange capacity (meq/gm.)
1.	2.	3.	4.	5.
1.	QPPF	1/6	0.96	-
		1	2.70	2.08
		2	2.84	2.80
		5	3.65	3.02
		24	4.70	3.42
2.	CPPF	1/6	1.12	-
		1	2.83	2.70
		2	2.90	2.85
		5	3.71	3.02
		24	4.97	3.02

Table VII- T-21

Exchange capacity (Copper ion)

NO. 1.	Resin 2.	Exchange capacity (Copper ion) (in meq/gm.) 3.
1.	QPPF	1.52
2.	CPPF	1.63

Table VII- T-22

Copper Titration

NO.	Resin	Meq copper(II) taken/gm of dry resin	Exchange capacity realised (copper ion) (in meq/gm.)
1.	QUF	0.40	0.36
		1.03	0.72
		1.78	0.97
		2.78	1.12
		4.78	1.26
2.	CPPF	0.41	0.37
		0.76	0.64
		1.76	1.18
		2.47	1.30
		4.32	1.61

CHELATING POLYMERS

B : CROSSED-LINKED POLYMERIC NETWORKS AS ION-EXCHANGE RESINS

VIII DISCUSSION

CHELATING POLYMERS

B : CROSSED-LINKED POLYMERIC NETWORKS AS ION-EXCHANGE RESINS

VIII DISCUSSION

VIII (a) General :

Phenolics would be formed by the polycondensation of the phenol derivative with formaldehyde[31] and aminoplasts by the polycondensation of amine or amide derivative with formaldehyde[32]. Phenolic resins have been used as cation exchange resins. In recent years, attempts have been made to obtain resins by the polycondensation of phenol derivative (chelating agent) with formaldehyde. Salicylic acid-formaldehyde condensation resins have been reported by Topp[33], De Geiso et. al[34], Komiya et. al[35], Rabeck et. al[36], Davies et. al[37], etc. Anthranilic acid-formaldehyde condensation resin has been studied by Gregor[38] and gallic acid-formaldehyde resin by Hojo[39]. Resins from naphthoquinone/anthraquinone derivatives and formaldehyde have been studied by Soloway[40], Manecke[41], Izoret[42], etc.

Amphoteric resins from phenol derivatives, melamine and formaldehyde have been studied by Trivedi and Krishnaswamy[28]. We have prepared ion exchange resins exhibiting amphoteric nature using different chelating (complexing) phenol derivatives and different amines/amides. The phenol derivatives used possess the following structural characteristics :

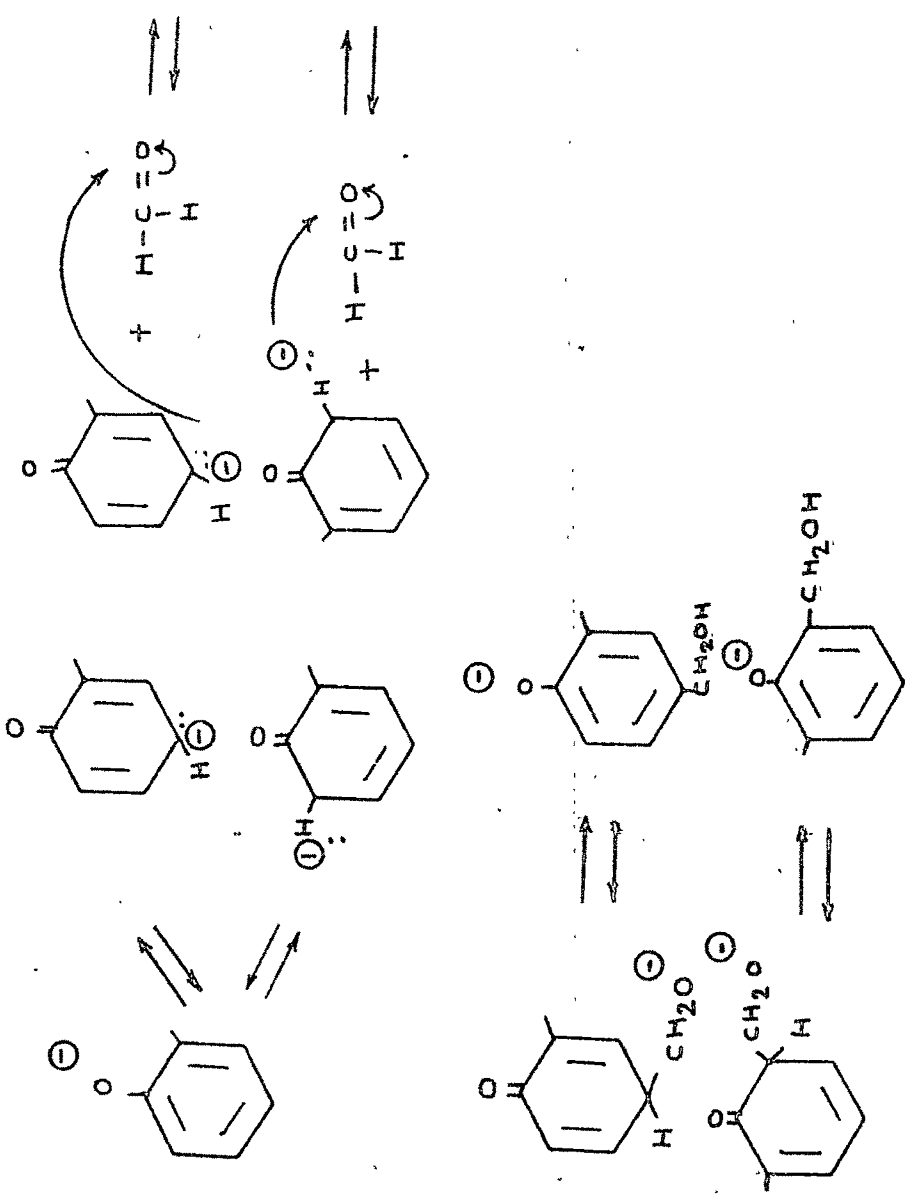
(i) two phenolic groups in ortho, meta or para positions on a phenyl ring, (ii) three phenolic groups on a phenyl ring, (iii) one phenolic group and one carboxy (CO) group in ortho position on phenyl ring, (iv) one phenol group and one ring nitrogen. The amine/amide derivatives used were di and tri amine/amide.

The mechanism of condensation of phenolate and formaldehyde can be represented as (i) base-catalysed hydroxy methylation of phenol derivative with formaldehyde (VIII- E-1) and (ii) polymerisation to cross-linked resin by ring-alkylation reaction through hydroxy methyl groups (VIII- E-2)[43].

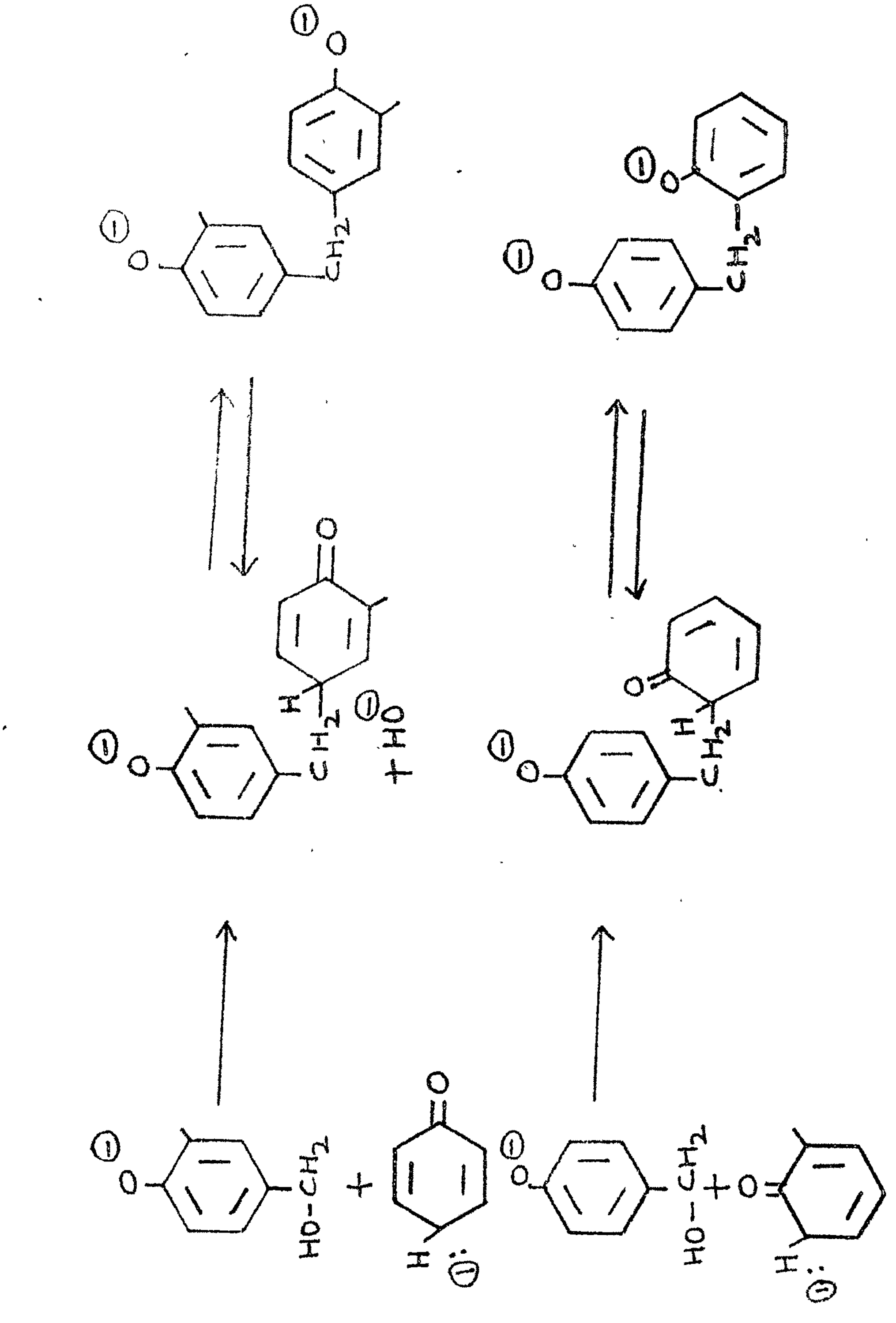
VIII (b) Chelating polymers (phenol-melamine series) :

VIII (b-1) Preparation :

Alkaline condensation of phenolate and melamine with formaldehyde yields amphoteric ion exchange polymers (VIII- E-3). Amphoteric ion exchange resin which may be termed "zwitter-ion resin" would behave like an amphoteric



VIII−E−1



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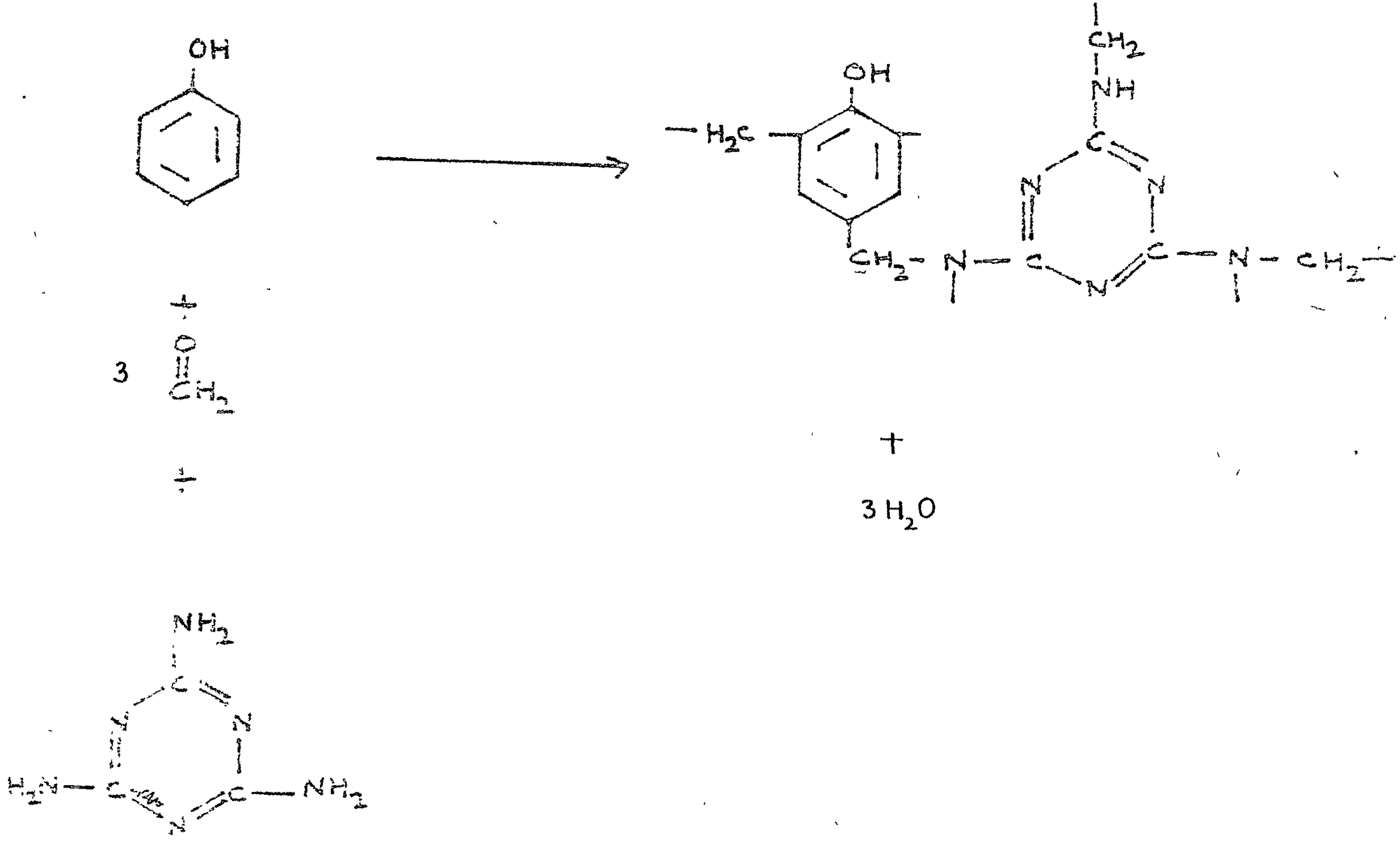


VIII - E - 5

substance. It would exhibit titration curves similar to those of amino acids and proteins and hence would be of potential interest as model compound for the study of the behaviour of proteins and wool[44]. Harwood and Cassidy[45] studied hydroquinone-polypeptide resin. Recently, amino group, sulphonic acid group and dihydroxy (or trihydroxy) benzene are introduced into methylene styrene-divinyl benzene matrix and the product is studied for its amphoteric nature[46]. And carboxylic acid resin is condensed with optically active amino acid to obtain optically active resin[47].

The formation of the resin is characterised by the gel point. Gel point or gel period is related to the branching ability and hence to the functionality of the monomers involved in condensation[48]. Linear chains would be obtained if condensing monomers exhibit functionality of two. If the condensing monomers exhibit the functionality greater than two, branching may be obtained and gelation will take place. Greater the functionality (f) exhibited by the monomers, shorter can be the period of gelation. In the phenol-melamine series under investigation, the observed gelation period in increasing order for the resins is

SAMF < NAMF < RAMF < SSAMF < ASAMF
RMF < CMF < QMF < GMF < RAMF
CMF < OQMF SAMF < SMF (VIII- E-4).

We suggest that (i) blocking an active site by introducing a substituent in salicylic acid molecule reduces the functionality and hence increases the gelation period, (ii) in dihydroxy benzenes, the position (o, m or p) of the groups has not a very marked influence on the gelation period, (iii) introduction of a third group (OH or CO_2H) in dihydroxy benzene increases gelation period, (iv) ring nitrogen has an effect comparable to second hydroxy group on phenol on gelation and (v) substitution of carboxylic group by aldehydo group increases considerably the gelation period.

Curing involves the thermosetting of the gel. It is observed that curing period is shorter for dihydroxy benzenes and their derivatives and longer for salicylaldehyde. Thus

CMF $<$ SAMF $<$ SMF (VIII- E-5).

VIII (b-2) General properties and structures :

These resins do not melt and are found to be insoluble in water and various organic solvents. They are fairly stable to the action of 3N hydrochloric acid and 3N sodium hydroxide.

On the basis of their analysis (%C, %H and %N) and their behaviour, the most probable structures of these resins are shown as (i) SAMF (VIII- S-1), (ii) SSAMF (VIII-S-2), (iii) RAMF (VIII- S-3), (iv) NAMF (VIII- S-4), (v)

(v) ASAMF (VIII- S-5), (vi) RMF (VIII- S-6), (vii) CMF (VIII- S-7), (viii) QMF (VIII- S-8), (ix) GMF (VIII- S-9), (x) SMF (VIII- S-10) and (xi) OQMF (VIII- S-11).

Trivedi and Krishnaswamy[28] obtained resin from salicylic acid, melamine and formaldehyde containing 25.8% N and seems to have the same structure and nature as our product.

The study of these structures leads us to some generalisations : (i) salicylic acid and its derivatives condense with melamine in the molar ratio of 1:2, (ii) dihydroxy benzenes condense with melamine in the molar ratio of 2:1, (iii) dihydroxybenzene with a substituent condense with melamine in the molar ratio of 1:1, (iv) salicylaldehyde and 8-hydroxyquinoline condense with melamine in the molar ratio of 1:1 and products seem to have similar linear polymeric structures and (v) sulphonic, carboxylic and aldehyde groups are considered to have condensed with amino group of melamine forming sulphonamide, amide and schiff base respectively. Ion exchange studies support this consideration.

VIII (b-3) Percentage moisture :

Percentage moisture of the resins in H-form varies between 12 and 23. Known values[49] of percentage moisture for commercial resins in H-form are 45.0 for Zeocarb 225, 38.0 for Tulsion 14 and 5.4 for Duolite E S 63. Thus the resins under study have intermediate range of percentage moisture. Percentage moisture of the resins in OH-form varies between 10 and 16. Difference in values for the resins in H- and OH- forms is small and hence the resins can stand recycling to a good degree.

VIII (b-4) <u>Exchange capacity</u> :

Cation exchangers containing free sulphonic acid group are strong and those containing carboxylic or phenolic groups are weak. As suggested in the structural formulations and as observed in later investigations, the cation exchange capacity of these resins cannot be related to free sulphonic or carboxylic acid groups. Hence cation exchange capacity is to be related to the phenolic groups. If we write the cation exchange capacity of the resin as

$$CEC_{cal} = \frac{1000}{M/n} \qquad \text{(VIII- E-6)}$$

where M and n are the "mer weight" on dry basis and number of phenolic groups per unit, the observed capacity (CEC_{ob}) can be compared with the calculated capacity (CEC_{cal}) as presented in Table VIII- T-1. Three ranges exist : (i) value of CEC_{ob}/CEC_{cal} is close to 1, (ii) value of CEC_{ob}/CEC_{cal} is close to 1/2; and (iii) value of CEC_{ob}/CEC_{cal} is close to 3/2. Low values ($\sim$ 1/2) of the ratio are observed in case of polyhydroxy benzenes. If it is suggested that only one phenolic group in such compounds is involved in ion exchange, the ratio will turn out to be close to one. In the case of some acid derivatives, the value of the ratio is high (~3/2) and may be attributed to the contribution of weakly acidic amide group in such cases.

VIII (b-5) pH Titration :

The observations of pH titration for all the resins are studied graphically. Plots (not presented) of pH versus meq. of alkali taken/gm. of dry resin indicate that they show similar very weakly acidic groups. Similarly plots (not presented) of pH versus meq. of acid taken/gm. of dry resins indicate that they all show weak base nature.

(i) Apparent pK_C and pK_A of the resins :

Plots of cation (or anion) exchange versus pH of the solution at equilibrium are presented in figures VIII- F-1. From these plots pK_C and pK_A values of the resins are calculated as follows :

pK value of an acid group RH is defined as the negative logaritham of the equilibrium constant K of the dissociation equilibrium

$$RH \rightleftharpoons R^- + H^+ \qquad \text{(VIII- E-7)}$$

$$K = [R^-][H^+]/[RH], \; pK = -\log K \qquad \text{(VIII- E-8)}.$$

The degree of dissociation (α) and pH of resin are defined as

$$\alpha = \frac{[R^-]}{[R^-]+[RH]} \qquad \text{(VIII- E-9)}$$

$$pH_r = -\log[H^+] \qquad \text{(VIII- E-10).}$$

Hence, $pH_r = pK - \log (1-\alpha)/\alpha$ (VIII- E-11).

When $\alpha = 0.5$, it corresponds to 50% conversion of the resin from H form to Na form and (apparent) pK of the group is

$$pK = pH_r \qquad \text{(VIII- E-12)}$$

pH in the resin is now to be related to pH in the solution. As a first approximation, it can be assumed that the ratio $[Na^+]/[H^+]$ is the same in the ion exchanger$_{(r)}$ and in the aqueous phase$_{(s)}$. Hence $[Na^+]_s/[H^+]_s = [Na^+]_r/[H^+]_r$ (VIII- E-13)

i.e. $[H^+]_r = [Na^+]_r\,[H^+]_s \,/\, [Na^+]_s$ (VIII- E-13a).

At 50% conversion,

$$[Na^+]_r = \frac{[R^-] + [RH]}{2} \qquad \text{(VIII- E-14).}$$

Hence $pK = pH + \log(Na^+)_s - \log\frac{[R^-]+[RH]}{2}$ (VIII- E-15) .

If E represents exchange capacity in meq./gm. and Z represents water content (%) of half-converted resin, the total concentration of ionogenic groups $[RH] + [R^-]$ at half conversion is $E(100-Z)/Z$ meq/gm. water.

The acid dissociation of the amphoteric resin in cation exchange process can be represented as

$$H^+R^- \rightleftharpoons H^+ + R^- \qquad \text{(VIII- E-16).}$$

And acid dissociation constant in cation exchange (K_C) as

$$K_C = [H^+][R^-]/[H^+R^-] \qquad \text{(VIII- E-17).}$$

Since K_C corresponds to acid ionisation in cation exchange, pK_C can be calculated from pH titration involving cation exchange using (VIII- E-15).

Acid dissociation of the amphoteric resin in anion exchange can be represented as

$$H^+RH \rightleftharpoons H^+R^- + H^+ \qquad \text{(VIII- E-18)}$$

and acid dissociation constant in anion exchange (K_A) as

$$K_A = [H^+R^-]\ [H^-]/[H^+RH] \qquad \text{(VIII- E-19).}$$

Now it can be shown that for a weak base

when $\alpha = 0.5$

$$pK_A = pH - \log[Cl^-]_s + \log\frac{[H^+RH] + [RH]}{2} \qquad \text{(VIII- E-20)}$$

Since K_A corresponds to anion exchange, pK_A can be calculated from pH titration involving anion exchange, using (VIII- E-20).

Values of pK_C and pK_A calculated by above relations are presented in Table VIII- T-2. The values are in decreasing order as

for pK_C : SAMF > ASAMF > RAMF > NAMF > SSAMF

RMF > CMF > QMF > GMF

OQMF > RMF (VIII- E-21)

for pK_A : SSAMF > SAMF > RAMF > ASAMF > NAMF
RMF > GMF > QMF > CMF
OQMF > RMF (VIII- E-22).

(ii) Isoionic point :

Isoelectric point is defined as that pH at which net positive and negative charge on a particle or on a surface is zero and there is no motion in an electric field. On the other hand, isoionic point is defined as that pH at which number of positive and negative groups which arise exclusively from proton exchange are equal to each other. It is evident that the isoelectric and isoionic points are identical only if zwitter ion combines with no other than H- ions.

Isoionic point of a simple zwitter ion can be calculated as follows :

If ^{+}A, $^{+}A^{-}$ and A^{-} represent cation, zwitter ion and anion respectively of the simple ampholyte (such as glycine), we write the ionisation equations as :

$$^{+}A \rightleftharpoons {}^{+}A^{-} + H^{+} \qquad \text{(VIII- E-23)}$$

$$^{+}A^{-} \rightleftharpoons A^{-} + H^{+} \qquad \text{(VIII- E-24)}$$

Acid dissociation constants (K_1, K_2) for these two ionisations are

$$K_1 = [H^{+}][^{+}A^{-}]/[^{+}A] \qquad \text{(VIII- E-25)}$$

$$K_2 = [H^{+}][A^{-}]/[^{+}A] \qquad \text{(VIII- E-26)}$$

Combining the two equations to eliminate $(^{+}A^{-})$, we have

$$[H^{+}]^{2} = K_1 \ K_2 [^{+}A]/[A^{-}] \qquad \text{(VIII- E-27)}$$

At isoionic point, $[^{+}A] = [A^{-}]$. Hence at isoionic point

$$(H^{+}) = \sqrt{K_1 \ K_2} \qquad \text{(VIII- E-28)}$$

or,

$$pH_1 = \frac{1}{2} (pK_1 + pK_2) \qquad \text{(VIII- E-29)}$$

where pH_1 represents pH at isoionic point.

Isoionic point for glycine is 5.97 ($pK_1 = 2.34$, $pK_2 = 9.60$)

Using equations (VIII- E-15), (VIII- E-17), (VIII- E-19) and (VIII- E-20), we write for isoionic point(IP)

$$IP = \frac{1}{2} (pK_C + pK_A) \qquad \text{(VIII- E-30)}$$

The values of isoionic point (IP) calculated for these resins are presented in Table VIII- T-2. The values are increasing in order :

$$\text{RAMF} < \text{ASAMF} < \text{NAMF} < \text{SSAMF} < \text{SAMF}$$
$$\text{GMF} < \text{QMF} < \text{CMF} < \text{RMF} < \text{OQMF} \qquad \text{(VIII- E-31)}$$

(iii) Ion exchange equlibria- adsorption relationships :

Boedeker[50] suggested that we may describe ion exchange by the equation

$$X = Ka^{n} \qquad \text{(VIII- E-32)}$$

where X = quantity exchanged per gm. of resin a = initial concentration

k,n = constants

Krocker[51] suggested the equation

$$\log \frac{a}{c} = km. \qquad \text{(VIII- E-33)}$$

where m = quantity exchanged per gm. of resin

a = initial concentration

c = equilibrium concentration

k = constant

Wiegner and Jenny[52] expressed the relation

$$\frac{X}{M} = k \left(\frac{c}{a-c}\right)^{1/p} \qquad \text{(VIII- E-34)}$$

where $\frac{x}{m}$ = quantity exchanged per gm. of resin

a = initial concentration

c = equilibrium concentration

k, p = constants

Weisz[53] tested these relationships and concluded that none of these relations was sufficiently satisfactory over a wide range of conditions.

Plots corresponding to these equations are presented in figures VIII- F-2, VIII- F-3, VIII- F-4.

It is observed from figure VIII- F-2 that only in case of some resins from dihydroxy benzenes straight line curves are obtained. Hence it can be stated that the curves, in general do not satisfy the relation VIII- E-32.

It is seen from figure VIII- F-3 that curves drawn according to VIII- E-33 are quite abnormal and unsatisfactory.

Similarly it is found from figure VIII- F-4 that curves drawn according to VIII- E-34 are unsatisfactory.

Hence we conclude that adsorption relationships cited above give unsatisfactory results.

(iv) Ion exchange equlibria : mass action relationship :

Ganssen[54] suggested that the equilibrium be represented as

$$\frac{X}{u-x} = K\,\frac{c}{x} \qquad \text{(VIII- E-35)}$$

where U = exchange capacity

X = quantity exchanged per gm. of resin

c = equilibrium concentration

k = constant

Rothmund and Kornfeld[55] modified the relationship as

$$\frac{X}{u-x} = k\left(\frac{c}{x}\right)^{p} \qquad \text{(VIII- E-36)}$$

where p = constant.

However, Kerr[56] may be accredited with the first true analysis of the application of the law of mass action to ion exchange system. He showed that for the equation

$$A_r + B_s \rightleftharpoons A_s + B_r \qquad \text{(VIII- E-37)}$$

where A_r, B_r, A_s, B_s represent A and B monovalent ions in resin phase and solution phase respectively, the equilibrium constant may be expressed by

$$K = [B_r][A_s]/[B_s][A_r] \qquad \text{(VIII- E-38)}$$

$$\text{or} \quad K = \frac{[B_r]/[A_r]}{[B_s]/[A_s]} \qquad \text{(VIII- E-39)}$$

If $(n_A)_r$, $(n_B)_r$, $(n_A)_s$ and $(n_B)_s$ represent the number of moles of A and B in the resin phase and solution phase respectively, the equilibrium constant termed selectivity coefficient **is** written as

$$K_A^B = \frac{(n_B)_r/(n_A)_r}{(n_B)_s/(n_A)_s} \qquad \text{(VIII- E-40)}$$

If Z_A and Z_B represent the equivalent fractions of A and B on the resin phase such that $Z_A + Z_B = 1$, and if S_A AND S_B represent the equivalent fractions of A and B in solution phase such that $S_A + S_B = 1$,

$$K_A^B = \frac{Z_B/(1-Z_B)}{S_B/(1-S_B)} \qquad \text{(VIII- E-41)}$$

Exchange isotherms are obtained by plotting

Z_B versus C_x/C_y (where C_x and C_y represent the equilibrium and initial concentrations respectively of exchangeable sodium ion (or chloride ion) in solution as presented in figure (VIII- F-5). Deviation from the expected nature of the curves can be explained as follows : In the previous derivations it was tacitly implied that the ion exchanger is homogeneous and that all its fixed ionic groups are identical in their behaviour. For monofunctional addition polymers, especially styrene type ion exchangers, this assumption usually holds well. However, it is by no means generally valid.

A characteristic behaviour is observed, say, by polyfunctional ion exchangers, i.e. resins containing different types of ionogenic groups. Each individual group exhibits its characetristics, but different types of groups may well counteract one another. Cornaz and Deuel[57] studied ion exchange isotherms of a bifunctional cation exchanger and of a mixture of cation exchangers (VIII- F-6). They found that the behaviour of a polyfunctional resin is similar to that of a mixture of different monofunctional resins containing, in total, the same amounts of various ionogenic groups. However, there is no quantitative agreement as the environment of the groups may be quite different in the two systems. Even the behaviour of a fixed ionic group depends not only on its chemical structure but also on its environment. Many ion exchange resins, particularly the condensation polymers are inhomogeneous in colloidal dimensions. They consist of "islands" of high cross-linking and fixed charge molality embedded in regions of much lower cross-linking and fixed charge molality. The degree of cross-linking can affect selectivity[58]. Abnormalities would also be observed if the ion exchanger exhibits discontinuous lattice rearrangement and hysteresis[59,60].(VIII F-7). These arguments may also hold good for various adsorption expressions stated earlier. And the earlier controversy as to whether ion exchange obeys mass action law or adsorption isotherm seems beside the point, since there are theoretical relations between the mass action law and adsorption isotherm[61,62].

VIII (b-6) Rate of exchange :

Rate of cation (or anion) exchange of various resins is presented graphically in figure (VIII F-8). From the plots of the fraction of the exchange capacity versus time, we determined time for 50% exchange. The values are presented in table (VIII T-3). The results show that time for half exchange increases in order :

for cation exchange

GMF < SSAMF < ASAMF < QMF < RMF < OQMF < CMF < RAMF < SAMF

for anion exchange

GMF < CMF < QMF < RAMF < SSAMF < RMF < NAMF < ASAMF < SAMF < OQMF (VIII E-42).

Relatively long times for half exchange may be attributed primarily to the weak acid, weak base characters of these ion-exchange resins. The results show that sulphonic acid group is not associated with ion exchange process.

VIII (b-7) Copper exchange :

The exchange capacity of the resins in H-form for copper ion is presented in the table (VII T-7). The capacity values in range of 1.07 to 1.76 (in meq/gm of dry resin).

From the study of the exchange of copper ion for different concentrations of copper ion in solution, plots of copper ion exchange versus copper ion taken are drawn as presented in figure (VIII F-9). The curves confirm the exchange capacity observed separately.

Exchange isotherms are obtained by plotting Z_B versus C_x/C_y (where Z_B represents equivalent fraction of copper ion on the resin phase and C_x and C_y represent the equlibrium and initial concentrations respectively of copper ion in solution) as presented in figure (VIII F-10). The results show that these resins have a selectivity for copper ion and are comparable in their behaviour.

VIII (c) Chelating polymers-(phenol-urea series) and phenol-thiourea series) :

VIII (c-1) Preparation :

We have already reported the condensation of salicylic acid and salicylaldehyde with dimethylol urea. We now report the condensation of phenol derivatives (resorcinol, hydroquinone, pyrocatechol, salicylaldehyde, salicylic acid and 8-hydroxyquinoline) with urea (or thiourea) and formaldehyde under alkaline conditions.

In case of urea series, gel period is increasing in order

QUF < CUF < SAUF < SUF < RUF (VIII E-43),

while in case of thiourea series, gel period is between 6 and 9 hours.

VIII (c-2) General properties and structure :

These resins do not melt and are found insoluble in water and various organic solvents. They are fairly stable to the action of 3N hydrochloric acid and 3N sodium hydroxide.

On the basis of their analysis (%C, %H, %N) and their behaviour, the most probable structures are shown as

(i) SAUF (VIII- S-12), (ii) QUF (VIII- S-13), (iii) CUF (VIII- S-14), (iv) RUF (VIII- S-15), (v) SUF (VIII- S-16), (vi) OQTF (VIII- S-17), (vii) RTF (VIII- S-18), (viii) QTF (VIII- S-19), (ix) CTF (VIII- S-20) and (x) STF (VIII- S-21).

The study of these structures leads us to some generalisations: (i) dihydroxy benzenes condense with urea in the molar ratio of 1:1 or 2:1, and with thiourea in the molar ratio of 3:1 or 2:1, (ii) salicylaldehyde condenses wi with urea in the ratio of 2:1 and with thiourea in the ratio of 1:1.

VIII (c-3) <u>moisture content and exchange capacity</u> :

Moisture content of these resins is comparable to that of the resins of melamine series presented earlier. Difference in the values for the resins in H- and OH- forms is not large.

Cation exchange capacity of the resins increases in the order :

QTF < CTF < RTF < RUF < SAUF < CUF < SUF < QUF

and anion exchange capacity increases in order :

CUF < QUF < RTF < RUF < SUF < SAUF (VIII- E-44).

The results show that cation exchange capacity of thiourea resins is less than that of urea resins.

It indicates that thiourea moiety is not involved in cation exchange process.

VIII (C-4) pH titration :

Results of pH titration are studied graphically. Plots (not presented) of pH versus meq. of alkali (or acid) taken per gm. of dry resin indicate weak acid (or base) nature of the resins. Plots of cation (or anion) exchange versus pH of the solution at equilibrium are presented in figure (VIII F-11). From these plots pK_C and pK_A are calculated as shown in VIII (b-5). Values of pK_C and pK_A are presented in table (VIII T-4).

The values are in increasing order as

for pK_C

RTF < CUF < QUF < SUF < RUF < SAUF

and for pK_A

SUF < RUF < RTF < CUF < QUF < SAUF (VIII E-45).

Isoionic point (IP) for the resins is calculated as shown in VIII (b-5) and presented in table (VIII T-4). The values are increasing in order,

CUF < QUF < SUF < RUF < RTF < SAUF

Exchange isotherms are obtained by plotting Z_B versus C_x/C_y as shown in VIII (b-5) and are presented in figure (VIII F-12). As discussed in VIII (b-5), the abnormalities may be attributed to polyfunctional nature of the resins, their inhomogeneity, selectivity, etc.

VIII (c-5) Rate studies :

Rate of ion exchange of various resins is presented graphically in figure (VIII F-13). From the plots of the fraction of exchange capacity versus time, time for 50% exchange is evaluated and presented in table (VIII T-5). The results show that time for half exchange increases in order

for cation exchange

SAUF < RTF < CUF < RUF < SUF < QUF

FOR anion exchange

CUF < QUF < SUF < SAUF < RTF < RUF (VIII E-46).

Relatively long times for half exchange may be attributed primarily to the weak acid - weak base character of these resins.

VIII (c-6) Copper exchange :

Exchange capacity of these resins in H-form for copper ion is presented in table (VII T-15). In contrast to melamine series, urea (thiourea) series gives varying values of capacity. The exchange capacity is increasing in order

CTF < QTF < SUF < SAUF < RTF < RUF < CUF < QUF

(VIII E-47).

The results show that thiourea resins have a smaller exchange capacity than the urea resins and indicate the absence of interaction of c=s with copper ion.

VIII (d) Chelating polymers (phenol-p-phenylenediamine series) and (phenol-o-aminopyridine series) :

VIII (d-1) preparation :

We considered that other amines be tried for studies. Hence we selected p-phenylenediamine and o-amino pyridine for the purpose. Phenol derivatives used were salicylic acid, catechol and hydraquinone. Condensation products could be obtained after relatively long gel periods.

VIII (d-2) General properties and structure :

These resins do not melt and are found insoluble in water and various organic solvents. However, some of them are soluble in alkali solution. On the basis of their analysis (%C, %H, %N) and their behaviour, the most probable structures are shown as (i) SAAPF (VIII S-22), (ii) QAPF (VIII S-23), (iii) CAPF (VIII S-24), (iv) QPPF (VIII S-25) and (v) CPPF (VIII S-26).

The study of these structures leads us to some generalisations: (i) phenol derivatives condense with o-amino pyridine in the ratio of 2:1 and (ii) phenol derivatives condense with p-phenylenediamine in the ratio of 3:1.

VIII (d-3) Moisture content and exchange capacity :

Moisture content of these resins is comparable to that of the resins presented earlier.

Cation exchange capacity of these resins increase in order

CAPF $<$ QAPF $<$ SAAPF $<$ QPPF $<$ CPPF

Anion exchange capacity of amino pyridine series could not be determined because of the solubility of these resins in concentrated alkali solutions. Anion exchange capacity of QPPF is higher than that of CPPF.

VIII (d-4) pH titration :

Results of pH titration are studied graphically. Plots of cation (or anion) exchange versus pH of the solution at equilibrium are presented in figure (VIII F-14). From these plots, pK_C and pK_A are calculated as shown in VIII (b-5). Values of pK_C and pK_A are presented in table (VIII T-6). The values are higher for CPPF than for QPPF. Isoionic point for these resins is also calculated as shown in VIII (b-5) and presented in table (VIII T-6).

Exchange isotherms are obtained by plotting Z_B versus C_x/C_y as shown in VIII (b-5) and are ~~x~~presented in figure (VIII F-15).

VIII (d-5) Rate studies :

Rate of ion exchange of various resins is presented graphically in figure (VIII-F-6) . From the plots of the fraction of exchange capacity versus time, time for 50% exchange is evaluated and presented in table (VIII-T-7). Relatively long times for half exchange are observed for these resins.

VIII (d-6) Copper exchange :

Exchange capacity of CPPF for copper is found to be 1.8 meq/gm. dry resin.

From the study of the exchange of copper ion for different concentrations of copper ion in solution, plots of copper ion exchange versus copper ion taken are drawn for QUF and CPPF as presented in figure (VIII-F-17) and exchange isotherms are obtained by plotting Z_B versus C_x/C_y as suggested in (VIII-b-7) and presented in figure (VIII-F-18). The results show that CPPF does not have slectivity for copper ion.

VIII (e) General :

VIII (e-1) Ion exchange in soils :

Since soil particles exhibit amphoteric ion exchange behaviour, related studies and considerations on soils are presented here.

The ion exchange property of soil is due almost entirely to the clay and silt fractions and the organic matter. The soil particles carry a net negative charge, arising essentially either by isomorphic ion substitution or by ionisation of hydroxyl groups attached to silicon of broken tetra-hedral planes. In addition, negative charges may also originate from humic, phosphoric and silicic acids, constituting more or less integral part of the clay particle surface.

The amphoteric nature of the clay fraction requires, however, the existence of positive charges. These may arise from hydrous oxides of iron, aluminium and manganese and from the exposed octahedral groups which react as bases by accepting protons from the surrounding soil solution, thus acquiring a positive electric charge. The basic groups of humus are due to nitrogen.

The electric charge and surface charge density are not constant but vary more or less with pH of the solution. The negative charge grows and the positive charge decreases with rising pH as a result of increasing ionisation of acid groups and dreasing proton addition to the basic groups.

The decrease of the net negative charge below pH 6 is supposed to be caused not by an actual decrease of the negative charge itself but by an increase in the positive charge which at a certain pH balances the negative charge and renders the clay particles isoelectric.

The carboxylic groups of the humus ionise in the acid part of the pH scale, and the phenolic hydroxyls mainly above pH 6. The basic groups are weak and since acid properties predominate, humus never becomes isoelectric.

Because of the irregular shape of the clay particles and non-uniform distribution of charges throughout the particles, the surface change density varies not only with the kind of material but also on the same particle.

The capacity of soils to adsorb and exchange cations and anions varies with the content of clay and organic matter and the minerological composition. Generally, CEC of mineral soils is smaller than that of organic soils.

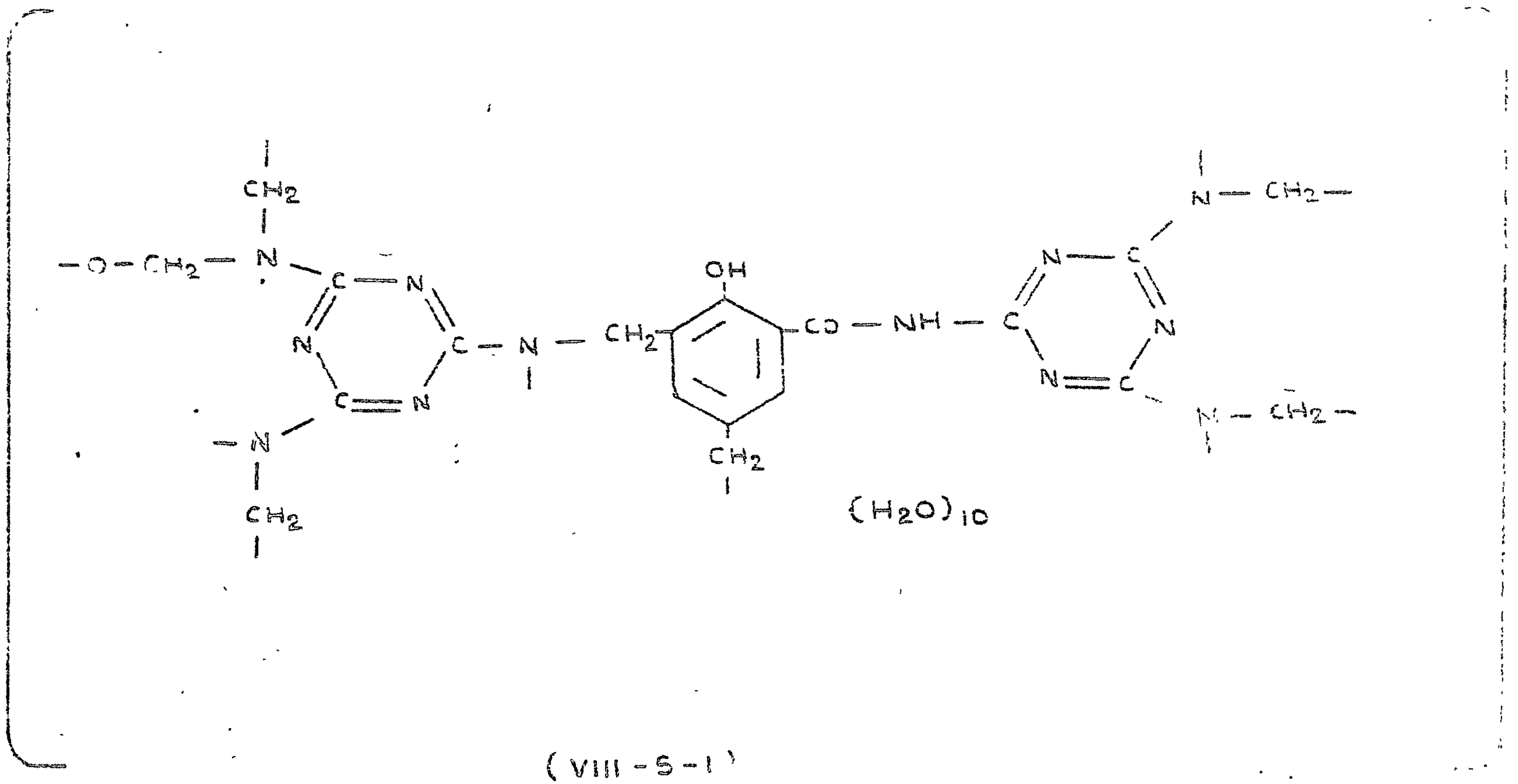
The cation exchange would proceeds just as fast as ions from the solution are supplied to the exchanger surface. A condition for rapid attainment of equilibrium is, of course, that the soil be moist before exchange, as the moistening process may take sometime. But a rapid exchange is feasible only if the exchangeable ions are directly accessible to the ions in solution. If the exchange has to be proceeded by diffusion of ions to the inner surface of the clay particles or the interior of the aggregate with narrow pores, the exchange may require considerably more time. In this connection it should be pointed out that to reach equilibrium in the neutralisation of acid clays, humus and soils with alkali requires much longer time than does ordinary ion exchange, often many hours or even days. Hystereis has also been encountered to varying degree with soils, clay minerals, etc.[63]

VIII (e-2) <u>Kienetics of ion exchange</u> :

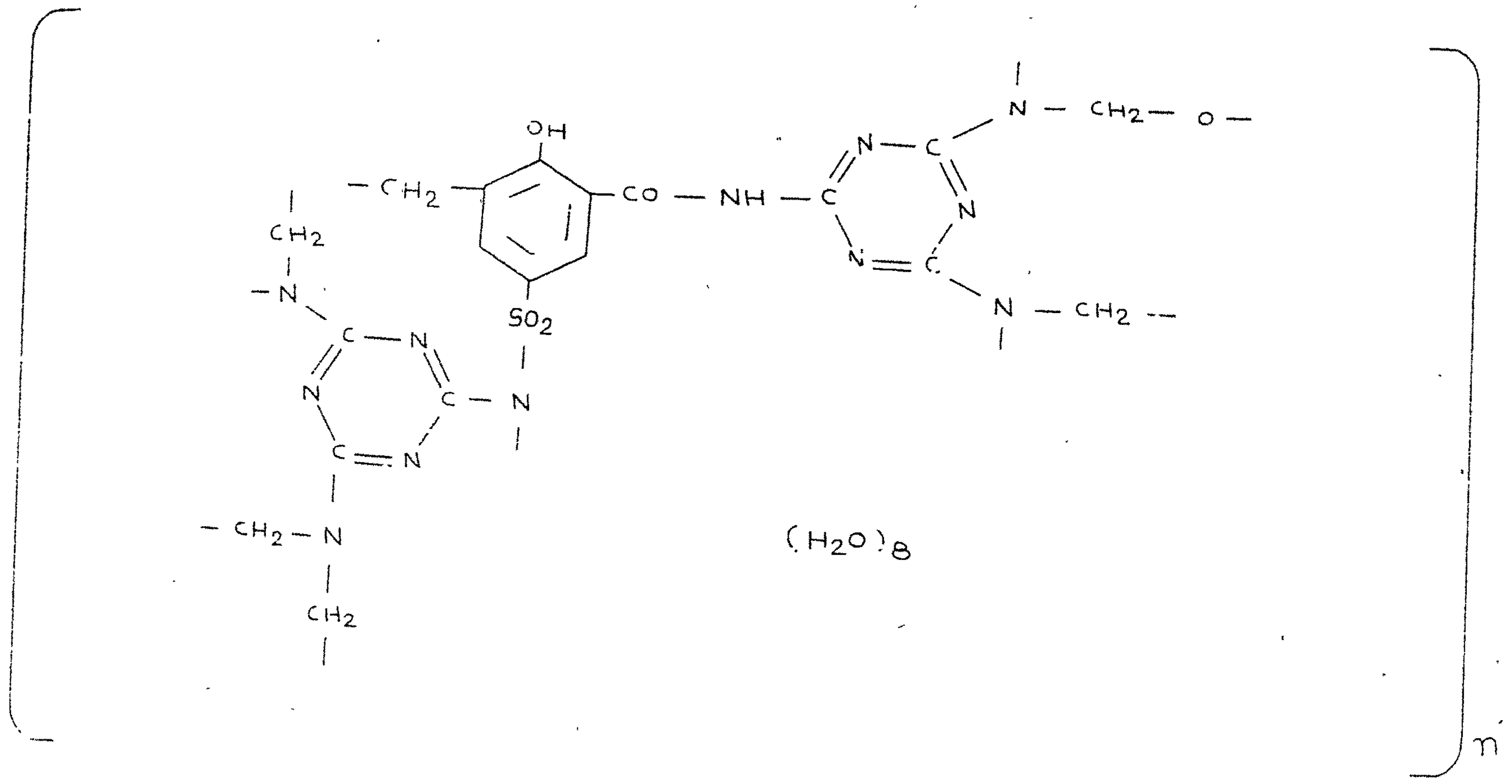
Ordinary ion exchange is essentially a redistribution of the exchanging counter ions A and B by diffusion, a process in which neither co-ions nor fixed ionic groups are considered to play an active role. Counter ion diffusion, however, is subject to the restriction of electroneutrality, as ions of species A move into the solution, a stoichiometrically equivalent amount of species B must move into the ion exchanger to balance the electric charges of the fixed ionic groups.

In an exchange of counter ions, the rate controlling step was shown to be diffusion[64] either in the ion exchanger particle itself or in an adherent stagnant liquid layer called the film[65]. In an intermediate range of conditions both mechanisms may affect the rate. Two other possible rate-controlling steps, passage through particle -solution interface and chemical reaction at fixed ionic groups, cannot be ruled out[66,67], however, whereas interfacial resistance to diffusion is highly unlikely for theoretical reasons, chemical reaction may indeed be slow enough to become rate controlling, if counter ions from sluggishly reacting complexes. Further, the assumption that ion exchange is a redistribution of counter ions is in error if ion exchange is accompanied by chemical reactions, such as neutralisation, hydrolysis, complex formation etc. Thus for the ionisation of a weakly dissociated fixed ionic group (say, -COOH) by reaction with a co-ion, somewhat different behaviour must be anticipated. Two mechanisms, both involving particle diffusion, are possible in principle. The first mechanism is interdiffusion of counter ions (say, H and Na) in the particles and differs from ordinary particle diffusion in that the process is greatly slowed down by association of H ions with fixed ionic groups. The second mechanism is invasion by Na and OH ions across the outer shell in Na form to the inner core still in Hform. OH ion abstracts a proton from -COOH forming H_2O while Na ion takes over the task of compensating the charge of newly formed -COO ion[68-70].

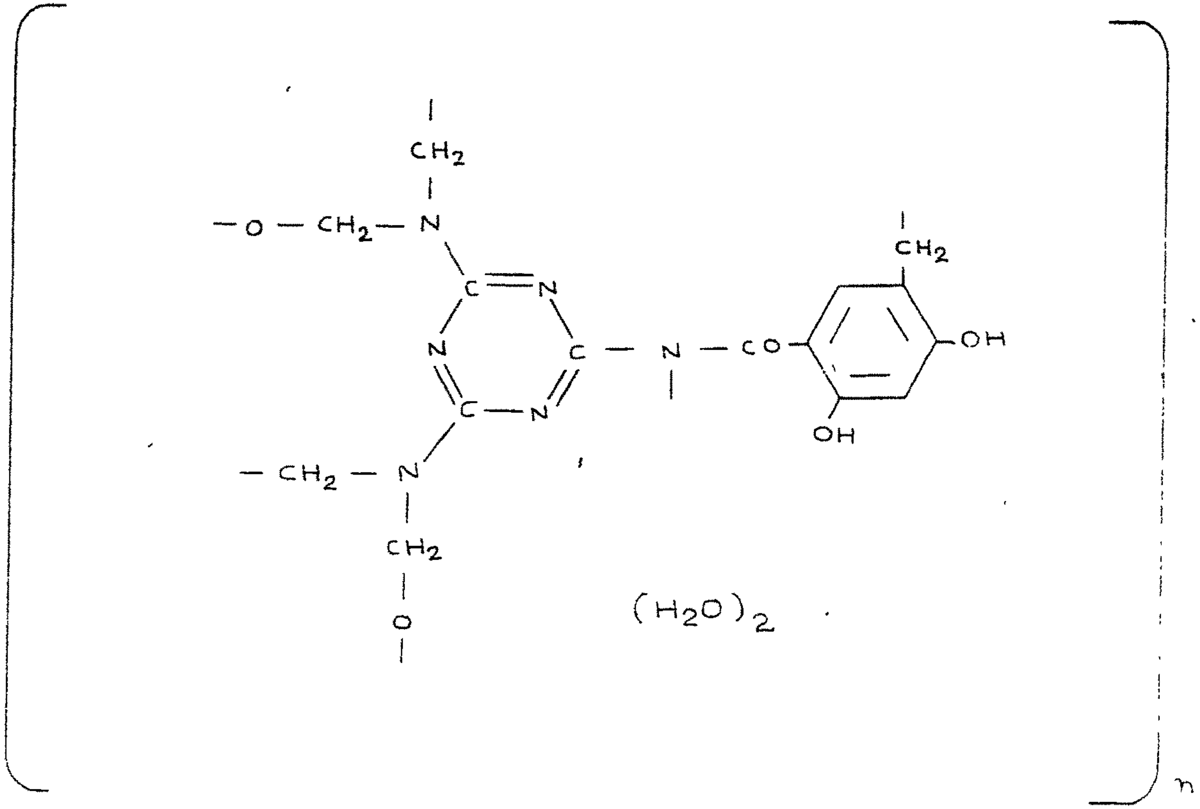
We consider that the complexing or chelating ability of the group in the chelating polymers make ion exchange a sluggish process. We further suggest that the amphoteric nature of chelating ion exchange resins under study will have a stable zwitter ion form which will retard the ion exchange process. Thus the slow rate of exchange observed in the present investigations can be attributed to various factors, such as weak nature of the fixed ionic groups, complexing/chelating behaviour of the group, zwitter ion formation, particle size, gel density, etc.



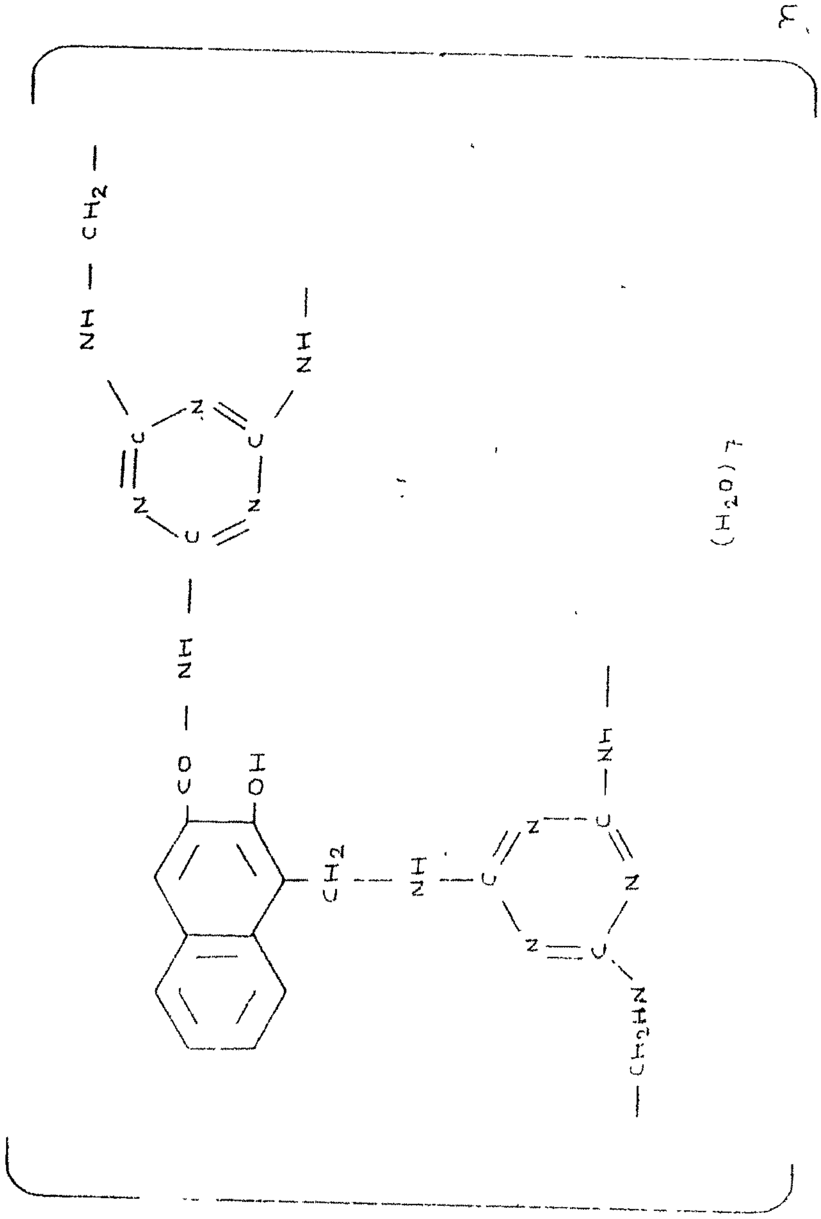
(VIII-S-1)
SAMF



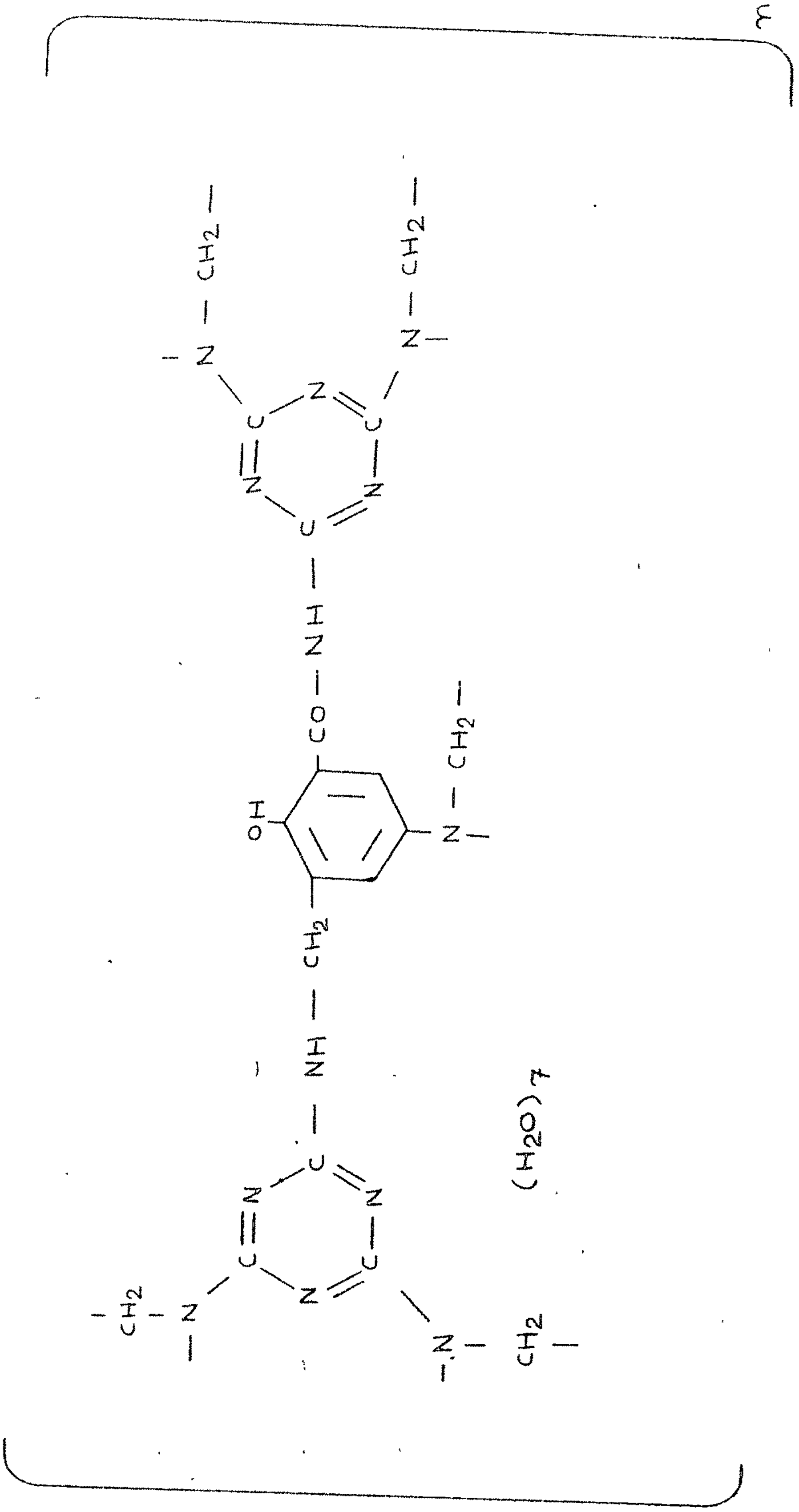
VIII - 5 - 2
SSAMF



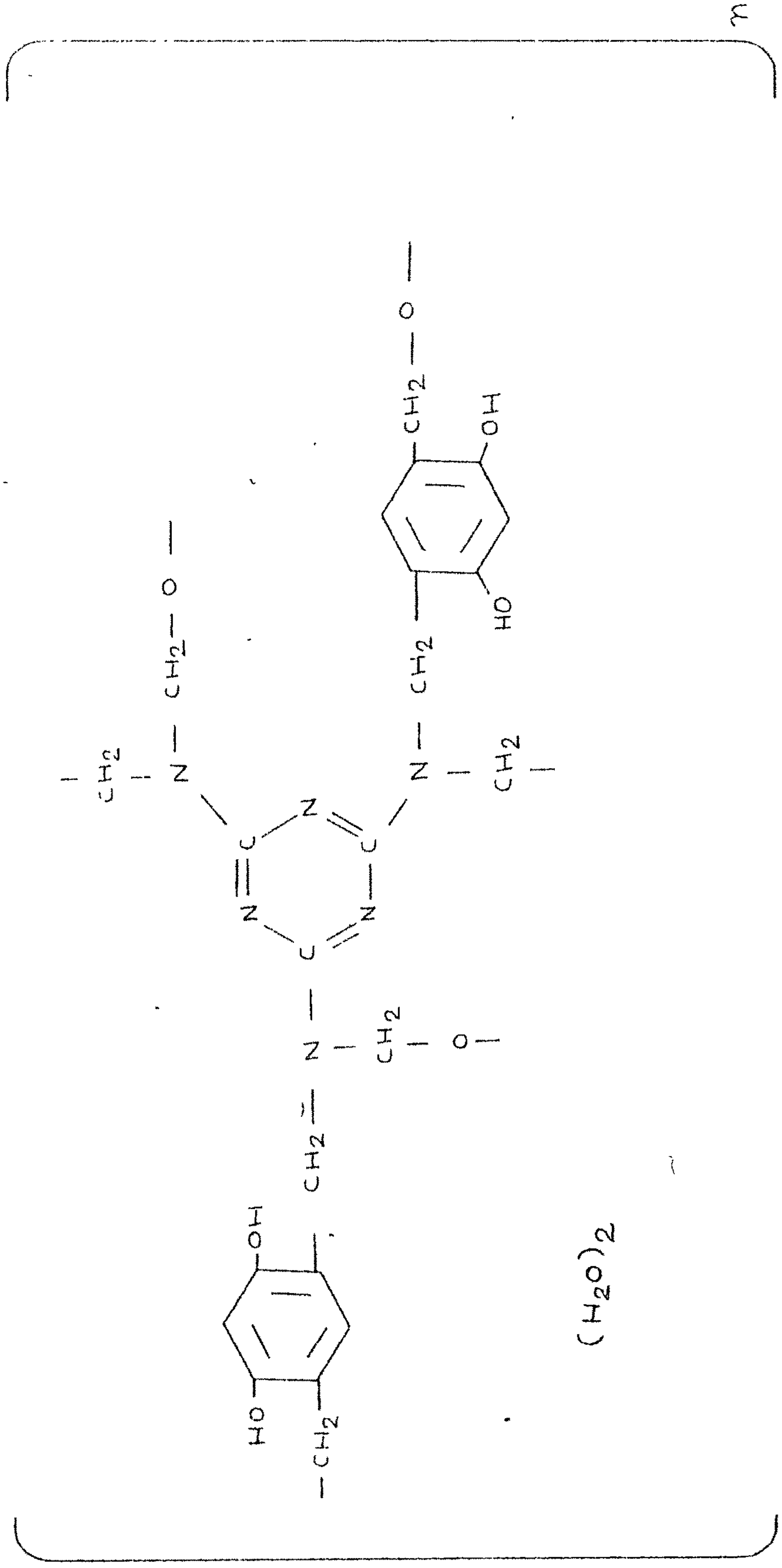
VIII - 5 - 3
RAMF



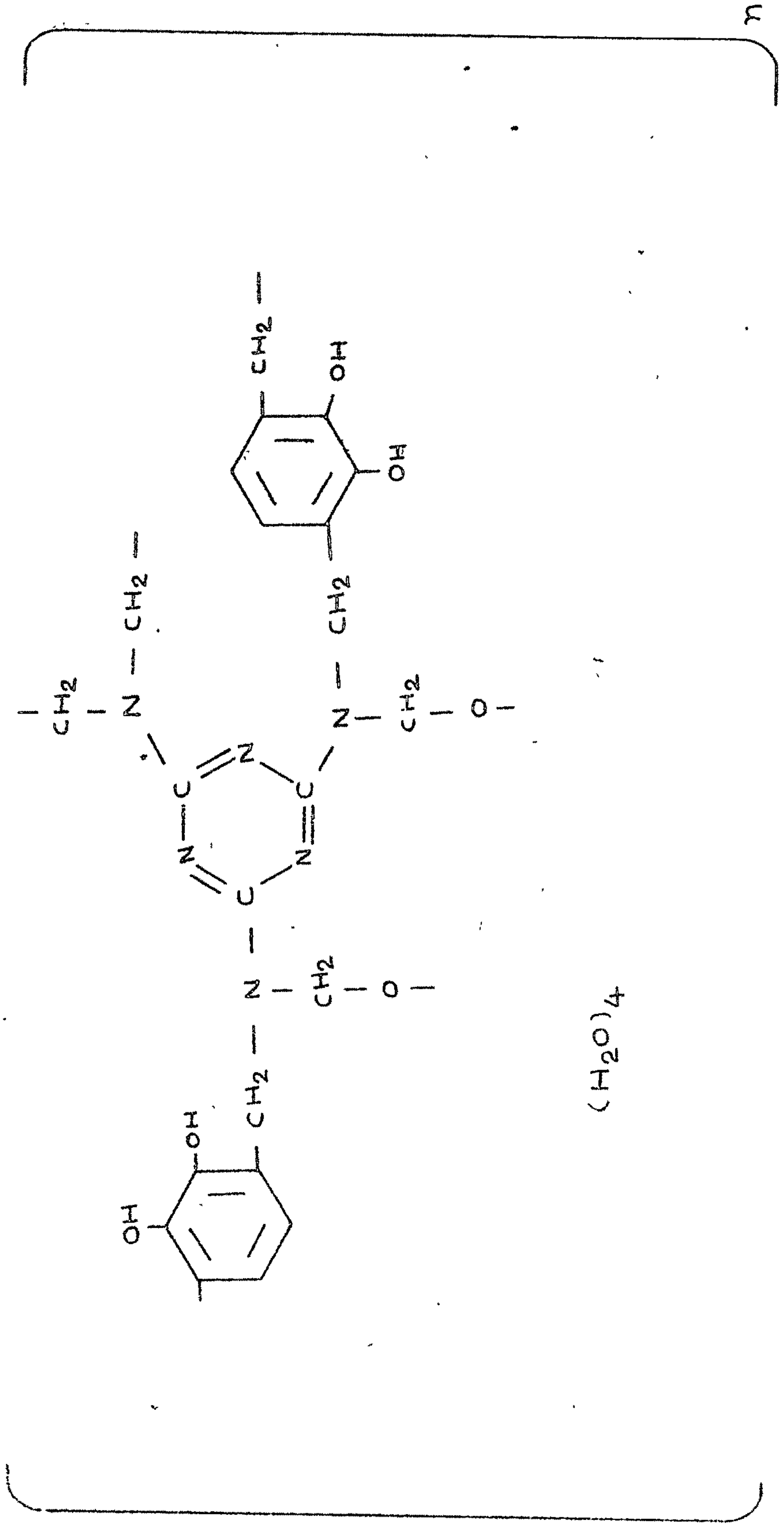
VIII-S-4
NAMF



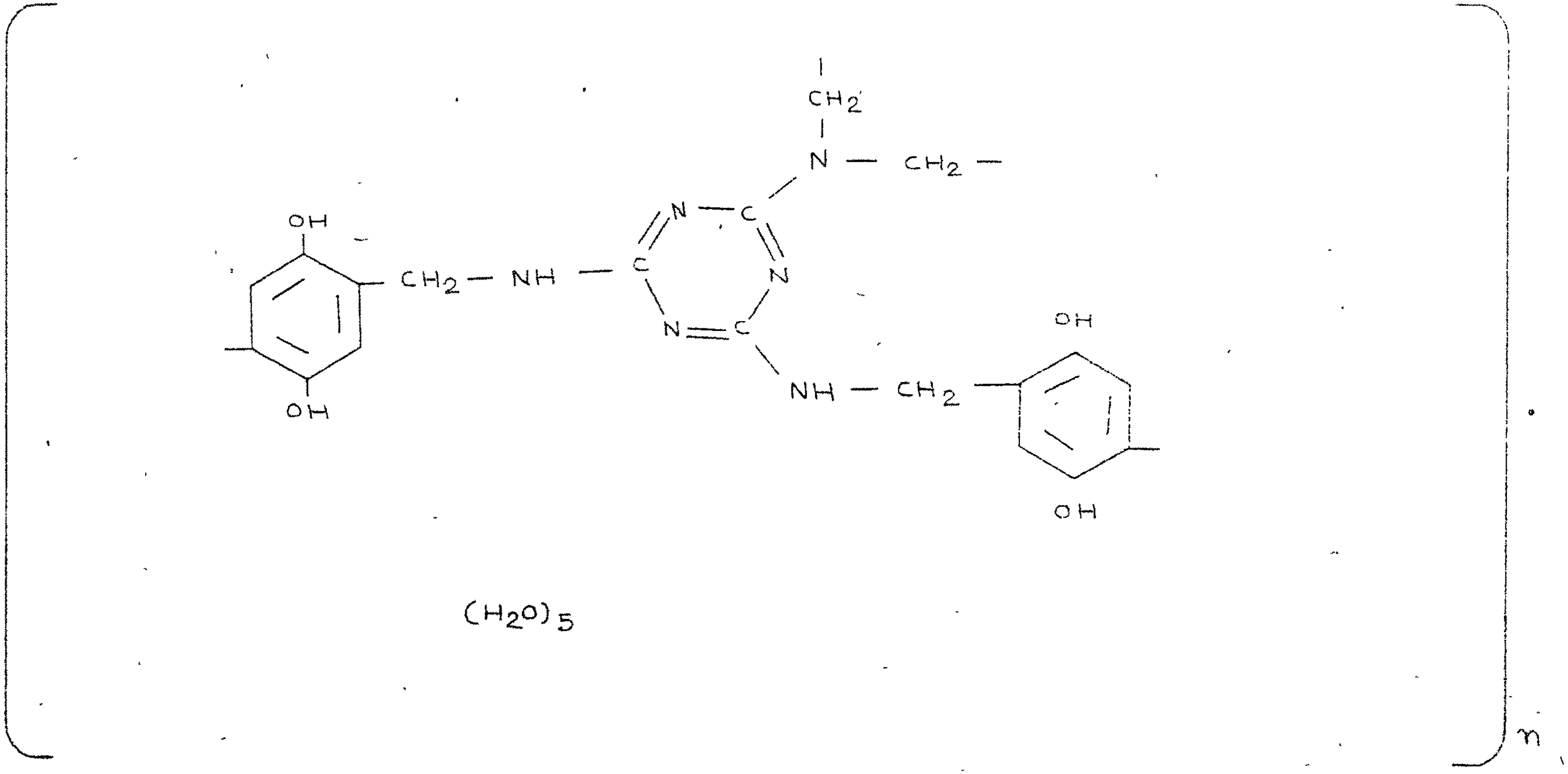
VIII-5-5
ASAMF



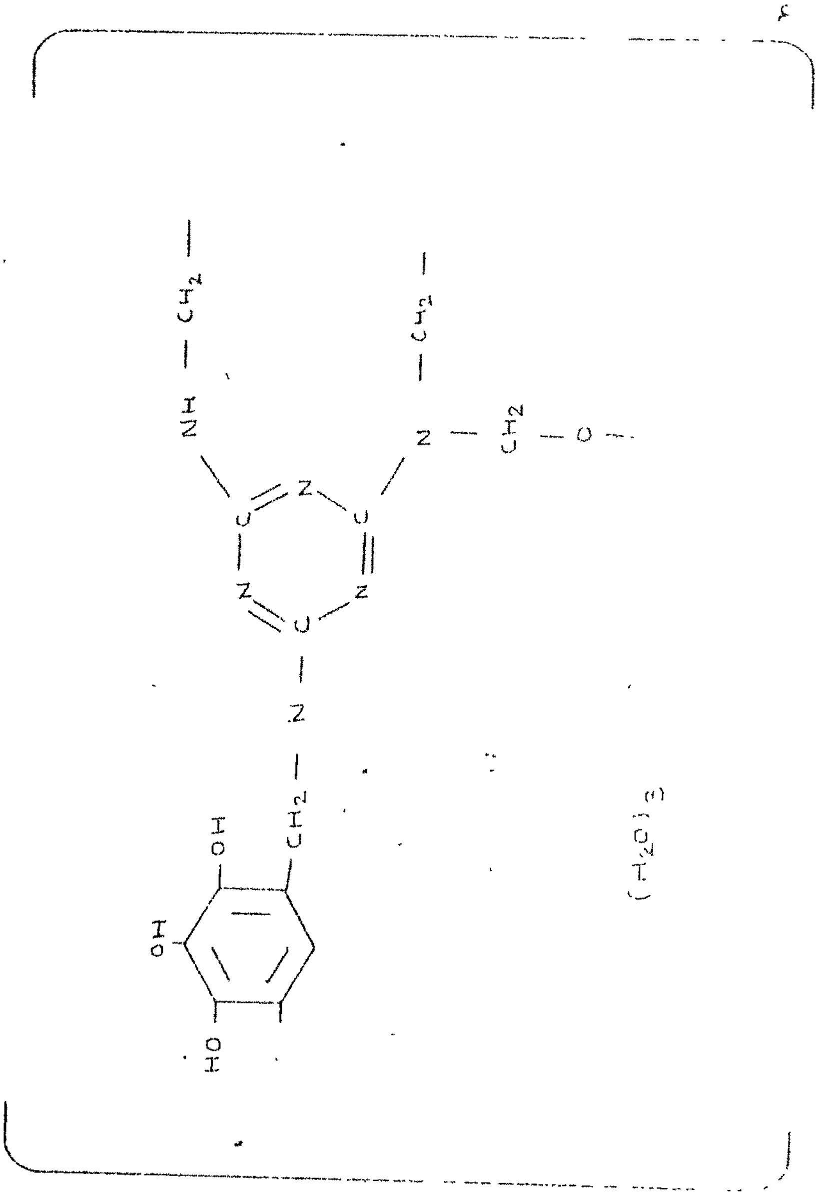
VIII-5-6
RMF



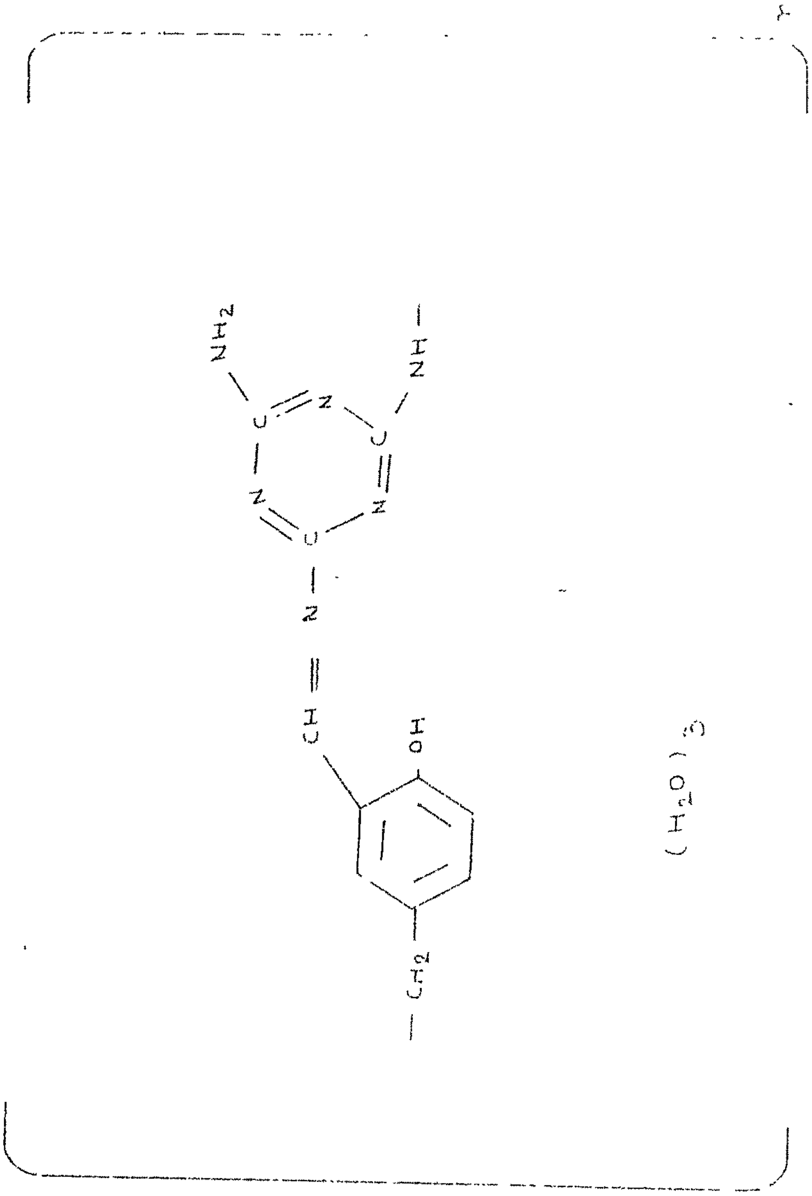
VIII-5-7
CMF



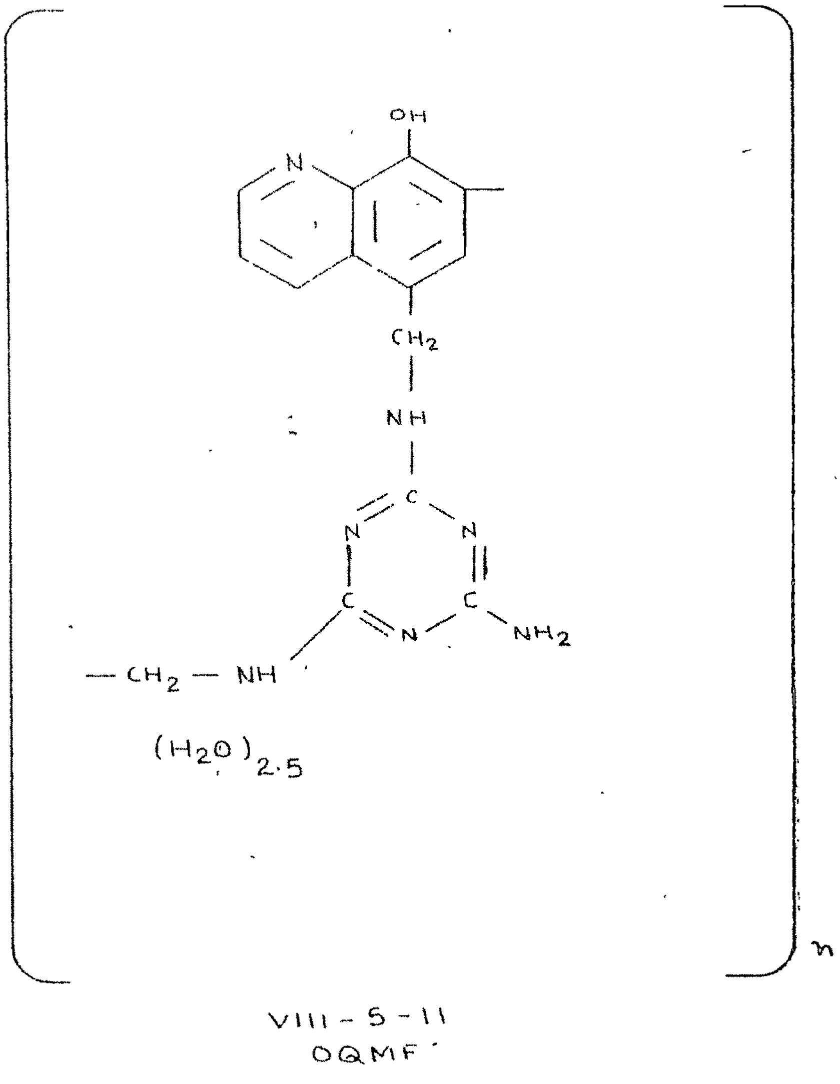
VIII-5-B
QMF



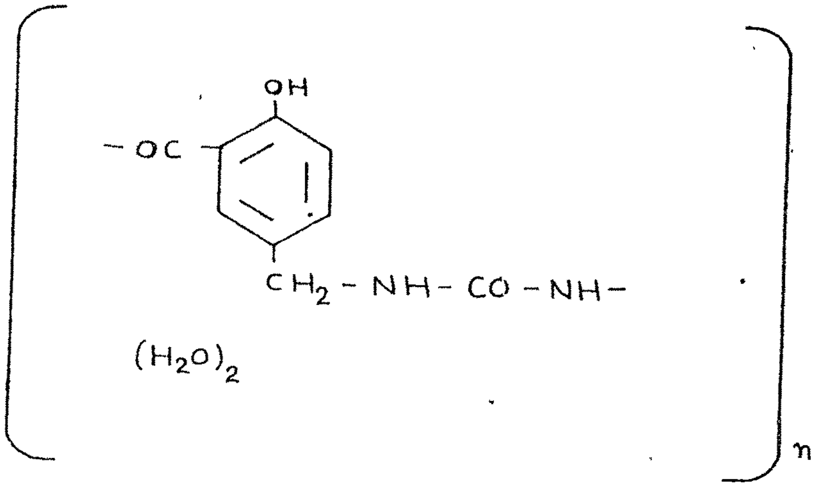
GMF



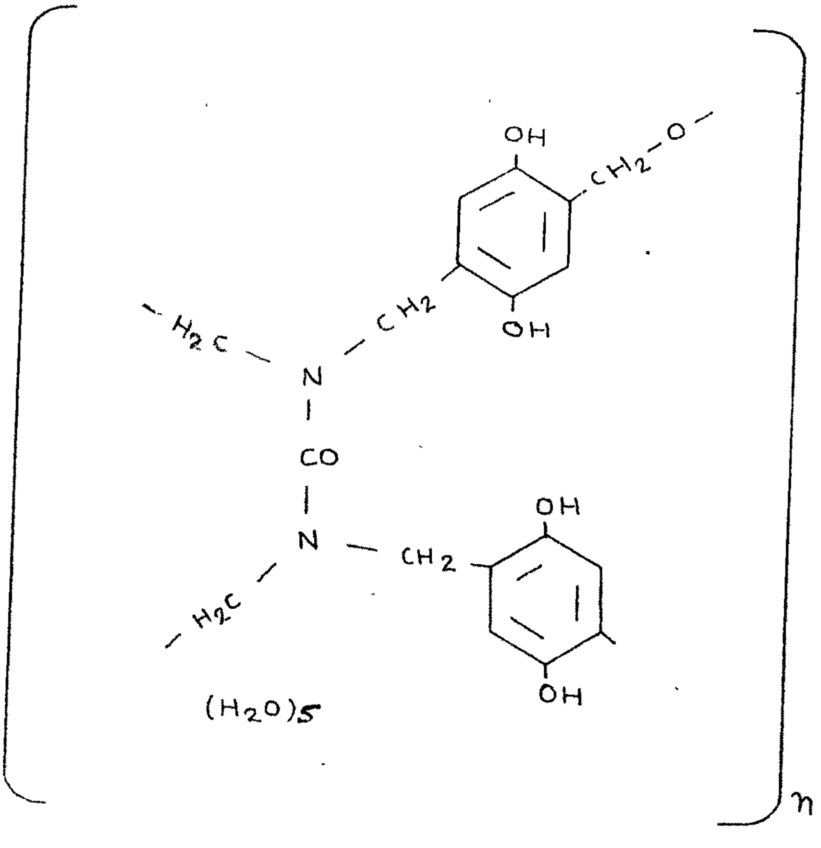
VIII-5-10
SMF



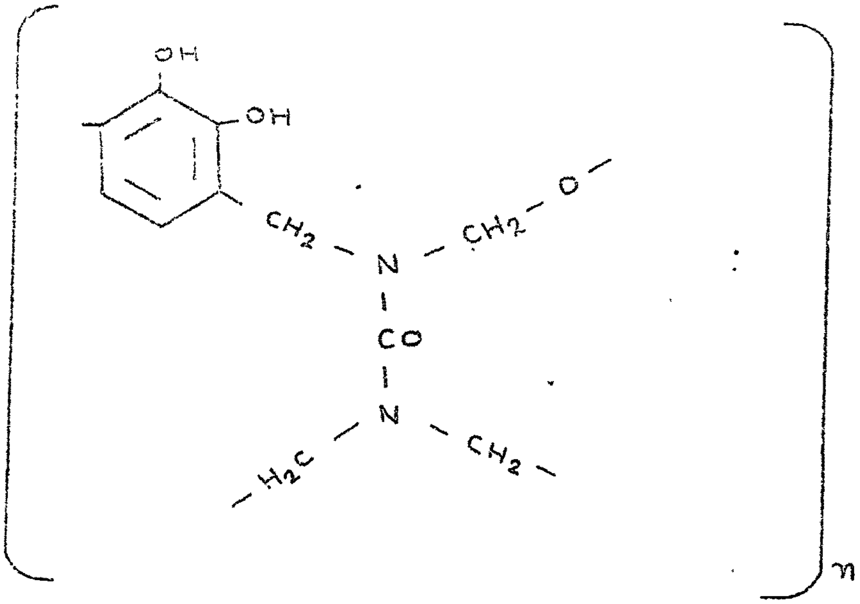
VIII-5-11
OQMF



VIII - 5 - 12
SAUF

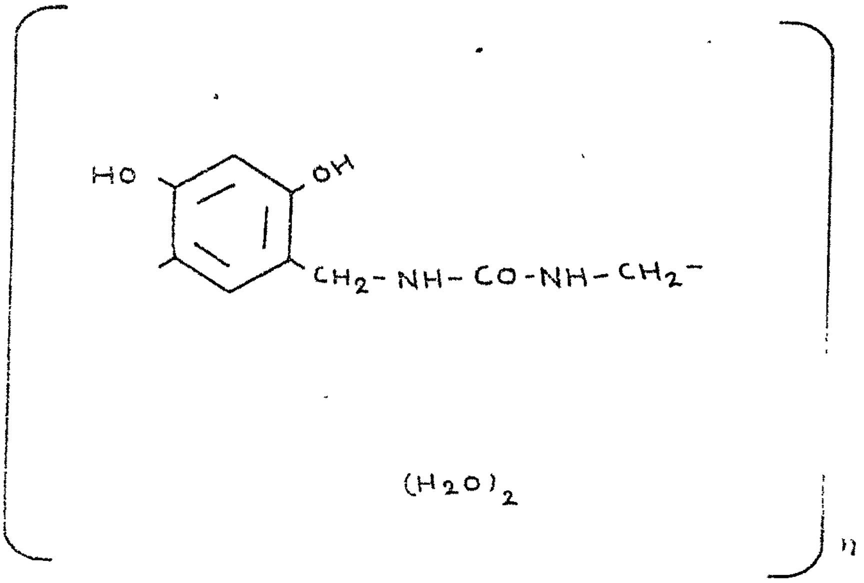


VIII - 5 - 13
QUF



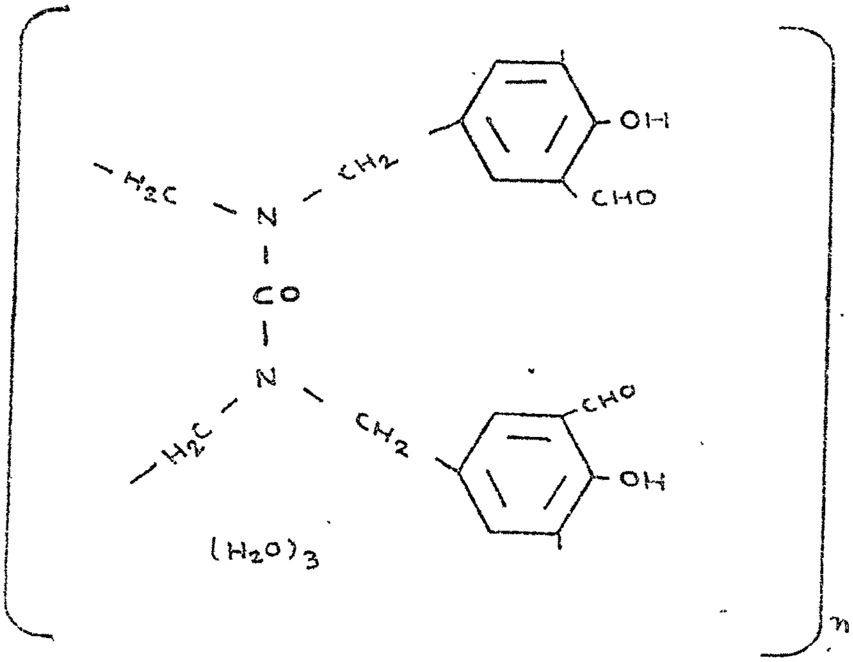
VIII - S - 14

CUF

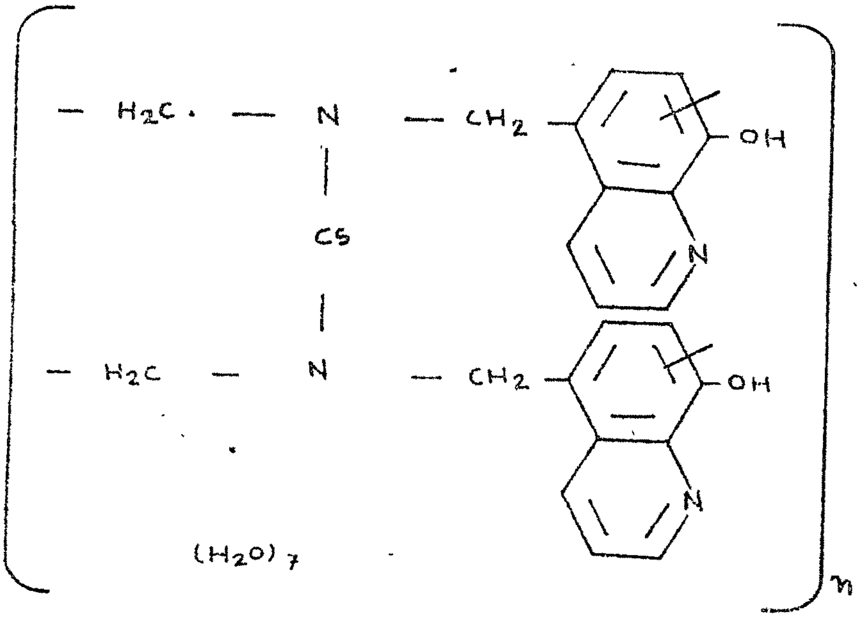


VIII - S - 15

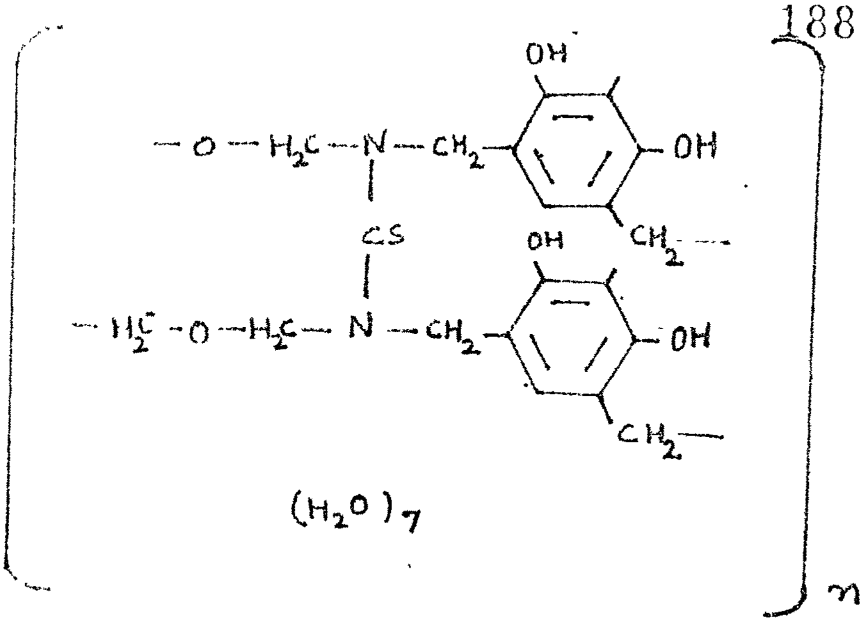
RUF



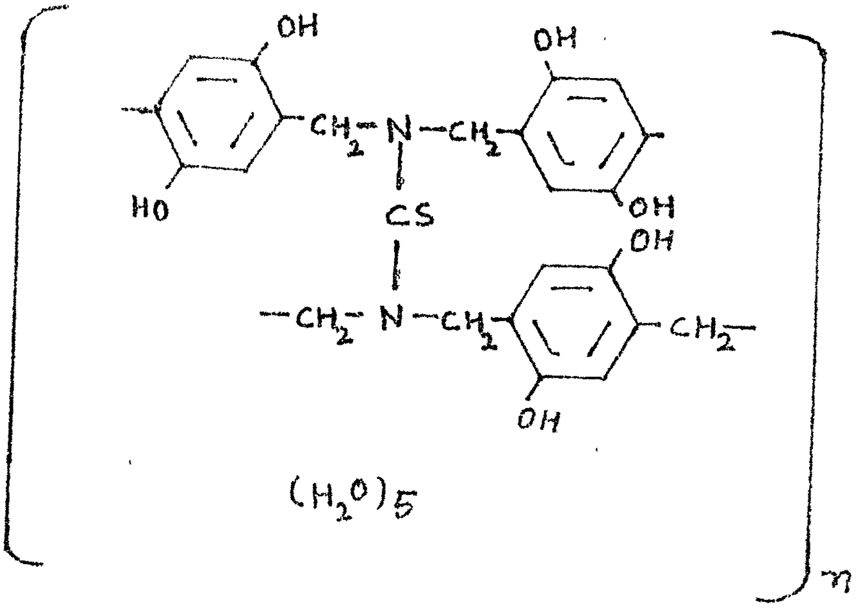
VIII - 5 - 16
SUF



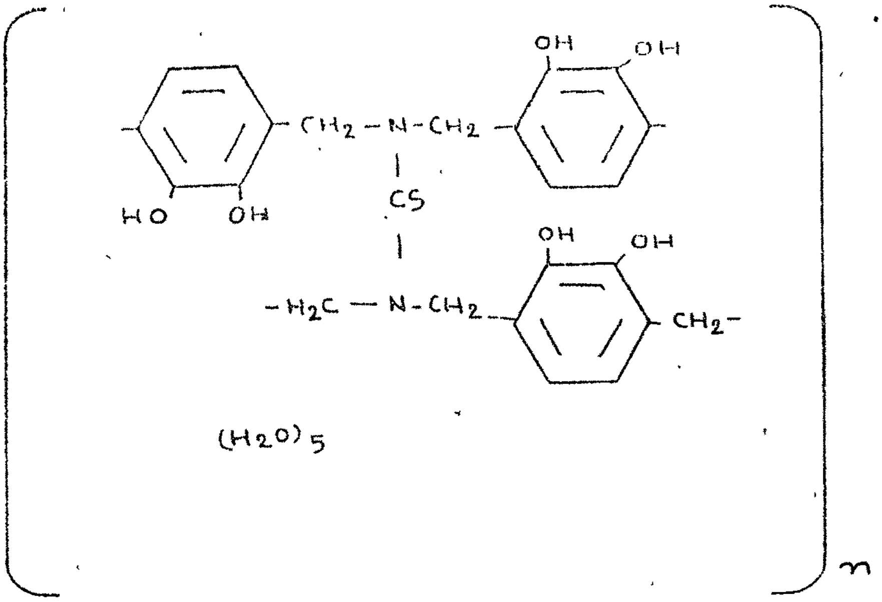
VIII - 5 - 17
OQTF



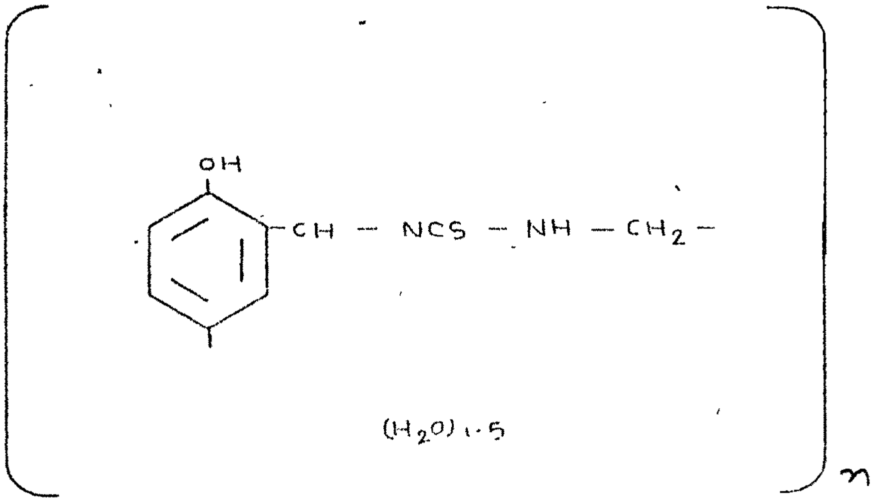
VIII-S-18
RTF



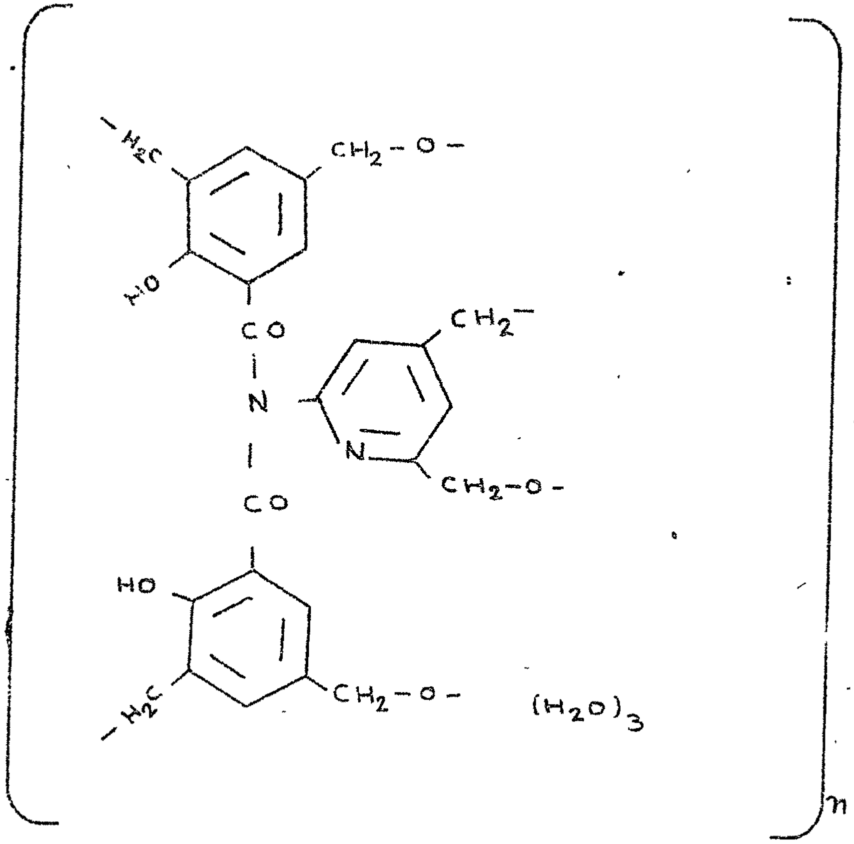
VIII - S - 19
QTF



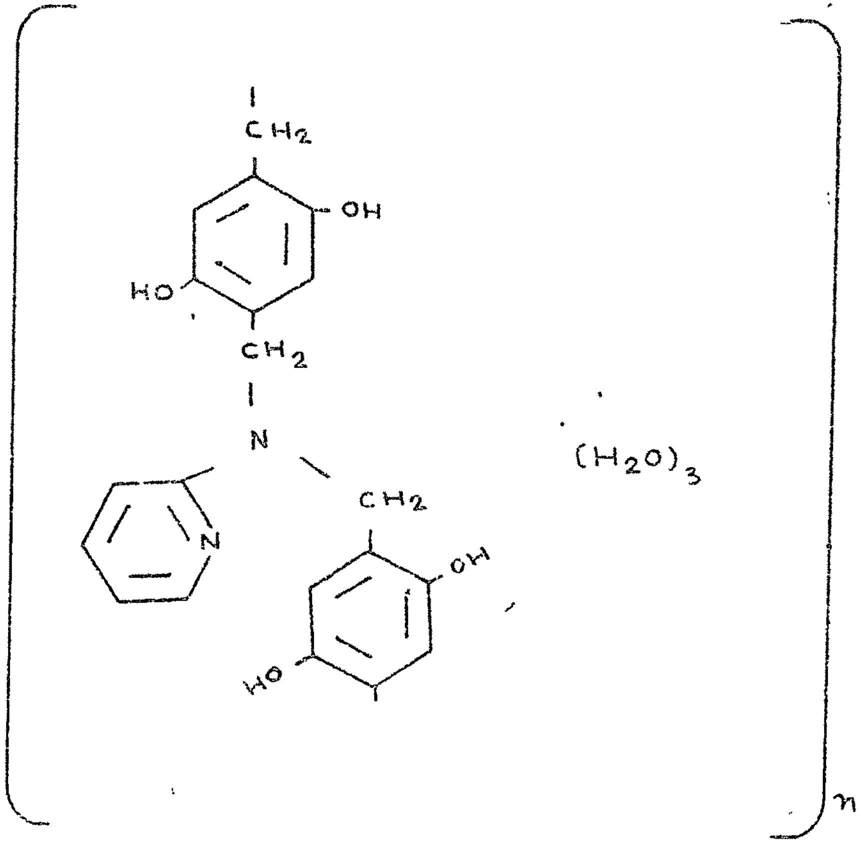
VIII - S - 20
CTF



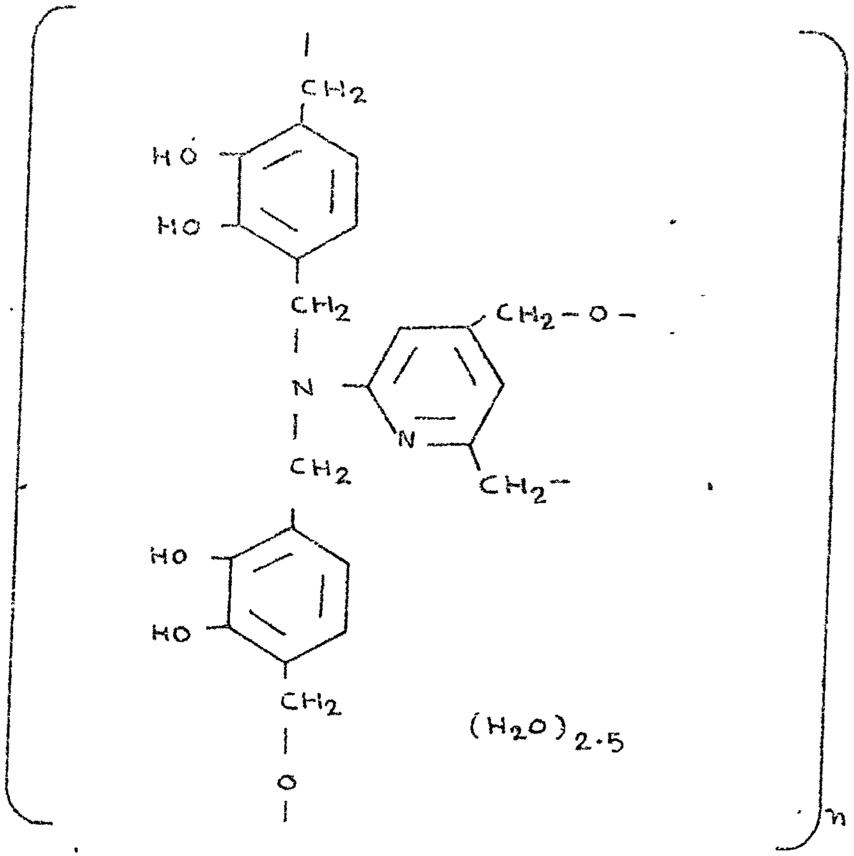
VIII - S - 21
STF



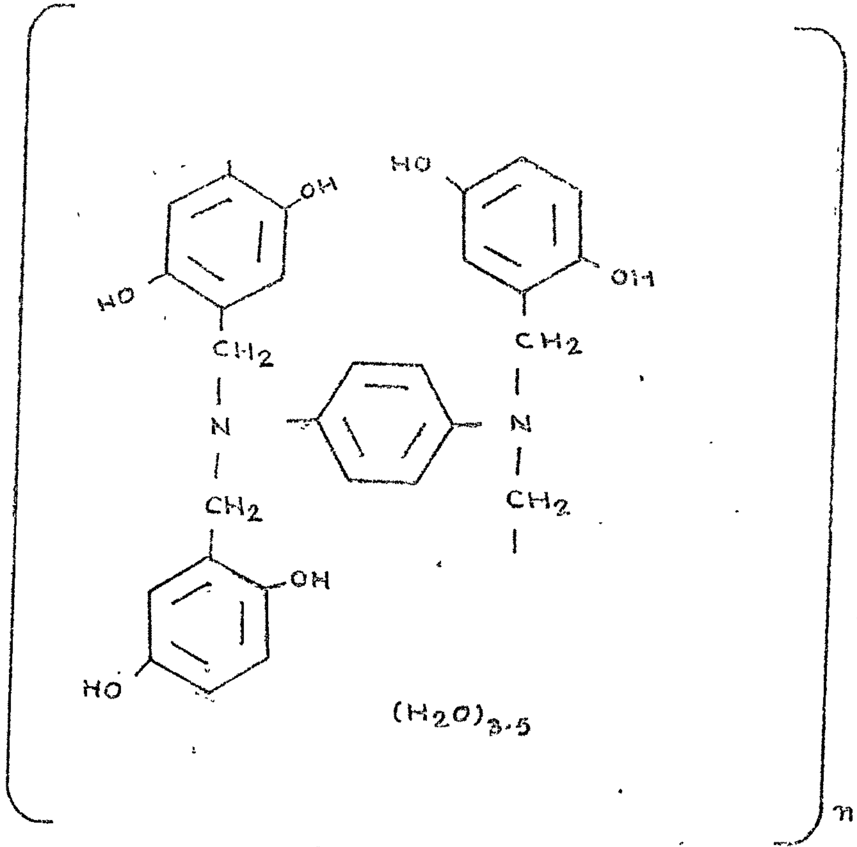
VIII - S - 22
SAAPF



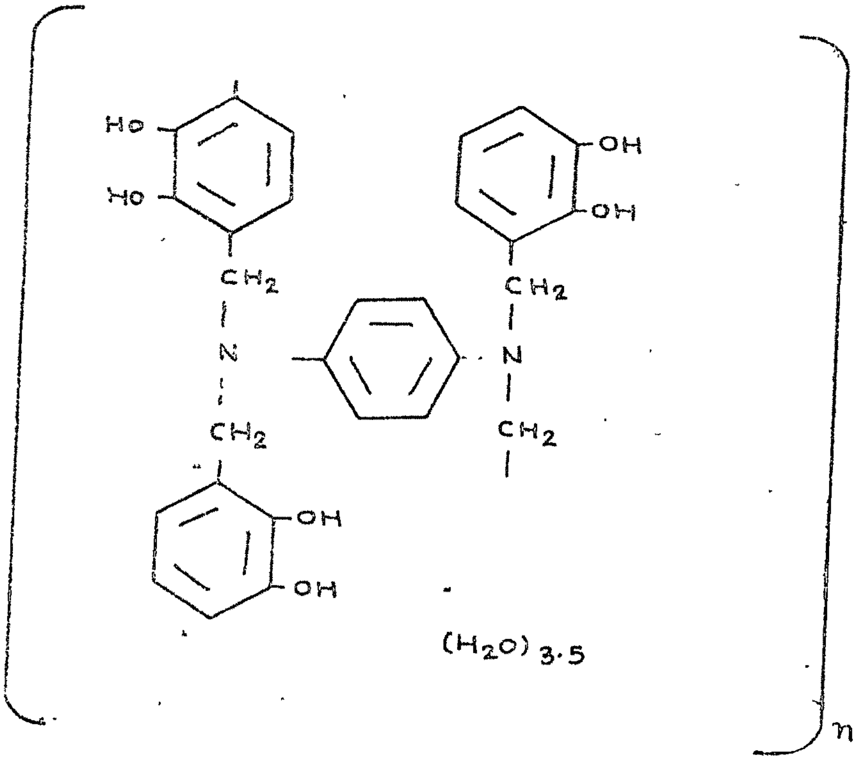
VIII - S - 23
QAPF



VIII - 5 - 24
CAPF



VIII - 5 - 25
QPPF



VIII-5-26
CPPF

Table VIII- T-1

Cation exchange capacity

NO.	Resin	CEC_{obs}	CEC_{cal}	CEC_{obs} / CEC_{cal}
1.	SAMF	3.2	2.1	1.5
2.	SSAMF	3.3	1.8	1.8
3.	RAMF	3.8	5.6*	0.7
4.	NAMF	2.6	2.2	1.2
5.	ASAMF	2.4	2.2	1.1
6.	RMF	4.2	8.0*	0.5
7.	CMF	4.4	8.6*	0.5
8.	QMF	4.2	10.0*	0.4
9.	GMF	3.5	9.3*	0.4
10.	SMF	3.5	4.1	0.9
11.	OQMF	2.8	3.3	0.9

* polyhydroxy benzene derivative.

Table VIII- T-2

NO.	Resin	% Moisture (average of values for resin in H and OH form)	pH(α=0.5) (resin in H form)	pK_C (resin in H form)	pH(α=0.5) (resin in OH form)	pK_A (resin in OH form)	Isoionic point (IP)
1.	2.	3.	4.	5.	6.	7.	8
1.	SAMF	13.1	11.3	10.27	3.0	4.22	7.24
2.	SSAMF	14.3	10.0	9.01	3.2	4.30	6.65
3.	RAMF	17.3	10.5	9.54	2.0	2.98	6.26

Table VIII- T-2 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.
4.	NAMF	11.3	10.2	9.19	1.5	2.69	6.44
5.	ASAMF	14.5	10.7	9.85	1.5	2.73	6.29
6.	RMF	19.0	11.2	10.25	2.5	3.31	6.75

Table VIII- T-2 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.
7.	QMF	13.8	10.7	9.56	2.3	3.23	6.39
8.	CMF	17.7	10.9	9.89	2.2	3.03	6.46
9.	GMF	17.7	9.3	8.39	2.3	3.31	5.85
10.	OQMF	13.5	11.4	10.44	2.2	3.47	6.95

Table VIII- T-3

rate studies

No.	Resin	Time (inminutes) for 50% exchange	
		cation exchange	anion exchange
1.	2.	3.	4.
1.	SAMF	285	117
2.	SSAMF	27	27
3.	RAMF	117	15
4.	NAMF	69	90
5.	ASAMF	51	114

Table VIII- T-3 (cont.)

*1.	2.	3.	4.
6.	RMF	57	30
7.	CMF	108	425
8.	QMF	54	12
9.	GMF	9	9
10.	OQMF	87	252

Table VIII- T-4

NO.	Resin	% Moisture (average of values for resin H and OH-form)	pH(α=0.5) (resin in H-form)	pK$_C$ (resin in H-form)	pH(α =0.5) (resin in OH-form)	pK$_A$ (resin in OH-form)	IP
1.	2.	3.	4.	5.	6.	7.	8
1.	SAUF	12.6	11.0	10.87	2.4	3.40	7.14
2.	QUF	14.2	10.0	8.88	2.3	2.94	5.91
3.	CUF	12.9	10.0	8.84	2.3	2.92	5.88

Table VIII- T-4 (cont.)

1.	2.	3.	4.	5.	6.	7.	8.
4.	RUF	12.9	10.7	9.66	2.1	2.90	6.28
5.	SUF	14.0	10.6	9.46	2.0	2.78	6.12
6.	RTF	11.6	9.4	8.37	2.1	2.91	6.64

Table VIII- T-5

rate studies

NO.	Resin	Time(in minutes) for 50% exchange	
		cation exchange	anion exchange
1.	SAUF	21	18
2.	QUF	57	7
3.	CUF	28	4
4.	RUF	39	45
5.	SUF	54	15
6.	RTF	27	42

Table VIII- T-6

NO.	Resin	% Moisture (average of values for resin H and OH form)	pH (α =0,5) (resin in H-form)	pK_C (resin in H-form)	pH (α=0.5) (resin in OH-form)	pK_A (resin in OH-form)	IP
1.	2.	3.	4.	5.	6.	7.	8.
1.	CPPF	10.9	10.9	9.60	2.3	3.40	6.50
2.	QPPF	14.0	10.4	9.24	2.2	3.22	6.23

Table VIII- T-7

rate studies

NO.	Resin	Time (in minutes) for 50% exchange	
		Cation exchange	Anion exchange
1.	QPPF	21	45
2.	CPPF	54	27

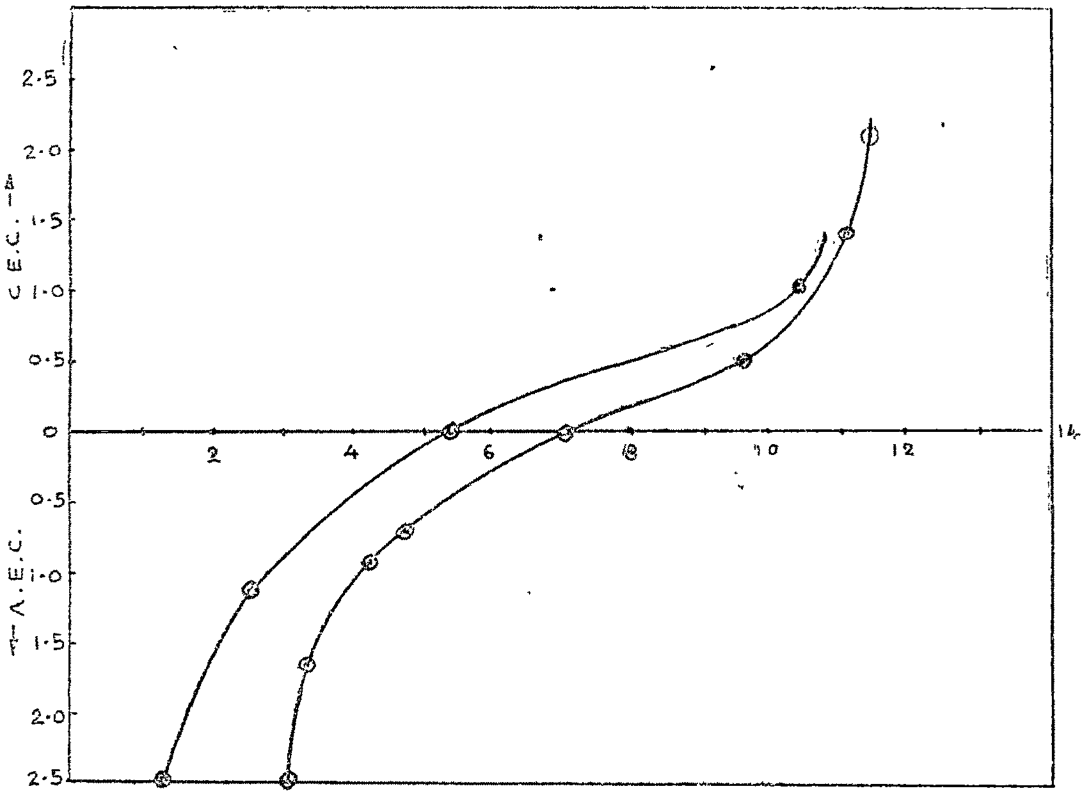


FIG. VIII - F-1(a) pH TITRATION OF SAMF [⊙,⊙] AND ASAMF [⊗,⊗]

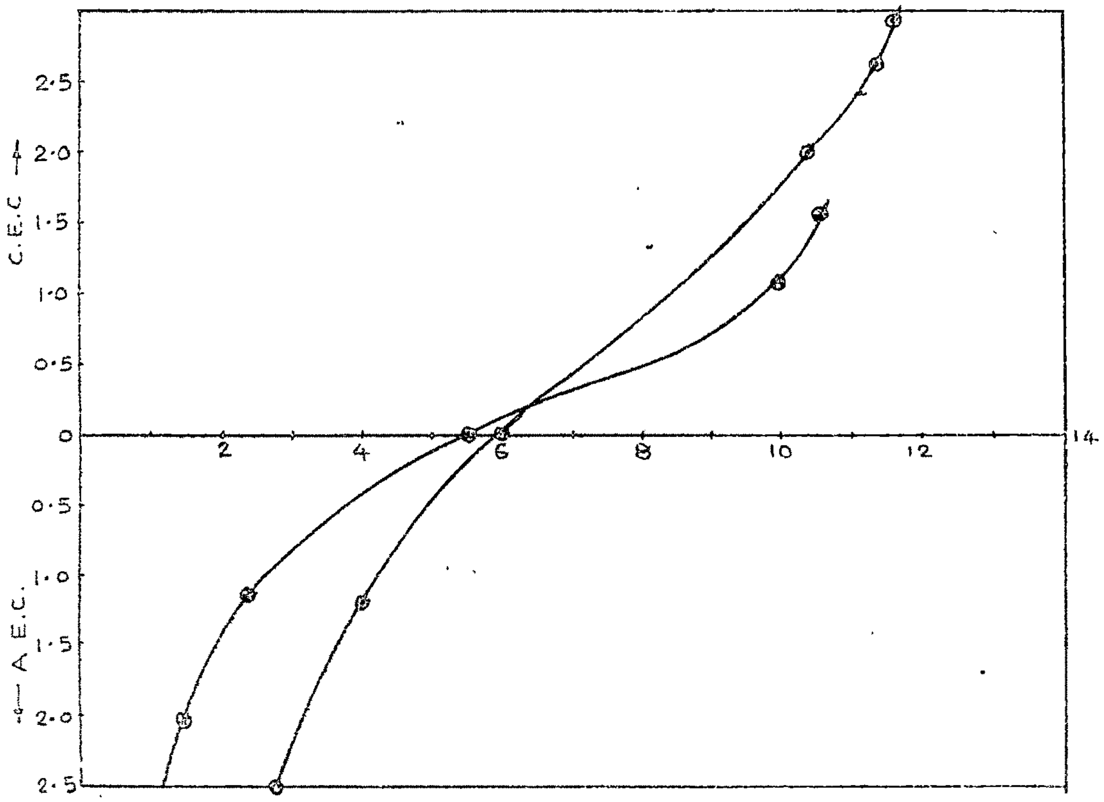


FIG VIII - F-1(b) pH TITRATION OF SSAMF [⊙,⊙] AND NAMF [⊗,⊗]

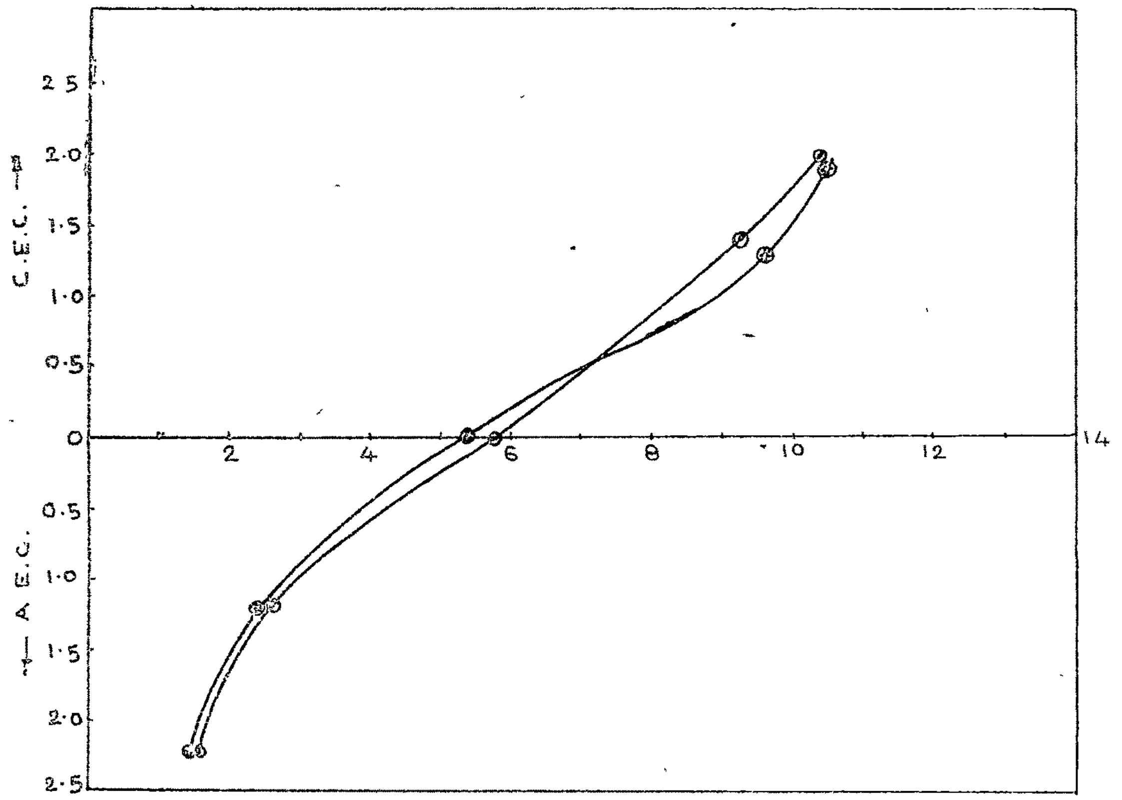


FIG. VIII-F-1(c) p^H TITRATION OF RAMF [⊙,⊙] AND CMF [⊗,⊗]

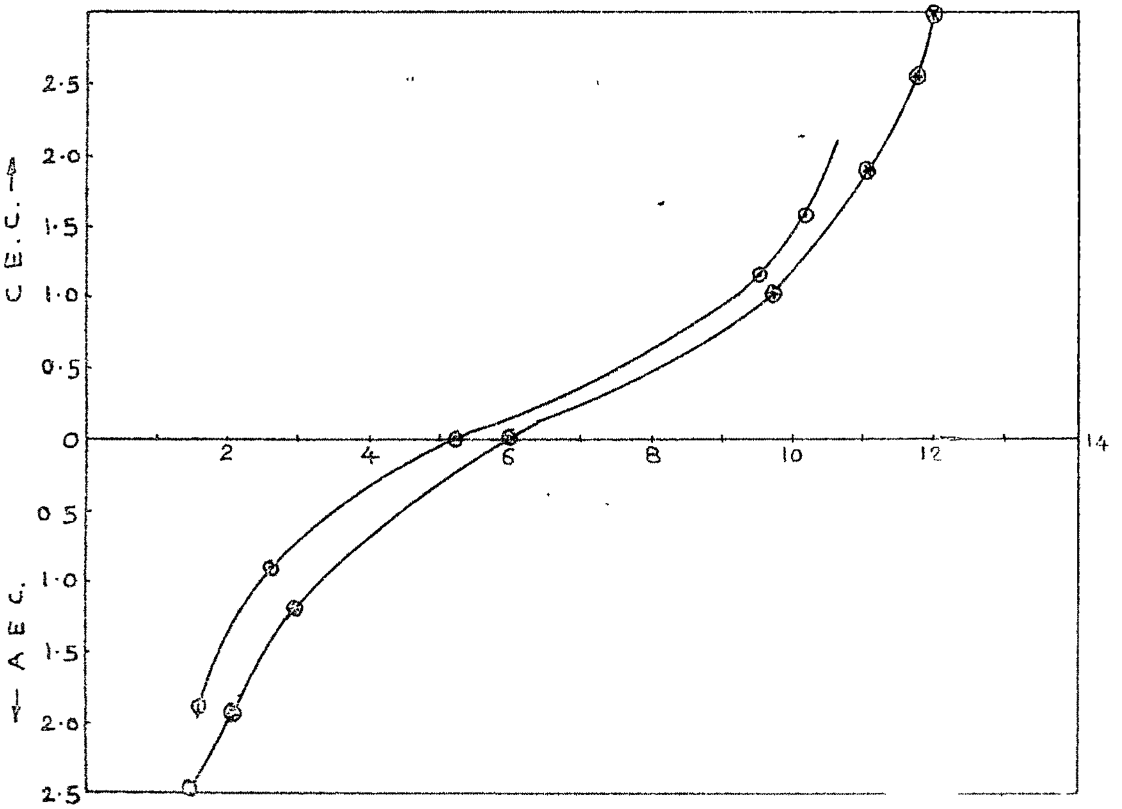


FIG. VIII-F-1(d) p^H TITRATION OF QMF [⊙,⊙] AND RMF [⊗,⊗]

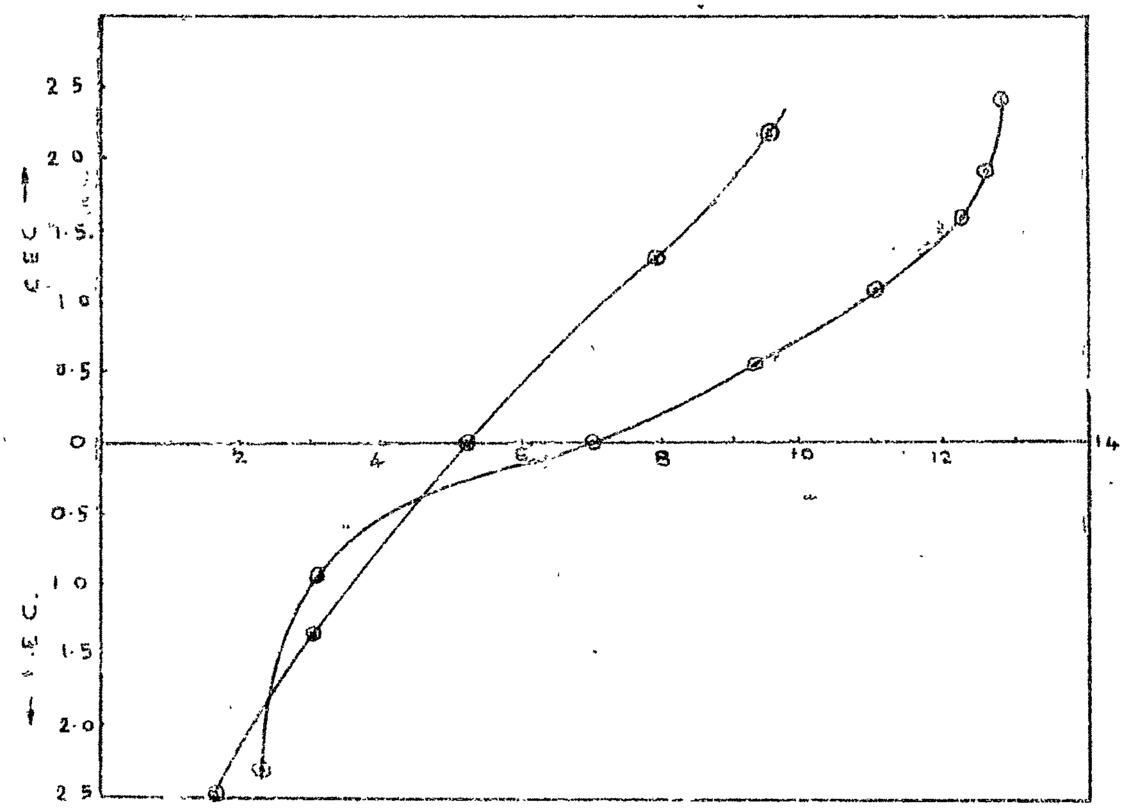


FIG VIII - Γ-1(e) pH TITRATION OF OQMF [⊙⊙] AND GMF [⊗ ⊗]

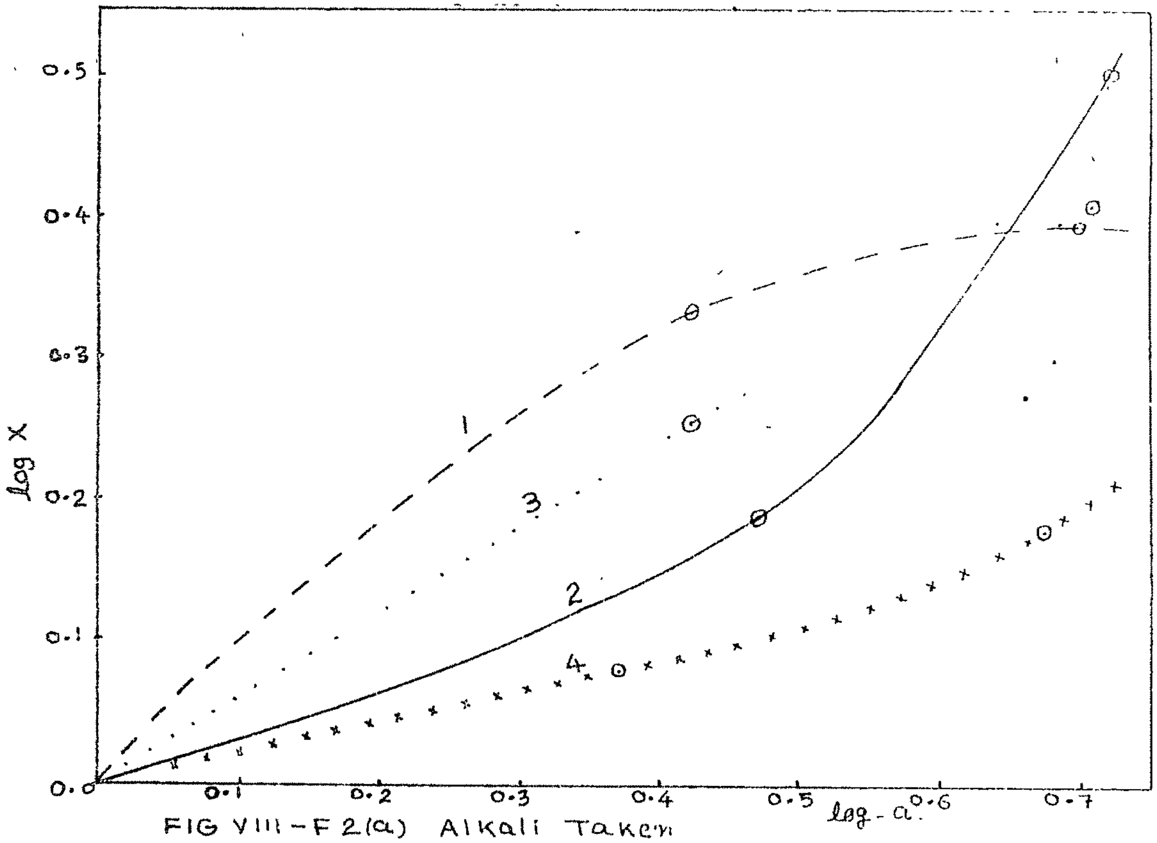


FIG VIII - F 2(a) Alkali Taken
(1) SAMF (2) SSAMF (3) RMF (4) OQMF

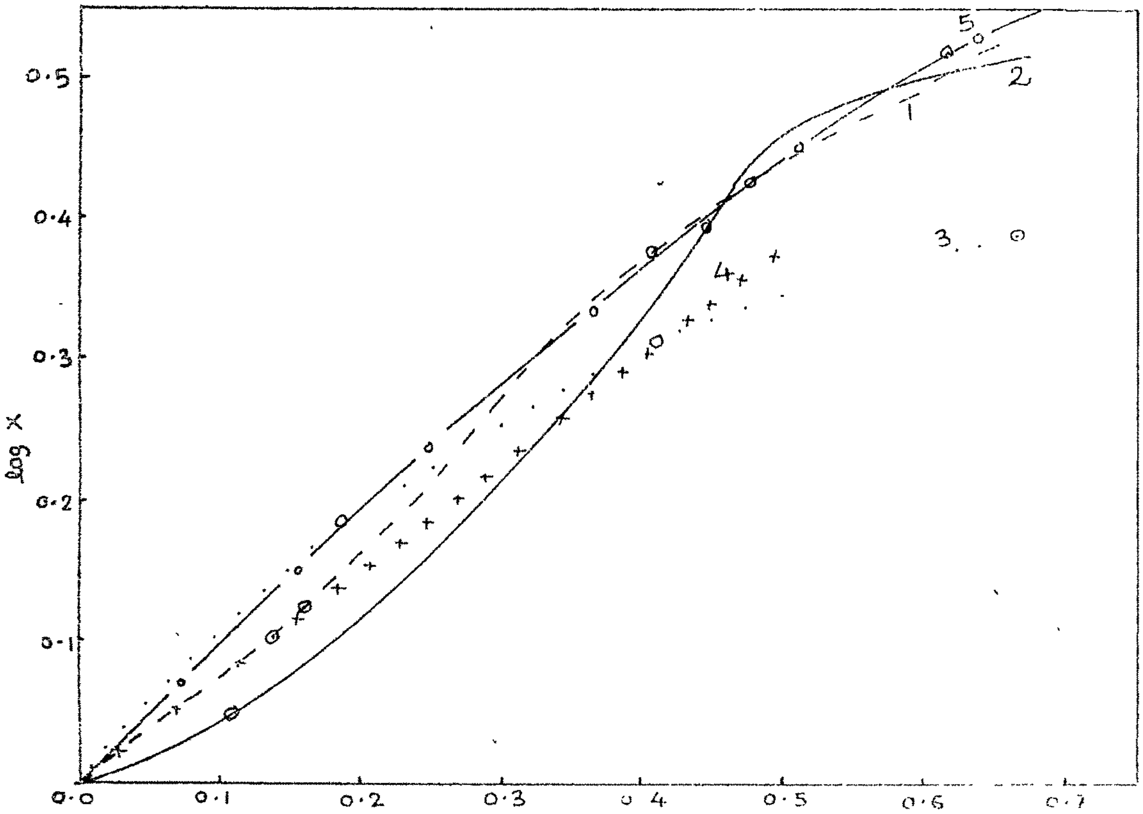


FIG VIII - F 2(b) Acid Taken
(1) SAMF (2) SSAMF (3) RMF (4) CMF (5) OQMF

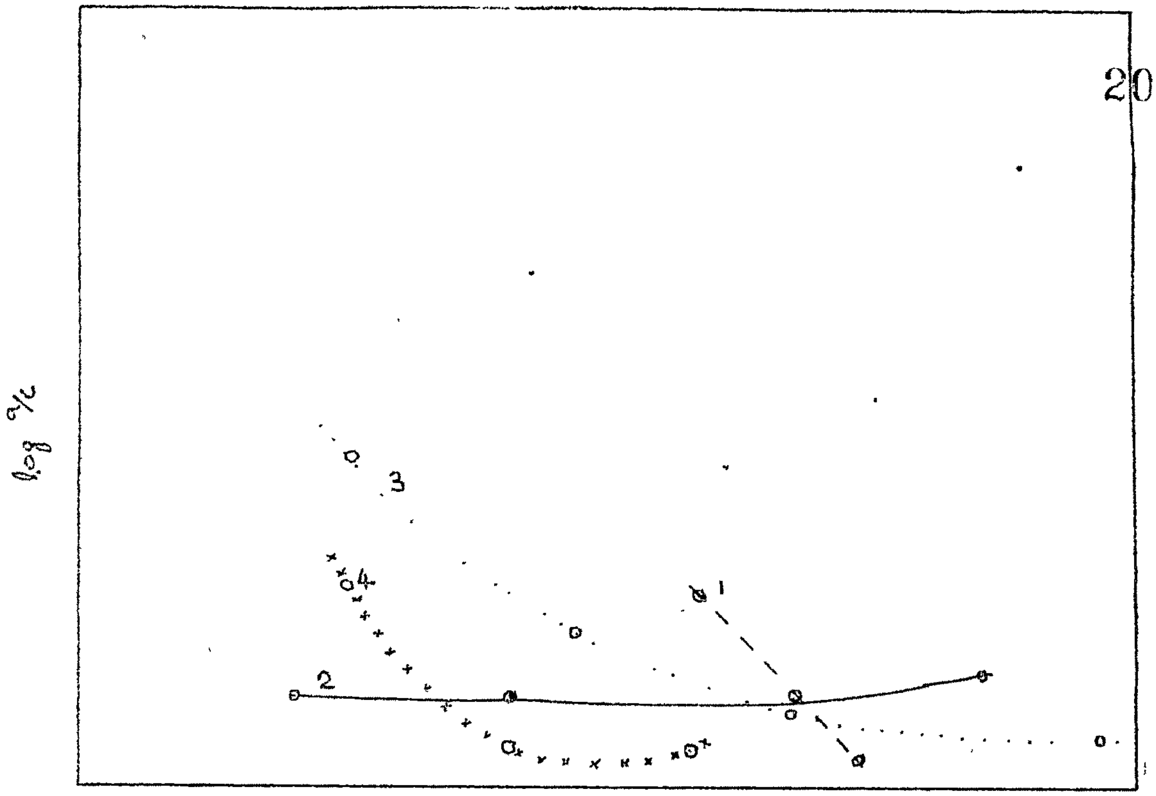


Fig VIII - F - 3 (a) Alkali taken,
sorption by (1) SAMF (2) SSAMF (3) RMF (4) OQMF

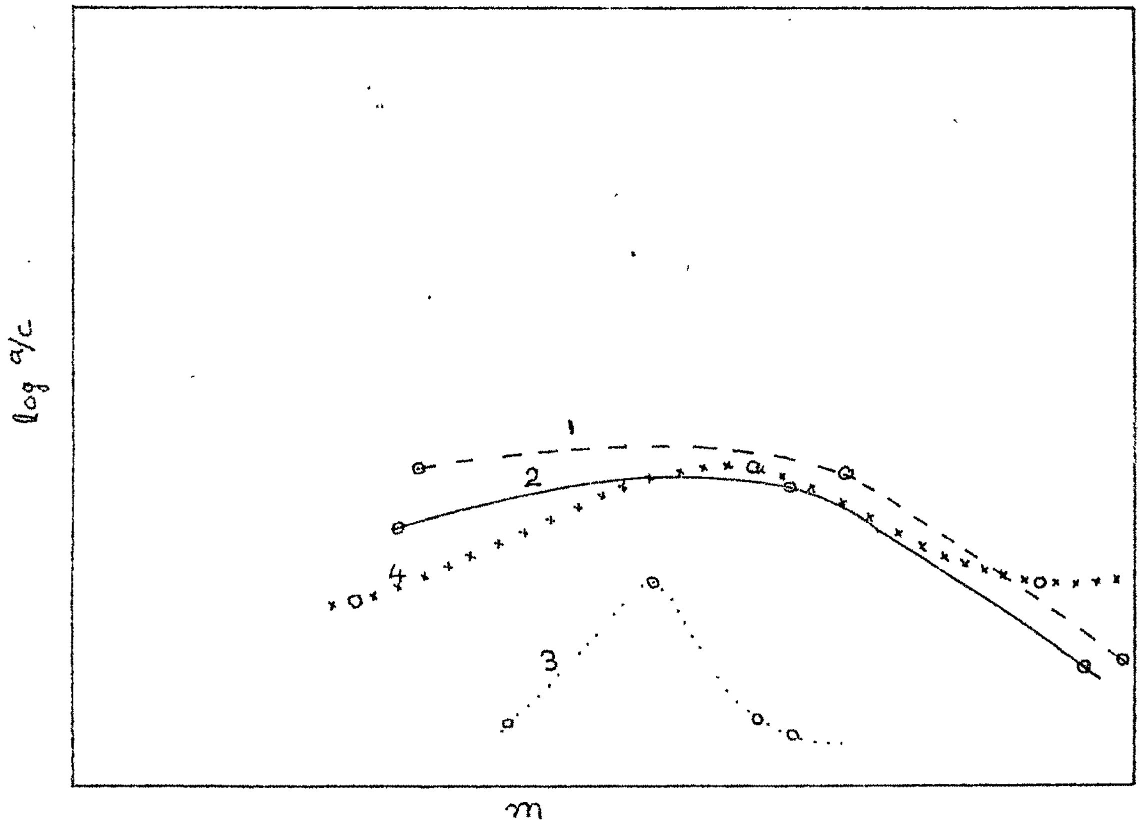


Fig VIII - F - 3 (b) Acid taken,
sorption by (1) SAMF (2) SSAMF (3) RMF (4) OQMF

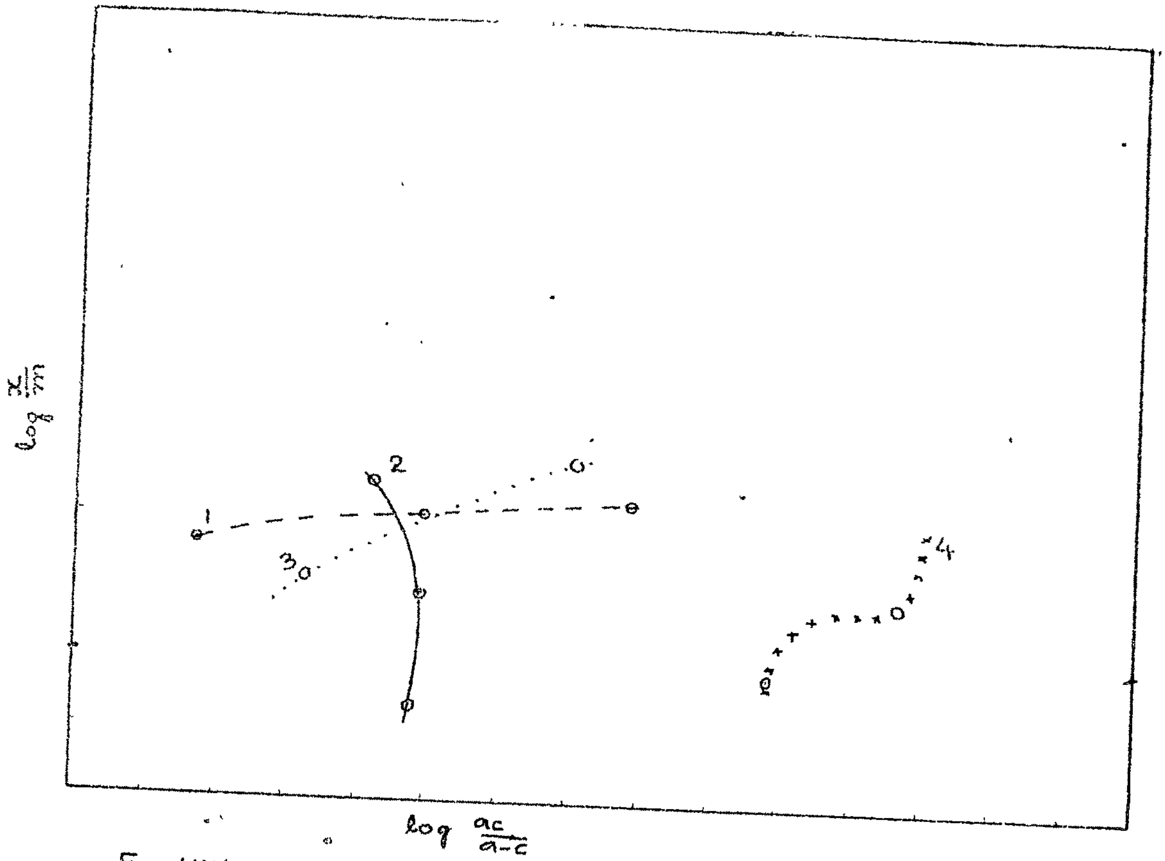


Fig VIII - F - 4(a) Alkali taken,
Sorption by (1) SAMF (2) SSAMF (3) RMF (4) OQMF

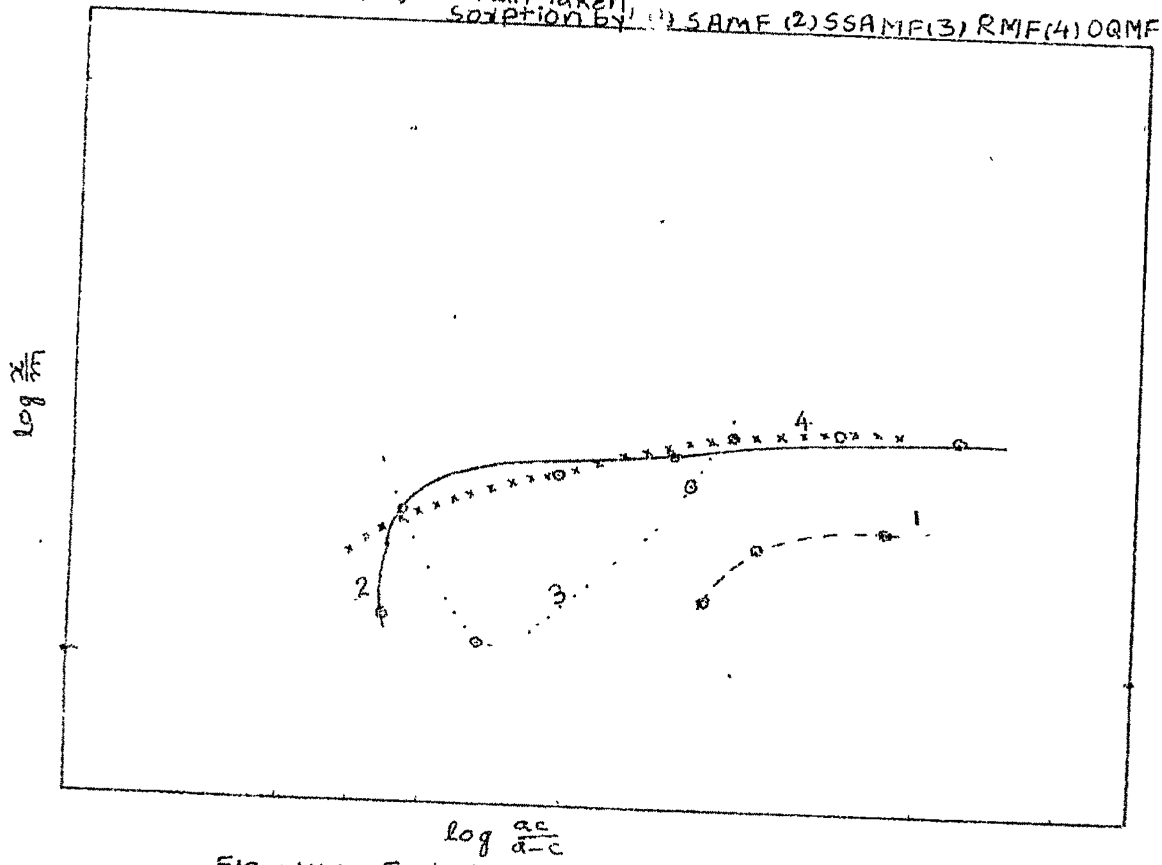
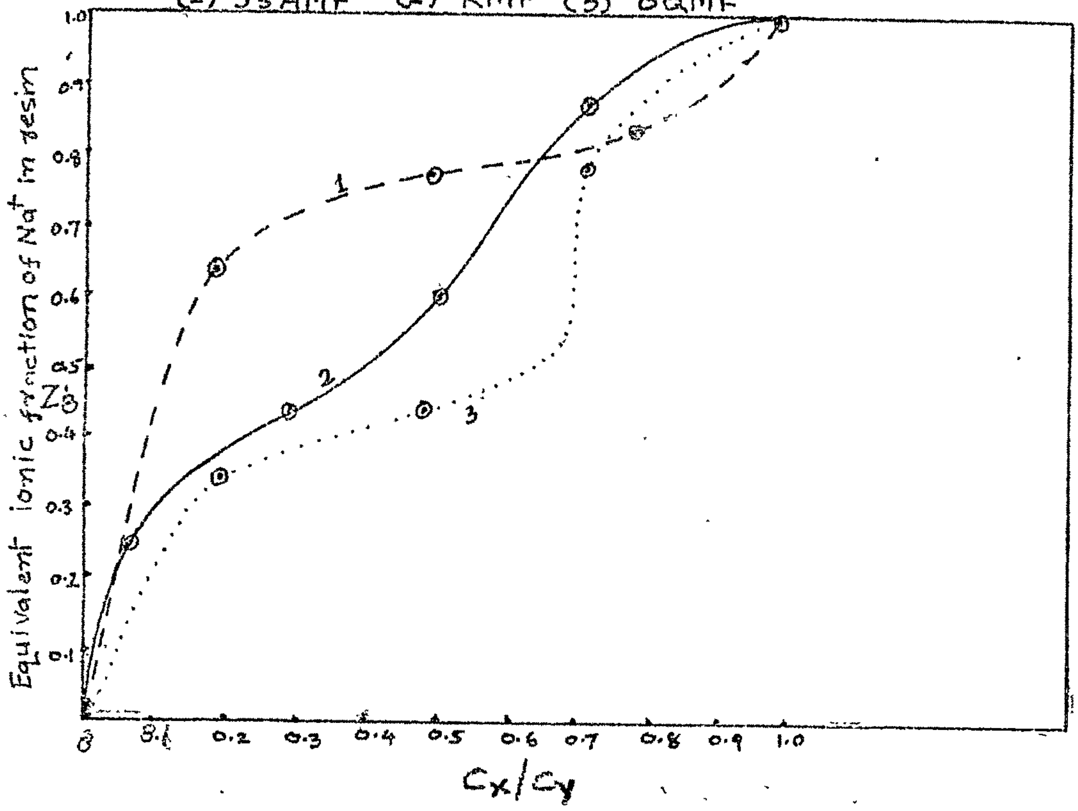


Fig - VIII - F - 4(b) Acid taken,
Sorption by (1) RMF (2) SAMF (3) RAMF (4) OQMF

Fig: VIII - F - 5(a) Isotherms for ion exchange H^+/Na^+ on ion exchangers:
(1) SSAMF (2) RMF (3) OQMF



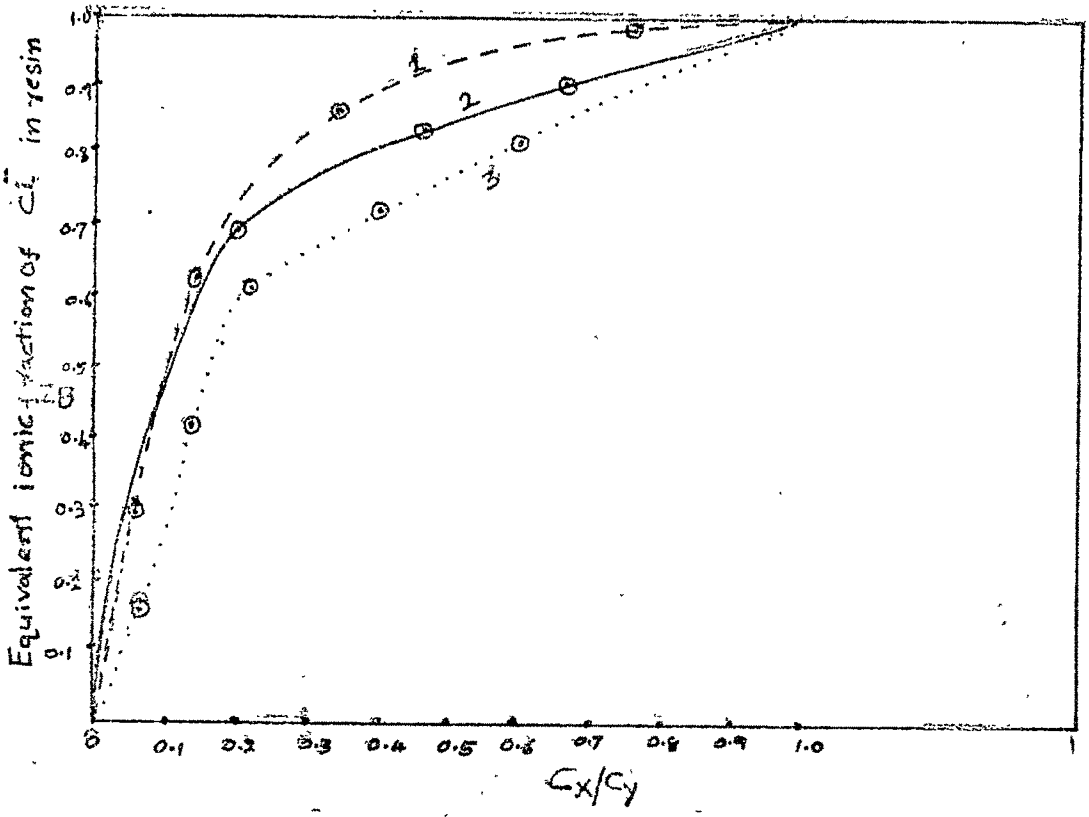
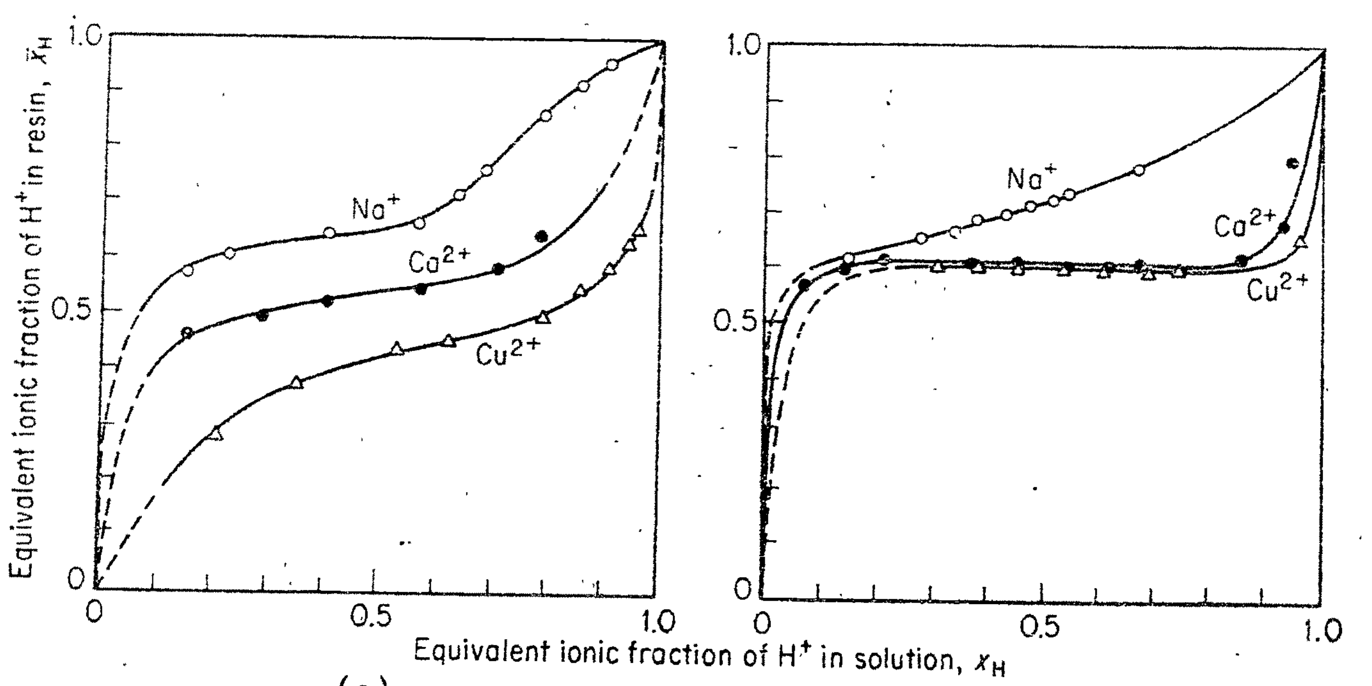


Fig - VIII-F-5(b) Isotherms for ion exchange OH^-/Cl^- on ion exchangers:
(1) SSAMF (2) RMF (3) OQMF



(a) (b)

Fig. VIII - F-6

Ion exchange isotherm of (a) bifunctional cation exchanger and (b) mixture of two monofunctional cation exchangers.

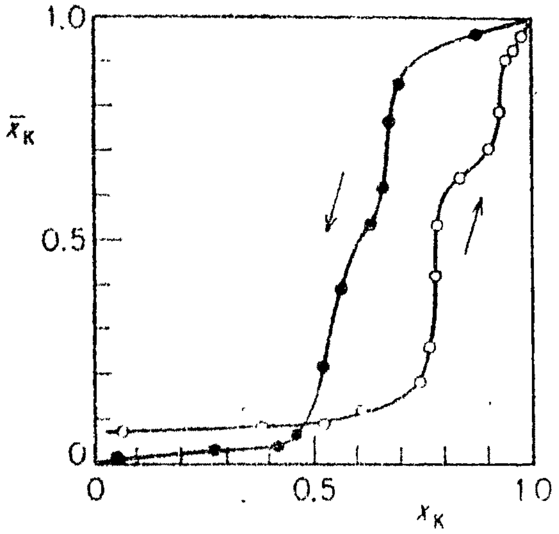
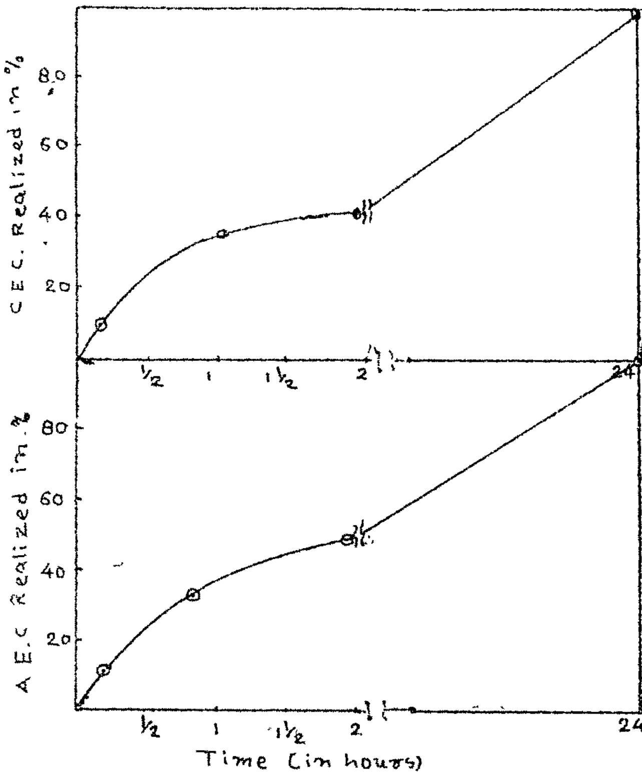


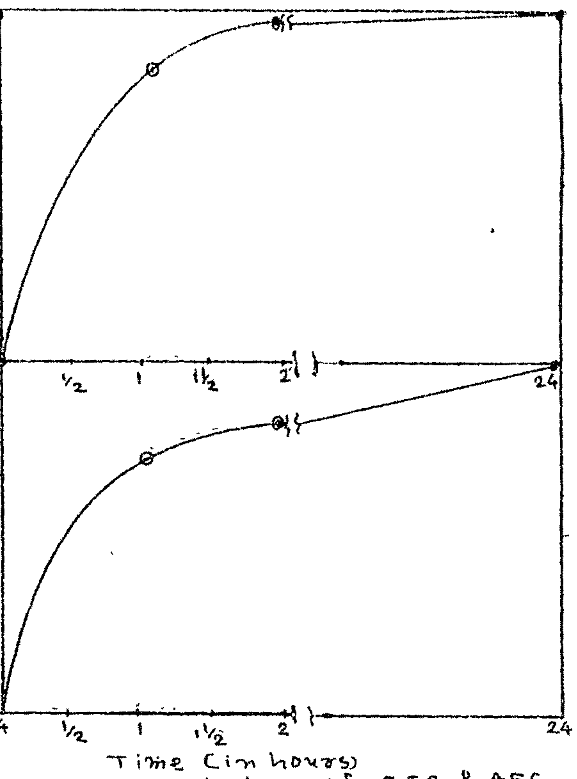
Fig. VIII - F-7

Ion exchange isotherm (equivalent ionic fraction of K^+ in the resin versus equivalent ionic fraction of K^+ in solution) of analcite - leucite at 110° C. (System with discontinious lattice rearrangement and hysteresis)



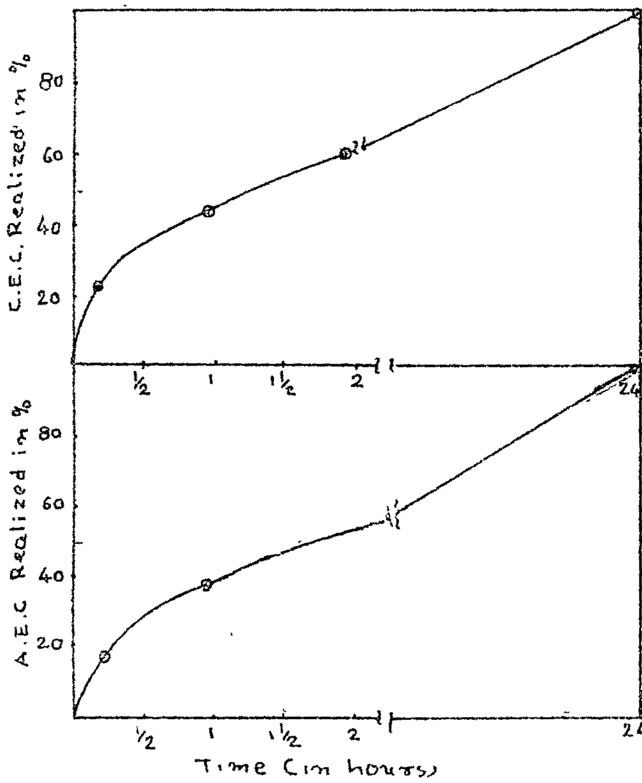
Rate studies of CEC AND AEC of SAMF

FIG - VIII - F - B (a)



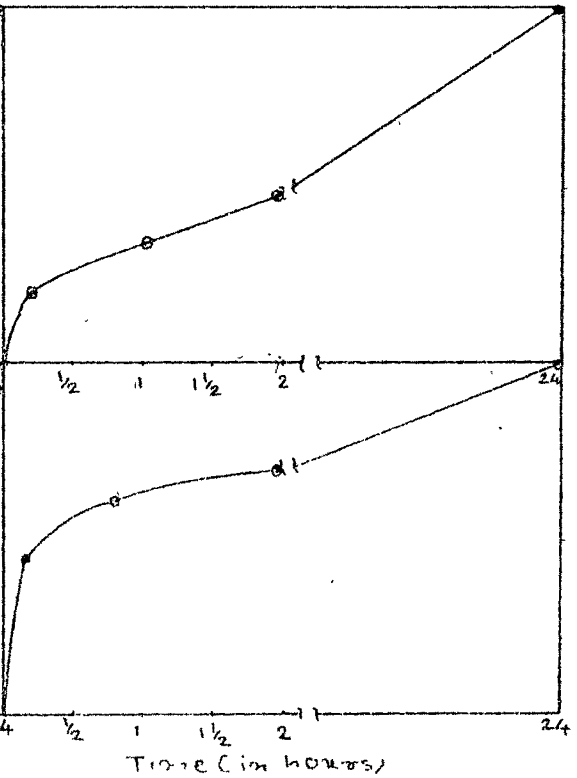
Rate studies of CEC & AEC of SSAMF

FIG - VIII - F - B (b)



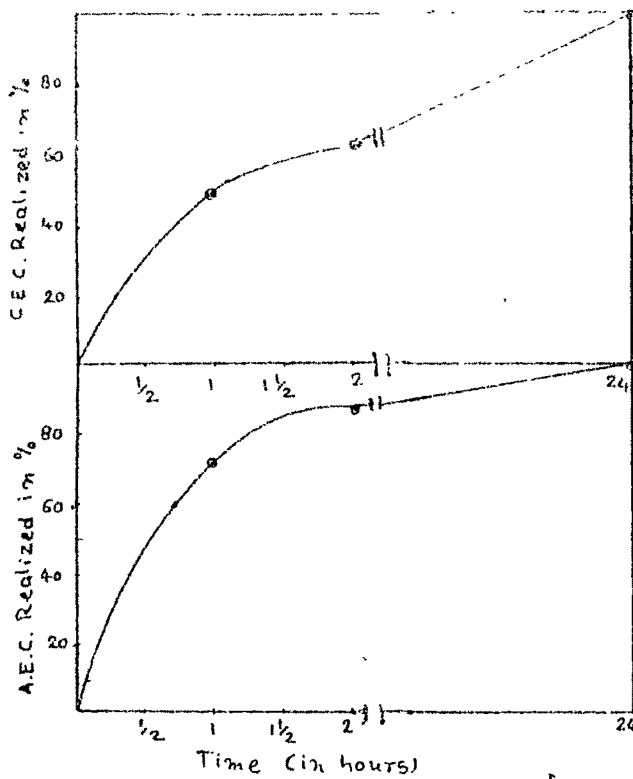
Rate Studies of CEC & AEC of NAMF

FIG - VIII - F - B (c)



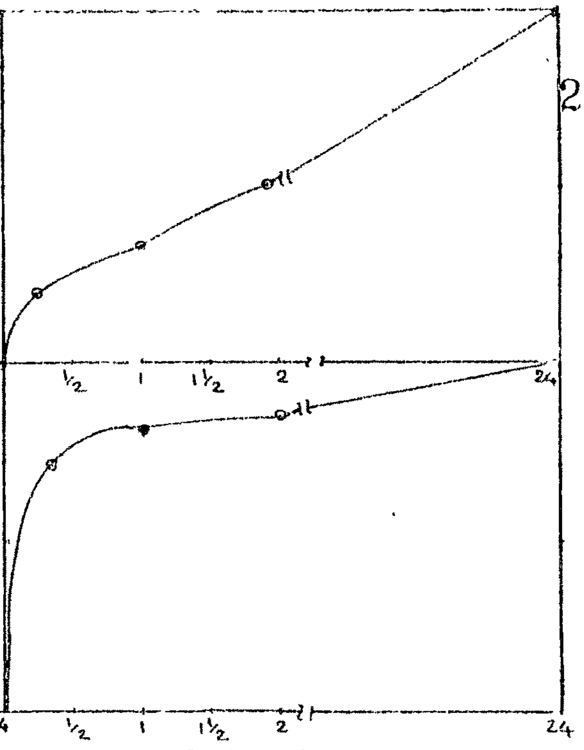
Rate studies of CEC & AEC of RAMF

FIG - VIII - F - B (d)



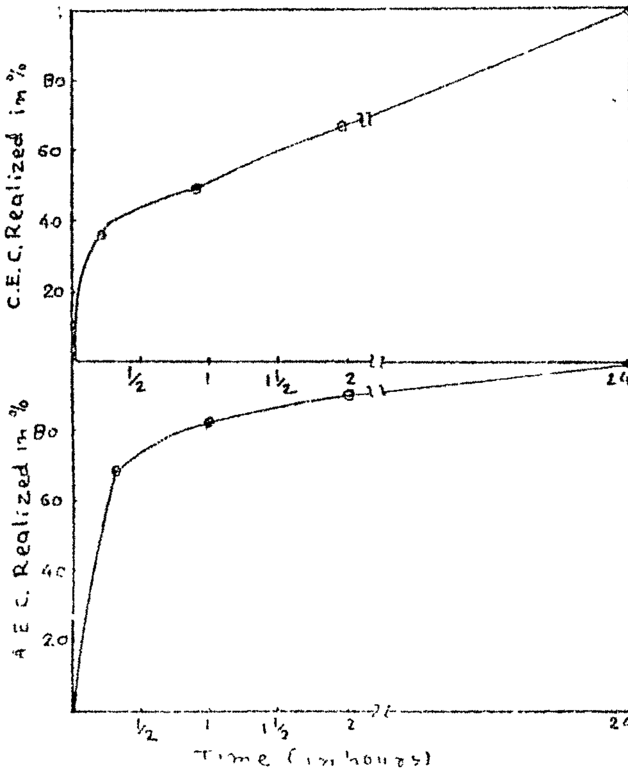
Rate Studies of CEC & AEC of RMF

FIG - VIII - F - 8(e)



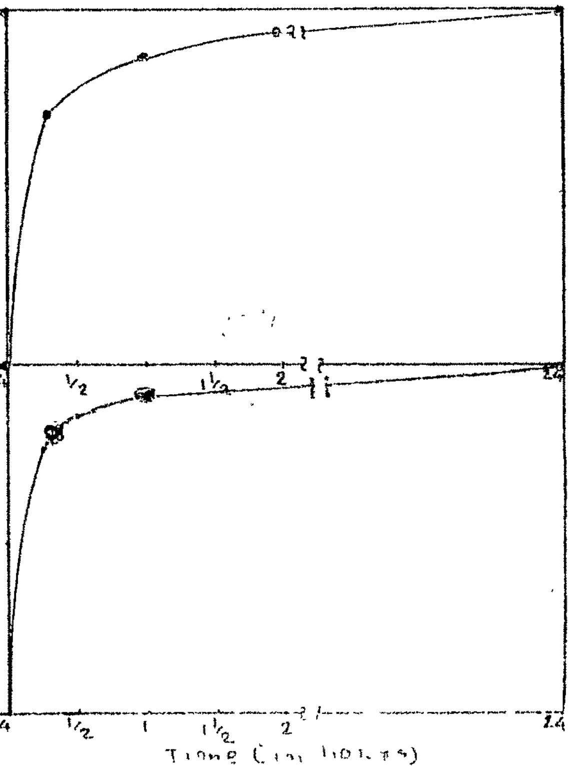
Rate Studies of CEC & AEC of CMF

FIG - VIII - F - 8(f)



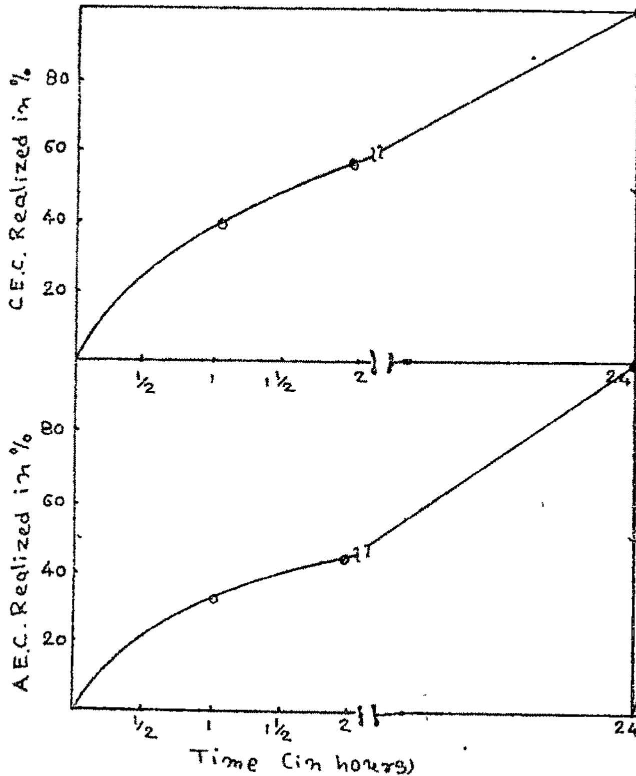
Rate Studies of CEC & AEC of QMF

FIG - VIII - F - 8(g)

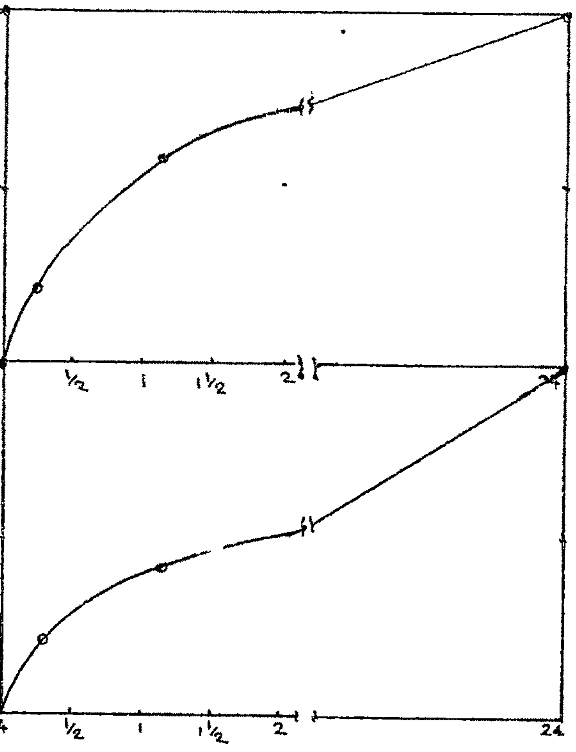


Rate Studies of CEC & AEC of GMF

FIG - VIII - F - 8(h)



Rate Studies of CEC & AEC of
<u>OQMF</u>
FIG - VIII - F - 8 (i)



Rate Studies of CEC & AEC of
<u>ASAMF</u>
FIG - VIII - F - 8 (j)

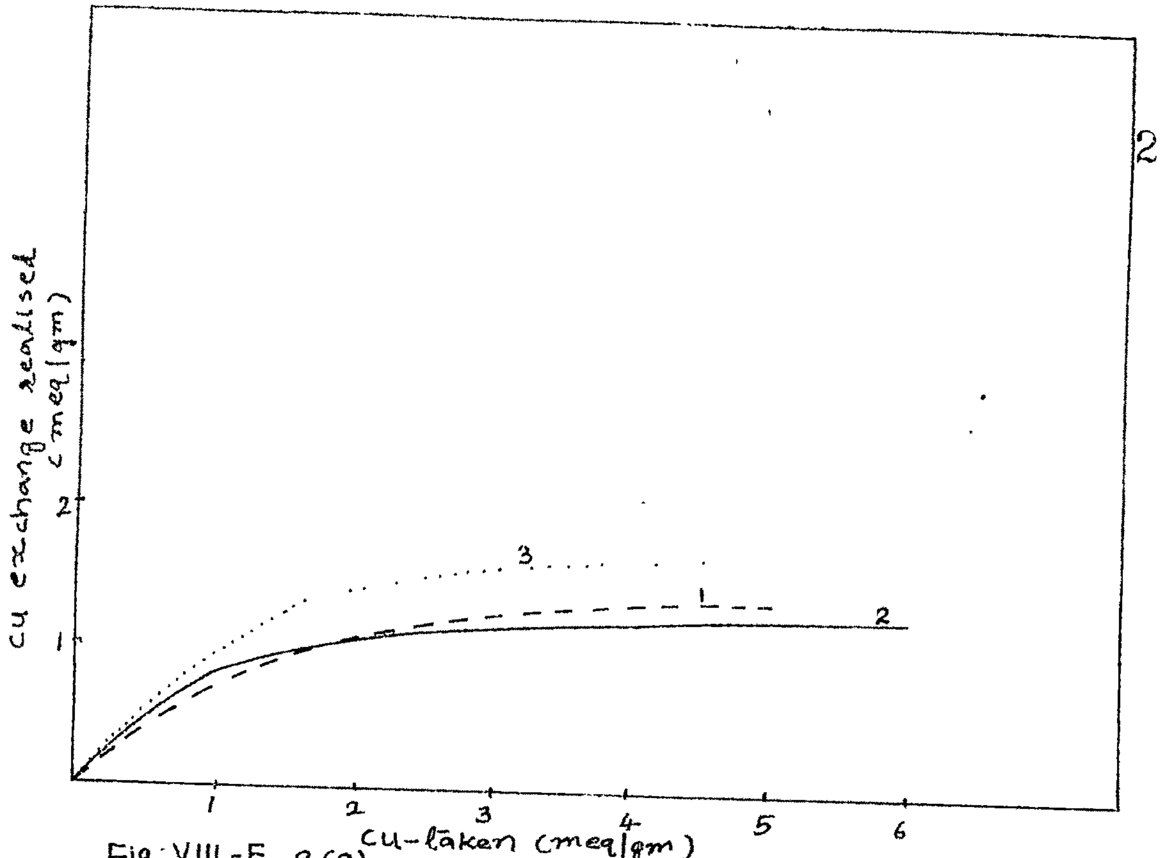


Fig: VIII-F 9.(a) cu-exchange: (1) RAMF (2). NAMF (3). RMF

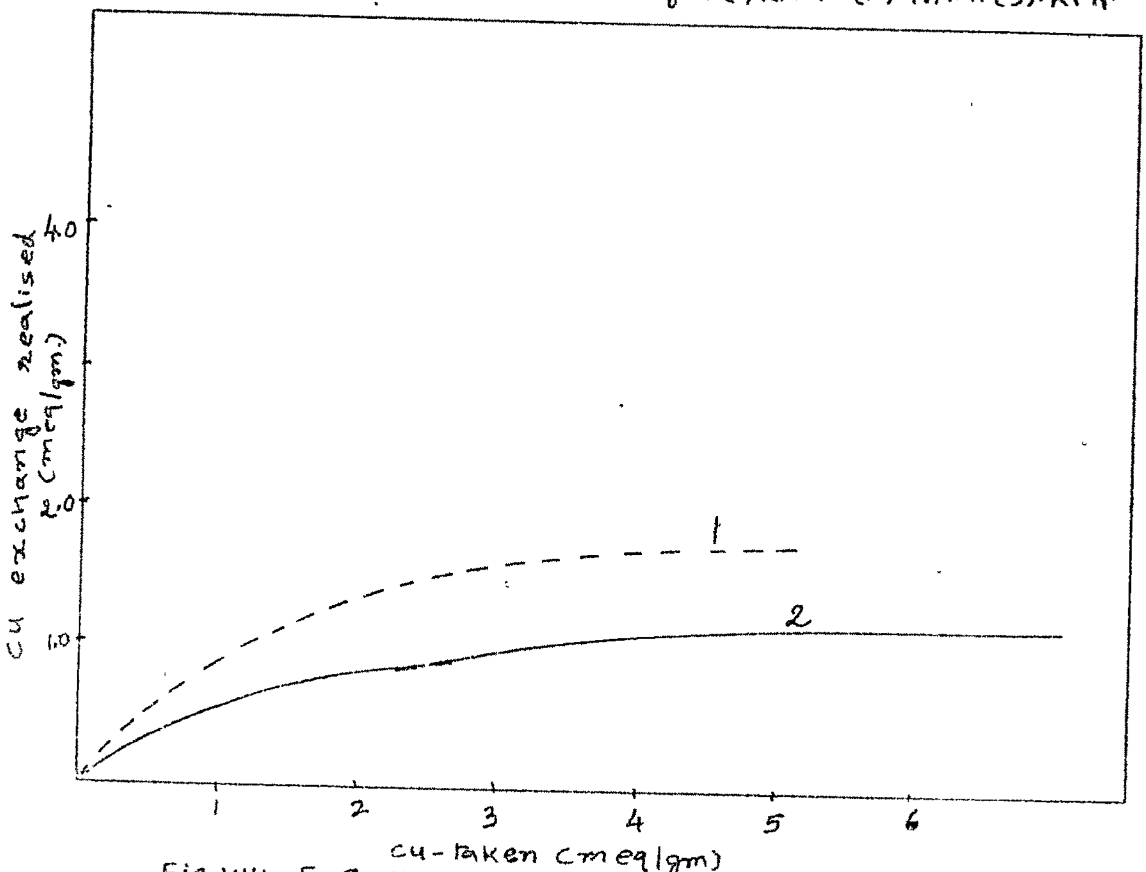


Fig. VIII-F-9 (b) cu-exchange: (1) GMF (2) CMF

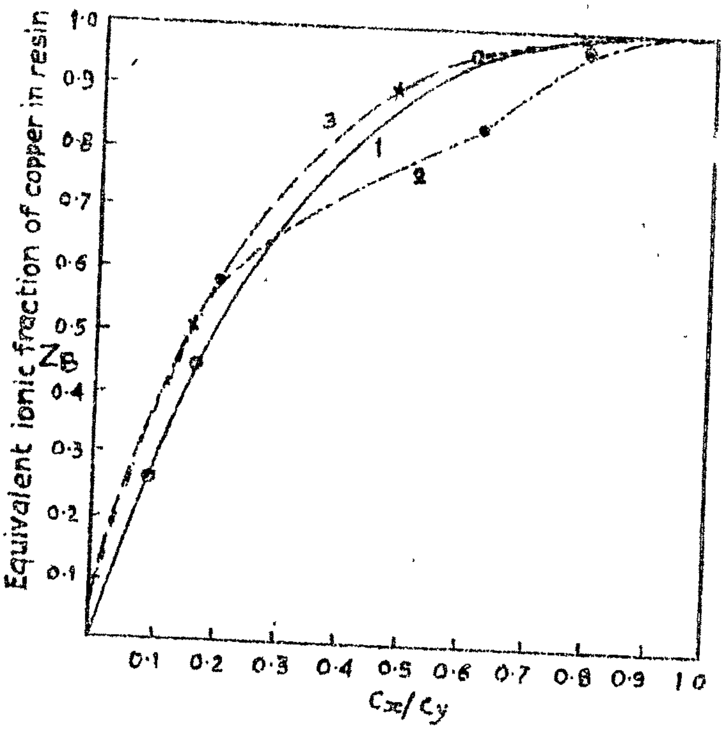
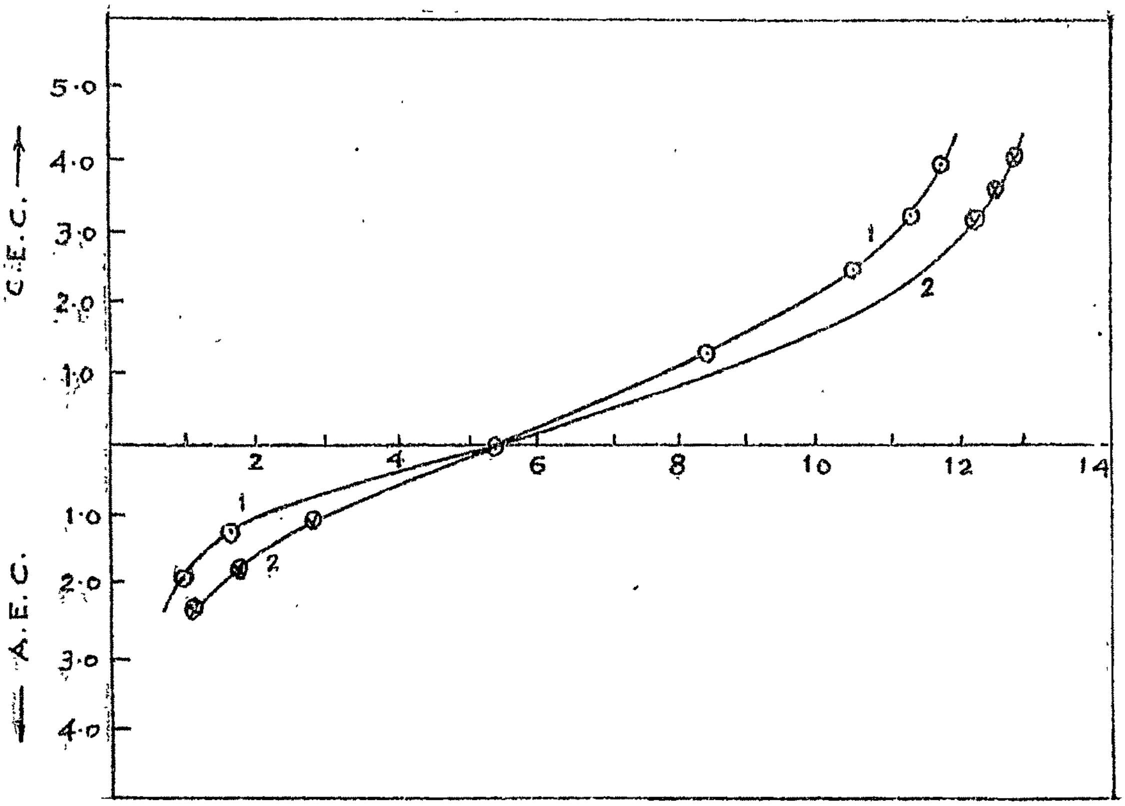
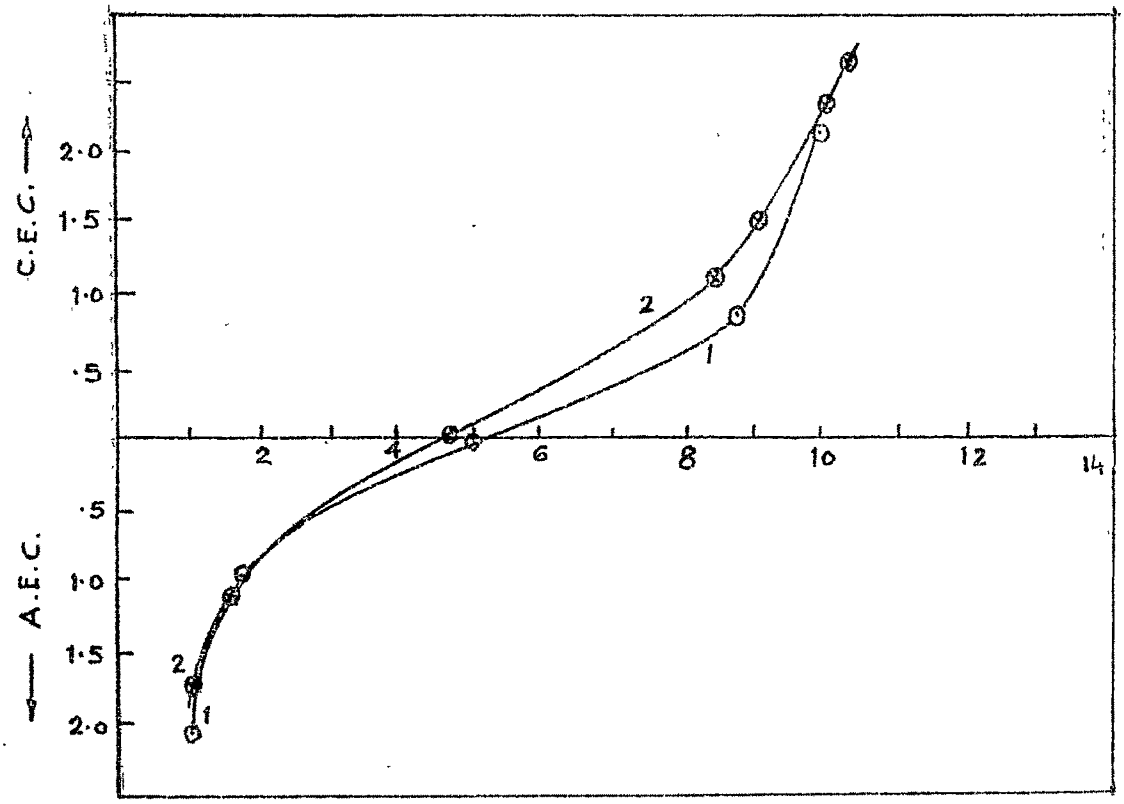


Fig. VIII-F-10 Isotherms for ion exchange
(1) RMF (2) NAMF (3) GMF



p^H Titration of S.U.F ($\odot_1\odot$) and SAUF($\otimes_2\otimes$)
Fig. VIII - F - II (a)



p^H Titration of QUF ($\odot_1\odot$) and RTF ($\otimes_2\otimes$)
Fig. VIII - F - II (b)

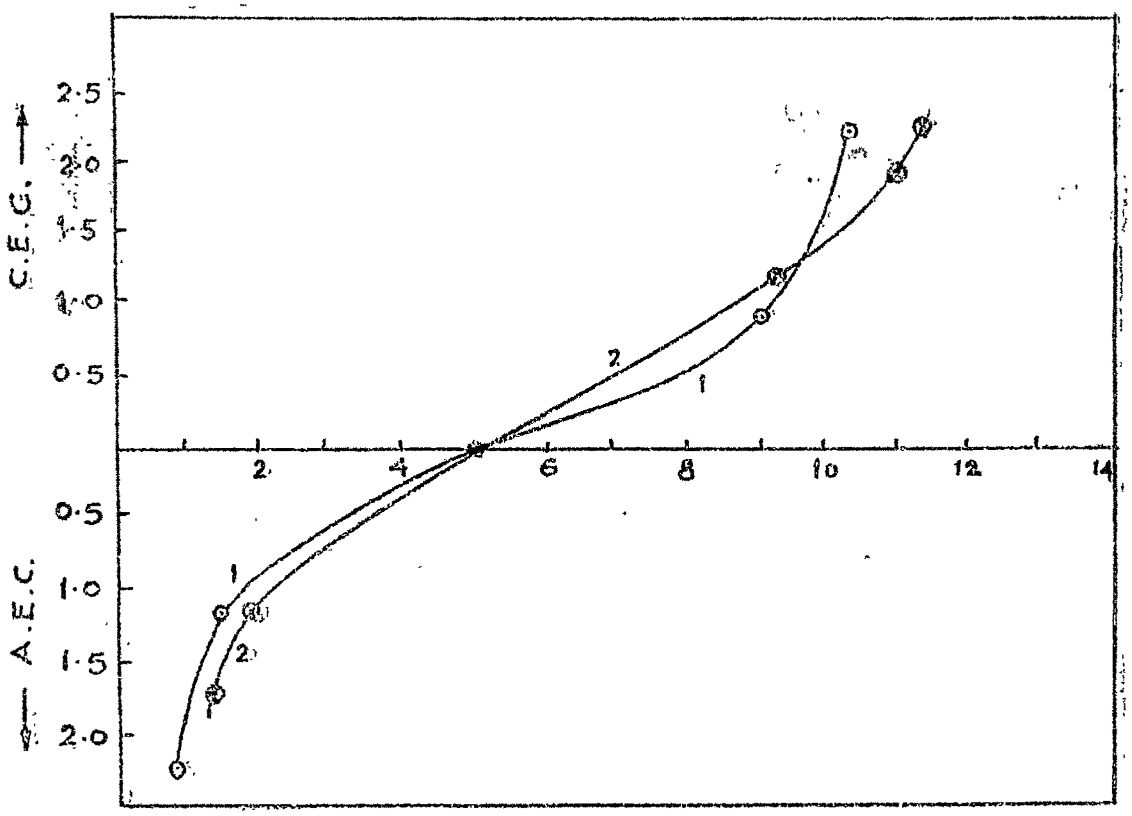


Fig. VIII-F-II(c) P^H Titration of $\overset{C}{\bullet}$UF$(\odot\underset{1}{-}\odot)$ and R$\overset{U}{\bullet}$F$(\otimes\underset{2}{-}\otimes)$

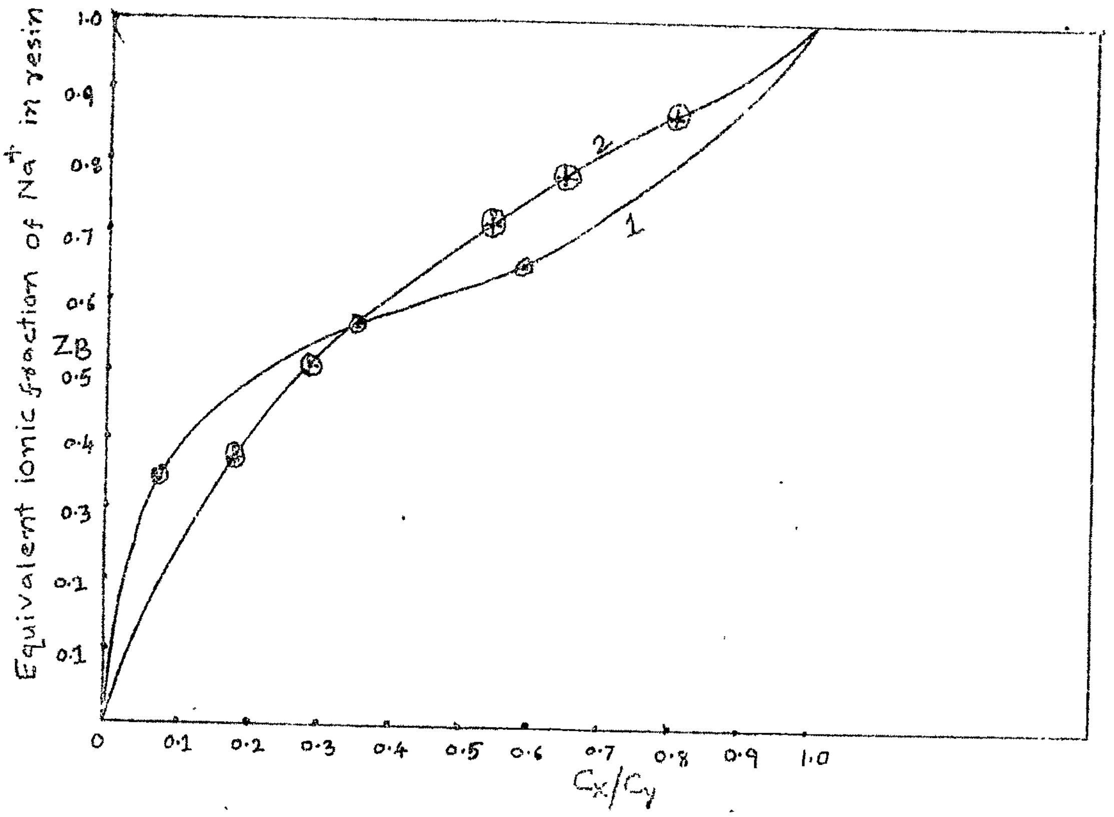
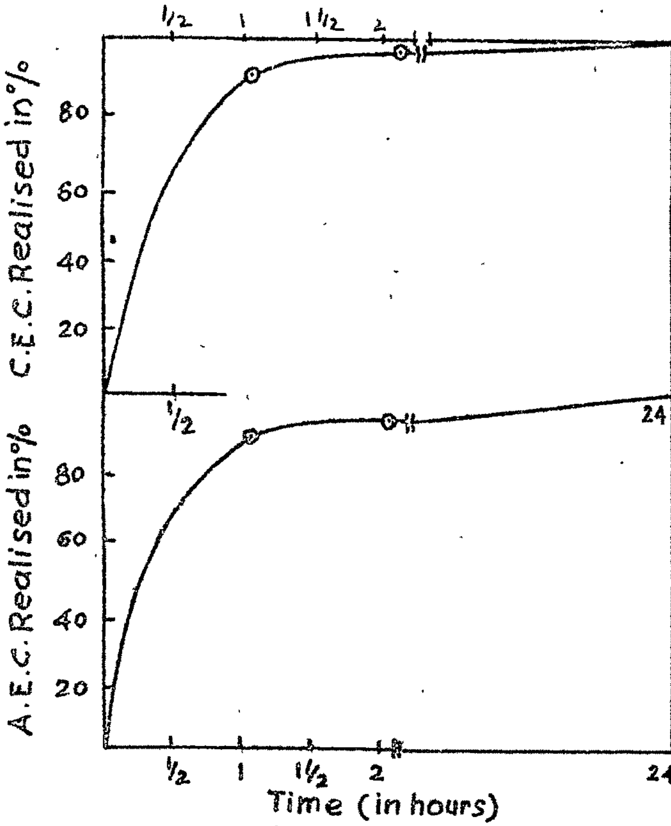
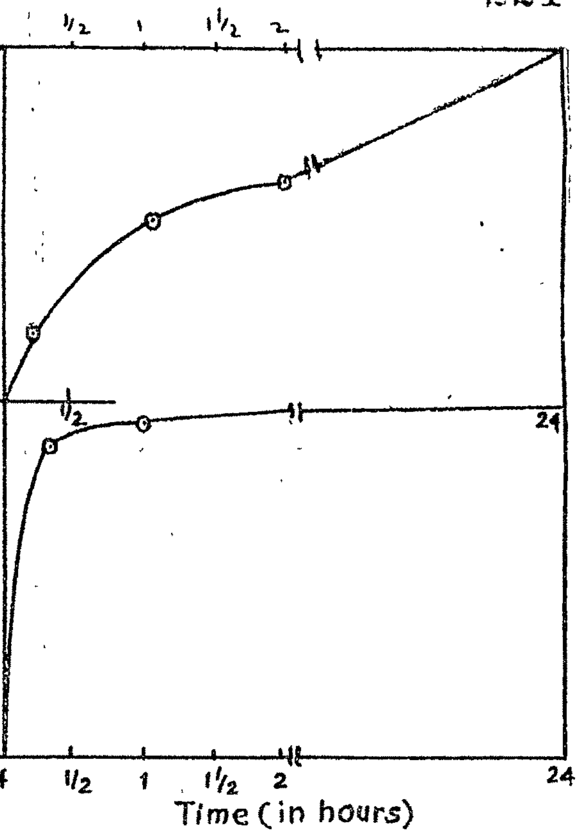


Fig - VIII - F - 12. Isotherms for ion exchange H^+/Na^+ on ion exchangers : (1) RUF[⊙⊙] (2) RTF[⊗⊗]



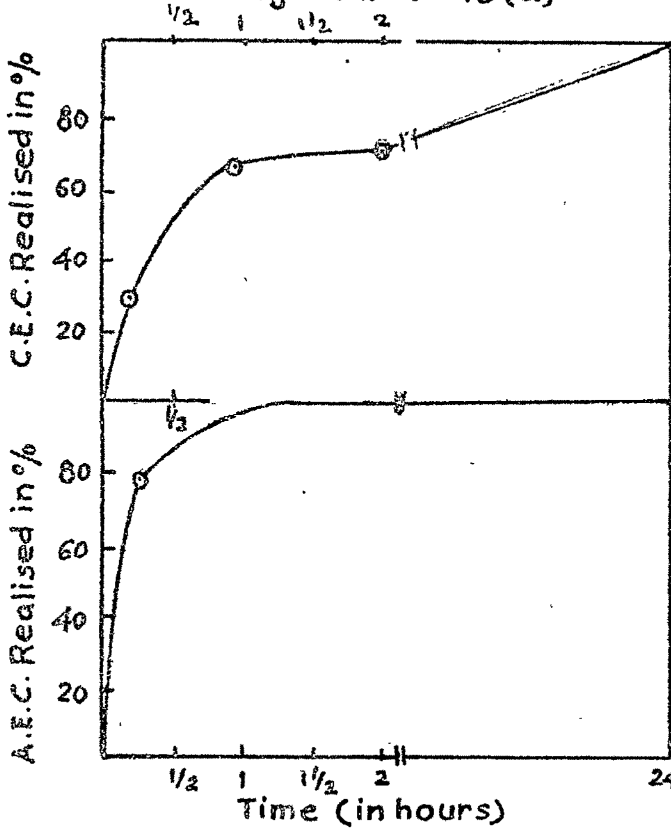
Rate studies of CEC & AEC of SAUF

Fig.- VIII - F - 13 (a)



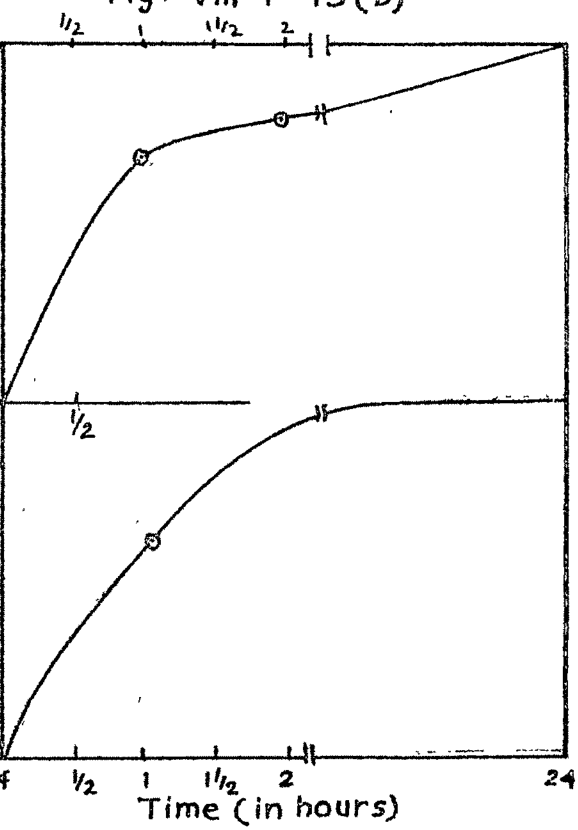
Rate studies of CEC & AEC of QUF

Fig.- VIII - F - 13 (b)



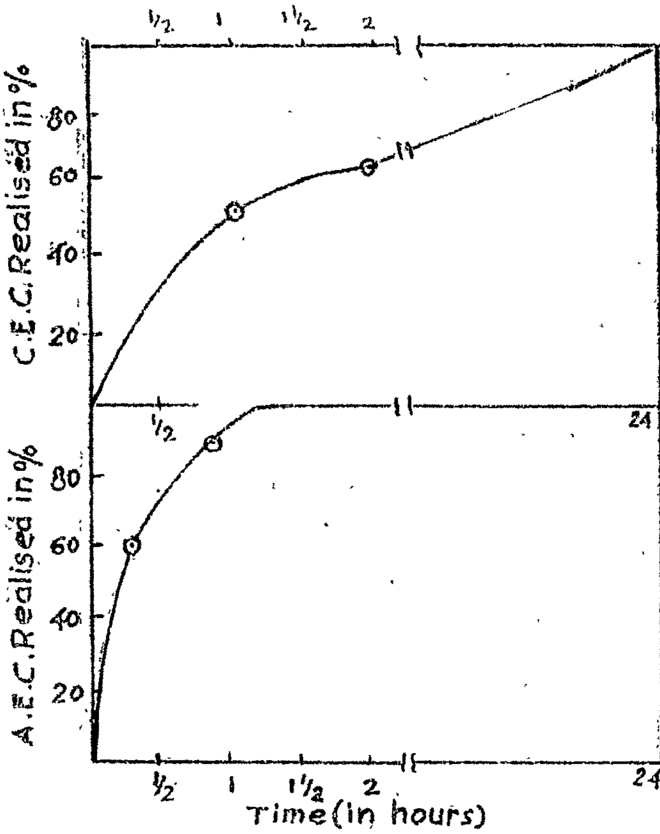
Rate studies of CEC & AEC of CUF

Fig.- VIII - F - 13 (c)



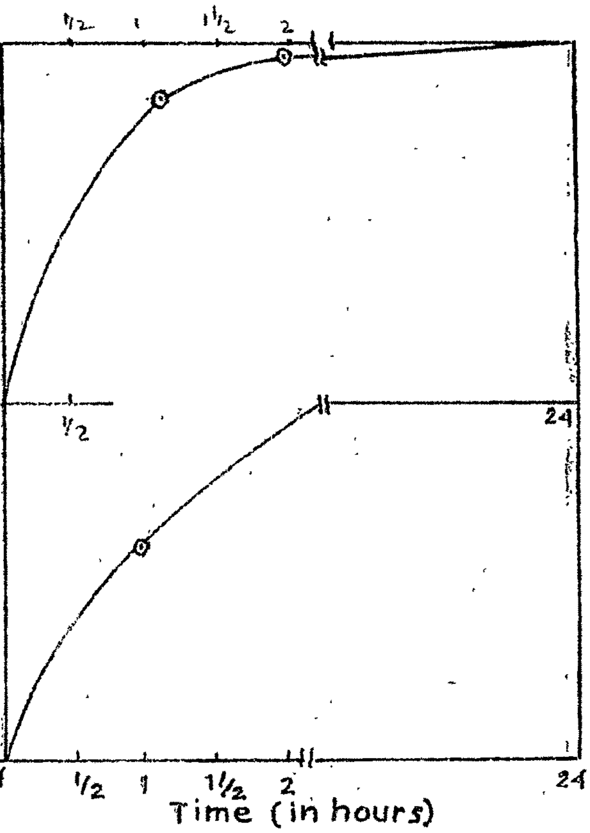
Rate studies of CEC & AEC of RUF

Fig.- VIII - F - 13 (d)



Rate studies of CEC & AEC of SUF

Fig. VIII - F - 13 (e)



Rate studies of CEC & AEC of RTF

Fig. VIII - F - 13 (f)

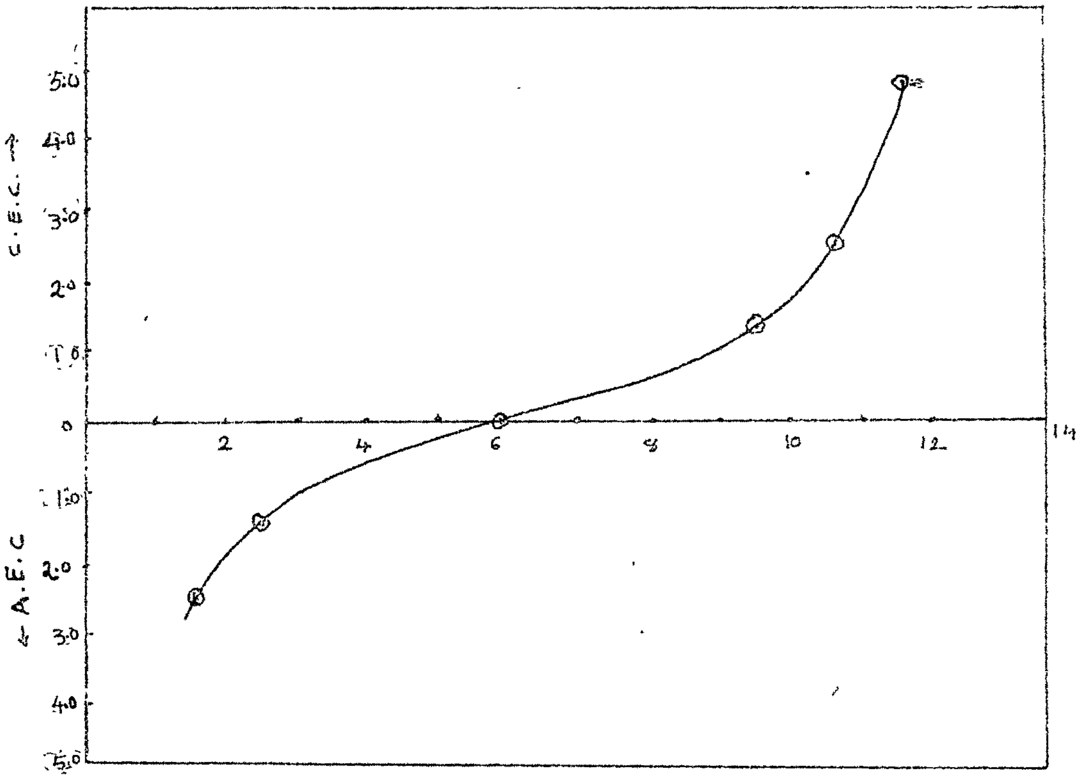


Fig - VIII - F - 14(a) pH Titration of CPPF

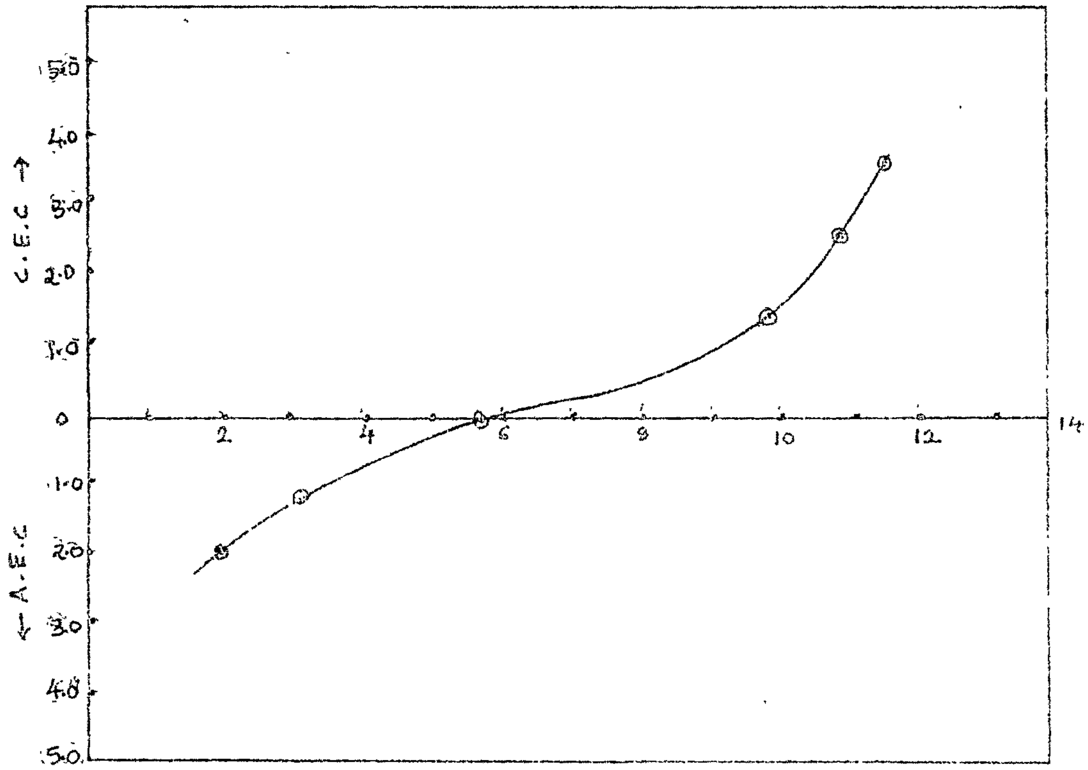
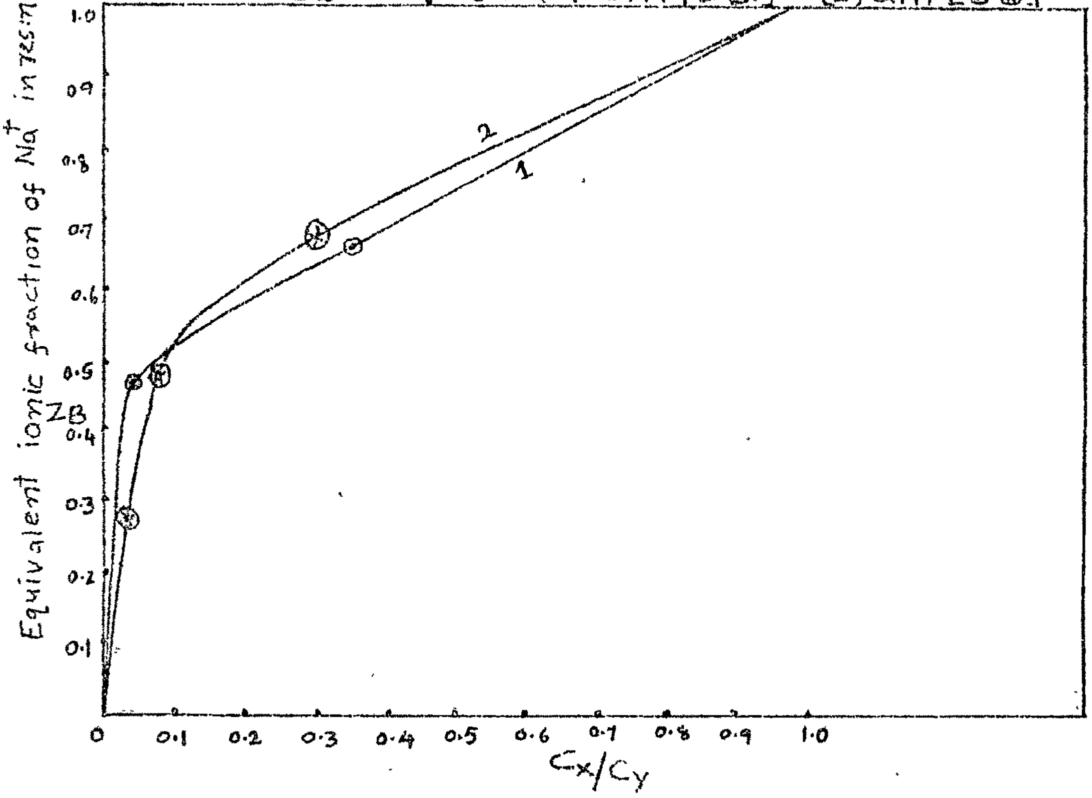


Fig - VIII - F - 14(b) pH Titration of GPPF

Fig- VIII - F - 15(a) Isotherms for ion exchange H^+/Na^+ on ion exchangers: (1) CPPF[⊙⊙] (2) QPPF[⊗⊗]



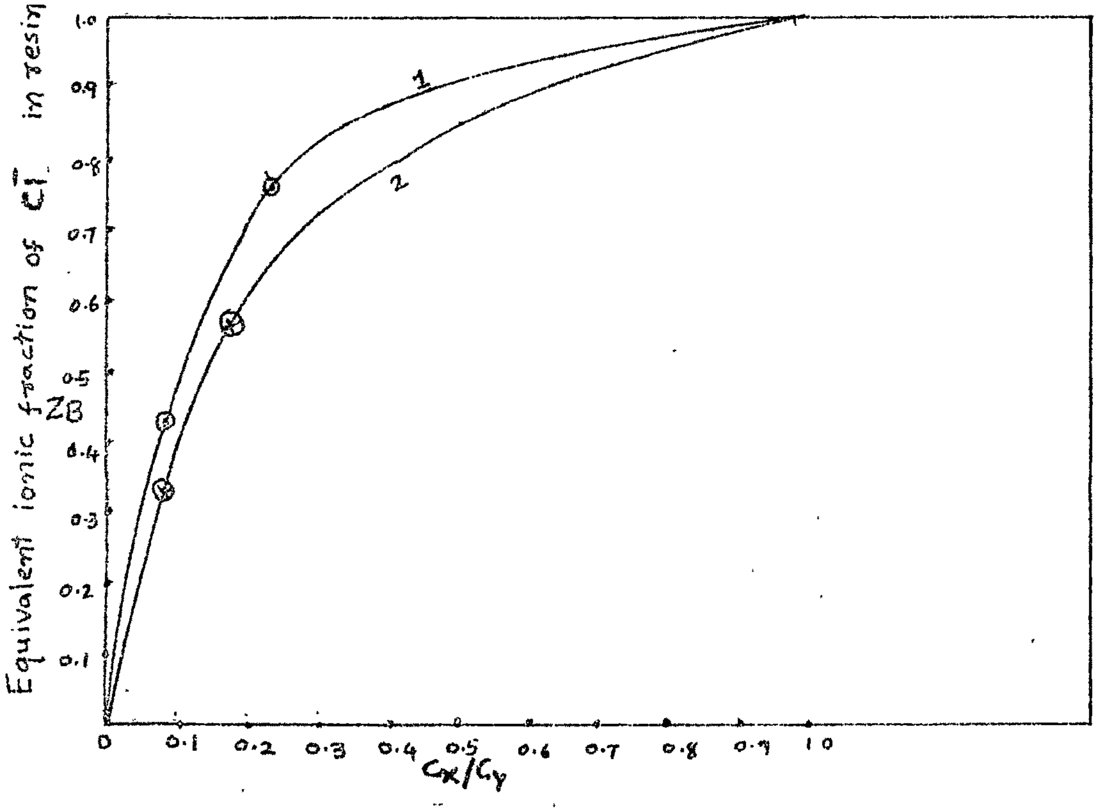
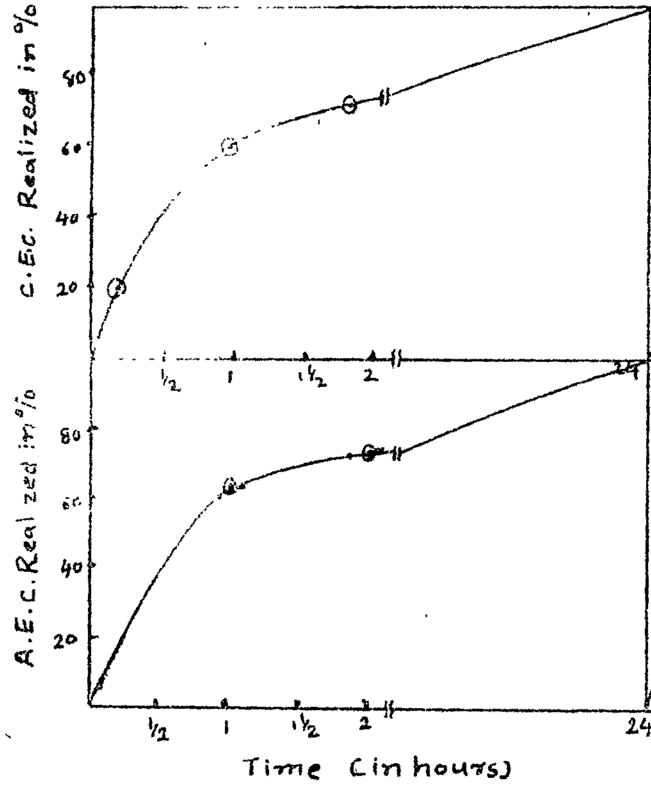
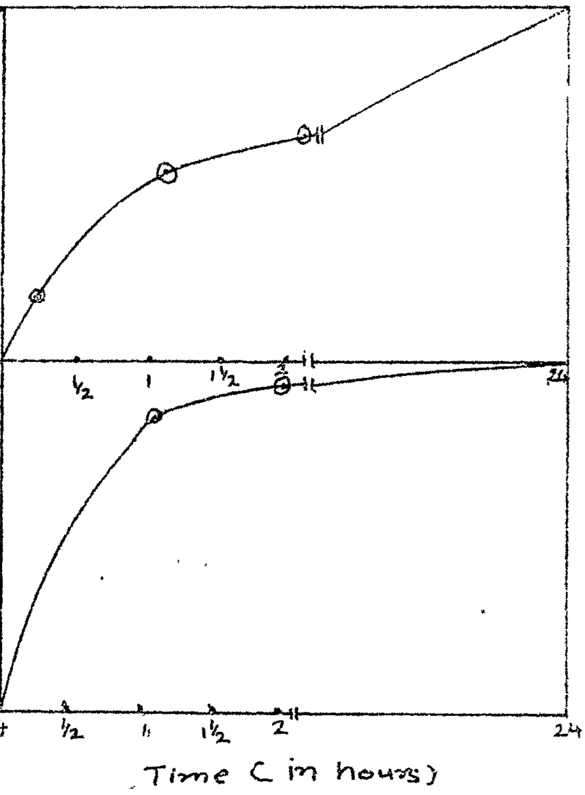


Fig- VIII - F - 15(b) Isotherms for ion exchange OH^-/Cl^- on ion exchangers: (1) CPPF[⊙⊙] (2) QPFF[⊗⊗]



Rate studies of CEC & AEC of GPPF

Fig- VIII- F - 16 (a)



Rate studies of CEC & AEC of CPPF

Fig-VIII- F- 16 (b)

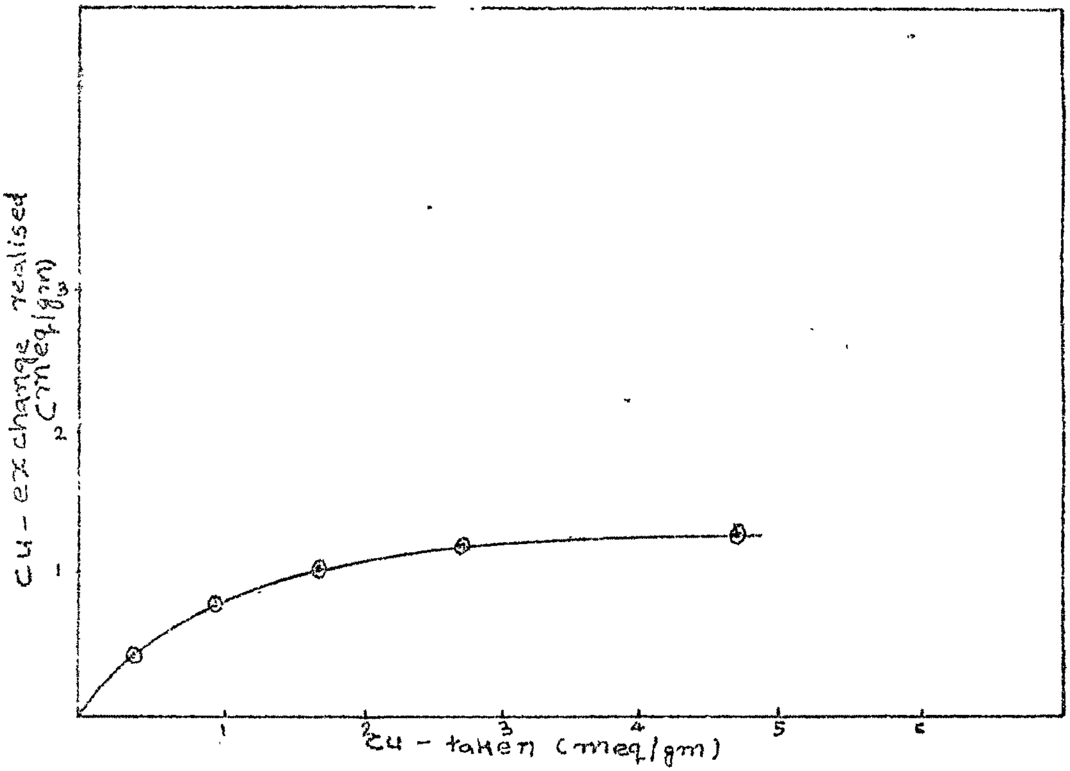


Fig. VIII – F – 17(a) Cu-exchange QUF

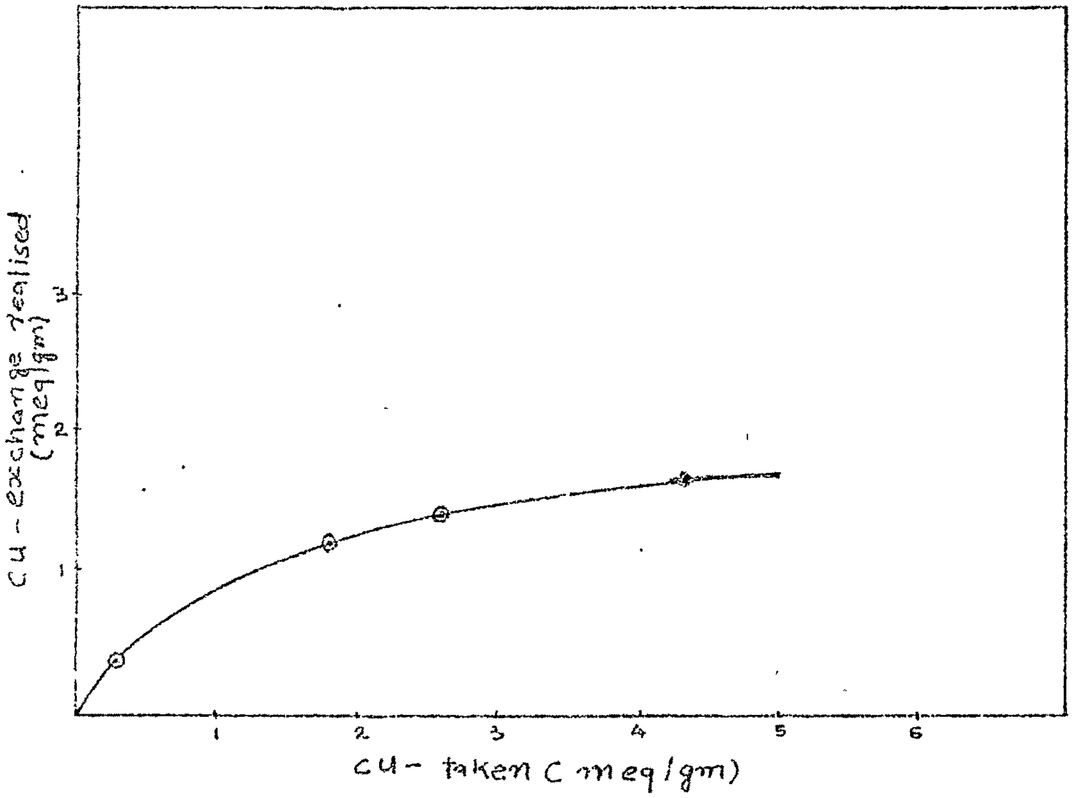


Fig. VIII – F – 17(b) Cu-exchange CPPF

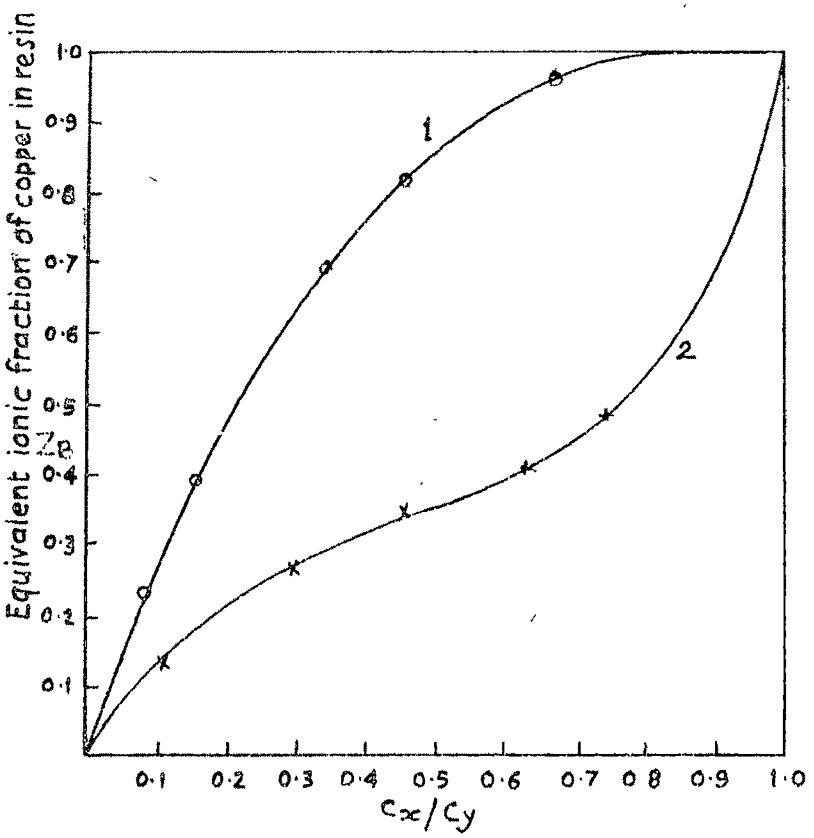


Fig. VIII-F-18 Isotherms for ion exchange
(1) QUF (2) CPPF

CHELATING POLYMERS

B : CROSSED-LINKED POLYMERIC NETWORKS AS ION-EXCHANGE RESINS

IX REFERENCES

CHELATING POLYMERS

B: CROSSED-LINKED POLYMERIC NETWORKS AS ION-EXCHANGE RESINS

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