CHAPTER I

I Poly (vinyl alcohol) - Phenolic Derivatives Type Ion-Exchange Resins

EXPERIMENTAL

I (a) Synthesis of ion-exchange resins

Phenolic derivatives such as anthranilic acid, gallic acid, p-hydroxybenzaldehyde, pyrogallol, 8-hydroxyquinoline, salicylic acid, hydroquinone or β-resorcylic acid (1 mole) were dissolved in 50 ml DMF and taken in 250 ml round bottom flask to this 2 moles of poly (vinyl alcohol) dissolved in 50 ml DMF was added. 4 gms of p-toluene sulphonic acid was added as initiator to the reaction mixture. The mixture was vigorously stirred and refluxed at 150^0c for 16 hours. Gel formation takes place in about 1 hour. A hard mass was obtained which varied in colour brown to dark brown to black for different phenolic monomers listed above. The gel product formed was washed with ethanol to remove unreacted monomer and low molecular weight product. The hard mass was cured at temperature 100^0c and crushed to -60 to 100 BSS mesh size as needed.

The resins were conditioned by alternate treatment with 0.1N HCl and 4% NaOH solution. After several regeneration cycles, the resins were washed free of regenerant and dried in an oven below 100^0c and stored in polyethylene bottles.

I (b) Moisture content of resins : (71)

Moisture content of the resins (H^+ form and OH^- form) was determined by drying an exactly weighed sample (0.5gm) (H^+ form or OH^- form) of the resin in an oven at 110^0-115^0c for 24 hours

and reweighing it after cooling it in a desiccator.

The calculation is,

$$\frac{\text{Weight of oven dried resin} \times 100}{\text{Weight of resin before drying}} = \% \text{ solid}$$

$$100 - \% \text{ solid} = \% \text{ moisture}$$

The values of % moisture content of resins are presented in Table - PA-3.

I (c) Density of resins

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

True density of resins (H^+ form and OH^- form) was determined by the specific gravity bottle method. A definite amount of the resin (H^+ form or OH^- form) was taken in a specific gravity bottle whose weight was determined previously and was weighed. There it was (1) filled with water in presence of resin and (2) alone and weighed. Hence the true density (d_{res}) was determined as follows :

$$d_{res} = \frac{W_r - W}{(W_s - W_{rs}) + (W_r - W)}$$

Where W = Weight of the specific gravity bottle,

W_r = Weight of the specific gravity bottle containing resin,

W_s = Weight of the specific gravity bottle containing water.

W_{rs} = weight of the specific gravity bottle containing water and resin.

(ii) Apparent density of resins : (d_{col})

Apparent or column density of resin (H^+ form or OH^- form) was determined as follows :

A definite amount of the resin (H^+ form or OH^-) form was suspended in water. The suspension was introduced into a graduated glass column which was plugged at the lower end. Resin was allowed to settle as water gradually flows through the plug. Some more water was passed through the plug and when all excess passes out, the volume of the column was read. The resin was then taken out and allowed to dry at room temperature till constant weight, hence the column density (d_{col}) was determined as follows :

$$d_{col} = \frac{\text{Weight of resin}}{\text{Volume of resin bed}}$$

The values of d_{res} and of d_{col} are presented in Table-PA-4.

(iii) Void volume of resins :

The following three methods are known for the determination of void volume.

(1) Simple volume measurements

(2) Titration

(3) Calculation from density data.

We have adopted the third method, since the results obtained by first two methods are usually low about 5%.

The void volume is calculated by following formula :

Void volume fraction = $1 - d_{col} / d_{res}$

The results are presented in table - PA - 5

I (d) (i) Total ion-exchange capacity : (72)

Approximately 10 gms of the resin were weighed and taken in the beaker and converted into H^+ form with one litre of one normal hydrochloric acid. The resin was filtered, washed to neutrality with distilled water. The sample was made (air-dried). Then the sample was stored in polyethylene bottles. Similarly, resin was converted into OH^- form with one litre of 4% sodium hydroxide solution.

About one gram (exactly weighed) sample of the resin (H^+ form or OH^- form) prepared as above, was taken in dry 250ml erlenmeyer flask. A similar sample was used to determine the moisture content as suggested earlier. To the sample (of H^+ form) in erlenmeyer flask, were added 200 ml of standardized 0.1 N sodium hydroxide in 1 N sodium chloride solution and to the sample of (OH^- form) in erlenmeyer flask, were added 200ml of standardized 0.1N hydrochloric acid in 1N sodium chloride solution. The mixture was kept for 24 hours, 50 ml aliquots of the supernatant liquid were titrated with standard 0.1N acid and standard 0.1N alkali solution. The total cation exchange capacity is calculated as follows :

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

Milliequivalents of cation exchange capacity = CEC gms. of dry H^+ form resin. Similarly, total anion exchange capacity is calculated as,

$$\frac{(200 \times N.HCl) - 4(ml.\ base \times N.base)}{Sample\ weight \times (\%\ solid) / 100}$$

Milliequivalents of anion exchange capacity =
AEC gm. of dry OH form resin.

(ii) Volume capacity of resins :

From the weight capacity of resins volume capacity of the resins is evaluated as follows :

Concentration of fixed ionogenic groups (Cr)

For the resin is evaluated by the following relation :

$$C_r = d_{res} \times \frac{(100 - \%\ moisture)}{100} \times EC$$

Where EC is the exchange capacity (weight) of the resin, Hence the volume capacity (Q) of the resin is evaluated as follows :

$$Q = (1 - \text{void volume fraction}) \times C_r$$

The values of total exchange capacity, concentration of ionogenic groups and volume capacity of resins are presented in Table-PA-6A and Table-PA-6B.

I (e) 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 10% ammonia solution. The mixture was kept for 24 hours. 50 ml aliquots of the supernatant liquid were titrated with standard 0.05M EDTA Solution. The copper exchange capacity is calculated as follows :

$$\frac{(200 \times N \text{ Copper II}) - 4\ (\text{ml EDTA} \times N.\ \text{of EDTA})}{\text{Sample weight} \times (\%\ \text{solid})\ /100}$$

= Milliequivalents of Cu-exchange/gms of dry H^+ form resin

= (Cu ion) Exchange capacity

The results are presented in Table-PA-6A.

I (f) Rate of exchange :

The H^+ form (or OH^- form) of the resin (0.5gm) (-60 + 100 mesh) was accurately weighed into eight to nine different stoppered bottles. 100ml 0.1 N NaoH in 1N NaCl (or 100ml 0.1N HCl in 1N NaCl) added to each bottle and the resin is allowed to remain in contact for different periods of time, with intermittent shaking. At definite predetermined intervals, the solutions were decanted and an aliquot was titrated against standard acid or standard alkali and from this the capacity realized at different time intervals was calculated. The values of the capacities of the resins were plotted against time and shown in figs 1 to 4 and presented in Table-PA-7.

I (g) pH-titration studies and Apparent pK_a and pK_b values : (72)

The OH^- form of the resin (0.1 gm) (-60 to 100 mesh) was accurately weighed into different stoppered bottles and to each bottle 0.1N HCl in 1 N NaCl and 1 N NaCl solutions were added in different proportion to make up the volume to 150 ml and to give solutions of varying pH in the range 1-7. Similarly, in different stoppered bottles, accurately weighed H^+ form (0.1gm) of the resin was treated with 0.1 N NaOH in 1 N NaCl and 1 N NaCl

solution in different proportions to make up the volume to 150 ml and to give solutions of varying pH in the range 7-12. The resin was kept in equilibrium with the mixture for 24 hours and then residual acidity or basicity and pH were determined . The values of the capacities of the resins were plotted against the pH of the solution and shown in figs. 5 to 7.

The apparent pK_a and pK_b values for these resins are presented in Table-PA-8. The pH meter used for the practical purpose was Digital pH meter, Digichem 8201.

I (h) Effect of temperature of equilibration on capacity of resins : (73)

Definite amounts (0.5gm) of the resin (H^+ or OH^- form) (-60 to 100 mesh) were allowed to equilibrate with 100 ml each of standard NaOH in 1 N NaCl solution or standard HCl in 1 N NaCl solution at room temperature (30^0C) for 2 hours and then the capacity of the samples determined. The same experiment was repeated at 50^0 and 70^0 using a thermostat. The results are presented in Table-PA-9.

I (i) Oxidation resistance test : (74)

Exactly weighed (0.5gm) (-60 to 100 mesh) free acid or free base form of the resin was treated with 10-20 ml of 6% (W/V) hydrogen peroxide solution in 100ml conical flask at 45^0 C for 72 to 95 hr. Then the resin was quantitatively transferred from the flask and subjected to the moisture content determination as usual.

The results are presented in Table-PA-10A and Table-PA 10B.

I (j) Swelling behaviour : (75)

Swelling behaviour of resins in non-aqueous solvents were determined by adopting following procedure.

30 to 40 ml of the dried resin (H^+ form OH^- form) were poured into 100 ml of graduated cylinder without shaking or tapping and the initial volume was read to the nearest 0.5 ml. The resin was then covered with the solvent to 100 ml mark. After 120 hours the volume was again read and percent swelling was calculated as follows.

$$\% \text{ Swelling} = 100 \times \frac{\text{Final volume - Initial volume}}{\text{Initial volume}}$$

The results are presented in Table - PA - 11 A and Table PA-11B.

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RESULTS AND DISCUSSION

General :

Recently PVA is the most wide used domestic plastic and adhesive of the day but its thermal instability still is regarded as the most important draw back. Keeping in view the more important attempts to modify PVA, which will be highlighted in the following pages - The present research claims at modifying some of the important properties of PVA through incorporation of reactive moieties in the PVA chain by a simple-OH displacement reaction. This research is also concerned with the synthesis and characterization of a novel ion exchanger.

General Characteristics and Structure :

The ion-exchange resins, in general are fairly porous in nature with average physical stability and good chemical resistance to 3N acids and alkalis and exhibit no change when converted from the free acid form to sodium form or from free base form to chloride form.

It is not possible to assign definite structures for the polymeric composition and hence attempts have been made to assign the most likely structures of these resins on the basis of analytical data. (Table-PA-2). Apparently the structure is linear and fairly cross-linked. It is the most probable structure for the polymeric resins, and their physico-chemical studies are

shown as -

(i)	Poly-A-Anthra	(ii)	Poly-A-Galli
(iii)	Poly-A-PHyBe	(iv)	Poly-A-Pyro
(v)	Poly-A-8Hyqui	(vi)	Poly-A-Sali
(vii)	Poly-A-Hyqui	(Viii)	Poly-A-βRes

(a) The study of these structures leads us to believe that the various end products are not identical.

(b) All phenolic derivatives get condensed with PVA in molar ratio of 1:2

Gelling and Curing :

The formation of the resin is characterised by the gel point. Gel point or gel period is related to branching ability and hence the functionality of the monomer involved in condensation (76). If the condensing monomers exhibit functionality of two, a linear chain would result of the condensing monomers, exhibit the functionality greater than two, branching may be obtained and gelation. Curing involves the thermosetting of gel. In the series under investigation, gelling time and curing period for all the resins are same, hence we suggest that gelling time and curing period are directly related to phenolic compounds functionality only.

Moisture retention% :

Percentage moisture of the resins are presented in Table-PA-3. The percentage moisture of the resins in H^+ form varies between 2.27 to 7.16, while the percentage moisture of the resins in OH^- form varies between 2.35 to 6.15. Low range of percentage moisture suggest that the resins have a fairly good degree of

cross-linking.

The moisture content of resins can be related to

(a) Concentration, valency and solvation tendency of counter ions,

(b) Concentration and solvation tendency of the fixed ionogenic groups.

(c) Degree of cross-linking, and

(d) Electrostatic interaction of ions in the resins. The degree of cross-linking in resin is neither controlled nor known, even then it can be suggested that higher degree of cross-linking may lead to lower moisture content. Influence of structure feature of condensing agent is however apparent. We find in general that the moisture content of resin increases in terms of the condensing agent.

Poly-A-8Hyqui < Poly-A-sali < Poly-A-βRes < Poly-A-Anthra
> Poly-A-PHYSC ≒ Poly-A-pyro ≒ Poly-A-Hyqui < Poly-A-Galli

Difference in the value for the resins in H^+ form and OH^- form is small and hence we suggest that the resins can stand recycling to a good degree.

Density of resins :

The results of true density (d_{res}) and apparent density (d_{col}) are presented in Table-PA-4. The values are ranging from 0.39 to 0.55 gm/cm3 for H^+ form of resins and 0.45 to 0.50 gm/cm^3 for OH^--form of resins. We observed that, in the case of resin Poly-A-Anthra and Poly-A-8Hyqui d_{res} for OH^- form is slightly higher than that of H^+ form.

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

We have also evaluated the apparent (column) density (d_{col}) of the resins (Table-PA-4). The values are ranging from 0.21 to 0.33 gm/ml for H^+ form and 0.26 to 0.35 gm/ml for OH^- form of resins. Known values (77) of apparent density for commercial resins in H^+ form are 0.69 gm/ml for IRC 50/75 and 0.74 gm/ml for IRC-84. Thus the resins under study have low range of density (d_{col}) for H^+ form.

The column density for the commercial resins are 0.74 gm/ml for IRA-68 (Weak base-$N(R)_2$). 0.67 gm/ml for 1R-45 (weak base-$N(R)_2$, - $NH(R)$,-NH_2) and 0.64 gm/ml for IRA-93 ($N(R)_2$ weak base) in OH^- form. Thus the OH^- form of the resins have values lower than that of similar type of commercial resins.

Void volume of resins :

The values of void volume fraction of resins are presented in Table-PA-5. It is observed that the values of void volume fraction vary between 0.25 to 0.53 for H^+ form and 0.29 to 0.41 for OH^- form of the resins. We suggest that as the resins have large void volume fraction, the diffusion of ions and hence the rate of ion exchange may be facilitated.

Ion-exchange capacity :

The cation or anion exchange capacity of these resins were calculated using the formula as described in I-(d) . The observed capacity CEC_{obs} (cation exchanger) or AEC_{obs} (anion exchanger) can be compared with the calculated CEC_{cal} or AEC_{cal} as reported

in Table-PA-6A and Table-PA-6B respectively.

For the values of ratio CEC_{obs}/CEC_{cal}, two range exist,

(1) Values of $\frac{CEC_{obs}}{CEC_{cal}}$ is approximately close to 1

(2) Values of $\frac{CEC_{obs}}{CEC_{cal}}$ is approximately close or less to 1/2

Low values (1/2) of the ratio may be attributed to any one phenolic group (in such resins) involved in ion exchange.

Ion-exchange resins as cation exchanger show following decreasing order for cation exchange capacity.

Poly-A-Galli > Poly-A-Hyqui > Poly-A-Pyro >Poly-A-βRes > Poly-A-Sali > Poly-A-Anthra > Poly-A-8Hyqui > Poly-A-PHyBe

Concentration of ionogenic groups :

The data regarding the concentration of ionogenic groups are presented in Table-PA-6A for cationic form of resins. Excluding few exceptions, the total exchange capacity is related to the concentration of ionogenic groups. Higher the exchange capacity, higher is the concentration of ionogenic groups. The increase in concentration of ionogenic groups may be due to higher concentration of condensing reagent.

Metal (Cu) exchange capacity :

Results of copper ion-exchange capacity of these resins (H^+ form) are presented in Table-PA-6A. It is observed that copper ion exchange capacity of these resins range between 0.71 to 2.96

meq/gm. The decreasing order for the copper ion-exchange capacity of these resins was observed as

Poly-A-Galli > Poly-A-Hyqui > Poly-A-Pyro > Poly-A-βRes > Poly-A-Sali > Poly-A-Anthra > Poly-A-8Hyqui > Poly-A-PHyBe.

Recover of copper from industrial wastes by ion-exchange was considered from time to time by various research worker (78-84), M.C. Burney (85) presented a resin showning high selectivity for copper. Gregor (86) and pepper (87) synthesised chelating resins and investigated their specificity for copper.

We suggest that at pH (10.6 to 10.8) understudy, resin in H^+ form would get transformed in Cu-form via NH_4^+ form and resin not converted into Cu-form at equilibrium would be in H^+ form. Hence the overall reaction under experimental condition would be

$$HR + Cu^{+2} \rightleftharpoons (CuR)^+ + H^+$$

$$HR + (CuR)^+ \rightleftharpoons CuR_2 + H^+$$

Rate of exchange

Figs 1 to 4 represent the rate of cation exchange as well as anion exchange resins.

A perusal of the trends rate of exchange for cation exchanger and as anion exchanger reveals that the rate of ion-exchange is very fast and hence a continues stirring procedure is adopted.

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

(i) Complete exchange occurs in 20 to 40 minutes

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

Poly-A-Galli > Poly-A-Hyqui > Poly-A-pyro > Poly-A-βRes > Poly-A-Sali > Poly-A-Anthra > Poly-A-8Hyqui > Poly-A-PHyBe.

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

(i) Complete exchange occurs in 15 minutes

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

Poly-A-8Hyqui > Poly-A-Anthra

It is observed that the rate of anion exchanger is faster than that of cation exchanger. The shape of the curves also suggest the porous nature of matrices. The dependence of the porosity of the exchanger could not be brought about due to lack of facility.

pH-titration

pH titration curves for the resins are presented in figs. 5 to 7. These resins exhibit good cation exchange capacity over the pH range 8 to 12. It is evident from the fig 5 and 7 that the resins Poly-A-Anthra and Poly-A-8Hyqui are amphoteric in nature. These resins can be used as anion exchanger as well as cation exchanger, depending upon pH of the solution. In the pH range 1-7 the resins Poly-A-Anthra, Poly-A-8Hyqui acted as anion exchanger (fig 5,6) and curves over this range are characteristic of weakly basic resin and may be compared with pH titration curves of commercially available weakly basic an anion exchanger. (Tulsion WB) (88).

The cation exchange behaviour of these resins reveals the weakly acidic nature of ion exchanger resins prepared. As a typical cation exchanger does not have much significance as the phenolic hydroxyl groups. They ionise only at relatively higher pH values.

Apparent pK_a and pK_b

Plot of cation and an anion exchange capacity versus pH of the solution at equilibrium are presented in Fig. 5 to 7.

From these plots pK_a and pK_b values of the resins are calculated as follows :

pK value of acid group RH is defined as the negative logarithm of the equilibrium constant K of the dissociation equilibrium.

$$RH = R^- + H^+ \quad \ldots\ldots\ldots\ldots\ldots\ldots (1)$$

$$K = \frac{[R^-]\ [H^+]}{[RH]} \qquad p^k = -\log K \ldots\ldots (2)$$

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

$$\alpha = \frac{[R^-]}{[R^-]+[RH]} \quad \ldots\ldots\ldots\ldots (3)$$

$$pHr = -\log [H^+] \quad \ldots\ldots\ldots\ldots\ldots (4)$$

$$\text{Hence } pHr = pk - \log (1-\alpha)/\alpha \quad \ldots\ldots (5)$$

When $\alpha = 0.5$ it corresponds to 50% conversion.

Conversion of the resin from H^+ form to Na form and (apparent) pK

of the group is

$$p^K = p^{Hr} \quad \ldots\ldots\ldots\ldots\ldots\ldots (6)$$

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).

$$\text{Hence } [Na^+]_s \; / \; [H^+]_s = [Na^+]_r / [H^+]_r \quad \ldots\ldots\ldots\ldots\ldots (7)$$

$$\text{i.e. } = [H^+]_r = \frac{[Na^+]_r \; [H^+]s}{[Na^+] \; s} \quad \ldots\ldots\ldots\ldots\ldots (7a)$$

As 50% conversion

$$[Na^+]_r = \frac{[R^-] + [RH]}{2} \quad \ldots\ldots\ldots\ldots\ldots\ldots (8)$$

$$\text{Hence } p^k = p^H + \log [Na^+]s - \frac{\log [R^-] + [RH]}{2} \quad \ldots\ldots\ldots\ldots (9)$$

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 resin in the cation exchange process can be represented as

$$H^+ \; R^- \rightleftharpoons \quad H^+ + R^- \quad \ldots\ldots\ldots\ldots (10)$$

and acid dissociation constant in cation exchange (K_A) AS

$$K_A = [H^+]\ [R^-]\ /\ [H^+\ R^-] \quad \ldots\ldots\ldots\ldots (11)$$

Since K_A corresponds to acid ionization in cation exchange. pK_a can be calculated from pH titration involving cation exchange using equation (9).

The acid dissociation of the resin in anion exchange can be represented as

$$H^+RH \rightleftharpoons H^+R^- + H^+ \quad \ldots\ldots\ldots\ldots (12)$$

and acid dissociation constant in anion exchange (K_B) as

$$K_B = [H^+\ R^-]\ [H^+]\ /\ [H^+\ RH] \quad \ldots\ldots\ldots\ldots (13)$$

Now it can be shown that for a weak base when $\alpha = 0.5$

$$pK_b = pH - \log [Cl^-]_s + \log \frac{[H^+\ RH] + [RH]}{2} \quad \ldots (14)$$

Since K_B corresponds to anion exchange, PK_b can be calculated from pH titration involving anion exchange using equation (14).

The apparent pK_a and pK_b values calculated from pH titration curves and using above relations (9) and (14) respectively, are presented in Table-PA-8.

It is seen that the range of pK_a obtained for overall cation exchange process in general for various ion exchangers studies varies between 9.89 to 11.46 which is slightly higher than values of phenolic hydroxyl group and that of pK_b obtained for the overall anion exchange process for these resins lies between

2.82 to 3.32 which is slightly higher than of a characteristic of bases of weak strength. pK_a values for the resins are in the following decreasing order :

Poly-A-Sali > Poly-A-Pyro > Poly-A-βRes > Poly-A-8Hyqui > Poly-A-PHyBe > Poly-A-Hyqui > Poly-A-Anthra > Poly-A-Galli

Where as the pK_b values for the resins are in the following decreasing order :

Poly-A-Anthra > Poly-A-8Hyqui

ISOIONIC POINT :

Isoelectric point is defined as that hydrogen ion concentration of the solution in which a particular amino acid does not migrate under the influence of an electric field, Isoionic point (ip) define as that" hydrogen ion concentration at which the number of positive and negative groups which arise exclusively from proton exchange are equal to each other."

Isoelectric and isoionic are same only if zwitter ion combines only with H-ions.

Isoionic point of a Zwitter ion (x^-) can be obtained follows :

$$^+X \rightleftharpoons {}^+X^- + H^+ \quad \text{.....(i)}$$

$$^+X^- \rightleftharpoons X^- + H^+ \quad \text{.....(ii)}$$

Equations (i) and (ii) are related to cation and anion exchange processes respectively.

Thus acid dissociation constant [K_{AC} and K_{AA}]

for ionisation are

$$K_{AC} = [^{+}X^{-}]\ [H^{+}] \quad \ldots\ldots\ldots\ldots (iii)$$

$$K_{AA} = \frac{[X^{-}]\ [H^{+}]}{[^{+}X^{-}]} \quad \ldots\ldots\ldots\ldots (iv)$$

Combining the two equations (iii) and (iv), we get

$$[H^{+}]^{2} = K_{AC} \times K_{AA}\ [^{+}X] / [X^{-}] \quad \ldots\ldots\ldots (v)$$

At isoionic point

$$[X^{+}] = [X^{-}]$$

Hence

$$[H^{+}]^{2} = K_{AC} \times K_{AA}$$

pH ip for isoionic point is pH ip = 1/2 $[P^{k}AC + P^{k}\ AA]$

The values of isoionic point (ip) are presented in Table-PA-8. The values vary in the range of 6.69 to 6.87 . It is observed that the resins under study have the isoionic values comparable with threonine, cysteine and proline. The values are in the decreasing order as :

Poly-A-Anthra > Poly-A-8Hyqui

Effect of temperature of equilibration on the capacity of the resin :

The data regarding the effect of varying temperature of equilibration on the capacity of the resin are presented in Table-PA-9.

It can be seen that the anion exchange capacity of resin

increases with the increasing temperature of equilibration. This is because, on heating the resin, certain basic gaseous decomposition products (such as NH_3 resulting from anthranilic acid & 8-hydroxyquinoline used for the synthesis of resin) are produced which neutralize a part of the acid during equilibration, thus giving an apparent high value of the anion exchange capacity of resin.

While the lowering of the cation exchange capacity of the resin with the increasing temp. of equilibration may be due to loss of the ionogenic groups. Similar results were obtained by Kapadia & Vyas. (89 - 93).

Oxidation resistance :

Result of oxidation resistance test of different ion exchangers as cation exchanger as well as anion exchanger are presented in Table-PA-10A. Table-PA-10B respectively. Resin Poly-A-PHyBe exhibits the lowest increase in % water, content as cation exchanger and as anion exchanger and this is most resistant to oxidation. We observed that the oxidative degradation for amphoteric resins as anion exchanger exhibit high increase in percentage water content than cation exchanger. Hence we suggest that cationic form is less susceptible to oxidation than the anionic form Cation exchanger show the following decreasing order for their stability on oxidative degradation.

Poly-A-Galli > Poly-A-8Hyqui > Poly-A-pyro > Poly-A-Sali
> Poly-A-Hyqui > Poly-A-Anthra > Poly-A-βHyqui > Poly-A-PHyBe

Anion exchanger show the following decreasing order for their

stability on oxidative degradation.

Poly-A-8Hyqui > Poly-A-Anthra

Behaviour in non-aqueous solvents

The results of behaviour of these resins as cation exchanger and some anion exchanger in non-aqueous solvents are reported in Table-PA-11A and Table-PA-11B.

It is observed that

1. Polar solvents produce more extensive swelling than nonpolar hydrocarbons.
2. In polar solvents (H_2O, CH_2OH, CH_2COOH) the swelling behaviour of cation exchanger as well as anion exchange is fairly comparable.

The amount of resin swelling is always an important consideration in designing equipment. The use of ion-exchange resins in such application as solvent purification and catalysis of organic reaction has directed the attention of investigators.

The decreasing order of porosity of cation exchanger is as follows.

Poly-A-Pyro > Poly-A-Sali > Poly-A-βRes > Poly-A-8Hyqui > Poly-A-Hyqui > Poly-A-Galli > Poly-A-Anthra > Poly-A-PHyBe

The decreasing order of porosity for anion form of the resins is as follows :

Poly-A-8Hyqui > Poly-A-Anthra

TABLE : PA-1

Abbreviation

No.	Resin	Abbreviation
1	Poly (vinyl alcohol) - Anthranilic acid	Poly-A-Anthra
2	Poly (vinyl alcohol) - Gallic acid	Poly-A-Galli
3	Poly (vinyl alcohol) - p-Hydroxybenzaldehyde	Poly-A-PHyBe
4	Poly (vinyl alcohol) - Pyrogallol	Poly-A-Pyro
5	Poly (vinyl alcohol) - 8-Hydroxyquinoline	Poly-A-8Hyqui
6	Poly (vinyl alcohol) - Salicylic acid	Poly-A-Sali
7	Poly (vinyl alcohol) - Hydroquinone	Poly-A-Hyqui
8	Poly (vinyl alcohol) - β-Resorcylic acid	Poly-A-βRes

TABLE : PA-2

Analyses, Formula etc. of resins

No.	Resin	Formula	Analysis					
			Calculated			Observed		
			%C	%H	%N	%C	%H	%N
1	Poly-A-Anthra	$C_{10}H_{20}O_5N_2$	64.04	5.61	7.86	64.5	6.00	8.2
2	Poly-A-Galli	$C_{19}H_{18}O_{11}$	54.02	4.26	-	54.5	4.6	-
3	Poly-A-PHyBe	$C_{19}H_{18}O_5$	69.93	5.52	-	70.10	5.61	-
4	Poly-A-Pyro	$C_{19}H_{18}O_7$	61.07	5.38	-	61.4	5.6	-
5	Poly-A-8Hyqui	$C_{19}H_{18}O_3N_2$	77.52	5.61	7.86	78.1	6.1	8.1
6	Poly-A-Sali	$C_{19}H_{20}O_7$	64.04	5.02	-	64.3	5.6	-
7	Poly-A-Hyqui	$C_{19}H_{18}O_5$	67.54	5.96	-	68.0	5.3	-
8	Poly-A-βRes	$C_{19}H_{18}O_9$	58.46	4.61	-	59.0	5.1	-

TABLE-PA-3

% Moisture content of ion-exchange resins

No.	Resin	% Moisture	
		H^+ - form	OH^- - form
1	Poly-A-Anthra	5.04	6.15
2	Poly-A-Galli	7.16	-
3	Poly-A-PHyBe	5.29	-
4	Poly-A-Pyro	5.39	-
5	Poly-A-8Hyqui	2.27	2.35
6	Poly-A-Sali	4.82	-
7	Poly-A-Hyqui	5.95	-
8	Poly-A-βRes	5.01	-

TABLE : PA-4

Density of resins

No.	Resin	True density of resins (d_{res}) (gm/cm^3)		Apparent (column) density of resins (d_{col}) (gm/ml)	
		H^+-form	OH^--form	H^+-form	OH^--form
1	Poly-A-Anthra	0·403	0·45	0.26	0.26
2	Poly-A-Galli	0·556	-	0.33	-
3	Poly-A-PHyBe	0·394	-	0.29	-
4	Poly-A-Pyro	0·444	-	0.31	-
5	Poly-A-8Hyqui	0·469	0·5027	0.21	0.35
6	Poly-A-Sali	0·420	-	0.26	-
7	Poly-A-Hyqui	0·532	-	0.31	-
8	Poly-A-βRes	0·509	-	0.26	-

TABLE-PA-5

Void volume fraction of resins

No.	Resin	Resin d_{col}/d_{res}	in H^+-form void volume fraction $(1-d_{col}/d_{res})$	Resin d_{col}/d_{res}	in OH^--form void volume fraction $(1-d_{col}/d_{res})$
1	Poly-A-Anthra	0.23	0·358	0.26	0·496
2	Poly-A-Galli	0.25	0 395	-	-
3	Poly-A-PHyBe	0.28	0·259	-	-
4	Poly-A-Pyro	0.26	0·287	-	-
5	Poly-A-8Hyqui	0.21	0·538	0.35	0·707
6	Poly-A-Sali	0.23	0·373	-	-
7	Poly-A-Hyqui	0.25	0·413	-	-
8	Poly-A-βRes	0.23	0·482	-	-

TABLE : PA-6 A

Capacity and concentration of ionogenic groups of resins as cation exchanger

No.	Resins	Total Capacity $CEC_{obs.}$ (meq/gm)	Total Capacity $CEC_{cal.}$ (meq/gm)	$\frac{CEC_{obs}}{CEC_{cal.}}$	Concentration of ionogenic group Cr (meq/gm)	Volume Capacity Q (gm.eq/l)	Cu-exchange Capacity (meq/gm)
1	Poly-A-Anthra	2.17	2.80	0.77	2.26	0.53	0.95
2	Poly-A-Galli	5.63	15.83	0.35	6.82	1.75	2.96
3	Poly-A-PHyBe	1.69	9.20	0.18	1.67	0.47	0.71
4	Poly-A-Pyro	4.25	14.97	0.28	4.76	1.26	2.35
5	Poly-A-8Hyqui	1.32	2.68	0.49	1.32	0.28	0.78
6	Poly-A-Sali	2.25	8.38	0.26	2.41	0.56	0.99
7	Poly-A-Hyqui	4.58	9.93	0.46	5.31	1.34	2.67
8	Poly-A-βRes	2.74	2.74	0.21	2.97	0.68	1.03

TABLE : PA-6 B

Capacity and concentration of ionogenic groups of resins as anion exchanger

No.	Resins	Total Capacity $CEC_{obs.}$ (meq/gm)	Total Capacity $CEC_{cal.}$ (meq/gm)	$\frac{CEC_{obs}}{CEC_{cal.}}$	Concentration of ionogenic group Cr (meq/gm)	Volume Capacity Q (gm.eq/l)
1	Poly-A-Anthra	1.22	5.61	0.21	1.14	0.30
2	Poly-A-8Hyqui	1.26	5.37	0.23	1.23	0.43

TABLE : PA-7

Rate of exchange of resins

No. Resin	Time in Minute	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1. Poly-A-Anthra	5	0.86	0.51
	10	0.86	0.61
	15	1.13	0.71
	20	1.16	0.71
	40	1.27	0.81
	60	1.27	0.91
	80	1.27	1.02
	100	1.27	1.02
	120	1.41	1.02
2. Poly-A-Galli	5	2.80	-
	10	3.22	-
	15	3.30	-
	20	3.38	-
	40	3.72	-
	60	3.72	-
	80	4.13	-
	100	4.30	-
	120	4.63	-
3. Poly-A-PHyBe	5	0.84	-
	10	0.93	-
	15	1.13	-
	20	1.23	-
	40	1.23	-
	60	1.33	-
	80	1.33	-
	100	1.33	-
	120	1.33	-
4. Poly-A-Pyro	5	1.87	-
	10	2.28	-
	15	2.77	-
	20	2.94	-
	40	3.06	-
	60	3.26	-
	80	3.76	-
	100	3.76	-
	120	3.76	-

CONTINUED.....

No.	Resin	Time in Minute	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
5.	Poly-A-8Hyqui	5	0.64	0.97
		10	0.84	1.06
		15	1.03	1.11
		20	1.13	1.16
		40	1.13	1.16
		60	1.13	1.16
		80	1.13	1.16
		100	1.13	1.16
		120	1.32	1.16
6.	Poly-A-Sali	5	0.95	-
		10	1.17	-
		15	1.20	-
		20	1.28	-
		40	1.28	-
		60	1.28	-
		80	1.28	-
		100	1.28	-
		120	1.28	-
7.	Poly-A-Hyqui	5	1.79	-
		10	1.95	-
		15	2.03	-
		20	2.28	-
		40	2.28	-
		60	2.44	-
		80	2.61	-
		100	2.77	-
		120	2.94	-
8.	Poly-A-βRes	5	0.71	-
		10	1.04	-
		15	1.12	-
		20	1.20	-
		40	1.36	-
		60	1.44	-
		80	1.69	-
		100	1.77	-
		120	2.17	-

TABLE : PA-8

Apparent pK_a and pK_b Values and Isoionic Point of resins

No.	Resin	Apparent pK_a values	Apparent pK_b values	Isoionic Point
1	Poly-A-Anthra	10.41	3.32	6.87
2	Poly-A-Galli	9.89	-	-
3	Poly-A-PHyBe	10.42	-	-
4	Poly-A-Pyro	11.07	-	-
5	Poly-A-8Hyqui	10.56	2.82	6.69
6	Poly-A-Sali	11.46	-	-
7	Poly-A-Hyqui	10.42	-	-
8	Poly-A-βRes	10.93	-	-

TABLE : PA-9

Effect of temperature of equilibration on the capacity of the resins

Equilibration period = 2 hr. Amount of resin = 0.5 gm

No.	Resin	Total AEC (meq/gm) of absolutely dry resin as determined at temperature (^{0}C)			Total CEC (meq/gm) of absolutely dry resin as determined at temperature (^{0}C)		
		30^0	50^0	70^0	30^0	50^0	70^0
1	Poly-A-Anthra	1.02	1.21	1.40	1.02	1.02	1.02
2	Poly-A-Galli	-	-	-	4.63	4.14	4.21
3	Poly-A-PHyBe	-	-	-	1.33	1.21	4.21
4	Poly-A-Pyro	-	-	-	3.76	3.46	3.36
5	Poly-A-8Hyqui	1.16	1.34	1.39	1.32	1.24	1.12
6	Poly-A-Sali	-	-	-	1.28	1.26	1.10
7	Poly-A-Hyqui	-	-	-	2.94	2.61	2.04
8	Poly-A-βRes	-	-	-	2.17	2.16	2.16

TABLE : PA-10A

Oxidation resistance of ion-exchange resins as cation exchanger

No.	Resin	% Moisture		Increase in % water content
		Untreated exchanger	H_2O_2 treated exchanger	
1	Poly-A-Anthra	5.0	7.6	2.5
2	Poly-A-Galli	7.1	16.8	9.6
3	Poly-A-PHyBe	5.2	6.0	0.7
4	Poly-A-Pyro	5.9	12.4	6.4
5	Poly-A-8Hyqui	2.2	10.2	7.9
6	Poly-A-Sali	4.8	10.6	5.7
7	Poly-A-Hyqui	5.9	10.2	4.2
8	Poly-A-βRes	5.0	7.2	2.1

TABLE : PA-10B

Oxidation resistance of ion-exchange resins as anion exchanger

No.	Resin	% Moisture		Increase in % water content
		Untreated exchanger	H_2O_2 treated exchanger	
1	Poly-A-Anthra	6.1	16.8	10.7
2	Poly-A-8Hyqui	2.3	15.6	13.2

TABLE :PA-11A

% Swelling of resins as cation exchange in various solvents

No.	Resin	% Swelling in								
		Glacial Acetic acid	Water	DMF	Dio-xane	Alco-hol	THF	Ben-zene	Acetone,	pet. Ether
1	Poly-A-Anthra	1.9	4.5	1.3	1.2	1.7	0.4	0.5	0.4	0
2	Poly-A-Galli	2.2	5.6	1.8	1.3	1.9	0.5	0.3	0.5	0
3	Poly-A-PHyBe	1.7	2.9	1.1	0.8	1.3	0.2	0.3	0.2	0
4	Poly-A-Pyro	2.4	7.9	1.2	1.6	1.9	0.9	0.2	0.7	0
5	Poly-A-8Hyqui	4.9	6.8	3.1	2.5	3.2	1.0	0.3	0.7	0
6	Poly-A-Sali	3.8	7.4	2.4	1.5	3.7	0.7	0.3	0.6	0
7	Poly-A-Hyqui	3.4	6.6	1.8	1.9	3.2	0.6	0.3	0.4	0
8	Poly-A-βRes	2.8	6.9	1.8	1.3	3.1	1.0	0.4	0.5	0

TABLE :PA-11 B

% Swelling of resins as cation exchange in various solvents

No.	Resin	% Swelling in								
		Glacial Acetic acid	Water	DMF	Dio-xane	Alco-hol	THF	Ben-zene	Acetone,	pet. Ether
1	Poly-A-Anthra	1.39	4.93	1.44	1.11	1.09	6.65	0.54	0.43	0
2	Poly-A-8Hyqui	3.78	6.81	3.03	2.63	2.13	0.79	0.26	0.81	0

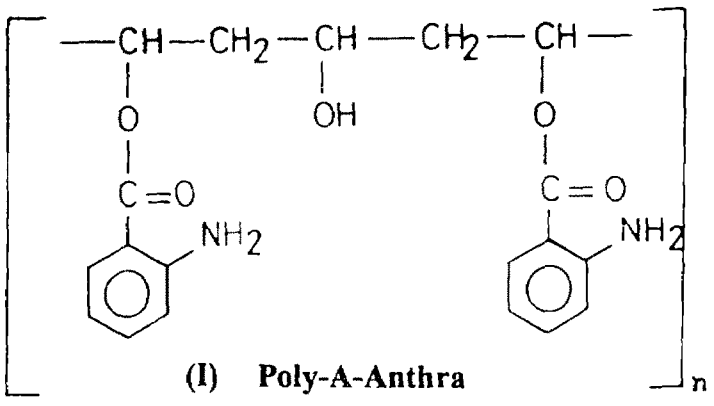
Table-A-I

Major peaks observed in the infrared spectra of resins

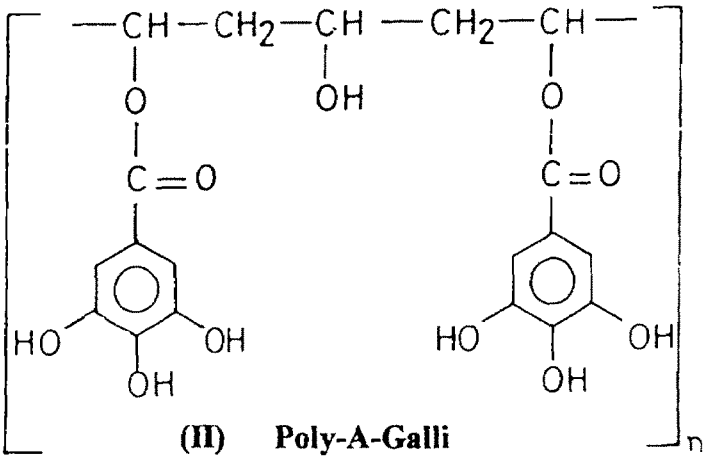
No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
1.	Poly-A-Anthra	3600-3200	broad	-0H stretching absorption and $-NH_2$ group
		1680-1720	medium	Conjugated ester >C=0
		1620-1580	medium	>C=C< group
2.	Poly-A-Galli	3600-2400	broad	-OH Stretching absorption
		1720-1650	medium	Conjugated ester >C=0
		1620-1580	medium	aromatic >C=C< absorption
3.	Poly-A-PHyBe	3600-2400	broad	Free -OH stretching absorption
		1680-1580	medium	Conjugated >C=0
		960-990	medium	$(-CH_2-CH-)_n$
4.	Poly-A-Pyro	3600-2600	broad	Free-OH stretching and -0H bending
		1600-1500	medium	aromatic >C=C< absorption
		1200-1190	Small	-C=0 ether absorption
5.	Poly-A-8Hyqui	3600-3000	broad	-OH Stretching absorption
		1200-1190	medium	-C=O ether absorption
		990-900	medium	$-CH_2$-CH-absorption
6.	Poly-A-Sali	3700-3000	broad	-OH Stretching absorption
		1720-1650	medium	conjugated ester absorption >C=0

Continued.....

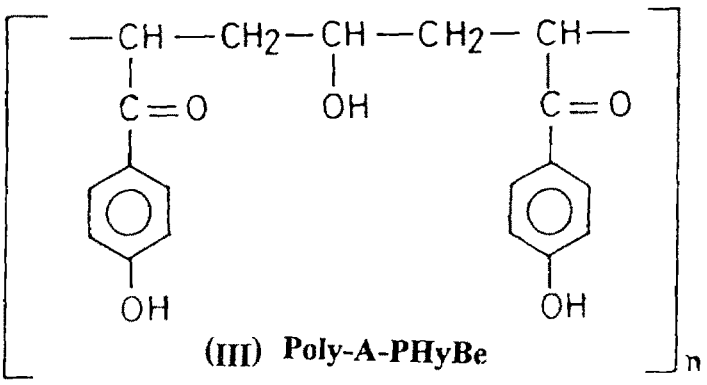
No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
7.	Poly-A-Hyqui	3700-3000	broad	-OH stretching absorption
		1540-1500	medium	aromatic >C=C<
		1180-1220	medium	-C-O ether stretching absorption
8.	Poly-A -βRes	3700-2900	broad	Free -OH stretching absorption and
		1685-1680	medium	>C=0 conjugated ether stretching
		1600-1500	medium	aromatic >C=C< stretching absorption



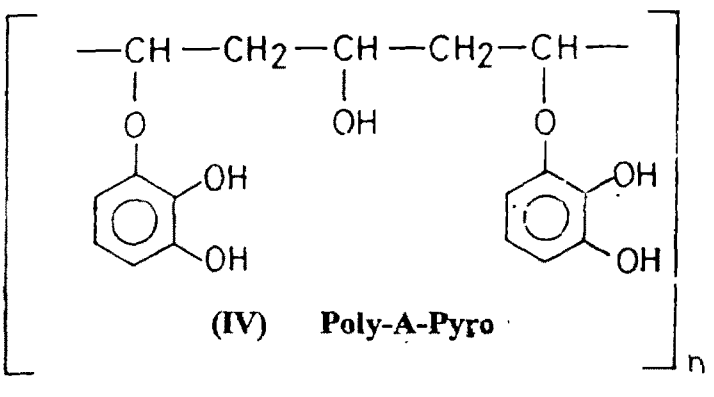
(I) **Poly-A-Anthra**



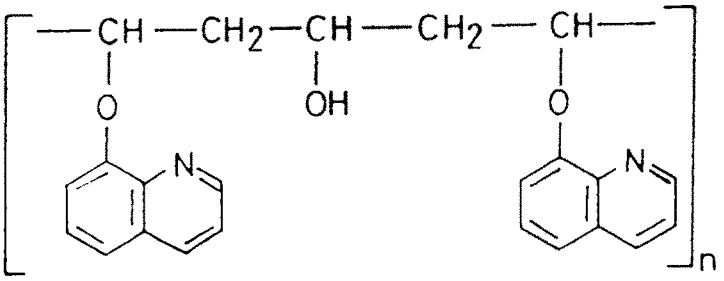
(II) **Poly-A-Galli**



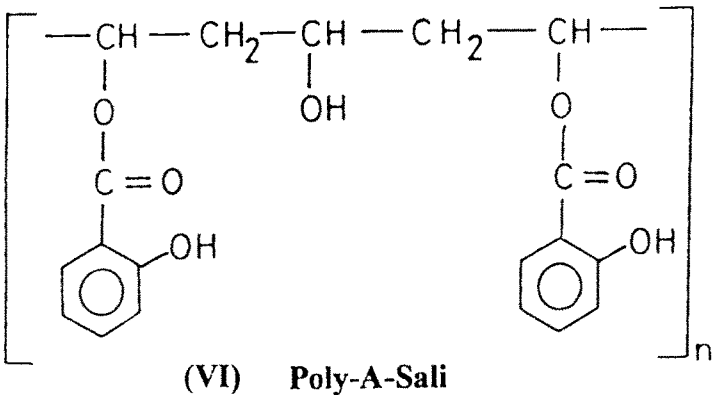
(III) **Poly-A-PHyBe**



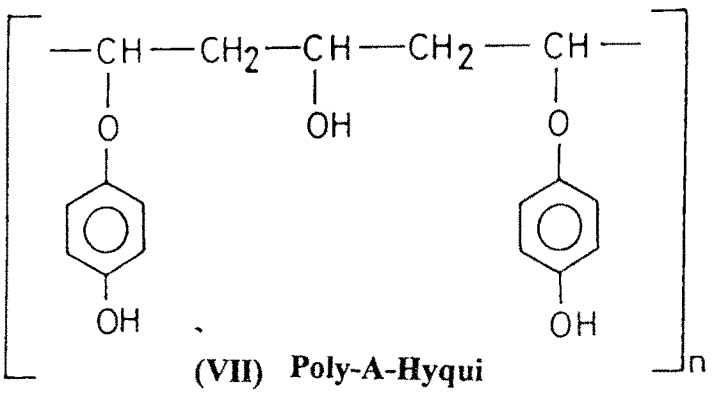
(IV) **Poly-A-Pyro**



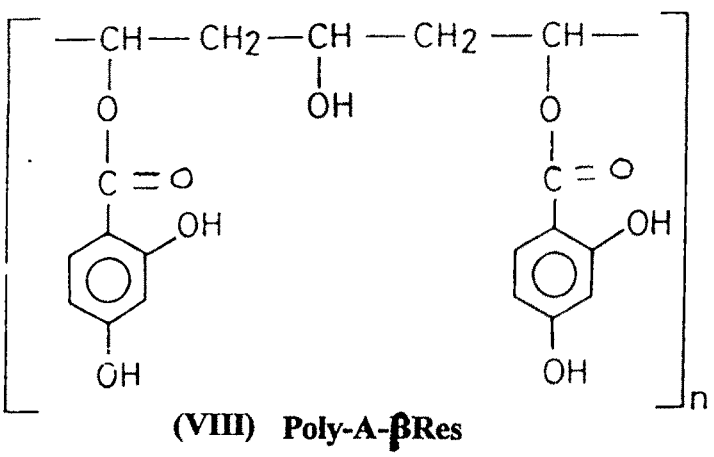
(V) **Poly-A-8Hyqui**



(VI) **Poly-A-Sali**



(VII) **Poly-A-Hyqui**



(VIII) **Poly-A-βRes**

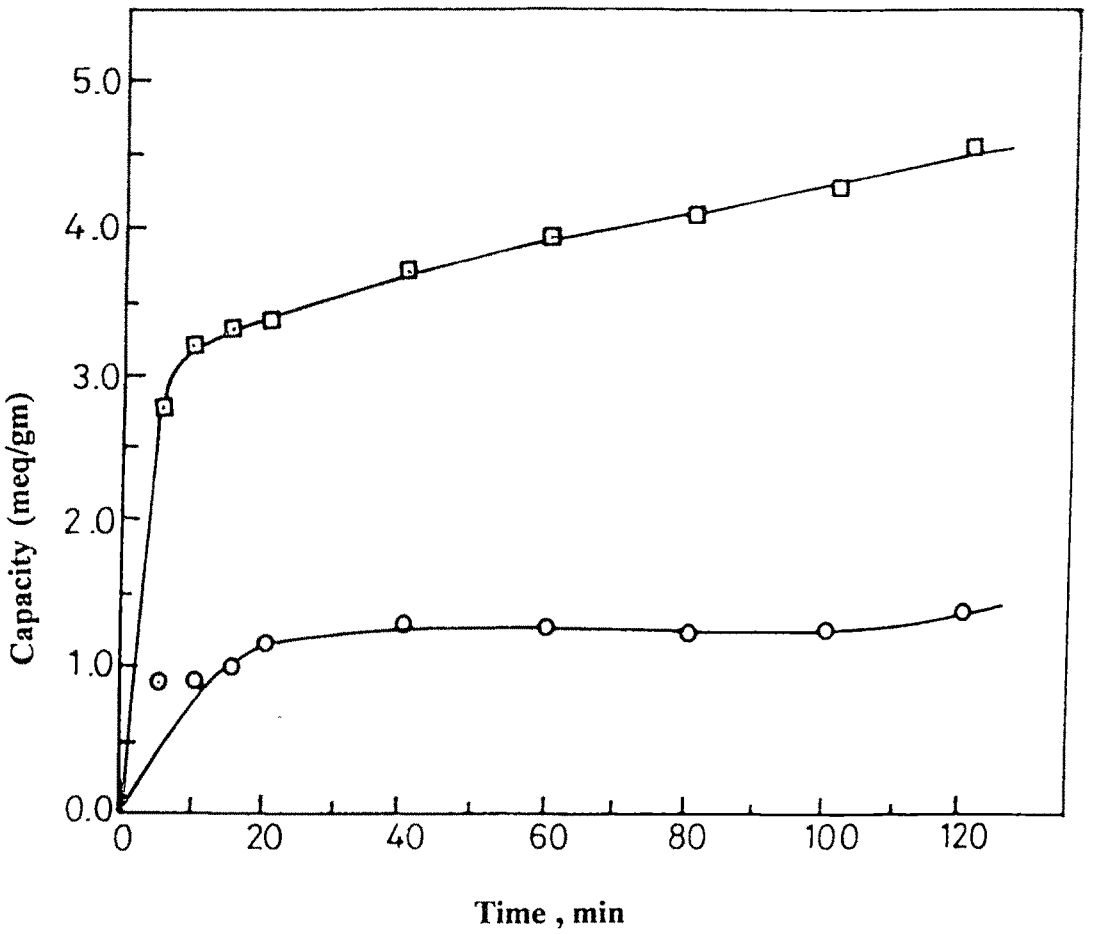


Fig.1 Rate of cation exchange of Poly-A-Anthra (⊙), Poly-A-Galli (⊡)

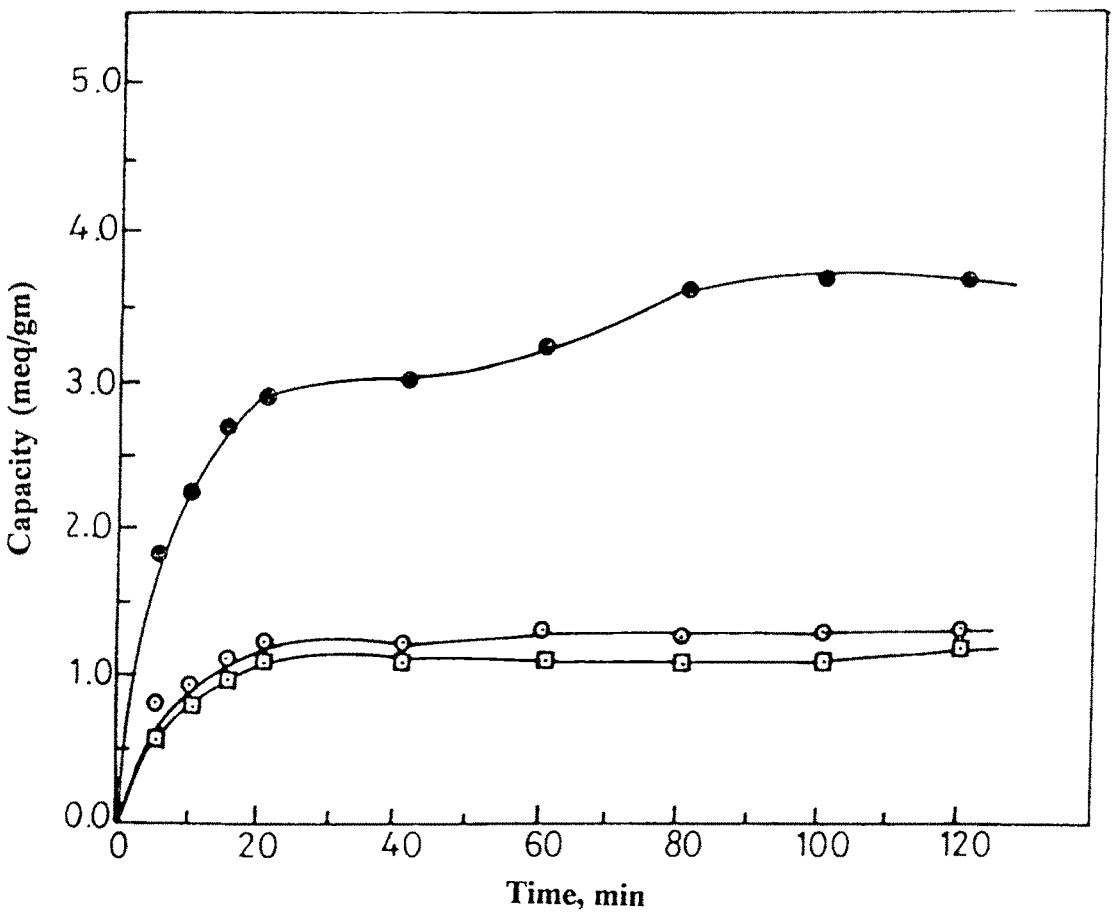


Fig.2 Rate of cation exchange of Poly-A-PHyBe (⊙), Poly-A-Pyro(●), Poly-C-8Hyqui (⊡)

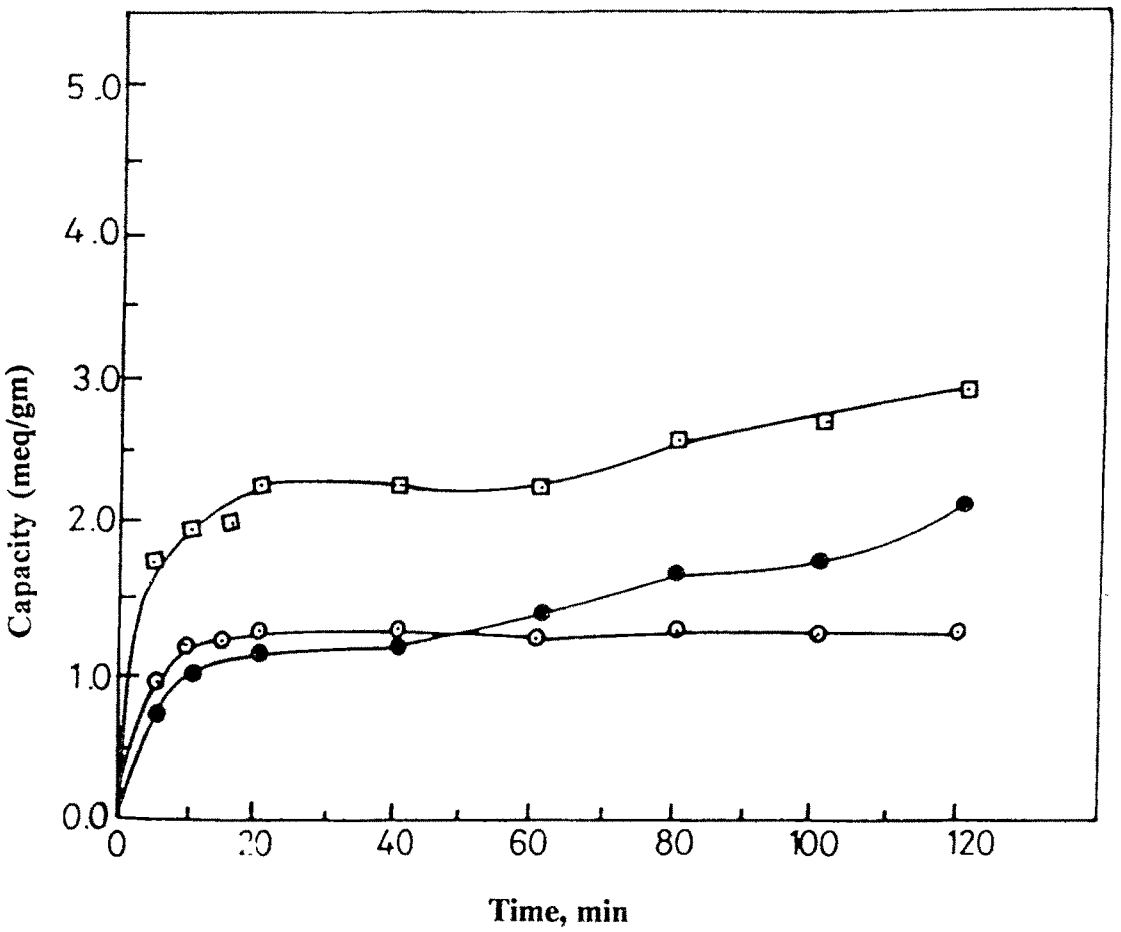


Fig.3 Rate of cation exchange of Poly-A-Sali (⊙), Poly-A-Hyqui (⊡), Poly-A-βRes (●)

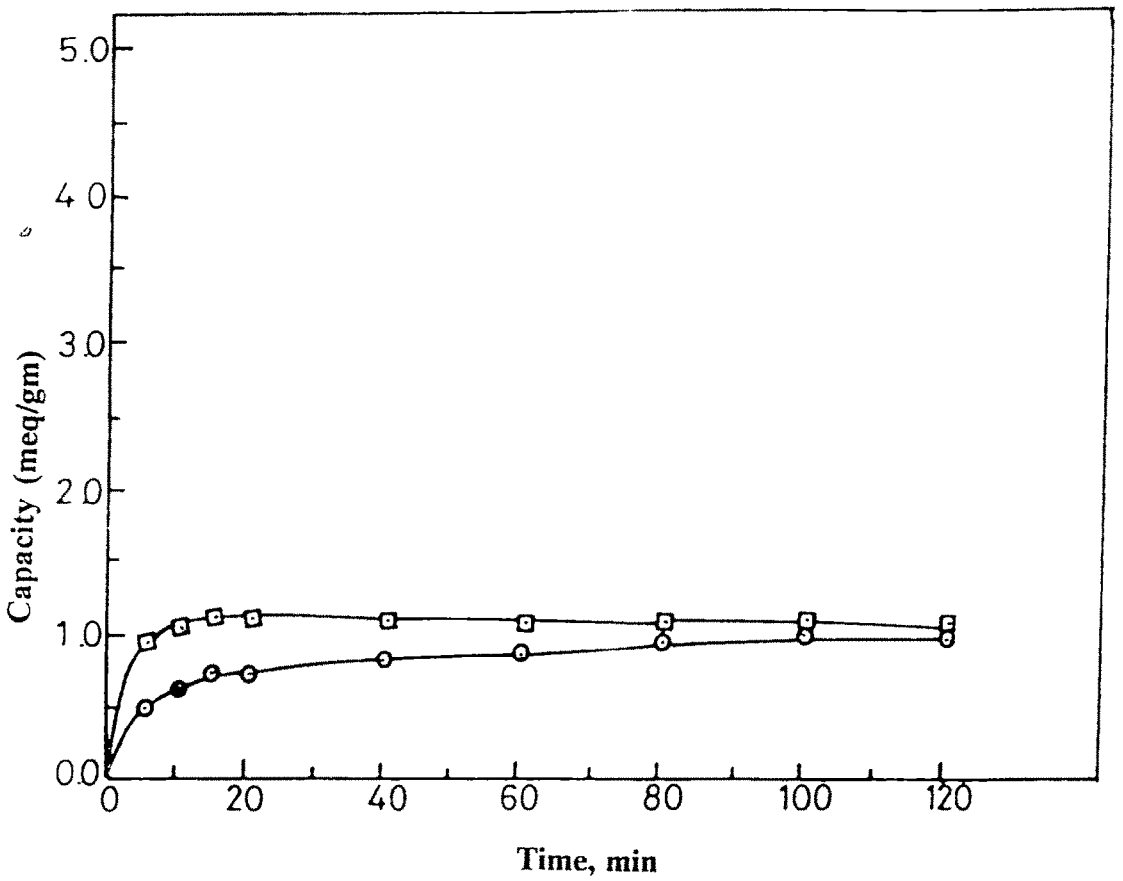


Fig.4 **Rate of anion exchange of Poly-A-Anthra (⊙), Poly-A-8Hyqui (⊡)**

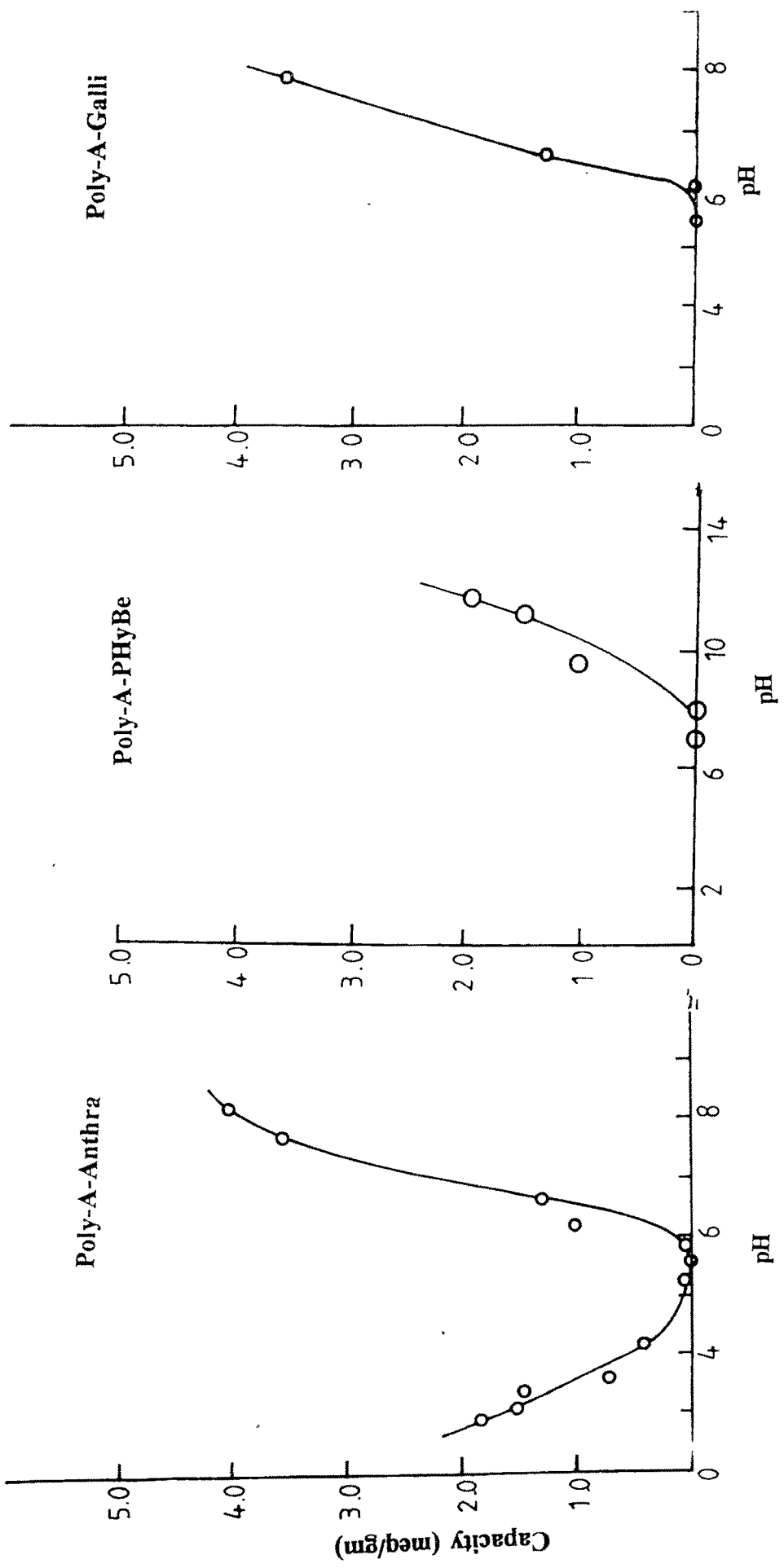

Poly-A-Anthra
Poly-A-PHyBe
Poly-A-Galli
Capacity (meq/gm)
pH
pH
pH
5.0
4.0
3.0
2.0
1.0
0
2
4
6
8
10
14

Fig. 5.

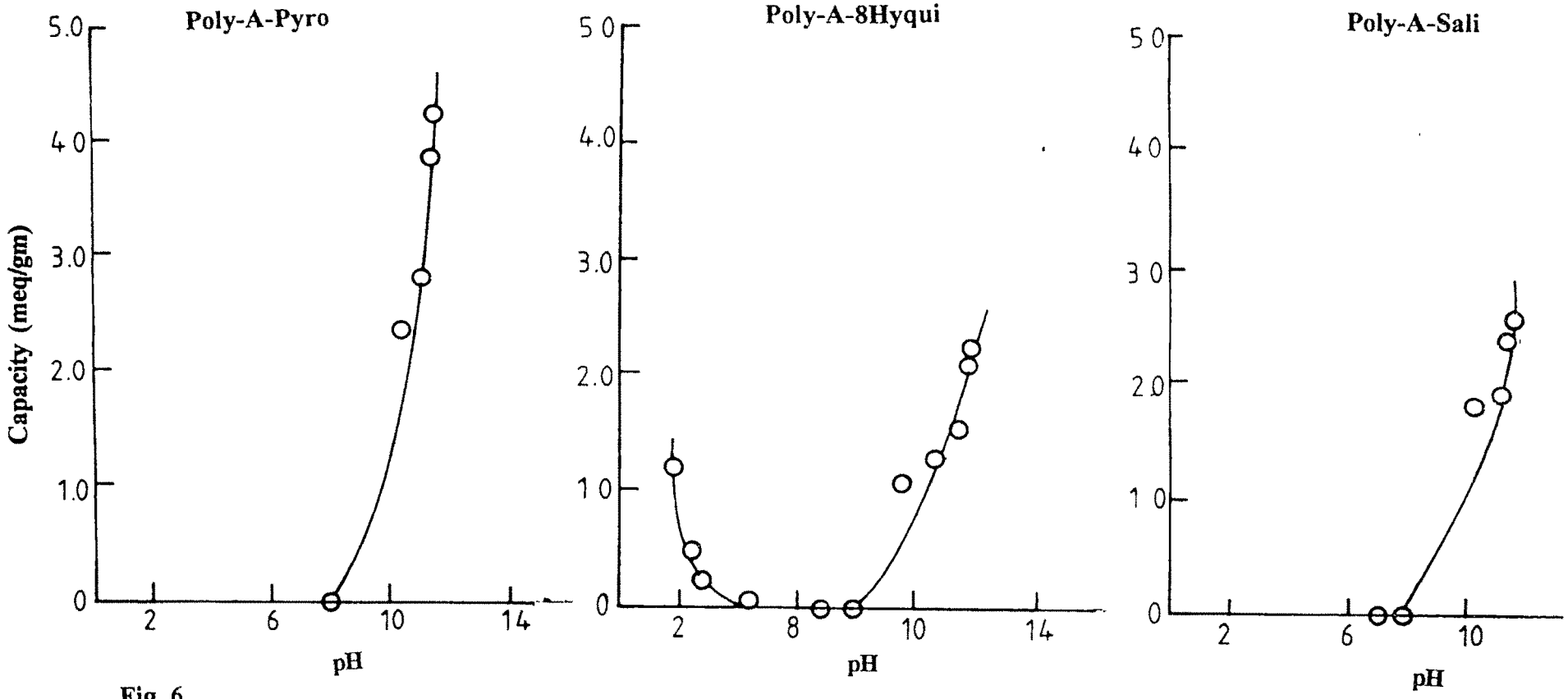
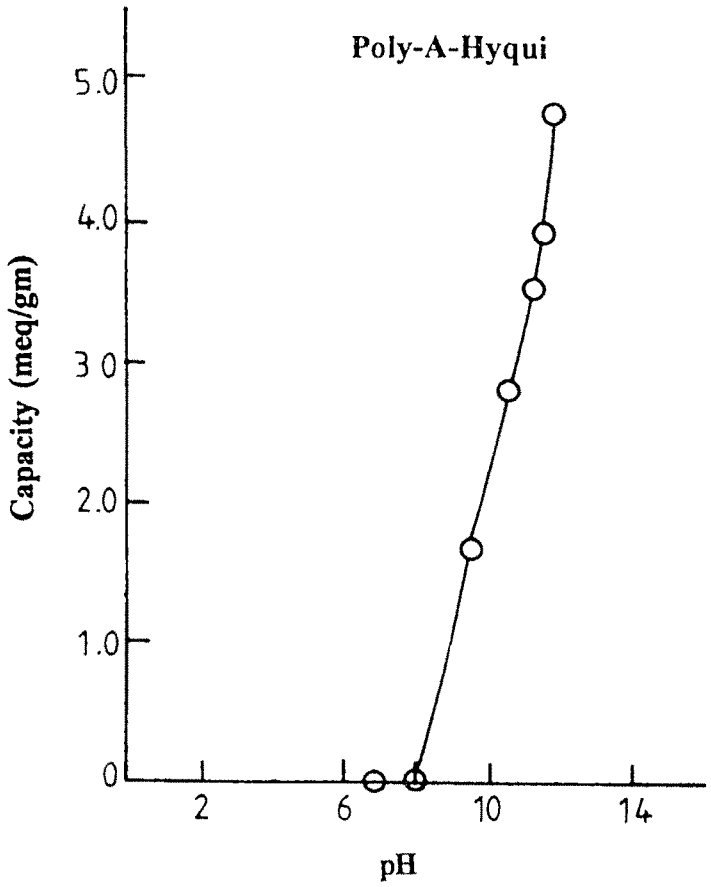

Poly-A-Pyro
Poly-A-8Hyqui
Poly-A-Sali
Capacity (meq/gm)
5.0
4.0
3.0
2.0
1.0
0
2
6
10
14
8
pH

Fig. 6.


Poly-A-Hyqui
Capacity (meq/gm)
5.0
4.0
3.0
2.0
1.0
0
2
6
10
14
pH

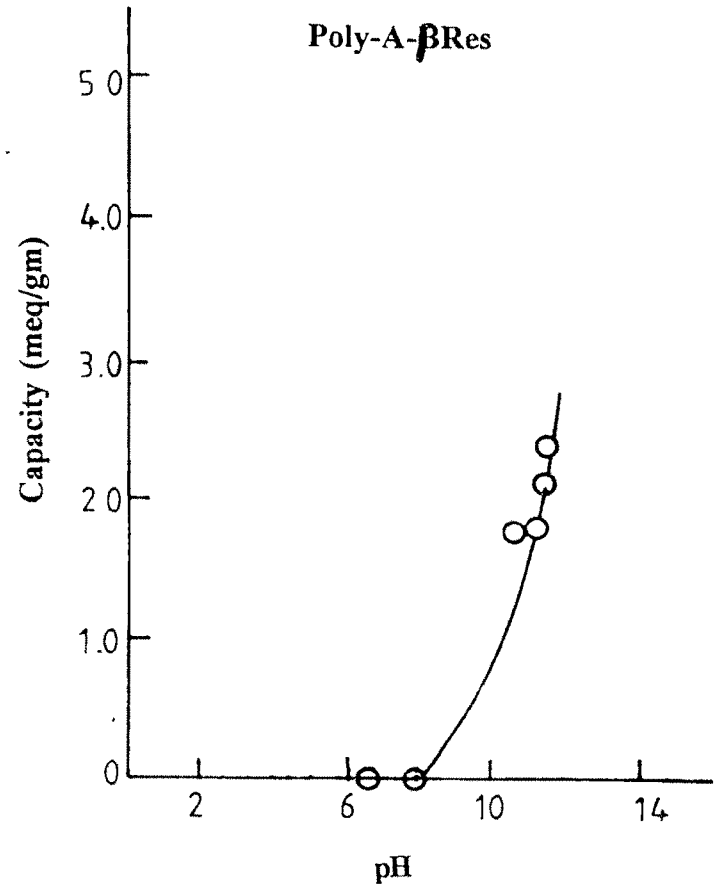
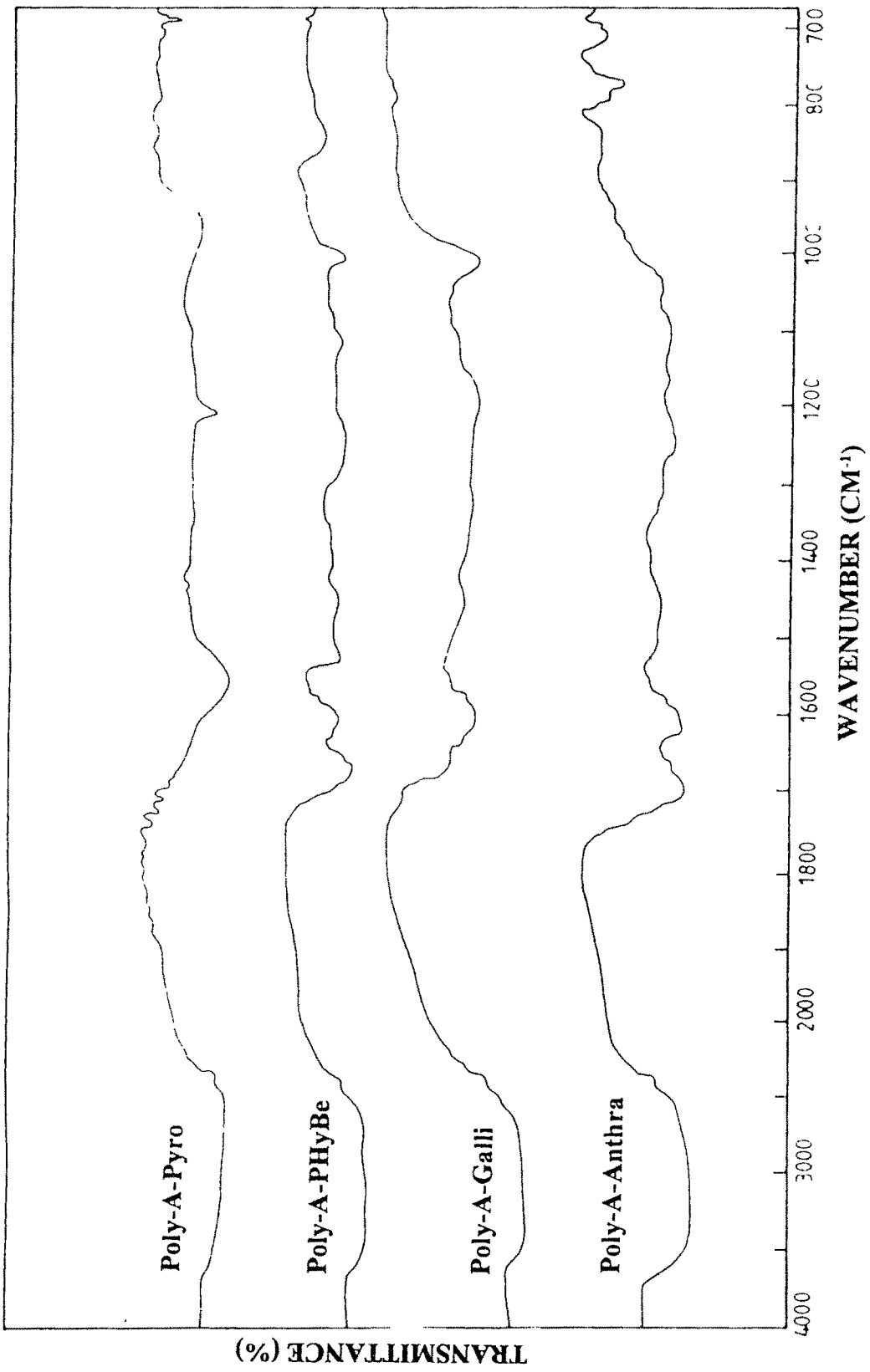
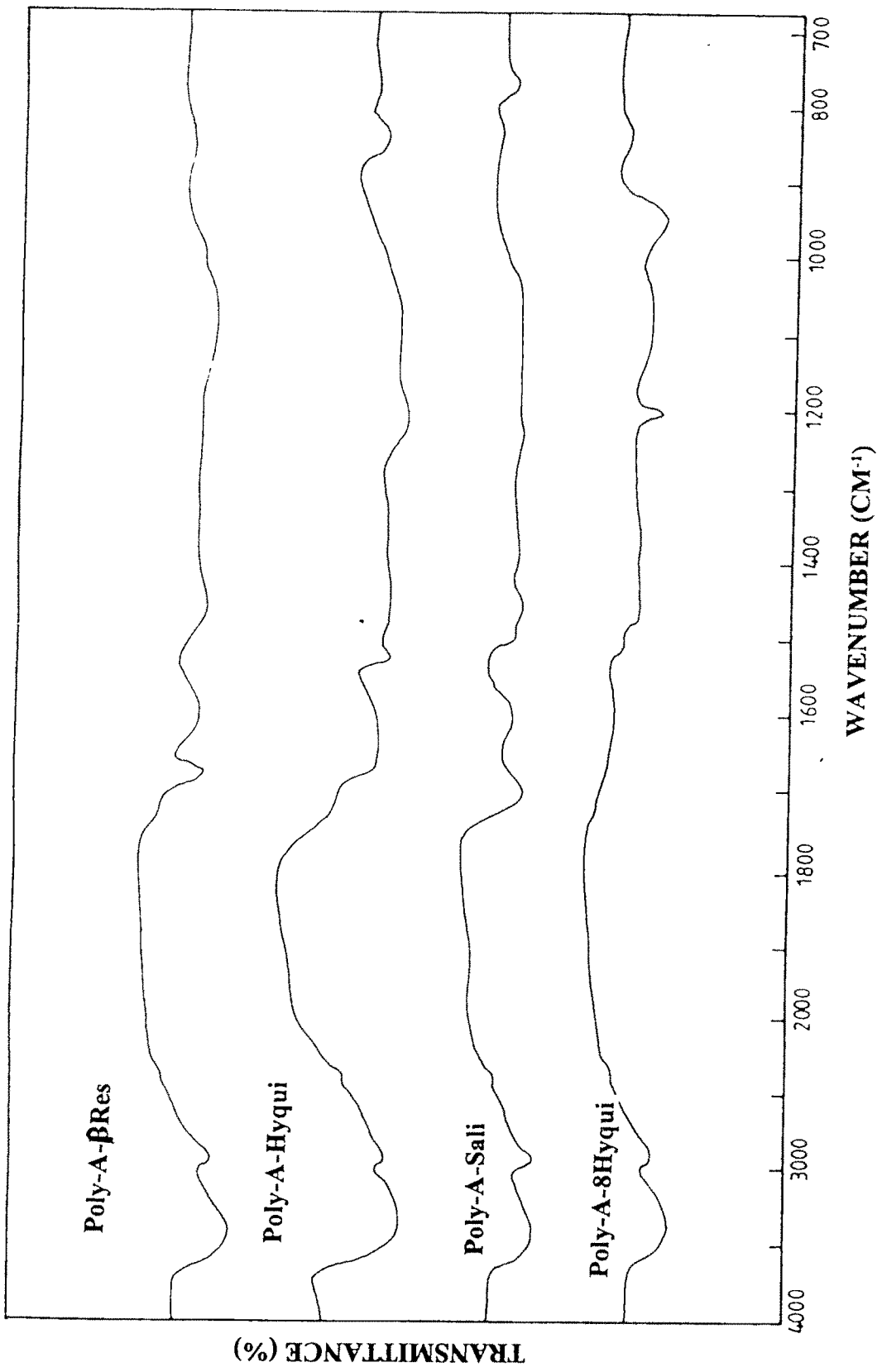

Poly-A-βRes
Capacity (meq/gm)
5.0
4.0
3.0
2.0
1.0
0
2
6
10
14
pH

Fig. 7.


Poly-A-Pyro
Poly-A-PHyBe
Poly-A-Galli
Poly-A-Anthra
4000
3000
2000
1800
1600
1400
1200
1000
800
700
WAVENUMBER (CM⁻¹)
TRANSMITTANCE (%)


Poly-A-βRes
Poly-A-Hyqui
Poly-A-Sali
Poly-A-8Hyqui
TRANSMITTANCE (%)
4000
3000
2000
1800
1600
1400
1200
1000
800
700
WAVENUMBER (CM-1)