CHAPTER IV

INTRODUCTION

In recent times, the evergrowing vista of applicability of ION-EXCHANGE RESINS in various field such as analytical and preparative chemistry, pharmacy and industry, stimulated a rush for finding new ION-EXCHANGE RESINS.

ION-EXCHANGE RESINS

These are synthetic organic ion-exchange materials prepared by the incorporation of appropriate functional groups into polymeric structures. The structure may be based upon polystyrene and divinylbenzene, phenol and formaldehyde or similar stable polymeric chemical structures. To function as a cation exchanger, the resin is substituted with either sulfonic acid groups (for strong cation exchangers). Anion exchangers are obtained by introducing primary and secondary amino groups into the polymeric lattice.

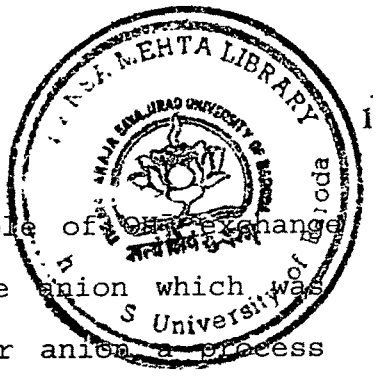
The first use of ion-exchangers was more than a century ago, and until the introduction of the synthetic ion-exchange resins in 1935 the inorganic naturally occurring zeolites were used for ion exchange studies and water softening. The first synthetic ion exchangers were prepared in 1935 using a phenol-formaldehyde polymer for the cation exchanger and a phenylenediamine-formaldehyde for the anion exchanger. More recent advances in this field include the development of chelating resins and amphoteric ion-exchange resins.

ION-EXCHANGER :

Ion-exchangers are solid and suitably insolubilized high molecular weight polyelectrolytes possessing labile or mobile ions which can exchange their mobile ions for ions of equal charge from the surrounding medium, without altering the general physical nature of the ion-exchanger. These ions are cations in a cation exchanger and anions in an anion-exchanger. Thus it can be seen that a cation exchanger consists of a polymeric anion and labile cations and an anion exchanger of a polymeric cation and labile anion.

Ion-exchanger may be defined as the reversible interchange of ions between a solid phase (Ion-exchange material) and a liquid phase in which there is no permanent change in structure, "Reversible" and "no permanent change" are the key points in this definition. However, a study of ion-exchange, either in laboratory or in the literature, shows that the use of ion-exchange material extend considerably beyond this definition.

Viewed in a different light, ion exchangers can be considered high molecular weight acids or bases with a high molecular weight cation, which can exchange their hydrogen or hydroxyl ions for equally charged ions and thus are converted into high molecular weight salts. If such a solid acid is neutralized with a base in to the salt, however, the cations bound to the polyelectrolytes can again be displaced by other cations. The resulting process is known as cation exchange and the polyelectrolytes is the cation exchanger. In the second



case, a solid base is obtained which is capable of ion exchange and can be neutralized with an acid, and the anion which was bound first can again be displaced by another anion, a process then known as anion exchange. The polyelectrolytes taking part in this process is called the anion exchanger.

Since the exchanger groups are hydrophilic and resin matrix with such groups are soluble in water , and as the groups are attached to the polymeric exchanger structure, they tend to draw the whole exchanger into solution also. To prevent this the polymer structure in the synthetic resins is held together with cross-linkers in order to form a three dimensional molecule, while a type of crosslinking of a somewhat similar nature exists in the nature materials. These cross-linkers restrain the tendency of the resin to dissolve.

For practical purpose the desirable characteristics of an ion-exchanger are that it should provide an insoluble chemically stable stationary phase possessing mechanical strength in a particle size able to flow reasonably easily for column packing.

Polymerization Processes :

There are two principal types of polymerization processes for polymer formation.

(A) Condensation polymerization/Polymer

Condensation polymerization in which the monomers interact by an ionic reaction mechanism, involving the elimination of small

molecules such as water, alcohol or ammonia and forming new C-C, C-N, C-O or other bonds. The structure of the monomer being such that the process can repeat itself in building up of the polymer molecule. Since molecules are lost, the ultimate analysis of the polymer is different from that of the monomer from which it was formed (4-S-1).

(B) Addition polymerization/Polymer

Addition polymerization in which the monomers interact by the free radical mechanism without forming any other products and the polymer chains contains only C-C bonds. These are polymers in which the molecular formula of the repeating unit is identical with that of the monomer, and the molecular weight of the polymer is a simple summation of the molecular weights of all combined monomers units in the chain (4-S-2).

Ion-exchange materials

Ion-exchange materials are of wide variety. These may be organic or inorganic, natural or synthetic. Synthetic materials are usually superior because their properties can be better controlled. The most important class of ion-exchangers are the organic ion-exchange resins. They are typical gels, their framework, the so-called matrix, consists of irregular, macromolecular, three dimensional network of hydrocarbon chains. Depending on the acidity or basicity of functional group attached to the matrix , the ion-exchange resins are classified as cation exchange resins (weakly or strongly acidic) and anion exchange resins (weakly or strongly basic).

Cation-exchange resins :

An ion-exchange resin capable of exclusively exchanging cation is classified as a cation exchanger. The early cation exchangers were naturally occurring zeolites, but these have been almost completely superseded by the synthetic ion-exchangers.

The first synthetic ion-exchangers were prepared in 1935 using a phenol-formaldehyde polymer for the cation exchanger. The synthetic cation exchangers are classified into two main groups, the weak-acid cation exchangers with hydroxyl (-OH) and carboxylic acid (-COOH) groups (4-S-3) and the strong acid cation exchangers with sulfonic ($-SO_3H$) acid groups (4-S-4). The strong acid cation exchangers are made either by sulfonation of phenol - formaldehyde polymers (sulfonation of sytrene-divinylbenzene polymers) or by polymerization of phenolsulfonic acid with formaldehyde.

Recently, other cation exchangers with different properties and acid strengths have been developed. These resins carry phosphoric ($-PO_3^{2-}$), phosphonic ($-HPO_2^-$), arsenic ($-AsO_3^{-2}$) and selenonic acid ($-SeO_3^-$) groups. Cation exchange also can contain two different functional groups with the same charge, such as sulfonic acid and carboxyl groups, such resins are called "bifunctional" or "polyfunctional".

Reaction Mechanism of Cation Exchange Resins :

The reaction of phenol with formaldehyde in the absence of some suitable catalyst is relatively slow. The nature of the

reaction product depends considerably upon whether an acidic or basic catalyst is used. The mechanism of the addition of formaldehyde to a phenol is still not clearly understood, However, the phenolic hydroxyl group activates the benzene ring so that a methylol (CH_2OH) group always enters the nucleus in ortho and para position to the hydroxyl group. When one or more of the ortho and para positions are already occupied, the reaction becomes slower and when no position is available the reaction stops.

When alkaline catalysts are used, the primary reaction products are phenol alcohols, which are called "Resoles". In the presence of acidic catalyst, the primary reaction products are also phenol alcohols, but they rearrange rapidly to yield diphenylmethane derivative, to which the name "Novalcs" has been given (4-S-5).

A three stage mechanism for the condensation in acidic catalyst have been proposed.

(i) Resol formation : This represents the initial condensation product of phenol and formaldehyde giving mainly a phenol alcohol.

(ii) Resitol formation : This is the second stage of condensation wherein the molecular weight is increased to such an extent that the product is no longer soluble in alkalis. The product is partially or completely soluble in oxygenated organic solvents. Cross- linking has just started at this stage and the resin is still soft and plastic while

hot, although hard and brittle when cold.

(iii) Resite formation : In this final stage of polymerization , a large amount of cross-linking has occurred and the resin is completely insoluble and infusible and there is formation of methylene ($-CH_2$) bridge.

In fact, the ionic character of the group is the same in the resin phase as it is in a simple organic compound, Thus all sulfonic acid exchange resins are strongly acidic in comparison to carboxylic acid resins, just as phenolsulfonic acid as strong in comparison to salicylic acid.

The ion-exchange behaviour of the resins is chiefly determined by the fixed ionic groups. The number of groups determines the ion-exchange capacity. The capacities of the weakly acidic exchangers are functions of the pH and the titration curves, i.e. curves of exchange capacity against pH have the form shown in (4-F-1) . on the other hand, the capacities of the strongly acidic exchangers are substantially independent of pH, the capacity falling only at the extreme ends of the pH scale as shown in (4-F-2) . The highest point on the titration curve represents the total capacity of the exchanger.

There has been considerable activity in the field of ion-exchange polymers in recent years. The research schools which contributed considerably towards the preparation and understanding of the nature and behaviour of polymers are those of Bauyer (1) Blasius (2) Gregor (3) Hearing (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 interms of functional groups introduced in them through specific ligand. Because of its specificity , an ion exchanger can sorb (exchange) one ionic species to the exclusion of others under broad range of conditions.

In recent years, attempts have been to obtain resins by polycondensation of phenol derivative with formaldehyde. Topp (9) De Geiso et al (10) Komiya et al (11) Rabeck et al (12) Davies et al (13) have reported salicylic acid formaldehyde condensation resins Dimitric et al (14) reported synthesis of Novalcs type ion-exchange resins from furfural and phenol. Muslimov kh I et al (15) reported a synthesis of electron exchange polymers from furfural and pyrogallol . Askarov M.A. (16,17) and Tsveshko G.S. (18) reported the synthesis of cation exchange resins based on products of the polycondensation of furfural and salicylic acid or p-hydroxybenzoic acid. Askarov et al (19,20) and Tsveshko (21) reported the synthesis of ion-exchange resins from furfural-salicylic acid, furfural-p-toluene sulphonic acid and furfural-hydroxyformamide polyethylene polyamine and studied radiation resistance and thermal stability. Biswas and Packirisamy (22) synthesized cation exchange resin from tetrahydrofuran and furfural and characterized by its total and salt splitting capacities, thermal behaviour and pH-metric titration.

Recently great deal of effort, has been directed towards the synthesis of complexing resin structures (23-26) and ion selective resins, amphoteric ion-exchange resins, inter polymeric resins and pellicular resins, etc. for various reasons. such polymers can find use in column chromatography, thin layer chromatography, ligand exchange chromatography, membrane formation, desalination, waste water treatment etc.,

Literature survey throws some light on the type of the work done on furfural type resins. We are planned to synthesis, resins by Condensation of schiff base (furfural - 1,4-phenylenediamine) with anthranilic acid, gallic acid, p-hydroxy-benzoic acid, pyrogallol and 8-hydroxyquinoline and by condensation of schiff base (furfural - benzidine) with gallic acid, p-hydroxybenzoic acid, salicylic acid and hydroquinone.

They are,

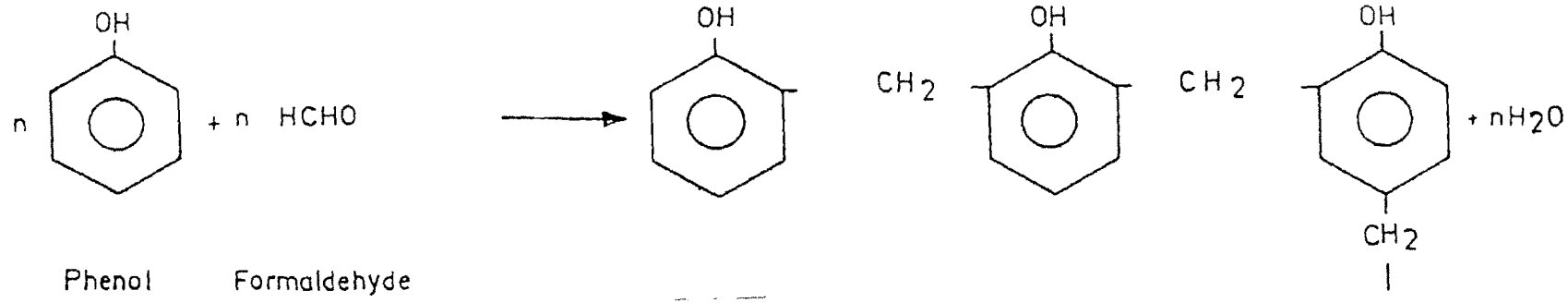
(1) Furfural - 1,4-phenylenediamine - Anthranilic acid Fu(PH)AN
Furfural - 1,4-phenylenediamine - gallic acid Fu(PH)GA
Furfural - 1,4-phenylenediamine - p-hydroxybenzoic acid Fu(PH)PHy
Furfural - 1,4-phenylenediamine - pyrogallol Fu(PH)Py
Furfural - 1,4-phenylenediamine - 8-hydroxyquinoline Fu(PH)8Hy

(2) Furfural - benzidine - gallic acid Fu(Ben)GA
Furfural - benzidine - p-Hydroxybenzoic acid Fu(Ben)PHy
Furfural - benzidine - salicylic acid Fu(Ben)SA
Furfural - benzidine - hydroquinone Fu(Ben)Hy

So to evaluate them with respect to its pertinent and distinguistable properties such as the total capacity, moisture

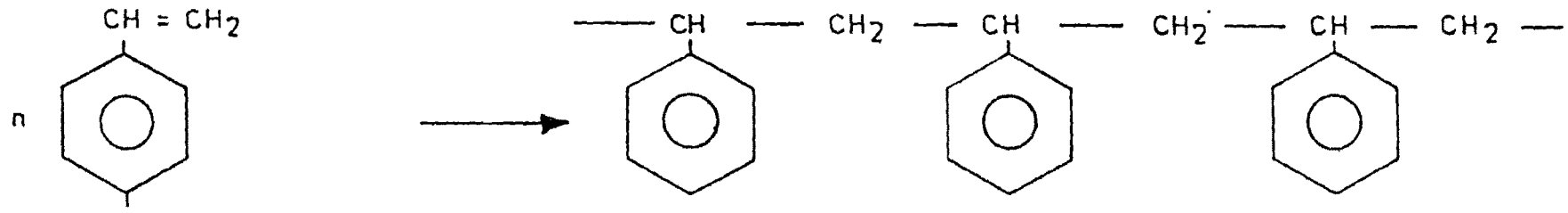
retention ability, density , void volume fraction, rate of exchange, pH titration behaviour, apparent pK_a, pK_b and isoelectric point values , oxidation resistance, the effect of equilibration at different temperature on the capacity of the resin and swelling behaviour in various solvent have been studied.

Investigations carried out with the above considerations in view and the results obtained are discussed in the following pages.



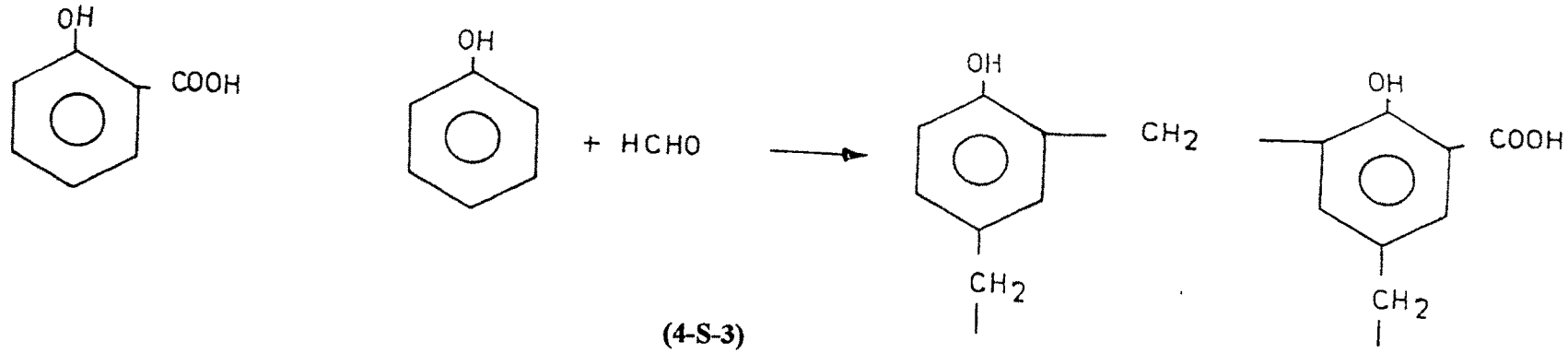
Phenol Formaldehyde

(4-S-1)

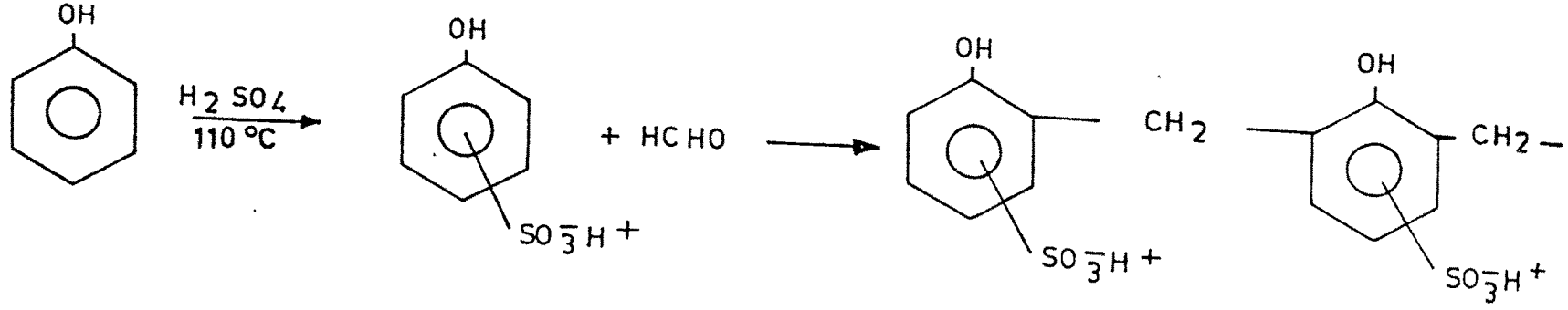


Styrene Polystyrene

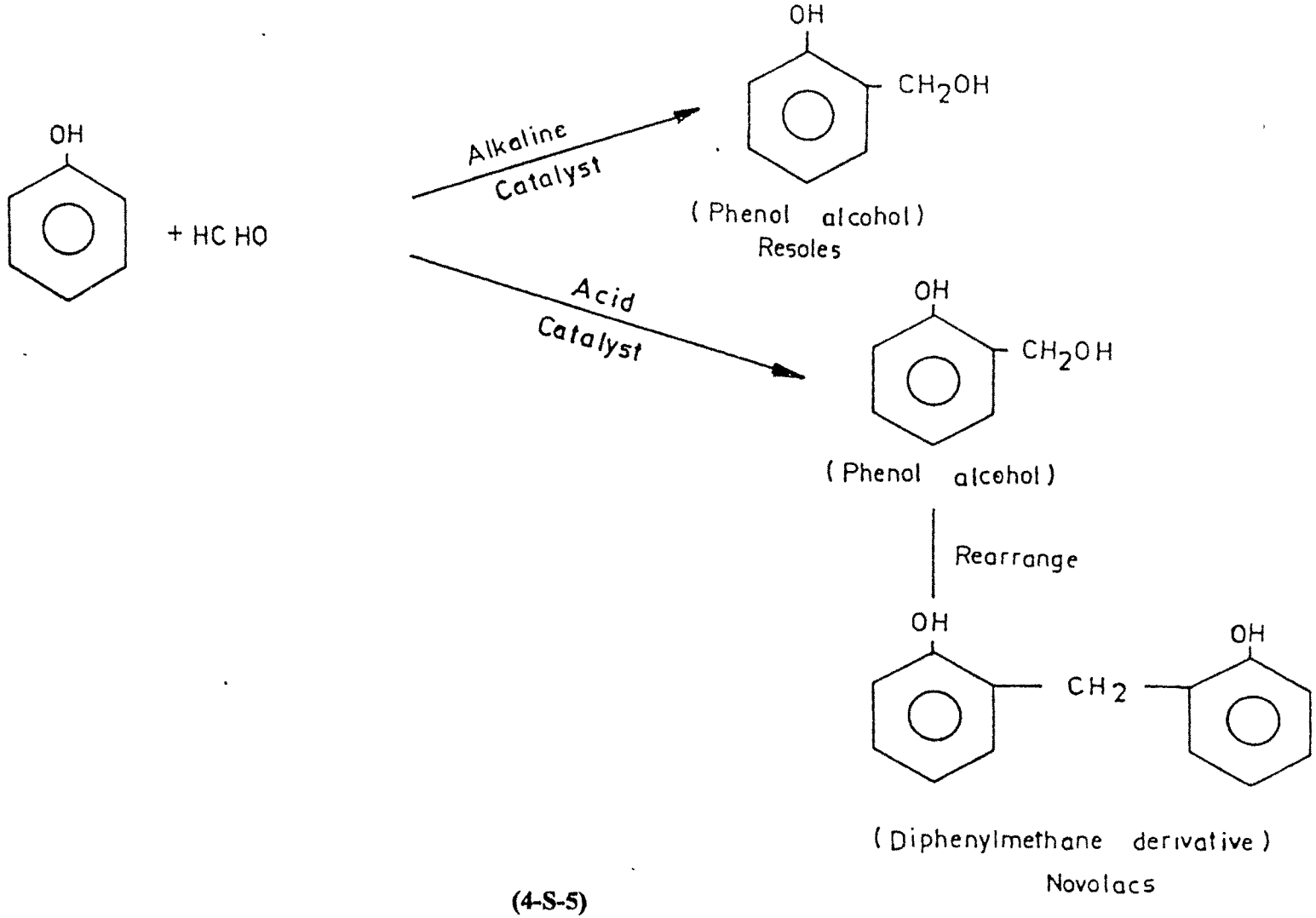
(4-S-2)


OH
COOH
OH
+ HCHO
OH
CH2
CH2
OH
COOH
CH2

(4-S-3)


OH
H2 SO4
110 °C
OH
SO3H +
+ HCHO
OH
CH2
SO3H +
OH
CH2
CH2 —
SO3H +

(4-S-4)


OH
+ HC HO
Alkaline
Catalyst
OH
CH2OH
(Phenol alcohol)
Resoles
Acid
Catalyst
OH
CH2OH
(Phenol alcohol)
Rearrange
OH
CH2
OH
(Diphenylmethane derivative)
Novolacs

(4-S-5)

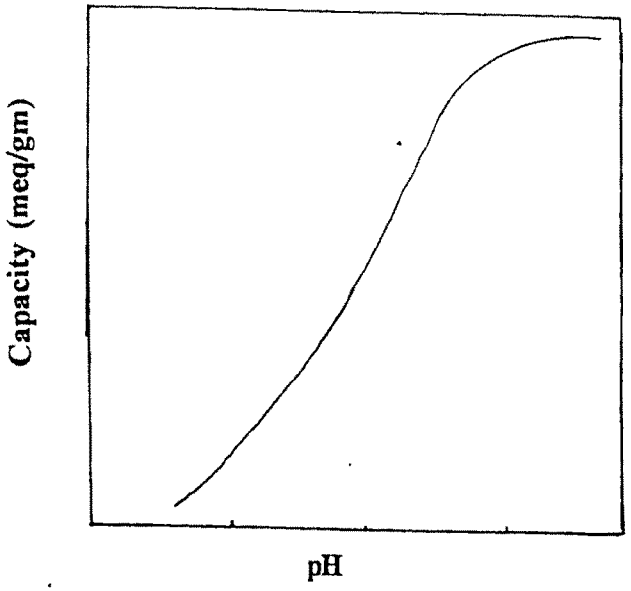


FIG (4-F-1)) TITRATIONCURVE OF
A TYPICAL UNIFUNCTIONAL WEAKLY
ACIDIC RESIN

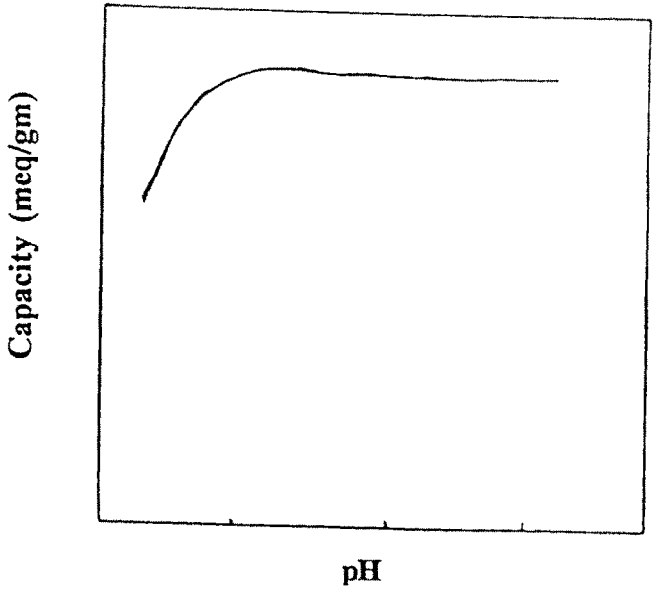


FIG ((4-F-2)TITRATIONCURVE OF
A TYPICAL UNIFUNCTIONAL STRONGLY
ACIDIC RESIN

IV (i) Furfural - 1,4-Phenylenediamine - Phenolic Derivatives and
(ii) Furfural - Benzidine - Phenolic Derivatives Types Amphoteric Ion-Exchange Resins.

EXPERIMENTAL

(a) Synthesis of amphoteric ion-exchange resins.

(i) Schiff bases (furfural - 1,4-phenylenediamine) are synthesised by using 2 moles of furfural and 1 mole of amine,using ethyl alcohol as solvent. 2 moles of anthranilic acid , gallic acid, p-hydroxybenzoic acid, pyrogallol, 8-hydroxyquinoline salicylic acid or hydroquinone was taken in 250ml round bottom flask and dissolved in DMF solvent, 1 mole of schiff base added in it, pTSA was used as initiator and refluxed for 3hrs.

(ii) Similarly schiff base (furfural - benzidine) was synthesised by using 2 moles of furfural and 1 mole of benzidine, using ethyl alcohol as solvent 2 moles of gallic acid, p-hydroxybenzoic acid, salicylic acid or hydroquinone was taken in 250ml round bottom flask and dissolved in DMF solvent. 1mole of schiff base added in it. PTSA was used as initiator and refluxed for 3hrs.

In both cases gel formation takes place in about 1/2h. A hard mass was obtained which was dark brown to black colour, for different phenolic monomers listed above. The cured hard mass was then crushed to -60 to 100 Bss mesh size as needed and washed with ethanol.

(b) Moisture content of resins

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

The values of % Moisture content of the resins (H^+ form OH^- form) are presented in Table-Sch-A-3 and Table-Sch-B-3 respectively.

(c) Density of resins

(i) True density (d_{res}) (ii) Apparent density (d_{col}) and (iii) void volume fraction of the resins (H^+ form and OH^- form were determined as described in 1-(c) (i), (ii) and (iii).

The values of d_{res} and d_{col} of the resins (H^+ form and OH^- form) are presented in Table-Sch-A-4 and Table-Sch-B-4 respectively.

The values of void volume fraction of the resins (H^+ form and OH^- form) are presented in Table-Sch-A-5 and Table-Sch-B-5 respectively.

(d) (i) Total ion-exchange capacity and (ii) concentration of ionogenic groups.

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

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

The values of total ion-exchange capacity concentration of

ionogenic groups and volume capacity of the resins as cation exchanger as well as anion exchange are presented in Table-Sch-A-6A and 6B, Table-Sch-B-6A and 6B respectively.

(e) Metal (Cu) exchange capacity.

Metal (Cu) exchange capacity of the resins (H^+ form) were determined by following the procedure described in I-(e) and the values are presented in Table-Sch-A-6A and Table-Sch-B-6A respectively.

(f) Rate of exchange

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

The values of the capacities of the resins were plotted against time and shown in figs. 4.1 to 4.8 and presented in Table-Sch-A-7 and Table-Sch-B-7 respectively.

(g) pH-titration studied and apparent pK_a and pK_b values.

pH titration studies and apparent pK_a and pK_b values of the resins were determined as described in 1(g).

The values of the capacities of the resins were plotted against the pH of the solution as shown in Figs 4.9 to 4.12.

The apparent pK_a and pK_b values for the resins are present in Table-Sch-A-8 and Table-Sch-B-8 respectively.

(h) Effect of the temperature of equilibration on the capacity of the resin.

The study of the effect of varying equilibration temperature on the capacity of the resins (H^+ form and OH^- form) were carried out according to the method described in I-(h). The results are presented in Table-Sch-A-9 and Table-Sch-B-9 respectively.

(i) Oxidation resistance test

Oxidation resistance of the resins in free acid and free base form were carried out as described in I-(i). The results are presented in Table-Sch-A-10A,10B and Table-Sch-B-10A,10B respectively.

(j) Swelling Behaviour

Swelling behaviour of the resins (H^+ form and OH^- form) in various solvents were studied as described in I-(j).

The results are presented in Table-Sch-A-11A,11B and Table-Sch-B-11A,11B respectively.

IV (i) Furfural - 1,4-Phenylenediamine - Phenolic Derivatives and (ii) Furfural - Benzidine - Phenolic Derivatives Types Amphoteric Ion-Exchange Resins.

RESULT AND DISCUSSION

GENERAL

In recent years, attempts have been made to obtain resins by polycondensation of phenol derivatives with furfural. Dimitric et al (27) reported synthesis of novalc type ion-exchange resins from furfural and phenol. Muslimov kh I et al (15) reported a synthesis of electron-exchange polymers from furfural and pyrogallol. Askarov M A (16,17) and Tsveshko G S (18) reported the synthesis of cation exchange resins based on products of the polycondensation of furfural and salicylic acid or p-hydroxybenzoic acid. Askarov et al (19,20) and Tsveshko (21) reported the synthesis of ion-exchange resins from furfural-salicylic acid, furfural -p-toluene sulphonic acid and furfural - hydroformamide polyethylene polyamine and studied radiation resistance and thermal stabi lity. Biswas and Packirisamy (22) synthesized cation exchange resin from tetrahydrofuran and furfural. Kapadia and Dalal(28) synthesized phenol furfural type chelating ion-exchange resin and characterised by its total exchange capacity and pH-metric titration.

We have synthesized amphoteric ion exchangers from various phenolic derivatives and schiff base.(which were synthesized from furfural - 1,4-phenylenediamine or benzidine)

The condensate (resins) are insoluble in methanol, ethanol and benzene in which the individual components are soluble . Therefore the material (resins) appears to be a condensate product of the various phenolic derivatives with schiff base. The phenolic derivatives employed for synthesising resins possess the following structural features.

(a) One amino group and one carboxyl group in ortho position on a phenyl ring.

(b) Two phenolic groups meta and one phenolic group is para position to the carboxyl group on a phenyl ring.

(c) One phenolic group and one carboxyl group in para position on a phenyl ring.

(d) Three phenolic group are ortho position to each other on a phenyl ring.

(e) One phenolic group and one ring nitrogen.

(f) One phenolic group and one carboxyl group are in ortho position on phenyl ring.

(g) Two phenolic groups in a para position to each other.

The most probable structures of these resins on basis of analytical data and physico-chemical studies are shown as :

(i) Fu(PH)AN	(ii) Fu(PH)GA	(iii) Fu(PH)PHy
(iv) Fu(PH)Py	(v) Fu(PH)8Hy	
(i) Fu(Ben)GA	(ii) Fu(Ben)PHy	(iii) Fu(Ben)SA
(iv) Fu(Ben)Hy		

Gelling and curing

Curing involves the thermo-setting of gel. In the phenol-schiff base series under investigation, gelling time and curing period for all the resins are same, infers that gelling time and curing period is directly related to phenolic compounds

functionality only.

General Characteristics and structures :

The amphoteric ion exchangers, in general are fairly porous in nature with average physical stability and good chemical resistance to 3N acid and alkalis and all resins are black in colour.

In the present, investigation the polymers were obtained by poly - condensation under mild reactions and curing conditions cross-linking possible by formation of-C-C- Linkages, although on the basis of analytical data and other physico-chemical studies, we may have postulated structure as shown in fig.S.4.1 and S.4.2.

Moisture retention %

Percentage moisture of the resins are presented in Table-Sch-A-3 & Tab-Sch-B-3. Percentage moisture of the resins in H^+ form for resin synthesised from 1,4- phenylenediamine varies between 4.08 to 7.6. Percentage moisture of the resins in the OH^- form varies between 5.93 to 8.34 . This suggests that the amphoteric resins have a high degree of cross-linking. It is known that the degree of cross-linking is inversely proportional to the moisture content.

In case of resins synthesised from benzidine moisture of H^+ form varies between 4.02 to 5.22 and for OH^- form 4.93 to 6.26 . This also suggest that the degree of cross-linking very high.

Density of resins

(i) True density (d_{res})

The data obtained for the density d_{res} of the resins in H^+ form and OH^- form for both series are presented in Table-Sch-A-4 and Table-Sch-B-4 respectively. The values vary from 1.22 to 1.88 for H^+ form and 1.12 to 1.60 for OH^- form for 1,4-phenylenediamine series. In case of benzidine the values for H^+ form varies between 1.20 to 1.31 & for OH^- form varies between 1.10 to 1.28. In case of Fu(Ben)GA and Fu(Ben)SA the values are same.

(ii) Apparent density (d_{col})

We have also evaluated the apparent column density (d_{col}) of the amphoteric resins on Table-Sch-A-4 and Table-Sch-B-4 respectively . The values are ranging from 0.24 to 0.32 for H^+ form, 0.24 to 0.31 for OH^- form for 1,4-phenylenediamine series.

The values vary form 0.24 to 0.32 for H^+ form and 0.25 to 0.31 for OH^- form benzidine series.

Known values (29) of apparent density for commercial resins in H^+ form are 0.69 for IRC-50/57 and 0.75 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 for IRA -68 [weak base $-N(R)_2$], 0.61 for IR -45 [weak base $-N(R)_2$, $-NH(R)$, $-NH_2$] and 0.64 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 of resins are presented in Table-Sch-A-5 & Table-Sch-B-5 respectively. It is observed that the values of void volume fraction vary between 0.76 to 0.82 for cationic form and 0.77 to 0.80 for anionic form of the amphoteric resins in case of 1,4-phenylenediamine series and values varies between 0.7 to 0.76 for H^+ form and 0.71 to 0.80 for OH^- form in case of benzidine series. We suggest that as the resins have a large void volume fraction, the diffusion of ions and hence the rate of ion-exchange may be facilitated. The large void volume fraction suggests the porous nature of the resins.

Ion-exchange capacity.

The cation or anion exchange capacity of the amphoteric resins can be calculated using the formula described in chapter 1.

The observed capacity CEC_{obs} (cation exchanger) or AEC_{obs} (anion exchanger) can be compared with the calculated capacity CEC_{cal} or AEC_{cal} as reported in Table-Sch-A-6A, Table-Sch-B-6A and Table Sch-A-6B, Table-Sch-B-6B, respectively.

For ion-exchange resins synthesised from 1,4-phenylene-diamine, one range exist for CEC_{obs}/CEC_{cal} value of CEC_{obs}/CEC_{cal} is less than 1.

Amphoteric resins as cation exchanger show the following decreasing order for cation exchange capacity.

Fu(PH)Py > Fu(PH)GA > Fu(PH)PHy > Fu(PH)8Hy > Fu(PH)AN

Amphoteric resins as anion exchanger show the following decreasing order for anion exchange capacity.

Fu(PH)AN > Fu(PH)8Hy > Fu(PH)PHy > Fu(PH)Py > Fu(PH)GA

In the case of ion-exchange resins synthesised from benzidine, two ranges exist for CEC_{obs} / CEC_{cal}.

(1) Value of CEC_{obs}/CEC_{cal} is less than 1,

(2) Value of CEC_{obs}/CEC_{cal} is slightly higher than 1.

The observed capacity AEC_{obs} can be compare with AEC_{cal} as presented in Table-Sch-B-6A and Table-Sch-B-6B.

Amphoteric resins as cation exchanger show the following decreasing order for cation exchange capacity.

Fu(Ben)GA > Fu(Ben)Hy > Fu(Ben)PHy > Fu(Ben)SA

Amphoteric resins as anion exchanger show the following decreasing order for anion exchange capacity.

Fu(Ben)GA $\geq$ Fu(Ben)PHy > Fu(Ben)Hy > Fu(Ben)SA

Concentration of ionogenic groups :

The data regarding the concentration of ionogenic groups are presented in Table-Sch-A-6A, Table-Sch-A-6B, Table-Sch-B-6A, and Table-Sch-B-6B for resins synthesised from 1,4-phenylenediamine and benzidine respectively.

It is seen that , the total exchange capacity is related to the concentration of ionogenic groups. Higher the exchange

capacity , higher is the concentration of ionogenic groups.

Metal (Cu) Exchange capacity.

Result of copper ion-exchange capacity of these resins (H^+ form) are presented in Table-Sch-A-6A, and Table-Sch-B-6A respectively.

It is observed that the copper ion-exchange capacity of resins synthesised from 1,4-phenylenediamine range between 2.40 to 3.24 meq/gm. The decreasing order for the copper ion-exchange capacity of these resins were observed as.

Fu(PH)Py > Fu(PH)GA > Fu(PH)8Hy > Fu(PH)AN > Fu(PH)PHy.

Similarly copper ion-exchange capacity of the resins synthesised from benzidine ranges between 2.20 to 3.14 meq/gm. The decreasing order for the copper ion- exchange capacity of these resins were observed as

Fu(Ben)GA > Fu(Ben)Hy > Fu(Ben)PHy > Fu(Ben)SA.

Rate of exchange:

Figs 4.1 to 4.4 represent the rate of cation exchange as well as anion exchange of amphoteric resins synthesised from 1,4-phenylenediamine.

A perusal of the trends of the rate of exchange for amphoteric resins as cation exchanger as well as anion exchanger reveals that the rate is very fast.

In case of amphoteric resins as cation exchange it is observed that

(i) Complete exchange occurs in 20 to 40 min.

(ii) The rate of exchange for these resins is in the following decreasing order.

Fu(PH)Py > Fu(PH)GA > Fu(PH)8Hy > Fu(PH)AN > Fu(PH)PHy

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

(i) Complete exchange occurs in 40 to 60 min.

(ii) The decreasing order for the rate of exchange of these resins is

Fu(PH)Py > Fu(PH)AN ≒ Fu(PH)8Hy > Fu(PH)GA > Fu(PH)PHy

Similarly, perusal of the trends of the rate of exchange for amphoteric resins synthesised from benzidine as cation exchanger as well as anion exchanger reveals that the rate is very fast and it is represented in figs 4.4 to 4.8.

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

(i) Complete exchange occurs in 40 to 60 min.

(ii) The rate of exchange for these resins is in the following decreasing order

Fu(Ben)GA > Fu(Ben)Hy > Fu(Ben)PHy > Fu(Ben)SA

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

(i) Complete exchange occurs in 60 to 80 min.

(ii) The decreasing order for the rate of exchange of these resins is

Fu(Ben)PHy> Fu(Ben)GA > Fu(Ben)Hy > Fu(Ben)SA

pH- titration study

The result of pH-titration curves (Figs. 4.9 to4.12) reveal the amphoteric nature of ion-exchange resins prepared. They exhibit good cation and anion exchange capacity over the pH range 1 to 12. These resins can be used as anion exchanger as well as cation exchanger depending upon the pH of the solution. In the pH range 1 to 7 , resins acted as anion exchanger (Figs 4.10 and 4.12), and curves over this range are characteristic of weakly basic resin and may be compared with pH titration curve of commercially available weakly basic anion exchange resin, Tulsion WB (30) . The cation exchange behaviour of these resins is similar to weak resin (31).

Apparent pK_a and pK_b values

The apparent pK_a and pK_b values of the resins under study were obtained from pH titration curves and calculated using equation (9) and (14) as described earlier in chapter I and and are reported in Table-Sch-A-8 and Table-Sch-B-8 respectively for the resins synthesised from 1,4-phenylenediamine and benzidine.

In case of resins synthesised from 1,4-phenylenediamine pK_a obtained for cation exchange process in general for various ion exchange studied between 11.01 to 11.86.

The pK_a values for the resins are in the following decreasing order.

Fu(Ben)Hy > Fu(Ben)GA > Fu(Ben)PHy > Fu(Ben)SA

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

Fu(Ben)Hy > Fu(Ben)GA > Fu(Ben)PHy > Fu(Ben)SA

Isoionic Point

The values of Isoionic point (ip) are presented in Table-Sch-A-8 and Table-Sch-B-8 for these resins synthesised form 1,4-phenylenediamine and benzidine.

The values vary in the range of 7.33 to 7.83 for resins synthesised from 1,4-phenylenediamine and the value vary in the range of 3.37 to 8.10 for resins synthesised from benzidine. For histidine the value of ip 7.3 (32) which is comparable with resins under study.

The isoionic point values are in the decreasing order as, for resins, synthesised from 1,4-phenylenediamine.

Fu(PH)PHy > Fu(PH)AN > Fu(PH)8Hy > Fu(PH)GA > Fu(PH)Py

The isoionic point values are in the decreasing order for resins synthesised from benzidine as

Fu(Ben)Hy > Fu(Ben)GA > Fu(Ben)PHy > Fu(Ben)SA

Effect of temperature of equilibration on the capacity of resin.

The results of the effect of varying temperature of equilibration on the capacity of the resins are reported in

Table-Sch-A-9 and Table-Sch-B-9 for the resins synthesised from 1,4-phenylenediamine and benzidine respectively.

From the data it is revealed that the anion exchange capacity of amphoteric resins increased with the rise in temperature equilibration. This can be explained as follows on heating the resin, certain basic gaseous decomposition products (such as NH_3 resulting from 1,4-phenylenediamine & benzidine used in the preparation of resins) are produced which neutralize a part of the acid during equilibration, thus giving apparently higher value for the anion exchange capacity of the resin. The loss in cation exchange capacity of the resins with the rise in equilibration temperature may be due to the loss of ionogenic groups.

Oxidation resistance

Results of oxidation resistance test of different amphoteric exchangers as cation exchanger are presented in Table-Sch-A-10A & Table-Sch-B-10B for Schiff base synthesised from 1,4-phenylene-diamine and benzidine respectively.

We observed that, the oxidative degradation for amphoteric resins cation exchanger exhibit high increase in percentage water content than the amphoteric resins as anion exchanger. Hence we suggest that anionic form is less susceptible to oxidation than cationic form.

Amphoteric resins as cation exchangers show the following decreasing order for their stability on the oxidation degradation

for resins synthesised from 1,4-phenylenediamine.

Fu(PH)8Hy > Fu(PH)AN > Fu(PH)Py > Fu(PH)GA > Fu(PH)PHy.

Amphoteric resins as cation exchanger show the following decreasing order for their stability on the oxidative degradation for resins synthesised from benzidine.

Fu(Ben)SA > Fu(Ben)PHy > Fu(Ben)Hy > Fu(Ben)GA

Amphoteric resins as anion exchanger show the following decreasing order for their stability on oxidative degradation for resins synthesised from 1,4-phenylenediamine and benzidine respectively.

Fu(PH)PHy > Fu(PH)AN > Fu(PH)Py > Fu(PH)8Hy > Fu(PH)GA
Fu(Ben)Hy > Fu(Ben)GA > Fu(Ben)SA > Fu(Ben)PHy

Behaviour in non-aqueous solvents

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

It is observed that,

(i) Polar solvent produce more extensive swelling than non polar hydrocarbons. Swelling of an ion-exchange resin in water and other polar solvent is chiefly caused by hydration tendency of the fixed ionic groups and counter ions, the osmotic activity of counter ions and the electrostatic repulsion between neighboring fixed ionic groups. The

elastic matrix expands until swelling equilibrium is attained.

(ii) In polar solvents (H_2O, CH_3OH, CH_3COOH) with some exception amphoteric resins as anion exchanger swell more than cationic type,

(iii) Percentage swelling of amphoteric resins in acetic acid as anion exchanger as well as cation exchanger is much greater than would be anticipated. This is explained on page 43

(iv) The decreasing order of porosity of amphoteric resin synthesised from 1,4-phenylenediamine as cation exchanger is as follows.

Fu(PH)GA > Fu(PH)Py > Fu(PH)PHy > Fu(PH)8Hy > Fu(PH)AN

The decreasing order of porosity of amphoteric resin, as cation exchanger are as follows which were synthesised from benzidine.

Fu(Ben)PHy > Fu(Ben)SA > Fu(Ben)GA > Fu(Ben)Hy

(v) The decreasing order of porosity for amphoteric resins an anion exchanger are as follows. Which were synthesised from 1,4-phenylenediamine.

Fu(PH)Py > Fu(PH)GA > Fu(PH)AN > Fu(PH)8Hy > Fu(PH)PHy

The decreasing order of porosity for amphoteric resins as anion exchanger are as follows which were synthesised from benzidine.

Fu(Ben)SA > Fu(Ben)GA > Fu(Ben)PHy > Fu(Ben)Hy

TABLE-Sch-A-1

Abbreviation

No.	Resin	Abbreviation
1.	Furfural-1,4-Phenylenediamine - Anthranilic acid	Fu(PH)AN
2.	Furfural-1,4-Phenylenediamine - Gallic acid	Fu(PH)GA
3.	Furfural-1,4-Phenylenediamine - p-Hydroxybenzoic acid	Fu(PH)PHy
4.	Furfural-1,4-Phenylenediamine - Pyrogallol	Fu(PH)Py
5.	Furfural-1,4-Phenylenediamine - 8-Hydroxyquinoline	Fu(PH)8Hy

TABLE-Sch-B-1

Abbreviation

No.	Resin	Abbreviation
1.	Furfural- Benzidine - Gallic acid	Fu(Ben)GA
2.	Furfural- Benzidine - p-Hydroxybenzoic acid	Fu(Ben)PHy
3.	Furfural- Benzidine - Salicylic acid	Fu(Ben)SA
4.	Furfural- Benzidine - Hydroquinone	Fu(Ben)Hy

TABLE-Sch-A-2

Analyses, formulae etc. of amphoteric resins

Resin	Formula	Calculated			Observed		
		%C	%H	%N	%C	%H	%N
Fu(PH)AN	$C_{30}H_{22}O_4N_4$	71.71	4.38	11.15	68.80	4.58	10.63
Fu(PH)GA	$C_{30}H_{20}O_{10}N_2$	63.38	3.52	4.92	59.68	4.48	4.05
Fu(PH)PHy	$C_{30}H_{20}O_6N_2$	71.42	3.96	5.55	62.76	4.67	5.66
Fu(PH)Py	$C_{28}H_{20}O_8N_2$	65.62	3.90	5.46	62.29	4.92	5.21
Fu(PH)8Hy	$C_{34}H_{22}O_4N_4$	74.18	4.00	10.18	64.85	4.94	9.52

TABLE-Sch-B-2

Analyses, formulae etc. of amphoteric resins

Resin	Formula	Calculated			Observed		
		%C	%H	%N	%C	%H	%N
Fu(Ben)GA	$C_{36}H_{24}O_{10}N_2$	67.08	3.72	4.34	67.72	5.04	2.35
Fu(Ben)PHy	$C_{36}H_{24}O_6N_2$	74.48	4.13	4.82	70.42	5.08	3.26
Fu(Ben)SA	$C_{36}H_{24}O_6N_2$	74.48	4.13	4.82	73.79	5.35	4.46
Fu(Ben)Hy	$C_{34}H_{24}O_6N_2$	73.38	4.31	5.03	70.73	5.16	2.58

TABLE-Sch-A-3

% Moisture content of amphoteric resins

No.	Resin	% Moisture	
		H^+ - form	OH^- - form
1.	Fu(PH)AN	4.08	6.62
2.	Fu(PH)GA	7.6	8.34
3.	Fu(PH)PHy	5.89	5.93
4.	Fu(PH)Py	5.9	6.34
5.	Fu(PH)8Hy	5.32	6.03

TABLE-Sch-B-3

% Moisture content of amphoteric resins

No.	Resin	% Moisture	
		H^+ - form	OH^- - form
1.	Fu(Ben)GA	5.22	6.26
2.	Fu(Ben)PHy	4.9	5.15
3.	Fu(Ben)SA	4.02	4.93
4.	Fu(Ben)Hy	5.01	5.98

TABLE-Sch-A-4

Density of resins

No.	Resin	True density of resins d_{res} (gm/cm^3)		Apparent (Column) density of resin (d_{col}) (gm/ml)	
		H^+ - form	OH^- - form	H^+ - form	OH^- - form
1.	Fu(PH)AN	1.48	1.49	0.30	0.30
2.	Fu(PH)GA	1.24	1.23	0.29	0.28
3.	Fu(PH)PHy	1.22	1.12	0.24	0.24
4.	Fu(PH)Py	1.88	1.60	0.32	0.31
5.	Fu(PH)8Hy	1.38	1.48	0.31	0.31

TABLE-Sch-B-4

Density of resins

No.	Resin	True density of resins d_{res} (gm/cm^3)		Apparent (Column) density of resin (d_{col}) (gm/ml)	
		H^+ - form	OH^- - form	H^+ - form	OH^- - form
1.	Fu(Ben)GA	1.11	1.10	0.29	0.30
2.	Fu(Ben)PHy	1.31	1.23	0.32	0.29
3.	Fu(Ben)SA	1.00	1.10	0.28	0.31
4.	Fu(Ben)Hy	1.01	1.28	0.24	0.25

TABLE-Sch-A-5

Void volume fraction of resins

No.	Resin	Resin in H^+ - form		Resin in OH^- - form	
		$\frac{d_{col}}{d_{res}}$	void volume fraction $(1-d_{col}/d_{res})$	$\frac{d_{col}}{d_{res}}$	void volume fraction $(1-d_{col}/d_{res})$
1.	Fu(PH)AN	0.20	0.79	0.20	0.79
2.	Fu(PH)GA	0.23	0.76	0.22	0.77
3.	Fu(PH)PHy	0.19	0.80	0.21	0.78
4.	Fu(PH)Py	0.17	0.82	0.19	0.80
5.	Fu(PH)8Hy	0.22	0.77	0.20	0.79

TABLE-Sch-B-5

Void volume fraction of resins

No.	Resin	Resin in H^+ - form		Resin in OH^- - form	
		$\frac{d_{col}}{d_{res}}$	void volume fraction $(1-d_{col}/d_{res})$	$\frac{d_{col}}{d_{res}}$	void volume fraction $(1-d_{col}/d_{res})$
1.	Fu(Ben)GA	0.25	0.74	0.27	0.72
2.	Fu(Ben)PHy	0.24	0.75	0.23	0.76
3.	Fu(Ben)SA	0.27	0.72	0.28	0.71
4.	Fu(Ben)Hy	0.23	0.76	0.19	0.80

TABLE-Sch-A-6A

Capacity and concentration of ionogenic groups of ion-exchange resin as cation exchanger

Resin	Total capacity $CEC_{obs.}$ (meq/gm)	Total capacity $CEC_{cal.}$ (meq/gm)	$\frac{CEC_{obs.}}{CEC_{cal.}}$	Concentration of ionogenic groups Cr (meq/cm^3)	Volume capacity gm eq/l Q	Cu-exchange capacity meq/gm
Fu(PH)AN	1.01	1.99	0.50	1.43	0.29	2.45
Fu(PH)GA	5.22	10.56	0.49	5.98	1.39	3.04
Fu(PH)PHy	3.12	3.96	0.78	3.58	0.70	2.40
Fu(PH)Py	6.13	11.71	0.52	10.84	1.84	3.24
Fu(PH)8Hy	1.25	1.90	0.65	1.63	0.36	2.94

TABLE -Sch-A-6B

Capacity and Concentration of ionogenic groups of ion-exchange resins as anion exchanger

Resin	Total Capacity $AEC_{obs.}$ meq/gm	Total Capacity $AEC_{cal.}$ meq/gm	$\frac{AEC_{obs.}}{AEC_{cal.}}$	Concentration of ionogenic groups Cr meq/cm^3	Volume capacity gm eq/l Q
Fu(PH)AN	5.81	7.96	0.73	8.05	1.62
Fu(PH)GA	2.00	3.52	0.56	2.25	0.51
Fu(PH)PHy	3.01	3.96	0.75	3.17	0.67
Fu(PH)Py	3.59	3.90	0.91	5.37	1.04
Fu(PH)8Hy	5.98	7.27	0.82	8.31	1.74

TABLE-Sch-B-6A

Capacity and concentration of ionogenic groups of ion-exchange resin as cation exchanger

Resin	Total Capacity $CEC_{obs.}$ (meq/gm)	Total capacity $CEC_{cal.}$ (meq/gm)	$\frac{CEC_{obs.}}{CEC_{cal.}}$	Concentration of ionogenic groups Cr meq/cm^3	Volume capacity gm eq/l Q	Cu-exchange capacity meq/gm.
Fu(Ben)GA	5.99	9.31	0.58	0.53	0.13	3.14
Fu(Ben)PHy	4.65	3.44	1.34	0.62	0.15	2.49
Fu(Ben)SA	4.13	3.44	1.19	0.47	0.13	2.20
Fu(Ben)Hy	5.01	7.19	0.69	0.48	0.11	3.00

TABLE-Sch-B-6B

Capacity and concentration of ionogenic groups of ion-exchange resins as anion exchanger

Resin	Total Capacity $AEC_{obs.}$ meq/gm	Total Capacity $AEC_{cal.}$ meq/gm	$\frac{AEC_{obs.}}{AEC_{cal.}}$	Concentration of ionogenic groups Cr. meq/cm^3	Volume capacity gm eq/l Q
Fu(Ben)GA	5.45	3.10	1.92	0.47	0.12
Fu(Ben)PHy	5.51	3.44	1.59	0.56	0.13
Fu(Ben)SA	5.38	3.44	1.56	0.47	0.13
Fu(Ben)Hy	5.41	3.59	1.50	0.55	0.11

TABLE-Sch-A-7

Rate of exchange of resins

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1.	Fu(PH)AN	5	0.20	0.53
		10	0.25	2.00
		15	0.35	3.01
		20	0.45	3.85
		40	0.50	4.85
		60	1.10	5.53
		80	1.10	5.80
		100	1.03	5.75
		120	1.03	5.81
2.	Fu(PH)GA	5	0.52	0.55
		10	2.51	1.05
		15	2.80	1.55
		20	4.02	1.85
		40	4.61	2.01
		60	4.85	2.02
		80	4.75	2.04
		100	4.90	2.05
		120	5.01	2.06
3.	Fu(PH)PHy	5	1.01	0.25
		10	1.52	1.25
		15	1.03	1.35
		20	2.05	1.95
		40	2.51	2.92
		60	2.82	4.01
		80	3.09	4.50
		100	3.01	4.23
		120	3.05	4.25
4.	Fu(PH)Py	5	2.01	1.01
		10	3.75	1.90
		15	3.50	2.44
		20	4.50	2.81
		40	5.20	3.06
		60	5.41	3.55
		80	5.42	3.53
		100	5.25	3.50
		120	5.53	3.51

CONTINUED.....

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
5.	Fu(PH)8Hy	5	0.51	1.01
		10	0.90	1.76
		15	1.02	2.55
		20	1.40	2.74
		40	1.52	4.03
		60	1.95	5.01
		80	1.95	5.56
		100	1.95	5.54
		120	1.95	5.52

TABLE-Sch-B-7

Rate of exchange of resins

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1.	Fu(Ben)GA	5	0.50	2.02
		10	2.15	2.98
		15	1.0	3.26
		20	3.05	3.52
		40	4.45	5.25
		60	4.95	5.5
		80	4.95	5.76
		100	5.0	6.05
		120	5.0	6.25
2.	Fu(Ben)PHy	5	1.00	1.00
		10	1.00	2.5
		15	2.5	3.0
		20	4.0	4.0
		40	4.25	4.51
		60	4.43	5.0
		80	4.50	5.40
		100	4.50	5.40
		120	4.50	5.40
3.	Fu(Ben)SA	5	0.5	0.25
		10	1.35	3.0
		15	1.50	3.25
		20	3.40	3.65
		40	3.50	4.30
		60	4.15	4.55
		80	4.15	4.55
		100	4.0	4.60
		120	4.25	4.75
4.	Fu(Ben)Hy	5	0.5	2.0
		10	1.5	2.7
		15	2.0	3.85
		20	4.0	3.0
		40	4.5	4.85
		60	4.20	4.75
		80	4.35	5.05
		100	5.05	5.25
		120	5.05	5.25

TABLE-Sch-A-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.	Fu(PH)AN	11.76	3.77	7.77
2.	Fu(PH)GA	11.52	3.59	7.56
3.	Fu(PH)PHy	11.71	3.96	7.83
4.	Fu(PH)Py	11.01	3.65	7.33
5.	Fu(PH)8Hy	11.86	3.35	7.61

TABLE-Sch-B-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.	Fu(Ben)GA	11.82	3.65	7.73
2.	Fu(Ben)PHy	11.41	3.50	7.45
3.	Fu(Ben)SA	11.40	3.34	7.37
4.	Fu(Ben)Hy	12.20	4.01	8.10

TABLE-Sch-A-9

Effect of temperature of equilibration on the capacity of the resin
equilibration period = 2hr. Amount of Resin = 0.5 gm.

No.	Resin	Total AEC (meq/gm) of absolutely dry resin as determined at temp. (^{o}C)			Total CEC (meq/gm) of absolutely dry resin as determined at temp. (^{o}C)		
		30^{0}	50^{0}	70^{0}	30^{0}	50^{0}	70^{0}
1.	Fu(PH)AN	4.03	3.93	3.90	5.29	5.31	5.33
2.	Fu(PH)GA	5.13	5.09	5.01	5.49	5.56	5.67
3.	Fu(PH)PHy	3.26	3.21	3.20	5.02	5.10	5.15
4.	Fu(PH)Py	6.09	5.83	5.80	6.32	6.39	6.41
5.	Fu(PH)8Hy	4.790	4.80	4.800	5.89	5.91	5.93

TABLE-Sch-B-9

Effect of temperature of equilibration on the capacity of the resin
equilibration period = 2hr. Amount of resin = 0.5 gm

No.	Resin	Total AEC (meq/gm) of absolutely dry resin as determined at temp. (°C)			Total CEC (meq/gm) of absolutely dry resin as determined at temp. (°C)		
		30^{o}	50^{o}	70^{o}	30^{o}	50^{o}	70^{o}
1.	Fu(Ben)GA	5.21	5.22	5.31	5.34	5.31	5.29
2.	Fu(Ben)PHy	5.13	5.14	5.23	4.62	4.34	4.23
3.	Fu(Ben)SA	5.23	5.34	5.43	4.13	4.09	4.08
4.	Fu(Ben)Hy	5.31	5.43	5.54	5.04	4.93	4.81

TABLE-Sch-A-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.	Fu(PH)AN	4.08	12.45	8.37
2.	Fu(PH)GA	7.60	17.93	10.33
3.	Fu(PH)PHy	5.89	14.16	12.27
4.	Fu(PH)Py	5.90	14.98	9.08
5.	Fu(PH)8Hy	5.32	13.42	8.16

TABLE-Sch-A-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.	Fu(PH)AN	6.62	14.32	7.70
2.	Fu(PH)GA	8.34	16.96	8.62
3.	Fu(PH)PHy	5.93	12.34	6.41
4.	Fu(PH)Py	6.34	14.28	7.94
5.	Fu(PH)8Hy	6.03	14.13	8.10

TABLE-Sch-B-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.	Fu(Ben)GA	5.23	14.03	8.81
2.	Fu(Ben)PHy	4.9	12.48	7.58
3.	Fu(Ben)SA	4.02	11.59	7.57
4.	Fu(Ben)Hy	5.01	13.56	8.55

TABLE-Sch-B-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.	Fu(Ben)GA	6.26	12.93	6.67
2.	Fu(Ben)PHy	5.15	12.43	8.28
3.	Fu(Ben)SA	4.93	12.03	7.10
4.	Fu(Ben)Hy	5.98	11.34	5.36

TABLE-Sch-A-11A

% Swelling of resin in various solvents for cation exchanger

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	pet. ether
Fu(PH)AN	4.01	2.54	2.03	1.92	2.34	1.53	1.50	0	0
Fu(PH)GA	8.53	5.03	3.24	2.53	3.05	2.08	1.53	1.02	0
Fu(PH)PHy	4.64	3.12	2.05	1.85	2.35	1.51	1.25	0	0
Fu(PH)Py	8.02	6.93	4.63	3.03	5.67	2.95	2.45	1.13	0
Fu(PH)8Hy	4.34	3.84	4.84	3.55	3.17	2.66	2.08	1.23	0

TABLE-Sch-A-11B

% Swelling of resin in various solvents for anion exchanger

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	pet. ether
Fu(PH)AN	5.35	3.46	3.12	2.13	2.43	2.61	1.53	0	0
Fu(PH)GA	8.93	6.13	4.34	3.61	3.15	3.14	2.45	0	0
Fu(PH)PHy	4.04	3.64	3.13	2.94	3.93	2.91	2.45	0	0
Fu(PH)Py	9.93	7.34	4.52	3.12	6.78	3.14	3.45	0	0
Fu(PH)8Hy	4.83	4.34	4.93	4.46	4.12	3.13	3.45	0	0

TABLE-Sch-B-11A

% Swelling of resin in various solvents as cation exchanger

Resin .	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	pet. ether
Fu(Ben)GA	6.62	4.60	1.49	1.46	2.46	1.50	0.73	1.55	0
Fu(Ben)PHy	7.33	4.88	2.26	1.33	2.47	1.63	0.68	1.34	0
Fu(Ben)SA	6.74	4.65	2.89	1.87	2.87	1.51	0.93	1.39	0
Fu(Ben)8Hy	5.76	4.24	1.13	0.84	1.49	0.81	0.61	1.03	0

TABLE-Sch-B-11B

% Swelling of resin in various solvents as anion exchanger

Resin	Glacial acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	pet. ether
Fu(Ben)GA	6.62	4.60	1.49	1.46	2.46	1.50	0.73	1.55	0
Fu(Ben)PHy	4.33	4.28	2.26	1.33	2.47	1.63	0.68	1.34	0
Fu(Ben)SA	6.44	4.65	2.89	1.87	2.87	1.51	0.93	1.39	0
Fu(Ben)8Hy	3.76	4.24	1.13	0.84	1.49	0.81	0.61	1.03	0

Table-SchA-I

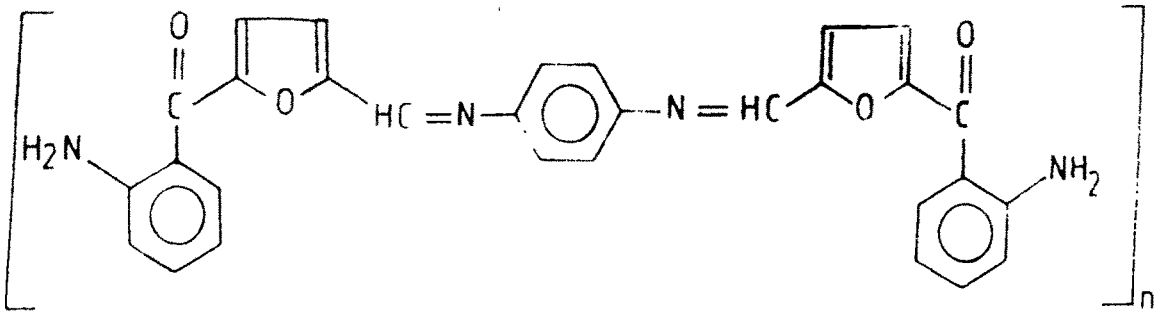
Major peaks observed in the infrared spectra of resins

No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
1.	Fu(PH)AN	3600-3400	medium	-NH stretching absorption
		1670-1700	medium	conjugated ester >C=0
		1170-2000	medium	-C-O-C- stretching absorption of ether
		1480-1520	medium	>C=N stretching absorption
2.	Fu(PH)GA	3500-2800	broad	-OH Stretching absorption
		1700-1670	medium	conjugated >C=0 group
		1620-1540	medium	>C=N stretching absorption
		1780-1200	medium	C-O ether linkage
3.	Fu(PH)PHy	3600-2500	broad	-OH stretching absorption
		1780-1620	medium	conjugated >C=0
		1290-1150	medium	C-0 stretching absorption of ether
4.	Fu(PH)Py	3600-2500	broad	-OH stretching absorption
		1600-1550	medium	>C=C< stretching
		1200-1190	medium	-C-O ether stretching
5.	Fu(PH)8Hy	3600-2800	broad	-OH-stretching absorption
		1600-1550	medium	>C=C< stretching absorption
		1540-1510	medium	>C=N- Stretching
		1190-1210	medium	-C-O stretching

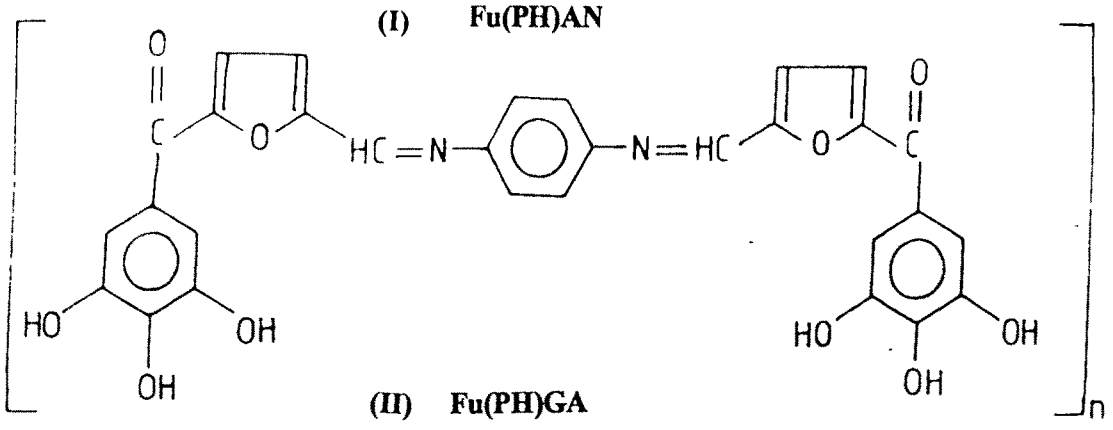
Table-SchB-I

Major peaks observed in the infrared spectra of resins

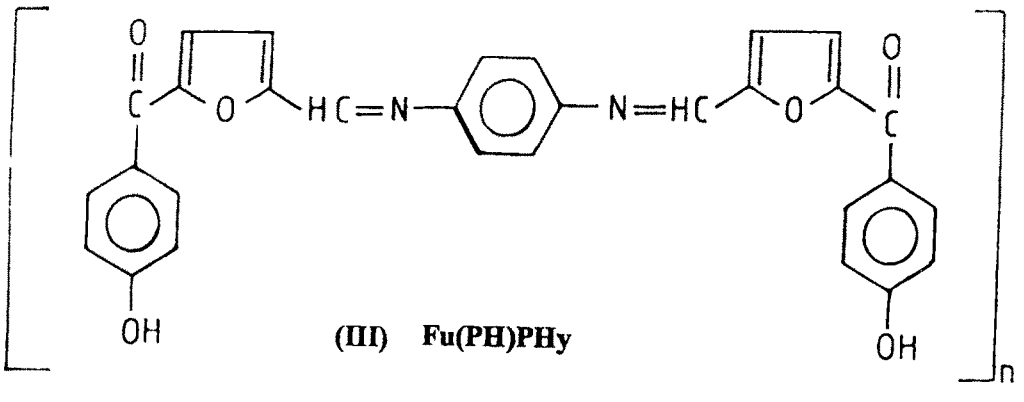
No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
1.	Fu(Ben)GA	3600-3200	broad	-OH Stretching
		1710-1670	medium	Conjugated >C=0
		1590-1500	medium	>C=N Stretching absorption
		1190-1150	medium	-C-O ether absorption
2.	Fu(Ben)PHy	3600-3200	broad	-OH Stretching absorption
		1710-1670	medium	Conjugated >C=0
		1610-1590	medium	>C=C< stretching
		1170-1130	medium	-C-O ether stretching
3.	Fu(Ben)SA	3600-3200	broad	-OH stretching absorption
		1600-1550	medium	>C=C< absorption
		1190-1150	medium	-C-O stretching Of ether
4.	Fu(Ben)Hy	3600-3200	broad	-OH stretching absorption
		1600-1500	medium	>C=C< aromatic stretching absorption
		1550-1600	medium	>C=N stretching absorption



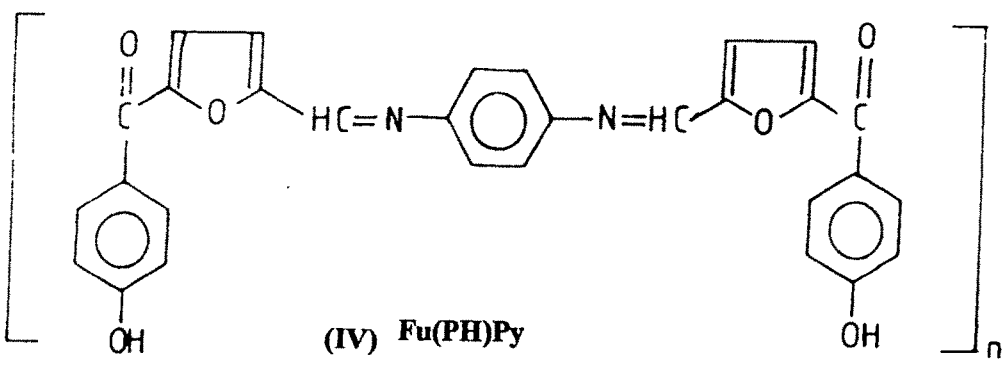
(I) Fu(PH)AN



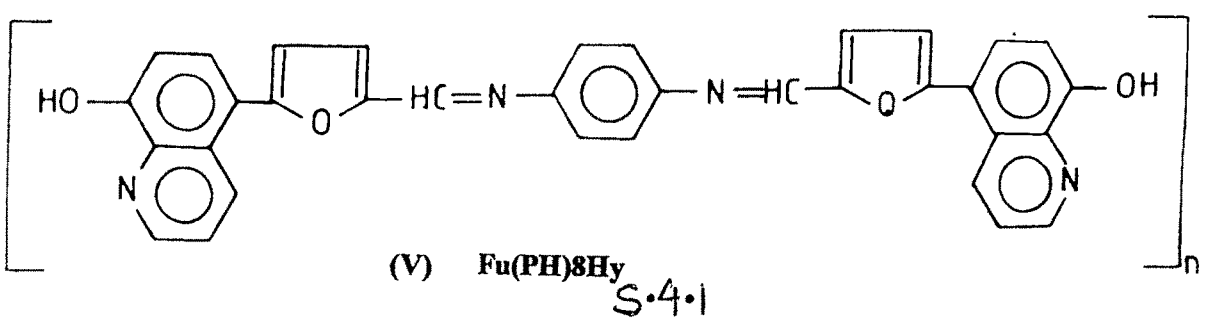
(II) Fu(PH)GA



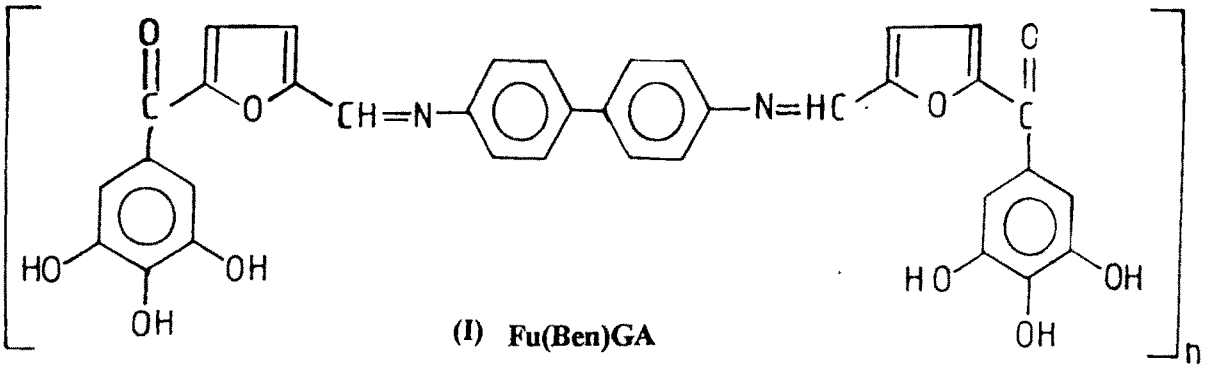
(III) Fu(PH)PHy



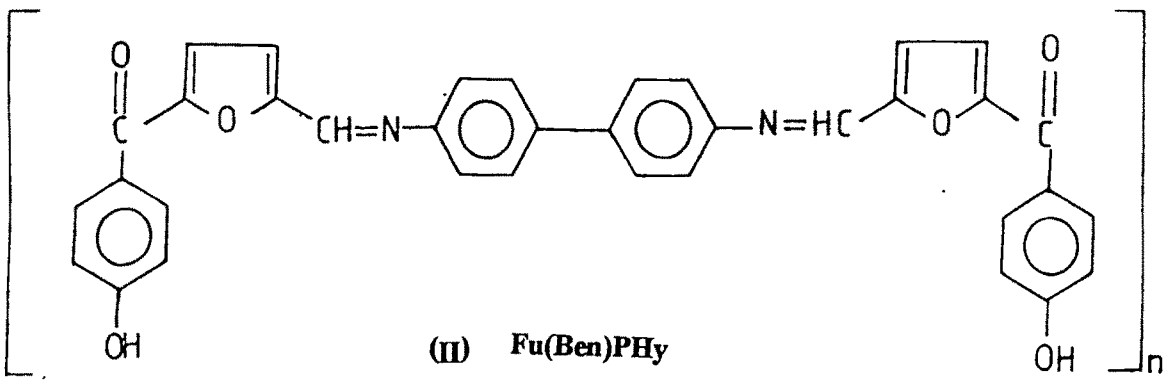
(IV) Fu(PH)Py



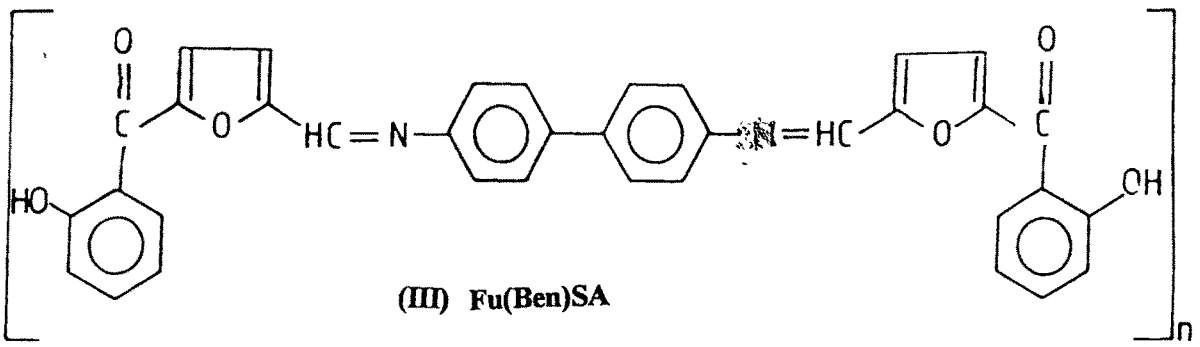
(V) Fu(PH)8Hy



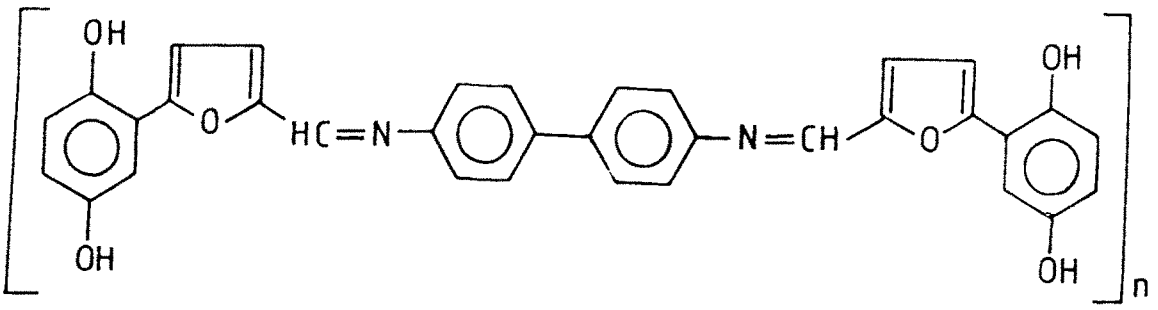
(I) Fu(Ben)GA



(II) Fu(Ben)PHy



(III) Fu(Ben)SA



(IV) Fu(Ben)Hy

S.4.2

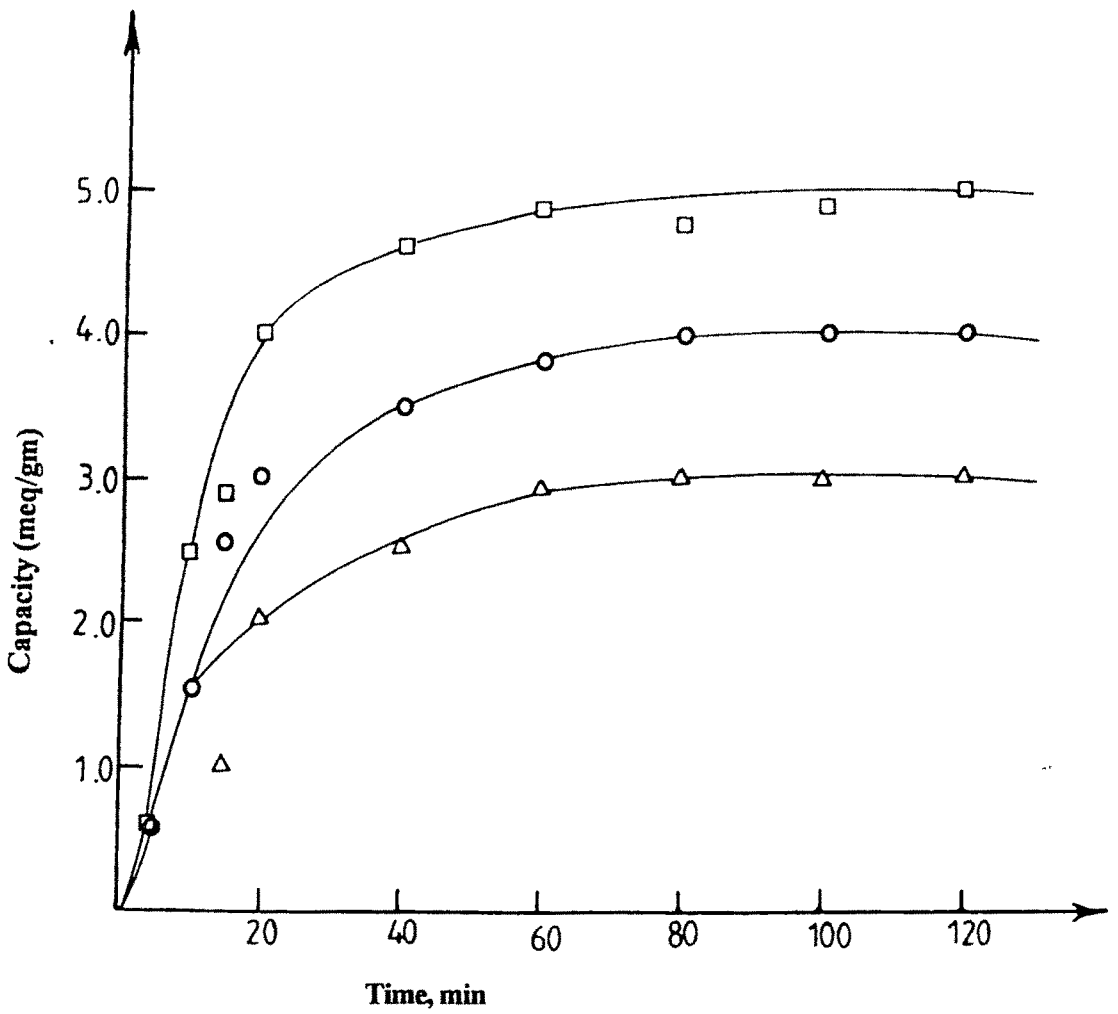


Fig.4.1 Rate of cation exchange of Fu(PH)AN (○), Fu(PH)GA (□), Fu(PH)PHy (△)

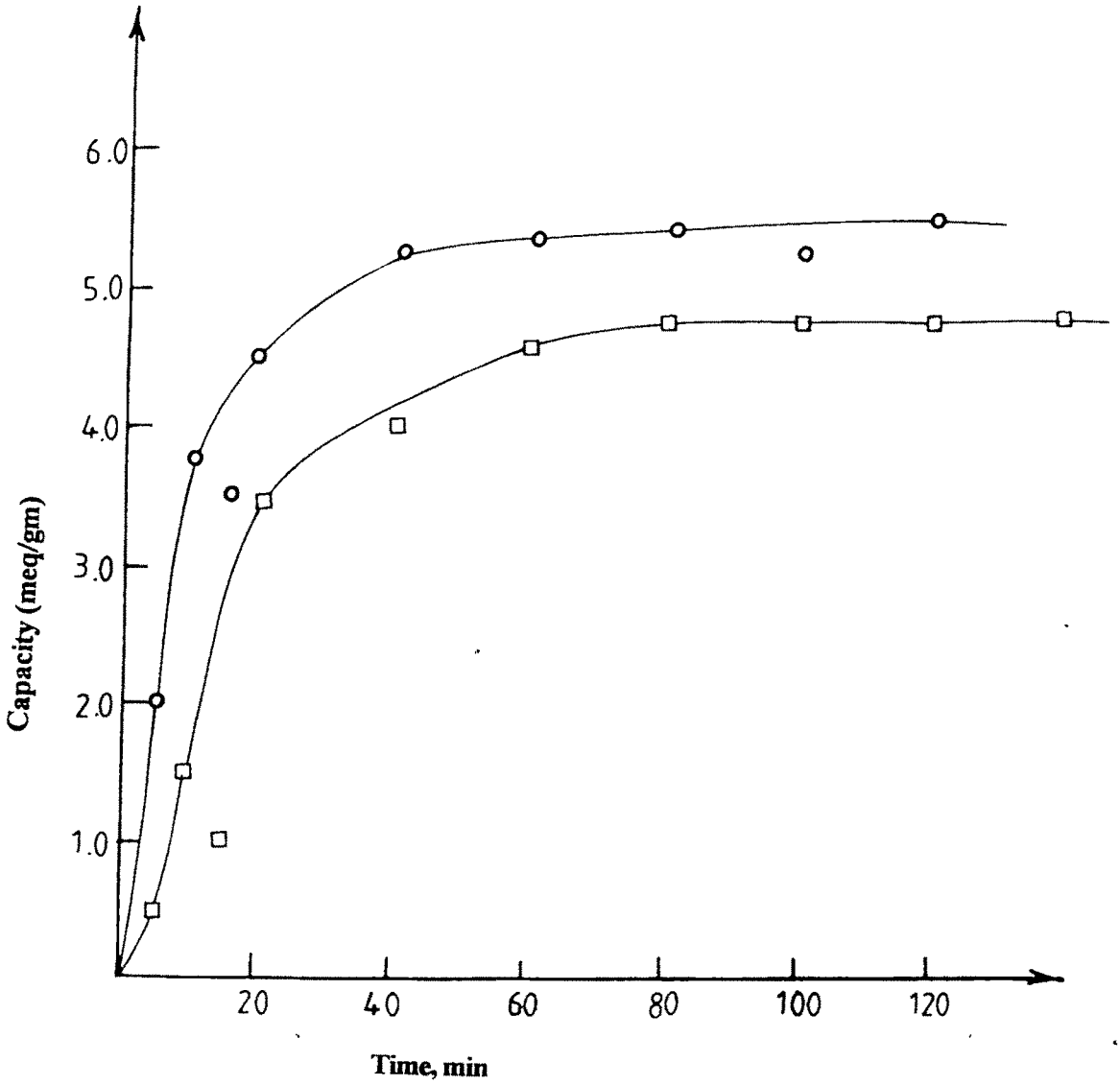


Fig.4.2 Rate of cation exchange of Fu(PH)Py (○), Fu(PH)8Hy (□)

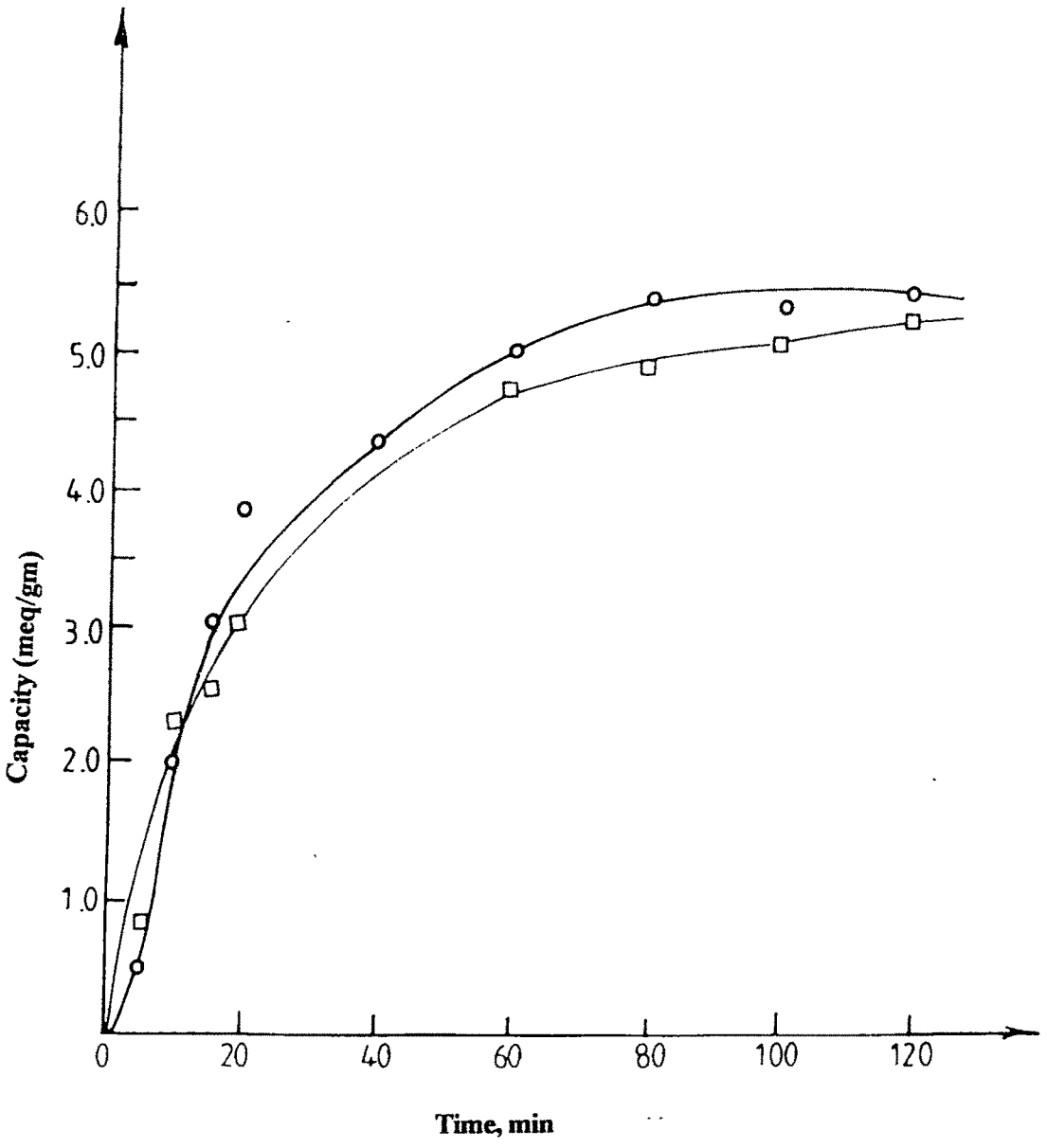


Fig.4.3 Rate of anion exchange of Fu(PH)AN (O), Fu(PH)GA (□)

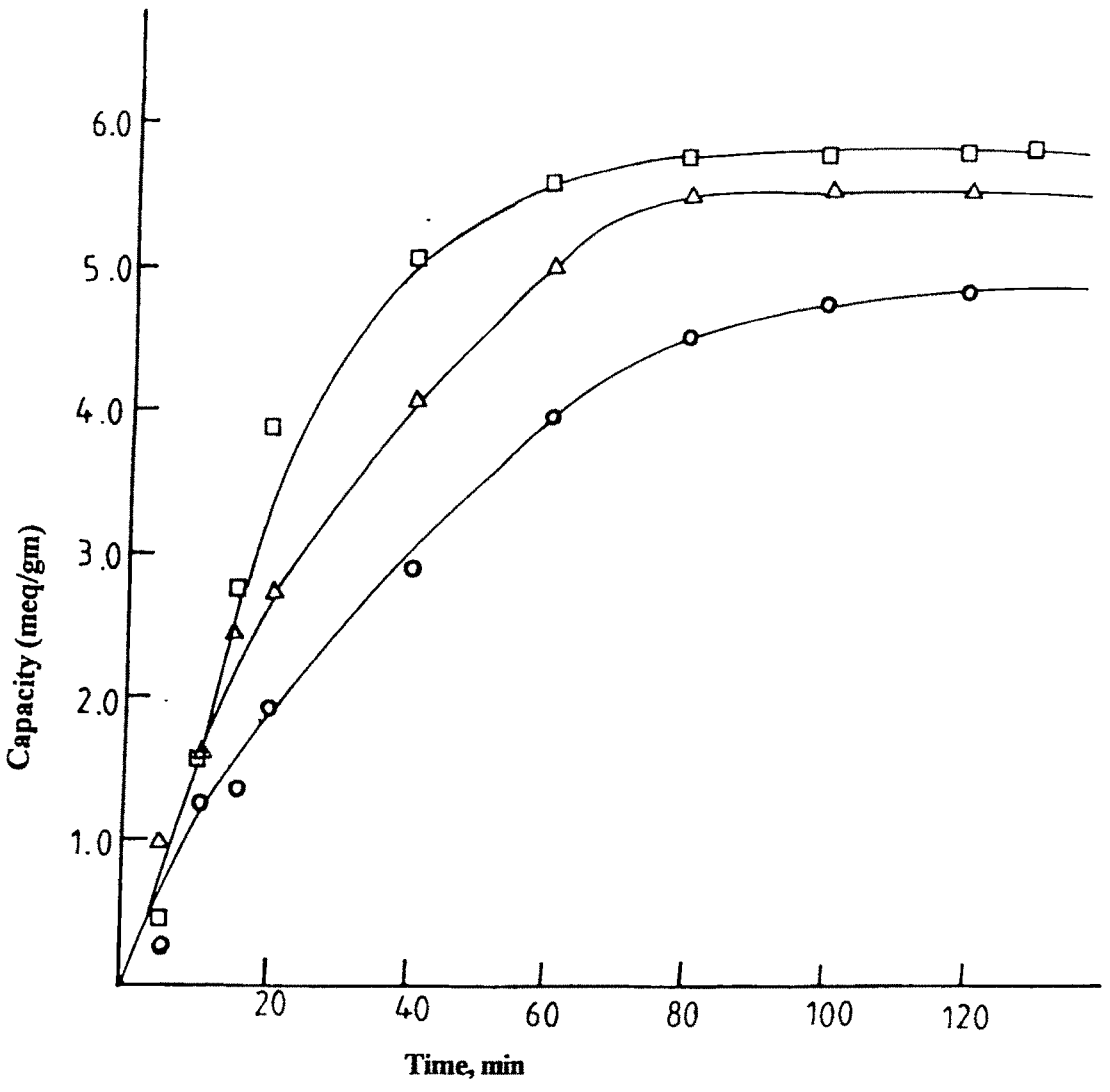


Fig.4.4 Rate of anion exchange of Fu(PH)8Hy (△), Fu(PH)PHy (○), Fu(PH)Py (□)

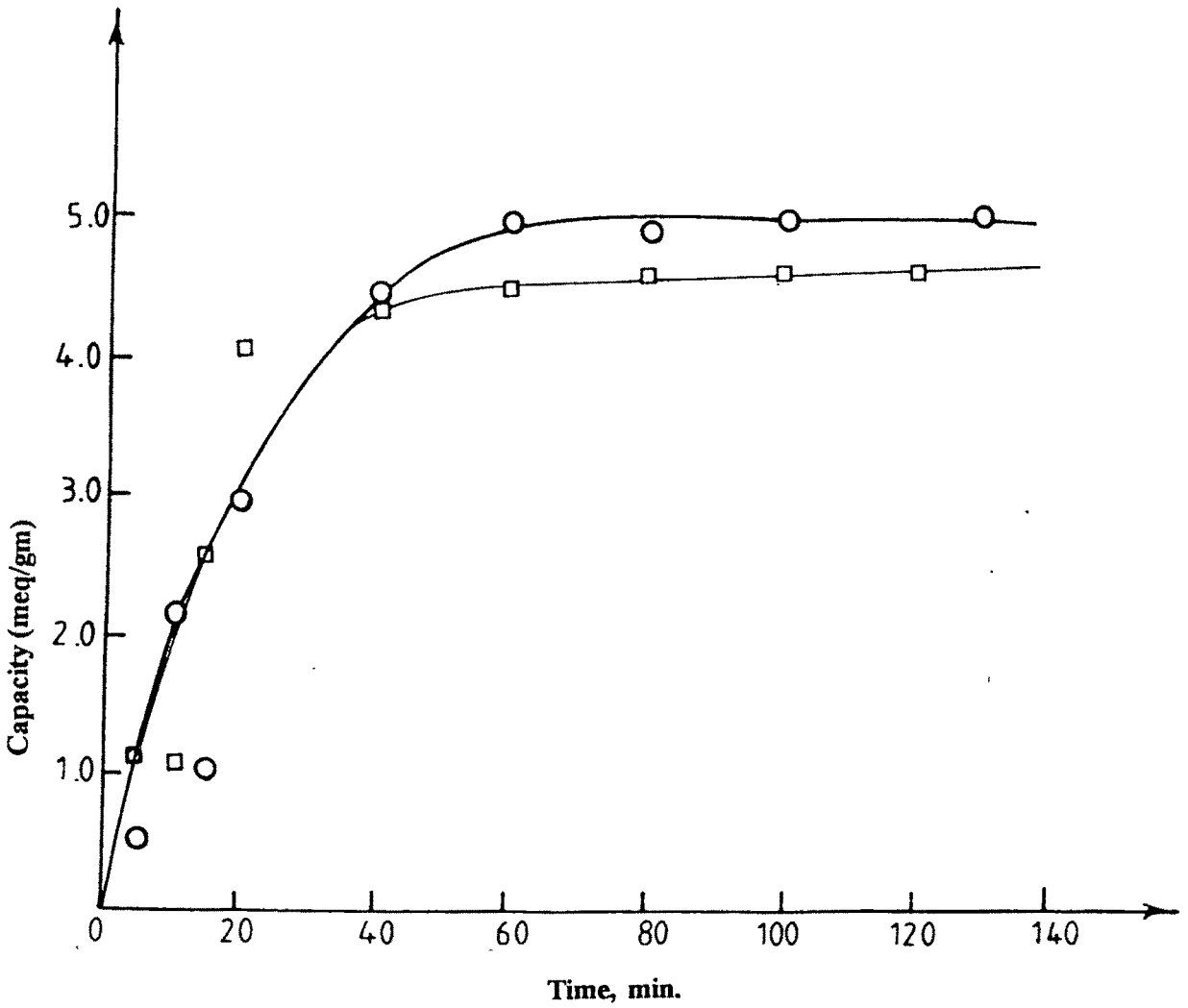


Fig.4.5 Rate of cation exchange of Fu(Ben)PHy (□), Fu(Ben)GA (○)

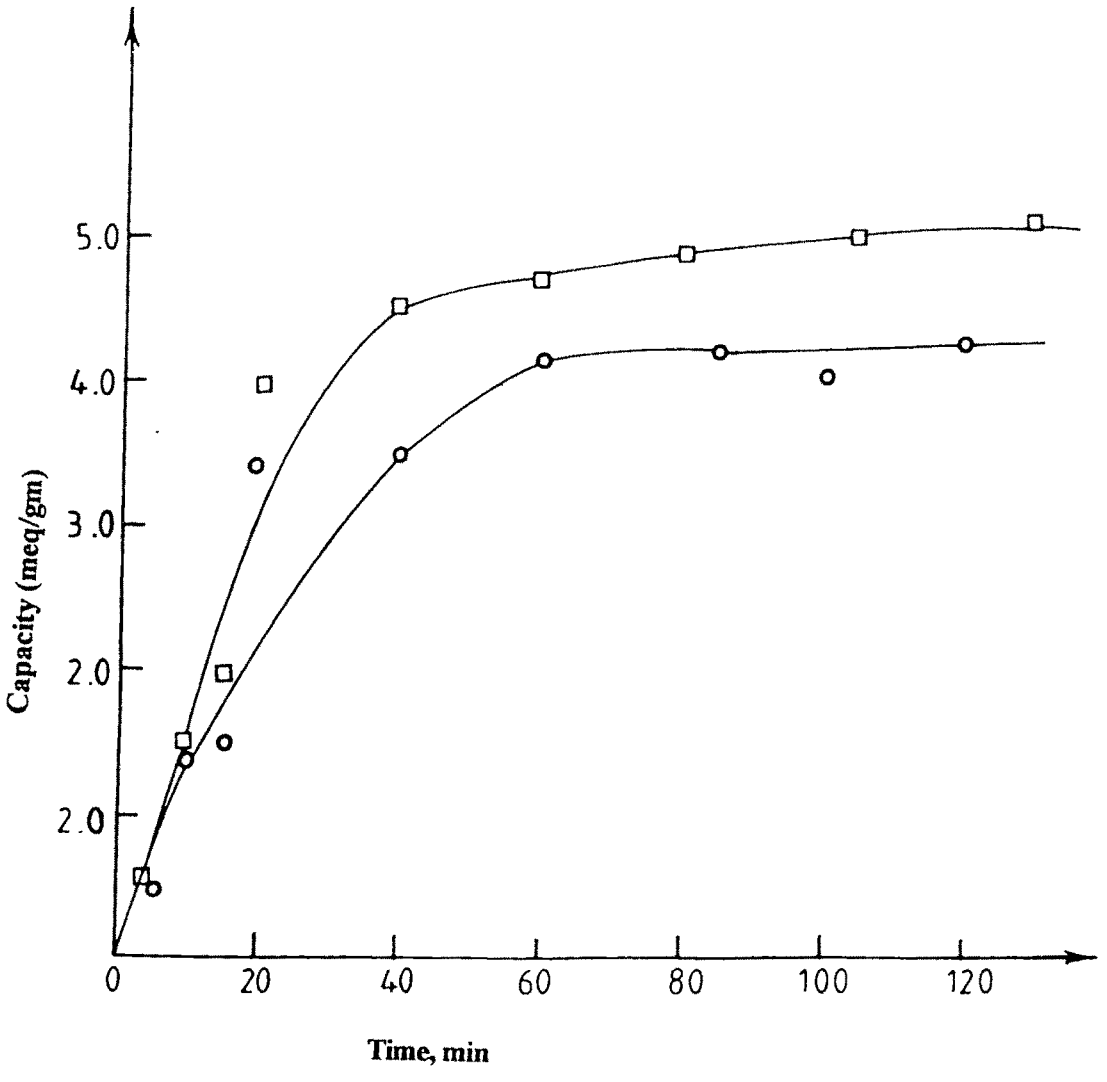


Fig.4.6 **Rate of cation exchange of Fu(Ben)SA (O), Fu(Ben)Hy (□)**

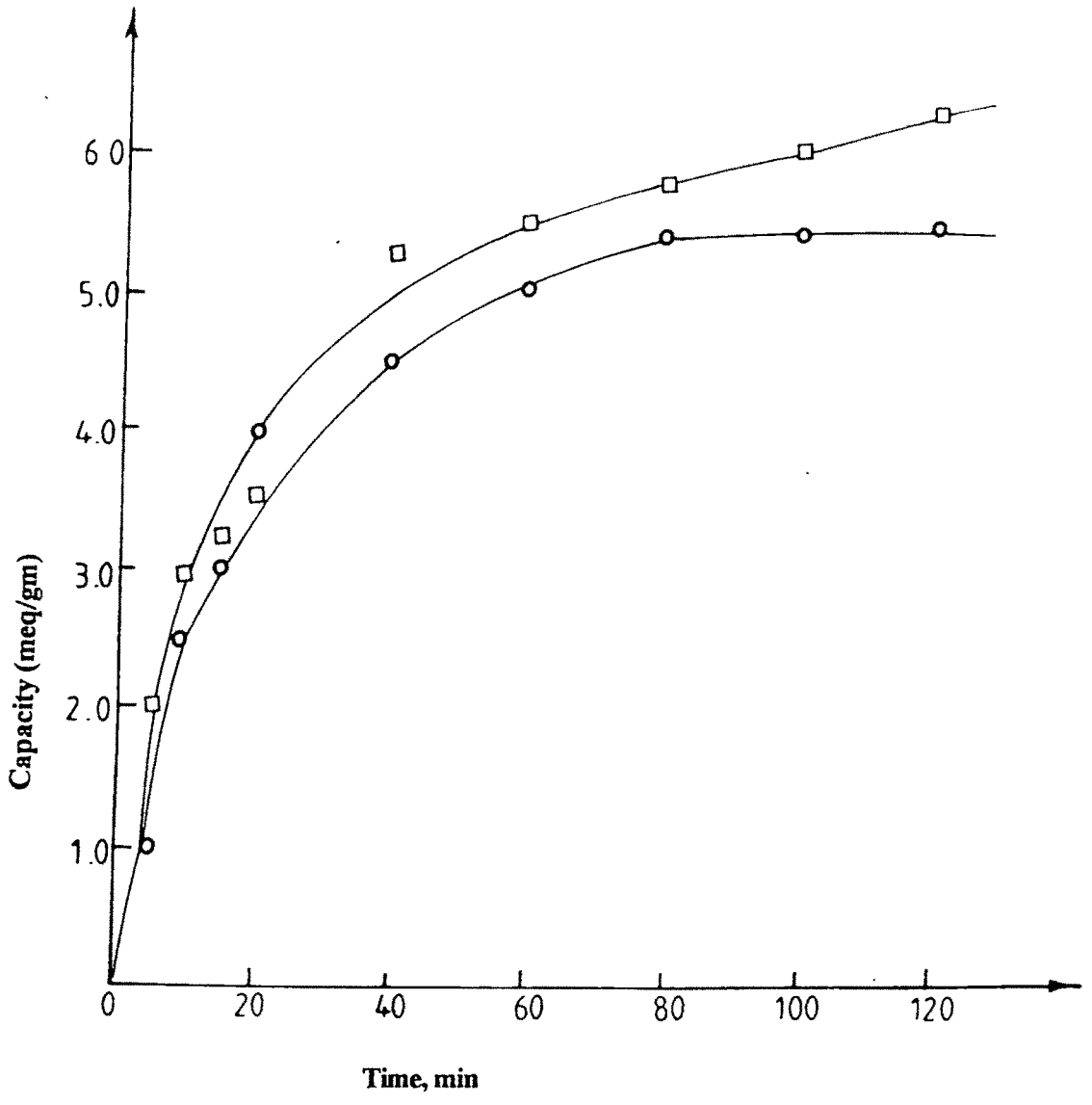


Fig.4.7 Rate of anion exchange of Fu(Ben)PHy (○), Fu(Ben)GA (□)

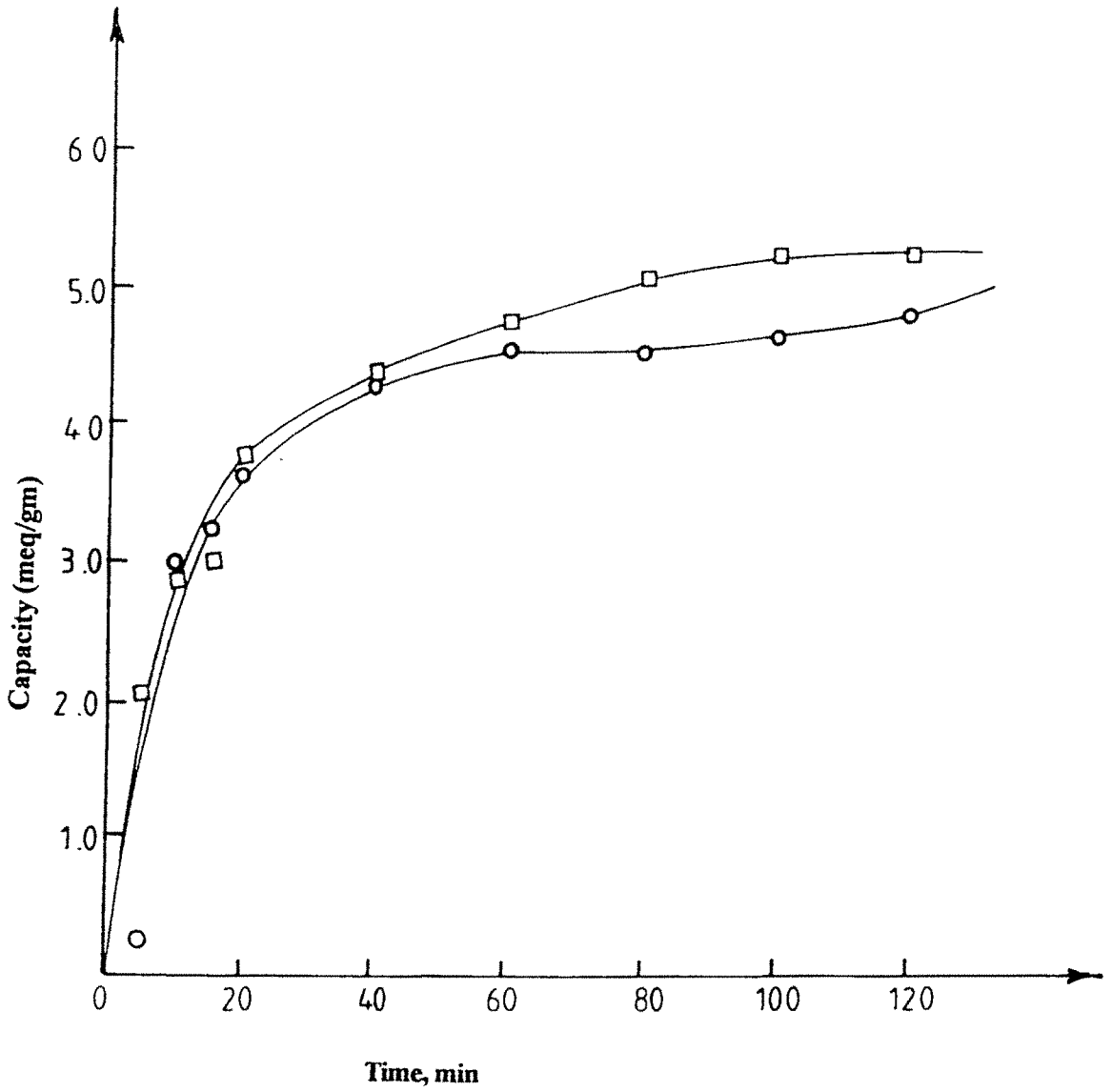


Fig.4.8 **Rate of anion exchange of Fu(Ben)SA (○), Fu(Ben)Hy (□)**

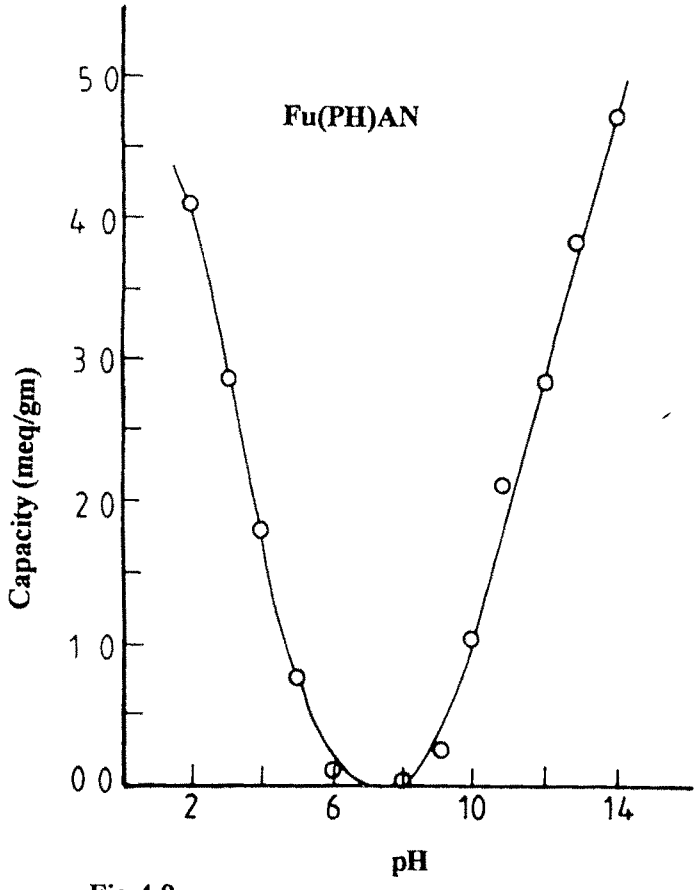
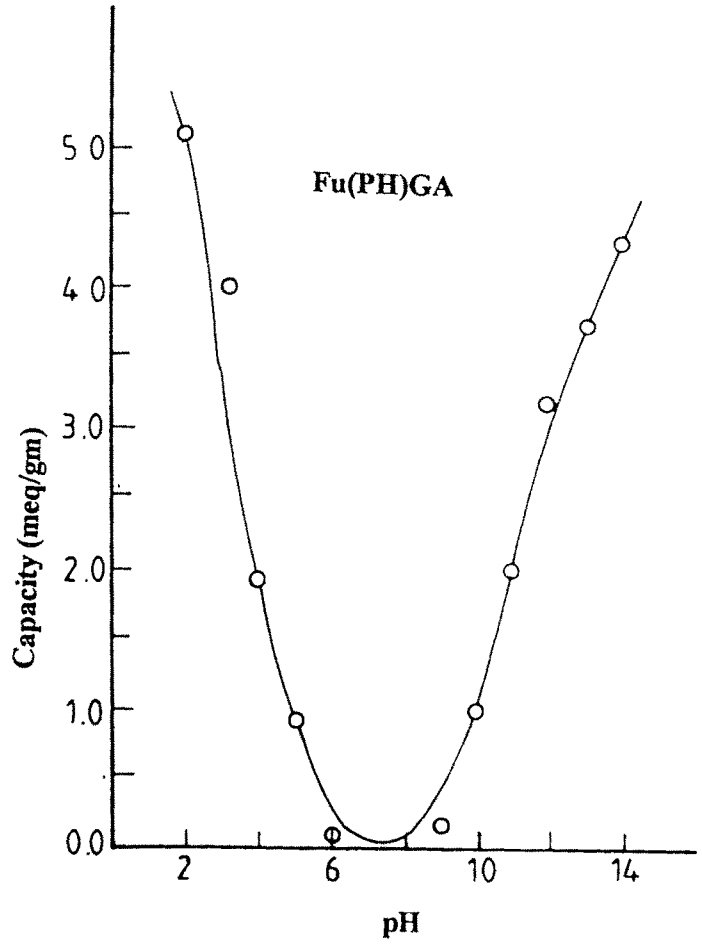

Fu(PH)AN
Capacity (meq/gm)
5 0
4 0
3 0
2 0
1 0
0 0
2
6
10
14
pH

Fig.4.9


Fu(PH)GA
Capacity (meq/gm)
5 0
4 0
3.0
2.0
1.0
0.0
2
6
10
14
pH

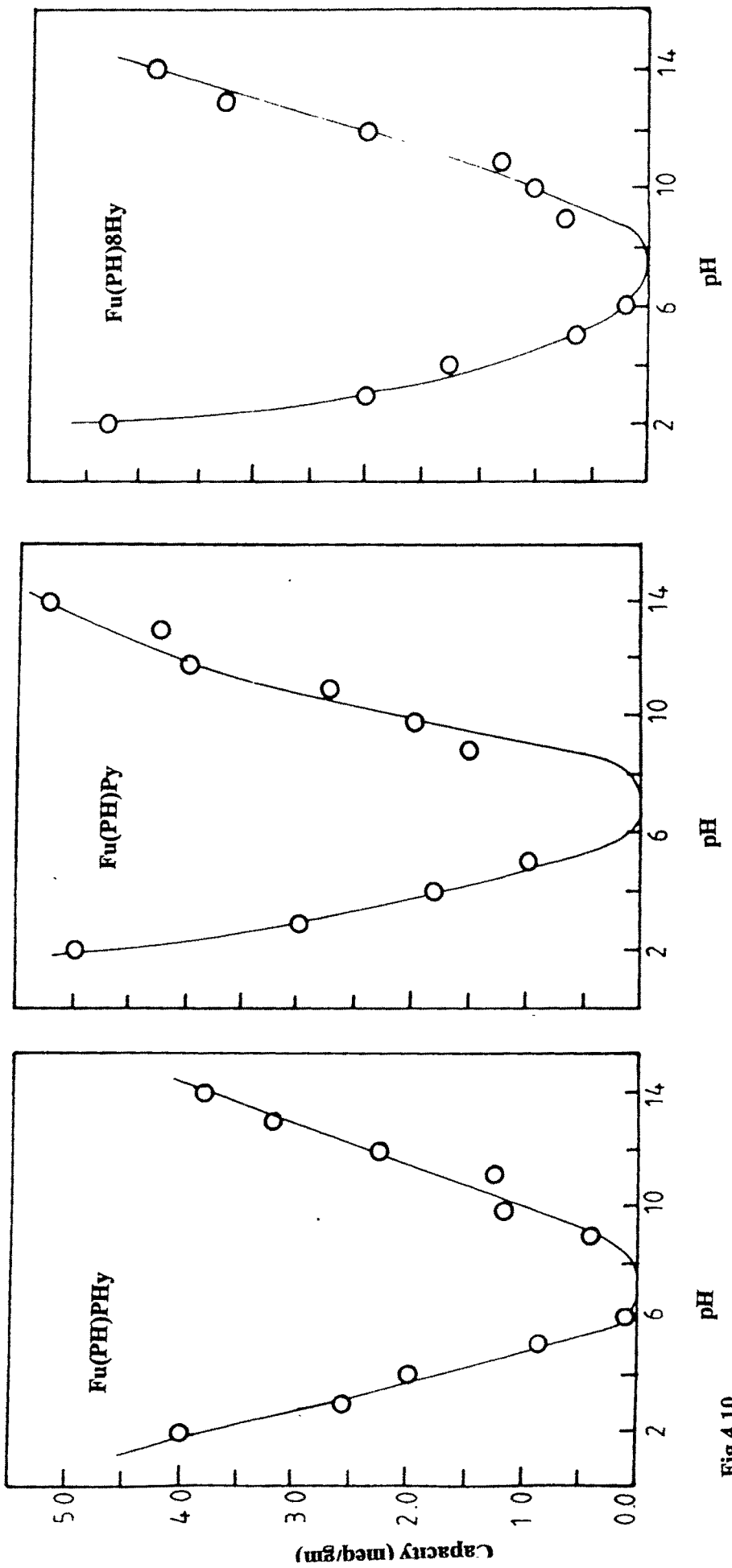

Fu(PH)PHy
Fu(PH)Py
Fu(PH)8Hy
Capacity (meq/gm)
pH
pH
pH
0.0
1.0
2.0
3.0
4.0
5.0
2
6
10
14

Fig.4.10

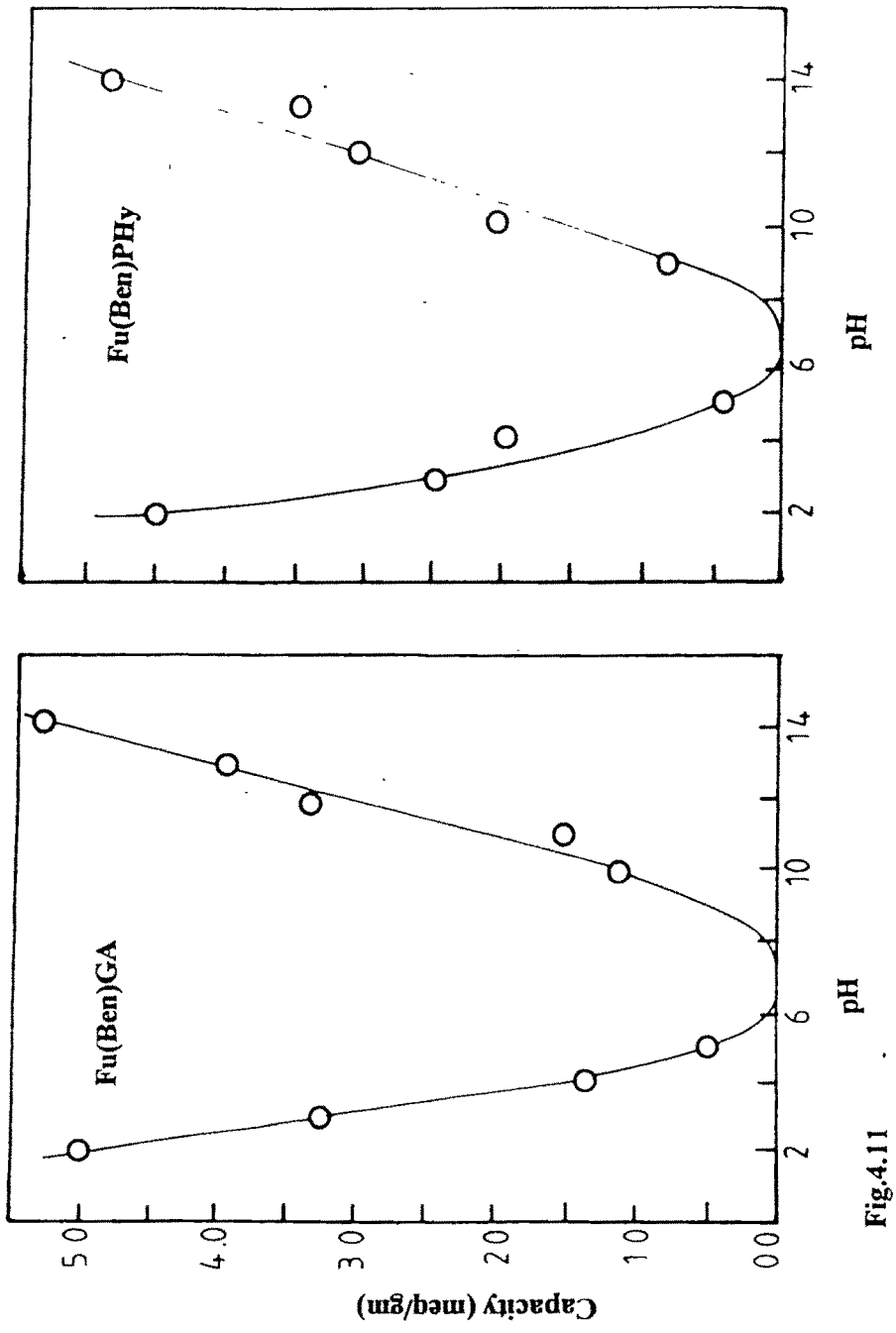

Fu(Ben)PHy
Fu(Ben)GA
Capacity (meq/gm)
pH
pH
0.0
1.0
2.0
3.0
4.0
5.0
2
6
10
14

Fig.4.11

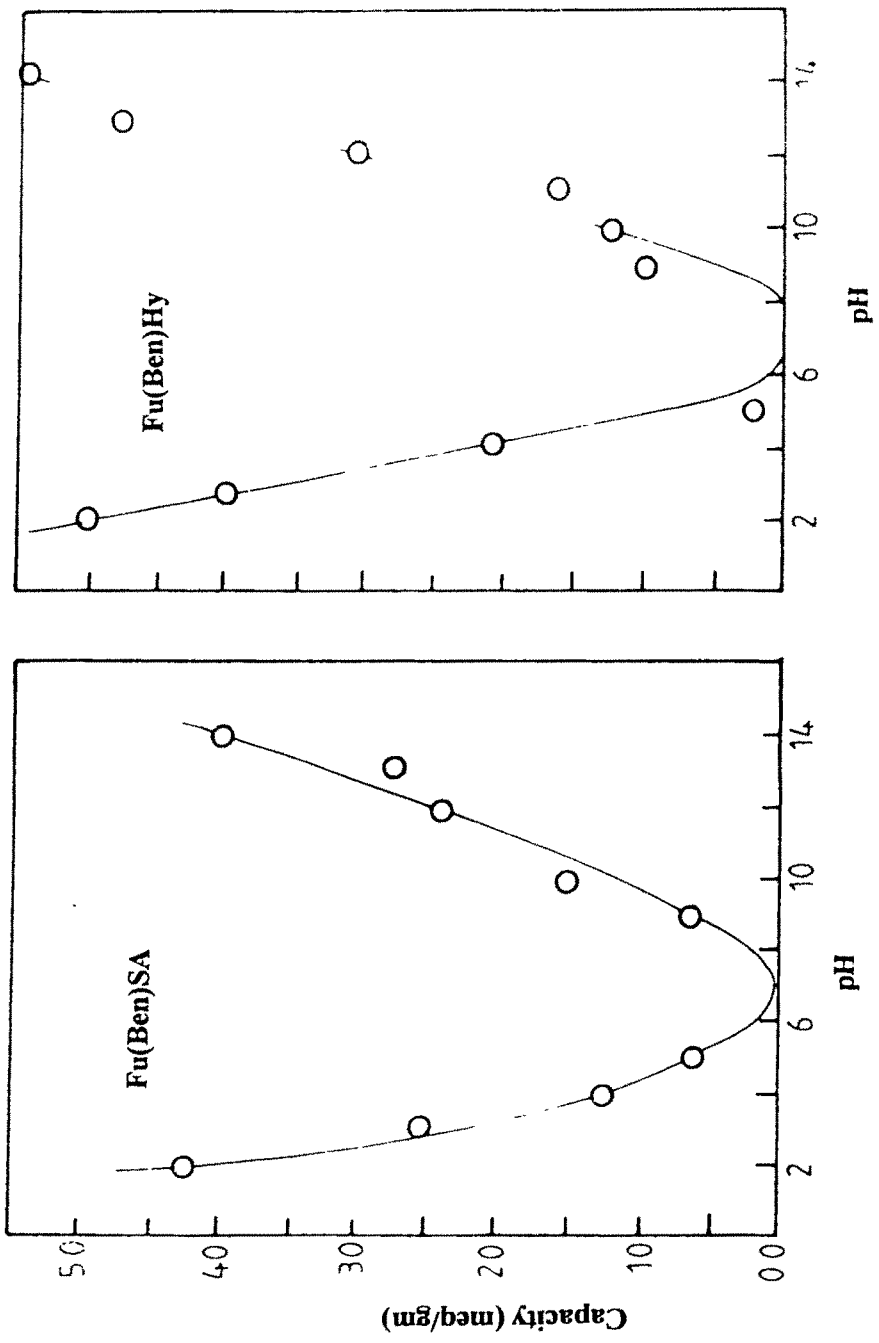
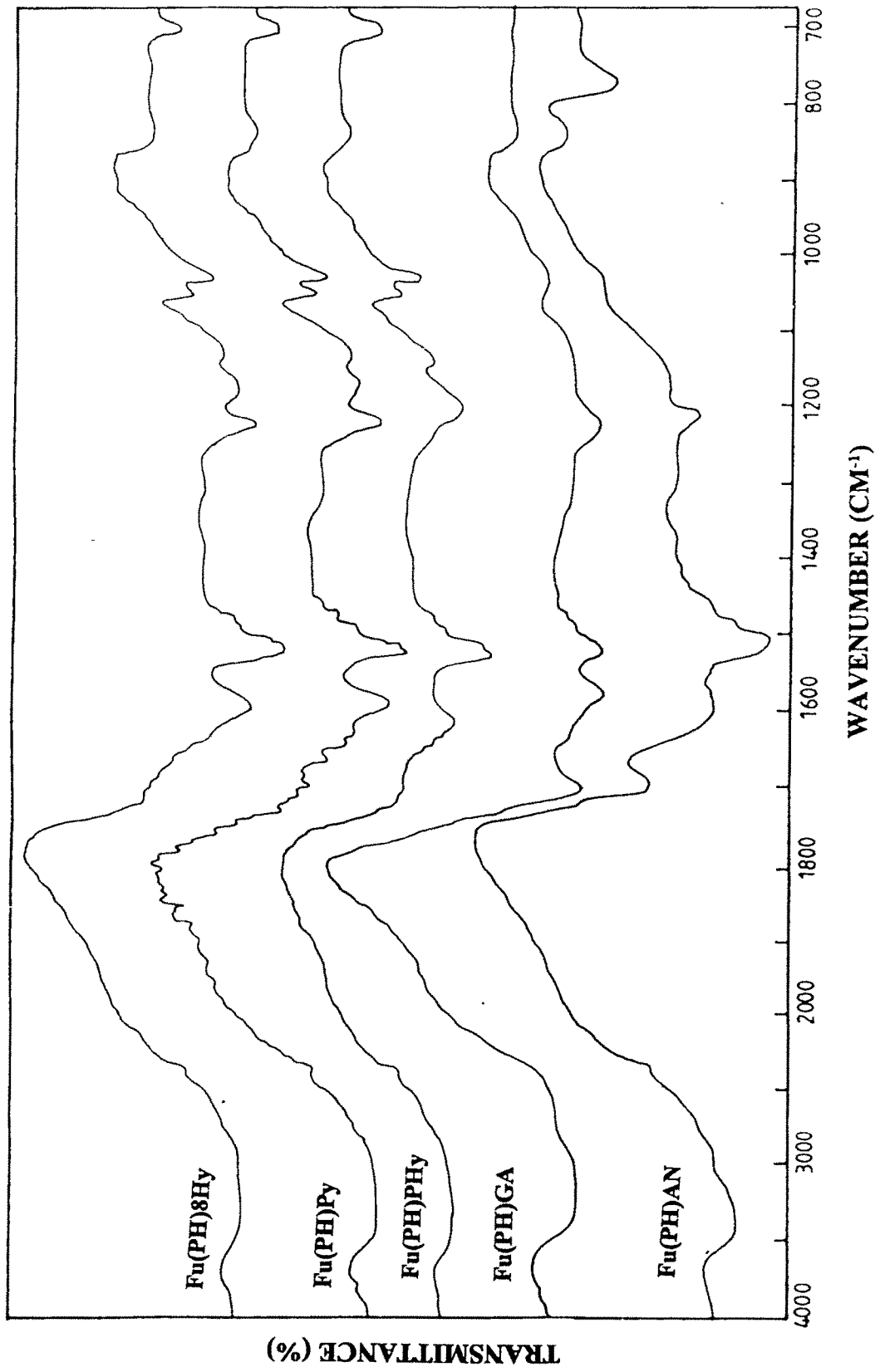
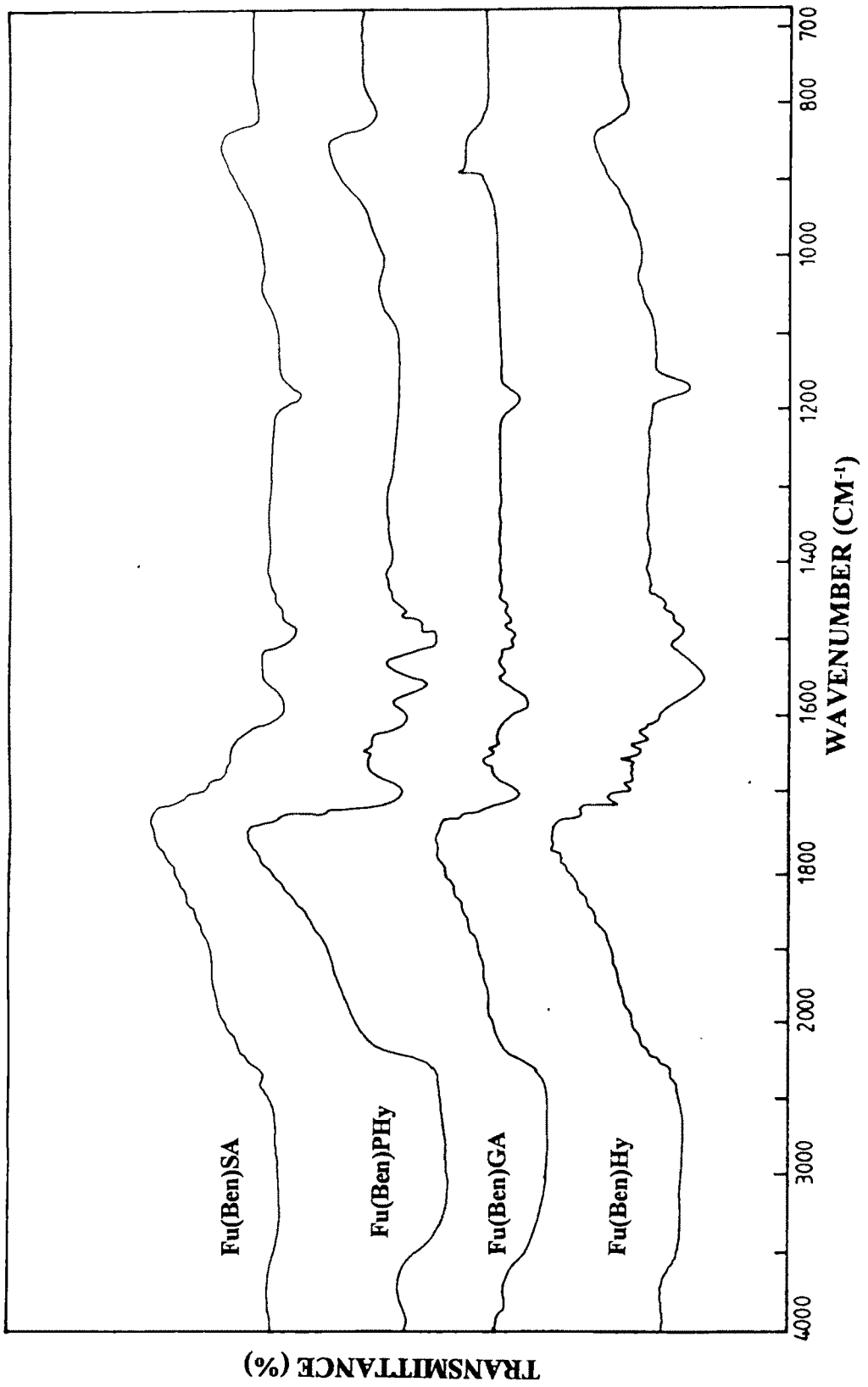


Fig.4.12


Fu(PH)8Hy
Fu(PH)Py
Fu(PH)PHy
Fu(PH)GA
Fu(PH)AN
4000
3000
2000
1800
1600
1400
1200
1000
800
700
WAVENUMBER (CM-1)
TRANSMITTANCE (%)


Fu(Ben)SA
Fu(Ben)PHy
Fu(Ben)GA
Fu(Ben)Hy
4000
3000
2000
1800
1600
1400
1200
1000
800
700
WAVENUMBER (CM-1)
TRANSMITTANCE (%)

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