CHAPTER III

III Poly(vinyl acetate) - Aromatic Phenolic Derivatives Type Ion-Exchange Resins

EXPERIMENTAL

III (a) Synthesis of ion-exchange resins

1 mole of poly(vinyl acetate) ($\bar{M}$ wt. = 45,000) was dissolved in 100ml glacial acetic acid. To this anthranilic acid, gallic acid, p-hydroxy benzoic acid, pyrogallol, salicylic acid, hydroquinone or β-resorcylic acid (1 mole) was added 2gms of p-tolunesulphonic acid was added as initiator. The mixture was vigorously stirred and refluxed on low flame on sand bath for 24 hours. Gel formation takes place in about 1 hour.

III (b) Moisture content of resins

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

The values of % moisture content of the resins (H^+ form and OH^- form) are presented in Table-PAC-3.

III (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 I-(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-PAC-4. The values of void volume fraction of the resins (H^+ form and OH^- form) are presented in Table-PAC-5.

III (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 exchanger are presented in Table-PAC-6A and Table-PAC-6B respectively.

III (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-PAC-6A.

III (f) Rate of exchange

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.3.1 to 3.4 and presented in Table-PAC-7.

III (g) pH-titration studies 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 I-(g).

The values of the capacities of the resin were plotted against the pH of the solution and shown in Figs. 3.5 & 3.6.

The apparent pK_a and pK_b values for the resins are presented in Table-PAC-8.

III (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-PAC-9.

III (i) Oxidation resistance test

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

III (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-PAC-11A and Table-PAC-11B respectively.

III Poly (vinyl acetate) - Aromatic Phenolic Derivative Type Ion-Exchange Resin

RESULT & DISCUSSION

General

The most widely used polymer of a vinyl ester is poly (vinyl acetate). It is utilized not only as a plastic, primarily in the form of emulsions but also as the precursor for two polymers. Which can not be prepared by direct polymerization lower molecular weight polymers are brittle but become gum like when masticated. Poly(vinyl acetate) is water sensitive in certain physical properties, such as strength and adhesive but does not hydrolyze in neutral systems. One major use of poly (vinyl acetate) is in the production of water based emulsion paints. The low cost, stability, quick drying and quick recoatability of emulsion paints have led their wide acceptance.

The first chemical reaction on a totally synthetic polymer is probably the nitration of poly (styrene) in 1845 (96) an important step for modification. A poly (vinyl acetate) (97) forward in 1914 was the development by standinager of the concept of the polymer analogous reaction.

Keeping all this point in mind we through of modify the properties of poly (vinyl acetate) as ion exchanger by incorporating different aromatic phenolic derivatives.

We have synthesised a ion-exchange resin from poly(vinyl acetate) and aromatic phenolic derivatives. The condensate is insoluble in sodium hydroxide , hydrochloric acid and dioxane in

which individual components are miscible or soluble. Therefore the resin appears to be a condensate product of phenolic derivative with poly (vinyl acetate).

General Characteristics and structure

The phenolic derivatives employed for synthesizing the resins possess the following structural characteristics.

(1) One phenolic and one amino group in o- position on a phenyl ring.

(2) Two phenolic groups meta position and one phenolic group para position to the carboxylic group on a phenyl ring.

(3) One phenolic group para position to carboxylic group on a phenyl ring.

(4) Three phenolic groups on a phenyl ring (pyrogallic acid) on 1,2 and 3 position.

(5) One phenolic group and one carboxylic group in ortho position on a phenyl ring.

(6) Two phenolic groups in a para position on a phenyl ring.

(7) One phenolic group in meta position and one phenolic group ortho position to carboxyl group on a phenyl ring.

The ion exchangers, in general are fairly porous in nature with average physical stability and good chemical resistance to 3N acids and alkalis. In present investigation the polymers were obtained by poly condensation under mild reaction and curing condensations, crosslinking is possible by formation of -C- linkaged, although on the basis of analytical data and other physico-chemical studies, we have some generalisation viz,

(1) Aromatic hydroxy derivatives get condensed with poly (vinyl acetate) in the molar ratio of 1:1.

The most likely structures of these resins on the basis of analytical data and their physico-chemical studies and are shown as

(i)	Poly-AC-Anthra	(ii)	poly-AC-Galli
(ii)	poly-AC-PHyBe	(iv)	poly-AC-Pyro
(v)	poly-AC-Sali	(vi)	poly-AC-Hyqui
(vii)	poly-AC-βRes		

Moisture retention %

Percentage moisture of resins are presented in table-PAC-3 percentage moisture of the resins in H^+form varies between 0.0133 to 0.2045 and 0.035 for OH^-. Low range of percentage moisture suggest that the resins have a fairly good degree of cross-linking.

Density of resins

True density (d_{res})

The data obtained for the density (d_{res}) of the resins in H^+ form and OH^- form are presented in Table-PAC-6. The values are ranging from 0.4187 to 0.7934 for H^+form and for OH^- form of Poly-AC-Anthra is 0.6180. We observed in general that in the resin Poly-AC-Anthra under study, d_{res} for H^+form is slightly higher than that for OH^- form.

Apparent density (d_{col})

We have also evaluated the apparent (column) density (d_{col}) of the ion exchange resins (Table-PAC-6). The values are ranging from 0.3461 to 0.4462 for H-form and 0.4575 for OH- form of Poly-AC-Anthra known values (77) of apparent density for

commercial resins in H^+ form are 0.69 for IRC- 50/75 and 0.75 for IRC-84.

Thus the resins under study have low range of density (d_{col}) for H^+ form. Similarly for OH^- form of Poly-AC-Anthra d_{col} is low then commercial available resin.

The values of void volume of resins are presented in Table-PAC-5. It is observed that the values of void volume fraction vary between 0.1734 to 0.4655 for cationic form and 0.2598 is the value for anionic form of Poly-AC-Anthra . Further we observed that the void volume fraction of cationic form of Poly-AC-Anthra resin is higher than that of anionic form. 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 suggest the porous nature of the resins.

Ion-Exchange capacity

The cation or anion exchange capacity of the ion exchange resins can be calculated using the formula described I(d)(i) . The observed capacity CEC_{obs} (cation exchange) or AEC_{obs} (anion exchanger) can be compared with the calculated capacity CEC_{cal} or AEC_{cal} as reported in Table-PAC-6A and Table-PAC-6B respectively.

Three ranges exist,

(1) value of CEC_{obs} / CEC_{cal} is close to 1.
(2) value of CEC_{obs} / CEC_{cal} is close to 1/2.
(3) value of CEC_{obs} / CEC_{cal} is less than 1/2.

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

Poly-AC-Pyro > poly-AC-Galli > poly-AC-βRes > poly-AC-PHyBe > poly-AC-Hyqui > poly-AC-Sali > Poly-AC-Anthra

Concentration of ionogenic groups

The data on concentration of ionogenic groups are presented in Table-PAC-6A. and Table-PAC-6B. 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

The results copper ion exchange capacity of these resins are presented in Table-PAC-6A. It is observed that the copper exchange capacity of these resins ranges between 3.56 to 1.05 meq/gm.

The decreasing order for the copper ion exchange capacity of these resins was observed as

poly-AC-pyro > poly-AC-Galli > poly-AC-Hyqui > poly-AC-βRes > poly-AC-PHyBe > poly-AC-Sali > Poly-AC-Anthra

Rate of Exchange

Figs 3.1 to 3.4 represent the rate of cation exchange as well as anion exchange of ion-exchange resins. In the case of resins as cation exchanger, it is observed that (i) 50% exchange occurs in 40-50min. (ii) the rate of exchange for these resins follows the order.

Poly-AC-Sali < Poly-AC-Anthra < poly-AC-βRes ≃
Poly-AC-PHyBe < poly-AC-Hyqui < poly-AC-Galli ≃ poly-AC-pyro

In the case of resins as anion exchanger, It is observed that 50% exchange occurs in 5-10min.

pH Titration

The pH titration curves for the ion-exchange resins are presented in figs 3.5 to 3.6. It is evident from the figs 3.5 that the resin Poly-AC-Anthra is amphoteric in nature. This resin can be used as anion exchange as well as cation exchanger depending up on the pH of the solution.

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

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) described earlier in chapter I and are reported in Table-PAC-8.

It is seen that the range of pK_a values obtained for overall cation exchange process, in general ,for various ion exchange process, studied, is from 8.57 to 10.37 , which is characteristic of phenolic hydroxyl group, indicating considerably weakly

acidic nature of the phenolic hydroxyl group attached to the matrices.

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

poly-AC-PHyBe ≒ poly-AC-Sali > poly-AC-βRes > poly-AC-Hyqui > poly-AC-Galli > poly-AC-Pyro > Poly-AC-Anthra.

The pK_b value for Poly-AC-Anthra is 2.46 which is characteristic of bases of strong strength.

Isoionic point

The value for Isoionic point for Poly-AC-Anthra is presented in Table-PAC-8. The value is 5.52.

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

The variation of the capacity of various ion exchange resins with the varying equilibration temperature are presented in Table-PAc-9.

It is clear from the data the anion exchange capacity for Poly-AC-Anthra increases with the increasing equilibration temperature. This apparent higher value of anion exchange capacity of the resin is due to an additional neutralisation of the part of an acid during equilibration by decomposition products such as NH_3 , while lowering of cation exchange capacity of the resin with the increasing temperature of equilibration may be due to the loss of ionogenic groups.

Oxidation resistance

Results of oxidation resistance test of different ion exchangers as cation exchanger as well as anion exchanger are presented in Table-PAC-10A and Table-PAC-10B respectively.

Ion exchange resins as cation exchanger show the following decreasing order for the stability on oxidative degradation.

poly-AC-Galli > Poly-AC-Anthra > poly-AC-Pyro > poly-AC-Hyqui > poly-AC-Sali > poly-AC-PHyBe > poly-AC-βRes

Swelling behaviour in non-aqueous solvents

The results of behaviour in non-aqueous solvent of these resins as cation exchanger and as anion exchanger are reported in Table-PAC-11A and Table-PAC-11B respectively. It is observed that polar solvents produce more extensive swelling than non polar hydrocarbons, and the more porous resins swell more then their less porous analogs.

The amount of resin swelling is always an important consideration in design equipment. The use of ion-exchange resin in such applications as solvent purification and catalysis of organic reaction has directed the attention of investigators. The decreasing order of porosity for ion exchange resins as cation exchanger is as follows.

poly-AC-PHyBe > poly-AC-Sali > poly-AC-Hyqui > poly-AC-Galli > poly-AC-Pyro > poly-AC-βRes > Poly-AC-Anthra

TABLE-PAC-1

Abbreviation

No.	Resin	Abbreviation
1	poly(vinyl acetate)-Anthranilic acid	Poly-AC-Anthra
2	poly(vinyl acetate)-Gallic acid	Poly-AC-Gallic
3	poly(vinyl acetate)-p-Hydroxybenzoic acid	Poly-AC-pHyBe
4	poly(vinyl acetate)- Pyrogallol	Poly-AC-Pyro
5	poly(vinyl acetate)-Salicylic acid	Poly-AC-Sali
6	poly(vinyl acetate)-Hydroquinone	Poly-AC-Hyqui
7	poly(vinyl acetate)-β-Resorcylic acid	Poly-AC-βRes

TABLE-PAC-2

Analyses, formulae etc. of ion-exchange resins

No.	Resin	Formula	Analysis					
			Calculated			Observed		
			% C	% H	% N	% C	% H	% N
1	Poly-AC-Anthra	$C_{21}H_{20}O_6N_2$	79.19	5.82	3.21	79.34	5.77	3.19
2	Poly-AC-Gallic	$C_{21}H_{18}O_{12}$	67.15	4.56	-	67.87	4.98	-
3	Poly-AC-pHyBe	$C_{21}H_{18}O_8$	76.04	6.78	-	76.40	6.77	-
4	Poly-AC-Pyro	$C_{21}H_{18}O_8$	68.05	6.79	-	68.01	6.38	-
5	Poly-AC-Sali	$C_{21}H_{18}O_8$	79.56	6.95	-	79.36	6.92	-
6	Poly-AC-Hyqui	$C_{19}H_{18}O_6$	73.47	6.50	-	73.41	6.11	-
7	Poly-AC-βRes	$C_{21}H_{18}O_{10}$	74.23	5.78	-	74.71	5.99	-

TABLE-PAC-3

% Moisture content of ion-exchange resins

No.	Resin	% Moisture	
		H^+-form	OH^--form
1	Poly-AC-Anthra	0.016	0.035
2	Poly-AC-Galli	0.204	-
3	Poly-AC-pHyBe	0.037	-
4	Poly-AC-Pyro	0.128	-
5	Poly-AC-Sali	0.013	-
6	Poly-AC-Hyqui	0.056	-
7	Poly-AC-βRes	0.051	-

TABLE-PAC-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-AC-Anthra	0.70	0.61	0.46	0.46
2	Poly-AC-Galli	0.56	—	0.44	—
3	Poly-AC-pHyBe	0.62	—	0.44	—
4	Poly-AC-Pyro	0.41	—	0.35	—
5	Poly-AC-Sali	0.79	—	0.42	—
6	Poly-AC-Hyqui	0.77	—	0.44	—
7	Poly-AC-βRes	0.65	—	0.42	—

TABLE-PAC-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	Poly-AC-Anthra	0.61	0.38	0.74	0.25
2	Poly-AC-Galli	0.79	0.20	—	—
3	Poly-AC-pHyBe	0.70	0.29	—	—
4	Poly-AC-Pyro	0.82	0.17	—	—
5	Poly-AC-Sali	0.53	0.46	—	—
6	Poly-AC-Hyqui	0.57	0.42	—	—
7	Poly-AC-βRes	0.64	0.35	—	—

TABLE-PAC-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 Q gm eq/1	Cu.Exchange Capacity (meq/gm)
Poly-AC-Anthra	2.38	2.52	0.94	0.70	0.43	1.05
Poly-AC-Galli	7.03	12.98	0.54	0.56	0.44	3.01
Poly-AC-pHyBe	3.96	5.02	0.78	0.62	0.44	2.15
Poly-AC-Pyro	7.88	16.04	0.49	0.41	0.34	3.56
Poly-AC-Sali	3.18	15.07	0.21	0.79	0.22	2.03
Poly-AC-Hyqui	3.90	5.84	0.66	0.77	0.44	2.93
Poly-AC-BRes	4.63	9.30	0.49	0.64	0.42	2.54

TABLE-PAC-6B

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

No.	Resin	Total capacity CEC_{obs} (meq/gm)	Total Capacity CEC_{cal} (meq/gm)	$\frac{CEC_{obs}}{CEC_{cal}}$	Concentration of ionogenic groups Cr meq/cm^3	Volume capacity Q gm.eq/1
1	Poly-AC-Anthra	2.01	5.05	0.39	0.61	0.45

TABLE-PAC-7

Rate of exchange of resins

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1	Poly-AC-Anthra	5	0.31	0.27
		10	0.39	0.37
		15	0.51	0.44
		20	0.70	0.53
		40	1.25	0.67
		60	3.14	0.81
		80	3.30	0.90
		100	3.34	0.99
		120	3.49	1.02
2	Poly-AC-Galli	5	1.37	
		10	1.92	
		15	2.19	
		20	2.51	
		40	3.61	—
		60	4.01	
		80	4.36	
		100	5.14	
		120	5.50	
3	Poly-AC-pHyBe	5	0.51	
		10	0.51	
		15	0.51	
		20	0.51	
		40	0.51	—
		60	2.97	
		80	2.97	
		100	2.97	
		120	3.86	
4	Poly-AC-Pyro	5	1.09	
		10	1.09	
		15	1.09	
		20	1.09	
		40	1.09	—
		60	3.58	
		80	3.58	
		100	3.58	
		120	5.62	

CONTINUED.....

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
5	Poly-AC-Sali	5	0.14	
		10	0.44	
		15	0.55	
		20	0.65	
		40	0.87	–
		60	1.26	
		80	1.83	
		100	2.26	
		120	2.48	
6	poly-AC-Hyqui	5	0.00	
		10	0.47	
		15	0.59	
		20	0.63	–
		40	1.49	
		60	1.96	
		80	2.54	
		100	3.89	
		120	4.16	
7	Poly-AC-βRes	5	0.27	
		10	0.47	
		15	0.63	
		20	0.86	–
		40	1.57	
		60	2.63	
		80	2.98	
		100	3.76	
		120	3.84	

TABLE-PAC-8

Apparent pK_a and pK_b Values and Isoionic point of resins

No.	Resin	Apparent pK_a values	Apparent pK_b	Isoionic Point
1	Poly-AC-Anthra	8.57	2.47	5.52
2	Poly-AC-Galli	9.27	-	-
3	Poly-AC-PHyBe	10.37	-	-
4	Poly-AC-Pyro	9.20	-	-
5	Poly-AC-Sali	10.37	-	-
6	Poly-AC-Hyqui	10.09	-	-
7	Poly-AC-βRes	10.15	-	-

TABLE-PAC-9

Effect of temperature of equilibration on the capacity of the resin

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

No.	Resin	Total AEC (meq/gm) of absolutely dry resin as determined at temperature (°C)			Total CEC (meq/gm) of absolutely dry resin as determined at temperature (°C)		
		30^0	50^0	70^0	30^0	50^0	70°
1	Poly-AC-Anthra	1.23	1.34	1.39	2.46	2.43	2.40
2	Poly-AC-Galli	-	-	-	6.98	6.88	6.83
3	Poly-AC-pHyBe	-	-	-	3.95	3.89	3.82
4	Poly-AC-Pyro	-	-	-	7.74	7.70	7.68
5	Poly-AC-Sali	-	-	-	3.29	3.20	3.02
6	Poly-AC-Hyqui	-	-	-	3.61	3.60	3.55
7	Poly-AC-βRes	-	-	-	4.25	4.06	4.00

TABLE-PAC-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-AC-Anthra	0.017	10.8	10.78
2	Poly-AC-Galli	0.20	18.4	18.20
3	Poly-AC-PHyBe	0.04	5.8	5.79
4	Poly-AC-Pyro	0.13	10.2	10.07
5	Poly-AC-Sali	0.01	7.2	6.99
6	Poly-AC-Hyqui	0.06	8.2	8.14
7	Poly-AC-βRes	0.05	4.0	3.95

TABLE-PAC-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-AC-Anthra	0.035	8.4	8.37

TABLE-PAC-11A

% Swelling of resins as cation exchange in various solvents

Resin	% Swelling in								
	Glacial Acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Pet. Ether
Poly-AC-Anthra	4.2	8.4	3.9	1.0	2.4	1.5	1.8	1.7	0
Poly-AC-Galli	3.5	9.4	3.6	2.3	2.9	2.7	1.8	2.5	0
Poly-AC-PHyBe	4.7	13.0	3.4	2.6	2.9	1.9	1.0	2.4	0
Poly-AC-Pyro	3.0	8.7	3.5	1.1	3.7	2.9	1.4	2.6	0
Poly-AC-Sali	5.9	12.9	4.6	2.9	3.7	4.0	2.4	3.4	0
Poly-AC-Hyqui	4.6	10.6	4.8	2.2	3.2	3.9	1.5	4.3	0
Poly-AC-BRes	3.1	8.6	4.1	1.9	1.2	2.9	1.8	2.9	0

TABLE-PAC-11B

% Swelling of resins as anion exchange in various solvents

Resin	% Swelling in								
	Glacial Acetic acid	Water	DMF	Dioxane	Alcohol	THF	Benzene	Acetone	Pet. Ether
Poly-AC-Anthra	4.01	6.32	2.13	1.02	2.13	1.03	1.53	1.12	0

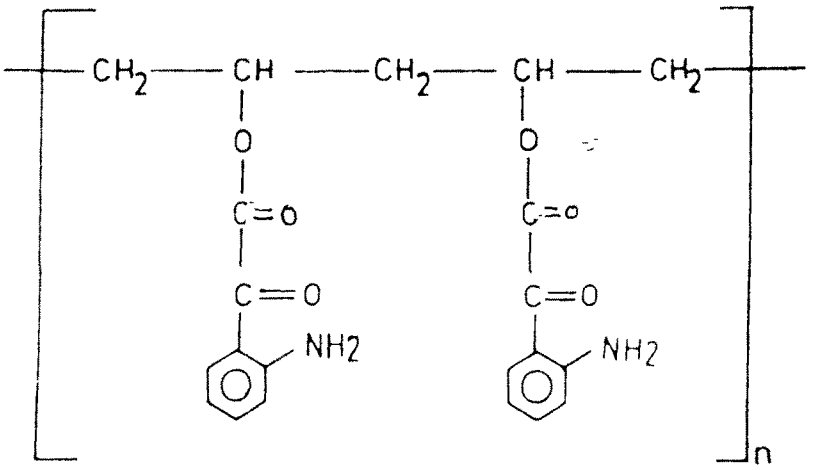
Table-AC-I

Major peaks observed in the infrared spectra of resins

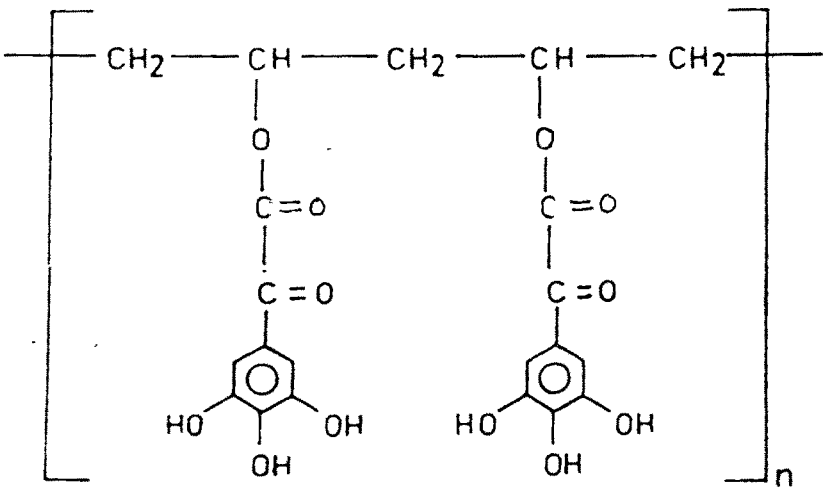
No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
1.	Poly-AC-Anthra	1660	medium	N-H bending
		1320-1280	weak	C-N vibration
		1150	sharp	-O-ether linkage
		1710-1730	broad	-O-C-C- conjugated carbonyl group
2.	Poly-AC-Galli	3600-3000	broad	-OH Stretching absorption
		1720-1680	medium	-O-C-C- conjugated carbonyl group
		1550-1610	sharp	>C=C< aromatic ring
3.	Poly-AC-PHyBe	3700-3200	broad	-OH stretching absorption
		1740-1700	medium	-O-C-C- conjugated carbonyl group
		1590	sharp	>C=C< aromatic ring
4.	Poly-AC-Pyro	3600-2800	broad	-OH stretching absorption
		1550-1350	broad	-O- ether linkage stretching
5.	Poly-AC-Sali	3600-3000	broad	-OH Stretching absorption
		1720-1680	medium	-O-C-C- conjugated carbonyl group

Continued.....

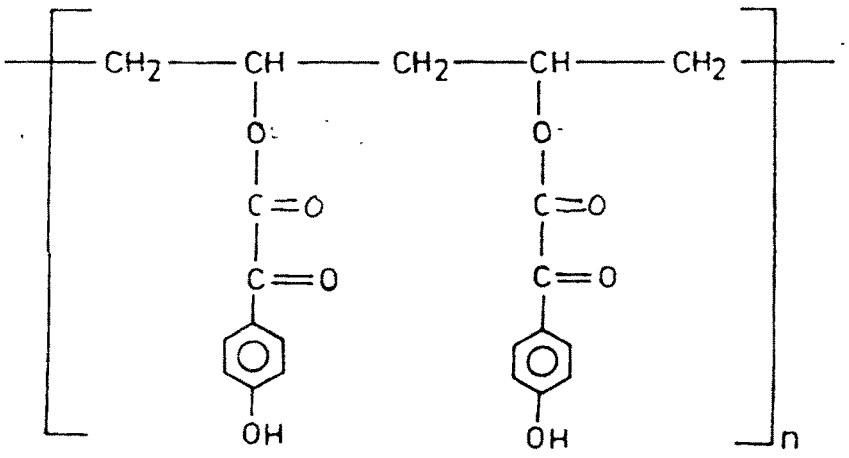
No.	Resin	Wave number cm^{-1}	Nature of peak	Probable assignment
6.	Poly-AC-Hyqui	3600-3000	broad	-OH stretching absorption
		1740-1700	medium	-O-C- ether group
		1620-1580	medium	>C=C< aromatic group
7.	Poly-AC-βRes	3600-2500	broad	-OH stretching absorption
		1740-1700	medium	-O-C-C- conjugated carbonyl group
		1620-1580	medium	>C=C< aromatic ring



(I) **Poly-AC-Anthra**

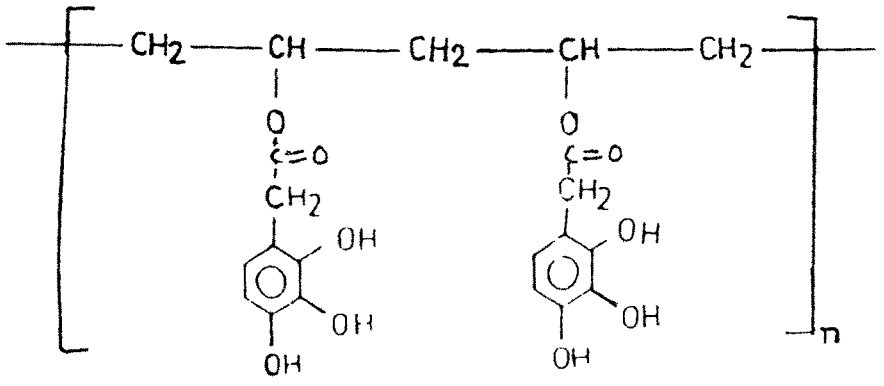


(II) **Poly-AC-Galli**

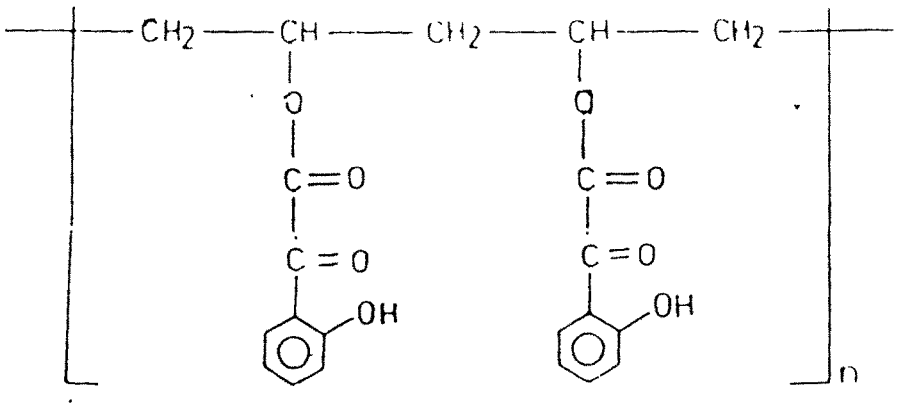


(III) **Poly-AC-PHyBe**

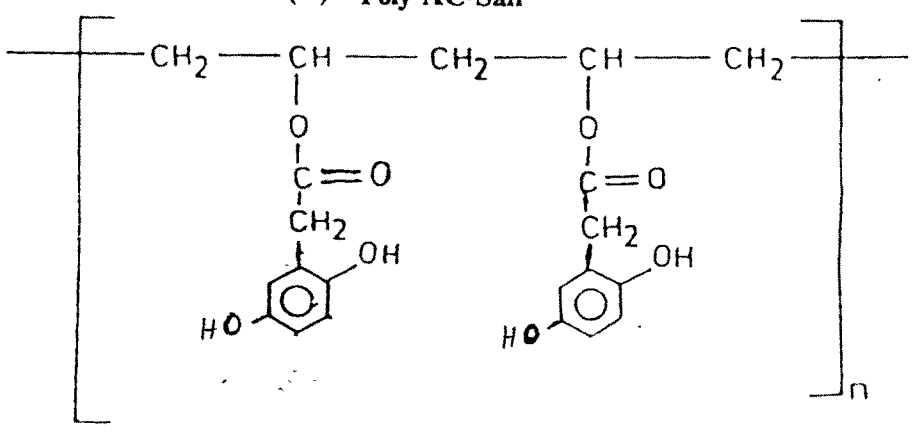
S.3.1



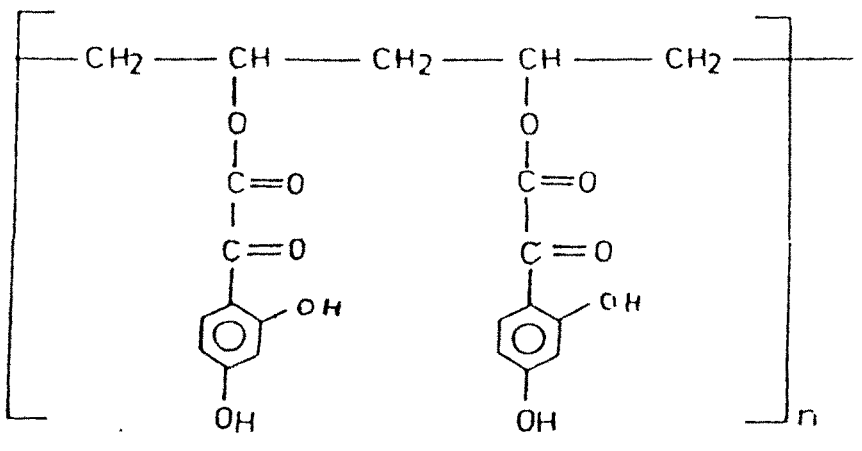
(IV) Poly-AC-Pyro



(V) Poly-AC-Sali



(VI) Poly-AC-Hyqui



(VII) Poly-AC-BRes

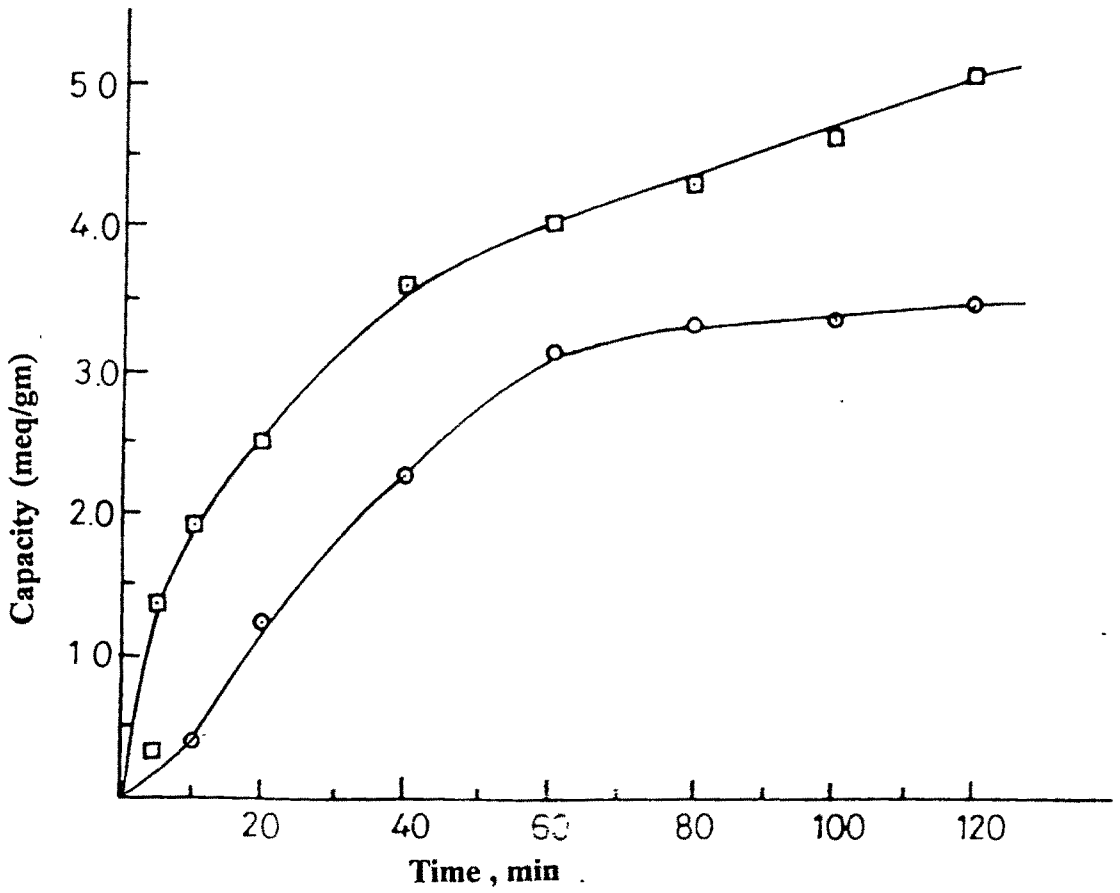


Fig.3.1 **Rate of cation exchange of Poly-AC-Anthra (⊙), Poly-AC-Galli (⊡)**

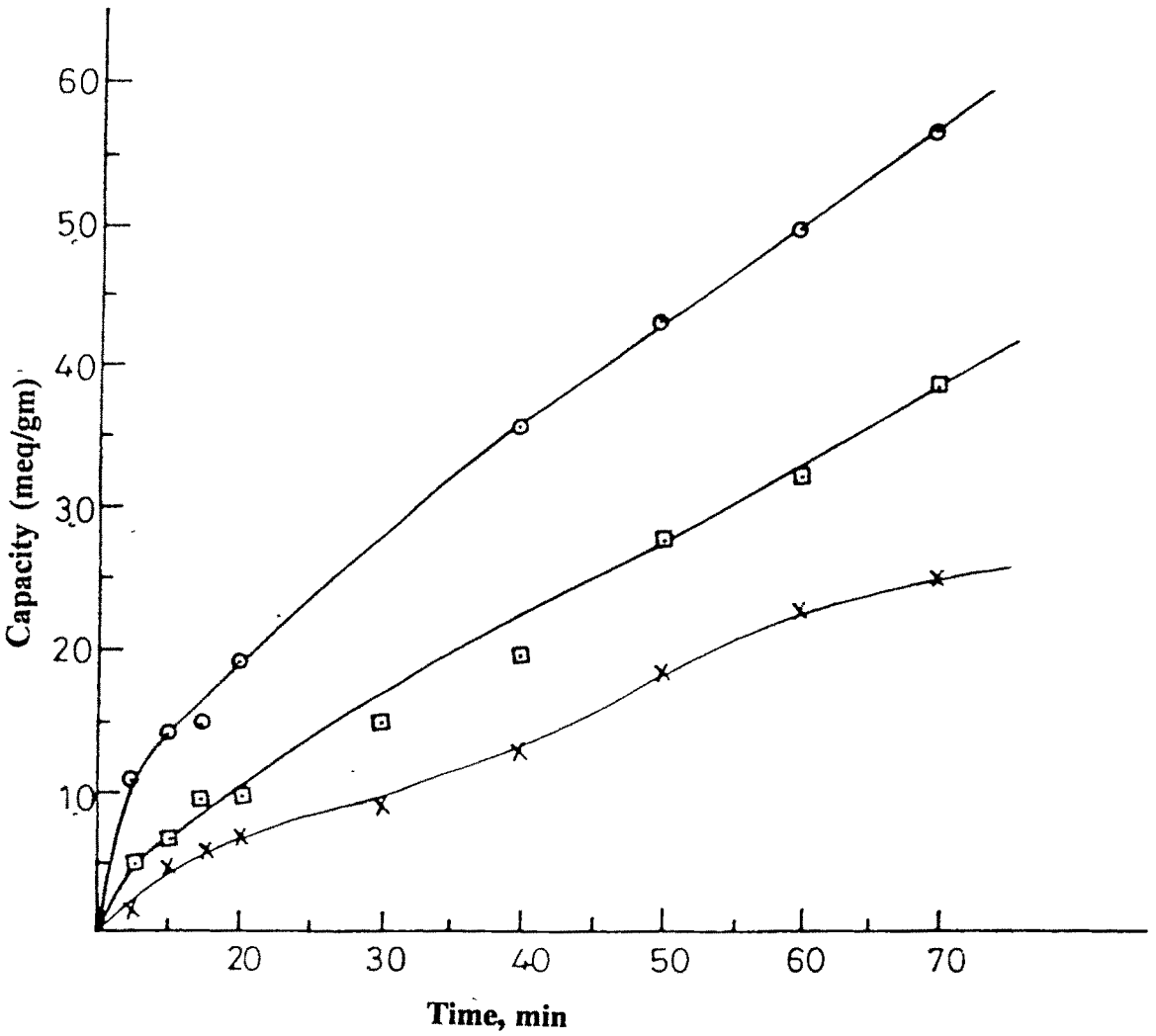


Fig.3.2 Rate of cation exchange of Poly-AC-Pyro (⊙), Poly-AC-PHyBe (⊡), Poly-AC-Sali (×)

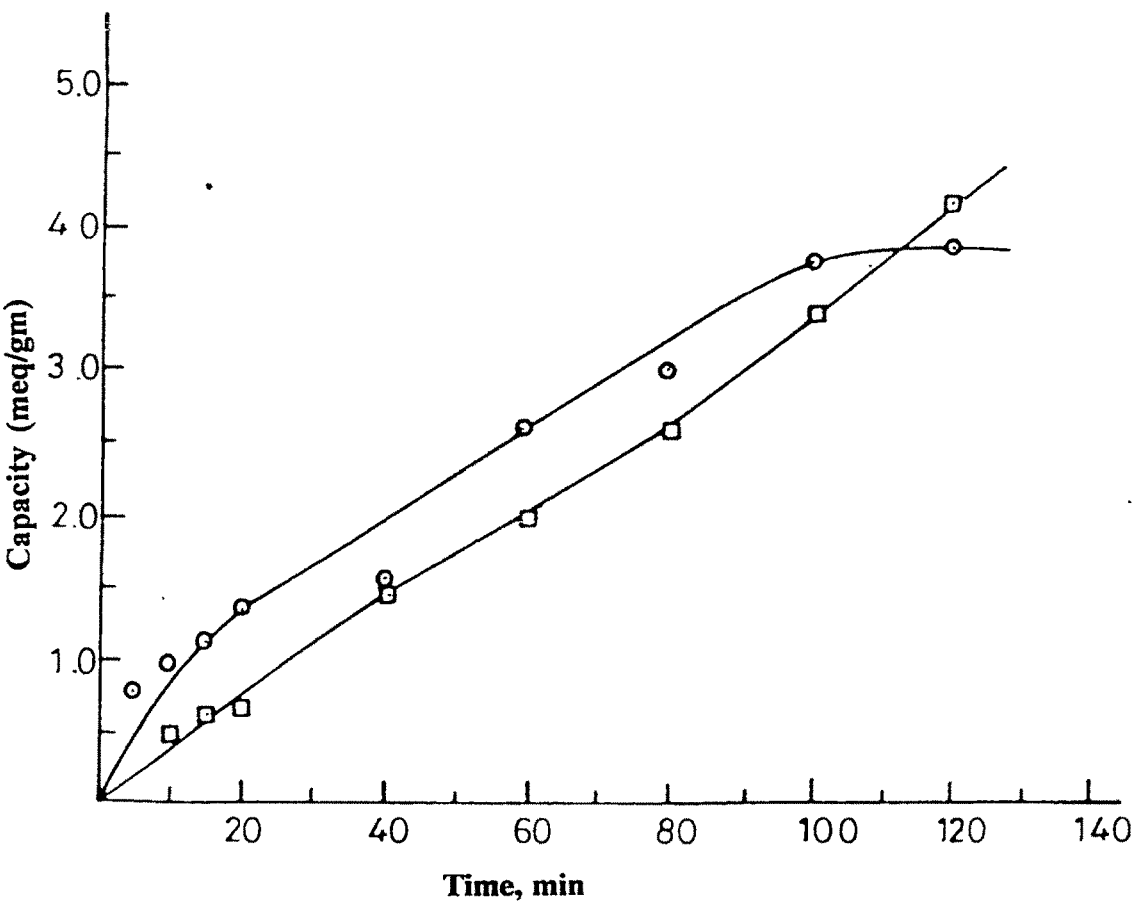


Fig.3.3 **Rate of cation exchange of Poly-AC-Hyqui (⊙), Poly-AC-BRes (⊡)**

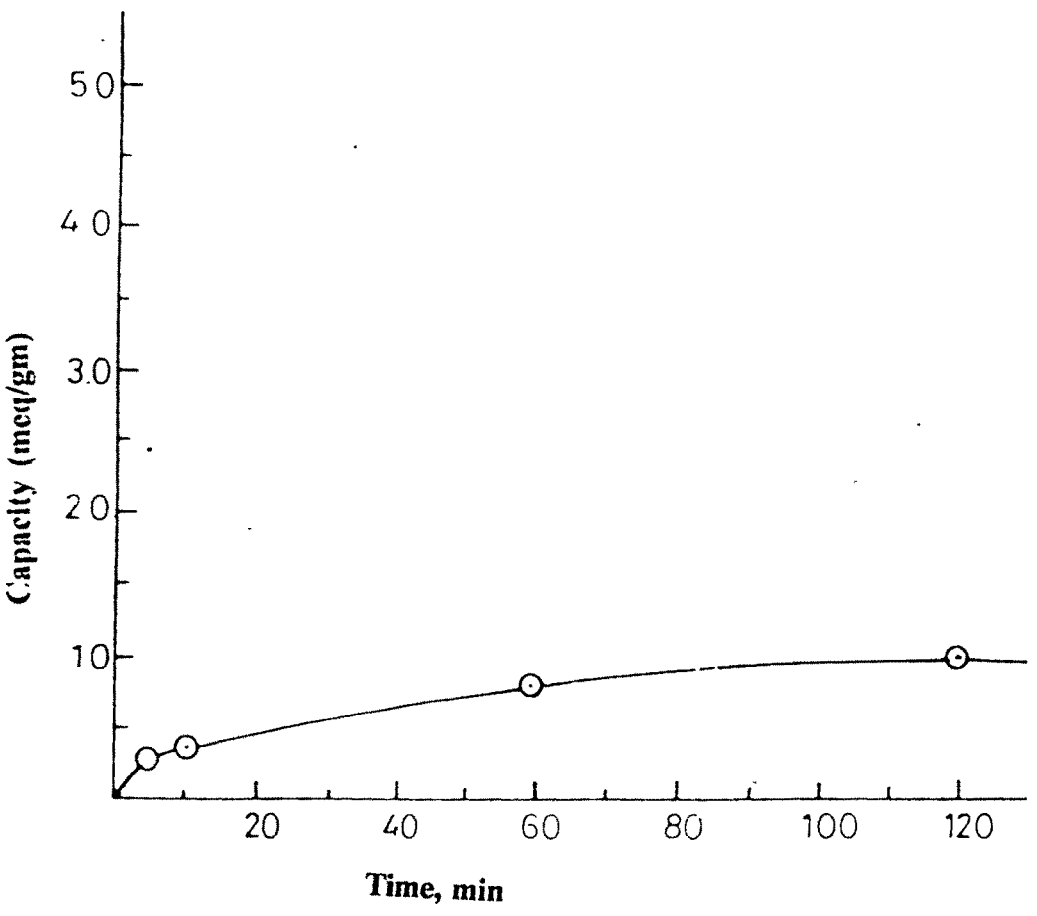


Fig.3.4 **Rate of anion exchange of Poly-AC-Anthra (⊙),**

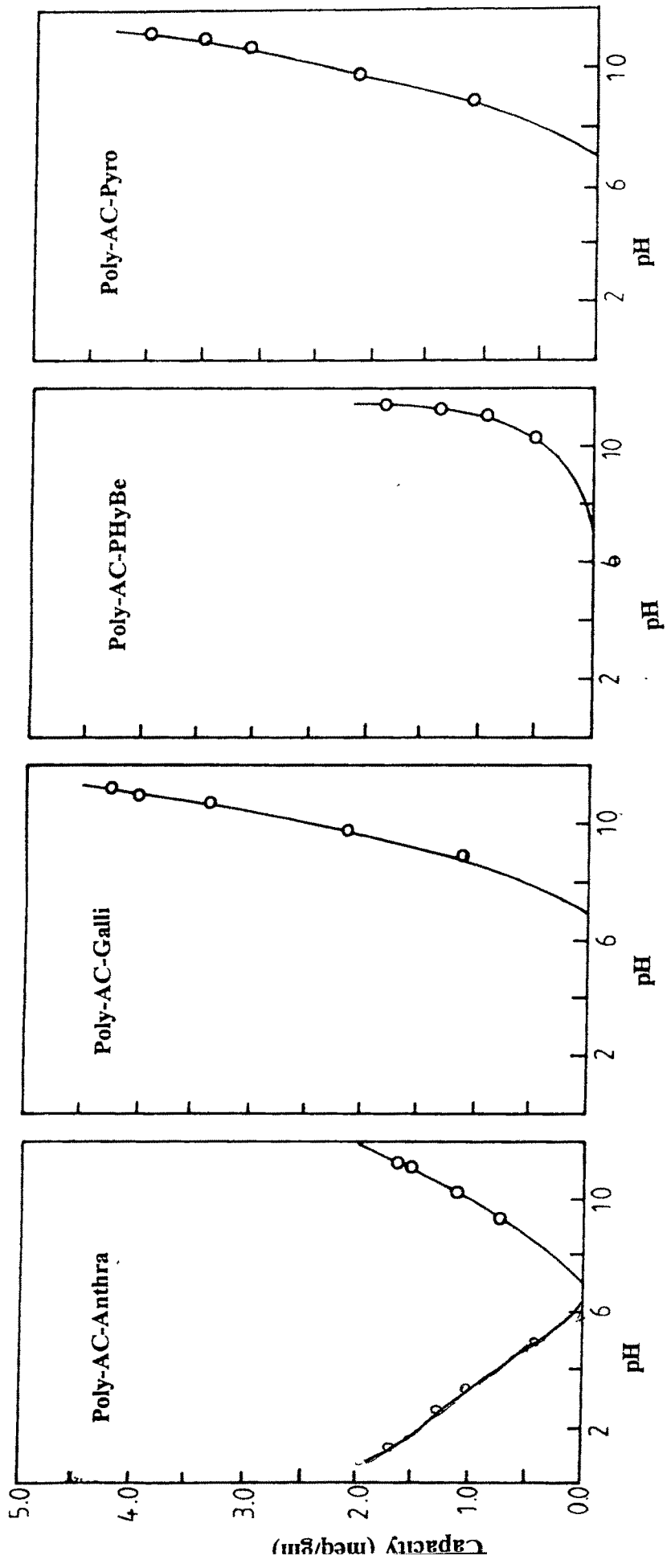

Poly-AC-Anthra
Poly-AC-Galli
Poly-AC-PHyBe
Poly-AC-Pyro
Capacity (meq/gm)
pH
5.0
4.0
3.0
2.0
1.0
0.0
2
6
10

Fig.3.5

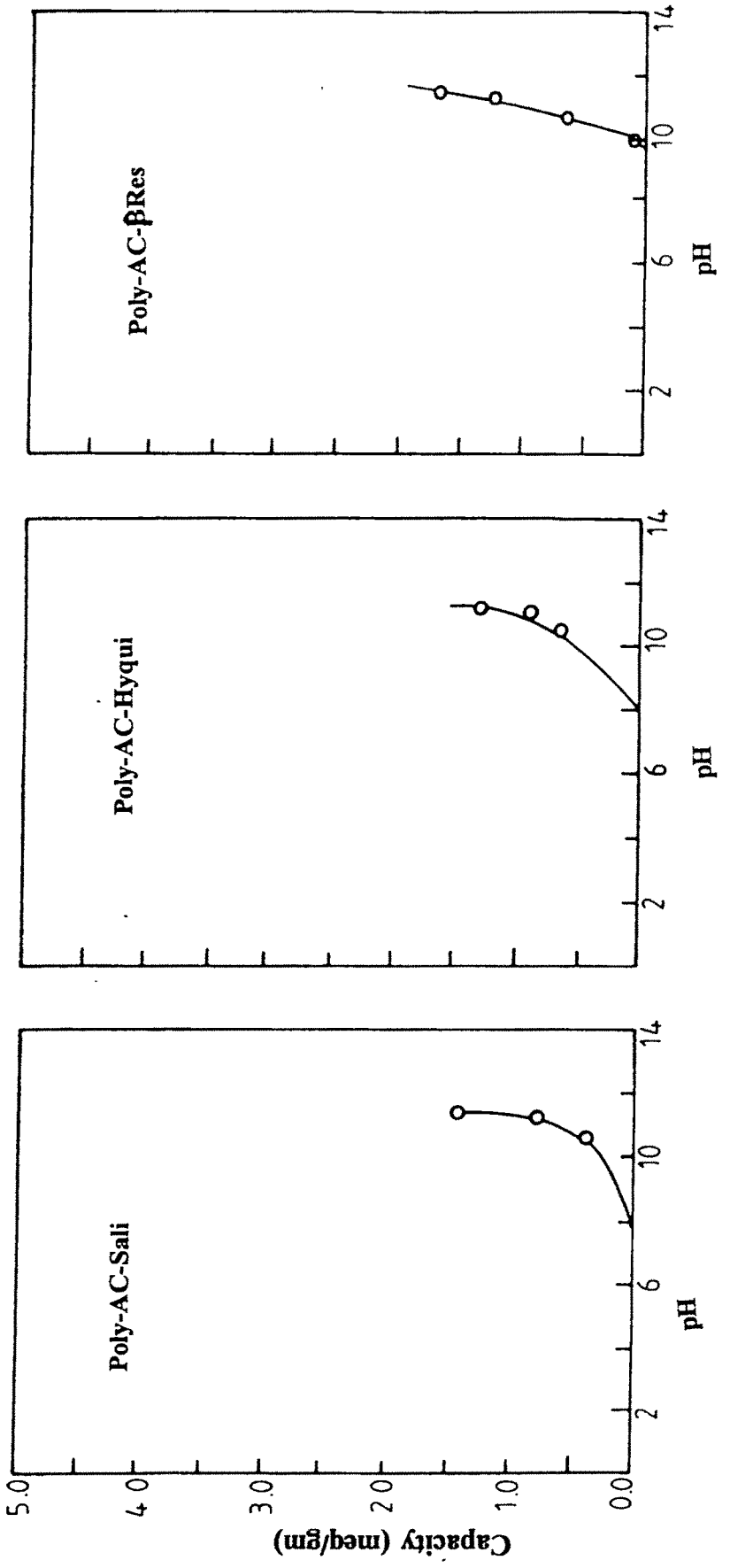
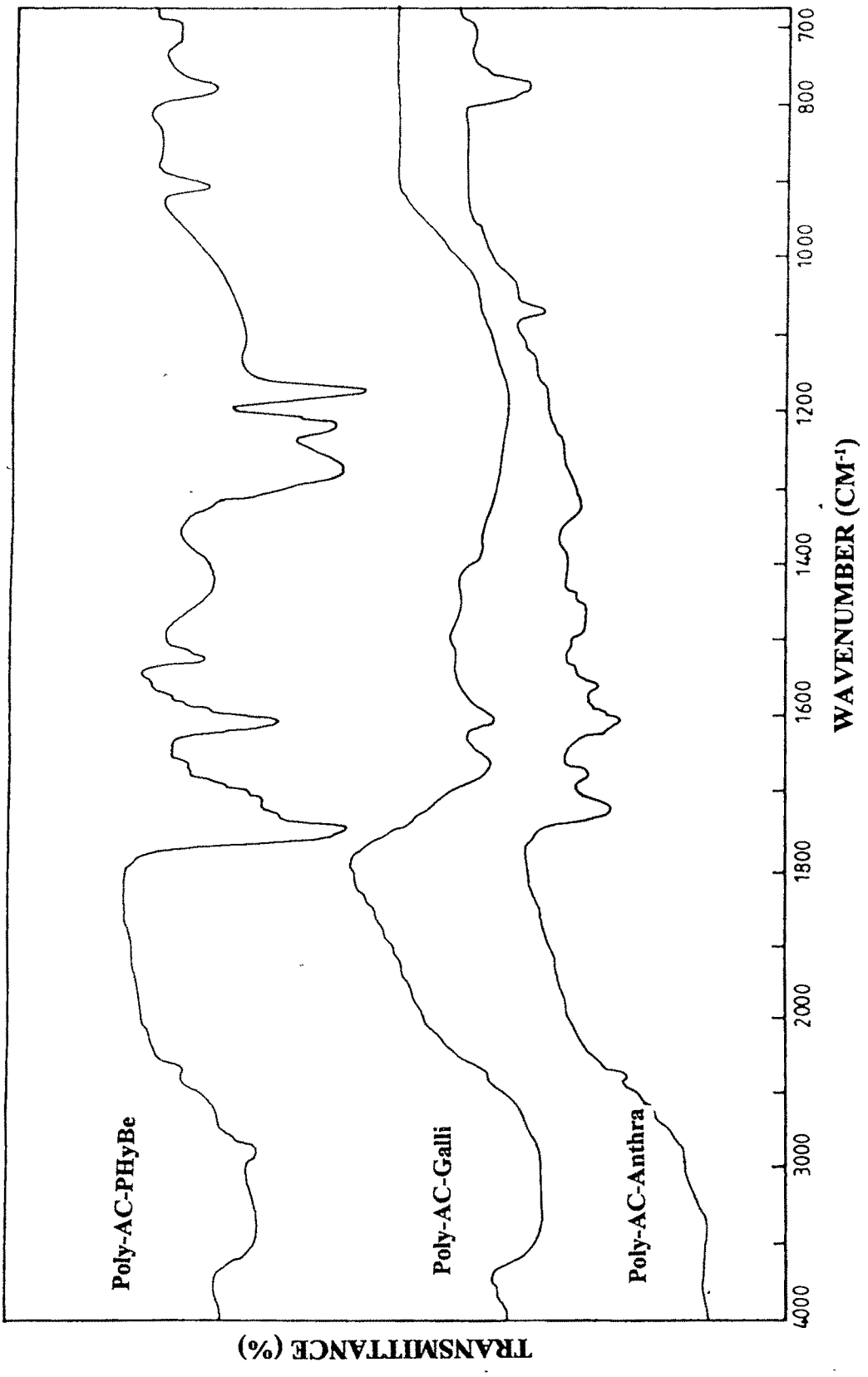
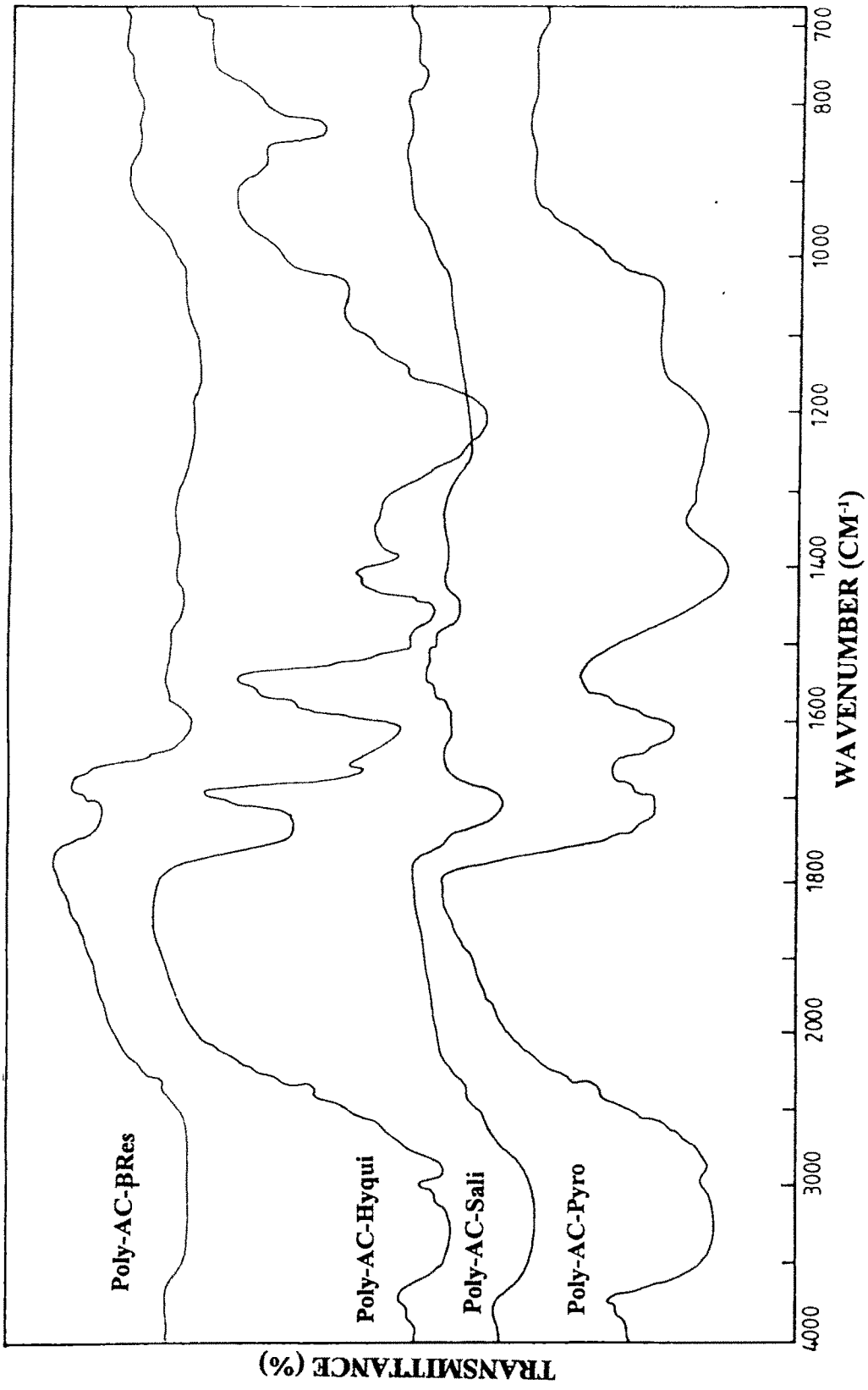

Poly-AC-Sali
Poly-AC-Hyqui
Poly-AC-βRes
Capacity (meq/gm)
pH
0.0
1.0
2.0
3.0
4.0
5.0
2
6
10
14

Fig.3.6


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


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

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