CHAPTER - I

I Phenol-Epichlorohydrin-Diethylenetriamine Type Chelating Amphoteric Ion-Exchange Resins

EXPERIMENTAL

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

The phenolic derivatives such as catechol, 8-hydroxyquinoline, hydroquinone, salicylic acid, sulfosalicylic acid, 3-hydroxy-2-naphthoic acid, p-hydroxybenzoic acid, β-resorcylic acid and anthranilic acid (0.06 mole) were dissolved in 50-75 ml of toluene and were mixed with epichlorohydrin (0.4 mole) in a 500 ml round bottom three necked flask fitted with a stirrer, a thermometer and a condenser. The mixture was vigorously stirred all the while keeping the temperature between 0° - 5°C. To the above cooled mixture, Diethylenetriamine (0.05 mole) was added slowly in fractions maintaining the temperature below 4°C shaking the mixture all the while. The condensation was carried out by maintaining the temperature below 10°C for two hours. A gel formed was then heated on steam bath for 5-6 hours and then cured in an oven below 90°C for 10 hours. The cured hard mass then crushed to -20 + 30 or - 60 + 100 BSS mesh size as needed and washed with acetone and ethyl alcohol to remove the unreacted monomers and polymer of low molecular weight from the resin.

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

I - (b) <u>Moisture content of resins:</u> (97)

Moisture content of the resins (H^+ form and OH^- form) was determined by drying an exactly weighed sample (0.5 gm) (H^+ form or OH^- form) of the resin in an oven at 110° - 115°C 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 - DT-3.

I - (c) Density of resins:

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

True density of resins (H^+ form and OH^- form) is determined by the specific gravity bottle method. A definite amount of the resin (H^+- form or OH^- - form) is taken in a specific gravity bottle whose weight is determined previously and is weighed. Then it is filled with water in presence of resin and (ii) alone and weighed. Hence the true density (dres) is 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 and OH^- form) is determined as follows:

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

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

The values of d_{res} and d_{col} are presented in Table-DT-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-DT-5.

I - (d) (i) Total Ion Exchange Capacity: (98)

Approximately 10 gms of the resin were weighed and taken in the funnel and converted into H-form with one litre of one normal hydrochloric acid. The resin was filtered, washed to neutrality with distilled water and dried in an oven below 100°C. 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 250 ml 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 1N sodium chloride solution and to the sample (of OH^--form) in Erlenmeyer Flask, were added 200 ml of standardized 0.1 N hydrochloric acid in 1 N sodium chloride solution. The mixture was kept for 24 hours. 50 ml aliquots of the supernatant liquid were titrated with standard 0.1 N acid and standard 0.1 N 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,

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

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

(ii) <u>Volume capacity of resins:</u>

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

Concentration of fixed ionogenic groups (C_r) for the resin is evaluated by the following relation:

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

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-DT-6 and Table-DT-7.

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 0.05 N copper acetate in 10% ammonia solution. The mixture was kept for 24 hours. 50 ml aliquots of the supernatant liquid were titrated with standard 0.05 M E.D.T.A. solution. The copper exchange capacity is calculated as follows:

$$\frac{(200 \times N\ \text{copper II}) - 4\ (\text{ml E.D.T.A.} \times \text{N. of E.D.T.A})}{\text{Sample weight} \times (\%\ \text{solid})/100}$$

= Milliequivalents of Cu - exchange gms of dry
H - form resin

= (Cu ion) Exchange capacity.

The results are presented in Table - DT-6.

I - (f) Rate of exchange:

The H - form (or OH-form) of the resin (0.5 gm) (-60 + 100 mesh) was accurately weighed into eight to nine different stoppered bottles. 100 ml 0.1 N NaOH in 1N Nacl (or 100 ml 0.1 N Hcl in 1 N Nacl) added to each bottle and the resin is allowed to remain in contact for different periods of time, with intermittent shaking. At definite pre-determined intervals, the solutions were decanted and an aliquot was titrated against standard acid or standard [redacted] alkali and from this the capacity realized at different time intervals was calculated. The values of the capacities of the resins ~~resin~~ were plotted against time and shown in Figs 1 to 6 and presented in Table - DT-8.

I - (g) pH - titration studies and Apparent pKa & pKb values: (98)

The OH-form of the resin (0.5 gm) (-60+100 mesh) was accurately weighed into different stoppered bottles and to each bottle 0.1 N Hcl in 1 N Nacl and 1 N Nacl solutions were added in different proportions to make up the volume to 50 ml and to give solutions of varying pH in the range 1 - 7. Similarly, in different stoppered bottles, accurately weighed H - form (0.5 gm) of the resin was treated with 0.1 N NaoH in 1 N Nacl and 1 N Nacl solutions in different proportions to make up the volume to 50 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.7 to 9.

The apparent pKa and pKb values for these resins are presented in Table - DT-9.

I - (h) Thermal stability:

Thermal stability of these resins in free acid, free base, sodium and chloride form were determined by adopting following procedure.

The resin (in desired form and of known capacity) about 10 grams (-60 +100 mesh) was heated in an electric oven at a pre-determined temperature for eight hours. The capacity of a portion of the heated sample (1 gm) was determined by directly equilibrating with standard alkaline or acidic solution. Another portion of the heated resin (1 gm) was regenerated with acid or alkali and the capacity determined. The experiment was repeated by heating the resin to different temperature in the range of 80° - 140°C.

The results are presented in Table-DT-10 and Table - DT-11.

I - (i) Effect of temperature of equilibration on capacity of resins: (99).

Definite amounts (0.5 gm) of the resin (H^+-or OH^--form) (-60 + 100 mesh) were allowed to equilibrate with 50 ml each of standard NaoH in 1 N Nacl solution or standard Hcl in 1 N Nacl solution at room temperature (30°C) for 2 hours and then the capacity of the samples determined. The same experiment was repeated at 50° and 70°C, using a thermostat.

The results are presented in Table - DT-12.

I - (j) Oxidation resistance test: (100)

Exactly weighed (0.5 gm) (-60 + 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 100 ml conical flask at 45°C for 72 to 95 hours. Then the resin was quantitatively transferred from the flask and subjected to the moisture content determination as usual. The results are presented in Table - DT-13 and Table - DT-14.

I - (k) Swelling behaviour: (101)

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

30 to 40 ml of the dried resin (H-form or OH-form) were poured into 100 ml 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 per cent swelling was calculated as follows:

$$\% \text{ swelling} = 100 \times \frac{(\text{Final volume} - \text{Initial volume})}{(\text{Initial volume})}$$

The results are presented in Table - DT-15 and Table - DT-16.

I - (1) Study of sorption behaviour of some metal cations on cationic form (NH_4^+ - form) of the amphoteric resins from NH_4OAC - DMF media: (107)

The sorption behaviour of the cationic form (NH_4^+ - form) of the amphoteric ion exchange resins with reference to some selected pre-transitional, transitional and post-transitional bivalent metal cations from NH_4OAc - DMF media was studied according the procedure as follows:

The resin (10 gms) was converted into NH_4^+ form by treating with 10% NH_4Cl solution in 10% liquor ammonia (Sp.gr. 0.90) solution and the resin was made free from chloride (negative test with $AgNO_3$). This resin was air dried and stored in polyethylene bottles for the sorption study.

Standard aqueous solutions (ca.0.1 M) of metal ions were prepared from their acetates (BDH). Metals selected are Ca (II) and Mg (II) (pre-transitional), Co (II) and Ni (II) (transitional) and

Cu (II) and Zn (II) (post-transitional). Aqueous NH_4OAC solutions used were 0.02 M, 0.25 M and 1.0 M and reagent grade DMF used was 40%. Study was carried out at room temperature (35 ± 1°C). Buffer solution of pH = 10 (NH_4Cl/ammonia) was used for EDTA titrations. Other desired pH were obtained by maintaining the pH of the solution by addition of the required quantities of acid or alkali solution and by using the pH meter (Elico pH-meter model CL-44).

Distribution study was carried out as follows:

For the determination of distribution coefficient, Kd, by batch equilibrium method, exactly weighed (0.5 gm) air-dried resin (NH_4^+ - form) was equilibrated with the solution containing the metal ion, NH_4OAC and DMF (total volume 25 ml) for 24 hours with the intermittent shaking of the solution mixture. The resin was filtered and the fraction of metal ion remained in solution after equilibrium was determined titrametrically against E.D.T.A. solution and K_d values were obtained by using the formula,

$$K_d = \frac{\text{Amt. of metal (II) in the resin}}{\text{Amt. of metal(II) in the soln.}} \times \frac{\text{Vol. of soln.}}{\text{g. dry resin}}$$

The results are presented in Table - DT-17.

I Phenol - Epichlorohydrin - Diethylenetriamine Type Chelating Amphoteric Ion-Exchange Resins

RESULTS AND DISCUSSION

General:

Recently epichlorohydrins have become prominent polymer formers and cross-linkers with alkylene-polyamines, such as diethylenetriamine (103 - 110) and other polyethyethylenepolyamines (111 - 115). Products range from low viscosity syrups to highly cross-linked solids can be obtained, depending on reactant ratios and polymerisation conditions. Several other chlorohydrin amine reactions which yield weak base resins include poly (allyl amine) epichlorohydrin-diglycidyl ether (116), (epichlorohydrin - ammonia)-imidazole (117), Poly (allyl amine) - epichlorohydrin - dihydroxypropane (118), poly (N-vinylimidazole) - epichlorohydrin (119), and (ammonia - glycerohalohydrin)-heterocyclic polyamine (120).

Strizhak, N.P. et al (121) synthesized chelate forming ion exchanger by condensation of p - aminostyrene - divinylbenzene copolymer with 20% aqueous chloroacetic acid. ICI Australia Ltd. (122) synthesized amphoteric resins from chloromethylated DVB - styrene copolymer, PVC, thioglycolic acid and amines, which are capable of thermal regeneration. Itagaki, et al (123) obtained amphoteric ion exchangers by treating copolymers (derived from styrene and divinylbenzene having chloromethylated groups) with N, N-dimethylglycine derivatives, having inner salt forming capacity 0.95 meq/ml.

Samborskii, I.V. et al (124) synthesized an amphoteric ion exchanger having improved selectivity for Cu or, in its absence for Ni, via the polycondensation of epichlorohydrin with maleic dihydrazide, curing the oligomer obtained with a mixture of hydrazide hydrate and nonaqueous polyethylenepolyamine, and subsequently chloromethylating with chloroacetic acid. Murel, A. (125) carried out a synthesis of improved and inexpensive carrier ampholytes for isoelectric focusing, using N, N' - methylenebisacrylamides, acrylic acid and polyethylenepolyamines (triethylenetetramine and tetraethylenepentamine). Balakin, V.M. et al (126) synthesized complex forming ion exchangers with aminophosphonic acid groups, by the reaction of H_3PO_3 and HCHO with commercial anion exchangers AN-2F, AN-31, AV-16 and EDE - 10P, which contain in their structures both primary and secondary alkylamino groups. The prepared ANKF-1, ANKF-2, ANKF-3 and ANKF-4 have a high sorption capacity for Ca ions.

Valakin, V.M. et al (127) prepared ampholytes having a high exchange capacity for UO_2^{-2} and insignificant sorption for Fe^{+3}, Cu^{+2}, Ni^{+2} and Co^{+2} by treating chloromethylated styrene - divinylbenzene copolymer with a 4-fold excess of $R\text{-}NH\text{-}CH_2\text{-}CH_2\text{-}CN$ (R = H, Me, Et, Bu) at 120°.

Okida, Tsugio. et al (128) synthesized chelating resins having chelating capacities of Cu^{+2}, Cd^{+2}, Pb^{+2} and Hg^{+2} 29.3, 38.6, 81.3 and 142.0 g/L respectively and good mechanical strength.

We have synthesized chelating amphoteric ion exchange resins using various chelating (complexing) phenol derivatives, epichlorohydrin and diethylenetriamine. The phenolic derivatives employed for synthesising the resins possess the following structural characteristics:

(a) two phenolic groups in ortho or para positions on a phenyl ring,

(b) one phenolic group and one ring nitrogen,

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

(d) one phenolic group in ortho position to carboxyl group but in meta position to sulfonic group on a phenyl ring,

(e) one phenolic group and one carboxyl group in ortho position on a naphthalene ring,

(f) one phenolic group and one carboxylic group in para position on a phenyl ring,

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

(h) one amino group and one carboxyl group on a phenyl ring.

The title resins are prepared in granular form by condensation of phenolate with diethylenetriamine and epichlorohydrin. Amphoteric ion exchange resins which may be termed "Zwitter ion" resin would behave like an amphoteric material. Amphoteric resins would be of potential interest as a model compound for the study of behaviour of proteins and wool (129) because it would exhibit titration curves similar to those of amino acids and proteins.

General Characteristics and Structures:

The chelating amphoteric ion exchangers, in general, are fairly porous in nature with average physical stability and good chemical resistance to 3N acids and alkalis and exhibit no colour 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 - DT - 2) and their physico-chemical studies and are shown as (i) I-S-20, EP(CA)DT (ii) I-S-21, EP(HQ)DT (iii) I-S-22, EP(SA)DT (iv) I-S-23, EP(SS)DT

(v) I-S-24, EP(3-OH)DT (vi) I-S-25, EP(PHB)DT (vii) I-S-26, EP(BR)DT and (viii) I-S-27, EP(AN)DT.

The study of these structures leads us to believe that the various end products are identical and all the phenolic derivatives get condensed with diethylenetriamine in molar ratio of 1 : 1.

Moisture retention %. :

Percentage moisture of the resins are presented in Table - DT-3. The percentage moisture of the resins in H-form varies between 1.90 to 6.50, while the percentage moisture of the resins in OH-form varies between 2.70 to 7.80. Known values (130) of percentage moisture for commercial resins in H-form are 43.00 to 53.00 for IRC - 50/75 (weak acid, Active group -COO-) and 42.00 to 50.00 for IRC - 84 (weak acid, Active group -COO-). Thus resins under investigation have very low range of percentage moisture. This may be attributed to high degree of cross-linking. Difference in the values 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.

We observed that the ion exchange capacity is not related to the moisture retention ability for the resins under investigation.

Density of resins:

The results of true density (d_{res}) and apparent density (d_{col}) are presented in Table - DT - 4. It is seen that the values of d_{res} is ranging from 1.03 to 1.61 gm/cm^3 for H-form of resins and from 1.00 to 1.78 for OH-form of resins. We have also measured the column or apparent density (d_{col}) of the resins. The values vary between 0.14 to 0.31 gm/ml for H-form of resins and 0.25 to 0.46 gm/ml for OH-form of resins.

We observe in general that in case of amphoteric resins under study, the apparent density (d_{col}) of the resin in H-form is lower than that of the resin in OH-form. Further, we suggest that since the difference in density (d_{res}) of the resins in H - and OH - forms is small, the resins under study can stand recycling to a good degree.

Void volume fraction:

The results of the void volume fraction are presented in Table - DT - 5.

It is observed that the values of the void volume fraction vary between 0.71 to 0.90 for resins in H - form and between 0.62 to 0.81 for resins in OH - form.

The large void volume fraction suggests the porous nature of the resins and hence the diffusion of ions and the rate of ion exchange may be facilitated.

Ion exchange capacity:

The resins synthesized are polyfunctional in nature. They contain $-SO_3H$, - COOH, -OH and amine groups. The cation or anion exchange capacity can be calculated using the formula,

$$\begin{array}{c} CEC_{(cal)} \\ \text{or} \\ AEC_{(cal)} \end{array} = \frac{1000}{M/n}$$

where M = Molecular weight of the resin per unit on dry basis and

n = number of groups taking part in anion or cation exchange.

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 - DT - 6 and Table - DT - 7.

The results show that total anion exchange capacity of amphoteric resins is much higher than that of total cation exchange capacity.

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

EP(BR) DT > EP(SS)DT > EP(AN)DT >
EP(SA)DT > EP(PHB)DT > EP(HQ)DT >
EP(3-OH)DT > EP(8-OH)DT > EP(CA)DT.

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

EP(SA)DT > EP(BR)DT > EP(SS)DT >
EP(PHB)DT > EP(AN)DT > EP(HQ)DT >
EP(8-OH)DT > EP(CA)DT > EP(3-OH)DT.

Total exchange capacity of EP(PHB)DT [7.02 meq/gm], EP(BR)DT [7.92 meq/gm] and EP(SA)DT [8.9 meq/gm] as anion exchanger is comparable to that of commercial anion exchanger Duolite A - 4 (7.7 meq/gm) (granules) and Duolite A-2 (8.4 meq/gm) (granules), Duolite A-7 (9.1 meq/gm) (granules, weak base amino group condensation polymer).

Metal (Cu) exchange capacity:

Recovery of copper from industrial wastes by ion exchange was considered from time to time by various research workers (131 - 137). McBurney (68) patented a resin showing high selectivity for copper. Gregor (53) and Pepper (138) synthesized chelating resins and investigated their specificity for copper.

We have studied the copper ion-exchange by the resins in H - form from ammonical solutions. The observed values of copper ion-exchange capacity of these resins are presented in Table - DT - 6. It is seen that copper ion-exchange capacity of these resins ranges from 1.03 to 2.54 meq/gm. The copper ion-exchange capacity of these resins are in the decreasing order as,

EP(SS)DT > EP(SA)DT > EP(BR)DT >
EP(AN)DT > EP(HQ)DT > EP(3-OH)DT >
EP(PHB)DT > EP(CA)DT > EP(8-OH)DT.

We suggest that at pH range (10.6 to 10.8) under study, 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 6 show the rate of exchange of amphoteric resins as cation exchanger as well as anion exchanger.

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

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

(a) complete exchange occurs in 15 mins.,

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

EP(HQ)DT ≅ EP(SA)DT > EP(PHB)DT > EP(8-OH)DT > EP(CA)DT > EP(SS)DT > EP(AN)DT > EP(3-OH)DT > EP(BR)DT.

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

(a) complete exchange occurs in 15 minutes,

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

EP(3-OH)DT > EP(PHB)DT > EP(SS)DT >
EP(BR)DT > EP(HQ)DT > EP(SA)DT >
EP(AN)DT > EP(CA)DT > EP(8-OH)DT.

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

pH - titration study:

The pH titration curves for the amphoteric resins are presented in Figs. 7 to 9. The resins exhibit good cation and anion exchange capacities over the pH range 1 to 12. It is evident from the Figs. 7 to 9 that the resins are capable of exchanging anions or cations over the pH-range 1-12 and are amphoteric in nature. These resins can be used as anion exchanger as well as cation exchanger, depending upon the pH of the solutions.

In the pH range 1 to 7, the resins behave as anion exchanger (Figs. 7 to 9) and the curves over this range are characteristic of weakly basic resins and may be compared with the pH - titration curve of commercially available weakly basic anion exchange resin (Tulsion WB) (139). The cation exchange behaviour of these resins is similar to that of weak acid resin (140).

Apparent pK_a and pK_b values:

Plots of cation and anion exchange capacity versus pH of the solution at equilibrium are presented in Figs. 7 to 9. From these plots pK_a and pK_b values of the resins are calculated as follows:

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

$$RH \rightleftharpoons R^- + H^+ \qquad (1)$$

$$K = \frac{[R^-]\,[H^+]}{[RH]} \; ; \quad pK = -\log K \qquad (2)$$

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

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

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

Hence $pHr = pK - \log (1 - \alpha)/\alpha$ (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

$$pK = pHr \qquad (6)$$

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).

Hence $[Na^+]_s / [H^+]_s = [Na^+]_r / [H^+]_r$

...... (7)

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

At 50% conversion,

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

Hence $pK = pH + \log [Na^+]_s - \log \dfrac{[R^-] + [RH]}{2}$

..... (9)

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

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

$$H^+R^- \rightleftharpoons H^+ + R^- \qquad (10)$$

and acid dissociation constant in cation exchange (K_A) as

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

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

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

and acid dissociation constant in anion exchange (K_B) as

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

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

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

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 - DT - 9.

It is seen that the range of pK_a obtained for overall cation exchange process in general for various ion-exchangers studied varies between 10.89 to 11.13 which is slightly higher than a value of phenolic hydroxyl group and that of pK_b obtained for the overall anion exchange process for these resins lies between 2.8 to 3.10 which is a characteristic of bases of medium strength.

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

EP(AN)DT $\cong$ EP(SS)DT $>$ EP(BR)DT $>$
EP(SA)DT $>$ EP(3-OH)DT $>$ EP(PHB)DT $>$
EP(CA)DT $>$ EP(HQ)DT $>$ EP(8-OH)DT,

while the pK_b values for the resins are in the decreasing order as,

EP(SA)DT > EP(BR)DT > EP(SS)DT >
EP(PHB)DT > EP(HQ)DT > EP(8-OH)DT >
EP(CA)DT > EP(AN)DT > EP(3-OH)DT.

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 is defined 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 as follows:

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

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

Equations (i) and (ii) are related to cation and anion exchange processes respectively. Thus acid dissocation constant [K_{AC} and K_{AA}] for ionisation are

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

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

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

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

At isoionic point,

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

Hence,

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

pH_{ip} for isoionic point is

$$pH_{ip} = 1/2\ [pK_{AC} + pK_{AA}]$$

The values of isoionic point (ip) are presented in Table - DT - 9.

From the values of isoionic point [redacted] presented in Table - DT - 9, it can be seen that the values vary in the range of 6.90 to 7.10. Isoionic point for Proline is 6.3 and for Histidine is 7.3 (141). It is observed that the resins under study have values comparable with Proline and Histidine.

The values are in the decreasing order, as,

EP(SA)DT > EP(SS)DT > EP(BR)DT >
EP(AN)DT > EP(PHB)DT > EP(HQ)DT >
EP(3-OH)DT > EP(8-OH)DT > EP(CA)DT.

Thermal stability:

The results of thermal stability of amphoteric resins as cation exchanger in free acid and salt (Na-) form at different temperature are presented in Table - DT - 10 and as anion exchanger in free base form and in salt form such as chloride form are presented in Table - DT - 11.

It is revealed that no change in the total capacity for all the forms (H-, Na-, OH-and Cl-forms) of the resins are observed upto 80°C. Hence the amphoteric resins could be safely used upto the temperature 80°C. Above this temperature they show an increase in capacity when the heated resins were regenerated and tested could be due to

(i) destruction of some of the $-\underset{|}{\mathrm{CH}}-$ bridges, creating more gaps in the matrix thereby facilitating the acess of more - NH - groups,

(ii) removal of the decomposition products which had neutralized the ionogenic groups.

A thermal stability decreasing order for the H-form of the amphoteric resins is,

EP(CA)DT > EP(8-OH)DT > EP(HQ)DT >
EP(PHB)DT > EP(SS)DT > EP(AN)DT >
EP(SA)DT > EP(BR)DT > EP(3-OH)DT,

whereas a thermal stability decreasing order for the OH-form of the amphoteric resins is,

EP(CA)DT > EP(8-OH)DT > EP(PHB)DT >
EP(3-OH)DT > EP(HQ)DT > EP(AN)DT >
EP(SS)DT > EP(SA)DT > EP(BR)DT.

The salt forms (Na- and Cl- form) of the resins are found to be more stable than the free acid and free base form which is in conformity with the earlier observation of Hall et al (142).

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 - DT - 12.

It can be seen that the anion exchange capacity of amphoteric 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 diethylenetriamine used for the synthesis of the resin) are produced which neutralise a part of the acid during equilibration, thus giving an apparent higher value of the anion exchange capacity of the resin.

While the lowering of the cation exchange capacity of the resin with the increasing temperature of equilibration may be due to the loss of the ionogenic groups.

Oxidation resistance:

Results of oxidation resistance test of different amphoteric ion exchangers as cation exchanger as well as anion exchanger are presented in Table - DT-13 and Table - DT - 14 respectively.

Amphoteric resin EP(HQ)DT exhibits the lowest increase in % water content as cation exchanger and as anion exchanger and thus is the most resistant to oxidation. We observed that (with few exceptions), on oxidative degradation, amphoteric resins as anion exchanger exhibit greater increase in % water content than the amphoteric resins as cation exchanger.

Hence we suggest that the cationic form is less susceptible to oxidation than anionic form.

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

EP(HQ)DT > EP(CA)DT > EP(3-OH)DT >
EP(8-OH)DT > EP(AN)DT > EP(SS)DT >
EP(PHB)DT > EP(BR)DT > EP(SA)DT ,

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

EP(HQ)DT > EP(CA)DT > EP(AN)DT >
EP(8-OH)DT > EP(SS)DT > EP(PHB)DT >
EP(SA)DT > EP(3-OH)DT > EP(BR)DT.

Behaviour in non-aqueous solvents:

Ion exchangers in non aqueous solvents serve as catalysts. In some cases for purification purposes, non aqueous solvents are treated with ion exchangers. These applications have lead us to study the behaviour of ion exchangers in non aqueous phases. Bodamer and Kunin (101) showed that the behaviour in non aqueous solvents depends highly on the nature of the carbon chain of the exchange resin as well as its porosity and cross linking.

The results of behaviour in non aqueous solvents of these resins as cation exchanger as well as anion exchanger are reported in Table - DT - 15 and Table - DT - 16 respectively.

It can be easily seen that,

(i) polar solvents produce more extensive swelling than the non polar hydrocarbons,

(ii) in polar solvent, amphoteric resins as anion exchanger swell more than the cationic types,

(iii) % swelling of amphoteric resins in acetic acid as cation exchanger as well as anion exchanger is much higher than would be anticipated. This can be explained as follows:

Swelling of amphoteric resins with both weak acid and weak base groups is a function of pH of the solution and show a characteristic minimum near the isoelectric point of the resins. Here, the active groups of both types are practically undissociated, so that the osmotic pressure difference is small. When pH is increased or decreased, either the acid or base groups dissociate, this increasing the number of osmotically active particle within the resin. The result is an increase in swelling in either case,

(iv) the decreasing order of porosity (polar solvents) for amphoteric resins as cation exchanger is as follows:

EP(PHB)DT > EP(SS)DT > EP(SA)DT >
EP(AN)DT > EP(HQ)DT > EP(3-OH)DT >
EP(BR)DT > EP(CA)DT > EP(8-OH)DT and,

(v) the decreasing order of porosity (polar solvents) for amphoteric resins as anion exchanger is as follows:

EP(AN)DT > EP(PHB)DT > EP(SA)DT >
EP(8-OH)DT > EP(HQ)DT > EP(BR)DT >
EP(3-OH)DT > EP(SS)DT > EP(CA)DT.

(vi) Sorption behaviour of some bivalent metal cations on cationic form (NH_4^+ form) of the amphoteric resins from ammonium acetate - dimethylformamide media:

The results of sorption studies are presented in Table - DT - 17. We observed that,

(i) the sorption of metal ions decreases with the increasing concentration of NH_4OAc (DMF being constant). Largely, the metal forms a complex with the acetate ion and the sorption depends upon the nature of the complex formed. If the charge of the complex is positive, zero or negative, the sorption will be less(143). Various concentration of DMF have been tried and 40% concentration has been found to be the best for separation.

We suggest that on increasing the concentration of NH_4OAc, acetate ion replaces the co-ordinating water molecules resulting in the formation of complex species of a small positive charge, or neutral metal acetate is likely to be present in solution and consequently the K_d value is decreased. The most likely species in the resin phase is $[M^{II}(OAc)]^+$ or $[M^{II}(OAc)]^{+2}$ as reported by earlier workers (144, 145).

(ii) From the table for K_d values, we suggest that role of DMF is mainly to assist the formation of complex and does not exhibit a complexing ability in the system. [redacted]

(iii) From the Table - DT - 17, it is clear that Cu^{+2} has K_d value 253.6 as compared to 1.70 for Mg^{+2} at 0.02 M concentration of ammonium acetate, indicating the possibility of chromatographic separation of these two cations employing EP(SA)DT resin.

(iv) Similarly, we also suggest the possibilities of separation of Cu^{+2} and Mg^{+2} at 0.25 M concentration of ammonium acetate using EP(SA)DT, EP(3-OH)DT and EP(BR)DT resins.

(v) The resins EP(SA)DT and EP(BR)DT showed high uptake of Cu^{+2} whereas relatively low uptake of Mg^{+2} at 1.00 M concentration of ammonium acetate indicating the possibilities of chromatographic separation of these two metal cations employing EP(SA)DT and EP(BR)DT resin respectively.

(vi) Mg^{+2} ion has lower K_d values at all the molar concentrations of ammonium acetate which may be due to higher affinity of ammonium ions towards the resins as compared to Mg^{+2} and reverse is true for Cu^{+2}.

The following variation of sorption of cations with the concentration of ammonium acetate was observed.

$[NH_4OAc] = 0.02$ M

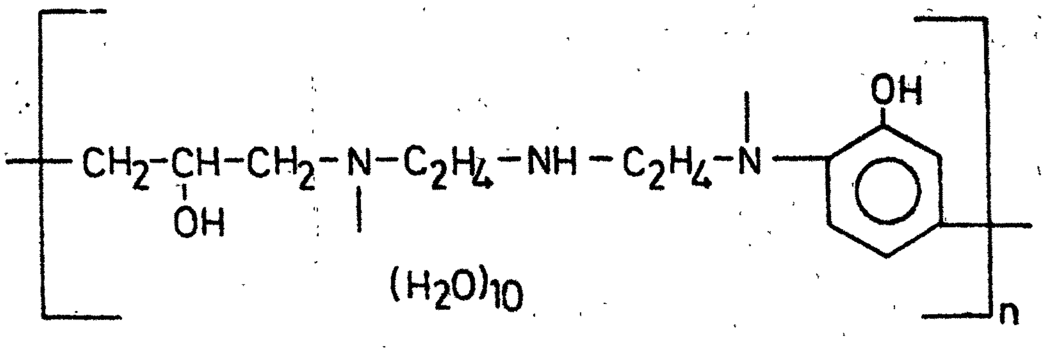
Resin	Sorption Order
EP(CA)DT	Cu > Ni > Co ≅ Ca > Zn > Mg
EP(8-OH)DT	Cu > Ca > Co > Zn > Ni ≅ Mg
EP(HQ)DT	Cu > Ni > Ca > Zn > Co ≅ Mg
EP(SA)DT	Cu > Zn > Ni > Co > Ca > Mg
EP(SS)DT	Cu > Ni > Zn > Ca > Co > Mg
EP(3-OH)DT	Cu > Ni ≅ Zn > Ca ≅ Co > Mg
EP(PHB)DT	Cu > Ni > Zn > Ca > Co > Mg
EP(BR)DT	Cu > Zn > Ni > Co > Ca > Mg
EP(AN)DT	Cu > Ni > Zn > Ca > Co > Mg

$[NH_4OAc] = 0.25$ M

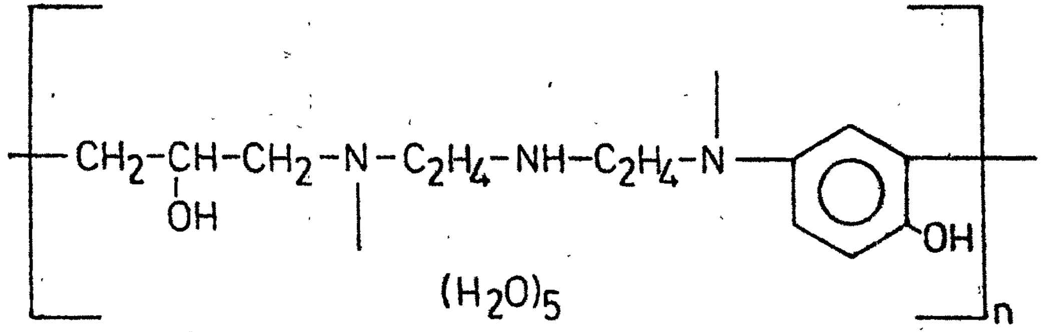
Resin	Sorption Order
EP(CA)DT	Cu > Co > Ca > Ni > Zn > Mg
EP(8-OH)DT	Cu > Co > Ni > Ca > Zn > Mg
EP(HQ)DT	Cu > Ni > Co > Ca > Zn > Mg
EP(SA)DT	Cu > Zn > Ni > Co > Ca > Mg
EP(SS)DT	Cu > Co > Ni > Zn > Ca > Mg
EP(3-OH)DT	Cu > Co > Ni > Zn ≅ Ca > Mg
EP(PHB)DT	Cu > Co > Ni > Zn > Mg > Ca
EP(BR)DT	Cu > Co > Ni > Zn > Ca > Mg
EP(AN)DT	Cu > Co > Ni > Zn > Ca > Mg

$[NH_4OAc] = 1.00$ M

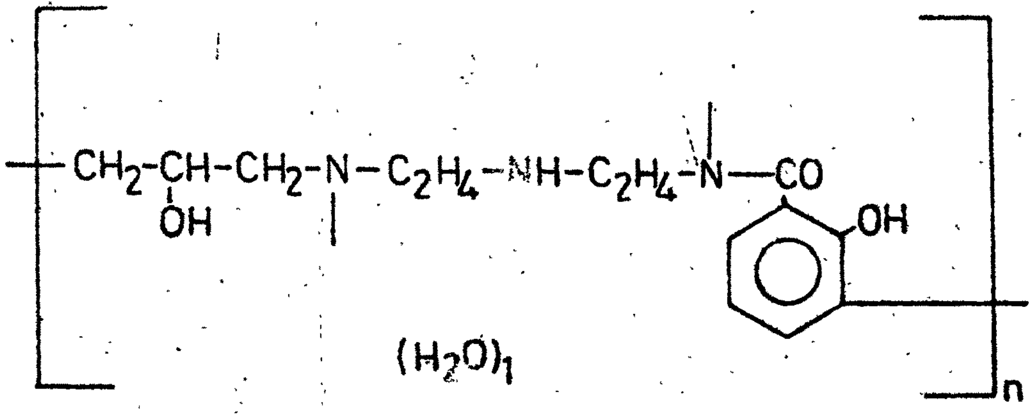
Resin	Sorption Order
EP(CA)DT	Cu > Ni > Ca > Co > Zn > Mg
EP(8-OH)DT	Cu > Ni > Zn > Co ≅ Ca > Mg
EP(HQ)DT	Cu > Ni > Ca > Zn > Mg > Co
EP(SA)DT	Cu > Ni > Zn > Ca > Co > Mg
EP(SS)DT	Cu > Ni > Zn > Ca > Mg > Co
EP(3-OH)DT	Cu > Zn > Ni > Ca > Co > Mg
EP(PHB)DT	Cu > Ni > Zn > Ca > Co > Mg
EP(BR)DT	Cu > Ni > Zn > Ca > Co ≅ Mg
EP(AN)DT	Cu > Ni > Zn > Ca > Co > Mg



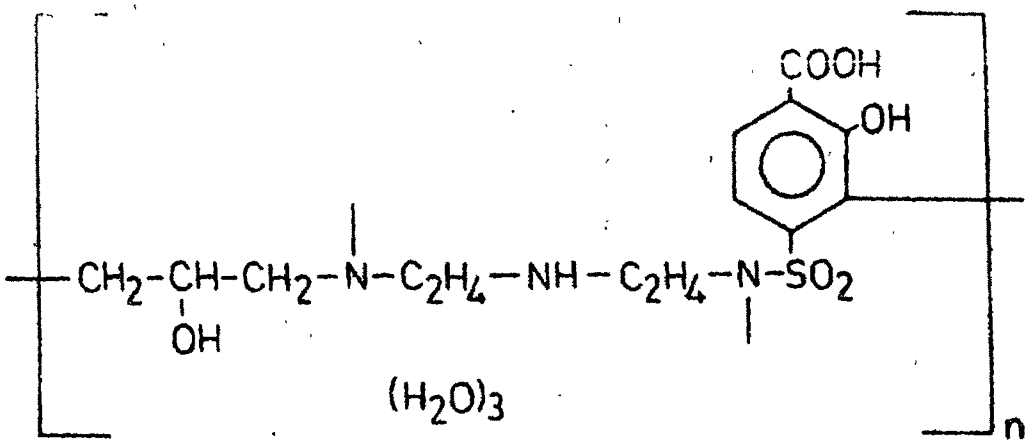
EP(CA)DT (I-S-20)



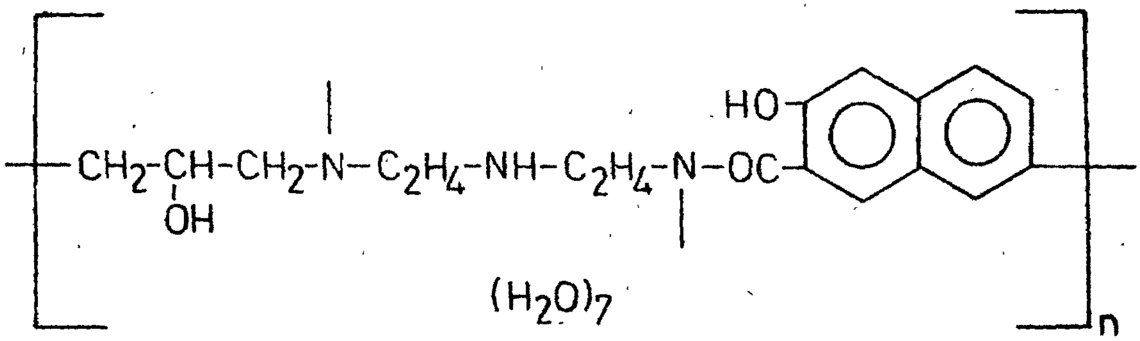
EP(HQ)DT (I-S-21)



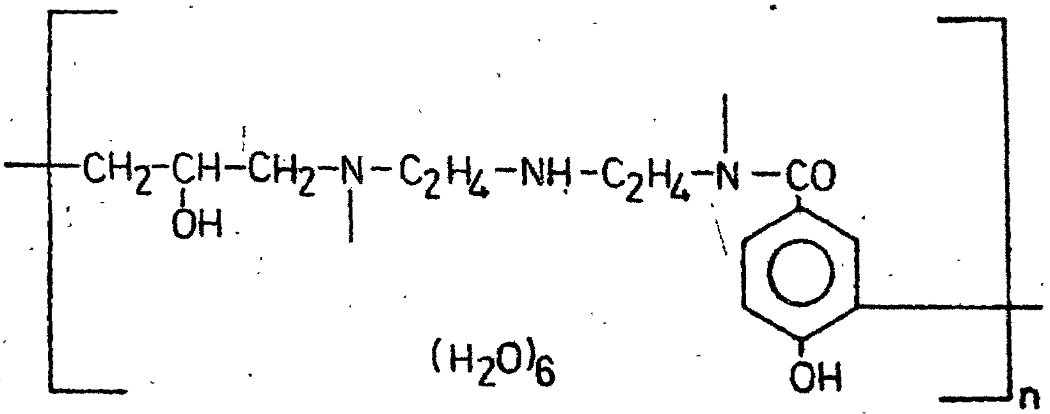
EP(SA)DT (I-S-22)



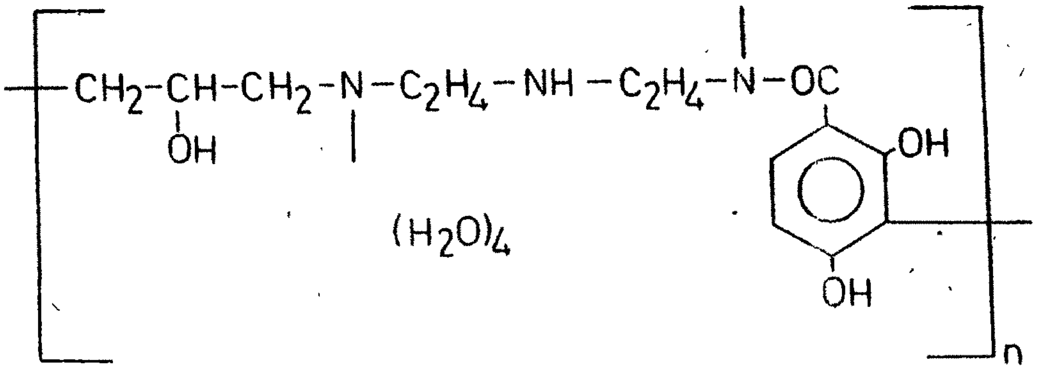
EP(SS)DT (I-S-23)



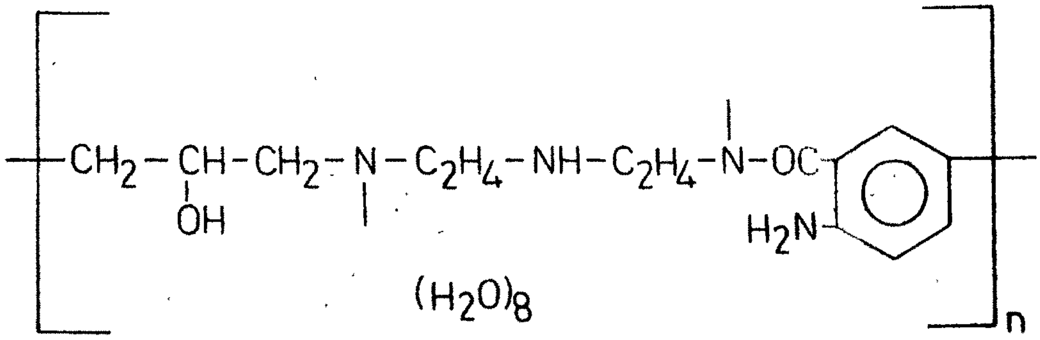
EP(3-OH)DT (I-S-24)



EP(PHB)DT (I-S-25)



EP(BR)DT (I-S-26)



EP(AN)DT (I-S-27)

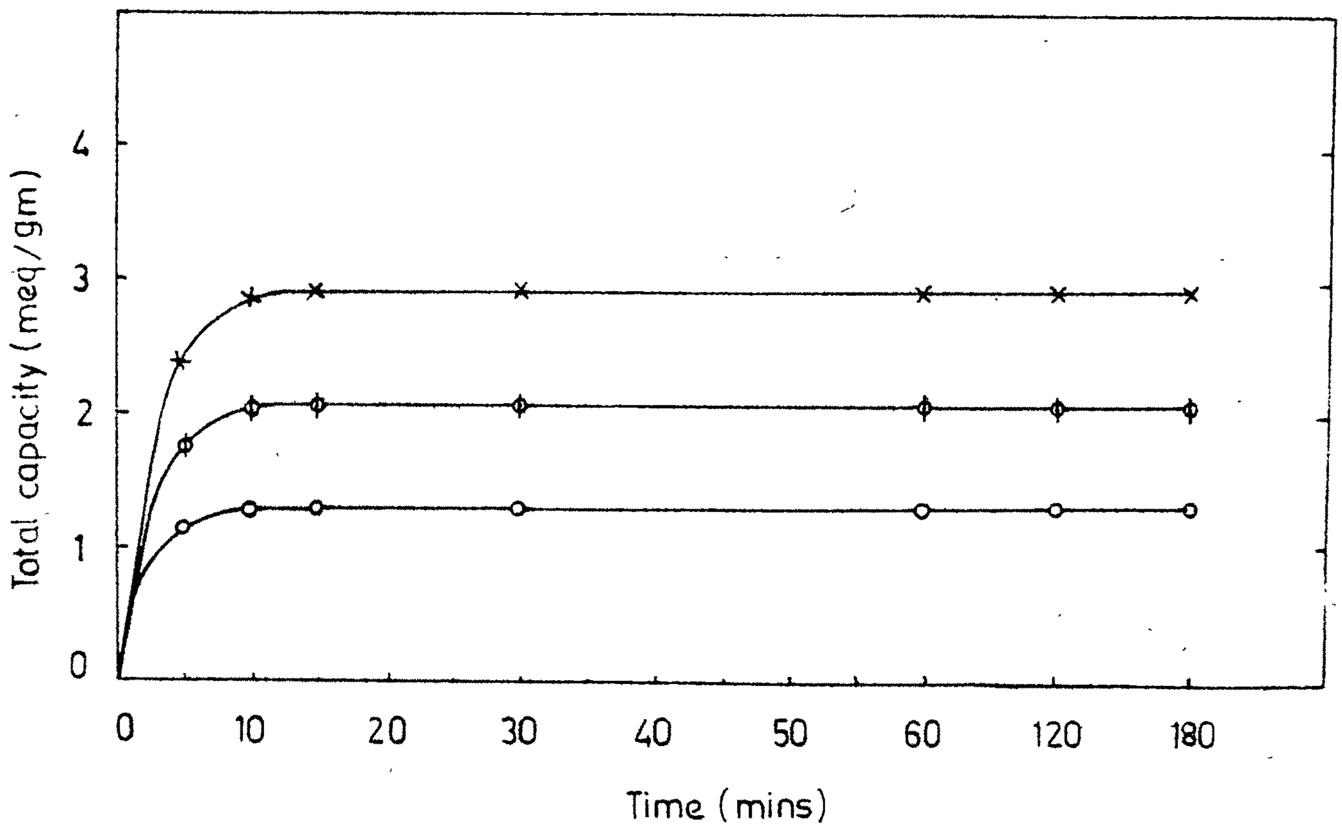


FIG 1 – RATE OF CATION EXCHANGE OF EP(SA)DT [×—×]
EP(HQ)DT [ϕ—ϕ] AND EP(CA)DT [o—o] RESINS

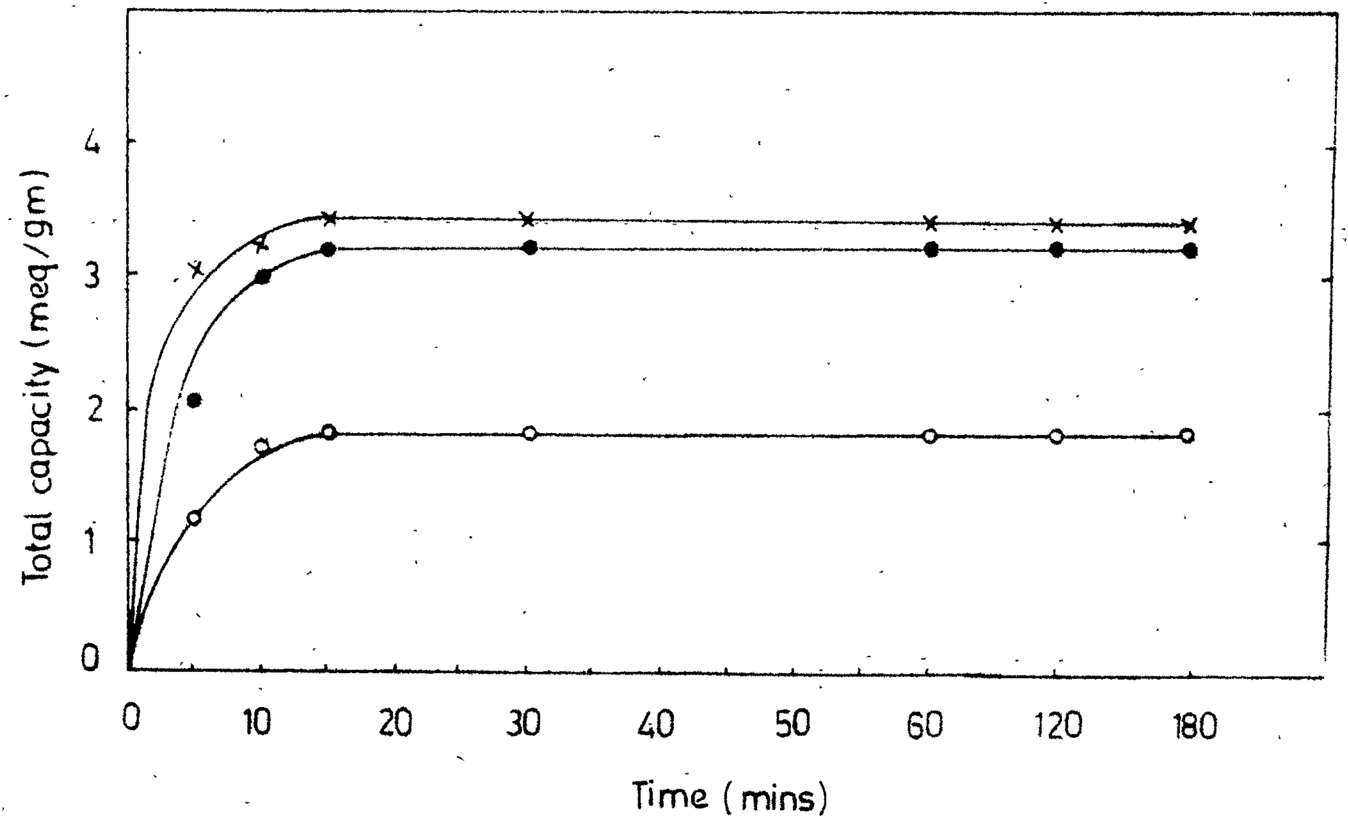


FIG 2 – RATE OF CATION EXCHANGE OF EP(BR)DT [×—×] EP(AN)DT [●—●] AND EP(3·OH)DT [○—○] RESINS

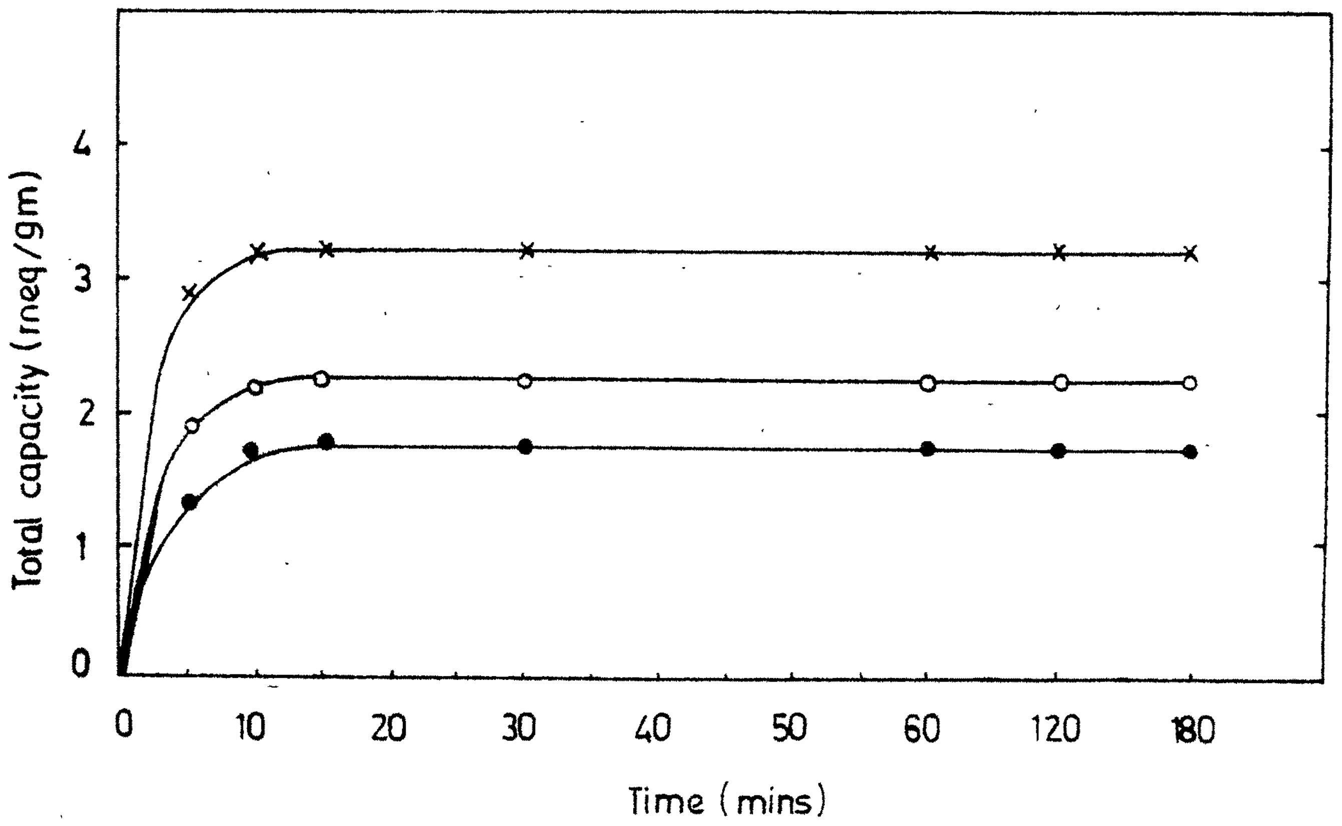


FIG 3 – RATE OF CATION EXCHANGE OF EP(SS)DT [×—×], EP(PHB)DT [○—○] AND EP(8-OH)DT [●—●] RESINS

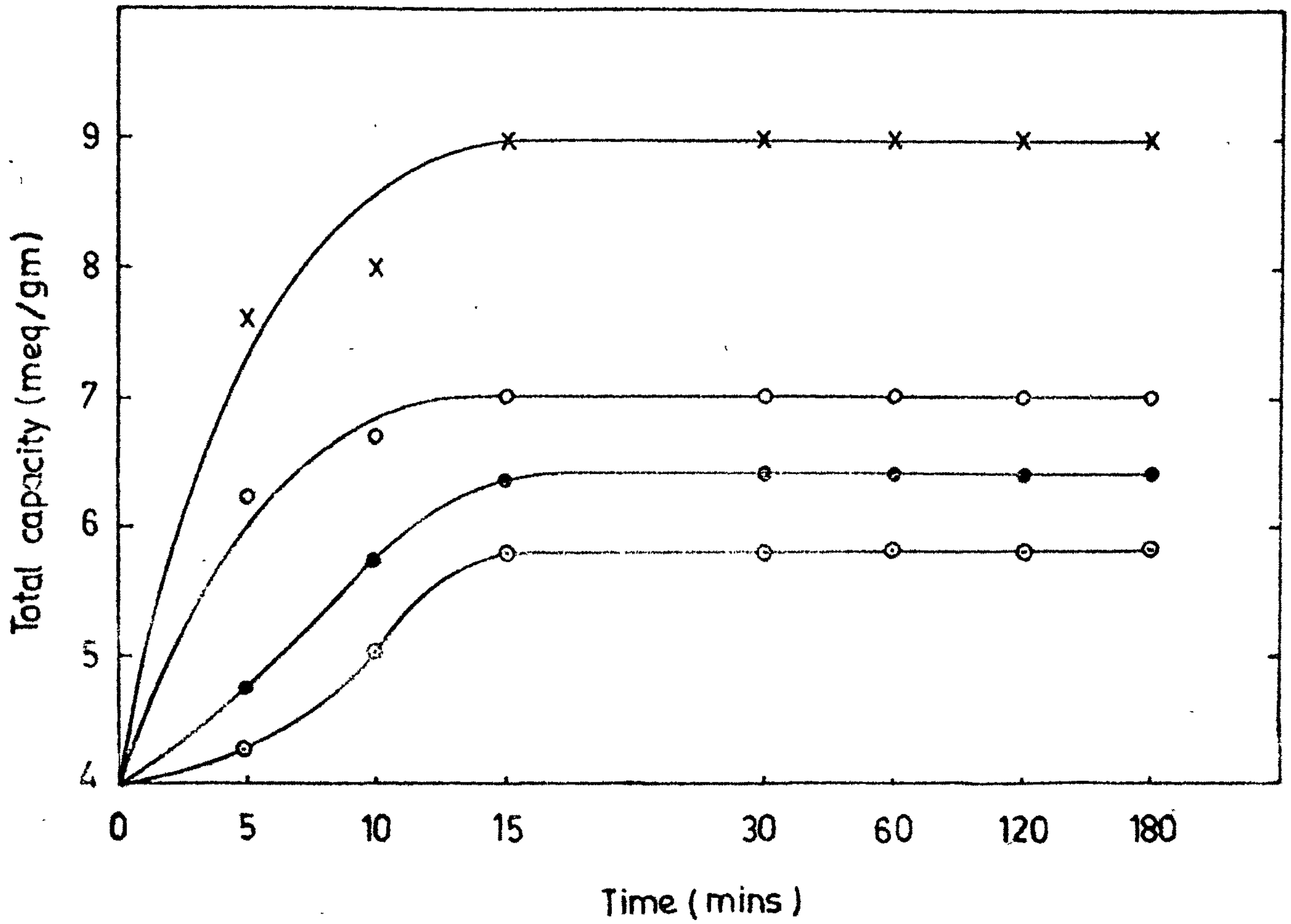


FIG 4 – RATE OF ANION EXCHANGE OF EP(SA)DT [×—×], EP(PHB)DT [○—○], EP(HQ)DT [●—●] AND EP(CA)DT [⊙—⊙] RESINS

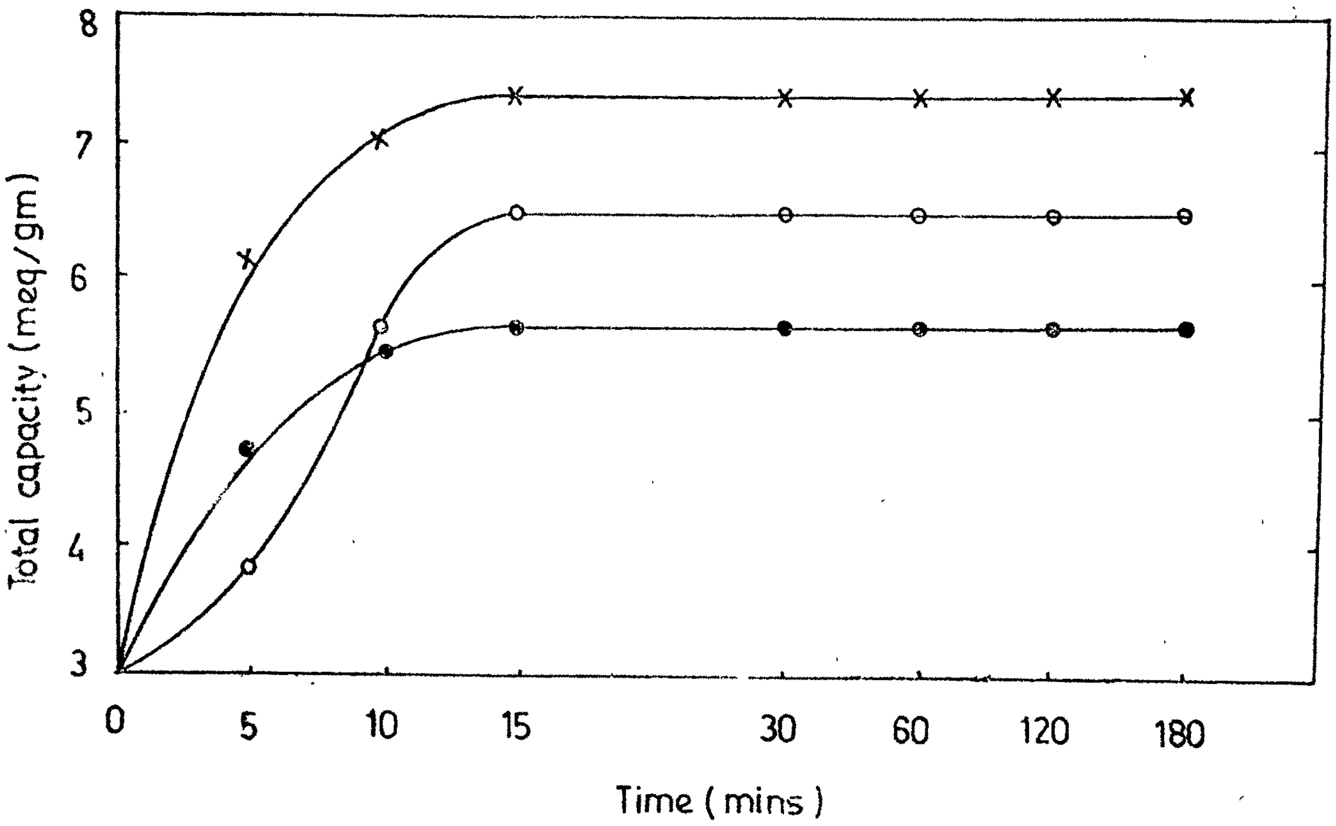


FIG 5 – RATE OF ANION EXCHANGE OF EP(SS)DT [x—x], EP(AN)DT [○—○] AND EP(3-OH)DT [●—●] RESINS

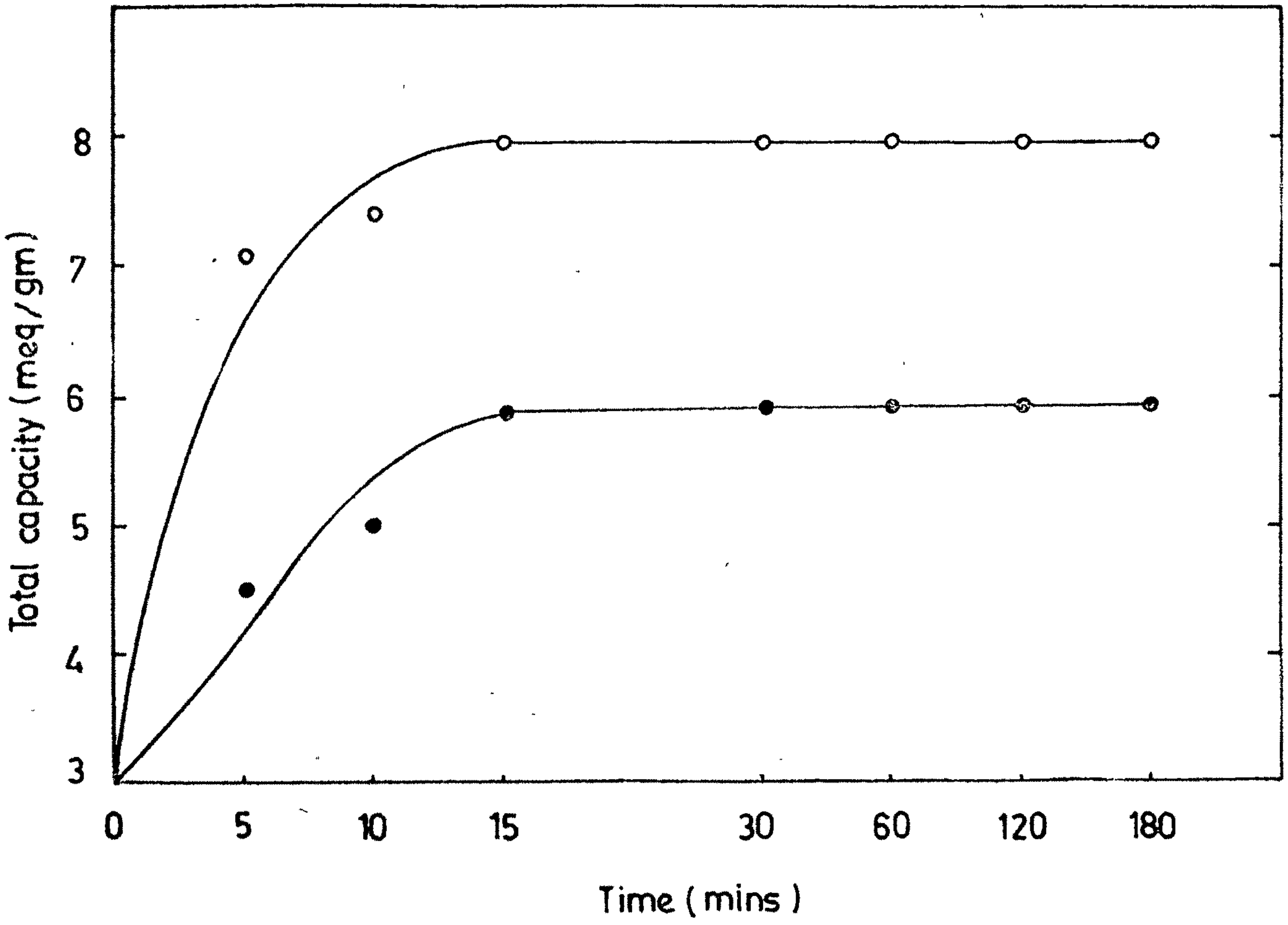


FIG 6 — RATE OF ANION EXCHANGE OF EP(BR)DT [○—○] AND EP(8-OH)DT [●—●] RESINS

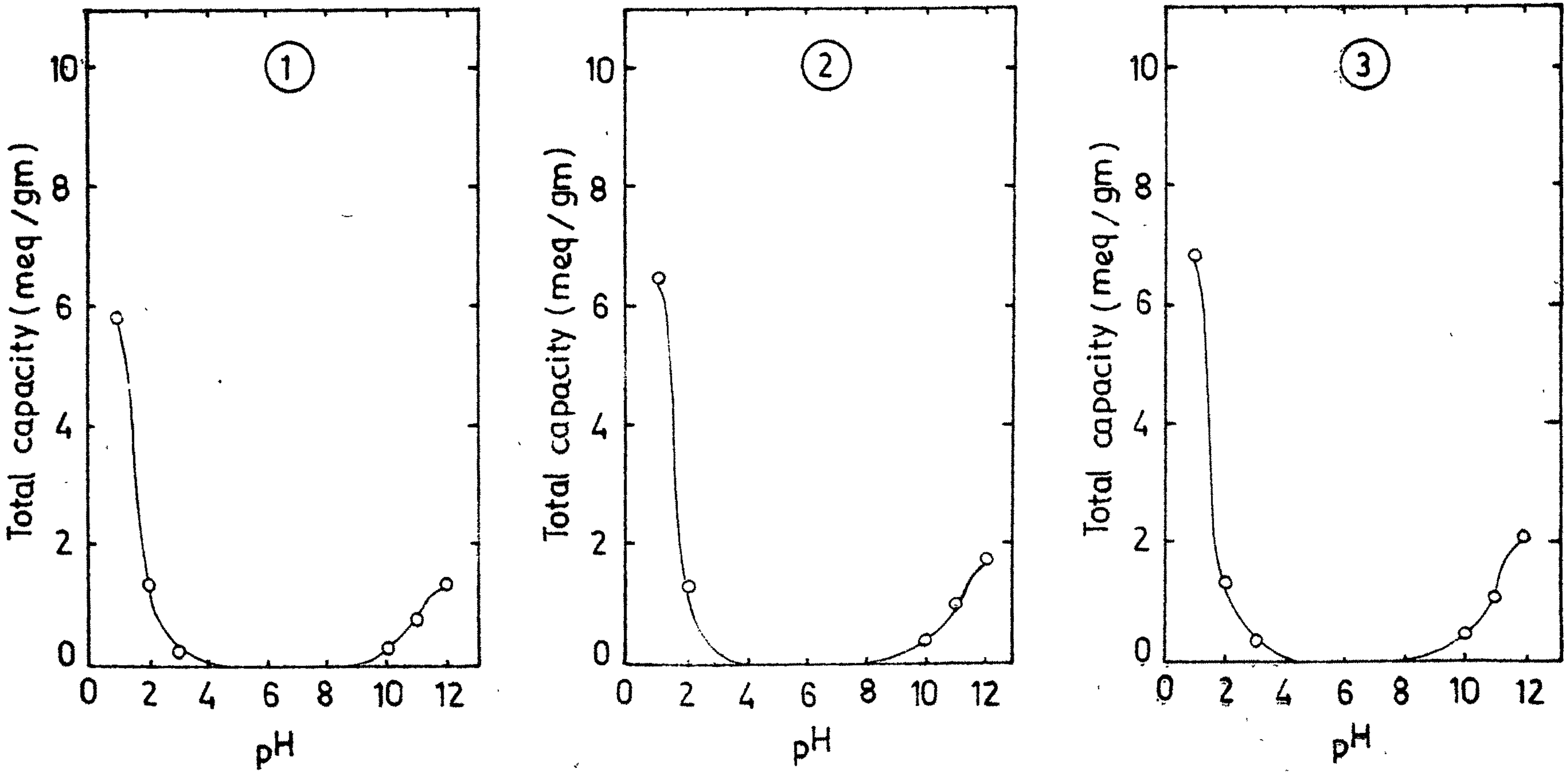


FIG 7 — PH-TITRATION CURVES OF ① EP(CA)DT ② EP(8-OH)DT ③ EP(HQ)DT RESINS

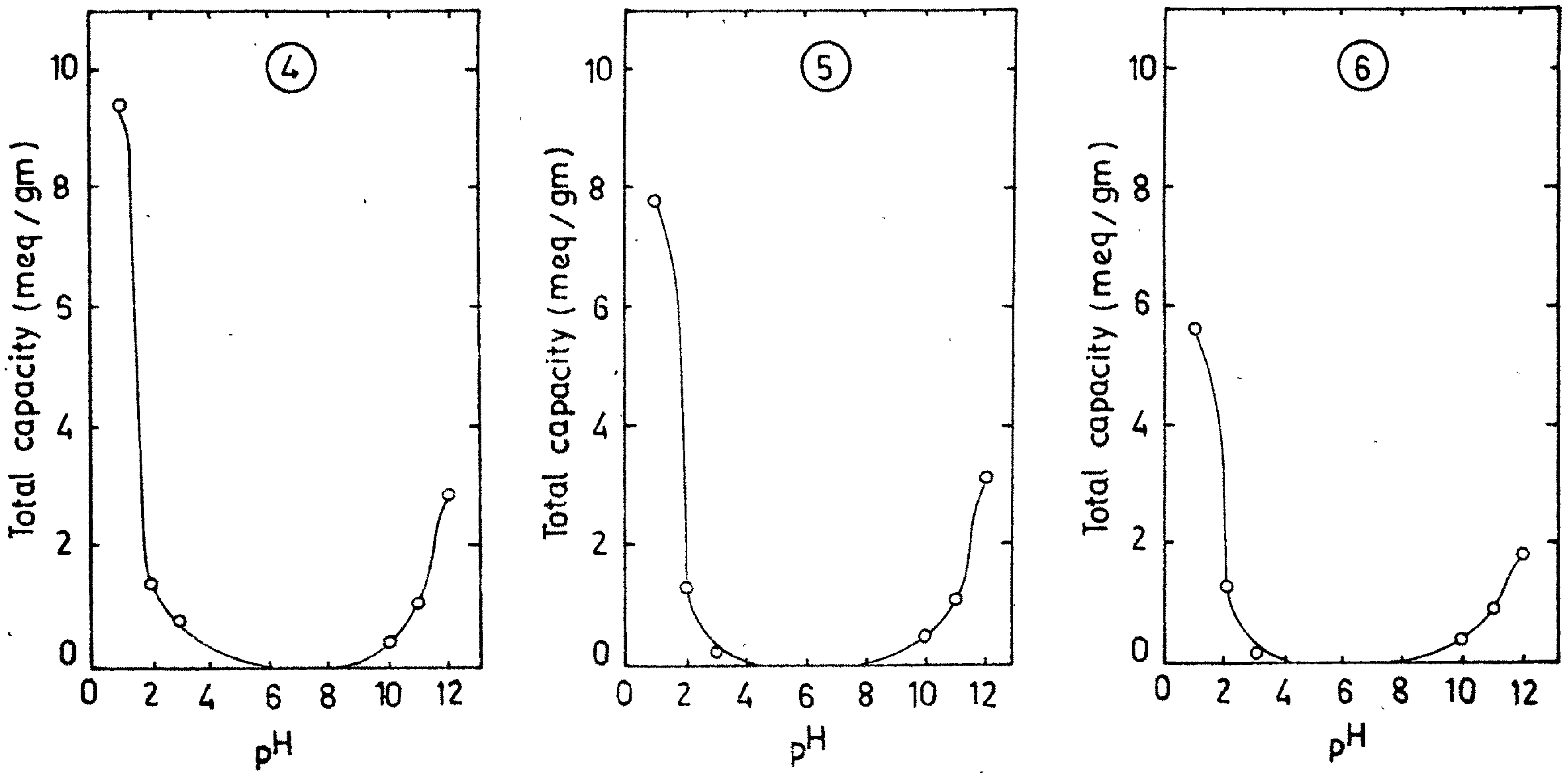


FIG 8 – pH-TITRATION CURVES OF ④ EP(SA)DT ⑤ EP(SS)DT ⑥ EP(3-OH)DT RESINS

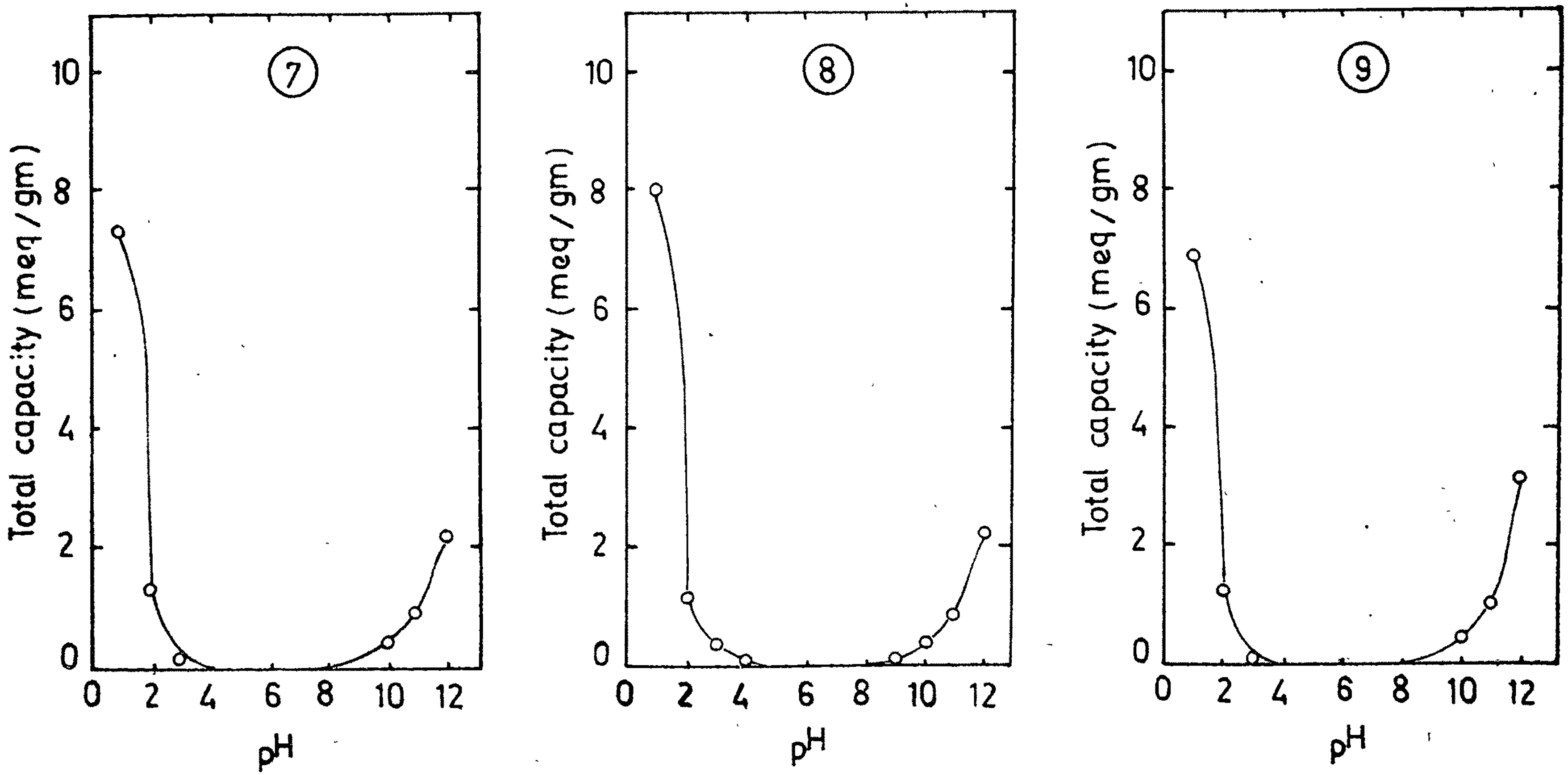


FIG 9 — pH-TITRATION CURVES OF ⑦ EP(PHB)DT ⑧ EP(BR)DT ⑨ EP(AN)DT RESINS

TABLE - DT - 1

Abbreviation

No.	Resin	Abbreviation
1	Epichlorohydrin - Catechol - Diethylenetriamine	EP(CA)DT
2	Epichlorohydrin - 8-hydroxyquinoline - Diethylenetriamine	EP(8-OH)DT
3	Epichlorohydrin - Hydroquinone - Diethylenetriamine	EP(HQ)DT
4	Epichlorohydrin - Salicylic acid - Diethylenetriamine	EP(SA)DT
5	Epichlorohydrin - Sulfosalicylic acid - Diethylenetriamine	EP(SS)DT
6	Epichlorohydrin - 3-hydroxy-2-napthoic acid - Diethylenetriamine	EP(3-OH)DT
7	Epichlorohydrin - p-hydroxybenzoic acid - Diethylenetriamine	EP(PHB)DT
8	Epichlorohydrin - β-resorcylic acid - Diethylenetriamine	EP(BR)DT
9	Epichlorohydrin - Anthranilic acid - Diethylenetriamine	EP(AN)DT

TABLE - DT - 2

Analyses, Formulae etc. of Amphoteric resins

No.	Resin	Formula	Analysis					
			Calculated			Observed		
			% C	% H	% N	% C	% H	% N
1	EP(CA)DT	$(C_{13}\ H_{39}\ O_{12}\ N_3)_n$	36.36	9.09	9.79	35.96	9.32	9.41
2	EP(8-OH)DT	-	-	-	-	-	-	-
3	EP(HQ)DT	$(C_{13}\ H_{29}\ O_7\ N_3)n$	46.01	8.55	12.39	45.80	8.34	12.09
4	EP(SA)DT	$(C_{14}\ H_{21}\ O_4\ N_3)_n$	56.95	7.11	14.23	56.52	6.70	14.19
5	EP(SS)DT	$(C_{14}\ H_{25}\ O_9\ N_3S)_n$	40.87	6.08	10.22	40.63	5.82	10.08
6	EP(3-OH)DT	$(C_{18}\ H_{35}\ O_9\ N_3\ )_n$	49.43	8.01	9.61	48.97	7.84	9.45
7	EP(PHB)DT	$(C_{14}\ H_{31}\ O_9\ N_3\ )_n$	43.63	8.05	10.91	43.31	7.75	10.88
8	EP(BR)DT	$(C_{14}\ H_{27}\ O_8\ N_3)_n$	46.03	7.40	11.50	45.77	7.12	11.35
9	EP(AN)DT	$(C_{14}\ H_{36}\ O_{10}\ N_4)_n$	40.00	8.57	13.33	39.81	8.44	13.02

TABLE - DT - 3

% Moisture content of Amphoteric resins

No.	Resin	% Moisture	
		H^+ form	OH^- form
1	EP(CA)DT	5.70	7.80
2	EP(8-OH)DT	4.10	7.60
3	EP(HQ)DT	2.70	7.00
4	EP(SA)DT	3.96	4.00
5	EP(SS)DT	2.73	2.70
6	EP(3-OH)DT	6.57	6.50
7	EP(PHB)DT	3.73	3.70
8	EP(BR)DT	1.90	3.40
9	EP(AN)DT	3.30	6.70

TABLE - DT - 4

Density of resins

No.	Resin	Resin in H^+ form		Resin in OH^- form	
		true density (d_{res}) (gm/cm^3)	apparent (column) density (d_{col}) (gm/ml)	true density (d_{res}) (gm/cm^3)	apparent (column) density (d_{col}) (gm/ml)
1	EP(CA)DT	1.0384	0.2977	1.3260	0.4471
2	EP(8-OH)DT	1.0385	0.2761	1.2500	0.4654
3	EP(HQ)DT	1.3387	0.2238	1.0050	0.3427
4	EP(SA)DT	1.5113	0.1440	1.3420	0.2511
5	EP(SS)DT	1.3980	0.1682	1.1360	0.3546
6	EP(3-OH)DT	1.6126	0.3144	1.7860	0.3653
7	EP(PHB)DT	1.2210	0.1851	1.1760	0.4040
8	EP(BR)DT	1.3300	0.1616	1.2000	0.2807
9	EP(AN)DT	1.4023	0.2510	1.4925	0.3495

TABLE - DT - 5

Void volume fraction of resins

No.	Resin	Resin in H^+ form		Resin in OH^- form	
		d_{col}/d_{res}	Void volume fraction $(1 - d_{col}/d_{res})$	d_{col} / d_{res}	Void volume fraction $(1 - d_{col} /d_{res})$
1	EP(CA)DT	0.2867	0.7133	0.3372	0.6628
2	EP(8-OH)DT	0.2659	0.7341	0.3723	0.6277
3	EP(HQ)DT	0.1672	0.8328	0.3410	0.6590
4	EP(SA)DT	0.0953	0.9047	0.1871	0.8129
5	EP(SS)DT	0.1203	0.8797	0.3121	0.6879
6	EP(3-OH)DT	0.1950	0.8050	0.2045	0.7955
7	EP(PHB)DT	0.1516	0.8484	0.3435	0.6565
8	EP(BR)DT	0.1215	0.8785	0.2339	0.7661
9	EP(AN)DT	0.1790	0.8210	0.2342	0.7658

TABLE - DT - 6

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

No.	Resin	Total capacity CEC_{obs} (meq/gm)	Total capacity CEC_{cal} (meq/gm)	$\frac{CEC_{obs}}{CEC_{cal}}$	Concentration of ionogenic groups Cr (meq/cm^3)	Volume capacity Q (gm.eq/l)	Cu-exchange capacity (meq/gm)
1.	EP(CA)DT	1.288	2.331	0.550	1.256	0.360	1.07
2	EP(8-OH)DT	1.751	-	-	1.881	0.500	1.03
3.	EP(HQ)DT	2.055	2.950	0.697	2.677	0.447	1.37
4	EP(SA)DT	2.875	3.390	0.848	4.173	0.398	2.20
5	EP(SS)DT	3.260	4.866	0.670	5.562	0.669	2.54
6	EP(3-OH)DT	1.800	2.288	0.787	2.794	0.545	1.22
7	EP(PHB)DT	2.182	2.597	0.840	2.614	0.396	1.21
8	EP(BR)DT	3.409	2.740	1.244	4.384	0.533	1.75
9	EP(AN)DT	3.162	2.380	1.328	4.288	0.767	1.63

TABLE - DT - 7

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

No.	Resin	Total capacity AEC_{obs} (meq/gm)	Total capacity AEC_{cal} (meq/gm)	$\frac{AEC_{obs}}{AEC_{cal}}$	Concentration of ionogenic groups Cr (meq/cm^3)	Volume capacity Q (gm. eq/l)
1	EP(CA)DT	5.80	4.662	1.244	7.091	2.390
2	EP(8-OH)DT	5.89	-	-	6.803	2.533
3	EP(HQ)DT	6.36	5.900	1.078	5.944	2.027
4	EP(SA)DT	8.90	6.780	1.312	11.460	2.144
5	EP(SS)DT	7.35	4.866	1.510	8.124	2.535
6	EP(3-OH)DT	5.61	4.576	1.226	9.368	1.916
7	EP(PHB)DT	7.02	5.194	1.351	7.950	2.731
8	EP(BR)DT	7.93	5.480	1.447	9.172	2.150
9	EP(AN)DT	6.44	7.142	0.902	8.968	2.100

TABLE - DT - 8

Rate of exchange of resins

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
1	EP(CA)DT	5	1.193	4.250
		10	1.273	5.050
		15	1.288	5.800
		30	1.288	5.800
		60	1.288	5.800
		120	1.288	5.800
		180	1.288	5.800
2	EP(8-OH)DT	5	1.303	4.502
		10	1.731	5.020
		15	1.751	5.890
		30	1.751	5.890
		60	1.751	5.890
		120	1.751	5.890
		180	1.751	5.890
3	EP(HQ) DT	5	1.800	4.750
		10	2.055	5.700
		15	2.055	6.360
		30	2.055	6.360
		60	2.055	6.360
		120	2.055	6.360
		180	2.055	6.360

(Table - DT - 8 contd....)

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realised (meq/gm)
4	EP(SA)DT	5	2.438	7.670
		10	2.875	7.940
		15	2.875	8.900
		30	2.875	8.900
		60	2.875	8.900
		120	2.875	8.900
		180	2.875	8.900
5	EP(SS)DT	5	2.937	6.100
		10	3.166	6.960
		15	3.260	7.350
		30	3.260	7.350
		60	3.260	7.350
		120	3.260	7.350
		180	3.260	7.350
6	EP(3-OH)DT	5	1.180	4.706
		10	1.700	5.400
		15	1.800	5.610
		30	1.800	5.610
		60	1.800	5.610
		120	1.800	5.610
		180	1.800	5.610

(Table - DT-- 8 contd.....)

No.	Resin	Time in minutes	Cation exchange capacity realized (meq/gm)	Anion exchange capacity realized (meq/gm)
		5	1.931	6.250
		10	2.163	6.710
		15	2.182	7.020
7	EP(PHB)DT	30	2.182	7.020
		60	2.182	7.020
		120	2.182	7.020
		180	2.182	7.020
		5	3.020	7.130
		10	3.210	7.400
		15	3.410	7.930
8	EP(BR)DT	30	3.410	7.930
		60	3.410	7.930
		120	3.410	7.930
		180	3.410	7.930
		5	2.050	3.820
		10	3.000	5.650
		15	3.162	6.440
9	EP(AN)DT	30	3.162	6.440
		60	3.162	6.440
		120	3.162	6.440
		180	3.162	6.440

TABLE - DT - 9

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.	EP(CA)DT	10.926	3.005	6.965
2.	EP(8-OH)DT	10.899	3.052	6.975
3	EP(HQ)DT	10.918	3.076	6.997
4	EP(SA)DT	11.078	3.215	7.146
5	EP(SS)DT	11.134	3.135	7.134
6	EP(3-OH)DT	11.071	2.892	6.981
7	EP(PHB)DT	10.998	3.103	7.050
8	EP(BR)DT	11.082	3.142	7.112
9	EP(AN)DT	11.135	2.981	7.058

TABLE - DT - 10

Thermal Stability of Amphoteric resins as cation exchanger

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration, %	
			H-form	Na-form	H-form	Na-form
80°	EP(CA) DT	1.288	NIL	NIL	NIL	NIL
	EP(8-OH) DT	1.751	NIL	NIL	NIL	NIL
	EP(HQ) DT	2.055	NIL	NIL	NIL	NIL
	EP(SA) DT	2.875	NIL	NIL	NIL	NIL
	EP(SS) DT	3.260	NIL	NIL	NIL	NIL
	EP(3-OH) DT	1.800	NIL	NIL	NIL	NIL
	EP(PHB) DT	2.182	NIL	NIL	NIL	NIL
	EP(BR) DT	3.410	NIL	NIL	NIL	NIL
	EP(AN) DT	3.162	NIL	NIL	NIL	NIL

(TABLE - DT - 10 contd....)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration, %	
			H-form	Na-form	H-form	Na-form
100°	EP(CA)DT	1.288	5.21	3.52	25.20	5.68
	EP(8-OH)DT	1.751	7.73	5.13	28.10	6.12
	EP(HQ)DT	2.055	9.20	7.17	19.30	6.50
	EP(SA)DT	2.875	13.51	11.18	18.21	7.40
	EP(SS)DT	3.260	11.10	9.13	14.30	10.20
	EP(3-OH)DT	1.800	15.70	12.01	31.50	15.09
	EP(PHB)DT	2.182	9.41	8.01	18.60	13.71
	EP(BR)DT	3.410	14.50	11.77	23.24	17.00
	EP(AN)DT	3.162	12.60	10.90	22.39	15.33

(TABLE - DT - 10 contd.......)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration, %	
			H-form	Na-form	H-form	Na-form
120°	EP(CA)DT	1.288	7.11	5.42	27.10	7.56
	EP(8-OH)DT	1.751	9.63	7.03	30.00	8.03
	EP(HQ)DT	2.055	11.10	9.07	21.20	8.40
	EP(SA)DT	2.875	15.41	13.08	20.11	9.30
	EP(SS)DT	3.260	13.00	11.05	16.32	12.10
	EP(3-OH)DT	1.800	17.60	14.00	33.40	17.02
	EP(PHB)DT	2.182	11.31	10.00	20.51	15.61
	EP(BR)DT	3.410	16.40	13.65	25.14	19.09
	EP(AN)DT	3.162	14.50	12.80	24.29	17.23

(TABLE - DT - 10 contd....)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration, %	
			H-form	Na-form	H-form	Na-form
140°	EP(CA)DT	1.288	10.21	8.52	30.20	10.70
	EP(8-OH)DT	1.751	12.73	10.13	33.15	11.15
	EP(HQ)DT	2.055	14.20	12.17	24.35	11.72
	EP(SA)DT	2.875	18.51	16.18	23.22	12.51
	EP(SS)DT	3.260	16.10	14.15	19.45	15.26
	EP(3-OH)DT	1.800	20.70	17.10	36.56	20.25
	EP(PHB)DT	2.182	14.41	13.20	23.59	18.79
	EP(BR)DT	3.410	19.50	16.75	28.29	22.37
	EP(AN)DT	3.162	17.60	15.99	27.52	20.34

TABLE - DT - 11

Thermal Stability of Amphoteric resins as anion exchanger

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating, %		Gain in capacity of absolutely dry resin as determined after regeneration, %	
			OH - form	Cl - form	OH - form	Cl- form
80°	EP(CA)DT	5.800	NIL	NIL	NIL	NIL
	EP(8-OH)DT	5.890	NIL	NIL	NIL	NIL
	EP(HQ)DT	6.360	NIL	NIL	NIL	NIL
	EP(SA)DT	8.900	NIL	NIL	NIL	NIL
	EP(SS)DT	7.350	NIL	NIL	NIL	NIL
	EP(3-OH)DT	5.610	NIL	NIL	NIL	NIL
	EP(PHB)DT	7.020	NIL	NIL	NIL	NIL
	EP(BR)DT	7.930	NIL	NIL	NIL	NIL
	EP(AN)DT	6.440	NIL	NIL	NIL	NIL

(TABLE - DT - 11 contd......)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration,%	
			OH - form	Cl - form	OH - form	Cl - form
	EP(CA)DT	5.800	3.35	2.07	5.20	2.88
	EP(8-OH)DT	5.890	3.46	2.51	6.31	3.16
	EP(HQ)DT	6.360	4.97	2.99	8.11	3.80
	EP(SA)DT	8.900	7.17	4.27	9.20	5.12
100°	EP(SS)DT	7.350	5.48	3.15	8.54	4.09
	EP(3-OH)DT	5.610	4.36	2.66	7.13	3.24
	EP(PHB)DT	7.020	3.92	2.53	6.71	3.48
	EP(BR)DT	7.930	8.11	4.45	10.20	4.96
	EP(AN)DT	6.440	5.18	3.10	7.31	4.22

(Table - DT - 11 contd.......)

Temp. °C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration,%	
			OH - form	C1 - form	OH - form	C1 - form
120°	EP(CA) DT	5.800	9.31	4.11	13.33	6.16
	EP(8-OH) DT	5.890	10.13	5.66	15.25	8.14
	EP(HQ) DT	6.360	15.18	6.21	22.75	10.23
	EP(SA) DT	8.900	19.40	8.07	25.73	12.49
	EP(SS) DT	7.350	15.76	7.00	23.06	11.19
	EP(3-OH) DT	5.610	14.40	5.94	21.00	8.85
	EP(PHB) DT	7.020	13.42	5.77	18.67	7.20
	EP(BR) DT	7.930	16.61	8.00	21.69	8.58
	EP(AN) DT	6.440	14.38	6.19	18.30	7.62

(TABLE - DT - 11 contd......)

Temp. ^{o}C	Resin	Original capacity (meq/gm) of absolutely dry resin	Gain in capacity of absolutely dry resin as determined after heating,%		Gain in capacity of absolutely dry resin as determined after regeneration,%	
			OH - form	C1 - form	OH - form	C1- form
140°	EP(CA)DT	5.800	13.45	9.55	15.74	10.52
	EP(8-OH)DT	5.890	15.10	11.27	17.83	12.80
	EP(HQ)DT	6.360	20.24	13.60	25.82	15.87
	EP(SA)DT	8.900	25.53	17.63	33.24	20.32
	EP(SS)DT	7.350	21.85	16.10	27.65	17.50
	EP(3-OH)DT	5.610	19.93	12.90	21.87	15.48
	EP(PHB)DT	7.020	17.79	12.02	20.71	13.31
	EP(BR)DT	7.930	21.00	14.22	23.73	13.02
	EP(AN)DT	6.440	18.75	12.43	20.39	12.30

TABLE - DT - 12

Effect of temperature of equilibration on the capacity of the resin

Equilibration period = 2 hrs.
Amount of resin = 0.5 gm
Normality of HCl / NaCl = 0.098 N
Normality of NaOH / NaCl = 0.097 N

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°	50°	70°	30°	50°	70°
1	EP(CA)DT	5.800	5.924	6.191	1.288	1.010	0.848
2	EP(8-OH)DT	5.890	6.116	6.380	1.751	1.564	1.356
3	EP(HQ)DT	6.360	6.461	6.666	2.055	1.747	1.542
4	EP(SA)DT	8.900	9.130	9.259	2.875	2.603	2.291
5	EP(SS)DT	7.350	7.493	7.815	3.260	2.713	2.570
6	EP(3-OH)DT	5.610	5.840	6.021	1.800	1.712	1.350
7	EP(PHB)DT	7.020	7.213	7.580	2.182	1.818	1.558
8	EP(BR)DT	7.930	8.177	8.540	3.409	2.500	2.440
9	EP(AN)DT	6.440	6.752	6.944	3.162	2.585	2.172

TABLE - DT - 13

Oxidation resistance of Amphoteric resins as cation exchanger

No.	Resin	% Moisture		Increase in % water content
		Untreated exchanger	H_2O_2 treated exchanger	
1	EP(CA)DT	5.70	14.74	9.04
2	EP(8-OH)DT	4.10	14.36	10.26
3	EP(HQ)DT	2.70	10.45	7.75
4	EP(SA)DT	2.60	17.10	14.50
5	EP(SS)DT	2.10	14.54	12.44
6	EP(3-OH)DT	4.70	14.35	9.65
7	EP(PHB)DT	2.90	15.71	12.81
8	EP(BR)DT	1.90	15.17	13.27
9	EP(AN)DT	3.30	14.58	11.28

TABLE - DT - 14

Oxidation resistance of Amphoteric resins as anion exchanger

No.	Resin	% Moisture Untreated exchanger	% Moisture H_2O_2 treated exchanger	Increase in % water content
1	EP(CA)DT	7.80	17.31	9.51
2	EP(8-OH)DT	7.60	19.72	12.12
3	EP(HQ)DT	7.00	14.10	7.10
4	EP(SA)DT	4.00	18.37	14.37
5	EP(SS)DT	2.70	15.79	13.09
6	EP(3-OH)DT	6.50	22.92	16.42
7	EP(PHB)DT	3.70	17.80	14.10
8	EP(BR)DT	3.40	27.03	23.63
9	EP(AN)DT	6.70	17.29	10.59

TABLE - DT - 15

Swelling of Amphoteric resins as cation exchanger in various solvents

No.	Resin	% swelling in				
		Glacial Acetic acid	Water	Methanol	Benzene	Acetone
1	EP(CA)DT	271.4	75.0	50.0	0	0
2	EP(8-OH)DT	150.0	66.7	33.3	0	0
3	EP(HQ)DT	161.5	115.0	69.2	0	0
4	EP(SA)DT	221.4	180.0	85.7	0	0
5	EP(SS)DT	360.0	220.0	100.0	0	0
6	EP(3-OH)DT	142.8	114.8	43.0	0	0
7	EP(PHB)DT	471.4	357.1	128.6	0	0
8	EP(BR)DT	180.0	81.8	40.0	0	0
9	EP(AN)DT	500.0	157.1	66.7	0	0

TABLE - DT - 16

Swelling of Amphoteric resins as anion exchanger in various solvents

No.	Resin	% swelling in				
		Glacial Acetic acid	Water	Methanol	Benzene	Acetone
1	EP(CA)DT	201.0	95.0	83.3	0	0
2	EP(8-OH)DT	273.0	193.0	71.0	0	0
3	EP(HQ)DT	319.0	171.2	150.0	0	0
4	EP(SA)DT	533.5	231.7	200.0	0	0
5	EP(SS)DT	212.0	124.0	100.0	0	0
6	EP(3-OH)DT	223.7	137.5	96.0	0	0
7	EP(PHB)DT	312.0	261.0	130.0	0	0
8	EP(BR)DT	190.0	165.0	100.0	0	0
9	EP(AN)DT	382.0	264.0	89.0	0	0

TABLE - DT - 17

Values of distribution coefficients (K_d) in NH_4OAC - DMF media (35 ± 1 °C)

No.	Resin	$[K_d]_{A^*}$					
		Ca(II)	Mg(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
1	EP(CA)DT	11.42	2.26	11.70	12.93	46.72	9.29
2	EP(8-OH)DT	11.23	2.22	6.37	2.34	26.81	4.86
3	EP(HQ)DT	9.21	2.19	2.04	42.84	59.34	8.25
4	EP(SA)DT	20.38	1.70	25.59	38.77	253.60	59.19
5	EP(SS)DT	9.35	2.19	6.44	40.44	41.96	39.80
6	EP(3-OH)DT	11.82	2.28	11.73	12.66	35.36	12.69
7	EP(PHB)DT	9.30	4.00	4.12	33.65	59.98	26.84
8	EP(BR)DT	7.39	2.74	11.25	24.63	106.80	28.90
9	EP(AN)DT	11.14	2.20	6.39	25.00	74.04	21.96

* A = 0.02 M (concentration of NH_4OAc)

(TABLE - DT - 17 contd.....)

No.	Resin	$[K_d]_B$*					
		Ca(II)	Mg(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
1	EP(CA)DT	19.19	3.46	23.33	15.37	94.16	10.08
2	EP(8-OH)DT	12.22	2.64	45.14	13.21	67.05	9.13
3	EP(HQ)DT	23.80	3.65	48.57	62.95	120.80	11.35
4	EP(SA)DT	37.45	2.80	47.04	53.27	361.10	61.72
5	EP(SS)DT	19.83	3.36	71.73	60.20	91.29	49.27
6	EP(3-OH)DT	15.21	3.50	52.76	16.52	224.17	15.41
7	EP(PHB)DT	12.17	22.13	49.06	41.43	122.10	36.83
8	EP(BR)DT	31.18	3.92	57.04	37.08	248.30	34.57
9	EP(AN)DT	26.85	4.60	57.87	36.80	187.90	29.32

* B = 0.25 M (concentration of NH_4OAc)

(TABLE - DT - 17 contd......)

No.	Resin	$[K_d]_{C^*}$					
		Ca(II)	Mg(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
1	EP(CA)DT	11.24	2.50	7.78	13.43	84.44	6.31
2	EP(8-OH)DT	3.52	1.84	3.63	10.56	60.21	5.54
3	EP(HQ)DT	11.07	2.76	1.77	48.04	114.00	9.77
4	EP(SA)DT	10.25	2.00	3.62	50.88	300.10	45.85
5	EP(SS)DT	6.60	2.74	1.79	52.60	86.43	43.35
6	EP(3-OH)DT	8.64	2.87	7.86	9.14	49.85	10.18
7	EP(PHB)DT	9.30	2.80	3.61	36.96	82.71	23.15
8	EP(BR)DT	10.97	3.33	3.55	34.59	213.50	25.10
9	EP(AN)DT	10.18	3.37	5.57	31.97	164.40	25.46

* C = 1.00 M (concentration of NH_4OAc)