

Synthesis and Characterization of Some New Chelating Amphoteric Ion-Exchange Resins

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Synopsis

Some new chelating amphoteric ion exchange resins have been synthesized by condensing catechol, 8-hydroxyquinoline, hydroquinone, salicylic acid, sulfosalicylic acid, 3-hydroxy-2-naphthoic acid, *p*-hydroxybenzoic acid, β -resorcylic acid, and anthranilic acid with epichlorohydrin employing diethylenetriamine as a cross linking agent in a nonaqueous medium, toluene. These resins are characterized by their physicochemical properties such as moisture retention ability, true density, apparent density, void fraction, concentration of ionogenic groups, volume capacity, total ion exchange capacity, copper exchange capacity, rate of ion exchange, pH titration curves, apparent pK_a and pK_b values, isoionic point values, oxidative degradation, thermal stability, the effect of temperature of equilibration on the capacity of the resin, swelling behavior in various solvents, and absorption specificity towards certain bivalent metal cations in ammonium acetate–dimethylformamide media.

INTRODUCTION

This paper throws light on the synthesis and physicochemical properties of some new chelating amphoteric ion exchange resins derived from (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-naphthoic acid–diethylenetriamine [EP(3-OH)DT], (7) epichlorohydrin–*p*-hydroxybenzoic acid–diethylenetriamine [EP(PHB)DT], (8) epichlorohydrin– β -resorcylic acid–diethylenetriamine [EP(BR)DT], and (9) epichlorohydrin–anthranilic acid–diethylenetriamine [EP(AN)DT].

EXPERIMENTAL

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 mol) were taken in 50–75 mL of toluene and were mixed with epichlorohydrin (0.4 mol) in a 500-mL round-bottom three-necked flask fitted with a stirrer, a thermometer, and a condenser. The mixture was vigorously stirred maintaining the temperature 0–5°C. The the above cooled mixture, diethylenetriamine (0.05 mol) was added slowly in fractions, keeping the temperature below 10°C for 2 h. A gel formed was then heated on steam bath for 5–6 h and then cured in an oven at 90°C ($\pm 1^\circ\text{C}$). The cured hard mass was then crushed to $-20 + 30$ or $-60 + 100$ BSS mesh size as

needed and washed with acetone and ethyl alcohol to remove unreacted monomers and polymers of low molecular weight from the resin. The yields of resins in the syntheses were 65%. The wash solvents acetone and ethyl alcohol used to extract monomers and low molecular weight polymers were 200 mL each.

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

AR grade chemicals were used for the synthesis and physicochemical study of these resins. Doubly distilled CO₂ free water was used throughout An Elico pH Meter (Model CL 44) and Model EXPAND pH METER pH 821 (Electronics Corporation of India, Ltd.) were employed for the pH measurements.

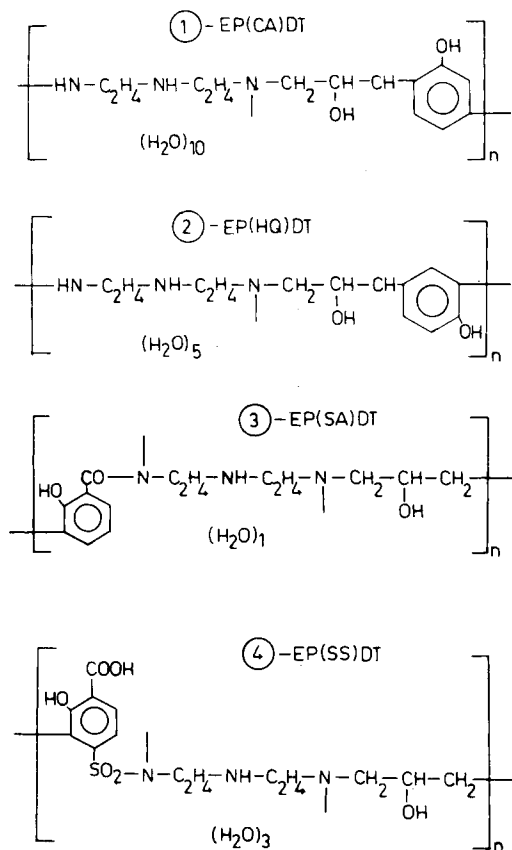
Total ion exchange capacity and moisture content of the resins were determined by the method reported by Kunin.¹ pH titrations for the resins were carried out according to the procedure described by Kunin.² True density, apparent density, void volume fraction, concentration of ionogenic groups, volume capacity, apparent pK_a and pK_b values, and the isoionic point of the resins were determined following the method reported by Helfferich.³ The rate of ion exchange and thermal stability of the resins were determined according to the procedure described by Krishnaswamy and Trivedi.⁴ Swelling behavior of these resins in various solvents was studied according to the method reported by Bodamer and Kunin.⁵ A study of oxidative degradation was carried out according to the method described by Dorfner.⁶ A study regarding the effect of temperature of equilibration on the capacity of the resins was carried out according to the process described by Krishnaswamy and Dasare,⁷ adsorption behavior of some bivalent metal cations on cationic form (NH₄⁺ form) of these amphoteric resins from ammonium acetate–dimethylformamide media was studied following the method described by Ghosh et al.⁸

RESULTS AND DISCUSSION

The most probable structures of these amphoteric resins on the basis of analytical data (Table I) are shown in Schemes I and II.

TABLE I
Analyses, Formulae, etc., of Amphoteric Resins

Resin	Formula	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 ₃ S) _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



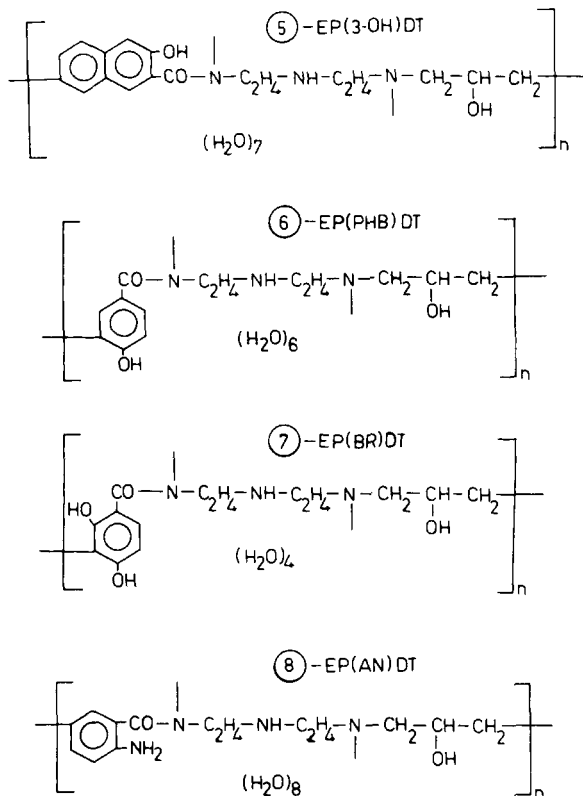
Scheme I.

Moisture Retention Ability, Density, and Void Volume Fraction

The moisture content of the resins are presented in Table II. The % moisture of the resins in the H form varies between 1.9 and 6.5 and that of OH form varies between 2.7 and 7.8. The known values of % moisture for the commercial resins (cationic form) are 43–53 for IRC-50/75 (weak acid, active group, COO⁻) and 42–50 for IRC-84 (weak acid, active group, COO⁻). Thus, the resins under investigation have very low range of % 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.

The true density (d_{res}) values are ranging from 1.03 to 1.60 gm/cm³ for anionic form of the resins whereas the apparent density (d_{col}) values vary from 0.14 to 0.31 gm/mL for cationic form and 0.25 to 0.45 gm/mL for anionic form of the resins. A small difference in the d_{col} values for these H and OH forms indicates that the resins can stand recycling to a good degree.

Data on void volume fraction (Table II) reveal that the values vary between 0.71 and 0.90 for the H form and from between 0.62 and 0.81 for the OH form.



Scheme II.

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

These polyfunctional ion exchange resins contain $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$, and amine groups. Types of the functional groups, detected are on the basis of the analytical data and the various physicochemical properties studied. The cation and anion exchange capacity can be calculated as

$$\text{CEC}_{\text{cal}} \quad \text{or} \quad \text{AEC}_{\text{cal}} = \frac{1000}{M/n}$$

where M = molecular weight of the resin per unit on dry basis and n = number of groups taking part in anion or cation exchange.

A comparative account of CEC_{obs} and CEC_{cal} (cation exchanger) and AEC_{obs} and AEC_{cal} (anion exchanger) is given in Tables III and IV. The results reveal that the total anion exchange capacity is much higher than the cation exchange capacity of these amphoteric ion exchange resins.

A decreasing order for the cation exchange capacity of these amphoteric resins is

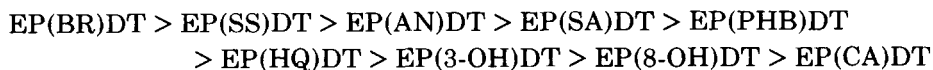


TABLE II
% Moisture, Density, and Void Volume Fraction of Resin

Resin	% moisture		True density (d_{res}) (gm/cm ³)		Apparent density (d_{col}) (gm/mL)		Void volume fraction ($1 - d_{col}/d_{res}$)	
	H form	OH form	H form	OH form	H form	OH form	H form	OH form
EP(CA)DT	5.70	7.80	1.03	1.32	0.29	0.44	0.71	0.66
EP(8-OH)DT	4.10	7.60	1.03	1.25	0.27	0.46	0.73	0.62
EP(HQ)DT	2.70	7.00	1.33	1.00	0.22	0.34	0.83	0.65
EP(SA)DT	3.96	4.00	1.51	1.34	0.14	0.25	0.90	0.81
EP(SS)DT	2.73	2.70	1.39	1.13	0.16	0.25	0.87	0.68
EP(3-OH)DT	6.57	6.50	1.61	1.78	0.31	0.35	0.80	0.79
EP(PHB)DT	3.73	3.70	1.22	1.17	0.18	0.40	0.84	0.65
EP(BR)DT	1.90	3.40	1.33	1.20	0.16	0.28	0.87	0.76
EP(AN)DT	3.30	6.70	1.40	1.49	0.25	0.34	0.82	0.76

TABLE III
Capacity and Concentration of Ionogenic Groups of Amphoteric Resins as Cation Exchanger

Resin	Total capacity CEC_{obs} (meq/g)	Total capacity CEC_{cal} (meq/g)	CEC_{obs} CEC_{cal}	Concentration of ionogenic groups C_r (meq/cm ³)	Volume capacity Q (g-eq/L)	Cu-exchange capacity (meq/g)
1. EP(CA)DT	1.28	2.33	0.55	1.25	0.36	1.07
2. EP(8-OH)DT	1.75	—	—	1.88	0.50	1.03
3. EP(HQ)DT	2.05	2.95	0.69	2.67	0.44	1.37
4. EP(SA)DT	2.87	3.39	0.84	4.17	0.39	2.20
5. EP(SS)DT	3.26	4.86	0.67	5.56	0.66	2.54
6. EP(3-OH)DT	1.80	2.28	0.78	2.79	0.54	1.22
7. EP(PHB)DT	2.18	2.59	0.84	2.61	0.39	1.21
8. EP(BR)DT	3.40	2.74	1.24	4.38	0.53	1.75
9. EP(AN)DT	3.16	2.38	1.32	4.28	0.76	1.63

TABLE IV
Capacity and Concentration of Ionogenic Groups of Amphoteric Resins and Anion Exchanger

Resin	Total capacity AEC _{obs} (meq/g)	Total capacity AEC _{cal} (meq/g)	$\frac{AEC_{obs}}{AEC_{cal}}$	Concentration of ionogenic groups C_r (meq/cm ³)	Volume capacity Q (g-eq/L)
1. EP(CA)DT	5.80	4.66	1.24	7.09	2.39
2. EP(8-OH)DT	5.89	—	—	6.80	2.53
3. EP(HQ)DT	6.36	5.90	1.07	5.94	2.02
4. EP(SA)DT	8.90	6.78	1.31	11.46	2.14
5. EP(SS)DT	7.35	4.86	1.51	8.12	2.53
6. EP(3-OH)DT	5.61	4.57	1.22	9.36	1.91
7. EP(PHB)DT	7.02	5.19	1.35	7.95	2.73
8. EP(BR)DT	7.93	5.48	1.44	9.17	2.15
9. EP(AN)DT	6.44	7.14	0.90	8.96	2.10

and, for anion exchange capacity, the decreasing order is

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 anion exchange capacity of resins EP(PHB)DT (7.02 meq/g), EP(BR)DT (7.92 meq/g), and EP(SA)DT (8.9 meq/g) are quite comparable with those of commercial anion exchangers, viz., Duolite A-2 [8.4 meq/g, (granules)], Duolite A-4 [7.7 meq/g, (granules)], Duolite A-7 [9.1 meq/g, (granules, weak base amino group condensation polymer)].

Rate of Ion Exchange

A perusal of the trends of the rate of cation exchange (Figs. 1 and 2) as well as that of anion exchange (Figs. 3 and 4) reveals that the rate is very high. In both the cases, a complete exchange occurs within 15 min. The decreasing order for the rate of cation exchange is

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

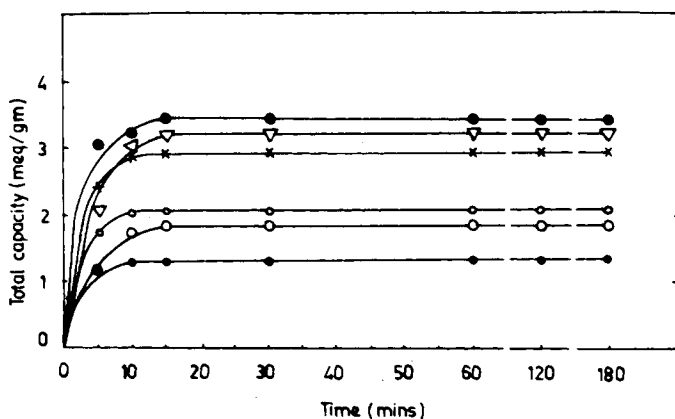


Fig. 1. Rate of cation exchange of EP(BR)DT (●), EP(AN)DT (▽), EP(SA)DT (×), EP(HQ)DT (○), EP(3-OH)DT (○), and EP(CA)DT (●) Resins.

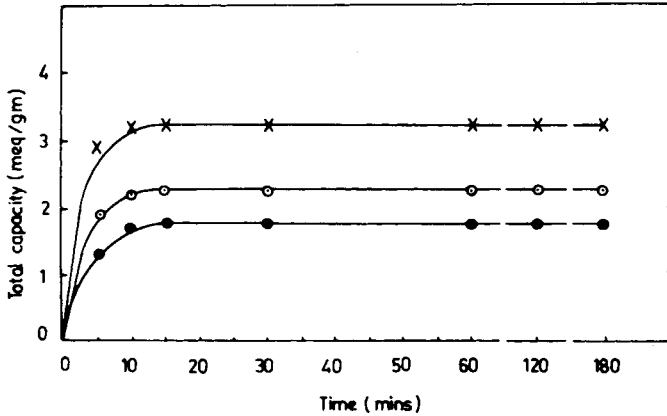
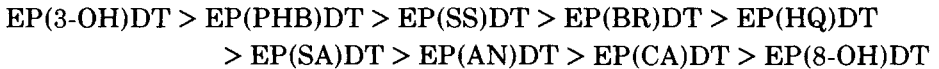


Fig. 2. Rate of cation exchange of EP(SS)DT (x), EP(PHB)DT (o), and EP(8-OH)DT (●) resins.

whereas for anion exchange the decreasing order is



The shape of the curve indicate the porous nature of matrices.

pH Titrations

From the pH titration curves (Figs. 5 and 6), it is seen that these resins are exhibiting good cation and anion exchange capacities over the pH range 1–12, and they are amphoteric in nature. The cationic and anionic nature of the resins have been characterized from the pH-titration curves. Thus resin can be used as anion exchanger as well as cation exchanger depending upon the pH of the solution.

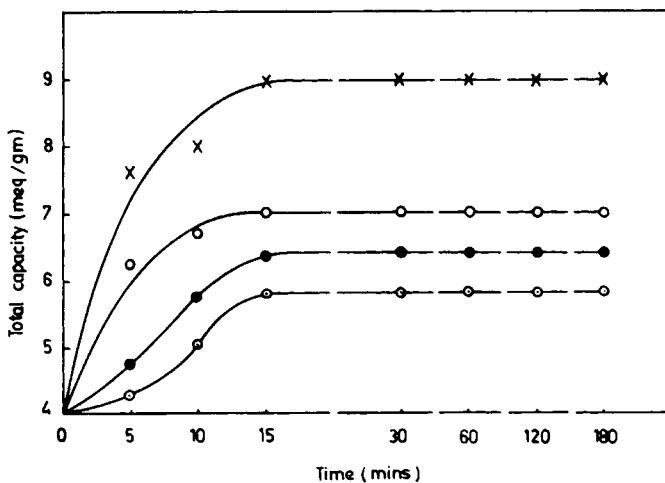


Fig. 3. Rate of anion exchange of EP(SA)DT (x), EP(PHB)DT (o), EP(HQ)DT (●), and EP(CA)DT (○) resins.

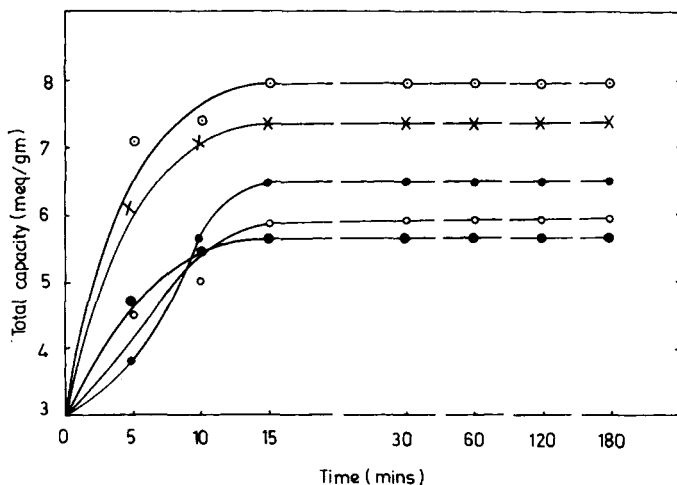


Fig. 4. Rate of anion exchange of EP(BR)DT (○), EP(SS)DT (×), EP(AN)DT (●), EP(8-OH)DT (○), and EP(3-OH)DT (●) resins

The pH-titration curves over the pH range 1–7 are characteristic of weakly basic resin and may be compared with the pH-titration curves of commercially available weakly basic anion exchange resin, Tulsion WB,⁹ while their cation exchanging behavior is similar to that of a weak acid resin.¹⁰

Apparent pK_a and pK_b Values and Isoionic Point

The apparent pK_a and pK_b values were obtained from the pH-titration curves, the appropriate values at 50% neutralization being inserted into the following Helfferich equation:

$$pK_a = pH + \log (Na^+) - \log X^{-/2}$$

$$pK_b = pH - \log (Cl^-) + \log X^{-/2}$$

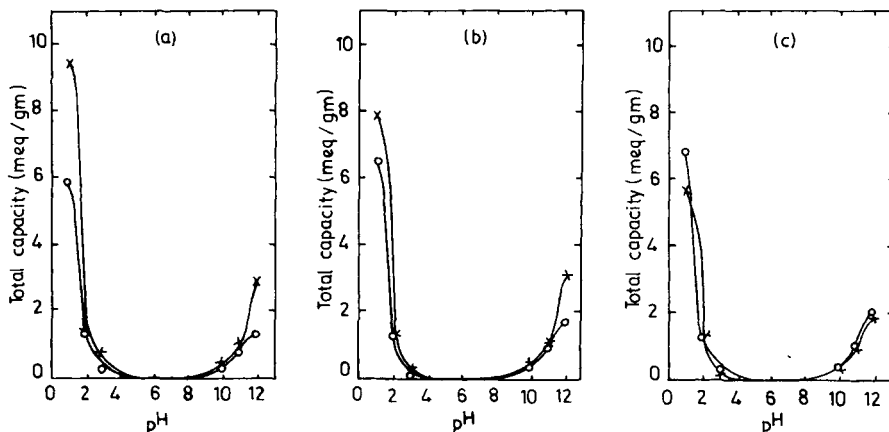


Fig. 5. pH-titration curves of (a) EP(CA)DT (○) and EP(SA)DT (×), (b) EP(8-OH)DT (○) and EP(SS)DT (×), and (c) EP(HQ)DT (○) and EP(3-OH)DT (×) resins.

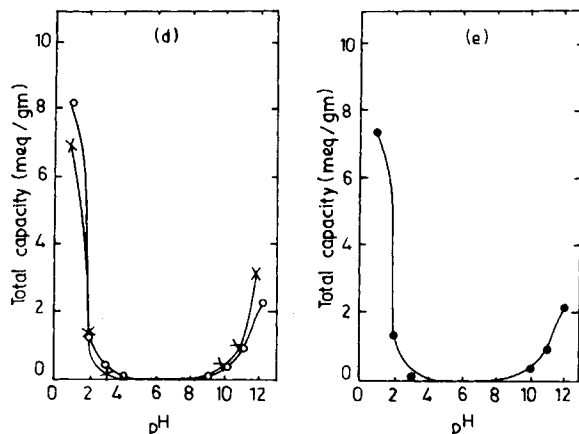


Fig. 6. pH-titration curves of (d) EP(BR)DT (O) and EP(AN)DT (X) and (e) EP(PHB)DT (●) resins.

where the term X^- represents the total concentration of both undissociated and dissociated ionogenic groups.

From Table V it is obvious that the apparent pK_a values obtained from overall cation exchange process in general for various ion exchangers vary in the range of 10.89–11.13, which is slightly higher than the value for phenolic hydroxyl group while apparent pK_b values vary from 2.80 to 3.10, which is characteristic of bases of medium strength. The values are in the following decreasing order as

for pK_a , EP(AN)DT > 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

for pK_b , 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

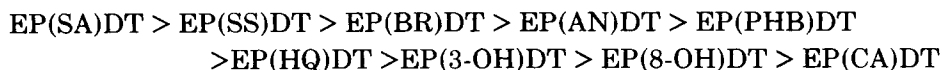
The values of the isoionic point pH_{ip} were calculated as

$$pH_{ip} = \frac{1}{2} (pK_a + pK_b)$$

TABLE V
 Apparent pK_a and pK_b Values and Isoionic Point Values of Amphoteric Resins

Resin	Apparent pK_a	Apparent pK_b	Isoionic point p^I
EP(CA)DT	10.92	3.00	6.96
EP(8-OH)DT	10.89	3.05	6.97
EP(HQ)DT	10.91	3.07	6.99
EP(SA)DT	11.07	3.21	7.14
EP(SS)DT	11.13	3.13	7.13
EP(3-OH)DT	11.07	2.89	6.98
EP(PHB)DT	10.99	3.10	7.05
EP(BR)DT	11.08	3.14	7.11
EP(AN)DT	11.13	2.98	7.06

The values of the isoionic point vary in the range 6.9–7.1. The isoionic point for Proline is 6.3 while for Histidine it is 7.59.¹¹ It is observed that the resins under study have intermediate values. The values are in the decreasing order as



Thermal Stability

From the data regarding the thermal stability of the amphoteric ion exchangers (Table VI), it is revealed that there is no change in the total capacity for all the forms (H—, Na—, OH—, and Cl—forms) of the resins up to 80°C. Hence these resins can be safely used up 80°C. Above this temperature, they show an increase in the capacity when the heated resins were regenerated and tested, which could be due to:

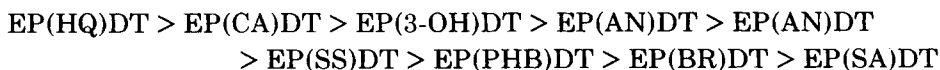
- (i) destruction of some of the —CH₂— bridges, creating more gaps in the polymer matrix thereby facilitating the access of more —NH— groups;
- (ii) removal of the decomposition products which had neutralized the ionogenic groups.

Effect of Temperature of Equilibration on the Capacity of the Resin

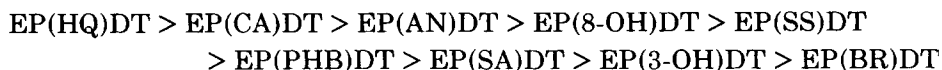
The data regarding the effect of varying temperature of equilibration on the capacity of the resin (Table VII) suggest that the anion exchange capacity of amphoteric resin increases with the increasing temperature of equilibration. This is because, on heating the resin, certain basic gaseous decomposition products (such as NH₃ resulting from diethylenetriamine used for the synthesis of the resin) are produced which neutralize 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 may be due to the loss of the ionogenic groups with the increasing equilibration temperature.

Oxidative Degradation

Data in Table VIII reveal that the amphoteric resin EP(HQ)DT exhibits the lowest increase in % water content as cation exchanger as well as anion exchanger and thus it is the most resistant to oxidation. We observed (with few exceptions) that, on oxidation, anionic forms exhibit greater increase in % water content than the cationic forms; hence anionic forms are more susceptible to oxidative degradation than the cationic forms. The cationic forms show the decreasing order as



and, for anionic forms, the decreasing stability order is



	EP(PHB)DT	2.18	7.02	9.41	8.01	3.92	2.53	18.60	13.71	6.71	3.48
	EP(BR)DT	3.41	7.93	14.50	11.77	8.11	4.45	23.24	17.00	10.20	4.96
	EP(AN)DT	3.16	6.44	12.60	10.90	5.18	3.10	22.39	15.33	7.31	4.22
120	EP(CA)DT	1.28	5.80	7.11	5.42	9.31	4.11	27.10	7.56	13.33	6.16
	EP(8-OH)DT	1.75	5.89	9.63	7.03	10.13	5.66	30.00	8.03	15.25	8.14
	EP(HQ)DT	2.05	6.36	11.10	9.07	15.18	6.21	21.20	8.40	22.75	10.23
	EP(SA)DT	2.87	8.90	15.41	13.08	19.40	8.07	20.11	9.30	25.73	12.49
	EP(SS)DT	3.26	7.35	13.00	11.05	15.76	7.00	16.32	12.10	23.06	11.19
	EP(3-OH)DT	1.80	5.61	17.60	14.00	14.40	5.94	33.40	17.02	21.00	8.85
	EP(PHB)DT	2.18	7.02	11.31	10.00	13.42	5.77	20.51	15.61	18.67	7.20
	EP(BR)DT	3.41	7.93	16.40	13.65	16.61	8.00	25.14	19.09	21.69	8.58
	EP(AN)DT	3.16	6.44	14.50	12.80	14.38	6.19	24.29	17.23	18.30	7.62
140	EP(CA)DT	1.28	5.80	10.21	8.52	13.45	9.55	30.20	10.70	15.74	10.52
	EP(8-OH)DT	1.75	5.89	12.73	10.13	15.10	11.27	33.15	11.15	17.83	12.80
	EP(HQ)DT	2.05	6.36	14.20	12.17	20.24	13.60	24.35	11.72	25.82	15.87
	EP(SA)DT	2.87	8.90	18.51	16.18	25.53	17.63	23.22	12.51	33.24	20.32
	EP(SS)DT	3.26	7.35	16.10	14.15	21.85	16.10	19.45	15.26	27.65	17.50
	EP(3-OH)DT	1.80	5.61	20.70	17.10	19.93	12.90	36.56	20.25	21.87	15.48
	EP(PHB)DT	2.18	7.02	14.41	13.20	17.79	12.02	23.59	18.79	20.71	13.31
	EP(BR)DT	3.41	7.93	19.50	16.75	21.00	14.22	28.29	22.37	23.73	13.02
	EP(AN)DT	3.16	6.44	17.60	15.99	18.75	12.43	27.51	20.34	20.39	12.30

TABLE VII
Effect of Temperature of Equilibration on the Capacity of the Resin^a

Resin	Total AEC (meq/g) of absolutely dry resin determined at			Total CEC (meq/g) of absolutely dry resin determined at		
	30°C	50°C	70°C	30°C	50°C	70°C
EP(CA)DT	5.80	5.92	6.19	1.28	1.01	0.84
EP(8-OH)DT	5.89	6.11	6.38	1.75	1.56	1.35
EP(HQ)DT	6.36	6.46	6.66	2.05	1.74	1.54
EP(SA)DT	8.90	9.13	9.25	2.87	2.60	2.29
EP(SS)DT	7.35	7.49	7.81	3.26	2.71	2.57
EP(3-OH)DT	5.61	5.64	6.02	1.80	1.71	1.35
EP(PHB)DT	7.02	7.21	7.58	2.18	1.81	1.55
EP(BR)DT	7.93	8.17	8.54	3.40	2.50	2.44
EP(AN)DT	6.44	6.75	6.94	3.16	2.58	2.17

^a Equilibration period = 2 h; amount of resin = 0.5 g; normality of HCl/NaCl = 0.098N; normality of NaOH/NaCl = 0.097N.

Swelling Behavior in Nonaqueous Solvents

From the data presented in Table IX, it can be seen that:

- (1) polar solvents produce more extensive swelling than the nonpolar solvents;
- (2) in polar solvents, the anionic form swells more than the cationic form of the amphoteric resin;
- (3) % swelling of amphoteric resins in acetic acid as cation exchanger as well as anion exchanger is much higher than would be anticipated, which can be explained as follows: Swelling of amphoteric resins with both weak acid and weak base groups is a function of the pH of the solution and show a characteristic minimum near the isoelectric point of the resins. Here, the active groups of both the types are practically undissociated, so that the osmotic pressure difference is small. When pH is increased or decreased, either the acid or base group dissociate; this increases the number of osmotically active particles within the resin. The result is an increase in swelling in either case.

TABLE VIII
Oxidation Resistance of Amphoteric Resins

Resin	Ion exchanger as cation exchanger			Ion exchanger as anion exchanger		
	% moisture		Increase in % water content	% moisture		Increase in % water content
	Untreated exchanger	H ₂ O ₂ -treated exchanger		Untreated exchanger	H ₂ O ₂ -treated exchanger	
EP(CA)DT	5.70	14.74	9.04	7.80	17.31	9.51
EP(8-OH)DT	4.10	14.36	10.26	7.60	19.72	12.12
EP(HQ)DT	2.70	10.45	7.75	7.00	14.10	7.10
EP(SA)DT	2.60	17.10	14.50	4.00	18.37	14.37
EP(SS)DT	2.10	14.54	12.44	2.70	15.79	13.09
EP(3-OH)DT	4.70	14.35	9.35	6.50	22.92	16.42
EP(PHB)DT	2.90	15.71	12.81	3.70	17.80	14.10
EP(BR)DT	1.90	15.17	13.27	3.40	27.03	23.63
EP(AN)DT	3.30	14.58	11.28	6.70	17.29	10.59

TABLE IX
Swelling of Amphoteric Resins in Nonaqueous Solvents

Resin		% swelling in				
		Glacial acetic acid	Water	Methanol	Benzene	Acetone
EP(CA)DT	(C)	271.4	75.0	50.0	0	0
	(A)	201.0	95.0	83.3	0	0
EP(8-OH)DT	(C)	150.0	66.7	33.3	0	0
	(A)	273.0	193.0	71.0	0	0
EP(HQ)DT	(C)	161.5	115.0	69.2	0	0
	(A)	319.0	171.2	150.0	0	0
EP(SA)DT	(C)	221.4	180.0	85.7	0	0
	(A)	533.5	231.7	200.0	0	0
EP(SS)DT	(C)	360.0	220.0	100.0	0	0
	(A)	212.0	124.0	100.0	0	0
EP(3-OH)DT	(C)	142.8	114.8	43.0	0	0
	(A)	223.7	135.5	96.0	0	0
EP(PHB)DT	(C)	471.4	357.1	128.6	0	0
	(A)	312.0	261.0	130.0	0	0
EP(BR)DT	(C)	180.0	81.8	40.0	0	0
	(A)	190.0	165.0	100.0	0	0
EP(AN)DT	(C)	500.0	157.1	66.7	0	0
	(A)	382.0	264.0	89.0	0	0

^a (C) = cationic form; (A) = anionic form.

(4) The decreasing order of porosity (polar solvents) for the cationic form is

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, for anionic form, the decreasing order is

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

Adsorption Behavior of Some Bivalent Metal Cations on Cationic Form (NH₄⁺ Form) of the Amphoteric Resins from Ammonium Acetate-Dimethylformamide Media

The results of sorption studies are presented in Table X. We observed that:

(i) The sorption of metal ions decreases with the increasing concentration of NH₄OAc (DMF being constant). Largely, the metal forms a complex with the acetate ion and the sorption depends on the nature of the complex formed. If the charge of the complex is positive, zero, or negative, the sorption will be less. Various concentration of DMF have been tried and 40% concentration (v/v) has been found to be the best for separation. We suggest that, on increasing the concentration of ammonium acetate, acetate ion replaces the coordinating water molecules resulting in the formation of complex species of a small positive charge,

TABLE X
Values of Distribution Coefficients (K_d) in NH_4OAc -DMF Media ($35 \pm 1^\circ\text{C}$)

Resin	$[K_d]_A^a$					
	Ca(II)	Mg(II)	Co(II)	Ni(II)	Cu(II)	Zn(II)
EP(CA)DT	11.42	2.26	11.70	12.93	46.72	9.29
EP(8-OH)DT	11.23	2.22	6.37	2.34	26.81	4.86
EP(HQ)DT	9.21	2.19	2.04	42.84	59.34	8.25
EP(SA)DT	20.38	1.70	25.59	38.77	253.60	59.19
EP(SS)DT	9.35	2.19	6.44	40.44	41.96	38.90
EP(3-OH)DT	11.82	2.28	11.73	12.66	35.36	12.69
EP(PHB)DT	9.30	4.00	4.12	33.65	59.98	26.84
EP(BR)DT	7.39	2.74	11.25	24.63	106.80	28.90
EP(AN)DT	11.14	2.20	6.39	25.00	74.04	21.96
	$[K_d]_B^a$					
EP(CA)DT	19.19	3.46	23.33	15.37	94.16	10.08
EP(8-OH)DT	12.22	2.64	45.14	13.21	67.05	9.13
EP(HQ)DT	23.80	3.65	48.57	62.95	120.80	11.35
EP(SA)DT	37.45	2.80	47.04	53.27	361.10	61.72
EP(SS)DT	19.83	3.36	71.73	60.20	91.29	49.27
EP(3-OH)DT	15.21	3.50	52.76	16.52	224.17	15.41
EP(PHB)DT	12.17	22.13	49.06	41.43	122.10	36.83
EP(BR)DT	31.18	3.92	57.04	37.08	248.30	34.57
EP(AN)DT	26.85	4.60	57.87	36.80	187.90	29.32
	$[K_d]_C^a$					
EP(CA)DT	11.24	2.50	7.78	13.43	84.44	6.31
EP(8-OH)DT	3.52	1.84	3.63	10.56	60.21	5.54
EP(HQ)DT	11.07	2.76	1.77	48.04	114.00	9.77
EP(SA)DT	10.25	2.00	3.62	50.88	300.10	45.85
EP(SS)DT	6.60	2.74	1.79	52.60	86.43	43.35
EP(3-OH)DT	8.64	2.87	7.86	9.14	49.85	10.18
EP(PHB)DT	9.30	2.80	3.61	36.96	82.71	23.15
EP(BR)DT	10.97	3.33	3.55	34.59	213.50	25.10
EP(AN)DT	10.18	3.37	5.57	31.97	164.40	25.46

^a A, B, and C are the molar concentrations of NH_4OAc , i.e., A = 0.02M, B = 0.25M, C = 1.00M.

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 $[\text{M}^{\text{II}}(\text{OAC})]^+$ or $[\text{M}^{\text{II}}(\text{OAC})]^{+2}$ as reported by earlier workers.^{12,13}

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

(iii) From the Table X, it is clear that Cu(II) has K_d value 253.6 as compared to 1.70 for Mg(II) at 0.02M concentration of NH_4OAc , indicating the possibility of chromatographic separation of these two cations employing EP(SA)DT resin.

(iv) Similarly, from the Table X, we also suggest the possibilities of separation of Cu(II) from Mg(II) at 0.25M concentration of NH_4OAc 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(II)

whereas there was relatively low uptake of Mg(II) at 1.00M concentration of NH₄OAc, indicating the possibilities of chromatographic separation of these two metal cations employing EP(SA)DT and EP(BR)DT resins.

(vi) Mg(II) ion has lower K_d values at all the molar concentrations of NH₄OAc, which may be due to higher affinity of ammonium ions towards the resin as compared to Mg(II) and the reverse is true for Cu(II).

(vii) The following variation of sorption of cations with the concentration of NH₄OAc was observed.

At 0.020M Concentration of NH₄OAc

<u>Resin</u>	<u>Sorption order</u>										
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

At 0.25M Concentration of NH₄OAc

<u>Resin</u>	<u>Sorption order</u>										
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

At 1.00M Concentration of NH₄OAc

<u>Resin</u>	<u>Sorption order</u>										
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

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