# Synthesis and Physicochemical Studies of Some New Amphoteric Ion Exchangers

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## **Synopsis**

Some new amphoteric ion exchangers have been synthesized by condensing salicylic acid, p-hydroxybenzoic acid, sulfosalicylic acid, gallic acid, 3-hydroxy-2-naphthoic acid,  $\beta$ -resorcylic acid, and resacetophenone with epichlorohydrin employing ethylenediamine as a crosslinking agent. Some of the physicochemical properties, such as moisture content, true density, apparent density, void volume fraction, concentration of ionogenic groups, exchange capacity, rate of exchange, pH-titration curves, pK values, isoionic point, thermal stability, oxidation resistance, and swelling behavior in different solvents, have been investigated.

## **INTRODUCTION**

This paper reports the synthesis and physicochemical studies of some new amphoteric ion-exchange resins derived from (1) salicylic acid-epichlorohydrin-ethylenediamine (SAEPED), (2) p-hydroxybenzoic acid-epichlorohydrin-ethylenediamine (HBAEPED), (3) sulfosalicylic acid-epichlorohydrinethylenediamine (SSAEPED), (4) gallic acid-epichlorohydrin-ethylenediamine (GAEPED), (5) 3-hydroxy-2-naphthoic acid-epichlorohydrin-ethylenediamine (HNAEPED), (6)  $\beta$ -resorcylic acid-epichlorohydrin-ethylenediamine (RCAEPED), and (7) resacetophenone-epichlorohydrin-ethylenediamine (RAPEPED) (see structures I-VII). The following properties of the resins synthesized were studied: (i) moisture content, (ii) true density, (iii) apparent density, (iv) void volume fraction, (v) concentration of ionogenic groups, (vi) exchange capacity, (vii) rate of exchange at room temperature, (viii) pH-titration curves, (x) apparent pK values, (xi) isoionic point, (xii) thermal stability at dif-



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ferent temperatures, (xiii) oxidation resistance, and (xiv) swelling behavior in different solvents.

All the chemicals used for the preparation of the resins were of AR grade. Doubly distilled  $CO_2$  free water was used throughout. An Elico-pH-Meter (Model CL 44) was used for pH measurements.

	Percent Moisture, Density, and Void Volume Fraction of Resins											
	% M	oisture	True d <sub>res</sub> (g	density (m/cm <sup>3</sup> )	Appare $d_{ m col}$ (§	Apparent density d <sub>col</sub> (gm/mL)		Void volume fraction $1 - d_{col}/d_{res}$				
Resin	H form	OH form	H form	OH form	H form	OH form	H form	OH form				
SAEPED	3.59	5.27	1.39	1.29	0.19	0.18	0.86	0.86				
HBAEPED	1.38	2.04	1.32	1.30	0.23	0.24	0.83	0.82				
SSAEPED	1.20	2.20	1.34	1.30	0.14	0.15	0.90	0.88				
GAEPED	5.36	3.84	1.32	1.32	0.19	0.18	0.86	0.86				
HNAEPED	4.46	4.56	1.30	1.22	0.17	0.18	0.87	0.85				
RCAEPED	3.28	6.15	1.37	1.48	0.20	0.19	0.85	0.87				
RAPEPED	6.57	1.10	1.24	1.47	0.26	0.22	0.79	0.85				

 TABLE I

 Percent Moisture, Density, and Void Volume Fraction of Resins

#### EXPERIMENTAL

The phenolic derivatives such as salicylic acid, or gallic acid, 3-hydroxy-2naphthoic acid,  $\beta$ -resorcylic acid, resacetophenone (0.05 mol), p-hydroxybenzoic acid, and sulfosalicylic acid (0.1 mol) were taken in a 500-mL round bottom three-necked flask fitted with a stirrer, a thermometer, and a condenser and were mixed with the requisite quantity of 6N sodium hydroxide at 0-5°C with stirring and to the cooled mixture epichlorohydrin (0.25 mol) and ethylenediamine (0.1 mol) was added slowly. The condensation was carried out by maintaining temperature below 10°C for 10 h. The gel formed was then heated at 80-90°C for 10 h. 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 the unreacted monomers and polymers of low molecular weight from the resin.

The resins were conditioned by alternate treatment with 0.1N NaOH and 1N HCl solution. After several alternate regeneration cycles, the resins were washed free of regenerant and finally with distilled water until they became neutral. The resins were air-dried to remove surface moisture.

Total exchange capacity and moisture content of resins were determined by the method reported by Kunin.<sup>1</sup> A pH-titration study of resins was carried out by the procedure described by Kunin.<sup>2</sup> True density, apparent density, void volume fraction, concentration of ionogenic groups, volume capacity, apparent  $pK_a$ ,  $pK_b$  values, and isoionic point of resins were determined by the method reported by Helfferich.<sup>3</sup> The rate of exchange and thermal stability of resins were carried out by the procedure described by Krishnaswamy.<sup>4</sup> The swelling behavior of these resins in different solvents was determined by the method reported by Bodamer.<sup>5</sup> The oxidation resistance test of resins was determined by the method described by Dorfner.<sup>6</sup>

## **RESULTS AND DISCUSSION**

#### % Moisture, Density and Void Volume Fraction

Data presented in Table I reveal the following points:

(i) The % moisture of the resins in H form varies from 1.2 to 6.5. The % moisture of the resins in OH form varies from 1.10 to 6.15. The difference in

Capa	acity and Concen	tration of Ion	ogenic Groups	of Amphote	ric Resins as Cation	Exchanger
No.	Resin	Total capacity CEC <sub>obs</sub> (meq/g)	Total capacity CEC <sub>cal</sub> (meq/g)	$\frac{\text{CEC}_{\text{obs}}}{\text{CEC}_{\text{cal}}}$	Concentration of ionogenic groups C <sub>r</sub> (meq/g)	Volume capacity Q (g meq·L)
1	SAEPED	3.45	3.05	1.68	4.62	0.65
2	HBAEPED	4.34	3.25	1.33	5.65	0.96
3	SSAEPED	3.96	1.56	2.54	5.24	0.52
4	GAEPED	3.11	2.28	1.36	3.89	0.55
5	HNAEPED	3.01	1.47	2.05	3.74	0.49
6	RCAEPED	3.01	1.66	1.84	4.04	0.61
7	RAPEPED	3.26	2.03	1.60	3.78	0.79

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1.8	DL	<i>ν</i> Γ <i>ν</i>	

values for the resins in H form and OH form is small, and hence the resins can stand recycling to a good degree.

(ii) The values of true density  $(d_{res})$  ranging from 1.24 to 1.39 gm/cm<sup>3</sup> for H-form resins and from 1.22 to 1.48 gm/cm<sup>3</sup> for OH-form resins. The values of apparent density  $(d_{col})$  ranging from 0.14 to 0.26 gm/mL for the resins in H form and from 0.15 to 0.24 gm/mL for the resins in OH form. Further, since the difference in density of the resins in H form and OH form is small, the resins can stand recycling to a good degree.

(iii) The value of the void volume fraction varies between 0.79 to 0.90 for resins in H form and between 0.82 to 0.88 for resins in OH form. The large void volume fraction suggest the porous nature of the resins, and hence the diffusion of ions and the rate of 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

$$\left. \begin{array}{c} \text{CEC}_{\text{cal}} \\ \text{or} \\ \text{AEC}_{\text{cal}} \end{array} \right\} = \frac{1000}{M/n}$$

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 Tables II and III and it reveals that:

(i) The values of the ratio  $\text{CEC}_{obs}/\text{CEC}_{cal}$  or  $\text{AEC}_{obs}/\text{AEC}_{cal}$  are high (~3/2) and may be attributed to the condensation of the weakly acidic amide group in such resins.

(ii) The total anion exchange capacity of amphoteric resins is quite a bit higher than that of the total cation exchange capacity.

(iii) Amphoteric resins as cation exchangers show the following decreasing order for cation exchange capacity:

HBAEPED > SSAEPED > SAEPED > RAPEPED > GAEPED > RCAEPED > HNAEPED.

Cap	Capacity and Concentration of Ionogenic Groups of Amphoteric Resins as Anion Exchanger											
No.	Resin	Total capacity AEC <sub>obs</sub> (meq/g)	Total capacity AEC <sub>cal</sub> (meq/g)	$\frac{AEC_{obs}}{AEC_{cal}}$	Concentration of ionogenic groups C <sub>r</sub> (meq/cm <sup>3</sup> )	Volume capacity Q (g•meq/g)						
1	SAEPED	8.80	4.11	2.14	10.75	1.55						
2	HBAEPED	5.65	3.25	1.74	7.20	1.30						
3	SSAEPED	7.31	4.70	1.55	9.29	1.12						
4	GAEPED	6.47	4.57	1.42	8.21	1.15						
5	HNAEPED	7.33	4.41	1.66	8.53	1.28						
6	RCAEPED	9.48	4.99	1.89	13.17	1.78						
7	RAPEPED	5.86	4.07	1.44	8.61	1.03						

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(iv) Amphoteric resins as anion exchangers show the following decreasing order for the anion exchanger capacity:

# RCAEPED > SAEPED > HNAEPED > SSAEPED > GAEPED > RAPEPED > HNAEPED.

(v) The total exchange capacity of SAEPED (8.8 meq/g), SSAEPED (7.31 meq/g), HNAEPED (7.33 meq/g), and RCAEPED (9.48 meq/g) as anion exchangers is comparable to that of the commercial anion exchanger, Duolite A-2 (8.4 meq/g) (granules), Duolite A-4 (7.7 meq/g) (granules), and Duolite A-7 (9.1 meq/g) (granules, weak base amino group, condensation polymer).

#### **Rate of Exchange**

Figures 1, 2, and 3 show the rate of exchange of amphoteric resins as cation exchanger as well as anion exchanger.

A persual of the trends of the rate of exchange for amphoteric resins as cation exchangers and as anion exchangers is fast.

In the case of amphoteric resins as cation exchangers, it is observed that:

(a) complete exchange occurs in 24 h;

(b) more than 50% of the total capacity is realized in about 144 min for SSAEPED and GAEPED, 156 min for HBAEPED, HNAEPED, RCAEPED, and RAPEPED, and 168 min for SAEPED;

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

 $\left. \begin{array}{l} \mathrm{SSAEPED} \\ \mathrm{GAEPED} \end{array} \right\} > \begin{array}{l} \mathrm{HBAEPED}, \, \mathrm{RCAEPED} \\ \mathrm{HNAEPED}, \, \mathrm{RAPEPED} \end{array} \right\} > \mathrm{SAEPED} \end{array}$ 

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

(a) complete exchange occurs in 24 h;

(b) more than 50% of the total capacity is realized in about 72 min for HNAEPED, 96 min for SAEPED, 108 min for SSAEPED, RCAEPED, and RAPEPED, 120 min for GAEPED, and 132 min for HBAEPED;

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

HNAEPED > SAEPED > SSAEPED, RCAEPED, RAPEPED

> GAEPED > HBAEPED



Fig. 1. Rate of exchange of (1) SAEPED as ( $\bullet$ ) cation exchanger and as (O) anion exchanger; (2) HNAEPED as ( $\bullet$ ) cation exchanger and as (O) anion exchanger.



Fig. 2. Rate of exchange of (1) HBAEPED as ( $\bullet$ ) cation exchanger and as ( $\circ$ ) anion exchanger; (2) GAEPED as ( $\bullet$ ) cation exchanger and as ( $\circ$ ) anion exchanger.



Fig. 3. Rate of exchange of (1) RCAEPED as ( $\bullet$ ) cation exchanger and as ( $\circ$ ) anion exchanger; (2) RCPEPED as ( $\bullet$ ) cation exchanger and as ( $\circ$ ) anion exchanger; (3) SSAEPED as ( $\bullet$ ) cation exchanger and as ( $\circ$ ) anion exchanger.

It is observed that the rate of exchange of amphoteric resins as anion exchangers is faster than that as cation exchangers.

The shape of curves indicate the porous nature of matrices with a rapid rate of exchange in initial stage followed by slowing down of exchange.<sup>7</sup>

## **pH-Titration Curves**

Figures 4, 5, and 6 show the pH titration curves for the amphoteric resins. They exhibit good cation and anion exchange capacities over a pH range 1-12.

It is evident from Figures 4, 5, and 6 that 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 exchangers as well as cation exchangers, depending on the pH of the solution.

In the pH range 1–7, resins act as anion exchangers and over this range are characteristic of weakly basic resin and may be compared with the pH-titration curve of commercially available weakly basic anion exchanger resin Tulsion WB.<sup>8</sup> The cation exchanger behavior of these resins was similar to weak acid resin.<sup>9</sup>

# Apparent $pK_a$ , $pK_b$ Values and Isoionic Point

The apparent  $pK_a$  and  $pK_b$  values were obtained from the pH-titration curve, the appropriate values at 50% neutralization being inserted into the following



Fig. 4. pH titration curves of SAEPED ( $\bullet$ ), HBAEPED ( $\Box$ ), and GAEPED ( $\Delta$ ) resins.

Helfferich equation:

$$pK_{a} = pH + \log (Na^{+}) - \log \overline{X}/2$$
$$pK_{b} = pH - \log (Cl^{-}) + \log \overline{X}/2$$

The term  $\overline{X}$  represents the total concentration of both undissociated and dissociated ionogenic groups.

From Table V, it is seen that the range of  $pK_a$  obtained for the overall cation exchange process in general for various ion exchangers studied varies between 9.67 to 9.89, which is characteristic of phenolic hydroxyl groups, and that of  $pK_b$ obtained for the overall anion exchange process for these resins lies between 2.42 to 2.64, which is characteristic of bases of weak strength. The values are in decreasing order as:

for 
$$pK_a$$
: RCAEPED > HNAEPED > RAPEPED > GAEPED > SAEPED > SAEPED > HBAEPED  
for  $pK_b$ : RAPEPED > RCAEPED, HNAEPED > GAEPED > SAEPED > SAEPED > HBAEPED

The values of isoionic point (pH<sub>ip</sub>) obtained as

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

The values of isoionic point varies in the range of 6.05 to 6.25. The isoionic point for isoleucine is 6.02 and for proline is  $6.30^{10}$ ; it is observed that resins under



Fig. 5. pH titration curves of HNAEPED ( $\bullet$ ) and RCPEPED ( $\triangle$ ) resins.



Fig. 6. pH titration curves of SSAEPED (O) and RCAEPED ( $\Delta$ ) resins.

		% N	12.73	10.06	14.06	11.37	11.97	14.25	11.84
	Observed	% H	8.99	7.66	7.30	7.20	8.45	8.40	8.54
TABLE IV Elemental Analysis of Resins		% C	41.42	46.57	41.06	46.22	45.39	43.69	43.98
		% N	11.52	9.09	13.17	12.78	12.35	13.98	11.40
	Calculated	₩ %	8.64	7.79	7.83	7.46	8.82	8.98	8.94
		% C	41.97	46.75	41.38	46.79	45.88	43.92	43.99
		Formula	$(C_{17}H_{43}N_4O_{11.5})_n$	$(C_{12}H_{24}N_2O_7)_n$	$(C_{22}H_{50}N_6O_{13}S)_n$	$(C_{17}H_{34}N_4O_9)_n$	$(C_{26}H_{60}N_{6}O_{14})_n$	$(C_{22}H_{53}N_6O_{12.5})_n$	$(C_{18}H_{43}N_4O_{11})_n$
		Resin	SAEPED	HBAEPED	SSAEPED	GAEPED	HNAEPED	RCAEPED	RAPEPED
		No.	1	2	က	4	5	9	2

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Apparent $pK_a$ and $pK_b$ Values and Isoionic Point of Amphoteric Resins										
No.	Resin	$\begin{array}{c} \text{Apparent} \\ \text{pK}_a \text{ values} \end{array}$	Apparent $pK_b$ values	Isoionic point						
1	SAEPED	9.72	2.56	6.14						
2	HBAEPED	9.67	2.42	6.05						
3	SSAEPED	9.75	2.54	6.15						
4	GAEPED	9.77	2.58	6.18						
5	HNAEPED	9.87	2.59	6.23						
6	RCAEPED	9.89	2.59	6.24						
7	RAPEPED	9.86	2.64	6.25						

TABLE V

study have intermediate values. The values are in decreasing order as RAPEPED > RCAEPED > HNAEPED > GAEPED > SSAEPED > SAEPED > HBAEPED

## **Thermal Stability**

From Tables VI and VII it is seen that no change in total capacity for all the forms (H, Li, Na, K, Oh, and Cl forms) of the resins are observed up to 80°C. Hence the amphoteric resins could be safely used up to 80°C. Above this temperature, they show an increase in capacity when the heated resins were regenerated and tested, which could be due to (i) destruction of some of the  $-CH_2$ —bridges, creating more gaps in the matrix thereby facilitating the access to more -NH— groups and (ii) removal of the decomposition products which had neutralized the ionogenic groups.

# **Oxidation Resistance**

From Table VIII, it is seen that amphoteric resin HNAEPED exhibits the lowest increase in % water content as cation exchanger and as anion exchanger and thus is most resistant to oxidation. It is observed that the oxidative degradation for amphoteric resins as cation exchangers exhibits higher increases in % water content than amphoteric resins as anion exchangers. Hence it is suggested that the anionic form is less susceptible to oxidation than the cationic form.

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

HNAEPED > SAEPED > HBAEPED > RCAEPED

> RAPEPED > GAEPED > SSAEPED

Amphoteric resins as anion exchangers show the following decreasing order for their stability on oxidative degradation:

HNAEPED > RCAEPED > HBAEPED > GAEPED

> RAPEPED > SAEPED > SSAEPED

# Swelling Behavior in Nonaqueous Solvents

From Table IX, it can be easily seen that:

(i) Polar solvents produce more extensive swelling than nonpolar hydrocarbon.

ĺ		-	Thermal Stal	T oility of Amphot	ABLE VI eric Resins at C	ation Exchange	e Resins			
		Original		,				dain in capacity	of absolutely	
Temp		capacity of absolutely		Gain in capacity resin as detected	of absolutely di after heating (9	(9) K.		dry resin as de regenerat	tected after ion (%)	
(0°)	Resin	dry (meq/g)	H form	Li form	Na form	K form	H form	Li form	Na form	K form
80	SAEPED	3.45	nil	nil	nil	nil	nil	lin	nil	nil
	HBAEPED	4.34	lin	nil	nil	nil	nil	nil	lin	nil
	SSAEPED	3.96	lin	nil	nil	nil	nil	lin	lin	nil
	GAEPED	3.11	nil	lin	nil	nil	nil	nil	nil	nil
	HNAEPED	3.01	nil	nil	nil	lin	nil	lin	nil	nil
	RCAEPED	3.05	nil	lin	nil	nil	nil	lin	nil	lin
	RAPEPED	3.26	lin	nil	nil	nil	nil	lin	nil	nil
100	SAEPED	3.45	5.63	liu	nil	liu	31.54	nil	lin	nil
	HBAEPED	4.34	nil	nil	nil	nil	nil	- nil	nil	nil
	SSAEPED	3.96	nil	liu	nil	lin	nil	nil	lin	nil
	GAEPED	3.11	12.5	liu	nil	nil	19.42	lin	nil	nil
	HNARPED	3.01	lin	lin	nil	lin	nil	lin	nil	nil
	RCAEPED	3.05	23.08	liu	liu	lin	nil	nil	lin	lin
	RAEPED	3.06	3.7	lin	nil	nil	5.63	nil	nil	nil
120	SAEPED	3.45	8.22	5.67	6.52	7.21	35.26	12.20	15.69	18.90
	HBAEPED	4.34	10.74	6.78	8.12	9.13	38.21	9.22	16.17	20.12
	SSAEPED	3.96	12.21	7.12	10.18	11.54	39.27	9.54	16.44	21.31
	GAEPED	3.11	16.55	9.67	14.17	15.57	28.24	14.26	17.27	18.33
	HNAEPED	3.01	14.11	8.19	12.14	13.24	24.29	12.14	16.19	17.21
	RCAEPED	3.05	33.34	7.54	11.44	12.39	41.49	11.23	15.83	16.03
	RAPEPED	3.26	12.46	7.29	11.03	11.93	20.33	10.17	14.34	15.28
140	SAEPED	3.45	12.15	7.63	9.27	12.10	43.21	15.19	19.31	25.41
	HBAEPED	4.34	14.36	10.11	12.16	13.94	45.12	17.51	20.22	26.28
	SSAEPED	3.96	17.08	. 11.45	14.08	16.42	47.25	18.79	21.83	27.19
	GAEPED	3.11	19.31	13.32	18.19	18.27	42.53	19.22	22.39	28.43
	HNAEPED	3.01	17.51	12.53	16.08	16.47	39.31	17.61	19.25	19.74
	RCAEPED	3.05	38.87	11.32	15.42	17.17	46.18	16.32	17.77	18.71
	RAPEPED	3.26	10.58	14.02	14.02	15.89	33.11	14.41	18.28	17.54

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		Original capacity	Gain in ca absol	apacity of utely	Gain in capacity of absolutely	
m		of absolutely	dry resin a	s detected	ary resin as	aetected
Temp	р :	dry resin	after hea	$\frac{(\%)}{(\%)}$	after regener	$\frac{ration(\%)}{Cl}$
(°C)	Resin	(meq/g)	OH form	Cl form	UH form	Cliorm
80	SAEPED	8.80	nil	nil	nil	nil
	HBAEPED	5.65	nil	nil	nil	nil
	SSAEPED	7.31	nil	nil	nil	nil
	GAEPED	6.47	nil	nil	nil	nil
	HNAEPED	7.33	nil	nil	nil	nil
	RCAEPED	9.48	nil	nil	nil	nil
	RAPEPED	5.86	nil	nil	nil	nil
100	SAEPED	8.80	2.35	1.06	4.21	1.87
	HBAEPED	5.65	2.47	1.52	5.32	2.15
	SSAEPED	7.31	4.07	1.98	7.12	2.79
	GAEPED	6.47	6.18	3.28	8.19	4.11
	HNAEPED	7.33	4.49	2.17	7.52	3.06
	RCAEPED	9.48	3.37	1.67	6.16	2.23
	RAEPED	5.86	2.91	1.54	5.72	2.46
120	SAEPED	8.80	8.32	3.12	12.33	5.17
	HBAEPED	5.65	9.14	4.67	14.26	7.15
	SSAEPED	7.31	14.19	5.22	21.77	9.24
	GAEPED	6.47	18.41	7.08	23.71	11.47
	HNAEPED	7.33	14.78	6.01	22.07	10.11
	RCAEPED	9.48	13.39	4.95	20.02	7.86
	RAPEPED	5.86	12.44	4.76	17.65	6.27
140	SAEPED	8.80	12.46	8.51	14.71	9.56
	HBAEPED	5.65	14.17	10.24	16.89	11.76
	SSAEPED	7.31	19.21	12.54	24.81	14.82
	GAEPED	6.47	24.52	16.66	32.14	19.27
	HNAEPED	7.33	20.81	14.80	26.61	16.43
	RCAEPED	9.48	18.92	11.72	20.78	14.41
	RAPEPED	5.86	16.67	10.99	19.36	12.25

TABLE	VII
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Thermal Stability of Amphoteric Resins as Anion Exchange Resins

(ii) In hydrocarbon, amphoteric resins as cation exchangers swell more than the anionic type.

(iii) The % swelling of amphoteric resins in acetic acid, as cation exchangers

	Oxidation Resistance of Amphoteric Resins											
		Oxidati exch	on resistance as angers (% moist	s cation cure)	Oxidat exch	ion resistance a angers (% mois	s anion ture)					
No.	Resin	Untreated exchanger	H <sub>2</sub> O <sub>2</sub> -treated exchanger	Increase in % water content	Untreated exchanger	H <sub>2</sub> O <sub>2</sub> -treated exchanger	Increase in % water content					
1	SAEPED	3.59	27.10	24.51	5.27	27.72	22.45					
2	HBAEPED	1.38	28.05	26.67	2.04	16.52	14.48					
3	SSAEPED	1.20	46.75	45.55	2.20	37.13	34.94					
4	GAEPED	5.36	38.49	33.13	3.84	23.62	19.78					
5	HNAEPED	4.46	26.39	21.93	4.56	15.25	10.69					
6	RCAEPED	3.28	30.70	27.42	6.15	19.25	13.10					
7	RAPEPED	6.57	38.57	32.00	1.10	21.59	20.49					

TABLE VIII Oxidation Resistance of Amphoteric Resir

No.	Resin	Water	Ethanol	CH <sub>3</sub> COOH	% Swelling in acetone	Benzene	Petroleum ether			
1	SAEPED(C) <sup>a</sup>	190	50	195	15	10	10			
	SAEPED(A) <sup>b</sup>	50	90	244	10	11	5			
2	HBAEPED(C)	190	66	275	19	25	8			
	HBAEPED(A)	160	62	382	6	6	6			
3	SSAEPED(C)	135	57	193	25	12	6			
	SSAEPED(A)	80	53	280	6	6	6			
4	GAEPED(C)	95	28	150	11	12	7			
	GAEPED(A)	150	57	264	13	7	7			
5	HNAEPED(C)	230	100	500	25	12	20			
	HNAEPED(A)	120	180	388	13	7	6			
6	RCAEPED(C)	160	38	133	17	22	17			
	RCAEPED(A)	180	88	241	11	6	6			
7	RAPEPED(C)	110	27	133	11	22	11			
	RAPEPED(A)	120	60	172	6	6	11			

TABLE IX Swelling of Amphoteric Resins in Nonaqueous Solvents

 $^{a}(C) = cation exchangers.$ 

<sup>b</sup> (A) = anion exchangers.

as well as anion exchangers, is much higher than would be anticipated. This can be explained as follows:

The swelling of amphoteric resins with both weak-acid and weak-base groups is a function of the pH of the solution and shows a characteristic minimum near the isoelectric point of the resin. Here, the active groups of both types are practically undissociated, so that the osmotic pressure difference is small. When the pH is increased or decreased, either the acid or the base groups dissociate, thus 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 exchangers are as follows:

# HNAEPED > SAEPED, HBAEPED > RCAEPED > SSAEPED > RAPEPED > GAEPED

(v) The decreasing order of porosity (polar solvents) for amphoteric resins as anion exchangers are as follows:

RCAEPED > HBAEPED > GAEPED > HNAEPED, RAPEPED > SSAEPED > SAEPED

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