몇가지 양쪽성수지의 제조 및 물리화학적 성질

민경은 · 이학기 · 이동호

경북대학교 공과대학 공업화학과

Synthesis of Amphoteric Ion-Exchange Resins and Their Physico-Chemical Properties

Kyung-eun Min, Hak-ki Lee and Dong-ho Lee

*Department of Industrial Chemistry College of
Engineering Kyungpook National University, Taegu, Korea*

Abstract: The ionic resins, amphoteric type, having both cationic and anionic group were prepared by introducing sulfonyl chloride group into a poly (styrene-co-divinylbenzene), letting it reacted with ethylamine, diethylamine, aniline, and diphenylamine in the presence of aqueons alkali, respectively. The polymer matrix was obtained by using suspension polymerization, and modified with chlorosulfonic acid. The reactivity of chlorosulfonated resin toward amine and Arrhenius alkali was studied by cationic capacity and elemental analysis data. And physicochemical properties of prepared amphoteric resins were also studied. It was observed that cationic and anionic exchange capacity of prepared resins were 1.84—3.20 meq./g and 1.1—1.5 meq./g, respectively. But these capacities could be regulated by treating the final product with strong acid, and more presumably by controlling amine/alkali ratio while preparing the resins.

1. INTRODUCTION

Organic ion-exchangers have been receiving considerable attention since Adams et al. first reported the synthesis of ion exchange resin[1]. Much effort has since been invested in developing the resins of similar and different types[2]. As a consequence, resins commercially available are; strong acid, weak acid, strong ba, v११k b१ se, and miscellaneous chelating types[3]. These resins are useful for transformation, fractionation, concentration, and removal of ionic substances. The usages of these resin have been described in many papers and summerized[4].

In 1951, Stach reported synthesis of a resin containing both acid and base group, namely amphoteric ion exchange resin[5]. But the properties of this interesting resin have so far not been studied. During the last three decades, there are nearly 100 papers about the synthesis of amphoteric resins and fibers[6].

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Most of these resins can either be prepared by copolymerization employing an appropriately functionalized comonomer or by chemical modification of non-functionalized polymer matrix.

Recently, Kapadia et al.[7] reported synthesis and properties of amphoteric resin by condensing organic acids with epichlorohydrin employing ethylenediamine as a crosslinking agent.

In this paper, we aimed to prepare the amphoteric resin both having sulfonic acid and sulfonamide group by introducing sulfonyl chloride residue into a poly(styrene-co-divinyl-benzene) chain, and making to react with ethylamine, diethylamine, aniline, and diphenyl amine in the pressence of aqueous alkali, respectively. And here we would like to report synthesis and some of the physico-chemical properties of these resins.

2. EXPERIMENTAL

2-1. Preparation of Polymer Matrix.

All the chemicals used for the preparation of resins were GR grade. Styrene (Wako, Japan) was freed from the inhibitor by shaking with 20% aqueous NaOH, washing and drying, followed by distillation under reduced pressure. Divinylbenzene (55% in ethylbenzene, Wako) was treated with similar manner. The polymer matrix was obtained by standard suspension polymerization[8]. The polymerization was carried out for 12 hours at $90\pm0.05°C$ in 700ml water jacketed reactor equipped with mechanical stirrer with two blades at different level. (cf. Fig. 1)

After polymerization the polymer matrix was washed several times with water and then leached using methanol. Finally they were dried at room temperature under vacuum to produce a virtually quantitative yield of dry
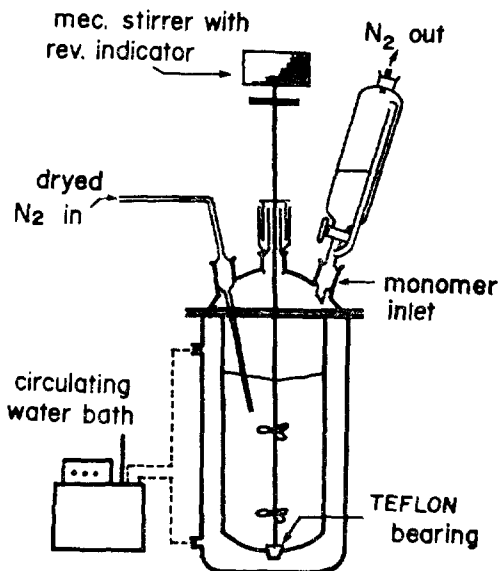

Fig. 1. Reactor system for preparing polymer matrix.

beads in the particle size range about 50 to 400μm. In this procedure, benzoyl peroxide was used as the initiator and the supension was stabilized by poly (vinyl alcohol).

2-2. Procedures for Chemical Modification

2-2-1. Chlorosulfonation

A mixture of 0.1g of silver sulfate (Wako) and 450ml of chlorosulfonic acid (Wako) was heated to about 80°C in 1 liter three necked flask equipped with stirrer, reflux condenser and thermometer. To this mixture, 100g of copolymer was added little by little. The reaction mixture was maintained at 90°C for 5 hours, and cooled under room temperature leaving for a few hours. The mixture was then poured into 2 liters of about 50 vol.% sulfuric acid solution. After the mixture cooled off again, it was diluted with water, and washed with plenty of water and the light chocolate colored beads were filtered by suction.

Chlorosulfonated resin (CSR) was dried in vacuum oven for over 24 hours at 30°C. The chlorine content of CSR prepared under these condition was about 85%.

2-2-2. Preparation of Amphoteric Resin

40g of CSR (about 0.2 mole) was stirred with 100ml of acetone at 30°C under nitrogen atmosphere in a 250ml flask and 0.2 mole of aliphatic or aromatic amine was added 30 minutes later.

Those amines were ethylamine (70% in water, Tokyokasei, Japan), diethylamine (Shimakyu, Japan), aniline (Wako), and diphenylamine (Kanto, Japan).

To the reaction mixture 0.02 mole of aqueous NaOH was added and stirred again in ultrasonic bath at 30°C for 48 hours. The reaction mixture was then poured into 500ml acetone and after an hour filtered off. The resin was washed on the filter with sufficient acetone to remove unreacted amine. The product was dried in a vacuum oven for 24 hours at room temperature.

2-3. Determination of Physicochemical Properties

The resins were conditioned by appropriate treatment with 1N HCl or 1N NaOH. This treatment was conducted by the method described in ASTM D-2187[9]. After several alternate treatment, the resin was washed free of regenerant and finally with doubly distilled water until the pH value of effluent became constant.

A pH titration curves and ion exchange capacity of resins were determined by the modified Helfferich method[10]. Water retention capacity and density were calculated by ASTM and Kunin's method[11]. Particle size distribution curves for resin were calculated from the sieve analysis data[12].

A Fisher pH meter (model 620, with combination electrode), Shimadzu 30BT thermal analyzer, Beckmann 4250 infrared spectrophotometer were employed for determination of related properties.
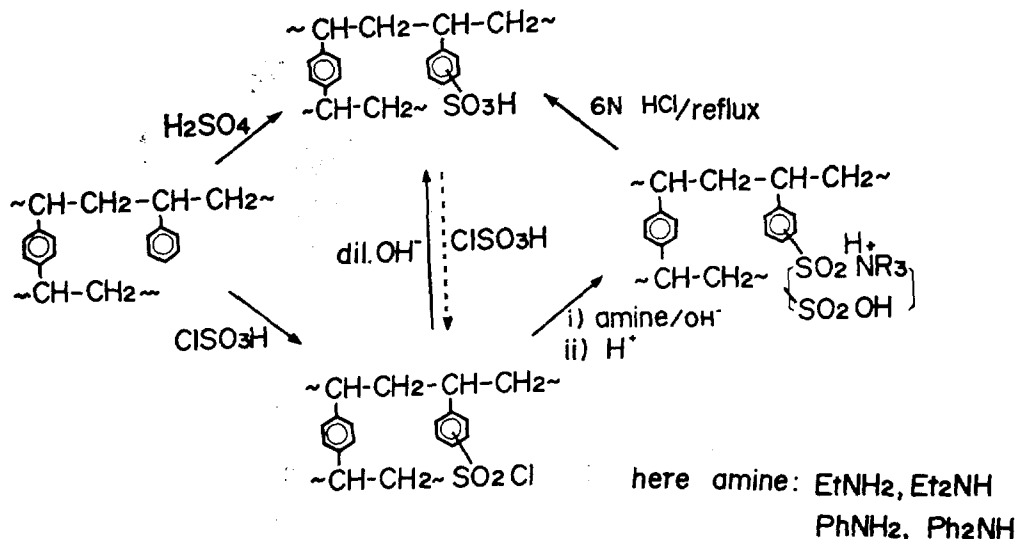

Overall Scheme

Table 1. Reaction Conditions for Preparing Polymer Matrix

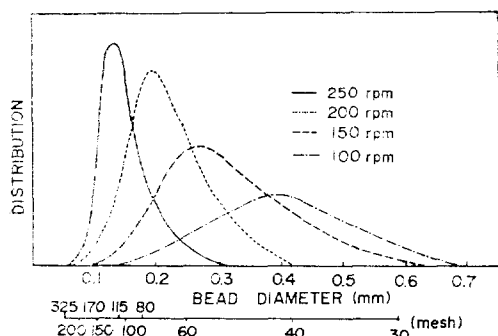| monomer (ml)		PVA (g)	BPO (g)	water (ml)	temperature (°C)	time (hr)	stirring speed (rpm)
ST	DVB						
50	5	0.5	0.5	400	90±0.05	12	200±10

Fig. 2. Effect of stirring speed on the particle size distribution.
* reaction conditions: same as shown in table 1 except stirring speed

3. RESULTS AND DISCUSSION

3-1. Preparation of Polymer Matrix

Because particle size of ionic resin affects to bulk density, pressure drop and exchange rate, it should be controlled by conditions of polymerization. The major factors controlling particle size are surface tension, densities and viscosity of aqueous phase, diameters of reactor and stirrer, and stirring speed in suspension reaction[13].

The most importanat experimental parameter we have examined to regulate particle size was stirring speed and relative amount of suspension stabilizer. In Figure 2 the results are given of the variation of the particle size distribution of polymer matrix as a function of stirring speed. However, as shown in Figure 3, amount of surfactant had any marked effect on particle size so far as same reaction system been used. This result is consistent with recent study of Balakrishnab[13].
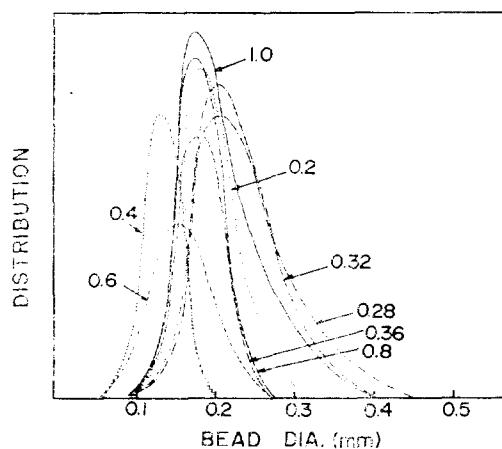

Fig. 3. Particle size distribution curves of polymer matrix in various suspension stabilizer concentration. Numbers in figure indicate gram of PVA
* reaction conditions: same as shown in table 1 except PVA amounts

Typical preparing conditions for copolymer are listed in Table 1, and large amount of polymer matrix was prepared under this condition. Figure 4 shows the optical microscopic picture of polymer matrix.

3-2. Chlorosulfonation of Polymer Matrix

It was considered that chlorosulfonation progresses from the outer shells toward the center of the particle and is accompanied by considerable swelling and evolution of heat. The matrix was strained rather severely, and beads might be cracked. This strain could be minimize by adding swelling reagent, but inthis procedure, swelling media was not introduced, because the most of swelling reagent was labile to chlorosulfonic acid, and difficulties of separation. However, the chlorosulfonated resin
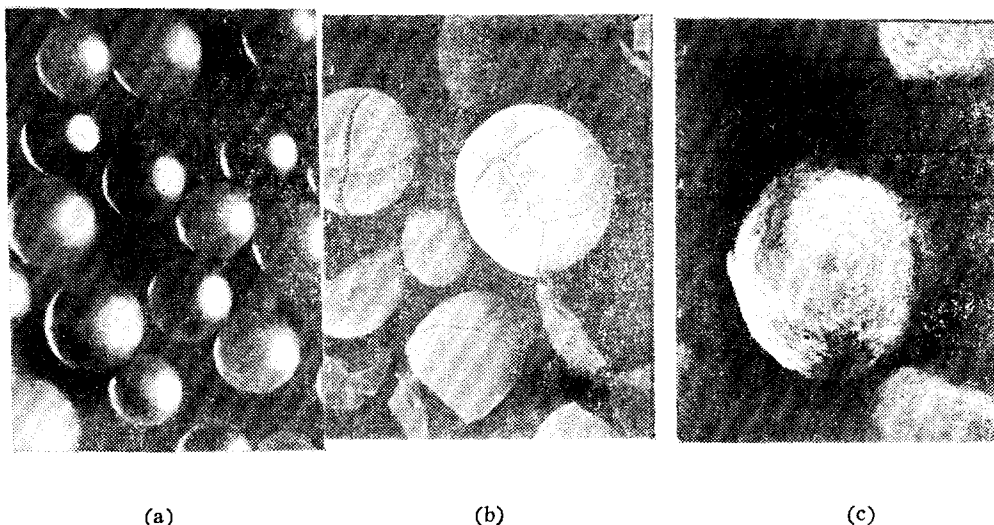
(a)   (b)   (c)

Fig. 4. Microscopic pictures of resins.
    A : Polymer matrix prepared by suspension reaction (optical, ×100).
    B : CSR separated by water (SEM, ×200).
    C : CSR separated by aqueous H_2SO_4 and stepwise dilution (SEM,×350).

CSR) was separated successively in aqueous sulfuric acid and stepwise dilution by water (cf. Fig. 4B,C).

Degree of chlorosulfonation was determined by using cationic capacity data of resin prepared by reaction of CSR with excess NaOH solution. It was found that effective chlorosulfonation occurred at 90°C for 48 hours in the presence of silver sulfate.

3-3. Preparation of Amphoteric Resin

Chlorine atom in sulfonyl chloride group can be replaced easily by various nucleophiles. Reaction of sulfonyl chloride compound with primary and secondary amines gives the corresponding sulfonamide[14], and with Arrhenius alkali gives sulfonic acid derivatives. The resin both having sulfonamide and sulfonic acid residue could be prepared by the reaction of CSR with amine in the presence of Arrhenius alkali.

Figure 5 shows cationic capacity of ANR resin produced by the reaction of CSR with aniline in various molar ratio, in the absence nd presence of aqueous NaOH. The higher cationic capacity value means the more sulfonic acid group presence than sulfonamide group in ANR resin. It is evident in Figure 5 that the OH^- ion not only competes with amine but acts as a catalyst.

An interesting feature of the cationic capacity shows in Figure 6 is that, in spite of sufficient amount of amine used, the cationic capacity increases with increasing of relative alkali concentration to CSR. It was considered that sulfonyl chloride group reacts predominantly with OH^- and gives more sulfonic acid group.

We prepared four kinds of resins by the reaction of CSR with equimolar amounts of various amines using one tenth mole of aqueous NaOH with swelling media in acetone. The expected structures and appearance of resins are listed in Table 2.

3-4 IR Characteristics

Infrared spectra were taken in KBr pellet method. Evidence[15] for the incorporation of sulfonyl chloride group in the CSR is provided

Table 2. Structure and Color of Prepared Resin[a]

used amine	structure[b]	color	abbreviation
Ethylamine	(P)—— $(SO_2\ NHEt)_x$ $(SO_3H)_y$	brown	EAR
Diethylamine	(P)—— $(SO_2NEt_2)_x$ $(SO_3H)_y$	golden brown	DEAR
Aniline	(P)——- $(SO_2NHPh)_x$ $(SO_3H)_y$	reddish brown	ANR
Diphenylamine	(P)—— $(SO_2NPh_2)_x$ $(SO_3H)_y$	dark green	DANR

a) Reaction condition:40g CSR+0.2mole amine+0.02mole NaOH 30°C, 48hrs, diluent;100ml acetone
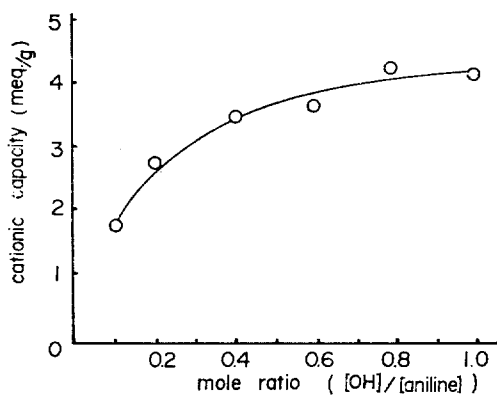b) Each x and y are not same, and (P) means polymer matrix

Fig. 5. Cationic capacity of ANR as a function of alkali/aniline mole ratio; [CS-R]/[aniline]=1, temperature=30°C, time=48 hours.

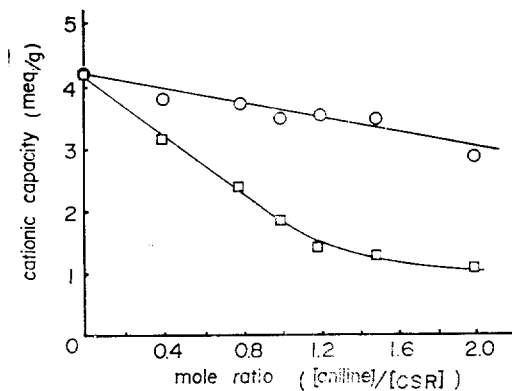**Fig. 6.** Changes of cationic capacity of ANR as a function of aniline/CSR concentration after alkali washing; (◯) ANR prepared in the absence of Na-OH, (□) ANR prepared in the presence of NaOH, [aniline]/[OH⁻]=10.

by the spectrum (cf. Fig. 7b) which possesses bands typical of S=O stretching 1135 and 1175cm⁻¹ and SO_2—Cl stretching at 1370cm⁻¹.

The spectrum of sulfonic acid resin (cf. Fig. 7c) produced from CSR by treating with 1N NaOH solution for several hours, does not reveal stretching band due to SO_2—Cl group at same position. This spectrum is identical with that of poly (p-styrene sulfonic acid) studied by Hart[16]. The broad strong band near 3400cm⁻¹ in Figure 7b was interpreted as by water molecule captured in CSR.

As shown in Figure 7d to 7g, the medium band near 1300 to 1350 cm⁻¹ appears to be consistent with the SO_2—N=stretching vibration, which is formed in resins obviously due to formation of sulfonamide.

3-5. Elmental Analysis

Chemical modification techniques have a little disadvantantages; for instance, it is impossible to predict the degree of functionalization of product exactly. However, it is possible to evaluate the average chemical formula of

each resin, from the elemental analysis data. The average degree of crosslinking (%) of polymer matrix prepared in this experiment was assumed 9.2% which was recalculated using Park's data[17] (cf. Table 3). And chemical formula should be $C_{8.2}H_{8.2}$ by the following relationship,
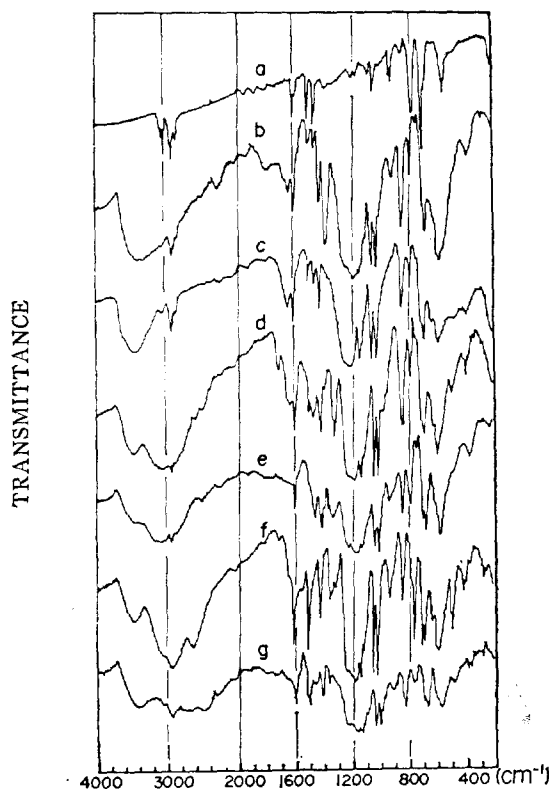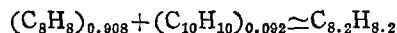

Fig. 7. Infrared spectra of resins; a) ST-DVB
b) CSR c) CSR treated with excess
alkali d) EAR e) DEAR f) ANR g)
DANR.

$$(C_8H_8)_{0.908} + (C_{10}H_{10})_{0.092} \simeq C_{8.2}H_{8.2}$$

When every benzene ring has chlorosulfonyl group, its chemical formula should be $C_{8.2}H_{7.2}SO_2Cl$, but in reality the observed value is $C_{9.7}H_{13}SO_3Cl_{0.99}$. It reveals that not only the chlorosulfonyl group is attached about 85% of benzene ring but each chlorosulfonyl group holds at least one molecule of water. It was supported by cationic capacity data (intercept of Fig. 5) and mentioned in discussion of IR spectrum already.

For EAR prepared from perfectly chlorosulfonated resin, contained 40% sulfonamide and 60% sulfonic acid group, should give rise to formula $C_9H_{10.2}SO_{2.6}N_{0.4}$, from
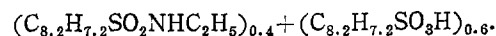
$$(C_{8.2}H_{7.2}SO_2NHC_2H_5)_{0.4} + (C_{8.2}H_{7.2}SO_3H)_{0.6}.$$

Table 4 shows calculated formula by using similar trial-and-error method and observed formular of resin estimated by analysis data. We believed that small difference in two values is caused by experimental error mainly inho-

Table 3. Relation between Monomer Feed Ratio and Degree of Crosslinking

cited data*			feed ratio (b)	deviation (a/b)
ST (ml)	DVB (ml)	% cross-link (a)		
80	1	1.25	1.23	1.0163
75	3	3.90	3.85	1.0130
75	6	7.50	7.41	1.0121
70	8.4	10.8	10.71	1.0084
70	12	14.8	14.63	1.0116
24	6	20.2**	20.00	1.0100

*See ref. 17; BPO 0.5g, $90 \pm 2°C$, 9 hrs
**BPO 0.5g, 87°C, 16hrs

Table 4. Elemental Analysis Data of Resins

resin	observed	calculated	reacted amine %
CSR	$C_{9.7}H_{13}SO_3Cl_{0.99}$	$C_{9.4}H_{10.54}SO_3Cl$	—
EAR	$C_{9.6}H_{13.4}SO_{4.6}N_{0.4}$	$C_{9.6}N_{12.48}S_{0.92}O_{3.84}N_{0.4}$	37.5
DEAR	$C_{11}H_{14.9}SO_{5.9}N_{0.27}$	$C_{11}N_{14.2}SO_{3.95}N_{0.27}$	22
ANR	$C_{13.8}H_{15.9}SO_{5.2}N_{0.56}$	$C_{13.8}H_{16}S_{1.1}O_{4.06}N_{0.56}$	42
DANR	$C_{9.9}H_{11.8}SO_6N_{0.11}$	$C_{9.9}H_{11.5}S_{0.91}O_{3.54}N_{0.11}$	10.5

mogeneity of chlorosulfonation degree and hydration of resins.

A tendency that primary amine reacts more easily than secondary amine with sulfonyl chloride was considered as influence of steric hindrance on amine molecule. The elemental analysis data and reactivity of amine to the CSR resin are shown in Table 4.

3-6. Ion Exchange Capacity

The weight capacity of an ion exchanger is defined as the number of counter ion equivalents in a specified amount of the material[10]. And the specific amount is defined as the amount which weighs one gram when the material is completely converted to the H^+ or Cl^- form and is devoid of sorbed solutes and solvents. Cationic capacity of prepared amphoteric resins was determined by converting the resin to H^+ form and back titrating H^+ concentration of aqueous Na_2SO_4 eluent. Anionic exchange capacity was evaluated by titrating the exchanged Cl^- ion by SO_4^{-2} with silver nitrate aqueous solution.

The capacities of resins measured by above method and theoretical capacity calculated using chemical formula are listed in Table 5.

3-7. Stabilities and Other Properties

Differences between moisture content(=water retention capacity) of H^+ and OH^- type resin may indicate either loss of functionalty or fouling of the ionic materials[9].

In Table 6, it is observed that the more

CSR aminated, the more differences of moisture contents are observed. The Cl^- type resin seemed to decompose during conversion to OH^- type. Therefore, we examined pH titration curve of resins.

Prior to determining the pH curve, the ionic resin was converted to the H^+ form according to ASTM method. The pH curves of cationic region for resins measured by Helfferich method are given in Figure 8. But pH curves of anionic region for OH^- form resins were difficult to be measured. Figure 8 is typical pH curves of strong acid type resin, and

Table 6. Moisture Content and Density of Resin

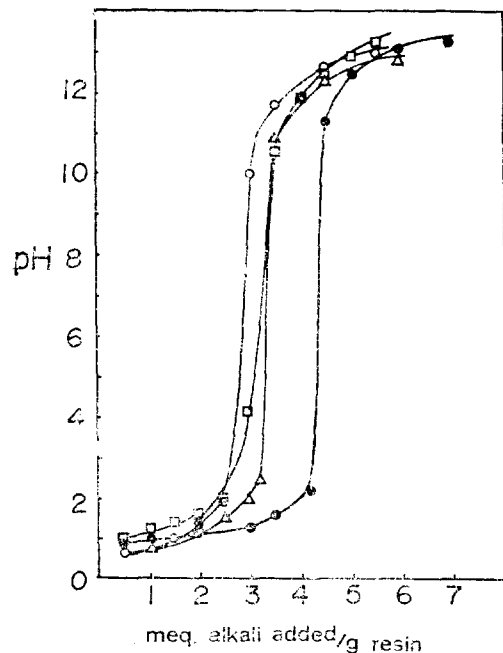| resins	moisture content(%)		density*
	H^+ form	OH^- form	
EAR	25.32	32.91	1.08
DEAR	20.93	23.63	1.15
ANR	30.38	38.51	1.19
DANR	38.85	39.22	1.26

*H form resin

Fig. 8. pH titration curves of resins; (○) EAR (△) DEAR (□) ANR (●) DANR.

Table 5. Ion Exchange Capacity of Resins
(unit : meq./g)

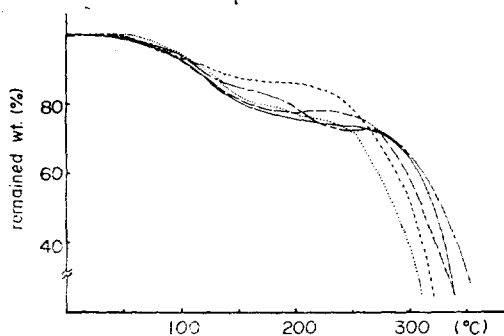| resin	cationic		anionic		total	
	observed	calcd.	observed	calcd.	observed	calcd.
EAR	2.38	2.47	1.41	1.65	3.79	4.12
DEAR	2.68	2.63	1.16	0.97	3.84	3.60
ANR	1.84	1.44	1.53	1.84	3.37	3.28
DEAR	3.20	3.42	1.14	0.42	4.34	3.84

Fig. 9. TGA thermograms of resins at a heating rate of 10°C/min in air;
(······) CSR (——) EAR (——) DEAR
(—·—) ANR (······) DANR.

capacity calcuated from the curve was different from capacity determined already and shown in Table 5. We believe that these differences are caused by weak-base-NH^+R_2 lose a proton and forming uncharged-NR_2, consequently increases cationic capacity when the pH is high. Those were the reason why we could not measure the pH titration curves of anionic region, and why we used aqueous Na_2SO_4 solution instead of alkali solution while determining cationic capacity.

All the prepared amphoteric resins were stable in all common solvents, except in concentrated HCl, and withstanded temperature near to 110°C. But anionic capacity began to detriorated above 60°C. Overberger indicated that sulfonamide group may decompose[18] and yield sulfonic acid group when it is treated in vigorous condition. Actually it is observed that cationic capacity of ANR was increased about 2.5 meq./g by refluxing with 6N HCl, 48 hours. As the results, we believe that each capacity could be regulated by treating the final product with strong acid, and more presumably by controlling amine/alkali ratio while preparing the amphoteric resins. The TGA thermogram of resins are shown in Figure 9.

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