Preparation of Ion-Exchange Celluloses.
I. Anion Exchange Celluloses

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Synopsis

Cellulose–poly(glycidyl methacrylate) graft copolymer (CPGMA) was treated with ammonia (AH), ethylamine (EA), diethylamine (DEA), and triethylamine (TEA). Factors affecting the reaction, such as reaction duration, temperature, liquor ratio, pH, and aminating agent/epoxide molar ratio were studied. A mechanism of the reaction was suggested. The anion exchange celluloses were characterized by studying its capacity, potentiometric titration, and durability to use. Potentiometric titration of the produced anion exchangers has been studied and pK_b values were found to be 6.1, 7.6, and 8.9 for DEA–CPGMA, EA–CPGMA, and AH–CPGMA, respectively.

INTRODUCTION

Anion-exchange celluloses have got great attention in the last decade. Amino ethyl cellulose was prepared by reacting cellulose with 2-amino ethyl sulfuric acid in the presence of sodium hydroxide[1-3] or by reacting cellulose with ethyleneimine.[4-7] A variety of chloro alkyl amines and amino alkyl hydrogen sulfate have been reacted with soda–cellulose[8] to form partial ethers with anion-exchange properties similar to those of 2-aminoethyl cellulose. Diethylamino ethyl cellulose was prepared by reacting B-chloroethyl diethyl amine hydrochloride either with cellulose in the presence of alkali[9-15] or with sodium cellulosate.[16,17] Diethyl amino ethyl cellulose was quaternized with alkyl halides,[18,19] giving rise to quaternary celluloses.

The aim of this work is to prepare anion-exchange celluloses via reacting cellulose–poly(glycidyl methacrylate) graft copolymer (CPGMA) with ammonia, ethyl amine, diethylamine, and triethylamine independently. Factors affecting these reactions, such as time, temperature, liquor ratio, pH, and aminating agent/epoxide molar ratio, are studied as well as characterization of the produced anion exchangers.

EXPERIMENTAL

Materials

Cellulose sheets, rayon grade pulp, kindly supplied by Misr. Co. for rayon and synthetic silk, were ground before use. The average degree of polymerization was determined and was found to be 500.

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Ammonium hydroxide solution (AH) of 25% NH_3, ethylamine solution (EA) of 33% $C_2H_5NH_2$, diethylamine (DEA), and triethylamine (TEA), chemically pure, were used.

Cellulose–poly(glycidyl methacrylate) copolymer (CPGMA) was prepared by grafting glycidyl methacrylate on cellulose pulp using hydrogen peroxide/ ferrous sulfate thiourea dioxide system as initiator according to a method described by Wally et al.[20]
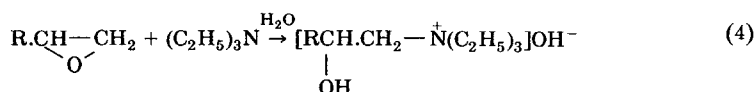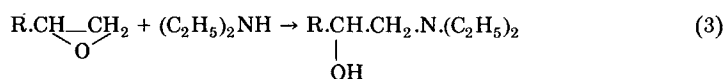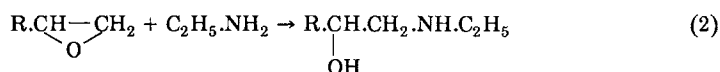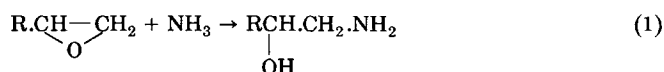
CPGMA Reaction

Round CPGMA (0.5 g) was reacted with an aqueous solution of the agent in a 30 mL stoppered glass bottle. The reaction was carried out in a thermostatic water bath at a specified temperature for a certain period of time. The sample was then thoroughly washed with ice-cold water, followed by acetone, and then dried at 50°C and finally over P_2O_5 for 24 h before analysis. The extent of amination reaction was traced by determining the nitrogen content (%N) using the Kjeldahl method. The remaining epoxide was determined according to a method described elsewhere.[20] Potentiometric titration of the prepared anion exchanger against a standard hydrochloric acid solution was performed according to Benerito et al.[19] Water solubility of the produced anion exchanger was determined according to the method of Kunin.[21]
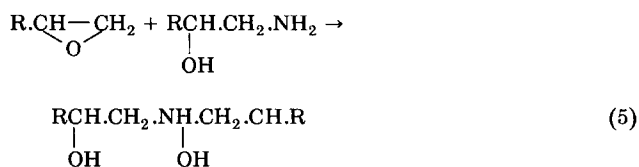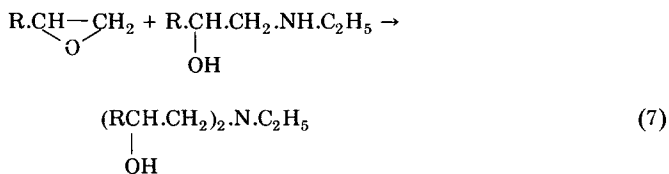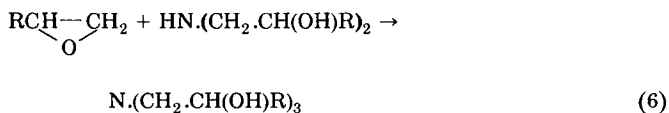
RESULTS AND DISCUSSION

It is known that ammonia and amines react with epoxides in aqueous media.[23-25] Accordingly cellulose–poly(glycidyl methacrylate) graft copolymers (CPGMA) may react with ammonia (AH), ethyl amine (EA), diethyl amine (DEA), and triethyl amine (TEA), in aqueous medium as follows.

(a) Amination reaction:

$$R.CH \overset{}{\underset{O}{\diagdown}} CH_2 + NH_3 \rightarrow \underset{\underset{OH}{|}}{R}CH.CH_2.NH_2 \qquad (1)$$

$$R.CH \overset{}{\underset{O}{\diagdown}} CH_2 + C_2H_5.NH_2 \rightarrow \underset{\underset{OH}{|}}{R}.CH.CH_2.NH.C_2H_5 \qquad (2)$$

$$R.CH \overset{}{\underset{O}{\diagdown}} CH_2 + (C_2H_5)_2NH \rightarrow \underset{\underset{OH}{|}}{R}.CH.CH_2.N.(C_2H_5)_2 \qquad (3)$$

$$R.CH \overset{}{\underset{O}{\diagdown}} CH_2 + (C_2H_5)_3N \overset{H_2O}{\rightarrow} [RCH.CH_2 \underset{\underset{OH}{|}}{—} \overset{+}{N}(C_2H_5)_3]OH^- \qquad (4)$$

(b) Crosslinking reaction:

$$R.CH \overset{}{\underset{O}{\diagdown}} CH_2 + \underset{\underset{OH}{|}}{R}CH.CH_2.NH_2 \rightarrow$$

$$\underset{\underset{OH}{|}}{R}CH.CH_2.NH.CH_2.\underset{\underset{OH}{|}}{C}H.R \qquad (5)$$

$$RCH \overset{}{\underset{O}{\diagup}} CH_2 + HN.(CH_2.CH(OH)R)_2 \rightarrow$$

$$N.(CH_2.CH(OH)R)_3 \qquad (6)$$

$$R.CH \overset{}{\underset{O}{\diagup}} CH_2 + R.CH.CH_2.NH.C_2H_5 \rightarrow$$
$$\underset{OH}{|}$$

$$(RCH.CH_2)_2.N.C_2H_5 \qquad (7)$$
$$\underset{OH}{|}$$

(c) Hydrolysis reaction:

$$R.CH \overset{}{\underset{O}{\diagup}} CH_2 + H_2O \rightarrow R.CH.CH_2.OH \qquad (8)$$
$$\underset{OH}{|}$$
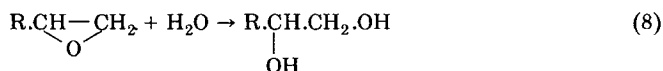
Effect of Time and Temperature

CPGMA (0.226 mol epoxide/100 g) was reacted with the aminating agents (AH, EA, DEA, and TEA) at different temperatures for varying lengths of time. Liquor/CPGMA ratio and aminating agent/epoxide molar ratio were 40 and 4, respectively. Table I shows the extents of amination reactions (expressed as %N) at different times and temperatures.

The data show that, in all cases, the reaction proceed initially fast, before slowing down with time and then leveling off. It is also seen that: (a) The nitrogen content increases by raising the reaction duration and temperature up to 90°C and then decreases most probably due to higher hydrolysis rate at 100°C. (b) The amination extent follows the order DEA > EA > AH > TEA. This can be attributed to the different rates of solubilities, ionization constants, and tendency towards crosslinking reaction of these reagents. The latter increases by increasing the number of labile hydrogen atoms in the aminating agent. The low extent of amination reaction in case of TEA may be attributed to its low solubility[25] and its catalytic effect on homopolymerization of the epoxide.[26,27] (c) These results show that the optimum amination conditions are 90°C and for 90 min.

For studying the mechanism of the reaction between the different amines and CPGMA, the amination extent, and the consumed epoxy groups were determined. Amination (%) was calculated as follows:

$$\% \text{ amination} = \frac{\text{aminated epoxide (mol)}}{\text{consumed epoxide (mol)}} \times 100$$

Table II shows the percentage of amination using AH, EA, DEA, and TEA. The data show that:

(a) For the same aminating agent the amination percent within 60 min is almost constant after which it slightly decreases. This means that both amination reaction and the side reactions (i.e., crosslinking, hydrolysis, and homopolymerization) occur instantaneously throughout the course of the process with almost constant ratio.

TABLE I

Extent of Amination (Expressed as Percent Nitrogen) of Cellulose Poly(glycidyl Methacrylate) Graft Copolymer (Epoxy Content of 0.226 mol/100 g) Using Different Amines at Different Temperatures[a]

Reaction time (min)	Percent nitrogen															
	50°C				70°C				90°C				100°C			
	AH	EA	DEA	TEA	AH	EA	DEA	TEA	AH	EA	DEA	TEA	AH	EA	DEA	TEA
20	0.09	0.17	0.38	0.07	0.15	0.27	0.60	0.14	0.43	1.10	1.70	0.32	0.59	0.76	1.26	0.26
40	0.15	0.29	0.76	0.12	0.27	0.49	1.10	0.22	0.65	1.60	2.30	0.46	0.69	1.20	1.90	0.40
60	0.21	0.37	1.00	0.17	0.35	0.69	1.30	0.32	0.81	1.70	2.60	0.56	0.77	1.47	2.30	0.50
90	0.24	0.51	1.31	0.22	0.44	0.89	1.70	0.39	0.94	1.80	2.70	0.64	0.80	1.71	2.60	0.60
120	0.27	0.60	1.60	0.27	0.50	1.00	1.90	0.45	1.00	1.80	2.80	0.67	0.80	1.80	2.70	0.65
150	0.29	0.65	1.60	0.29	0.54	1.10	2.00	0.47	1.00	1.90	2.80	0.68	0.80	1.80	2.70	0.65
180	0.31	0.67	1.64	0.31	0.55	1.10	2.00	0.47	1.00	1.90	2.80	0.68	0.80	1.80	2.70	0.65

[a] M:L ratio, 1:40; amine/epoxy ratio, 4:1; AH = ammonia; EA = ethyl amine; DEA = diethylamine; TEA = triethyl amine.

TABLE II
Percent Amination of CPGMA Reactions with AH, EA, DEA, and TEA as a Function of Time[a]

Reaction	Time (min)				
	20	40	60	80	100
AH–CPGMA	32.1	33.3	32.5	26.9	26.9
EA–CPGMA	55.5	52.9	51.1	48.3	48.3
DEA–CPGMA	90.9	90.5	90.0	87.1	85.7
TEA–CPGMA	22.2	21.4	22.2	22.2	21.2

[a] Temperature, 70°C; [amine], 1 mol/L; amine/epoxide, 4; liquor/CPGMA, 40.

(b) The percent of amination follows the order: DEA > EA > AH > TEA. This indicates that the percent amination (in case of the first three amines) increases with increasing the number of the labile hydrogen of the amines, which is in accordance with eqs. (1)–(7).

In the case of TEA the lower percent amination is due to its catalytic effect on the polymerization of the epoxides[26,27] as follows:

$$(n + 2)RCH\!-\!CH_2 + N(C_2H_5)_3 \rightarrow$$
$$\underset{O}{\smile}$$

$$RCH.CH_2.N.(C_2H_5)_3$$
$$\underset{O}{\diagdown}$$
$$(R.CH.CH_2)_n$$
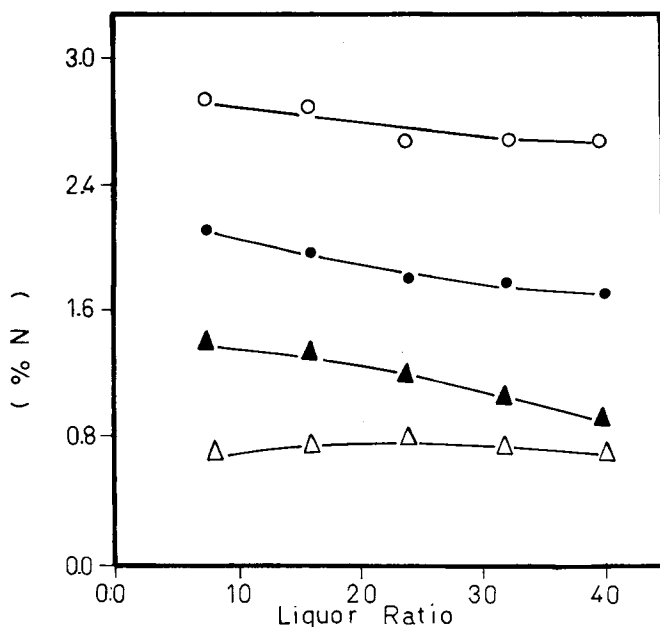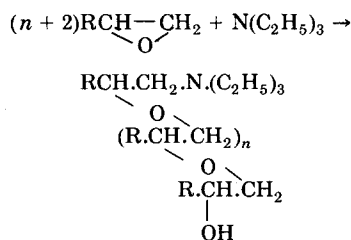$$\underset{O}{\diagdown}$$
$$R.CH.CH_2$$
$$|$$
$$OH$$

Fig. 1.   Effect of liquor ratio (LR) on the amination of cellulose poly(glycidyl methacrylate) graft copolymer. Aminating agent/epoxide molar ratio, 4; time, 90 min; temperature, 90°C; epoxy content, 0.226 mol/100 g; (▲) AH reaction; (●) EA reaction; (○) DEA reaction; (△) TEA reaction.
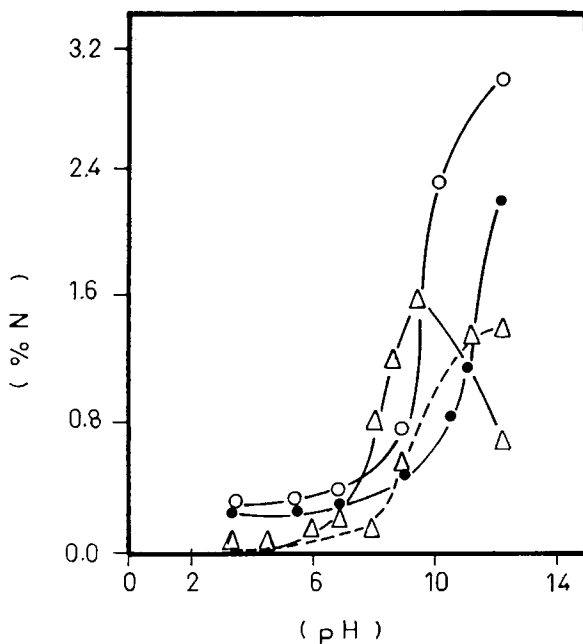
Fig. 2.   Effect of pH on the amination of cellulose poly(glycidyl methacrylate) graft copolymer. Aminating agent/epoxide molar ratio, 4; time, 90 min; temperature, 90°C; epoxy content, 0.226 mol/100 g; liquor ratio, 7.5; (▲) AH reaction; (●) EA reaction; (○) DEA reaction; (△) TEA reaction.

(c) In the case of DEA the side reaction is the hydrolysis reaction which consumes approximately 10% of the epoxide groups.

Effect of Liquor Ratio

The effect of liquor ratio (LR) on the course of amination reactions is shown in Figure 1. CPGMA (0.226 mol epoxide/100 g) was reacted with the aminating agents at 90°C for 90 min. The amount of aminating agent to epoxide was always kept at a molar ratio of 4. It was practically very difficult to carry out these reactions at a liquor ratio lower than 7.5.

Figure 2 shows that the %N decreases with the increase of LR in case of AH, EA, and DEA. However, it remains nearly constant at all LRs in the case of TEA.

In the case of AH, EA, and DEA the increase of LR increases the dilution of the reactants, and hence decreases the interaction between them.

In the case of TEA, the major part of this reagent is in the insoluble form. Any increase of LR in the range used in these experiments has practically no effect on the real concentration of the soluble part which remains nearly constant during the whole period of reactions.

Effect of pH

Figure 3 shows the %N as a function of pH of amination reactions, using CPGMA (of 0.226 mol epoxide per 100 g) at an aminating agent/epoxide
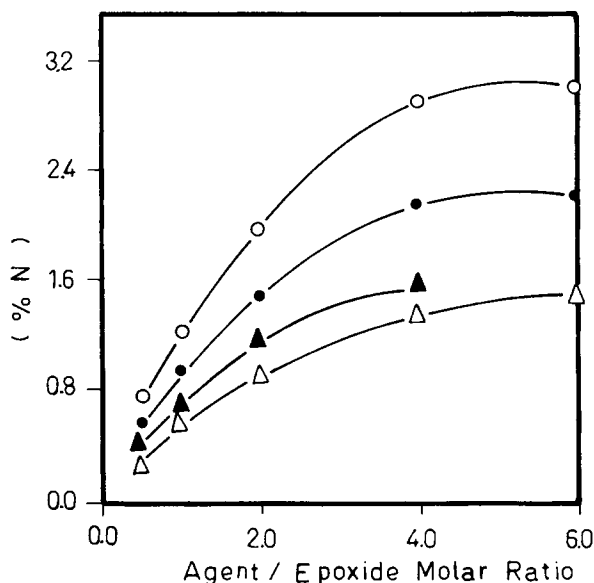
Fig. 3. Effect of the aminating agent/epoxide molar ratio on the amination of cellulose poly(glycidyl methacrylate) graft copolymer. Time, 90 min; temperature, 90°C; epoxy content, 0.226 mol/100 g; pH, original pHs in case of AH, EA, and DEA, while pH was 9.6 in case of TEA; liquor ratio, 7.5; (▲) AH reaction; (●) EA reaction; (○) DEA reaction; (△) TEA reaction.

molar ratio of 4. These reactions were carried out at temperature of 90°C, time of 90 min, and LR of 7.5 as was indicated before. The initial pHs were 11.4, 12.5, 12.6, and 12.3 for AH, EA, DEA, and TEA solutions, respectively. Lower pH values were obtained by addition of acetic acid.

It is observed in case of AH, EA, and DEA that the %N decreases with the decrease of pH. This means that amination is favored in alkaline medium. The addition of acetic acid results in the formation of the corresponding salts with the aminating agents. In this case two spontaneous reactions may take place. The first is the reaction of ammonium or alkylammonium ion with the oxirane ring that gives rise to an increase in the nitrogen content; this reaction predominates in alkaline medium. The second is the reaction of acetate ion with the oxirane ring[28,29] with no fixation of nitrogen; this reaction prevails in acidic medium.

In the case of TEA, it is observed (Fig. 2) that the decrease of pH from 12.3 is accompanied by an increase in nitrogen percent till it attained a maximum at pH 9.6. Further decrease in pH values is accompanied by a decrease in the nitrogen content. This may be due to the catalytic effect of protons on this reaction.[28] Thus, addition of acetic acid exerts H^+ ions that catalyze TEA reaction to reach a maximum at pH 9.6. Further addition of acetic acid has a reverse effect on the percent nitrogen and reaction of acetate ions with the oxirane ring predominates.

Effect of Aminating Agent/Epoxide Ratio

Figure 3 shows the effect of the aminating agent/epoxide molar ratio on the amination of CPGMA (of 0.226 mol epoxide/100 g). Reactions were carried

TABLE III
Capacity (meq/100 g) of the Produced Ion Exchangers

Resin	Effective function group	Epoxy content (m · mole/100 g)			
		90	164	226	300
AH–CPGMA	—NH$_2$	19	53	96	132
EA–CPGMA	—NH(C$_2$H$_5$)	41	94	143	214
DEA–CPGMA	—N(C$_2$H$_5$)$_2$	60	143	200	270
TEA–CPGMA	—Ṅ(C$_2$H$_5$)$_3$	25	65	111	—

out at a temperature of 90°C, a time of 1.5 h and an LR of 7.5. The pH was only adjusted in the case of the TEA reaction using acetic acid.

It is noticed that the nitrogen content increases with the increase of the aminating agent/epoxide molar ratio, up to 4 after which the percent nitrogen tends to level off.

Characterization of the Produced Anion Exchangers

Capacity

Table III shows the capacity of the anion exchangers produced by reacting AH, EA, DEA, and TEA with CPGMA at the optimum conditions. It is seen that: (a) The capacity of the anion exchanger depends on the initial epoxy content of the CPGMA; (b) on using definite epoxy content, the capacity
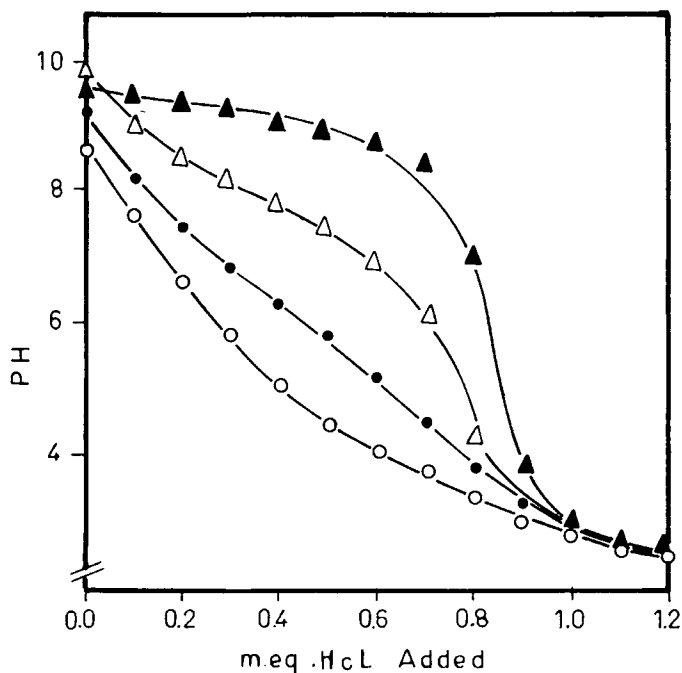

Fig. 4. Potentiometric titration of cellulose poly(glycidyl methacrylate) graft copolymer–(anion exchanger); (○) AH–CPGMA; (●) EA–CPGMA; (△) DEA–CPGMA; (▲) TEA–CPGMA.

TABLE IV
Stability of Anion Exchangers towards Use

Anion exchange	Capacity (meq/100 g)				% Loss in weight		
	0	10 cycles	20 cycles	50 cycles	10 cycles	20 cycles	50 cycles
AH–CPGMA	96	94	93	93	0.44	0.45	0.45
EA–CPGMA	143	144	143	142	0.54	0.54	0.55
DEA–CPGMA	208	208	208	208	0.81	0.83	0.83
TEA–CPGMA	111	110	108	208	1.12	1.24	1.24

follows the order

DEA–CPGMA > EA–CPGMA > TEA–CPGMA > AH–CPGMA
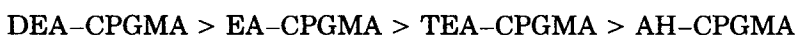
Potentiometric Titrations

Figure 4 shows the potentiometric titration curves of AH–CPGMA, EA–CPGMA, DEA–CPGMA, and TEA–CPGMA anion exchangers. The data show that the titration curve of TEA–CPGMA is like that of a strong base, while the other three exchangers behave like weak base anion exchangers. The strength of these anion exchangers follow the order: TEA–CPGMA > DEA–CPGMA > EA–CPGMA > AH–CPGMA. The strength of a weak anion exchanger (pK_b) can be obtained from the relationship

$$pK_b = 14 - pH\left(\tfrac{1}{2}\right)$$

where $pH(\tfrac{1}{2})$ is the pH at half capacity. pK_b values for these three weak base exchangers are 8.9, 7.6, and 6.1 for AH–CPGMA, EA–CPGMA, and DEA–CPGMA, respectively.

Stability of Anion Exchangers Towards Use

Table IV shows the percent loss in weight as well as the durability of anion exchanger capacity of the CPGMA-based exchangers. The data show that: (a) The main loss in weight takes place in the first 10 cycles of use (each cycle consists of exhaustion, washing, regeneration, and washing), after which no significant change takes place. (b) The percent loss in weight was in the order TEA–CPGMA > DEA–CPGMA > EA–CPGMA > AH–CPGMA, which seems to be connected with strength and capacity difference of these exchangers. (c) The capacity of these exchangers remains practically constant even after 50 cycles of use.

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