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Mono- and Diquaternary Ammonium Cellulose Cottons Prepared in Nonaqueous Media*

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Synopsis

Mono- and diquaternary ammonium cellulose anion exchangers in fabric form were prepared in nonaqueous media by reacting diethylaminoethyl (DEAE)-cotton with an alkyl halide, RX, or a dihaloalkane, $X(CH_2)_nX$, respectively. The alkyl group was varied from CH_3 to $C_{18}H_{35}$, and n varied from 5 to 10 in the dihaloalkanes. Electron emission spectroscopy for chemical analyses (ESCA) showed that approximately 70% of the amino groups in the original DEAE-cotton were free amines. ESCA data showed that highest degree of quaternization of the free amine groups was obtained with CH_3I but that diiodo and dibromo pentanes and decanes were also effective. Diquaternary ammonium cellulose exchangers of high nitrogen content had high wet and conditioned wrinkle recoveries, whereas the monoquaternary ammonium cellulose exchangers showed no improvement in wet or conditioned wrinkle recoveries. The monoquaternaries, like unmodified cottons and DEAE-cottons, were soluble in cupriethylenediamine hydroxide (cuene), and cross sections of their fibers expanded when subjected to layer expansion techniques. All diquaternaries were insoluble in cuene, and their cross sections did not layer.

INTRODUCTION

Weak-base cellulose anion exchangers, particularly diethylaminoethyl-(DEAE)-celluloses, have been used extensively. Conversions of DEAE-celluloses to strong-base quaternary ammonium cellulose anion exchangers were reported by Peterson and Sober,[1] Champetier,[2] and Porath.[3] More recently, the titration curves of DEAE-celluloses and their quaternaries formed with short-chain alkyl halides, such as CH_3I and C_2H_5Br, have been reported[4,5] and compared with titration curves of a quaternary ammonium cellulose anion exchanger formed by reacting cellulose with glycidyltrimethylammonium chloride.[5] The presence of more than one type of basic nitrogen group in the original DEAE-cellulose has also been reported.[6,7] Since biodegradable cellulose anion exchangers are of increasing importance in fractionations and purifications, we have investigated types of basic groups present in a variety of these exchangers. We have been particularly interested in changes of physical and chemical properties of the strong-base anion exchangers with type of organic group used to quaternize the tertiary amine groups of DEAE-cottons. This is a report of the preparation and characterization of a variety of quaternary ammonium cellulose anion exchangers prepared by reacting

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DEAE-cottons containing free amine groups, Cell-O-$C_2H_4\ddot{N}(C_2H_5)_2$, with an alkyl halide, RX, or a dihaloalkane, $X(CH_2)_nX$. With a given alkyl group, X was an iodide, bromide, or chloride. The monoquaternary products, Cell-O-$C_2H_4\overset{+}{N}(C_2H_5)_2R\bar{X}$, contained alkyl groups as small as CH_3 and as large as $C_{18}H_{35}$. In the diquaternary ammonium halides, n varied from 5 to 10. Fabric properties as well as solubilities of the strong-base anion exchangers were drastically changed by use of dihaloalkanes rather than alkyl halides as quaternizing reagents for DEAE-cottons.

EXPERIMENTAL

Reagents

Alkyl halides, dihaloalkanes, and tertiary butanol were reagent-grade chemicals from Eastman Organic Chemicals; the absolute anhydrous methanol was from Mallinckrodt Chemical Works, and β-chloroethyldiethylamine hydrochloride was from Matheson, Coleman, and Bell.

Fabrics

The nonaqueous preparations of sodium cellulosates in fabric form and their subsequent reactions at room temperature with β-chloroethyldiethylamine in *t*-butanol to form the free amine forms of diethylaminoethyl (DEAE)-cottons of varying nitrogen contents have been reported.[8,9] For a DEAE-cotton of approximately 0.6% N, cotton was reacted with 0.2*M* sodium methoxide, and the resultant sodium cellulosate was reacted for 5 hr with a 4% by weight solution of β-chloroethylamine in *t*-butanol. The fabric of 4.0% N required a 1.25*M* sodium methoxide solution to prepare the sodium cellulosate of higher degree of substitution. The cellulosate was subsequently reacted for 24 hr with a solution of β-chloroethyldiethylamine. The free amine form of the fabrics was then reacted again with 1.25*M* sodium methoxide and subsequently with β-chloroethyldiethylamine for another 24 hr.

Preparation of Monoquaternary and Diquaternary Ammonium Celluloses

The DEAE-cottons containing from about 0.5% to 4.0% nitrogen in free amine form were washed free of *t*-butanol with absolute methanol and then refluxed for about 5 hr in an ethanolic solution of about 10–20% of the alkyl halide or dihaloalkane. Treated fabrics were then washed in ethanol and dried.

Chemical Analyses

Nitrogen contents of all modified cottons were determined by the Kjeldahl method and reported as milliequivalents per gram of fabric (meq N/g fabric).

All quaternized DEAE fabrics were analyzed by conventional analytical procedures for halogen and halide ion and reported as meq X or $\bar{X}$ per gram of fabric.

Techniques of electron emission spectroscopy for chemical analyses

(ESCA) were applied to the DEAE-cottons before and after the quaternization reactions. A Varian IEE spectrometer Model VIEE-15 that had a MgK_α x-ray source was used. Spectra were obtained on samples of fabric and on samples of fabrics that had been ground to pass a 20-mesh screen. All binding energies were given against a Cl_s line of 285.6 electron volts (eV) as reference. Spectra were analyzed for relative amounts of nitrogen of high and low binding energies.

Titrations

Anion exchange fabrics in salt form were cut in a Wiley mill to pass a 20-mesh screen and regenerated to the base form in excess 0.05*M* NaOH. An accurately weighed sample of sufficient weight on the dry basis to furnish about one milliequivalent of replaceable anion was added to a specially designed titration flask containing exactly 50.00 ml of 1*M* NaCl solution prepared in conductivity water and kept in a nitrogen atmosphere. Experimental details were reported previously.[4] All pH measurements were made to 0.01 pH unit with a Beckman research pH meter.

Textile Testing

Physical properties of fabrics measured by standard ASTM methods were conditioned wrinkle recovery angles by Monsanto Tester,[10a] warp breaking strength, and elongation at break on strip ravelled to 80 threads,[10b] and abrasion resistance by flex method.[10c] Wet wrinkle recovery angles were determined as described previously.[11]

RESULTS AND DISCUSSION

Electron emission spectroscopy for chemical analyses (ESCA) was developed by Siegbahn[12] for use in obtaining information of the oxidative state and chemical environment of atoms in solid samples. Its use in determining

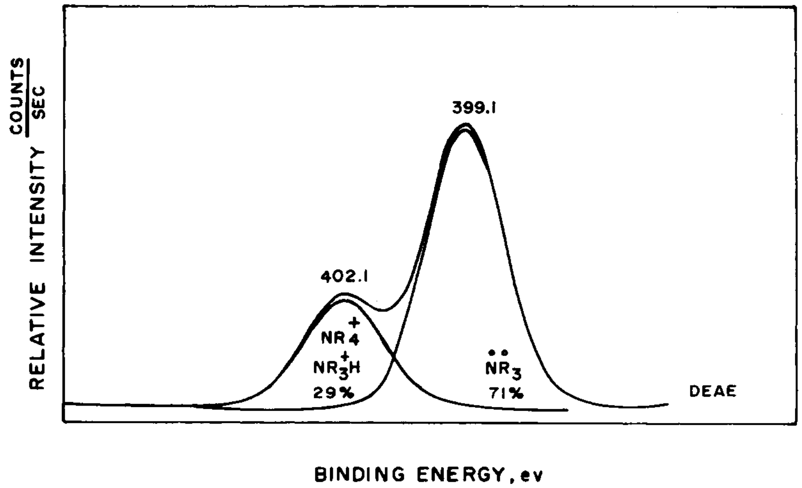

Fig. 1. Nitrogen 1_s ESCA spectrum of diethylaminoethyl (DEAE)-cotton prepared in nonaqueous medium from sodium cellulosate and β-chloroethyldiethylamine.

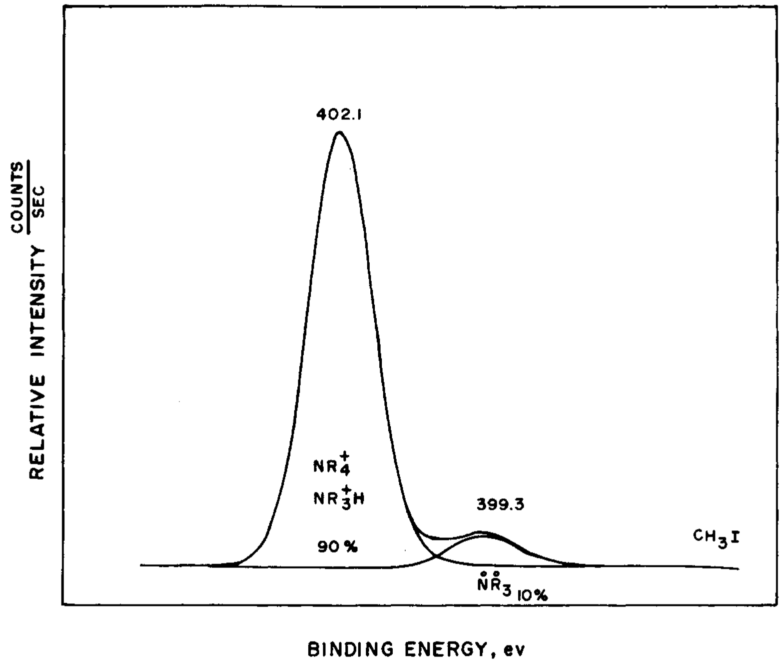

Fig. 2. Nitrogen 1_s ESCA spectrum of a DEAE-cotton after its quaternization with CH_3I.

binding energies of the $N1_s$ electrons in a series of inorganic and organic salts as well as in neutral molecules containing nitrogen has been reported.[13,14] Application of ESCA techniques to the analyses of DEAE-cottons showed presence of two types of nitrogen atoms with binding energies of 402.5 and 399.5 eV for the $N1_s$ electrons.[7]

A typical ESCA spectrum of the $N1_s$ electrons of a DEAE-cotton prepared in nonaqueous medium is shown in Figure 1, and that of the DEAE-cotton after quaternization with CH_3I, one of the most effective quaternizing reagents, is shown in Figure 2. Binding energies in eV are indicated on the deconvoluted curves. The DEAE-cottons contain about 70% free amine groups in which the nitrogen has the lower binding energy of about 399 eV. The higher binding energy is characteristic of a quaternized nitrogen. On the basis of ESCA spectra of pure compounds, it is possible to differentiate between free amine, $\ddot{N}R_3$, and quaternary ammonium ions, $\overset{+}{N}R_4$, as in the latter the binding energy of the $N1_s$ electron is 3 eV higher than in the free amine.[13] However, the binding energy of the $N1_s$ electron in a quaternary group having one hydrogen, $\overset{+}{N}R_3H$, differs from that in an $\overset{+}{N}R_4$ group by only 1 eV. This difference cannot be detected with the MgK_α x-ray source used in this study. In the preparation of DEAE-cottons, excess β-chloroethyldiethylamine can react as an alkylating reagent to quaternize some of the originally formed tertiary DEAE groups on cellulose. Or, hydrolysis of the chloroethylamine could result in the formation of a hydrochloride at some of the free tertiary amine sites. Such side reactions to form $\text{Cell-OC}_2H_4\overset{+}{N}(C_2H_5)_2(C_2H_4)\ddot{N}(C_2H_5)_2\bar{X}$ or $\text{Cell-OC}_2H_4\overset{+}{N}(C_2H_5)_2H\bar{X}$ might account for the two types of basic groups reported in the titrations of certain

TABLE I

Binding Energies of $N1_s$ Electrons of Cellulose Anion Exchangers[a]

Cellulose anion exchanger	Post treatment[b]	$(BE)_1$, eV $\overset{+}{N}R_4\overline{Cl}$ or $\overset{+}{N}R_3H\overline{Cl}$	$(BE)_2$, eV $\ddot{N}R_3$	$(BE)_1 - (BE)_2$, eV
DEAE	air	402.0	399.1	2.9
DEAE	HOH	402.0	399.2	2.8
DEAE	NaOH	402.3	399.6	2.7
DEAE	HCl	402.0	399.1	2.9
QI	air	402.9	400.2	2.7
QI	HOH	403.0	400.3	2.7
QI	NaCl	402.1	400.0	2.1
QI	NaOH	401.8	399.5	2.3
QI	HCl	401.8	399.5	2.3

[a] DEAE is diethylaminoethyl cotton in the free amine form; QI is DEAE after being quaternized with methyl iodide; $(BE)_1$ and $(BE)_2$ are binding energies in electron volts of quaternary and tertiary amino nitrogens, respectively.

[b] 0.1*M* solutions of acid, base, or salt were used in exchange treatments.

DEAE-celluloses[6] and explain the existence of two types of nitrogens with different binding energies as observed in ESCA spectra of DEAE-cottons.[7]

Data in Table I illustrate that the binding energies of the $N1_s$ electrons do not change appreciably as the anion of the DEAE-cotton or its quaternary is exchanged. However, with DEAE-cottons, relative areas under the two peaks change. It has been reported[7] that the lower energy component is increased at the expense of the higher binding energy component by treatment of a DEAE halide with sodium hydroxide.

Table II shows the high and low binding energies of the $N1_s$ electrons in the mono- and diquaternary ammonium celluloses investigated. Relative amounts of two forms of nitrogen are given as calculated from peak areas of ESCA spectra. In addition, an estimate of amount of DEAE-cotton quater-

TABLE II

Analyses of Quaternized DEAE-Cottons

	DEAE-Cottons of 0.6% N				DEAE-Cottons of 4.0% N			
			% Quaternized				% Quaternized	
Quaternization reagent	$N1_s$ Binding energies, eV		ESCA	Halide analyses	$N1_s$ Binding energies, eV		ESCA	Halide analyses
Iodomethane	402.7	400.0	69	89	402.7	399.3	80	95
1-Iodopentane	402.5	399.9	63	45	401.8	398.8	60	46
1,5-Diiodopentane	402.5	400.0	67	100	401.9	399.3	42	57
1-Iododecane	402.4	399.8	58	77	402.1	399.2	53	53
1,10-Diiodododecane	402.5	399.8	59	77	402.3	399.5	69	63
1-Iodooctadecane	402.9	400.4	46	80	402.1	399.1	42	26
Bromoethane	402.1	398.8	66	69	401.7	398.6	70	57
1-Bromopentane	402.5	400.1	58	54	401.5	398.4	52	17
1,5-Dibromopentane	401.7	399.4	55	66	401.8	398.8	67	41
1-Bromodecane	401.9	399.0	64	56	401.8	398.8	47	12
1,10-Dibromodecane	402.3	399.8	72	82	401.9	398.8	57	54
Chloropropane	402.3	399.4	30	27	401.9	398.9	30	25
1-Chloropentane	402.2	399.5	33	36	401.5	398.3	33	25
1,5-Dichloropentane	401.8	399.1	50	75	402.0	398.9	34	23
1-Chlorodecane	402.2	399.3	35	28	402.1	399.0	29	24
1,10-Dichlorodecane	402.7	399.7	42	34	401.9	398.9	28	21
DEAE-Cotton control	402.5	399.8	30		402.1	399.1	29	

nized on the assumption that all halide ion present is associated with a quaternary group is also given. It is to be noted that ESCA, although performed on ground samples of fabric exchangers, is a surface analysis only. These data show that neither the high binding energy peak (approximately 402 eV) nor the low binding energy peak (approximately 399 eV) is shifted significantly with change of halide ion, change of length of alkyl group, or with amount of amino groups within cellulose matrix. Greatest degree of quaternization was with the methyl iodide, and no significant quaternization was obtained with the chlorides. Of interest were the rather large degrees of quaternization with the diiododecane and with the dibromopentane.

ESCA spectra of the quaternary ammonium cellulose anion exchangers were also analyzed for shifts in binding energies of the halide with the type of alkyl group used to quaternize the DEAE-cottons. ESCA peaks in the vicinity of 620 eV, characteristic of the $I3d_{5/2}$ electrons, those of binding energies of 69 and 70 eV, characteristic of the $Br3d_{5/2}$ and $Br3d_{3/2}$ electrons, respectively, and those of the $Cl2p_{3/2}$ and $Cl2p_{1/2}$ electrons at 200 and 202 eV, respectively, were analyzed. With all mono- and diquaternary iodides, a single peak at 619.0 eV was obtained. The mono- and diquaternary bromides were characterized by a single peak that varied in binding energy from 65 to 69 eV. All DEAE-cottons after reaction with an alkyl chloride or dichloride gave one peak with a binding energy of 198 eV.

Fabric Properties

In earlier studies of the esterification of cotton in nonaqueous media,[15] it was shown that some built-in lubrication and conditioned as well as wet recovery could be imparted to cottons via monofunctional reagents that introduced long chain hydrophobic groups, such as palmitoyl or stearoyl groups. However, quaternization of tertiary amine groups in DEAE-cottons of low and high nitrogen contents with alkyl halides in which the alkyl group varied from a methyl to the octadecyl group resulted in fabrics of decreased wet wrinkle recoveries. Regardless of chain length of the alkyl group, conditioned wrinkle recoveries were equivalent to those of the DEAE-cotton controls even when a high degree of conversion to the monoquaternary was real-

TABLE III
Recovery Properties of Cotton Fabrics Containing Diquaternary Ammonium Groups

	DEAE-Cottons of 0.6% N			DEAE-Cottons of 4.0% N		
	Wrinkle recovery, (W + F)°			Wrinkle recovery, (W + F)°		
Dihalo alkane	Wet	Conditioned	Quaternary form, % N	Wet	Conditioned	Quaternary form, % N
$C_5H_{10}I_2$	157	190	100	305	280	57
$C_5H_{10}Br_2$	145	183	66	301	294	41
$C_5H_{10}Cl_2$	125	187	75	222	168	23
$C_{10}H_{20}I_2$	152	192	77	316	241	63
$C_{10}H_{20}Br_2$	155	172	82	—	260	54
$C_{10}H_{20}Cl_2$	165	188	33	—	122	21
DEAE control	189	183	—	223	124	—

ized. In contrast to earlier results of esterification of cottons, breaking strengths, elongations at break, and resistance to flex abrasion were not significantly improved by quaternization of DEAE-cottons with long-chain alkyl groups.

Data in Table III show that improved wrinkle recoveries were realized only when diquaternary ammonium celluloses were prepared from the DEAE-cottons of high nitrogen content. With DEAE-cottons of 0.6% nitrogen, no significant improvement in conditioned recovery was obtained regardless of the degree of conversion of the tertiary amino groups to diquaternary groups. However, there was a significant decrease in wet recovery. Only the diiodo and dibromo alkanes were effective in quaternizing enough tertiary amino groups of the DEAE-cottons of high nitrogen content to produce fabrics with high wet and high conditioned recovery angles. Some test fabrics curled too much in water to permit measurement of wet recovery angles. However, changes in moisture content or regain did not correlate with behavior of some of these fabrics in water. The percentages of moisture content and moisture regain of a DEAE-cotton of 4.0% N were 7.37% and 7.95%, respectively, com-

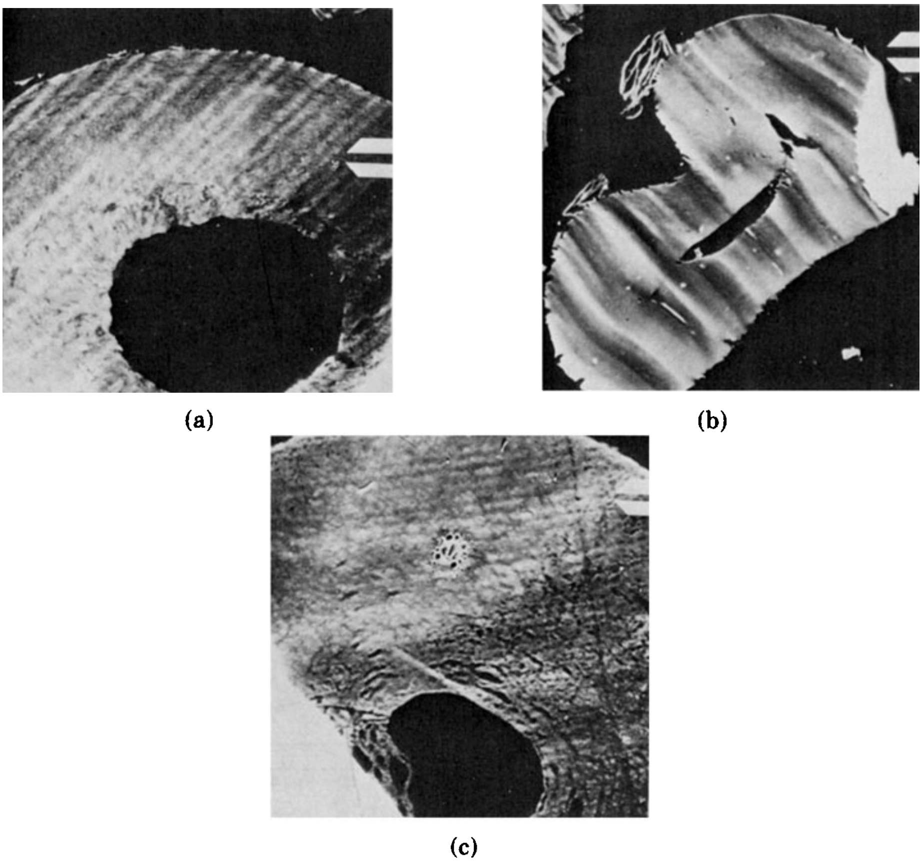
(a) (b) (c)

Fig. 3. Electron micrographs of methyl methacrylate expansion patterns of ultrathin cross sections of fibers removed from chemically modified cottons: (a) expansion pattern typical of diethylaminoethyl (DEAE)-cotton prepared in nonaqueous medium; (b) DEAE-cotton after quaternization with 1,5-diiodopentane to form a diquaternary; (c) DEAE-cotton after quaternization with 1-iodopentane to form a monoquaternary.

pared to values of 5.67% and 6.01% for the unmodified cotton control. After conversion to the diquaternary with either a dibromo or diiodo alkane, moisture content and moisture regain values were never more than 1.0% higher than the respective values of the DEAE-cotton controls. Regardless of degree of substitution, within the range studied, none of the diquaternary halides dissolved in water. X-Ray diffractograms of DEAE-cottons before and after quaternization with the dihalo alkanes showed no significant differences. With the high N content fabrics, patterns of cellulose I and cellulose II were present.

Microscopical Examinations

All DEAE-cottons and those reacted with alkyl halides were soluble in cupriethylenediamine hydroxide solution (cuene). Only DEAE-cottons reacted with dihaloalkanes were insoluble in cuene. Such insolubility in cuene has been attributed to presence of crosslinks between cellulosic chains. In the instances of reaction with a dihaloalkane, $X(CH_2)_nX$, intermolecular crosslinks would result in formation of diquaternary ammonium groups on different cellulosic chains. Even ultrathin cross sections of fibers of those DEAE-cottons quaternized with dihaloalkanes were insoluble in cuene.[16]

A typical electron micrograph of a cross section of a fiber from a DEAE-cotton showing layer expansion[17] is shown in Figure 3a. Cross sections of fi-

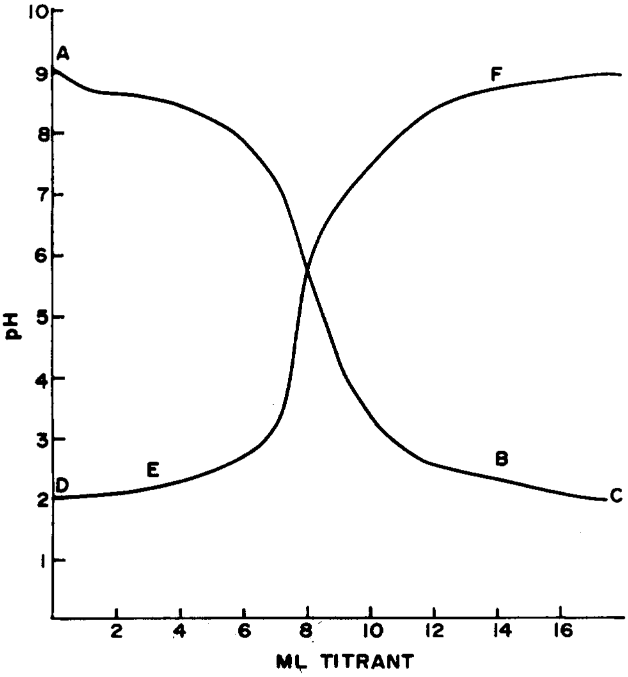

Fig. 4. Potentiometric titration curves for a diquaternary ammonium cellulose anion exchanger prepared from a DEAE-cotton of 0.61% N in free amine form and 1,5-diiodopentane. Curve ABC represents a sample containing 1.44 meq of N in the regenerated base form in 50.00 ml of 1*M* NaCl vs. 0.1020*N* HCl; curve DEF is the titration curve of the chloride form of the diquaternary, in slight excess HCl, vs. 0.1020*N* NaOH. Segments AB and EF represent titrations of exchangers.

bers from unmodified cotton also form concentric layers. Cross sections of those fibers from diquaternary exchangers showed either no layering or a small degree of layering, depending on the degree of conversion to the diquaternary form. For example, the solid cross section shown in Figure 3b is typical of a DEAE-cotton after reaction with 1,5-diiodopentane, an effective quaternizing reagent. Quaternizations of DEAE-cottons with all alkyl monohalides yielded cross sections that expanded and layered as shown in Figure 3c, which is that of a DEAE-cotton after reaction with 1-iodopentane.

Potentiometric Titrations

The diquaternary ammonium cellulose iodides and bromides were regenerated to the base forms in dilute aqueous NaOH and then titrated against standardized HCl in excess NaCl. The resultant chloride forms of the diquaternary exchangers in the presence of a slight excess of HCl were then titrated against standardized NaOH. Behaviors and shapes of the titration curves of the diquaternaries were not significantly different from those reported earlier for the monoquaternaries formed by reacting DEAE-cottons with the usual alkylating reagents, namely, either CH_3I or C_2H_5Br.[4] Typical titration curves illustrated in Figure 4 are for the diquaternary exchanger formed with the 1,5-diiodopentane.

Figure 5 shows similar curves obtained with the quaternary of the longest alkyl halide investigated. Curve ABC for the exchanger formed with 1-io-

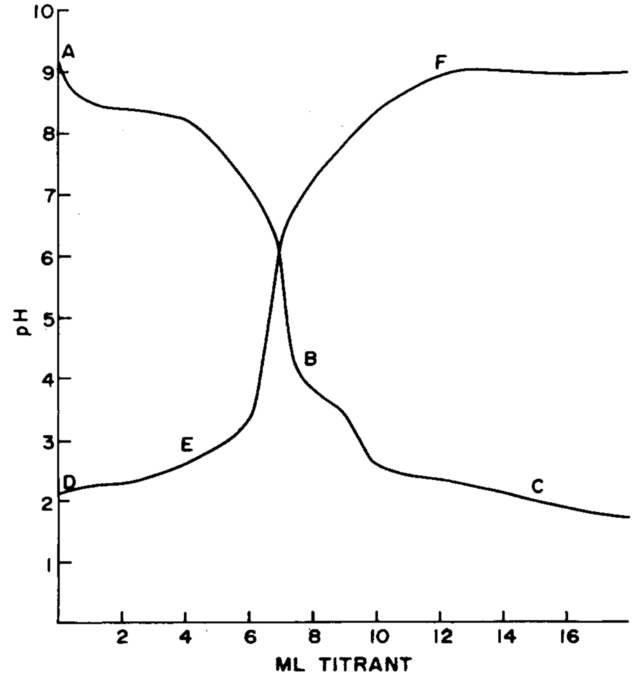

Fig. 5. Potentiometric titration curves for a monoquaternary cellulose anion exchanger prepared from a DEAE-cotton of 0.52% N in free amine form and 1-iodooctadecane. Curve ABC represents a sample containing 0.70 meq of N in the regenerated base form in 50.00 ml 1*M* NaCl vs. 0.1020*N* HCl; curve DEF is the titration curve of the chloride form of the quaternary in slight excess HCl vs. 0.1020*N* NaOH. Segments AB and EF represent titrations of the exchanger.

dooctadecane shows an unexplained break beyond the theoretical endpoint B. The long hydrophobic alkyl group attached to the charged nitrogen may have acted as a surface active reagent in entrapping a titrable impurity. The anomalous break was not observed in the reverse titration curve, DEF, of the chloride form versus NaOH.

SUMMARY

Mono- and diquaternary ammonium cellulose anion exchangers in fabric form were prepared in nonaqueous media by reacting (DEAE)-cotton in which most of the DEAE groups are in the free amine form with an alkyl halide, RX, or a dihaloalkane, $X(CH_2)_nX$, respectively. Electron emission spectroscopy was used to study effects of varying the halide with a given carbon chain length on the degree of conversion of the DEAE-cotton to the mono- or diquaternary ammonium cellulose. Effects of the number of carbon atoms in the alkyl group or dihaloalkane on the degree of quaternization and on final properties were determined. With a given carbon chain length, ion exchange and fabric properties of the monoquaternary ammonium cellulose exchanger differed from those of the respective diquaternary ammonium cellulose exchanger.

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