

Cellulosates of Group IA Metals—Their Preparation and Reactivity with β -Chloroethyldiethylamine*

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Synopsis

Mercerized cotton printcloth converted to a cellulosate of lithium, sodium, potassium, rubidium, or cesium by reaction with metal methoxide is a good substrate for the preparation of diethylaminoethyl (DEAE) cotton at low temperatures in nonaqueous media. The pretreatment to form the cellulosate of the alkali metal does not adversely affect mechanical properties of the cotton fabric. There is no advantage to using a cellulosate other than sodium cellulosate in reactions with β -chloroethyldiethylamine to form DEAE cotton. The reaction occurs in organic solvents of low and high dielectric constants. The hydrochloride of the amine rather than the free amine can be used to prepare DEAE cotton, provided the ratio of reactants is within specific limits. Consideration has been given to the mechanism of the reaction.

INTRODUCTION

Previously, conversion of cotton cellulose to a weak base anion exchanger, diethylaminoethyl (DEAE) cotton, was accomplished by application of 2-chloroethyldiethylamine hydrochloride prior to a treatment with aqueous bases.¹⁻³ Recently, by utilizing sodium cellulosate as the substrate, DEAE cotton of relatively high capacities was prepared in a totally nonaqueous system at room temperature.⁴ The latter method requires the use of the free amine rather than the 2-chloroethyldiethylamine hydrochloride.

More recently, the efficiency of converting cellulose to the cellulosate ion by using alkali metal alkoxides other than sodium methoxide in nonaqueous media was considered. This report deals with the extensive work with the methoxides of lithium, sodium, and potassium and limited experiments with methoxides of rubidium and cesium. Data are given for the reactions of cellulosates (of group IA metals) with 2-chloroethyldiethylamine under different conditions of time, temperature, concentration, and reaction medium. In addition, reactions between sodium cellulosate and the hydrochlorides of chloroalkylamines are reported.

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EXPERIMENTAL

Reagents. The 2-chloroethyldiethylamine was prepared from the hydrochloride according to the method described by McBay.⁵ All amine hydrochlorides, reagent-grade chemicals, were used without further purification. Sodium and lithium methoxides were obtained from Matheson, Coleman, and Bell Co.; potassium methoxide, from Pfaltz Bauer, Inc.; rubidium metal, from Alfa Inorganics; cesium metal, from Research Organic/Inorganic Chemical Co.

Alkoxide Solutions. Lithium, sodium, and potassium methoxide solutions were prepared by slowly adding the stock methoxides to anhydrous methanol. The rubidium and cesium methoxides were prepared by adding the metal to absolute methanol at Dry Ice-acetone temperatures as described by Ting.⁶ Molarities of the alcoholate solutions were determined by the addition of excess standardized acid and a back titration with standardized base to the phenolphthalein endpoint.

Fabrics. Desized, scoured, and bleached cotton printcloth (80 × 80), weighing 3.12 oz/yd², was used as the untreated control. Fabrics were premercerized for 30 min in 23% aqueous NaOH, washed free of excess base, neutralized with dilute acetic acid, and then washed with deionized H₂O. The fabrics were then solvent exchanged by washing five times with anhydrous methanol.

Preparation of Cellulosates. The cellulosates were prepared by a method similar to that described by Schwenker and Pacsu.⁷ The anhydrous cellulose fabric (10-g sample) was rolled and placed in 600 ml of a solution of the desired alkali metal alkoxide of known molarity for 1 hr at room temperature. After removal, the fabric was washed free of excess base with tertiary butanol. The fabrics were then stored in *t*-butanol saturated with dry N₂.⁴

Preparation of Anion Exchange Cottons. Prior to subsequent reactions in solvents other than *t*-butanol, the cellulosates were exchanged three times with the solvent to be used. The cellulosates, impregnated with the reaction solvent, were immersed in 250 ml of solution of the 2-chloroethyldiethylamine or one of the amine hydrochlorides and allowed to react at a given temperature for a specified period. Fabrics were washed in dilute acetic acid, then washed in hot tap water for 30 min, ironed dry, and allowed to air equilibrate for 24 hr before being subjected to chemical analyses or fabric testing.

Determination of Metal Ions in Cellulosates. Within each cotton fabric being converted to the cellulosate were rolled three smaller pieces of fabric of known weights. After conversion to the desired cellulosate, each of these fabrics was washed with *t*-butanol. Each fabric was then placed in 200 ml of deionized H₂O and allowed to stand for 24 hr. A known amount of standard HCl was added, and the excess acid was back-titrated with standardized NaOH. Triplicate analyses were used to determine the degree of conversion to the cellulosate. Results are reported as milliequivalents of metal ion per gram of original fabric (meq Me⁺/g fabric).

Analyses of Anion Exchange Celluloses. Alkali celluloses, which were only partially reacted with amine or amine hydrochloride, were also analyzed for metal ion remaining after conversion to the anion exchange celluloses. Such fabrics (10 g) were washed three times in *t*-butanol to remove unreacted amine and then placed in 300 ml of water and allowed to stand overnight. Fabrics were subsequently squeezed dry, removed from the solutions, washed in dilute acetic acid and water before being dried, and analyzed for nitrogen. The solutions were titrated to determine the amount of NaOH present and thus estimate the amount of unreacted sodium cellulosate. Nitrogen, as determined by the Kjeldahl method, was reported as milliequivalents of nitrogen per gram of fabric (meq N/g fabric) in the anion exchangers.

Textile Testing. Breaking strengths were determined by the strip method (80-thread count width) on a Scott Tester,^{8a} conditioned (dry) wrinkle recovery angles were determined by the Monsanto Method^{8b} with a 500-g weight, and abrasion resistance was valued by the flex method.^{8c} Wet wrinkle recovery angles were determined as described previously.⁹

RESULTS AND DISCUSSIONS

Alkali Metal Cellulosates

The previously reported method of preparing alkali metal cellulosate by use of sodium methoxide in methanol^{7,10} was applied by Berni⁴ to cotton fabrics. In the latter study, the degree of conversion to the cellulosate increased with the concentration of the sodium methoxide and with the degree of swelling of the starting cellulose. In a continuation of this study, we now report the effect of alkali metal ion of the methoxide on the conversion of cotton printcloth or of premercerized printcloth to the corresponding cellulosates.

In Figure 1 are graphed the degrees of cellulosate formation expressed as milliequivalents of metal ion per gram of fabric (meq/g) as a function of the molarity of the metal methoxide solution. These data are for solutions of methoxides more concentrated than 0.25*M* and for reaction times of 30 min at 25°C. Lines represent least-squares lines through experimental points. Both cotton (1A) and mercerized cotton (1B) showed an increase in conversion with an increase of the molarity of a given alkali metal methoxide.

With unmercerized fabric, the amount of alkali metal cellulosate formed increased with size of the metal ion only with the lowest molarity of alkali methoxide. At the higher concentrations of methoxides, the sodium methoxide gave a higher yield of metal ion cellulosate than did the lithium or potassium methoxides.

With premercerized fabrics, the amount of alkali metal cellulosate formed increased with size of the metal ion when Li⁺, Na⁺, and K⁺ methoxides of less than 1-molar concentration were used. At the highest molarities of

methoxides, sodium methoxide gave the highest yield of metal ion cellulose. Use of the larger cations Rb^+ and Cs^+ as the methoxides did not increase the amount of alkali metal cellulose formed. In Figure 1B, slopes of the least-squares lines were 1.58, 1.26, 1.24, 1.16, and 1.10 for Na^+ , K^+ , Cs^+ , Li^+ , and Rb^+ methoxides, respectively. These values indicate greatest change in amount of cellulose formation with increase in molarity of the methoxide for the sodium methoxide. It should be noted, however, that in the preparation of the celluloses of Li^+ , Na^+ , and K^+ from which data shown in Figure 1B were obtained, the starting fabric for these three

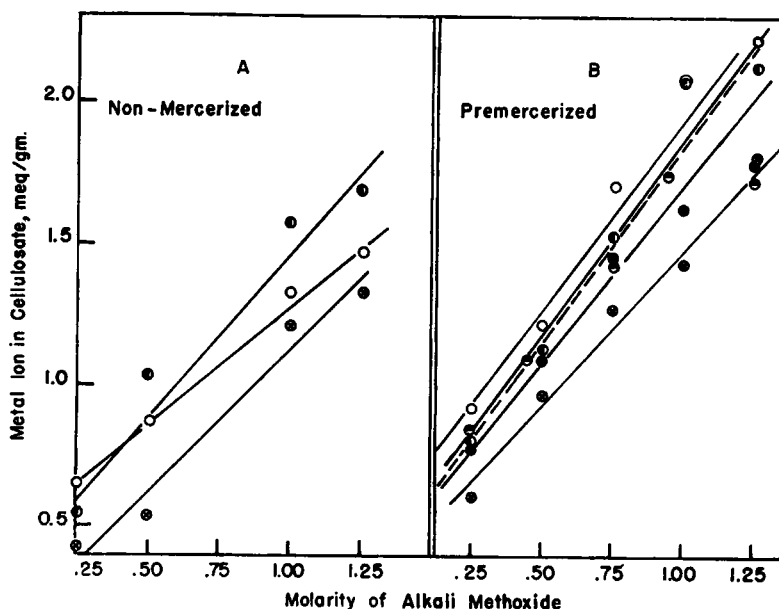


Fig. 1. Variation of metal ion content (meq/g) of cellulose with molarity of alkali methoxide used: (A) cotton fabric soaked first in DMF overnight; (B) premercerized cotton fabric. After either initial treatment, fabrics were solvent exchanged with methanol and then soaked in methanolic solutions of (\otimes) lithium methoxide, (\circ) sodium methoxide, (\bullet) rubidium methoxide, or (\ominus) cesium methoxide, for 30 min at 25°C. After unreacted methoxide was washed out with *t*-butanol, metal ion concentration was determined by titration.

celluloses was premercerized and solvent exchanged in the same container at the same time. The fabric utilized for the Rb^+ and Cs^+ celluloses, while from the same roll of untreated fabric, was premercerized and solvent exchanged by a like procedure, but at a different time.

Alkali metal celluloses of lithium, sodium, and potassium were neutralized with dilute acetic acid and then washed in hot tap water. Fabric properties of these regenerated unmodified fabrics, shown in Table I, indicate little change due to the treatment with the alkali metal methoxide.

TABLE I
Fabric Properties of Regenerated Cellulosates^a

Metal methoxide		Wrinkle recovery angles ($W + F$), ^b /degrees		Breaking strength, % retained	Elongation at break, %
Metal ion	Molarity	Wet	Cond.		
Li	0.25	200	162	78	37
Li	0.50	218	160	85	31
Li	1.00	220	159	97	32
Li	1.25	215	178	95	33
Na	0.25	210	158	97	31
Na	0.50	200	187	103	33
Na	1.00	222	188	80	31
Na	1.25	214	182	100	33
K	0.25	204	178	105	32
K	0.50	211	173	119	33
K	1.00	207	160	103	33
K	1.25	207	167	98	31
Control ^c	—	221	189	(57 lb)	27

^a Premercerized, water-free 80 × 80 cotton fabric, soaked in 250 ml methoxide at 25°C for 30 min, washed free of excess base with *t*-butanol, neutralized in dilute acetic acid, washed in hot tap water.

^b Average of three Monsanto recovery angles.

^c Premercerized, solvent-exchanged cotton fabric, washed three times with *t*-butanol, then soaked in dilute acetic acid solution and washed in hot tap water.

DEAE Cottons from Alkali Metal Cellulosates

Alkali metal cellulosates (10-g samples) prepared from premercerized cotton and containing various amounts of metal ion were reacted for 16 hr at 30°C with 10 ml 2-chloroethyldiethylamine in 240 ml *t*-butanol. Data in Figure 2 show variation in nitrogen content (expressed as milliequivalents of nitrogen per gram of fabric) of the DEAE cotton products as a function of the concentration of metal ion, Me⁺, in each cellulosate reagent.

At the higher metal ion concentrations, the amount of nitrogen begins to be independent of the metal ion concentration. It is apparent that the efficiency, (meq N/g)/(meq Me⁺/g), of converting the cellulosates to DEAE cotton decreases as the metal ion concentration increases. For any given metal ion concentration, the cellulosates of sodium and potassium are more efficient than those of rubidium and cesium, which are more efficient than the cellulosates of lithium. With all metal cellulosates, it is possible at the lowest metal ion concentrations to achieve an efficiency greater than 1. This indicates that the reaction is simply not one of reacting the amine at the site of every cellulosate ion.

Cellulosates of lithium, sodium, and potassium, prepared from premercerized fabrics and containing a given amount of metal ion per gram of cellulosate, were reacted for 16 hr with various molarities of the amine in *t*-butanol at 30°C. In Figure 3A are depicted changes in nitrogen con-

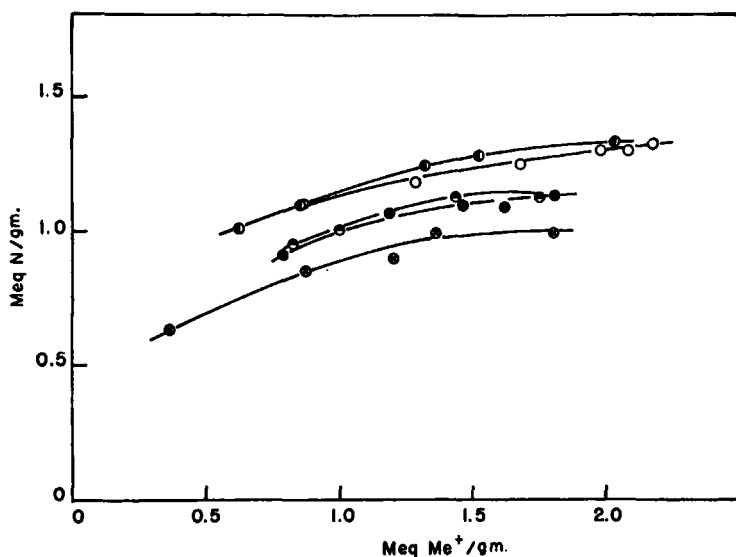


Fig. 2. Variation of nitrogen contents of DEAE cottons prepared from celluloses of various metal ion concentrations. Celluloses of indicated amounts of (\otimes) Li, (\odot) Na, (\circ) K, (\bullet) Rb, or (\ominus) Cs were immersed in 10 ml 2-chloroethyldiethylamine in 240 ml *t*-butanol for 16 hr at 30°C.

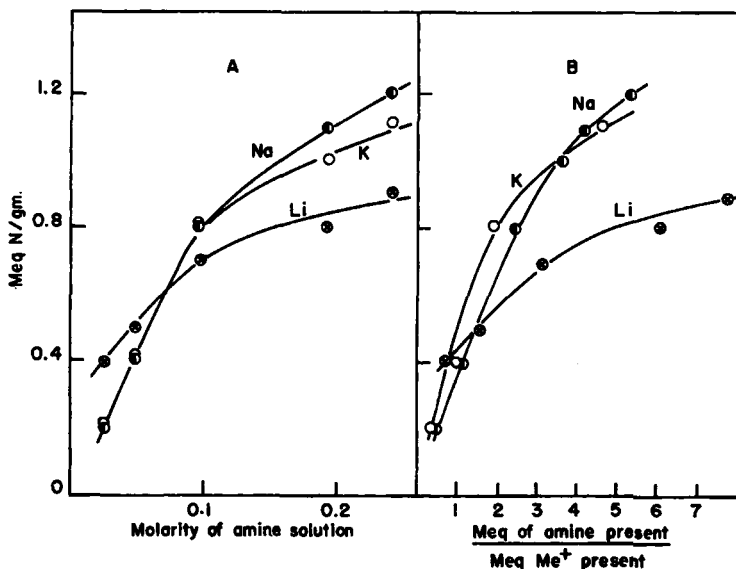


Fig. 3. (A) Variation of nitrogen contents of DEAE cottons prepared from approximately 9.5 g celluloses of a given metal ion content with molarity of β -chloroethyldiethylamine in *t*-butanol. Celluloses containing (\otimes) 0.8 meq Li⁺ per g, (\odot) 1.19 meq Na⁺ per g, (\circ) 1.34 meq K⁺ per g of fabric were reacted with indicated amount of 2-chloroethyldiethylamine for 16 hr at 30°C. (B) Variation of nitrogen contents of some fabrics vs. ratio of meq amine reactant/meq metal ion in cellulose.

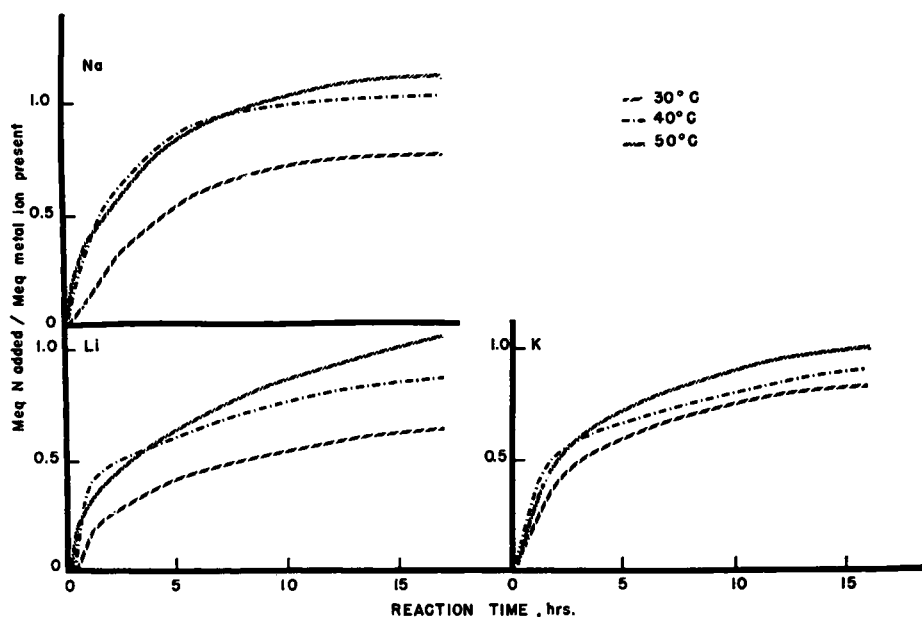
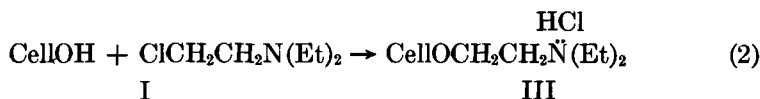
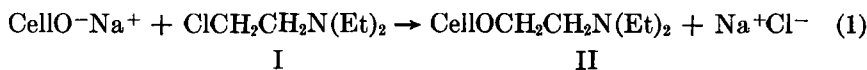


Fig. 4. Change of nitrogen content (meq/g) with time and temperature of reaction of alkali metal cellulosates with 0.27M β -chloroethyldiethylamine in *t*-butanol. Cellulosates contained 1.2–1.4 meq metal ion/g fabric.

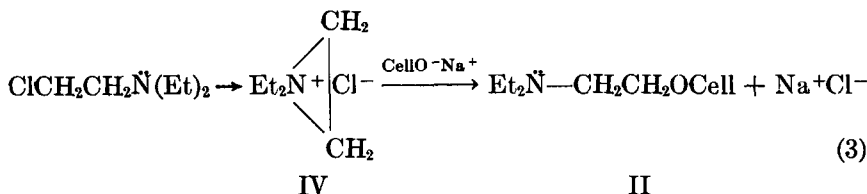
tents of the anion exchange product with molarity of amine used for reactions with cellulosates containing 8.5 meq of Li^+ , 11.8 meq of Na^+ , and 13.5 meq of K^+ per 10 g of reactant. There is an increase in conversion to DEAE cotton as the molarity of the amine solution increases. In Figure 3B, the meq N/g fabric product are plotted versus equivalent ratios of reactants, that is, meq of amine to meq metal ion, for each reaction. With the sodium and potassium cellulosates, the graphs are almost identical, and there is a decrease in slope at a ratio greater than 2. For the lithium cellulosate, the decrease in slope is observed at a ratio greater than 3. Initially, with cellulosates of sodium and potassium (Fig. 3B), the meq N/g product doubles as the ratio of meq amine/meq Me^+ doubles. This indicates that the rate of addition of nitrogen is first order with respect to amine until the product contains 0.8 meq N/g.

The effects of increasing temperature from 30° to 50°C on the reactions between alkali cellulosate and chloroalkylamine are shown in Figure 4. These graphs represent data obtained when cellulosates containing from 1.2 to 1.4 meq of Li^+ , Na^+ , or K^+ ions per gram fabric were reacted with 0.27M β -chloroethyldiethylamine in *t*-butanol. For the sodium and potassium cellulosates, the amine/ Me^+ ratio was between 2 and 3. In every instance, little reaction occurred during the first 20 min, and there was little difference during the first 5 hr in rates of reaction at 40° and 50°C. The temperature effect was least for the potassium cellulosate.

One mechanism for the formation of DEAE cotton is the direct reaction of the cellulosate ion with the chloroalkylamine as shown in eq. (1). Another is the reaction of the cellulose hydroxyl with the amine as shown in eq. (2):



The hydrochloride, III, can then react with a sodium cellulosate to regenerate a cellulosic hydroxyl group. Thus, both by eqs. (1) and (2), 1 meq of sodium cellulosate would be used per meq of nitrogen added to cotton. With the free amine,¹¹ it has been shown that diethylethylenimmonium chloride (IV) is formed. DEAE cotton (II) can be formed from IV according to eq. (3) as well as eq. (1):



The heterocyclic compound IV, relatively stable at low temperatures, can be formed only when there are free electrons on the amino nitrogen of the chloramine. Both I and IV can exist in the same solution.¹¹ The product, IV, can also react with the cellulose hydroxyls as well as with cellulosates. Both eqs. (1) and (3) involve ionic reactants, and one would expect to see a change in reaction as the dielectric constant of the solvent is varied. Reaction (3) would be more dependent upon dielectric constant of the medium, as even the formation of IV is favored by aprotic solvents of high dielectric constants.

To investigate the influence of solvent dielectric constants on the reaction, cellulosates of lithium, sodium, and potassium were reacted with solutions of β -chloroethyldiethylamine in solvents covering a wide range of dielectric constants. In an attempt to remove the *t*-butanol, which was used in the preparation of the cellulosates, fabrics were soaked three times in the respective solvents. However, it should be noted that the complete removal of *t*-butanol, which might be held in the solvated shell of ions in the alkali cellulosates, is difficult. Data in Table II show the conversions of the cellulosates to DEAE cotton in terms of meq of N per gram of product in solvents of various dielectric constant for reactions of 16 hr at 30°C. With the cellulosate of 0.68 meq Li⁺/g, there was complete conversion in solvents of dielectric constants ranging from 2.3 to 37.6. In DMSO, the

TABLE II
Effect of Solvent on Conversion of Cellulosates to Diethylaminoethyl Cotton^a

Solvent		Milliequivalents N/g sample from		
Name	Dielectric constant	LiOCell	NaOCell	KOCell
CCl ₄	2.2	0.55	0.73	0.67
Dioxane	2.2	0.51	0.68	0.71
Benzene	2.3	0.72	0.87	0.79
Chloroform	4.8	0.73	0.90	0.91
<i>t</i> -Butanol	10.9	0.78	1.13	1.11
Nitrobenzene	34.8	0.86	1.14	1.23
Dimethylformamide	37.6	0.76	1.16	1.14
Dimethylsulfoxide	48.9	1.07	1.39	1.21

^a Cellulosates of Li, Na, and K prepared from premercerized fabric and containing 0.68 meq Li⁺/g, 1.07 meq Na⁺/g, and 1.12 meq K⁺/g metal ion, respectively, were reacted at 30°C in 10 ml 2-chloroethyldiethylamine in 240 ml solvent for 16 hr.

efficiency, meq N/meq Me⁺, was 1.6. With the cellulosates of sodium and potassium, the efficiency approached unity as the dielectric constant approached 11; and in DMSO, the efficiency was less than with the lithium cellulosate.

Avny and Rebenfeld¹⁰ reported that with sodium cellulosate as a substrate for polymerization with vinyl-type monomers, some sodium cellulosate remained unreacted after the polymerization was complete. We have found the same to be true in the reaction of sodium cellulosates with 2-chloroethyldiethylamine. Cellulosates containing 1.9 meq Na⁺/g fabric were reacted with 0.27M amine in *t*-butanol for specified periods at 30°C. Figure 5 shows the variations in the nitrogen content of these fabrics

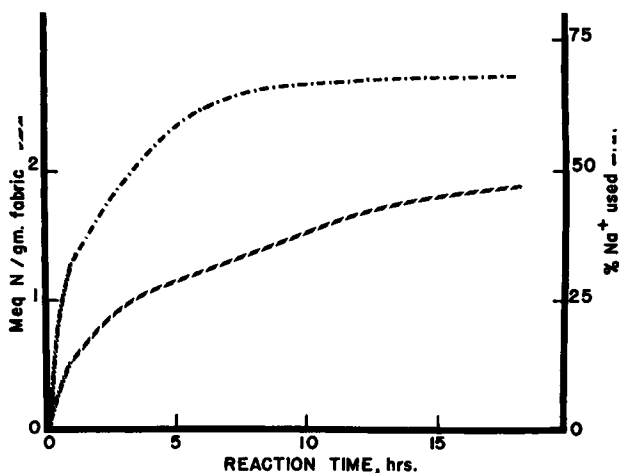


Fig. 5. Changes in nitrogen content added (meq/g) and changes in % Cello⁻ Na⁺ used with time of reaction of Cello⁻ Na⁺ containing 1.91 meq Na⁺/g reacted with 0.27M β -chloroethyldiethylamine in *t*-butanol at 30°C.

TABLE III
Effect of Time on Reaction of Sodium Cellulosate and 2-Chloroethyldiethylamine*

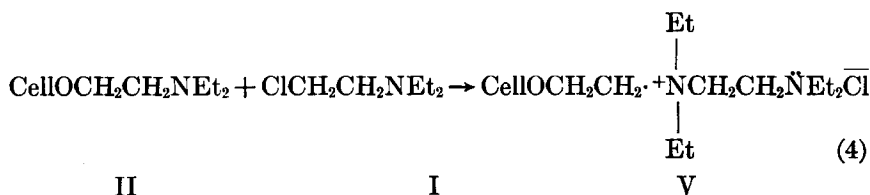
Reaction time, hr	Sodium cellulosate, meq Na ⁺			Nitrogen added, meq	meq N added/meq Na used
	Initial	Final	Used		
1	9.21	6.27	2.94	2.43	0.83
2	9.21	5.88	3.33	4.02	1.21
3	9.40	4.53	4.87	4.68	0.96
4	9.17	4.22	4.95	5.59	1.13
5	9.32	3.86	5.46	5.97	1.09
6	9.24	3.58	5.66	6.26	1.11
7	9.38	3.04	6.34	6.63	1.05
18	9.36	3.28	6.08	8.94	1.47

* Sodium cellulosate containing 1.9 meq Na⁺ per g fabric is immersed in a solution of 10 ml 2-chloroethyldiethylamine in 240 ml *t*-butanol at 30°C.

(meq N/g) and of percentage of original Na⁺ ion used with time of reaction. The rate at which sodium ion is used during the reaction decreases after 5 hr. After 18 hr, only two thirds of the available sodium ions of the cellulosate were used.

Data in Table III show that during the initial periods of reaction, 1 milliequivalent of sodium cellulosate is used per milliequivalent of nitrogen added. After two thirds of the originally available sodium cellulosate are used, the ratio of meq N added to meq Na⁺ used exceeds unity. In other experiments, we have found the meq N/g may exceed the original amount of metal ion in the cellulosate. This usually occurs after long times of reaction.

According to the previous equation, 1 equivalent of Na⁺ ion is used for every equivalent of N added. The following eq. (4) for the quaternization of some of the tertiary amine groups of DEAE cotton is proposed to account for the excess of nitrogen added over the amount of Cello⁻ used:



The chloroalkylamine (I) would react at the cellulosate sites initially. Then, after formation of product II, reaction between I and II or between IV and II can occur as depicted in eq. (4) to form some product V. Product V should contain both strong base and weak base groups. The titration curve of product V, after regeneration to the basic form, versus HCl showed two distinct breaks. The curve was similar to that of a mixture of a strong base and a weak base cellulose anion exchanger. Nitrogen may also be added to the fabric without consumption of sodium cellulosate ions if the

tertiary amine groups of the first product, II, act as an in situ catalyst for the base-catalyzed reaction of cellulosic hydroxyl groups with the amine according to eq. (2).

Reactions of Sodium Cellulosate with Hydrochlorides of Chloroalkylamines

In the preparation of DEAE cotton in an aqueous medium, where an excess of external base is used, the hydrochloride salt of 2-chloroethyldiethylamine can be used. However, with the alkali metal cellulosates in nonaqueous media, it was thought necessary to convert the hydrochloride salt to the free amine. This is time consuming and, in addition, the free amine has a tendency to dimerize to tetraethylpiperazinium dichloride¹¹ which is nonreactive toward cellulose. Also, the free amine irritates the eyes. Such disadvantages of the free amine can be circumvented by use of the hydrochloride salt of the amine.

Initially, with the alkali cellulosates, saturated solutions of the hydrochloride of 2-chloroethyldiethylamine in *t*-butanol were used. Although some nitrogen was added, the amount was much less than achieved with the free amine.

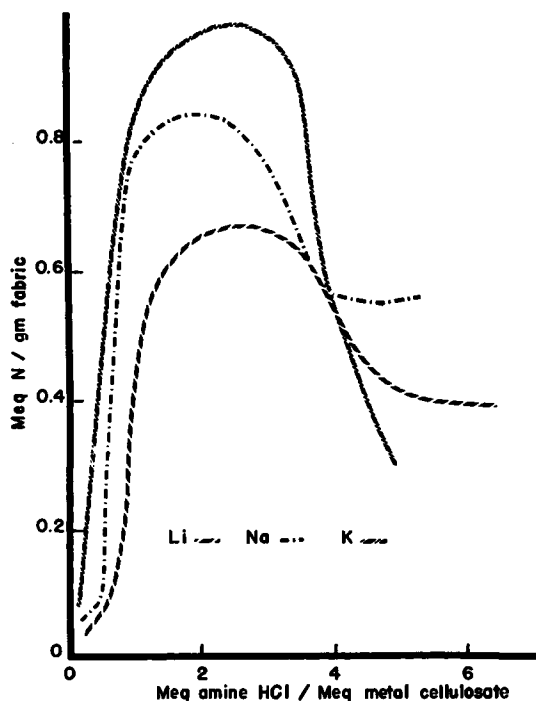


Fig. 6. Changes in nitrogen contents of fabric products (meq/g) with equivalent ratios of β -chloroethyldiethylamine HCl/CellO⁻. Cellulosates of Li containing 1.16 meq Li⁺/g, of Na containing 1.56 meq Na⁺/g, and of K containing 1.72 meq K⁺/g sample reacted for 16 hr at 50°C in 250 ml of *t*-butanol solution containing varying quantities of 2-chloroethyldiethylamine hydrochloride.

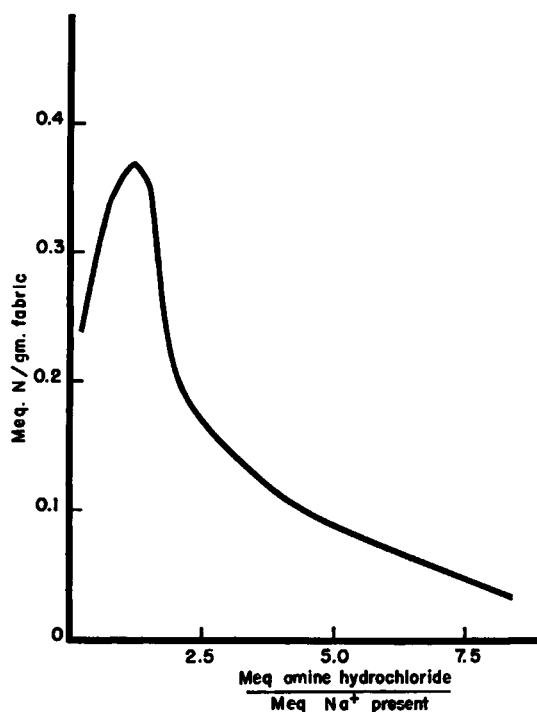
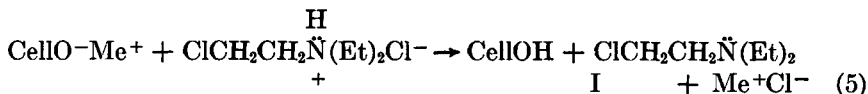


Fig. 7. Change in nitrogen contents of fabric products (meq/g) with equivalent ratio of 2-chloropropylidimethylamine HCl/Cello⁻ Na⁺. Sodium cellulosate containing 1.7 meq Na⁺/g fabric reacted for 16 hr at 50°C in *t*-butanol containing varying amounts of 2-chloropropylidimethylamine hydrochloride.

Cellulosates of lithium, sodium, and potassium were immersed in *t*-butanol solutions containing varying amounts of 2-chloroethyldiethylamine hydrochloride at 50°C. This temperature was selected in order to dissolve an amount of amine hydrochloride equivalent to the 0.27*M* free amine used in preceding experiments. As shown in Figure 6, maximum nitrogen (meq N/g fabric) resulted when the ratio of meqs amine hydrochloride to meq of metal ion was approximately 2. The amine hydrochloride will not react with cellulose unless base is present in aqueous media. Probably, in nonaqueous media, the first step in the addition of nitrogen is the conversion of the hydrochloride to the free amine by the basic cellulosate, as follows:



The free amine (I) can react according to eqs. (1), (2), or (3) to yield product II or III. In addition, the aziridine ring of compound IV can open in the presence of salt or by HCl catalysis and react with hydroxyls of cotton.

Sodium cellulosate (containing 1.7 meq Na^+ /g) was reacted for 16 hr at 50°C with *t*-butanol solutions containing varying concentrations of the following amine salts: 2-aminoethylsulfuric acid (AES), 2-chloroethylamine hydrochloride (CEA), 2-chloropropyl dimethylamine hydrochloride (2-CPDMA), 3-chloropropyl dimethylamine hydrochloride (3-CPDMA), and 2-chloroethyltrimethyl ammonium chloride (CETMACl). Neither AES nor the quaternary salt, CETMACl, reacted. Regardless of ratio of reactants, all fabrics had less than 0.05% N. The hydrochloride of CEA and of 3-chloropropyl dimethylamine (3-CPDMA), which is not capable of forming an aziridinium ion as does the β -chloroethyldiethylamine, were only slightly reactive with sodium cellulosate. The maximum N content was only 0.10%. The most reactive with sodium cellulosate was 2-CPDMA. Even though the latter can form the aziridinium ion, it was less reactive than the hydrochloride of β -chloroethyldiethylamine. Figure 7 is a graph showing the variation of N contents of products with equivalent ratio of reactants when cellulosates of 1.7 meq Na^+ /g were reacted for 16 hr at 50°C in *t*-butanol solutions of various molarities of 2-CPDMA. At every ratio of reactants, the N content was less than obtained with the hydrochloride of β -chloroethyldiethylamine. The latter gave a maximum N content of 0.8% at an equivalent ratio of reactants of approximately 2 (see Fig. 6). With 2-CPDMA, the maximum N content was less than 0.4% and was reached at a ratio between 1 and 1.5.

SUMMARY

Diethylaminoethyl (DEAE) cotton in fabric form has been prepared by reacting cellulosates of lithium, sodium, potassium, rubidium, and cesium with β -chloroethyldiethylamine in *t*-butanol at several temperatures and at various mole ratios of reactants. No advantage in using cellulosates of alkali metals other than sodium was realized. Initially, 1 meq nitrogen was added per 1 meq metal ion in the cellulosate. For long times of reaction, the ratio of meq N added to meq metal ion exceeded unity, and the ratio was higher in solvents of high dielectric constants. The hydrochloride of the amine could be used rather than the amine, provided the molar ratio of hydrochloride to the cellulosate ion was approximately 2.

Mention of a company and/or product by the U. S. Department of Agriculture does not imply approval or recommendation of the company or product to the exclusion of others which may also be suitable.

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