

Sodium Cellulosates—Preparation from Various Alkoxides and Reactivity toward 2-Chloroethyldiethylamine*

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Synopsis

Sodium cellulosates were prepared by reacting premercerized cotton fabrics with sodium salts of selected alcohols. The degree of conversion to the cellulosate was related to the Taft polar substituent constant, σ^* , of the alkoxide R group. Increase in size of the R group in the alkanol series did not decrease the degree of cellulosate formation. The extent of reaction of the cellulosates with 2-chloroethyldiethylamine in tertiary butanol to form diethylaminoethyl cellulose (DEAE-cotton) did not increase with the sodium ion content of the starting cellulosate substrate.

INTRODUCTION

Schwenker and Pacsu¹ reported the conversion of cotton fabric to sodium cellulosate in a nonaqueous system. They found that this substrate was suited for graft polymerization with vinyl monomers. Avny and Rebenfeld^{2,3} studied the physical properties of sodium cellulosate yarns and the reactivity of these cellulosates with acrylonitrile. Berni⁴ reported the preparation of diethylaminoethyl (DEAE) cotton fabrics of high anion exchange capacities by the reaction of sodium cellulosates with 2-chloroethyldiethylamine in nonaqueous media. Recently,⁵ the preparation of cellulosates of metals of the group IA elements and the reactivities of these cellulosates with 2-chloroethyldiethylamine to produce DEAE-cotton fabrics have been reported.

This report considers the effects of various sodium alkoxides on the preparation of sodium cellulosate in fabric form and on its subsequent conversion to DEAE-cotton.

EXPERIMENTAL

Reagents. The hydrochloride of 2-chloroethyldiethylamine, obtained from Michigan Chemical Corp., was used in the preparation of 2-chloro-

* Presented in part at the 160th National Meeting of the American Chemical Society, Chicago, Illinois, September 1970.

ethyldiethylamine according to the method described by McBay.⁶ All alcohols were reagent grade chemicals and were utilized without further purification. Sodium metal was obtained from J. T. Baker Chemical Co.

Alkoxide Solutions. Sodium alkoxides were prepared by the addition of sodium ribbon to the anhydrous alcohols. With the exception of sodium phenoxide, which was prepared in dioxane, each alkoxide was prepared in the corresponding alcohol. Most alcohols reacted immediately at room temperature. The more hindered alcohols (i.e., *t*-butanol, *i*-propanol) required heat to initiate the reaction.

Alkoxide solutions of known molarity ($\sim 0.2M$) were used in preparing the sodium cellulosates. Molarities of the alkoxides were determined by the addition of a measured quantity of excess standardized hydrochloric acid and back titration to the phenolphthalein endpoint with standardized sodium hydroxide.

Premercerization. Desized, scoured, and bleached cotton printcloth (80×80) weighing 3.1 oz/yd² was mercerized for 30 min in 23% aqueous NaOH, washed free of excess base, neutralized with dilute acetic acid, and washed with deionized water until free of acid. The fabrics were then washed five successive times with anhydrous methanol to remove water. The adhering methanol was removed by passing dry nitrogen through the fabrics for 2 hr prior to preparation of the sodium cellulosates.

Sodium Cellulosate Preparation. Details of the preparation have been described previously.⁴ Briefly, the dried fabrics (10-g samples) were loosely rolled and placed in 600 ml of a 0.2M sodium alkoxide solution for 1 hr at room temperature. Solutions were agitated by the dry nitrogen which bubbled through the vessel throughout the reaction time. After removal from solution, fabrics were washed with *t*-butanol until the wash solvent was neutral to water-wetted pH paper. These fabrics were used immediately after preparation for reaction with the 2-chloroethyldiethylamine.

DEAE-Cotton Preparation. Generally, the sodium cellulosate fabrics were immersed in 250 ml of *t*-butanol solutions of 0.27M 2-chloroethyldiethylamine for 3 hr at room temperature. In a few experiments, the reactions were carried out for longer time intervals at room temperature and at 37°C. Fabrics were removed, neutralized by washing in dilute acetic acid, washed in hot tap water, and then washed in deionized water.

Determination of Sodium Ion in Cellulosate. Within each cotton fabric being converted to the cellulosate were placed three smaller test fabrics of known weights. After the final *t*-butanol washing, each test fabric was removed and placed in 200 ml deionized water and allowed to stand overnight in an inert atmosphere. Following the addition of a known volume of excess standard HCl, the solutions were titrated to the phenolphthalein endpoint with standard NaOH. Triplicate analyses were used to determine the degree of conversion to the cellulosates. Results are reported as milliequivalents of sodium ion per gram of original fabric (meq Na⁺/g).

Analyses of DEAE-Cottons. The amount of bound nitrogen was determined by the Kjeldahl method. The results are reported as meq N/g fabric and represent the anion exchange capacities of the DEAE-cottons.

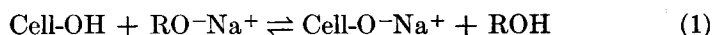
Amounts of sodium cellulosate remaining in fabrics after reaction with the 2-chloroethyldiethylamine were determined as follows: Fabrics were washed free of unreacted amine with *t*-butanol under anhydrous conditions. Fabrics were then soaked in deionized water which forms a milliequivalent of NaOH for each milliequivalent of sodium cellulosate remaining in the fabric. Total milliequivalents of base liberated were determined by titrations and results were reported as meq Na⁺/g fabric remaining in the DEAE-cottons.

RESULTS AND DISCUSSION

Cellulosate Formation

Previously,⁵ it was reported that sodium methoxide was as efficient as any methoxide of group IA metals in methanol for converting cotton fabric into an alkali metal cellulosate. With a given metal alkoxide, the amount of cellulosate formed increased with concentration of the alkoxide; with a given concentration of alkoxide, a higher conversion to cellulosate was obtained with a premercerized cotton than with an unmercerized fabric. Since no advantage was evident in the use of a methoxide other than sodium methoxide, it was of interest to see if the size or nature of the alkoxide anion, RO⁻, rather than the size of the cation, would affect significantly the degree of conversion of cotton to sodium cellulosate. In this study, premercerized fabric was used rather than unmercerized cottons, as one objective was to increase the ion exchange capacities of cottons prepared by reacting 2-chloroethyldiethylamine with the sodium cellulosates.

Conversion of cellulose to sodium cellulosate by its reaction with a sodium alkoxide in nonaqueous media is depicted in eq. (1):



The conversion might be visualized as displacement of hydrogen from the cellulosic hydroxyl groups by the electrophilic Na⁺ ions, or the nucleophilic attack of RO⁻ ions on the cellulose hydroxyl, resulting in the abstraction of hydrogen and the formation of ROH. By either mechanism, the degree of conversion of the cellulose to the cellulosate should be dependent on the relative base strengths of the RO⁻ and the cellulosate (Cell-O⁻) anions. It should be noted that in cellulose, the strength of the Cell-O⁻ anion is dependent on whether it originates from a primary C₆ hydroxyl, from the secondary C₂ hydroxyl, or the secondary C₃ hydroxyl groups.

The basicity of the RO⁻ anions depends on the relative negative charge residing on the oxygen. This charge increases with electron-donating power of the R group. The electron-donating or withdrawing nature of a group depends on its resonance energy and on its polar nature. The latter has been investigated by a study of the basic hydrolyses of selected esters in a given solvent at a given temperature. From many such experiments designed to neutralize steric and resonance effects, a series of values called σ^* , or the Taft polar substituent constants,⁷ have been determined for various R groups. These values were directly related to the logarithms of the

hydrolysis rates of the particular esters. Although σ^* values are empirical, their additives, and the correlations of these values with rate and equilibrium of numerous reactions, give credence to the conclusion that σ^* values are indeed measures of substituent polar effects.

These values were considered in the formation of cellulosate ion from the alkoxide, RO^- . A negative value of σ^* for a particular R group designates the group as electron donating, and such an RO^- anion would be more basic than an RO^- anion in which the R group, with a positive value of σ^* ,

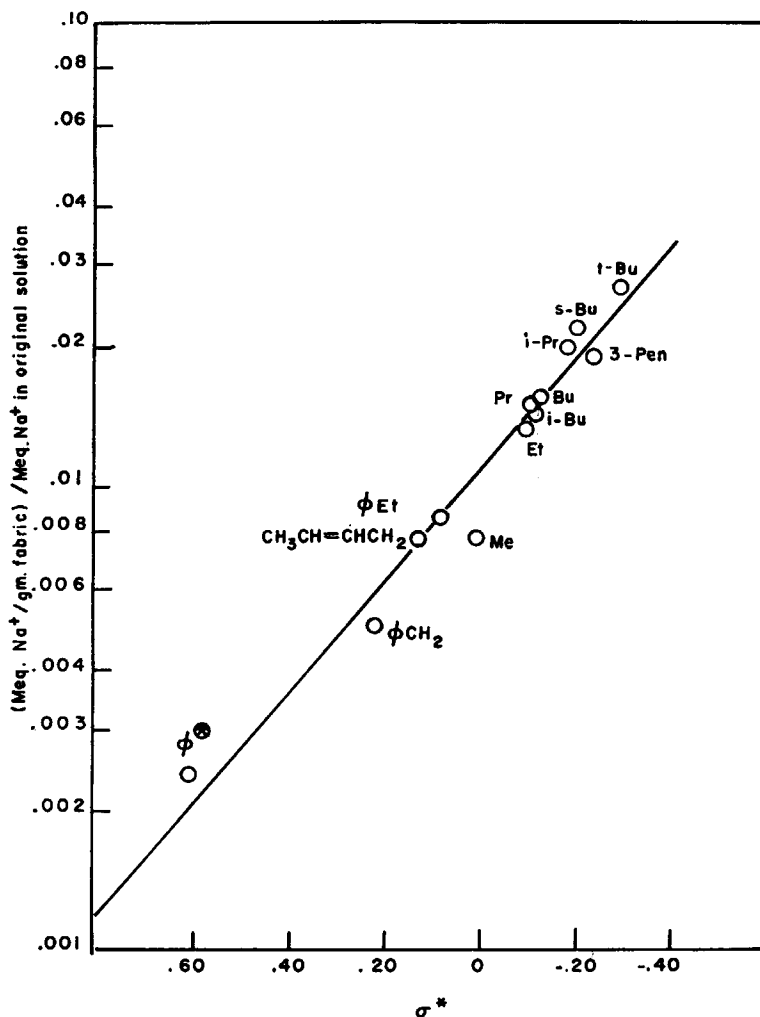


Fig. 1. The degree of conversion of cellulose to cellulosate vs. the Taft polar substituent constants σ^* of various R groups: t-Bu, *t*-butoxide; s-Bu, *s*-butoxide; 3-Pen, 3-pentoxide; i-Pr, *i*-propoxide; Bu, *n*-butoxide; Pr, *n*-propoxide; *i*-Bu, *i*-butoxide; Et, ethoxide; Me, methoxide; ϕEt , $\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{O}^-$; $\text{CH}_3\text{CH}=\text{CHCH}_2$, 2,3-butene-1-oxide; ϕCH_2 , $\text{C}_6\text{H}_5\text{CH}_2\text{O}^-$; ϕ , phenoxide. The \otimes indicates that this reaction was in dioxane rather than phenol.

is electron withdrawing. In an investigation of the effect of the σ^* value of the alkoxide on the conversion of cellulose to sodium cellulosate, it was necessary to consider the concentration of the sodium alkoxides. All sodium alkoxides, of known molarities, were $0.2 \pm 0.02M$. Therefore, the conversion of cotton to cellulosate within 1 hr at room temperature was expressed as milliequivalents of sodium cellulosate per gram of cotton per milliequivalent of sodium alkoxide in the original solutions. Figure 1 is a plot of the log of the conversion of cotton to the cellulosates versus the σ^* values of the R groups of the various sodium alkoxides. The linear relationship indicates excellent correlation between the Taft polar substituent constant σ^* and the degree of cellulosate formation. It also indicates that the steric hindrance of the R group is not a factor in the conversion.

Consideration was also given to the possibility of cotton swelling to different extents in the various alcohols. The degree of conversion to the cellulosate might also be expected to depend on the relative swelling characteristics of the alcohols. However, microscopic examinations indicated that the degree of swelling exhibited by premercerized cotton fabrics soaked in methanol, ethanol, and *t*-butanol was the same. Yet, conversion to sodium cellulosate was most efficient in *t*-butanol.

Under like experimental conditions, we have found the following:

1. Sodium alkoxides of the primary alkanols, with the exception of methanol, are equally effective in the conversion of cotton cellulose to sodium cellulosate.
2. For an alcohol of a given chain length, branching at the carbon directly attached to the hydroxyl increases the degree of conversion to the cellulosate.
3. The presence of unsaturation in the alcohol decreases the effectiveness of the RO^- ion in converting the cellulose to the cellulosate. The effect of unsaturation depends on its proximity to the carbon attached to the hydroxyl group.

Diethylaminoethyl Cotton

In earlier work, where sodium cellulosates were prepared from sodium methoxide,^{4,5} it was reported that approximately $\frac{2}{3}$ of the sodium cellulosate sites could be converted to tertiary amine groups by reacting the sodium cellulosates with 2-chloroethyldiethylamine in nonaqueous media. Although the degree of conversion to DEAE-cotton increased with the concentration of amine, increase in temperature, or with the time of reaction, a complete conversion was not realized in any organic solvent studied thus far. In fact, high-capacity anion exchange cottons could not be prepared simply by increasing the number of sodium cellulosate sites in cotton. That is, the ratio of meq N/g to meq Na^+ /g decreased for cottons containing the highest milliequivalents of Na^+ per gram fabric.

Sodium cellulosates, prepared from the various alkoxides and containing different concentrations of sodium ion, were reacted with $0.27M$ 2-chloroethyldiethylamine in *t*-butanol at room temperature. Figure 2 is a typical

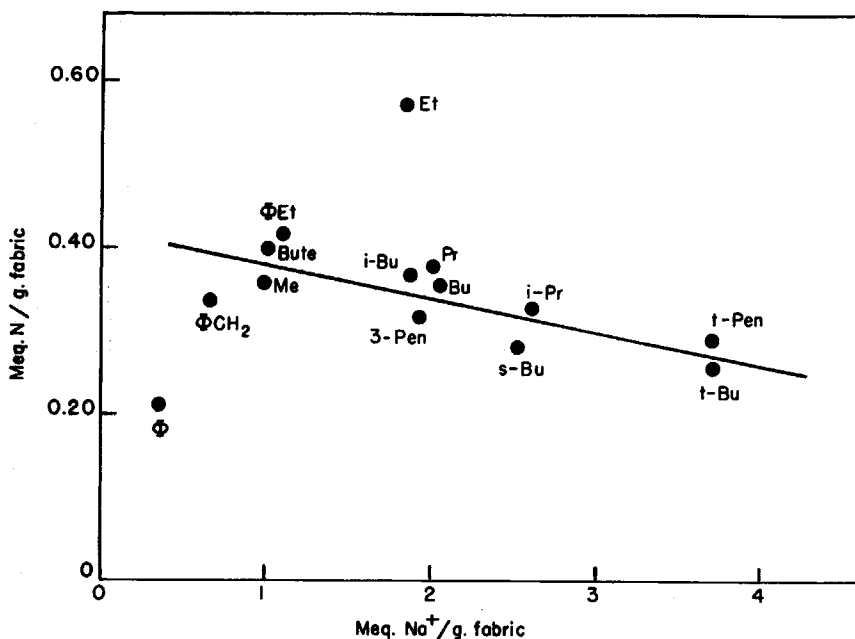
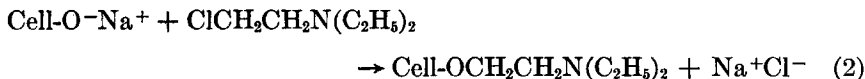


Fig. 2. Variations of nitrogen contents of DEAE-cottons with Na⁺ content of original cellulosates used in preparations. Sodium cellulosates prepared from the alkoxides indicated: t-Bu, *t*-butoxide; t-Pen, *t*-pentoxide; s-Bu, *s*-butoxide; i-Pr, *i*-propoxide; 3-Pen, 3-pentoxide; BU, *n*-butoxide; Pr, *n*-propoxide; i-Bu, *i*-butoxide; Et, ethoxide; Me, methoxide; ϕEt, C₆H₅CH₂O⁻; Bute, 2,3-butene-1-oxide; ϕCH₂, C₆H₅CH₂O⁻; ϕ, phenoxide.

plot of the conversion after 3 hr to DEAE-cotton expressed as meq N/g fabric versus the original sodium cellulosate content expressed as meq Na⁺/g fabric. The line shown represents the least-squares line through all experimental points, with the exception of those for the sodium ethoxide (Et) and sodium phenoxide (ϕ). The line has a slope of -0.04 , with a sample correlation coefficient of -0.76 . Even with the inclusion of all experimental points, the least-squares line has a slope of -0.02 . The degree of DEAE-cotton formation under the stated experimental conditions is independent of the initial sodium ion content of the cellulosate and independent of the sodium alkoxide from which the cellulosate was generated.

The formation of DEAE-cotton from sodium cellulosate and 2-chloroethyl-diethylamine might be considered as a Williamson synthesis. Displacement of halide from the chloroalkylamine by the nucleophilic cellulosate ion via an S_N2 mechanism can be depicted by eq. (2):



An increase in the concentration of cellulosate ions should produce a corresponding increase in the amount of DEAE-cotton, provided sufficient

TABLE I
Analyses of Cottons Before and After Reaction with 2-Chloroethyldiethylamine*

RO-Na ⁺	Orig. CellO-Na ⁺ , meq/g	Reaction time, hr	Temp., °C	Nitrogen, meq/g	Cell-O-Na ⁺ reacted, meq/g	Na ⁺ reacted, %
Methyl	0.67	3	37	0.59	0.52	77
	0.71	23	37	0.96	0.46	64
Ethyl	1.53	3	37	0.78	0.69	45
	1.48	23	37	1.45	1.02	67
	2.05	3	25	0.86	0.90	44
	2.05	6	25	1.00	1.14	55
	2.05	16	25	1.29	1.25	60
<i>n</i> -Butyl	1.75	3	37	0.76	0.69	40
	1.72	23	37	1.47	1.24	73
<i>s</i> -Butyl	2.62	3	37	0.60	0.74	28
	2.50	23	37	1.38	0.73	28
<i>i</i> -Propyl	2.45	3	37	0.74	0.83	33
	2.40	23	37	1.49	1.35	56
<i>t</i> -Butyl	2.40	3	37	0.51	0.53	22
	2.25	23	37	1.06	1.14	50
	2.22	3	25	0.28	0.26	12
	2.23	7	25	0.56	0.42	19
	2.20	16	25	0.86	0.94	42

* Sodium celluloses prepared from indicated alkoxide in the respective alcohol. Sodium cellulosate then reacted with 0.27*M* 2-chloroethyldiethylamine in *t*-butanol at indicated time and temperature.

chloroalkylamine is present for reaction. Data collected do not support this hypothesis. Sodium celluloses containing from 1 to 3.5 meq Na⁺ per gram of fabric reacted to give DEAE-cottons of equivalent nitrogen content during a 3-hr interval.

Side reactions such as the reversal of reaction depicted in eq. (1) and dimerization of the chloroalkylamine to form *N,N'*-tetraethylpiperazinium dichloride, which does not react with cotton, can occur. Nevertheless, a greater amount of DEAE-cotton would be anticipated from those cottons having the greater number of sodium cellulosate sites. It should also be noted that the amount of reaction with the chloroalkylamine will also be dependent upon the position of the ionic charge in the cellulose matrix. Cellulosate ions at secondary hydroxyl sites should be more reactive toward the *t*-butanol in exchanging by a reversal of eq. (1) than those located at the primary hydroxyl sites. Also, cellulosate anions at primary hydroxyl sites react with alkyl halides at different rates than those at secondary hydroxyl sites.

It was shown experimentally that reversal of eq. (1) was negligible when the sodium cellulosate was kept in *t*-butanol under nitrogen. Fabrics (10 g) containing from 0.6 to 4.0 meq Na⁺ per gram of fabric were soaked in 250 ml *t*-butanol for timed intervals up to 16 hr. Titration of deionized water solutions into which the fabrics were soaked, after various timed intervals, showed no loss of Na⁺ ion while fabrics were in the *t*-butanol.

Similar titrimetric analyses of DEAE-cottons were used in conjunction with nitrogen analyses to determine meq Na⁺ in fabrics before and after reaction with 2-chloroethyldiethylamine. Typical data for reactions of sodium cellulosate with 2-chloroethyldiethylamine in *t*-butanol at 37°C and 25°C are given in Table I. In most cases, 1 meq nitrogen was added to the sodium cellulosates per each meq Na⁺ used, regardless of which sodium alkoxide was used in the preparation of the sodium cellulosate. Only in a few instances did the meq N added significantly exceed the meq Na⁺ used. Sodium cellulosates prepared from sodium alkoxides of methyl and *s*-butyl alcohols were the only ones which reacted with the chloroalkylamine to add 2 meq nitrogen per each meq sodium cellulosate used, and this increase in ratio of nitrogen added to Na⁺ used occurred only after long periods of reaction. In every instance, even after long reaction periods, the DEAE-cottons had unreacted sodium cellulosate sites. As reported earlier for sodium cellulosates prepared from sodium methoxide,⁵ approximately 2/3 of the sodium cellulosate sites were used in the formation of DEAE-cottons even after long reaction periods. As indicated in the last column of Table I, the fraction of Na⁺ used was the same for the cellulosates prepared from the sodium alkoxides of the primary alcohols; the fraction of sodium cellulosate sites used in the cellulosates prepared from the sodium alkoxides of the branched alcohols was significantly less.

SUMMARY

The degree of conversion of cotton cellulose to sodium cellulosate can be increased by the use of the sodium alkoxide of a tertiary or secondary alcohol and it can be correlated with the Taft polar substituent constant σ^* of the alkoxide R groups. However, the subsequent conversion of the sodium cellulosates to DEAE-cottons cannot be increased by simply increasing the sodium content of the sodium cellulosates.

Mention of a company and/or product by the Department 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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Received September 22, 1971