

## Properties of Carboxymethylated Cotton Prepared in Nonaqueous Media

DOROTHY M. PERRIER and RUTH R. BENERITO, *Southern Regional Research Laboratory, Southern Region, Agricultural Research Service, U.S. Department of Agriculture, New Orleans, Louisiana 70179*

### Synopsis

Mercerized cotton printcloth was converted to sodium celluloses of various degrees of substitution by reaction with sodium methoxide in methanol. These sodium celluloses were reacted with sodium monochloroacetate in dimethyl sulfoxide at room temperature. The sodium hydroxide pretreatment affected not only the yield of the sodium cellulose but also the degree of conversion of cellulose to carboxymethyl (CM) cellulose. The nonaqueously prepared CM cottons had fabric properties that differed from the properties of CM cottons prepared by conventional aqueous methods. By the nonaqueous method, CM cottons of increased capacity, or degree of substitution (D.S.), were obtained by a one-treatment procedure. These CM cottons in the sodium salt or acid form were insoluble in water and in 23% NaOH. Those of D.S. of about 0.3, when in the acid form, possessed improved wrinkle recovery angles. The salt form of CM cotton acts as a built-in catalyst for the reactions of cotton with methylolated ureas such as dimethylolurea (DMU) and dimethylolethyleneurea (DMEU). However, only DMU was effective in imparting improved conditioned and wet wrinkle recovery to CM cotton. Initial replacement of  $\text{Na}^+$  ions of CM cotton by  $\text{H}^+$  was easily accomplished. After replacement of approximately half of the  $\text{Na}^+$  ions, it was more difficult to replace the remaining half of  $\text{Na}^+$  from CM cottons that had been prepared in nonaqueous media. Affinity of carboxylate ions in CM cottons prepared nonaqueously for cations did not decrease with size of cation even though affinity for  $\text{H}^+$  ions was greatest.

### INTRODUCTION

Carboxymethylated (CM) cotton yarns and threads, prepared aqueously with a degree of substitution (D.S.) of 0.17 to 0.25, become gelatinous and disintegrate in water but do not completely dissolve.<sup>1</sup> CM cotton with a D.S. of 0.3 is reported to be completely soluble in water. A D.S. of 0.3 could only be obtained by repetitive carboxymethylation of the purified cotton and by drastic increase of the reactant ratios. To obtain a D.S. of 0.3, yarns that had been either pressure-kiered or boiled in monoethanolamine were initially impregnated with 15% monochloroacetic acid and then treated with an aqueous 50% NaOH solution. These modified yarns were then retreated with 50% monochloroacetic acid and 50% NaOH solution.<sup>1</sup>

Recently, we have reported on the use of ion exchange cottons prepared aqueously as in situ catalysts for subsequent cellulose etherifications.<sup>2</sup> In this study, sodium cellulosate, prepared in nonaqueous media by the method of Schwenker and Pacsu,<sup>3</sup> was reacted with sodium monochloroacetic in dimethyl sulfoxide (DMSO) to prepare CM cotton in the fabric form.

Ion exchange fabrics with a high D.S. did not dissolve in water even when in the salt form. Effects of time, concentration of sodium cellulosate, concentration of sodium monochloroacetate, and of NaOH pretreatment of cotton before sodium cellulosate formation on CM cotton formation were studied. Fabric properties, ion exchange properties, and the ability of the substituted groups to act as in situ catalysts for subsequent chemical modification of these nonaqueously prepared CM cotton fabrics were determined.

## EXPERIMENTAL

**Reagents.** Sodium monochloroacetate was obtained from American Hoechst Corporation; dimethyl sulfoxide, from Crown Zellerbach; sodium methoxide, from Matheson Coleman and Bell; absolute anhydrous methanol, from Mallinckrodt Chemical Works; monochloroacetic acid, from Eastman Organic Chemicals; and dimethylolethyleneurea, from Badische Anilin and Soda-Fabrik. Dimethylolurea was a laboratory preparation.<sup>4</sup>

**Alkoxide Solutions.** Sodium methoxide was added slowly to methanol with rapid stirring. Molarities of these solutions were determined by titration with standardized acid to the phenolphthalein endpoint.

**Fabrics.** Desized, scoured, and bleached cotton printcloth (80 × 80) weighing 3.12 oz/yd<sup>2</sup> was used as the untreated control. Fabrics were pretreated for 30 min in aqueous base of concentrations ranging from 5% to 23% NaOH, washed free of excess base, neutralized with dilute acetic acid, and then washed with deionized water. The fabrics were then solvent exchanged by washing five times with anhydrous methanol before conversion to sodium cellulosates.

**Preparation of Sodium Cellulosates.** The solvent-exchanged fabrics were rolled and placed in vessels containing solutions of sodium methoxide of desired concentration. The vessels had provisions for agitation by dry nitrogen. After 1 hr of reaction at room temperature, the fabrics were washed free of excess base with tertiary butyl alcohol.<sup>3</sup>

A test fabric of known weight was rolled inside each fabric being converted to the cellulosate. After conversion to the sodium cellulosate, test fabrics were washed with tertiary butanol and then placed in 200 ml deionized water containing a known amount of standardized HCl. The excess acid was back-titrated with standardized NaOH.

**Nonaqueous Preparation of CM Cottons.** The sodium cellulosates were immersed in solutions of 2.5% sodium monochloroacetate in anhydrous DMSO and allowed to react at room temperature for a specified period

under completely anhydrous conditions in containers that allowed for agitation by dry nitrogen. The fabrics were either washed in deionized H<sub>2</sub>O or washed in methyl alcohol. A one-step treatment resulted in a fabric with a carboxymethyl content of approximately 1.7 meq/g, which corresponds to a D.S. of 0.3. Some CM cottons were maintained in the salt form. Others were converted to the acid form by soaking in either aqueous 2% HCl or one-molar acetic acid in methanol and then washing free of excess acid with appropriate solvent.

**Aqueous Preparation of CM Cottons.** Untreated cotton fabric was padded twice to a 100% wet pickup with an aqueous solution that was 8% with respect to both sodium hydroxide and monochloroacetic acid and cured at 125°C for 5 min.<sup>5</sup> The carboxymethyl content of fabric prepared by this method was 0.35 meq/g, which corresponds to a D.S. of 0.06. To yield a fabric with a D.S. of 0.27, this procedure had to be repeated four times.

**Analysis of Carboxyl Content.** The CM cottons were converted to the acid form with 2% HCl in water, washed to remove excess acid, and ironed dry. Weighed samples of the acid forms were placed in distilled water containing a known excess of standard NaOH. The excess base was back titrated with standardized HCl to the phenolphthalein endpoint. This acid method was used to determine the capacity expressed as meqs per gram, or degree of substitution, of carboxymethylated cotton.<sup>6</sup>

**Titrations of CM Cottons.** The cation exchange fabrics in the acid form were ground to pass a 20-mesh screen. After the exchanger in acid form was dried over P<sub>2</sub>O<sub>5</sub> under vacuum to constant weight, an accurately weighed sample containing approximately 0.7 meq of replaceable cation was placed in a specially designed titration flask. Conductivity water was used for all solutions, and titrations were in an inert atmosphere furnished by dried nitrogen. Experimental details for titrations were reported previously.<sup>7</sup> All pH measurements were made to 0.01 pH unit with a Beckman Research pH meter. Ion exchange capacities were expressed as meq/g.

**Cation Exchange Properties of CM Cottons.** The sodium salt forms of CM cottons, ground to pass a 20-mesh screen, were immersed in aqueous solutions of different molar concentrations of salts of various cations. After equilibration periods, supernatant solutions were analyzed for Na<sup>+</sup> ion concentrations by atomic adsorption methods and the amounts of exchanged cations were calculated.

**Chemical Finishing of CM Cottons.** CM cottons in the salt or acid form were padded twice with either a 10% solution of a dimethylolated urea in either water or DMF, dried at 60°C for 7 min and then cured for 5 min at a specific temperature. Fabrics were washed, ironed dry, and air equilibrated before being tested. Extents of reactions were determined by analyses for bound nitrogen and formaldehyde. Nitrogen analyses were by the Kjeldahl method, and formaldehyde analyses were by a chromotropic acid spectrophotometric method.<sup>8</sup>

**Textile Testing.** Physical properties of textiles measured by the standard ASTM methods were conditioned wrinkle recovery angles by Monsanto Tester,<sup>9a</sup> warp-breaking strength and elongation at break on strips ravelled to 80 threads,<sup>9b</sup> and abrasion resistance by the flex method.<sup>9c</sup> Wet wrinkle-recovery angles were determined as described previously.<sup>10</sup>

## RESULTS AND DISCUSSION

In Table I are data typical of CM cottons obtained by the nonaqueous method at room temperature and at 60°C. At room temperature, and with nitrogen bubbling through the container, a D.S. ranging from 0.04 to 0.2 could be obtained with a fabric containing 3.3 meq sodium cellulosate per gram fabric. Even with the large excess of monochloroacetate, complete conversion of all cellulosate sites to carboxymethyl groups, which would have resulted in a D.S. of 0.66, was not realized. Increase of reaction temperature to 60°C resulted in CM cottons of D.S. of approximately 0.25 in shorter reaction periods. Increase in time of reaction at the higher temperature did not increase extent of conversion of cellulosate sites to carboxymethyl groups. When the CM cottons were in the acid form, wet recovery angles were improved considerably. Maximum wet recoveries approaching 300 (W + F)° were obtained at maximum D.S., and only when the exchangers were in the acid form. Only small increases in conditioned recoveries were observed in the acid form of CM cottons.

TABLE I  
Effect of Time and Temperature on Degree of Carboxymethylation\*

Reaction conditions		Carboxymethyl substitution		Wrinkle recovery of acid form, (W+F)°	
Temp., °C	Time, hr	meq/g	D.S.	Wet	Conditioned
25	0.10	0.227	0.037	229	212
	0.25	0.366	0.060	244	191
	0.50	0.510	0.085	243	220
	0.75	0.583	0.100	252	213
	1.00	0.645	0.108	255	229
	2.00	0.817	0.139	276	202
	24.00	1.304	0.299	275	215
	Control				161
60	2.00	1.354	0.238	289	214
	4.00	1.484	0.261	289	205
	6.00	1.461	0.259	285	210
	16.00	1.337	0.234	270	203
	20.00	1.319	0.231	291	194
	48.00	1.649	0.295	292	202
	72.00	1.431	0.252	285	205
Control				218	192

\* Sodium cellulosate fabrics containing 3.3 meq Na<sup>+</sup>/g were treated with 2.5% sodium monochloroacetate in anhydrous DMSO at indicated temperature; approximately eight-fold excess of chloroacetate required for complete reaction with sodium cellulosate was used.

TABLE II  
Effect of Reagent Concentrations on Degree of Carboxymethylation<sup>a</sup>

Sodium mono- chloroacetate, meq	Carboxymethylated cotton, meq		
	24.13 <sup>b</sup>	37.80 <sup>b</sup>	65.80 <sup>b</sup>
31.41	4.28	9.78	15.20
63.34	5.10	12.86	22.00
126.81	9.32	13.64	24.10

<sup>a</sup> Sodium cellulosate fabrics containing indicated meq's of sodium cellulosate reacted in DMSO with indicated meq's of sodium monochloroacetate. Degree of conversion of cotton expressed as meq's of CM.

<sup>b</sup> Sodium cellulosate meq's.

Attempts were made to increase carboxymethyl contents of the CM cottons by using fabrics with maximum amounts of sodium cellulosate sites available and by using an excess of a saturated solution of sodium monochloroacetate in DMSO. Regardless of ratios of reactants used, cellulosate sites were never completely converted to carboxymethyl groups.

Data in Table II are typical of degrees of conversion of cellulosates to CM cotton. In this series, a given amount of sodium monochloroacetate, expressed as meq, was reacted under identical conditions with cottons containing three different amounts of sodium cellulosate sites, expressed as meq. Data in rows show that increasing the sodium cellulosate sites, while maintaining the same sodium monochloroacetate concentration, increased carboxymethyl substitution in the fabric. For fabrics containing the same meqs of cellulosate sites, increasing the sodium monochloroacetate concentration increased carboxymethyl substitution in the fabric, as evidenced by data in columns of Table II. However, even when the meq's of sodium monochloroacetate were five times that of the sodium cellulosate, less than 40% of the sodium cellulosate was converted to CM cotton (column 1, row 3). These results indicated that CM cottons of high D.S. could be obtained by reacting cellulosates of high D.S. with a slight excess of sodium monochloroacetate.

Pretreatment of cotton with aqueous sodium hydroxide of various concentrations before its conversion to sodium cellulosate in nonaqueous media affected not only the degree of conversion to the sodium cellulosate but also the degree of subsequent reaction between the sodium cellulosate and monochloroacetate. Typical data are shown in Table III. The extent of reaction of sodium methoxide with cellulose increased to a maximum with increased concentration of sodium hydroxide used in pretreatment. Maximum conversion, expressed as meq's Na<sup>+</sup> ions per g product, was obtained with the 15% sodium hydroxide pretreatment. With agitation by nitrogen gas and with the high concentration of sodium methoxide, 2.3M, or 13%, sodium cellulosate of 1.67 meq/g was obtained with fabrics not pretreated with base. In earlier studies<sup>11</sup> with lower concentrations of sodium methoxide, the cotton was not converted to cellulosate unless the

TABLE III  
Effect of Sodium Hydroxide Pretreatment on Formation and Properties of Carboxymethylated Fabrics<sup>a</sup>

Pretreatment NaOH, %	Conversion cellulosate, meq/g	Carboxymethyl substitution		CMC form <sup>b</sup>	Wrinkle recovery, (W + F) <sup>o</sup>		Breaking strength, lb	Elongation at break, %	Abrasion resistance, cycles
		meq/g	D.S.		Wet	Cond.			
0	1.676	0.167	0.03	salt acid	149	169	53	14	240
Control					158	190	54	13	235
5	3.117	0.814	0.14	salt acid	161	194	45	8	1319
					177	155	41	21	201
Control					219	192	30	14	134
10	3.101	1.079	0.19	salt acid	177	172	54	14	170
					182	142	42	19	171
Control					240	224	21	14	111
15	3.730	1.451	0.25	salt acid	188	175	53	16	230
					193	159	46	28	285
Control					282	225	28	21	207
23	3.696	1.478	0.26	salt acid	205	176	60	24	346
					202	147	53	41	334
Control					289	239	37	23	379
					204	178	60	33	768

<sup>a</sup> Control cotton pretreated with indicated concentration of aqueous NaOH solvent exchanged in methanol before being converted to sodium cellulosate by reacting in methanolic sodium methoxide. Sodium cellulosates of indicated concentrations then reacted with 2.5% sodium monochloroacetate in DMSO.

<sup>b</sup> CM cotton in sodium salt form. Acid formed by converting salt form by treatment with 0.24M aqueous HCl.

fabric had been pretreated. The degree of conversion to sodium cellulosate was dependent on the preswelling history of the fabric. Although fabrics pretreated with 5% and 10% sodium hydroxide contained the same meq's of cellulosate, the degree of conversion to CM cotton was greater in fabric pretreated with the 10% sodium hydroxide. Maximum conversion to cellulosate required pretreatment with at least 15% sodium hydroxide, the minimum concentration required to change cellulose I to the mixed cellulose I and II crystalline lattices. As the concentration of the sodium hydroxide increases, so does the swelling of the fabric. The moisture contents of the CM cotton made from cottons preswollen in 23% sodium hydroxide were 11.3% and 8.4% for the salt and acid forms, respectively. The moisture regain values were 12.8% and 9.2%, respectively, for the salt and acid forms. In contrast, the CM cotton made from the cottons having the 10% sodium hydroxide pretreatment had moisture contents and regain values of 8.2% and 9.0%, respectively, for the salt form and 8.0% and 8.8% for the acid form.

Even at maximum conversion, less than half of the cellulosate ions were converted to carboxymethyl groups. Previously, when sodium cellulosate was reacted with chloroethyldiethylamine to form diethylaminoethyl (DEAE) cotton, approximately two thirds of the sodium cellulosate groups were converted to tertiary amine groups.<sup>12</sup>

When fabrics received no preswelling treatment, the resultant CM cottons in the acid form had wet and dry wrinkle-recovery angles lower than those of native cotton. With increased concentration of sodium hydroxide used in the preswelling treatment or increase in D.S., wet and conditioned recoveries of the acid forms of CM cottons increased. A maximum value was reached with pretreatments of at least 15% NaOH. Regardless of concentration of sodium hydroxide used in pretreatments, the CM cottons in the sodium salt form had lower wet and conditioned recovery angles at all degrees of substitution than their respective controls. Each control was a cotton pretreated with the base used in pretreatment.

Previously, built-in acid groups were used as catalytic sites for subsequent reactions of the modified cottons with conventional finishing reagents such as DMEU.<sup>2</sup> CM cottons prepared aqueously, unlike sulfonoethylated and phosphonomethylated cottons, did not catalyze reactions between cotton and DMEU to give easy care cottons. However, Daul and coworkers have reported that aqueously prepared CM cottons in the acid form catalyzed reactions between cotton and urea or melamine formaldehyde resins.<sup>13</sup> In the present study, CM cottons prepared by the nonaqueous method were converted to the acid form via aqueous HCl solutions, reacted with 10% aqueous solutions of DMEU, dried, and cured immediately. Typical results in Table IV show that percentages of nitrogen and formaldehyde and conditioned recovery angles showed no improvement even when CM cottons of 0.26 D.S. were cured at 160°C.

When CM cottons of D.S. 0.26 in the sodium salt form rather than the acid form were reacted with a 10% aqueous solution of DMEU, nitrogen

TABLE IV  
Effect of Temperature on Properties of CM Cotton in Acid Form Treated with Aqueous DMEU<sup>a</sup>

Cure temp., °C	N, wt %	HCHO, wt %	Wrinkle recovery, (W+F) <sup>o</sup>		Breaking strength, lb	Elongation at break, %	Abrasion resistance, cycles
			Wet	Cond.			
25 <sup>b</sup>	0.06	0.04	271	208	43	28	306
100	0.06	0.05	273	219	46	29	301
120	0.10	0.07	270	208	40	24	293
160	0.10	0.15	299	199	37	23	284
CMC control			257	239	37	23	379

<sup>a</sup> Nonaqueously prepared carboxymethylated cottons of 0.26 D.S. converted to acid form by treatment with aqueous HCl, washed, dried, and then treated with 10% dimethylolethyleneurea in water. Fabrics were dried 7 min at 60°C and cured for 5 min at indicated temperature.

<sup>b</sup> Fabrics were dried but not cured.



TABLE V  
Effect of Temperature on Properties of CM Cottons in Salt Form Treated with Aqueous DMEU<sup>a</sup>

Cure temp. °C	N, wt %	HCHO wt %	Wrinkle recovery, (W + F)°		Breaking strength, lb	Elongation at break, %	Abrasion resistance, cycles
			Wet	Cond.			
			D.S. = 0.26				
25 <sup>b</sup>	0.01	0.01	217	180	50	31	432
100	0.08	0.14	191	194	52	29	381
120	0.25	0.25	201	192	50	26	298
160	1.08	1.51	206	183	51	32	365
CMC control			202	147	52	41	334
			D.S. = 0.06				
25 <sup>b</sup>	0.02	0.04	227	197	62	39	426
100	0.09	0.10	239	191	57	26	423
120	0.28	0.43	243	170	63	29	324
160	0.90	1.35	269	212	57	28	365
CMC control			226	186	60	32	571

<sup>a</sup> Nonaqueously prepared carboxymethylated cottons in sodium salt forms were treated with 10% dimethylolethyleneurea, dried at 60°C for 7 min, and cured at indicated temperatures for 5 min.

<sup>b</sup> Fabrics were dried but not cured.

TABLE VI  
Effect of Temperature on Properties of CM Cottons Treated with 10% DMEU<sup>a</sup> in DMF

Cure temp., °C	N, wt %	HCHO, wt %	Wrinkle recovery, (W+F) <sup>c</sup>		Breaking strength, lb	Elongation at break, %	Abrasion resistance, cycles
			Wet	Cond.			
			Acid Form <sup>b</sup>				
25 <sup>e</sup>	0.04	0.03	239	210	40	23	428
100	0.08	0.09	230	184	42	27	465
120	0.21	0.16	262	209	42	24	463
160	0.25	0.09	262	209	39	29	379
CMC control			214	158	49	34	326
			Salt Form				
25	0.02	0.05	193	148	48	32	288
100	0.02	0.01	176	169	52	37	304
120	0.01	0.01	182	173	51	26	215
160	0.02	0.03	175	163	48	33	399
CMC control			154	155	56	37	301

<sup>a</sup> Nonaqueously prepared carboxymethylated cottons of 0.26 D.S. were treated with 10% dimethylolethyleneurea in DMF, dried 7 min at 60°C, and cured for 5 min at indicated temperatures.

<sup>b</sup> Carboxymethylated cottons were converted to acid form by treatment with 1M HAc in methanol, washed in methanol, and then dried.

<sup>c</sup> Fabrics were dried but not cured.

and formaldehyde contents increased with temperature of cure, as shown in Table V. However, there were no improvements in the wet wrinkle-recovery angles and only small improvements in dry recovery angles. Included in Table V are similar data obtained with the sodium salt of a CM cotton with a D.S. of 0.06. Nitrogen and formaldehyde contents increased even with the CM cottons of low D.S. With the CM cottons of lower D.S., there was some improvement in wet recovery with increase of nitrogen and formaldehyde contents.

Data in Table VI were obtained with the CM cottons treated in a completely nonaqueous system. The CM cottons, converted to acid form via treatment with acetic acid in  $\text{CH}_3\text{OH}$ , were treated with 10% DMEU in DMF. Only small increases in nitrogen content were observed with increase of cure temperature, but wrinkle recovery angles improved slightly after a 120°C cure temperature. Included in Table VI are data for the salt form of CM cottons of D.S. 0.26 treated in completely nonaqueous systems. In completely nonaqueous systems, these fabrics had negligible add-ons of nitrogen and formaldehyde. This result was in contrast to the much larger add-ons of the salt form of CM cottons in aqueous DMEU.

Optical and electron-microscopic techniques were used to examine differences in fine structures of the modified cottons. Fibers removed from the premercerized control fabric and from CM cottons in the salt and acid forms all showed the same response when treated with cupriethylenediamine (cuene) and then subjected to the expansion technique. All dissolved in cuene and all had similar layer expansions. After reaction with the DMEU, the cation exchange products were still soluble in cuene, and all had similar layer expansion patterns. Cuene solubility and the layering observed with the conventional methacrylate embedding technique are indicative of the absence of crosslinking.<sup>14</sup> Usually, those cottons reacted with difunctional reagents even to a low D.S. do not readily dissolve in cuene or expand into layers when cross sections are embedded in methacrylate that is subsequently polymerized.

For comparative purposes, the weak cation exchange cellulose prepared aqueously, with a carboxymethyl capacity of 0.355 meq/g, and the nonaqueously prepared exchanger, with a carboxymethyl capacity of 1.55 meq/g, were potentiometrically titrated. Titration curves are shown in Figures 1 and 2, respectively. In each case, an amount of sample equivalent to 0.7 meq of exchangeable ion was used. The initial pH of the acid form of the aqueously prepared CM cottons was 2; the nonaqueously prepared CM cottons had an initial pH of 4. It is more difficult to replace the  $\text{Na}^+$  ions with  $\text{H}^+$  ions in the nonaqueously prepared CM cotton than in the aqueously prepared CM cotton. Shapes of the titration curves for the aqueously and nonaqueously prepared CM cottons were not similar. On back titration of the salt forms with acid, the nonaqueously prepared CM cottons, because of their high degree of substitution, did not convert completely to the acid form until a pH of 2.5 was reached.

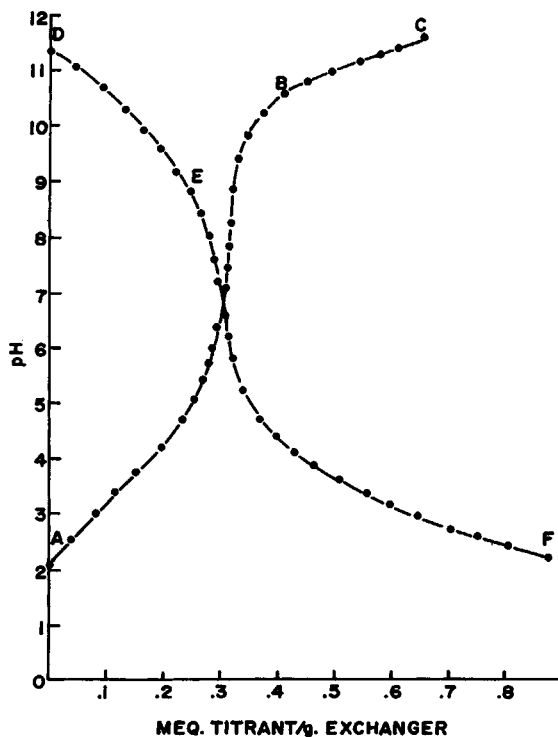
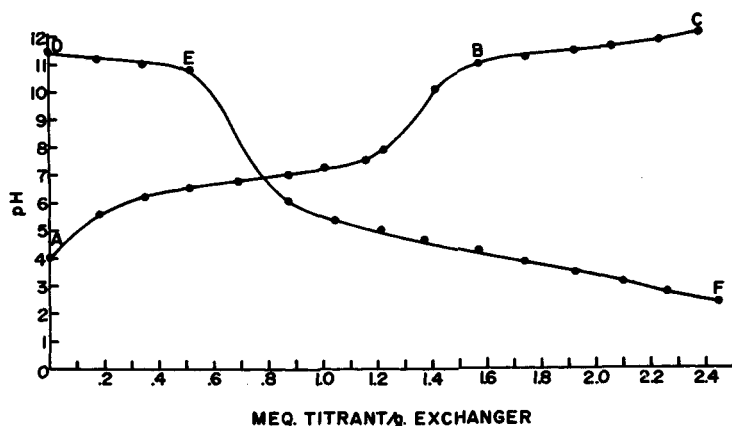


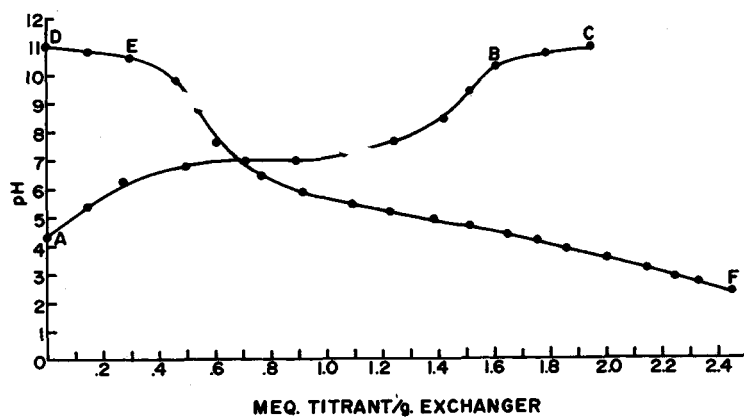
Fig. 1. Potentiometric titration curve of aqueously prepared carboxymethylated cotton. Curve ABC is the titration of the carboxymethylated cotton in the acid form vs.  $0.1M$  NaOH. Curve DEF is the titration curve of the excess NaOH and salt form vs.  $0.1M$  HCl. Capacity was  $0.355$  meq/g, and segment DE represents titration of excess base.

In Figure 1, curve ABC is the titration of the aqueously prepared CM cotton in the acid form versus  $0.1M$  NaOH. Curve DEF is the titration of the excess NaOH and the sodium salt form of the CM cotton versus standardized  $0.1M$  HCl. CM cotton, a weak acid cation exchanger, did not exchange its  $H^+$  ions very readily for  $Na^+$  ions; hence, the pH in the aqueous phase rose noticeably even in the early stages of the titration. At the endpoint, where the exchanger was changed completely to the salt form, there was a sharp change in pH.

In Figures 2a and 2b, typical of nonaqueously prepared CM cottons, curves ABC are the titration curves of the acid form versus  $1M$  NaOH or  $1M$  LiOH, respectively. Curves DEF represent titration curves of the alkali metal salt form versus  $1M$  HCl. Segments DE represent titration of the excess meq of base. Curves in Figures 2a and 2b indicate that for the nonaqueously prepared CM cotton, it is easy to replace  $H^+$  ions from the acid form with either  $Li^+$  ions or  $Na^+$  ions added as base. Both of these potentiometric curves yielded value of  $1.55$  meq/g as the capacity of the CM cotton. In the back titrations of the salt forms of CM cottons with



(a)



(b)

Fig. 2. Potentiometric titration curve of nonaqueously prepared carboxymethylated cotton. Curve ABC is the titration of the CM cotton in the acid form vs.  $1M$  NaOH (2a) or vs.  $1M$  LiOH (2b). Curve DEF is the titration curve of the excess base and salt form vs.  $1M$  HCl. Capacity was  $1.55$  meq/g, and segment DE represents titration of excess NaOH (2a) or excess LiOH (2b).

HCl, titration curves did not yield the theoretical capacity of the CM cotton. With both the lithium and sodium salt forms, only 40% of the alkali metal ions were replaced by the  $H^+$  ions on back titration with  $1M$  HCl. This result is in contrast to the ease of reversibility of the titration curves (Fig. 1) of CM cottons prepared aqueously.

In a study of the viscosity of carboxymethyl celluloses of high D.S.,<sup>15</sup> it was reported that conversion of the sodium salt to the acid form occurred over a wide range starting at about pH 6 and not being complete until about pH 2.5. Experimental data with the nonaqueously prepared CM cottons of relatively high D.S. indicated difficulty of replacing a bound cation with another cation.

TABLE VII  
Selectivity Order of Sodium Carboxymethylated Cotton for Monovalent Cations\*

Y <sup>+</sup> added, meq	% Na <sup>+</sup> replaced by Y <sup>+</sup>		
	H <sup>+</sup>	Li <sup>+</sup>	N(CH <sub>3</sub> ) <sub>4</sub> <sup>+</sup>
0.375	100	74	83
0.750	99	54	53
1.125	98	50	41
1.250	84	—	—

\* CM cotton containing 1.38 meq of Na<sup>+</sup> in salt form treated with a solution of YCl containing indicated meq's of Y<sup>+</sup>.

Data in Table VII are given to indicate difficulty of replacing a bound cation of the nonaqueously prepared CM cottons by another cation. These data also show that the ease of replacement of the Na<sup>+</sup> ion of the sodium salt form by a counter cation decreases as the fraction of the counter ion replaced increases. The selectivity is not dependent upon size of cation only, but selectivity series varies with amount of counter ion bound in the CM cotton. For example, the large tetramethylammonium ion is as effective as or a little more effective than the small Li<sup>+</sup> ion in replacing bound Na<sup>+</sup> ions from CM cotton initially. As a larger fraction of Na<sup>+</sup> ions are replaced, Li<sup>+</sup> ions enter the CM cotton matrix more easily to replace Na<sup>+</sup> ions than do the quaternary ions. In replacing Na<sup>+</sup> ions by H<sup>+</sup> ions, initially 100% of the added H<sup>+</sup> ions replace the Na<sup>+</sup> ions. On further addition of H<sup>+</sup> ions, it becomes increasingly harder to replace all Na<sup>+</sup> ions from the salt form of CM cottons.

Unlike CM cottons prepared in water, the nonaqueously prepared CM cottons were insoluble in aqueous base and were converted from salt to acid form with difficulty. These differences and the fact that only the nonaqueously prepared CM cottons in the acid form show improvement in conditioned recovery indicate that CM substitution occurs at different sites of the cellulose matrix in the two methods. Differences in properties are undoubtedly due to differences in overall H bondings.

### SUMMARY

Carboxymethyl (CM) cellulose in fabric form was prepared at room temperature by the reaction of sodium monochloroacetate and sodium cellulose in dimethyl sulfoxide. These cation exchange celluloses, prepared nonaqueously and with a degree of substitution (D.S.) as high as 0.3, do not dissolve when in either the acid or salt form in water or aqueous base. The relatively high-capacity exchangers were prepared by a one-step carboxymethylation treatment. Approximately one third of the sodium cellulose sites were converted to carboxymethyl groups under optimum conditions. Fabric properties of the nonaqueously prepared CM cottons differed from the properties of the aqueously prepared CM cottons of like D.S. In the acid form, CM cottons prepared nonaqueously

had improved wrinkle recoveries in both wet and dry states. The sodium salt forms could be used as in situ catalysts for reactions between cotton and dimethylolurea or dimethylolethyleneurea. Replacement of  $\text{Na}^+$  ions in the salt forms of CM cottons prepared in nonaqueous media by monovalent cations of various sizes was more difficult than replacement of  $\text{Na}^+$  ions in the salt forms of CM cottons prepared in water.

The authors wish to express their appreciation to Mildred Black and John Mason for nitrogen and formaldehyde determinations and to Louise Bosworth for textile testing.

The mention of trade names and companies does not imply endorsement by USDA over others not cited. Such mention is given merely to report experimental conditions explicitly.

### References

1. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Text. Res. J.*, **23**, 719 (1953).
2. D. M. Perrier and R. R. Benerito, *Text. Res. J.*, **41**, 680 (1971).
3. R. F. Schwenker and E. Pacsu, *Tappi*, **46**, 665 (1963).
4. R. M. Reinhardt, J. S. Bruno, and J. G. Frick, Jr., *Text. Res. J.*, **36**, 602 (1966).
5. R. M. Reinhardt and T. W. Fenner, *Ind. Eng. Chem. Prod. Develop.*, **4**, 82 (1965).
6. R. M. Reinhardt and T. W. Fenner, *Text. Res. J.*, **27**, 873 (1957).
7. R. R. Benerito, B. B. Woodward, and J. D. Guthrie, *Anal. Chem.*, **37**, 1693 (1965).
8. P. C. Mehta and R. D. Mehta, *Text. Res. J.*, **30**, 532 (1960).
9. American Society for Testing and Materials, Philadelphia, Pa., ASTM Designation (a), D 1295-67; (b) D 1682-64; (c) D 1175-64-T.
10. R. H. Fujimoto, R. M. Reinhardt, and J. D. Reid, *Amer. Dyestuff Repr.*, **52**, 329 (1963).
11. R. J. Berni, D. M. Soignet, and R. R. Benerito, *Text. Res. J.*, **40**, 999 (1970).
12. D. M. Soignet, R. J. Berni, and R. R. Benerito, *J. Appl. Polym. Sci.*, **15**, 155 (1971).
13. G. C. Daul, R. M. Reinhardt, and J. D. Reid, *Text. Res. J.*, **22**, 792 (1952).
14. M. L. Rollins, A. T. Moore, W. R. Goynes, J. H. Carra, and I. V. deGruy, *Amer. Dyestuff Repr.*, **54**, 512 (1965).
15. C. J. Brown and A. A. Houghton, *J. Soc. Chem. Ind.*, **60**, 254T (1941).

Received February 20, 1973

Revised May 1, 1973