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The Swelling of Cotton in Cadoxen, Ethylenediamine, and Cuprammonium Hydroxide

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Synopsis

This paper describes the swelling of cotton fiber in solutions of cadoxen, ethylenediamine, and cuprammonium hydroxide. The absorption of swelling agent and the increase in width of the fiber were measured. The degree of swelling in cadoxen solutions, in relation to the composition of these solutions, is complex; very high degrees of swelling can be attained. The effects of these swelling treatments on the fine structure of cotton, as measured by the infrared-deuteration method, density, acid hydrolysis, and an acetylation technique, are described and discussed in relation to the swelling behavior.

INTRODUCTION

Cadoxen [solutions of tris(ethylenediamine) cadmium dihydroxide in ethylenediamine–water mixtures] has received a considerable amount of investigation in respect to its use as a solvent for cellulose.[1,2] The oxidative degradation of cellulose in this solvent is thought to be small. Cadoxen has also been employed to a limited extent in studies of the structure of cellulose fibers,[3–7] e.g., Smith and co-workers[3] related the dissolution characteristics of a number of pulps and chemically modified celluloses to various chemical and morphological features of the cellulose fibers. Bergmann and co-workers[1] and Brown[2] have reviewed these various applications of cadoxen.

This paper describes the swelling of cotton fiber in cadoxen solutions of various concentrations. The absorption of swelling agent and the increase in width of the fiber were measured. These parameters characterize the swelling behavior sufficiently for the purposes of the present investigation: measurements of the actual degree of swelling as such (i.e., the increase in the volume of the cotton fiber) were not attempted. The effect of these treatments in cadoxen solutions on the fine structure of the fiber was also studied. It is of interest to compare the nature of the swelling behavior in cadoxen, and the structural changes produced, with that observed in aqueous solutions of caustic alkali, which are not solvents for cotton cellulose at any concentration.[8] As an initial step, the swelling and structural changes in cotton fiber immersed in ethylenediamine (EDA) and in EDA–water mixtures were studied. Published information on the structural effects of EDA and EDA solutions is referred to as appropriate below. For purposes of comparison, a brief investigation was also made of the swelling of cotton in dilute solutions of cuprammonium hydroxide. (Cuprammonium hydroxide is another solvent for cellulose at higher concentrations.)

EXPERIMENTAL

Materials

Scoured Acala 4-42 cotton was used throughout this investigation. In a few experiments a scoured and bleached poplin fabric was studied.

Saturated cadoxen solutions were prepared by adding excess cadmium oxide to various mixtures of redistilled EDA and water, ranging from 16% to 60% by weight EDA. The amount of cadmium that could be dissolved depended markedly on the concentration of EDA, reaching a maximum at about 30% EDA. Cadoxen solutions containing lower amounts of cadmium, in a particular EDA–water mixture, were prepared by dilution of these saturated solutions.

Cuprammonium hydroxide solutions of various concentrations of copper were prepared by diluting Shirley cuprammonium hydroxide (15 g copper and 200 g ammonia per liter) with ammonia solution of the same concentration.

Measurement of Swelling and Solubility

All swelling, washing, and drying treatments on fiber were done in the absence of any tension; swelling treatments were for 1 hr at 25°C unless otherwise stated. The swollen fiber was centrifuged at 1300 rcf for 7 min (in an enclosed container to prevent evaporation) and then weighed. The increase in weight is a measure of the amount of swelling agent absorbed into the cotton cellulose plus external swelling agent not removed by the centrifuging (i.e., remaining between the fibers and on the fiber surface). The amount of this external liquid is by no means negligible[9–11]; for example, with water as swelling agent it can be as much as 15%–20% of the weight of the dry fiber. It is not possible to estimate with any reliability the amount of this external liquid in the swelling systems under investigation and so no correction has been attempted. However, the amount will almost certainly be small compared with most of the swelling values measured in the present investigation, i.e., insufficient to affect any of the conclusions drawn. After being weighed, the centrifuged fiber was extracted for 16 hr in distilled water. The extracted EDA (plus, if present, cadmium) was estimated by titration with acid. Cadmium in the neutralized solution was determined by adjusting the solution to pH 6 with hexamine, adding a known amount of ethylenediaminetetraacetic acid, and back-titrating the excess of this acid with zinc sulfate solution.

The increase in width of cotton fibers produced by a particular swelling treatment was measured microscopically, 200 measurements being made on each sample of swollen fiber.[12]

The amount of cotton cellulose dissolved by a particular swelling treatment was determined from the weight of the washed, dried fiber.

Measurement of Acetylation

Some of the fiber samples, after being swollen and then washed in water, were solvent exchanged from this washed, never-dried condition to pyridine and then acetylated in this solvent; the acetylation was for 24 hr at 25°C in a 50/50 v/v mixture of acetic anhydride and pyridine.[13] The extent of acetylation produced by this nonswelling treatment (determined by saponification of the acetylated fiber in dilute sodium hydroxide, followed by back titration of the excess alkali) is thought to be a semiquantitative measure of the total "surface area" of the original, swollen fiber, i.e., of the degree of interfibrillar opening and separation produced by the swelling.[8]

Infrared-Deuteration Measurements

Samples of the cotton fiber, after being swollen, washed, and dried, were studied by the infrared-deuteration technique.[14–16] This technique measures order and disorder in the hydrogen bonding system in the cellulose and also provides information on the type of crystal lattice present.

The cotton fibers were prepared for infrared examination by forming them into a reasonably transparent film. In this procedure, the fibers were cut into short lengths, milled in an agate ball mill for 20 sec, sieved to give an even layer on the lower plate of a high-pressure die, and pressed for 20 min at 145,000 lb/in.^{2} Deuteration of the hydrogen bond disordered material was achieved in deuterium oxide vapor of 57% rh at room temperature for 5 hr (deuteration in saturated vapor leads to a rapid deterioration of the fiber film). The proportions of hydrogen bond ordered and disordered material were calculated from the relative intensities of the OH, OD, and CH bands in the 3μ region of the infrared spectrum of these partially deuterated fibers. The amount of hydrogen bond ordered cellulose deuterated by this deuteration treatment was calculated from the infrared spectrum of the fiber film after a suitable rehydrogenation treatment.[14,15]

The true 100% absorption line for each spectrum of deuterated fiber (lower than the nominal 100% absorption line because of unavoidable holes in the fiber film) was calculated from the OD band, since the OD band has been shown to be very similar in peak frequency, half-width, and shape for different forms of cellulose.[17,18] The relative amounts of cellulose I, II, and III in the hydrogen bond-ordered material were determined by comparing the OH band of the deuterated fiber with the OH bands calculated for known mixtures.

Measurement of Acid Hydrolysis and Levelling-Off Degree of Polymerization (LODP)

Samples of treated fiber, after being washed and dried, were hydrolyzed in refluxing 1.0*N* hydrochloric acid for 1 hr. The loss of weight produced was measured. The LODP of the cotton fiber was calculated from the intrinsic viscosity (*i*) of the hydrolysis residue in cuprammonium hydroxide at 20°C by means of the equation LODP = 175 *i*.[16]

Measurement of Density

Density was measured by immersing the dry fiber in either carbon tetrachloride or chloroform (depending upon the density of the fiber) and achieving a balance of density by change in temperature.

RESULTS AND DISCUSSION

The Effect of Solutions of Ethylenediamine on Cotton

The Effect of Concentration of EDA in EDA-Water Mixtures

Infrared-deuteration measurements on washed and dried samples (Fig. 1) showed that swelling in EDA–water mixtures produces no significant increase in the hydrogen bond disorder in cotton at concentrations of EDA of up to ca 40% by weight. At about 50% by weight EDA, there is a marked increase in the disorder produced, levelling off at about 60% EDA. This lack of any significant disordering effect up to about 40% EDA is in agreement with most previous work in this field.[19–21] None of the treatments

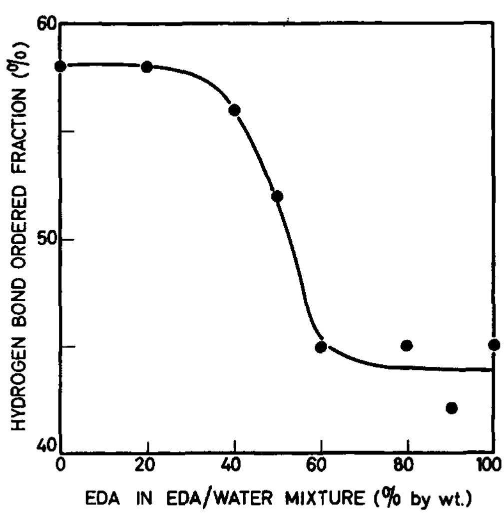

Fig. 1. Effect of swelling in mixtures of EDA and water on the fraction of hydrogen bond ordered material in cotton.

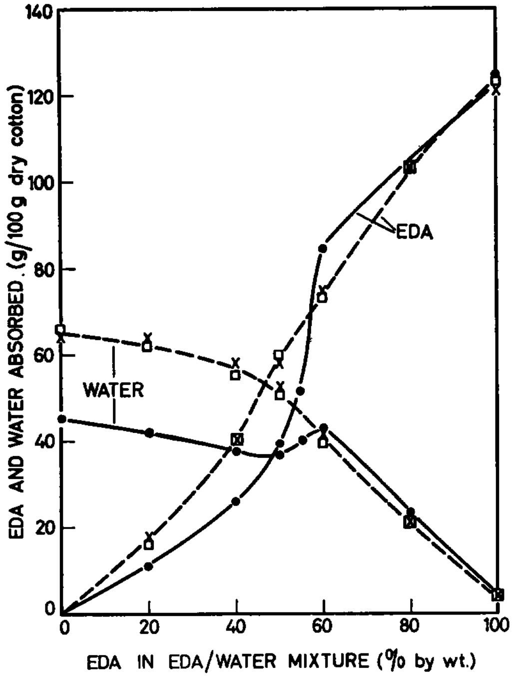

Fig. 2. Swelling of cotton fiber in mixtures of EDA and water: (●) scoured cotton; (□) mercerized cotton; (X) "decrystallised" cotton.

produces any change in the type of crystal lattice; this, again, is in agreement with previous work.[19,21–24]

This marked increase in disordering in the range 40%–60% EDA is associated with a marked and more or less sudden increase in the absorption of swelling agent in this range (Fig. 2, full lines). This increase in swelling is also shown by measurements of the width of the swollen cotton fiber (Fig. 3); it is associated mainly with a sudden increase in the uptake of EDA, not in the uptake of water (Fig. 2). The uptake of EDA increases comparatively slowly from 0% to 40% EDA, rapidly from about 50% to 60% EDA, and slowly again thereafter. The absorption of water decreases with EDA concentration from 0% to 50% EDA, rises slightly between about 50% and 60% EDA, and then falls again thereafter.

It has been suggested [19,20] that in EDA solutions "free" amine molecules are present only at concentrations of EDA greater than 50%–60% by weight and that this accounts for the fact that structural disordering occurs only in these more concentrated solutions. This explanation of the curves in Figures 2 and 3 was investigated by studying the swelling of mercerized fiber and fibers previously treated ("decrystallized") in pure EDA.

The results (Fig. 2, dashed lines) show clearly that mercerized and "decrystallized" cottons exhibit no discontinuous swelling behavior in the

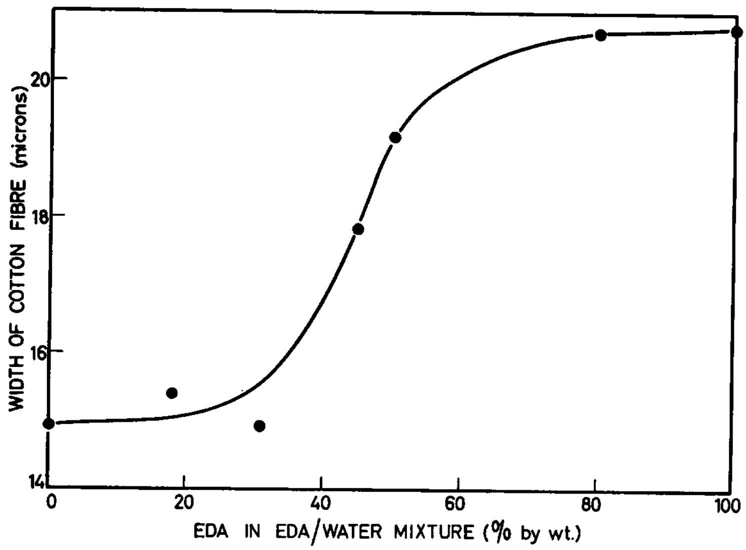

Fig. 3. Width of cotton fibers swollen in mixtures of EDA and water.

region of 40%–60% of EDA. It may thus be concluded that the discontinuous swelling and disordering behavior observed with scoured cotton in this range of EDA concentrations is not the result of changes in the nature of EDA–water mixtures in this range but is akin to the behavior observed in cotton treated in sodium hydroxide solutions over the "transition range" of concentrations: at about 40% EDA, the state of swelling of the cotton fiber is such that the EDA begins to penetrate, form complexes with, and thus eventually disorder the cellulose molecules in the interior of the microfibrils. Thus the discontinuity on Figure 2 for cotton is simply further evidence of a sudden increase in the accessibility of the sample to swelling agent; the increase in disorder over this concentration change was shown above in Figure 1. With the mercerized and "decrystallized" cottons, the higher accessibility is present at all concentrations of EDA (because of the pretreatment in alkali solution or EDA) and thus the swelling curves in Figure 2 show no marked discontinuity.

The Effect of Nonaqueous Washing Liquids

Infrared-deuteration studies have been made on cotton fibers that have been swollen in pure EDA at 25°C, washed in nonaqueous solvent at 25°C, and dried in air (Table I). With the exception of dimethyl formamide, removal of the EDA swelling agent by washing in a nonaqueous liquid gives a product with a hydrogen bond disordered fraction greater than that present in samples washed in water. This behavior, which has been noted previously,[22] must mean that these nonaqueous washes produce less recrystallization from the EDA-swollen state than washing in water. Some of the nonaqueous washes produce a small amount of the cellulose

TABLE I
Effect of Washing in Nonaqueous Solvents
on Disorder and Lattice Type of EDA-Treated Cotton Fiber Samples

Solvent used to wash out EDA	Hydrogen bond ordered cellulose, %	Cellulose III in ordered regions, % (approx.)
H_2O	45	0
Ethanol	41	10–15
Methanol	39	5–10
Dimethyl formamide	48	0
Acetone	41	0
Ethyl acetate	36	30
Isopropyl alcohol	34	35

III lattice in the hydrogen bond ordered regions, to judge from the OH-stretching band of these regions. This formation of cellulose III is known to take place in ethylamine-treated cotton fibers[27–29] if the ethylamine is removed by evaporation. The effect of nonaqueous washes in producing a more disordered product has been observed with other swelling agents and explanations have been suggested.[25,26]

Acetylation of EDA-Treated Fibers

Acetylation measurements on never-dried, solvent-exchanged samples suggest (Fig. 4) that the structural changes in EDA-swollen cotton in solutions of EDA concentration 40%–60% by weight (Figs. 1–3) are associated with a marked increase in internal surface area of the swollen fiber. This is presumably the result of a marked increase in the interfibrillar separation and "opening" in the swollen fiber and resembles the behavior observed in caustic soda solutions (the mercerization transition range is also associated with a marked increase in acetylation value). The internal surface is greater if the EDA–water swelling agent is washed out directly with pyridine (the acetylation solvent) than if it is washed out with water and then solvent exchanged to pyridine (Fig. 4). The intermediate wash in water must produce some collapse of the "open" fibrillar structure produced by the swelling agent.

Acid Hydrolysis, LODP, and Density Measurements

The weight loss after the standard acid hydrolysis treatment and the LODP value of swollen, washed, and dried fibers change markedly over the transition range, i.e., at approximately 40%–60% EDA. The weight loss (a qualitative measure of disorder) increases from 4.0% to 6.1%, as might be expected. The LODP decreases from 140 to about 100.

The density of the fiber decreases from 1.54 with untreated cotton to 1.46 with fiber treated in 100% EDA; the change in density as the concentration of EDA is increased is again most pronounced over the transition

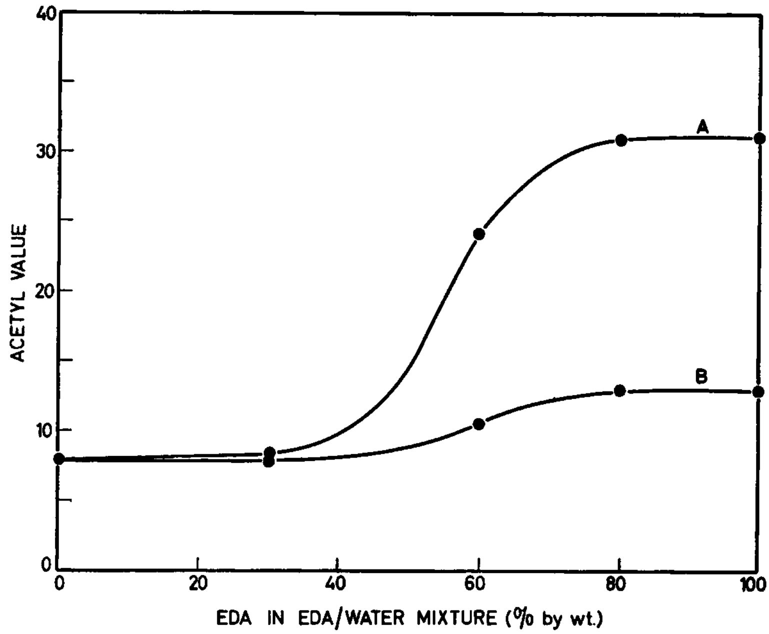

Fig. 4. Acetylation of cotton fiber swelled in EDA–water mixtures, solvent exchanged pyridine and acetylated: (A) swollen sample washed directly in pyridine; (B) swollen sample washed in water, then exchanged to pyridine.

range from about 40% to 60% EDA. These various results are in reasonable agreement with published values.[8]

Treatment of Cotton in Mixtures of EDA and Ethanol

Cotton fiber was treated in mixtures of EDA and ethanol for 2 hr at 25°C, washed in ethanol, and dried in air. As the concentration of EDA is increased, the hydrogen bond disorder in the fiber gradually increases (Table II); the disorder in 80% and 90% EDA appears to be slightly greater than in 100% EDA. At concentrations of EDA of 80% and more there is also

TABLE II
Infrared-Deuteration Studies on the Effect of Swelling Cotton Fiber in EDA–Ethanol Mixtures[a]

Concn. of EDA in ethanol, wt-%	Hydrogen bond ordered cellulose, %	Cellulose III in ordered regions, %
0	58	0
30	51	0
60	47	0
80	36	10
90	38	10
100	41	10–15

[a] EDA was washed out in ethanol in each case.

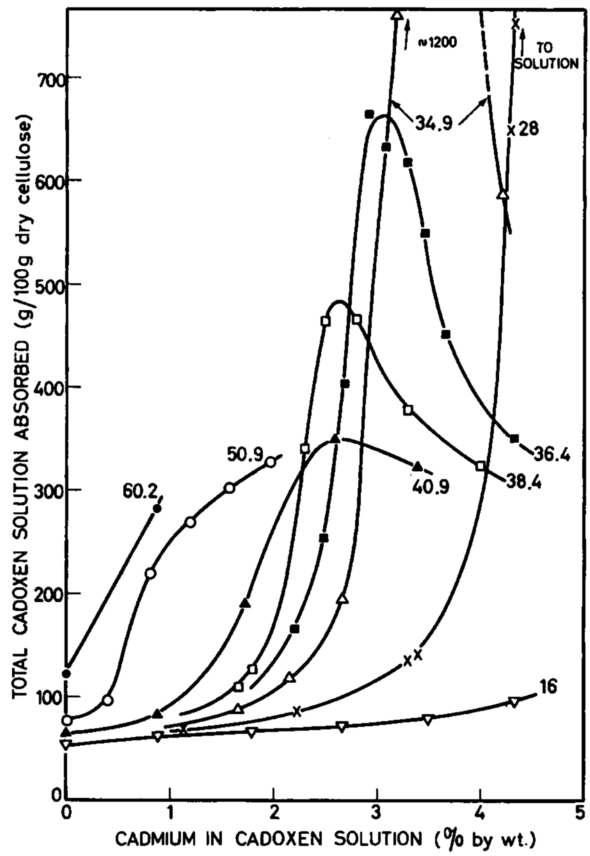

Fig. 5. Total absorption of cadoxen solution (cadmium, EDA, and water) by cotton fiber. The concentration of EDA in each cadoxen solution (wt-%) is indicated on the figure, i.e., each curve relates to a series of cadoxen solutions of the same concentration of EDA but of different concentrations of cadmium.

a small amount of cellulose III produced, to judge from the shape of the OH-stretching band.

The Effect of Cadoxen Solutions on Cotton

Swelling of Cotton Fibers in Cadoxen Solutions

The swelling of cotton fibers in various cadoxen solutions after 1 hr at 25°C is shown in Figure 5 (absorption of swelling agent) and Figure 6 (increase in fiber width). The swelling behavior is complex and can be summarized as follows, it being remembered that the limiting factor at each particular concentration of EDA is the maximum amount of cadmium that can be dissolved. In "dilute EDA" cadoxen solutions (16% by weight EDA), the degree of swelling is low at all concentrations of cadmium. In concentrated EDA solutions (>40%), the swelling increases with concen-

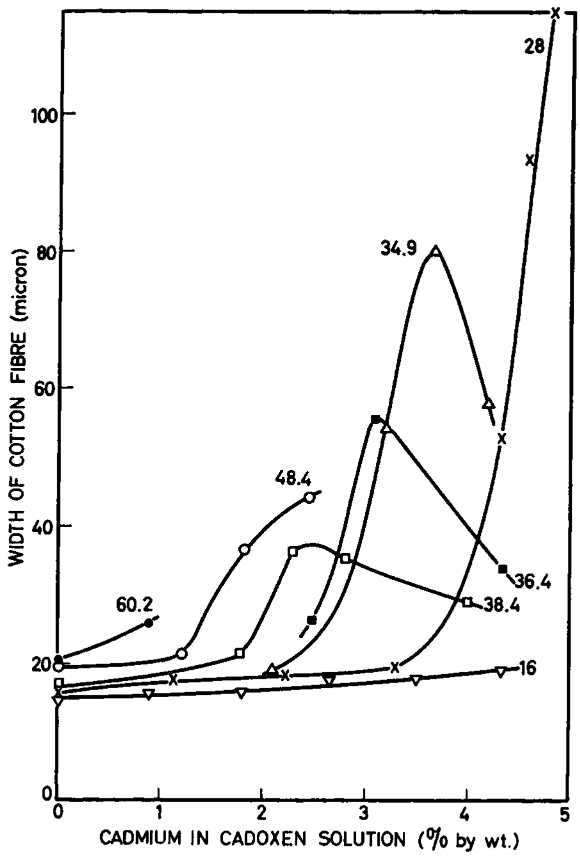

Fig. 6. Width of cotton fibers swollen in cadoxen solutions. The concentration of EDA (wt-%) in each cadoxen solution is indicated on the figure.

tration of cadmium in solution, tending to level off in the region of 300% absorbed solution. In EDA solutions of intermediate concentrations (34%–40%), the swelling first increases with cadmium concentration, passes through a maximum which varies from 350% to 1200% absorption, then decreases again. The degree of swelling at the maximum increases as the concentration of EDA decreases from 40% to 35%. In 28% EDA, the swelling increases slowly at first but then very rapidly with increase in cadmium concentration; very high degrees of swelling are obtained and the cellulose eventually dissolves, at first partially and then completely. This was the only concentration of EDA investigated in which any significant amount of solution (>5% by weight) took place (a small amount, about 5%, of the cotton dissolved at the maximum of the 34.9% EDA curve).

Microscopic examination revealed a change in the cross section of the fiber to a more rounded shape; the higher degrees of swelling in the cadoxen are accompanied by the rupture of the primary wall and the well-known associated phenomenon of "balloon" swelling.

Washing the cadoxen-swollen fiber in water causes in most cases a decrease in the degree of swelling of the fiber, though the level of swelling remains in general high. However, on the cadmium-rich side of the maxima in the swelling curves in Figures 5 and 6, the swelling of the water-washed material is higher than that of the fiber prior to washing. Solvent exchange of the water-washed fibers to ethanol or dimethyl sulfoxide causes no further change in the degree of swelling, provided that the differences in density of the three liquids are considered.

The Absorption of the Three Components of the Swelling Solution

Figures 7 and 8 illustrate the absorption by the cotton fiber of cadmium, EDA, and water from the swelling solution. The results can be summarized as follows:

(1) The cadmium is preferentially absorbed from solution relative to EDA and water, i.e., the concentration of cadmium in the absorbed solution is greater than in the external swelling solution. The amount of absorbed cadmium increases with increase in the concentration of cadmium in the

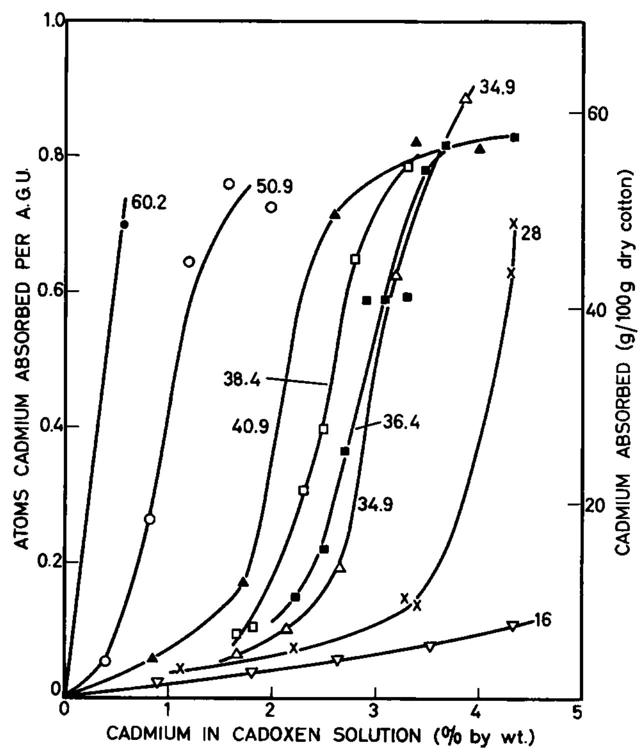

Fig. 7. Absorption of cadmium from cadoxen solutions by cotton fibers. The concentration of EDA (wt-%) in each cadoxen solution is indicated on the figure.

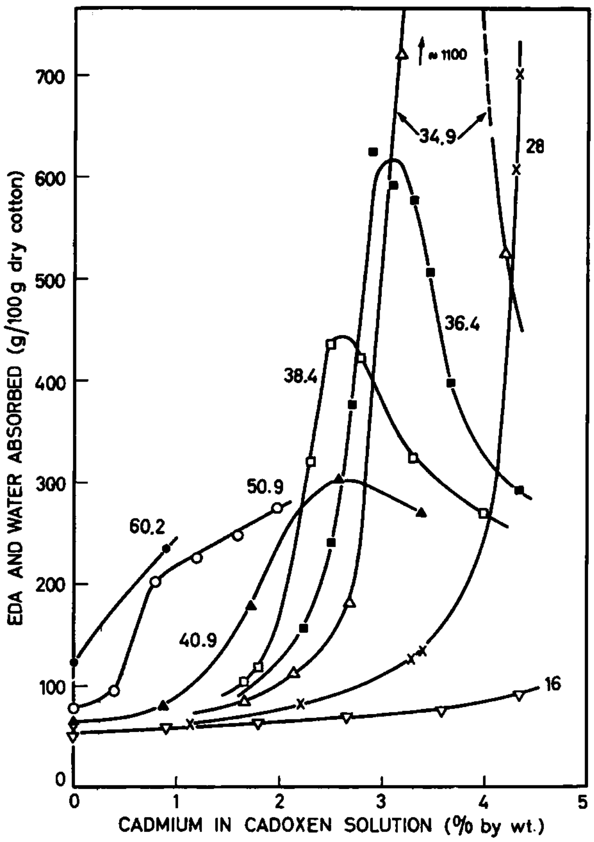

Fig. 8. Absorption of EDA and water from cadoxen solutions by cotton fibers. The concentration of EDA (wt-%) in each cadoxen solution is indicated on the figure.

swelling solution, tending to attain a maximum value of about 55–60 g cadmium per 100 g cellulose (i.e., 0.8–0.9 atoms Cd/a.g.u.) at nearly all EDA concentrations (Fig. 7). There is no peak in the absorption on any curve, i.e., the swelling maxima in the curves of total swelling (Figs. 5 and 6) are associated with maxima in the absorption of EDA and water (Fig. 8).

(2) The amount of cadmium absorbed from a solution of a particular cadmium concentration increases as the concentration of EDA in the solution increases.

(3) The absorbed solution contains slightly more EDA, relative to water, than the external swelling solution. Expressing the EDA concentration as percentage by weight of EDA in the EDA + water component, the difference is usually of the order of 2% to 3% (e.g., a concentration in the swelling solution of 40% and a concentration within the fiber of 43%). There is thus no marked preferential absorption of EDA compared with water.

Order and Disorder in Cadoxen-Treated Cotton Fibers

Infrared-deuteration measurements were made on cadoxen-treated cotton fibers after washing in water and drying in air. The results are presented in Figures 9 and 10. Some of the treatments increased the hydrogen bond disorder in the cotton (Fig. 9) and converted some cellulose I to cellulose II (Fig. 10). This is taken as evidence that intrafibrillar swelling takes place in fibers in these solutions. Other of the treatments produced no structural changes detectable by the infrared-deuteration technique. In general, the higher the concentration of cadmium at a particular EDA concentration, the more pronounced the structural effects. It is found, however, that the important factor is the concentration of cadmium in the absorbed solution, not the total swelling. Thus in solutions more concentrated in EDA, considerable structural changes take place at total degrees of swelling of only 280% (17% cadmium in absorbed solution), whereas in cadoxen solutions in more dilute EDA, degrees of swelling of as much as 700% produce only slight structural changes (6.5% cadmium in absorbed solution).

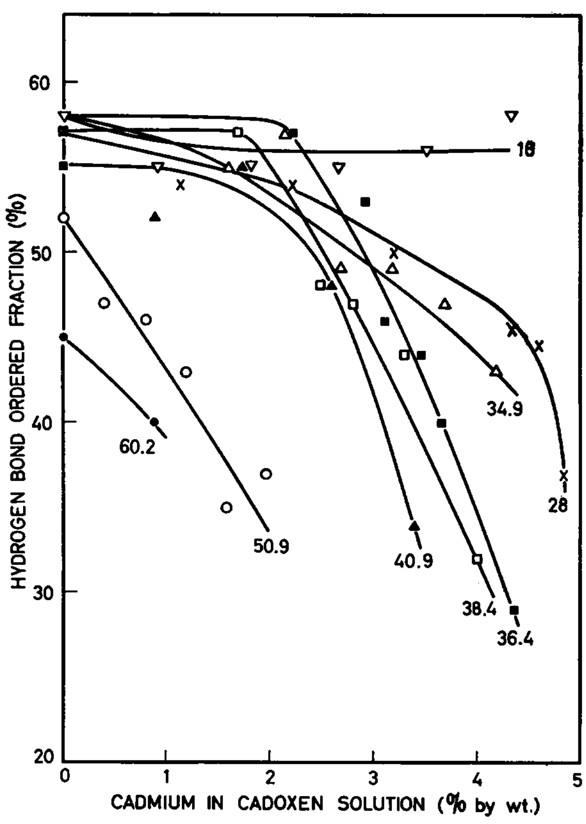

Fig. 9. Effect of swelling in cadoxen solutions on the hydrogen bond order in cotton. Samples washed in water and dried in air. The concentration of EDA (wt-%) in each cadoxen solution is indicated on the figure.

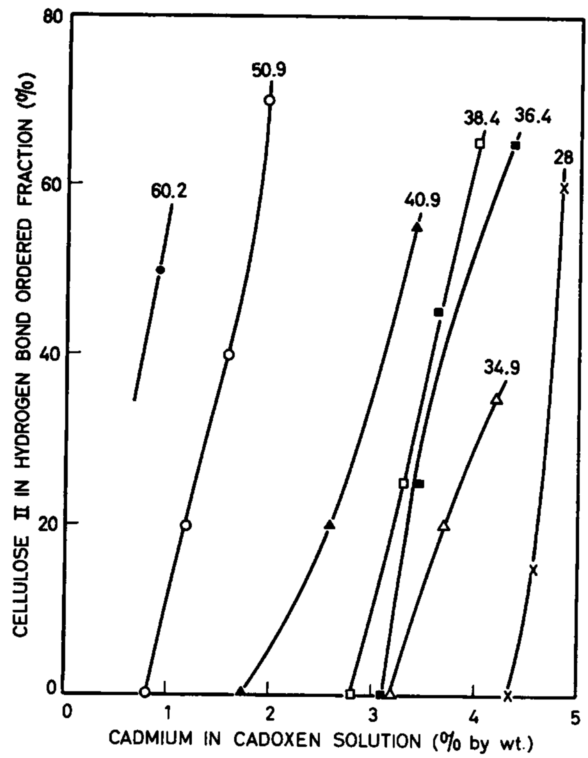

Fig. 10. Effect of swelling in cadoxen solutions on the fraction of cellulose II in the hydrogen bond ordered regions. Samples washed in water and dried in air. The concentration of EDA (wt-%) in each cadoxen solution is indicated on the figure.

With cadoxen treatments that produce little change in the structure of the cotton fiber, the effect on the structure of washing in ethanol instead of in water was at most small. However, with cadoxen swelling treatments that produce cellulose II in the water-washed fiber, washing in ethanol instead of in water had a marked effect: the ethanol wash tends to prevent the formation of any cellulose II component, with a corresponding increase in the hydrogen bond disordered fraction. This behavior is the opposite of that observed in the mercerization system (where washing in ethanol tends in general to prevent the formation of a cellulose I component[25,26]).

Table III lists values for the loss in weight during the standard hydrolysis treatment and the LODP of cotton samples treated in various cadoxen solutions, washed, and dried. The treated samples clearly lose more weight on hydrolysis than untreated cotton (indicating a higher degree of disorder, in agreement with the infrared-deuteration results), but the effect is at most small. The values, moreover, do not follow any systematic pattern and cannot be related to the nature and "swelling potential" of the cadoxen solution. The LODP values in general show a moderate decrease as a result of a prior treatment in cadoxen; at any one particular concentration of

TABLE III
Effect of Swelling in Cadoxen Solutions on Reactivity and Density of Cotton Fiber

Composition of swelling solution		Acetyl value, %	Acid hydrolysis		Density
EDA, wt %	Cd, wt %		Loss in wt, %	LODP	
50.9	1.74	18.4	5.2	108	1.531
36.4	2.69	10.9	4.3	141	1.532
36.4	3.00	13.1	4.8	133	1.513
36.4	3.49	16.7	4.8	126	1.515
34.9	3.15	13.4	5.3	132	1.516
34.9	4.5	19.7	4.8	82	1.508
27.9	4.28	12.3	4.0	135	1.509
28.6	2.56	8.6	—	—	—
28.6	4.94	23.25	—	—	—
0[a]	0[a]	7.75	4.0	140	1.54

[a] Swollen in water alone.

EDA, the LODP decreases as the concentration of cadmium in the solution increases.

Table III also shows that treatment in cadoxen solutions reduces the density of the fiber, indicating an increase in the disorder in the cotton fiber, again in general agreement with the infrared-deuteration results.

Acetylation Measurements

Measurements were made of the acetylation of samples of cotton fiber after being swollen in cadoxen, washed, and solvent exchanged to pyridine. Table III shows that all but one of the cadoxen treatments led to a larger internal surface than that present in cotton fibers swollen in water alone (acetylation value of 7.75%). In general, it appears to be the amount of cadmium absorbed, rather than the total degree of swelling, that is related to the acetylation value, i.e., to the degree of interfibrillar separation and opening up. It may be noted that the highest acetyl value (ca. 23%) is similar to that observed with solvent-exchanged mercerized fibers and also with fibers swollen and partially dissolved in dilute cuprammonium solutions (see below).

The Solubility and Swelling of Disordered Cellulose in Cadoxen Solutions

The solubility and swelling of disordered cellulose (produced by the non-aqueous saponification of secondary cellulose acetate[25]) in cadoxen solutions were investigated to clarify the importance of the type and nature of a cellulose in determining its behavior in cadoxen solutions. The results are listed in Table IV. The disordered cellulose, in the form of film or fiber, is completely soluble in cadoxen solutions that would not dissolve any significant amount of cotton cellulose. In all of the cadoxen solutions investigated there is at least partial solution of the disordered cellulose. The absorption

TABLE IV
Swelling and Solubility of Disordered Cellulose in Cadoxen Solutions

Sample	Composition of swelling solution		Amount dissolved, wt %	Degree of swelling[a]	Hydrogen bond ordered cellulose, %[b]
	EDA, wt %	Cd, wt %			
Fiber	17.7	1.5	30	340	27
	17.7	3.0	100	—	—
	28.3	0.5	20	245	28
	28.3	1.0	40	550	25
	28.3	2.0	100	—	—
	36.4	0.5	23	365	33
	36.4	1.0	100	—	—
	50.9	0.5	50	760	not meas.
	50.9	1.0	100	—	—
Film	28.3	2.0	100	—	—
	36.4	1.5	100	—	—
	50.9	1.0	100	—	—

[a] Grams swelling solution absorbed per 100 g of undissolved cellulose.
[b] Cellulose II.

of swelling agent by disordered cellulose fiber is also very much greater than that by cotton fiber in cadoxen solutions of the same composition.

Swelling of Cotton Fabric in Cadoxen Solutions

Table V shows that the cotton fabric absorbs much less cadoxen solution than does the cotton fiber. This behavior, which is similar to that observed in sodium hydroxide solutions, is presumably a result of the tensions

TABLE V
Swelling of Cotton Fabric in Cadoxen Solutions

Composition of swelling solution		Degree of swelling[a]	Degree of swelling after washing[b]
EDA, wt %	Cd, wt %		
28.9	0	50	55
28.9	1.13	56	56
28.9	2.22	65	58
28.9	3.29	88	60
28.9	4.33	305	107
34.9	3.25	129	82
36.4	3.10	126	75
36.4	4.35	121	90
38.4	2.80	120	81
50.9	1.96	100	79

[a] Grams swelling agent absorbed per 100 g cotton.
[b] Grams water in 100 g cotton after washing out the cadoxen in water.

on the fibers in the fabric structure. It should be emphasized, however, that the absorption can still be very high (as much as 300% by weight, which is higher than any degree of swelling attainable, even on free fiber, with sodium hydroxide solutions at 25°C).

Discussion

The absorption by cotton of a particular swelling agent is composed of two parts: (1) absorption of swelling agent between the microfibrils, leading to a lessening of interfibrillar cohesion and an expansion of the fibrillar arrangement (interfibrillar swelling), and (2) the absorption of swelling agent within the crystalline fibrils themselves (intrafibrillar swelling). It is thought that changes in lattice type and/or increased disorder in the washed and dried samples is a good criterion of intrafibrillar swelling. In the early stages of the swelling in cadoxen solutions (i.e., in solutions weak in cadmium), the swelling is probably interfibrillar only. In these early stages the absorbed cadmium must be associated with the cellulose on the surface only of the microfibrils; this would explain the lack of disordering or lattice change in these solutions. This "interfibrillar only" swelling can be very large (as much as 300%). At higher concentrations of cadmium, the absorbed cadmium begins to penetrate the fibrils, intrafibrillar swelling begins, and lattice change and increased disorder are observed in the washed and dried samples. At this stage the fibril surfaces are probably saturated with cadmium and interfibrillar hydrogen bonds become very few in number; this may promote a marked and more or less sudden increase in interfibrillar swelling. In the EDA–water system this probable association between the onset of the intrafibrillar swelling process and an increase in the degree of interfibrillar swelling is clearly suggested by a comparison of Figure 1 (the disordering being taken as an indication of intrafibrillar swelling) and Figure 4 (the acetyl value being a measure of the degree of interfibrillar swelling). There is good evidence of similar behavior in aqueous solutions of sodium hydroxide.[8,13] With cadoxen, however, the position on the swelling curves (in Figs. 5 and 6) of the start of intramolecular swelling, and the possible associated increase in intermolecular swelling, are less pronounced. As pointed out above, a large amount of interfibrillar swelling can apparently take place in cadoxen solutions in the absence of any intrafibrillar swelling.

The concentration of absorbed cadmium reaches a level-off value in cadoxen solutions of all EDA–water ratios, equivalent to almost one cadmium atom per a.g.u. This approximate 1:1 ratio just possibly corresponds to the complete formation of the cadmium–cellulose complex but is more likely to have no special significance, since in some instances at least part of the absorbed cadmium would be expected to be in the swelling solution present in the interfibrillar voids and capillaries. At the interfibrillar-only stage of swelling, the penetration of the microfibril by EDA and water will clearly be small. When intrafibrillar swelling takes place, there is possibly some entry of EDA into the microfibril, though direct evidence of this is not available.

As suggested above, it is probable that only when cadmium is absorbed into the microfibrils is there any possibility of lattice change or disordering. Structural change in the washed and dried cotton is always associated with a high absorption of cadmium, i.e., a good fraction of the "saturation" value of one cadmium atom per a.g.u. Admittedly, in certain cadoxen solutions (e.g., 4.3% Cd, 28.0% EDA) the amount of absorbed cadmium is high (48.6% in the example) and yet there is no lattice change or disordering produced. In these cases, however, the total swelling is very high (750% in the example given), and the large amount of absorbed cadmium can reasonably be accounted for in terms of the cadmium present in the large amount of interfibrillar liquid and absorbed on the fibrillar surfaces.

The effect of washing the cadoxen-swollen samples in ethanol shows that the intrafibrillar swelling may be different in character from that found in the mercerization system and suggests, in fact, that in cadoxen solutions the intrafibrillar swelling is the first stage in the dissolution of the cotton. Washing in ethanol is known to prevent recrystallization of cellulose that is disordered in the swollen state[25] and the fact that the ethanol-washed samples contain no cellulose II indicates that the cellulose II in water-washed samples is the result of a partial recrystallization, during the washing, of cellulose I regions that were "dispersed" and disordered during the intrafibrillar swelling process. Swelling in caustic soda solutions appears not to disorder the cellulose I lattice in the same manner, or to the same extent, since ethanol washing does not reduce the amount of cellulose II in the final product compared with washing in water.[25,26]

The Effect of Dilute Cuprammonium Hydroxide Solutions on Cotton

Samples of cotton were swelled in cuprammonium solutions of a range of concentrations. The treatment was for 1 hr at 25°C and was followed by a wash in ammonia solution of concentration 200 g/l., and then in water. In some cases a second treatment in cuprammonium was given.

Infrared-deuteration measurements on the dried samples showed that in no cuprammonium treatment (partially dissolving or not) was any cellulose I to II lattice change produced (Table VIa) and there was in general comparatively little increase in hydrogen bond disorder. The maximum increase measured was from 42% disorder (in untreated cotton) to about 55% disorder (in half-dissolved samples). A second treatment in cuprammonium solution increased the amount of cotton dissolved but did not produce any significant increase in the degree of structural change in the undissolved cotton (Table VIb).

The measurements of the degree of swelling of cotton in cuprammonium hydroxide were rather irreproducible. In measurements of fiber width this irreproducibility is difficult to understand, but in the measurements of weight of swelling agent absorbed is at least partially the result of the rapid evap-

TABLE VI

Effect of Treatment in Cuprammonium Hydroxide on Cotton Fiber[a]

(a)

Concn. of Cu, g/l.	Ratio of cotton to solution	Hydrogen bond ordered cellulose, %
0.76	0.4 g/50 ml	58
1.53	0.4 g/50 ml	59.5
2.29	0.4 g/50 ml	58.5
3.05	0.4 g/50 ml	55
3.82	0.4 g/50 ml	52
4.58	0.4 g/50 ml	50
7.63	0.4 g/4 ml	50
11.44	0 4 g/4 ml	51
2.29	10 g/750 ml	55
5.09	10 g/750 ml	46

(b)

	First treatment		Second treatment	
Concn. of Cu, g/l.	Cotton undissolved, wt %	Hydrogen bond ordered cellulose, %	Cotton undissolved, wt %	Hydrogen bond ordered cellulose, %
2.74	98.3	55	92.7	58
2.90	85.1	48	76.9	50
3.05	72.9	48	59.4	44
3.20	43.2	48	30.5	47
3.51	0	—	—	—

[a] The cotton solution ratio in Table VIa is 0.5 g/100 ml. The % undissolved cotton after the second treatment is a per cent of the *original* untreated sample of cotton. The hydrogen bond ordered cellulose is in each case cellulose I.

oration of ammonia from the sample during the centrifuging and weighing. The results are, however, sufficiently reliable to establish that high degrees of swelling are produced in both nondissolving and partially dissolving solutions. The swollen fibers had widths as high as 40–50μ and the increases in weight of the fibers during swelling were in the region 200%–500% (and possibly in some cases higher). The microscopic examination showed that ballooning took place in these highly swollen fibers.

Measurements of the acetylation in pyridine of swollen samples after being washed and solvent exchanged indicated that swelling in "nondissolving" cuprammonium solutions (e.g., 2.3 g copper per liter) did not produce any increase in internal surface over the increase produced by swelling in water alone. The partially dissolved samples had, however, a markedly increased acetylation value (23%), indicating a degree of interfibrillar swelling and separation in these solutions at least as great as that in solutions of sodium hydroxide of mercerizing strength and in cadoxen solutions.

SUMMARY AND CONCLUSIONS

Aqueous solutions of ethylenediamine (EDA), up to a concentration of about 40% by weight, swell cotton fiber to a moderate extent only and do not produce any significant change in the fine structure of the washed and dried cotton. In the range 40%–60%, however, the swelling increases markedly in magnitude, there is an increase in the internal surface area of the swollen fiber, and the treatments produce an increase in the disorder in the washed and dried cotton. Washing out the swelling agent with nonaqueous solvents in general leads to a product more disordered than that obtained by washing in water; some of these nonaqueous washes produced fibers containing a significant amount of cellulose III.

The swelling of cotton fiber in cadoxen solutions has been shown to be complex. In cadoxen solutions of some concentrations of EDA (16, 28, 50.9 and 60.2% by weight), the absorption of swelling agent increases steadily as the concentration of cadmium in the solution is increased to saturation; in 28% by weight EDA, the cotton dissolves in the more cadmium-rich solutions. In cadoxen solutions of intermediate concentrations of EDA (34.9, 36.4, 38.4, and 40.9% by weight), the curve relating the absorption of swelling agent to concentration of cadmium in solution at first increases and then, at the higher cadmium concentrations, decreases. The degree of absorption of cadoxen solutions by cotton fiber can be very high, as much as 2000% by weight. Cadmium is preferentially absorbed from solution, the absorption at each concentration of EDA tending to reach a maximum corresponding to almost one cadmium atom per anhydroglucose unit. Some of the cadoxen treatments increase the disorder in the cotton and produce some cellulose II regions; the important factor in these structural changes is the concentration of cadmium in the absorbed solution, not merely the total degree of swelling. Washing cadoxen-swollen cotton in ethanol tends to suppress the formation of cellulose II in the washed and dried structure. This is the opposite of the behavior found with cotton swollen with alkali solutions of mercerizing strength, where washing in ethanol tends to prevent the reformation of cellulose I in the washed and dried structure. Cotton fabric absorbs much less in cadoxen solution than does cotton fiber, as would be expected. The absorption can, however, still be very high, higher than any degree of swelling attainable, even on free fiber, with solutions of sodium hydroxide at 25°C. Disordered cellulose (prepared by the nonaqueous saponification of secondary cellulose acetate) swells and dissolves in cadoxen to a much greater extent than cotton. An extension of the present work to a wider range of celluloses, to elucidate more fully the relation between cellulose structure and swelling in cadoxen, would be rewarding.

Dilute solutions of cuprammonium hydroxide also swell cotton fiber highly (though not so highly as cadoxen solutions). None of these treatments in cuprammonium hydroxide, however, cause any change from cellulose I to cellulose II and there is in general comparatively little increase in hydrogen bond disorder, even in solutions strong enough to dissolve part of the cotton.

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