

## Deuteration of Cotton Fibers. I. Partially Decrystallized Celluloses

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### Synopsis

Deuteration of cellulose in the fiber form has been studied by the new technique developed recently. Infrared spectra in the  $3\text{-}\mu$  region were recorded to obtain four well-resolved bands due to H-bonded hydroxyl groups in the ordered regions. The peaks at  $3298$  and  $3400\text{ cm}^{-1}$  were assigned to cellulose I, while those at  $3445$  and  $3493\text{ cm}^{-1}$  were assigned to the cellulose II lattice structure. Cotton fibers containing both cellulose I and cellulose II lattice structures (50:50%) gave six bands in the  $3\text{-}\mu$  region at  $3230$ ,  $3298$ ,  $3350$ ,  $3400$ ,  $3445$ , and  $3493\text{ cm}^{-1}$ . Deuteration of swollen and decrystallized cotton fibers revealed that ethylenediamine brings about partial conversion of cellulose I lattice structure to cellulose II lattice structure, giving the characteristic cellulose II band at  $3493\text{ cm}^{-1}$ . Swelling mechanism with ethylenediamine to account for formation of cellulose II in cotton fibers has been put forward. Zinc chloride was found to retain the cellulose I structure intact. In both the decrystallized celluloses, the band at  $3400\text{ cm}^{-1}$  has been found to be completely wiped out. This band has been assigned to the group of H bonds mainly lying in rather imperfectly ordered crystalline regions in the fiber structure, which are attacked first during swelling treatment by both the swelling agents irrespective of their different mechanisms of swelling.

### INTRODUCTION

The main aim of the present paper is to report the findings on the changes brought about by different swelling agents in the lattice structure of cotton fibers using the infrared deuteration technique.

In an earlier communication,<sup>1</sup> it was shown that as a result of the new infrared deuteration technique developed in our laboratories, cellulosic material in the fiber form could be studied by the infrared deuteration method to give a better resolution of the four discrete OH bands in the  $3\text{-}\mu$  region. Description of the new deuteration technique developed forms the subject of the subsequent communication.

Frilette, Hanle, and Mark<sup>2</sup> developed the falling drop method in their deuteration studies on cellulose and established a two-step mechanism. These authors applied the H-D exchange reaction to characterize the fine structure of cellulose. Mann and Marrinan<sup>3,4</sup> extensively studied the H-bonded ordered regions of celluloses I, II, III, and IV using the infrared deuteration technique and reported the existence of H<sub>2</sub>O-resistant OD groups in cellulose. Tsuboi<sup>5</sup> observed four distinct bands due to OH stretching in the  $3\text{-}\mu$  region in case of fully amorphous cellulose and concluded that the "amorphous" cellulose contained a small fraction of crystalline material. Pennings,

Prins, Hale, and Ranby<sup>6</sup> carried out swelling and deuteration of regenerated cellulosic films simultaneously in NaOD solutions and concluded that intramolecular order in cellulose was retained longer during progressive swelling than intermolecular order.

Okajima and Inoue<sup>7,8</sup> carried out D<sub>2</sub>O exchange reaction at high temperatures and observed that liquid-phase deuteration, even at 210°C for 7 min, could not bring about 100% exchange reaction of hydroxyl groups. Jeffries<sup>9</sup> studied in detail the deuteration of disordered celluloses, and obtained cellulose I lattice structure in zinc chloride-treated as well as in ethylenediamine-treated bacterial cellulose. Dechant<sup>10</sup> found native cellulose to be more accessible toward deuterated ethanol (EtOD) than toward deuterated methanol (MeOD), whereas the reverse was true with respect to regenerated cellulose, indicating the difference in structure of accessible regions of both types of cellulose.

## EXPERIMENTAL

### Materials

**Fibers.** Long staple Sudanese cotton fibers were purified according to a standard procedure.<sup>11</sup> The fibers had the following specifications: degree of polymerization, 2250; copper number, 0.01; carboxyl content, 0.335 meq/100 g cotton.

**Chemicals.** Sodium hydroxide was of C.P. grade in the form of pellets. Anhydrous zinc chloride and ethylenediamine used in the swelling reaction were of C.P. grade. Deuterium oxide was 99.5% pure and was supplied by The Bhabha Atomic Research Centre, Bombay. The KBr used in the infrared studies was of spectroscopic grade supplied by Spex Industries, Inc., U.S.A. Other chemicals, e.g., methanol and ether, used in the preparation of swollen samples were also of C.P. grade.

### Methods

**Preparation of Cellulose I + Cellulose II Lattice Structures in the Same Fiber.** Cotton fibers were treated in 14% NaOH solution at 10°C for 5 min, followed by washing. The fibers contained approximately 50:50% cellulose I and cellulose II.

**Preparation of Swollen and Decrystallized Cotton Cellulose.** The swelling conditions chosen in case of zinc chloride were 65% concentration, 20°C, and 1 hr; while those for ethylenediamine were 70% concentration, 35°C, and 1 hr. After the swelling treatments, the samples were washed in a large volume of distilled water until the fibers were free from the traces of the swelling agents. Loosely held water was removed by suction and the final traces by the solvent exchange method (first dry methanol and then dry ether). The samples were then heated at about 35°C for 30 min and stored over P<sub>2</sub>O<sub>5</sub>. The dry cotton fibers were used in the deuteration studies.

**Infrared Deuteration Technique.** The liquid-phase deuteration technique was employed. The KBr-disc technique was used to record the spectra of deuterated cotton fibers. The detailed procedure of the new technique

has been described elsewhere.<sup>12</sup> Essentially, the new technique consists in carrying out deuteration of finely cut and accurately weighed cellulosic fibers in a dry box with running dry nitrogen atmosphere. The Mini-Press (manufactured by Wilks Scientific Corporation, U.S.A.) was employed after effecting a suitable modification by fabricating a set of screws with shorter arms, but exactly similar to the original ones except that they were hollow throughout, with a groove on the top to hold NaCl plates. A cap with a hole at the center was also fabricated which was screwed to the top of the groove holding the NaCl plate. KBr pellets containing the deuterated sample were pressed in the dry box using the Mini-Press. The screws of the Mini-Press containing a pellet were then replaced by the modified assembly containing the hollow screws to give an air-tight system obtained by using suitable rubber washers. This assembly was then mounted directly on the spectrophotometer for scanning the spectrum.

## RESULTS AND DISCUSSION

### Deuteration of Cellulose I + Cellulose II

From Table I, it can be seen that both cellulose I and cellulose II give four discrete bands in the  $3\text{-}\mu$  region after deuteration of the fibers. The bands at  $3230$  and  $3350\text{ cm}^{-1}$  are common for celluloses I and II. The bands at  $3298$  and  $3400\text{ cm}^{-1}$  are characteristic bands for cellulose I, while those at  $3445$  and  $3493\text{ cm}^{-1}$  are exclusive for the cellulose II lattice structure.

Cellulose fibers containing both cellulose I and cellulose II lattice structures (50:50%) were subjected to deuteration infrared studies with a view to obtain various OH bands in the  $3\text{-}\mu$  region and also to compare the frequen-

TABLE I  
Frequencies of Peaks in the  $3\text{-}\mu$  Region After Deuteration of Different Celluloses

Fiber	No.	Frequency ( $\nu$ ) of peaks, $\text{cm}^{-1}$	Quality of peaks
Cellulose I (cotton)	1	3230	small
	2	3298	prominent with sharp tip
	3	3350	broad and prominent
	4	3400	small but well resolved
Cellulose II	1	3230	broad and prominent
	2	3350	broad
	3	3397	additional small band due to splitting of $3350\text{ cm}^{-1}$ band
	4	3445	broad, prominent with scales at the tip
Cellulose I + cellulose II (50:50%)	5	3493	small but well resolved
	1	3230	broad and prominent
	2	3298	broad with scales at the tip
	3	3350	well defined, narrow, and prominent
	4	3400	broad with sharp tip
	5	3445	broad and prominent
	6	3493	very small

TABLE II  
Frequencies of Peaks in the 3- $\mu$  Region After Deuteration  
of Cotton Swollen in Different Swelling Agents

Swelling treatment	No.	Frequency ( $\nu$ ) of peaks, $\text{cm}^{-1}$		Peaks for cellulose I and/or cellulose II
		Unswollen cotton	Swollen cotton	
ZnCl <sub>2</sub> , 65%, 1 hr, 20°C	1	3230	3230	I + II
	2	3298	3298	I only
	3	3350	3350	I + II
	4	—	3375	as a result of approximate 23 $\text{cm}^{-1}$ shift toward each other in case of peaks at 3350 $\text{cm}^{-1}$ and 3397 $\text{cm}^{-1}$
	5	3400	—	I only
Ethylenediamine, 70%, 1 hr, 35°C	1	3230	3230	I + II
	2	—	3275	I only; as a result of shifting of 3298 $\text{cm}^{-1}$ peak
	3	3298	—	I only
	4	3350	3350	I + II
	5	—	3397	due to splitting of the peak at 3350 $\text{cm}^{-1}$
	6	3400	—	I only
	7	—	3493	II only

cies with those obtained separately for cellulose I and cellulose II structures. From Table I, it can also be seen that these fibers give six well-resolved hydroxyl bands in the 3- $\mu$  region at 3230, 3298, 3350, 3400, 3445, and 3493  $\text{cm}^{-1}$ . Thus, both the common bands for cellulose I and cellulose II structures at 3230 and 3350  $\text{cm}^{-1}$  were obtained. The two characteristic bands of cellulose I alone (3298 and 3400  $\text{cm}^{-1}$ ) and the other two bands for cellulose II alone (3445 and 3493  $\text{cm}^{-1}$ ) have also been observed.

### Deuteration of Swollen and Decrystallized Celluloses

Table II gives the results of deuteration studies of zinc chloride-treated and ethylenediamine-treated cotton fibers. It can be seen that the bands at 3230 and 3298  $\text{cm}^{-1}$  are unaffected by the swelling treatment with 65% zinc chloride solution at 20°C for 1 hr. The band at 3400  $\text{cm}^{-1}$ , however, is completely wiped out. A band at 3375  $\text{cm}^{-1}$  appears and happens to be equidistant from the two bands at 3350 and 3397  $\text{cm}^{-1}$  and arises as a result of splitting of the band at 3350  $\text{cm}^{-1}$ . It seems that this band is shifted to 3375  $\text{cm}^{-1}$  in the zinc chloride-treated cotton cellulose. The fact that one of the four discrete bands in the 3- $\mu$  region, viz., the band at 3400  $\text{cm}^{-1}$ , is wiped out as a result of swelling and decrystallization of cotton fibers by the 65% zinc chloride solution shows that a particular group of H bonds in the ordered regions of cellulose has been broken during the swelling reaction. Zinc chloride-treated cotton on deuteration, however, gives bands in the 3- $\mu$  region characteristic only of cellulose I structure and no band appears in the spectrum showing the trace of cellulose II lattice in the fibers. Therefore, it

seems that zinc chloride retains cellulose I structure of cotton cellulose during the swelling treatment.

The main features of the infrared spectrum in the  $3\text{-}\mu$  region of deuterated cotton fibers swollen in 70% ethylenediamine solution at  $35^\circ\text{C}$  for 1 hr are given in Table II. The common bands at  $3230$  and  $3350\text{ cm}^{-1}$  for cellulose I and cellulose II have been retained. Like in the case of zinc chloride-treated cotton cellulose, the band at  $3400\text{ cm}^{-1}$  is completely suppressed, while a cellulose I band at  $3298\text{ cm}^{-1}$  is shifted to  $3275\text{ cm}^{-1}$ . Incidentally, this band remains undisturbed in case of zinc chloride-treated cotton cellulose. The most important feature of this spectrum is the development of a new band at  $3493\text{ cm}^{-1}$ , which has been assigned exclusively to the cellulose II lattice structure.

These results indicate that the mechanisms of swelling and decrystallization of cotton fibers by zinc chloride and ethylenediamine are different and that the severity of decrystallizing action of these reagents with respect to breaking the H bonds in the ordered regions is different in different regions for the individual swelling agent. Thus, two different types of mechanism bring about different changes in the internal structure of cotton fibers resulting in the formation of cellulose II lattice structure as a result of decrystallizing action of ethylenediamine, zinc chloride retaining the cellulose I structure intact.

The fact that one and the same band, viz., the one at  $3400\text{ cm}^{-1}$  is eliminated as a result of swelling and decrystallizing action of zinc chloride and ethylenediamine shows that a particular group of H bonds in the ordered regions is broken during the treatments. These H bonds seem to be ruptured in the beginning of the attack on crystals of native cellulose and, therefore, lie on the crystallite surfaces, which are H bonded in the random amorphous manner. Okajima and co-workers<sup>7,13</sup> arrived at a similar conclusion from the x-ray diffraction and deuteration studies on *Valonia* cellulose.

### Mechanism of Conversion of Cellulose I into Cellulose II Lattice Structure by Diamines

Although ethylamine<sup>14,15</sup> has been found to change cellulose I lattice structure to celluloses II and III, there seems to be no information available in the literature so far with respect to such a result in case of treatments with ethylenediamine on cotton cellulose. Segal and co-workers<sup>16,17</sup> and Patil et al.<sup>18</sup> worked extensively on the swelling and decrystallizing action of aqueous solutions of ethylenediamine and reported that in case of cotton, the cellulose I structure is retained by washing out the diamine with water if the original cellulose is a native cellulose and a cellulose II lattice is formed if the original cellulose is a cellulose II structure. Segal and co-workers<sup>16,17</sup> put forward the mechanism of swelling action of ethylenediamine, according to which ethylenediamine solutions beyond the concentration of dihydrate brought about considerable swelling and decrystallization of cotton, the ethylenediamine molecule forming a bridge between the two cellulose chains. As a result of bridge formation, the cellulose I lattice structure was retained giving no evidence of the formation of cellulose II lattice structure.

Although in a solution of ethylenediamine of about 70% concentration the

ethylenediamine molecules exist in the form of monohydrates, it is likely that at the same time other types of swelling species of the diamine can exist in the same solution. Thus, this solution might contain a monohydrate, a dihydrate, free ethylenediamine, and even free water. Bridge formation of the ethylenediamine molecule across the two cellulose chains will be possible only when certain preconditions are satisfied, such as availability of enough space between two cellulose chains to accommodate the ethylenediamine molecule, availability of two OH groups on two separate chains of cellulose in the close vicinity of the end-NH<sub>2</sub> groups, and availability of both the —NH<sub>2</sub> groups in the ethylenediamine molecule. Although in the majority of cases all the above-mentioned conditions may be satisfied, it is, however, likely that under certain conditions of treatment either of these requirements or all of them may not be fulfilled. Thus, an ethylenediamine molecule, while penetrating in the crystalline region, may form an H bond with a hydroxyl group of a chain and, although the —NH<sub>2</sub> group at the other end of the ethylenediamine molecule is capable of forming a similar H bond with another OH group, may remain hydrated or free. This is the case of a monofunctional reagent. Under such conditions, as a result of lack of bridge formation, the anhydroglucose unit of a cellulose chain has complete freedom of rotation giving rise to the conversion of cellulose I structure into cellulose II lattice. It is also quite possible that all the ethylenediamine molecules capable of forming a three-dimensional network may not enter in the interchain bridge formation between the chains but some of them may enter into the intrachain bridging between the two OH groups either in the same anhydroglucose unit or across the two units on the same chain. In such cases, also the individual chain molecule has complete freedom of rotation; and, in addition to intrafibrillar swelling and decrystallization of cotton fibers, conversion of cellulose I into cellulose II could be possible.

Results of the present investigation suggest that careful manipulation of swelling conditions of cotton fibers with respect to the concentration of ethylenediamine, the time and temperature of treatment, the mode of removal of the swelling agent from the fibers, and repeating the swelling cycles either using the same or another swelling agent during certain intermediate cycles or mixtures of the two may bring about conversion of the cellulose I lattice structure into other lattice structures including cellulose II.

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