

Spectral Studies on Cellulose Treated with Sodium Deuterioxide

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Synopsis

Cellulose II and cellulose I samples were treated respectively with a strong solution of sodium deuterioxide in D_2O and a 99% solution of ethylenediamine. The complexes were washed with D_2O and the nature of the OD bands were studied after rehydrogenating the sample. The infrared spectra of these rehydrogenated samples showed well-resolved OD bands which are resistant to reexchange. The characteristic bands are discussed and compared with the predicted OH-OD frequency shifts.

INTRODUCTION

Extensive work has been reported on the spectral effects resulting from deuterium exchange between deuterium oxide and cellulose. This technique has become an important tool for the characterization of the cellulose structure. The nature of the changes in the OH stretching region in the infrared spectra of various celluloses deuterated in liquid D_2O was studied particularly by Mann and Marrinan,¹ Jeffries,² and Daruwalla et al.³ In these studies the nature of the resistant OD bands was not studied, as natural cellulose has only a limited accessibility toward deuterium oxide. As it is very difficult for the deuterium oxide to penetrate into the highly ordered regions and to form well-ordered deuterium bonds that are resistant to rehydrogenation, it was not possible to obtain a well-resolved vibrational spectrum in the OD region. Ranby et al.⁴ were able to carry out the deuteration on regenerated cellulose films by swelling in solutions of sodium deuterioxide.

Tsuboi⁵ has reported a few bands in the OD region from his studies on the polarization spectra of ramie fibers treated with a solution of NaOD in D_2O and subsequently washed with D_2O and dried and rehydrogenated. But the concentration of the NaOD solution used was not sufficient to effect any intracrystalline swelling thereby necessitating the study of polarization spectra for analyzing the OD bands. In the present work, NaOD treatment on natural cotton is studied for the first time and some interesting results regarding resistant OD bands characteristic of cellulose II and cellulose I by effecting intracrystalline swelling are reported.

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EXPERIMENTAL

Sudan cotton treated 50 times in sodium hydroxide solution and oven dried, known from an earlier study,⁶ to possess a pure form of cellulose II structure having high lateral order, was again treated with a solution of 20% NaOD in D₂O for 1 hr, washed with D₂O, and dried in nitrogen atmosphere. After drying, the sample was exposed to atmospheric conditions and allowed to rehydrogenate, and thereafter the sample was oven dried at 100°C. Another sample of Sudan raw cotton was treated with 99% ethylenediamine for 1 hr and washed with D₂O and dried in nitrogen atmosphere. As in the previous case, one half of the sample was allowed to rehydrogenate and was oven dried at 100°C.

The infrared spectra were recorded on a Perkin-Elmer Model 377 spectrophotometer using the KBr pellet technique. The KBr pellets of rehydrogenated samples were prepared using the ordinary 13-mm die, and the pellets of the samples before rehydrogenation were prepared under nitrogen atmosphere using a special die. The KBr used was of spectroscopy quality. However, a blank KBr pellet was always used in the reference beam.

For x-ray studies, nickel-filtered CuK α radiation from a Philips 1009 unit operated at 35 kV and 20 mA was used. Data were gathered by reflection technique using a divergence slit of 1°, a receiving slit of 0.05°, and a scatter slit of 1°. For the diffractometer studies the samples were cut with a pair of scissors, sieved through a 300-mesh screen, and made into rectangular pellets weighing exactly 100 mg with the aid of a special die as in earlier studies. All x-ray examinations were carried out at 50% R.H.⁷ The total order in the case of the cellulose I diffractogram was followed by measuring the half-width of the 002 peak.

RESULTS AND DISCUSSION

Cellulose II

It can be seen in the spectrum of the NaOD-treated highly ordered cellulose II sample shown in Figure 1 that the OD absorption in the 2500 cm⁻¹ region on rehydrogenation resolves itself into five well-defined bands at 2585, 2560, 2490, 2460, and 2360 cm⁻¹. These well-defined bands are due to the systematically arranged deuterium bonds in the crystalline region. The two bands at 2585 and 2560 cm⁻¹ are the most intense and well-defined bands and are typical of cellulose II structure. This corresponds to a similar observation in the OH region where two bands are observed above 3400 cm⁻¹ in cellulose II.

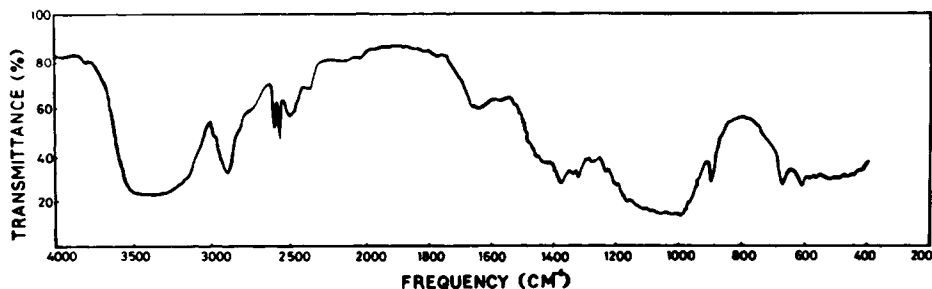


Fig. 1. IR spectrum of highly ordered cellulose II treated with 20% NaOD for 1 hr, washed with D₂O, dried, and rehydrogenated.

TABLE I
Cellulose II

OH Frequency, ⁸ cm ⁻¹	OD Frequency, cm ⁻¹		RI
	Computed	Observed	
3488	2598	2585	VS
3447	2560	2560	VS
3350	2490	2490	S
3305	2458	2460	Sh
3175	2367	2360	S

^a RI = Relative intensity; S = sharp; Sh = shoulder; VS = very sharp.

These frequencies are also in good agreement with those reported by Tsuboi.⁵ On comparison of these bands with the well-resolved OH bands in the polarization spectrum of cellulose II by Marchessault and Liang,⁸ it is found that there are five characteristic bands in the OH region assigned to cellulose II, and these have their counterparts in the OD region as well. The computed frequencies corresponding to these five OH bands using the usual isotope shift formula for OH to OD (see Appendix) are given in Table I together with observed frequencies.

Cellulose I

Figure 2 shows the spectra of 99% ethylenediamine-treated sample subsequently washed with D₂O, before and after rehydrogenation. These can be considered as cellulose I spectra, as treatment with 99% ethylenediamine is claimed not to effect any lattice change in cellulose during the first treatment, although some disruption in the cellulose I structure is shown by x-ray studies. After washing the EDA-cellulose complex with D₂O, the re-formation of deuterium bonds takes place in the same manner so as to revert to cellulose I. Such behavior in case of EDA-treated, H₂O-washed sample has been shown before. The OD band here shows a poorly resolved broad band with a relatively sharp peak at 2490 cm⁻¹ and three other bands at 2450, 2470 and 2540 cm⁻¹. The band at 2360 cm⁻¹ observed in the cellulose II spectrum is absent in the spectrum of EDA-treated sample. The profile of deuterium bands compares well with most of the OH bands reported by Liang and Marchessault⁹ for cellulose I, except the one at 2470 cm⁻¹. That these bands are due to cellulose I-type lattice with deuterium bonds is confirmed by the computed frequency shifts (Table II) calculated on the basis of OH values given by Liang and Marchessault.⁹

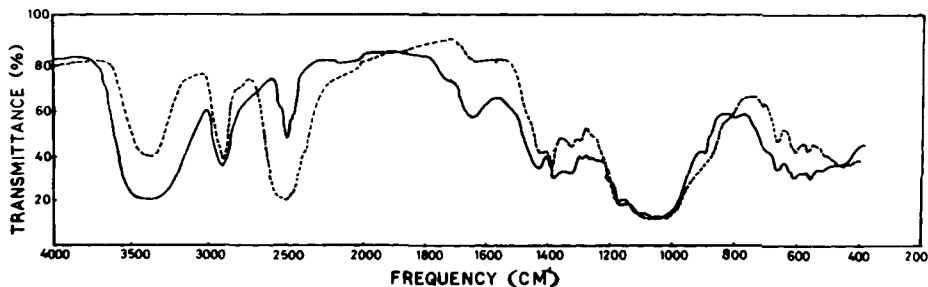


Fig. 2. IR spectra of native cellulose treated with 99% ethylenediamine for 1 hr, washed with D₂O, and dried before rehydrogenation (---) and after rehydrogenation (—).

TABLE II
Cellulose I

OH Frequency, ⁹ cm ⁻¹	OD Frequency, cm ⁻¹		
	Computed	Observed	RI
3405	2529	2540	Sh
3350	2490	2490	VS
—	—	2470	Sh
3305	2458	2450	Sh

The spectra of deuterated and rehydrogenated cellulose I are shown in Figure 3. The peak at 890 cm⁻¹ loses in intensity on deuteration, confirming the earlier findings of Higgins et al.¹⁰ on the sensitivity of this band to deuterium exchange indicating its close relationship with the easily accessible OH groups. On comparison of Figure 2 with Figures 1 and 3, it is seen that although the spectrum of the 99% ethylenediamine-treated sample is very similar to that of cellulose I, a close examination reveals some minor differences. It appears as though the structure has assumed an intermediate state between cellulose I and cellulose II. This may be due to the fact that on swelling with ethylenediamine and washing with water, most of the EDA-cellulose complex reverts back to the cellulose I lattice while, however, a small portion of the structure remains in a disrupted state although not conforming to the cellulose II-type structure.

In order to confirm whether this situation is due to a lowering in the lateral order or due to an inherent change in the molecular structure itself, x-ray examinations were carried out on raw cotton treated with 99% ethylenediamine for 1 hr and washed with water, dried, and afterward boiled in water and dried. Table III shows the half-widths of the 002 peaks, from which it may be noted that the structure is unable to revert to the original state on boiling in water thereby

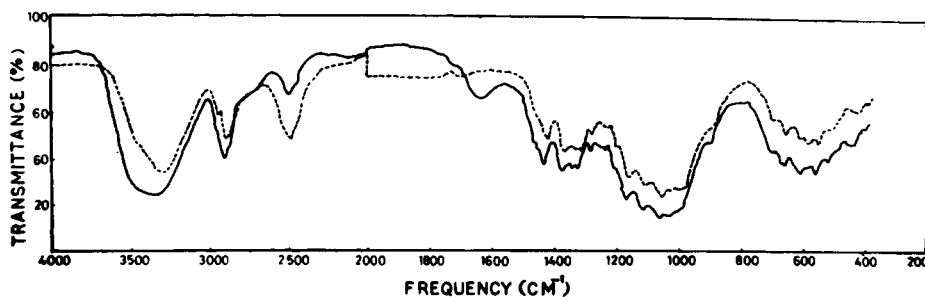


Fig. 3. IR spectra of native cellulose deuterated (---) and rehydrogenated (—).

TABLE III
Half-widths of 002 Peaks of Cotton Samples

Sample no.	Sample	Half-width of 002 peak, degree
1	Raw cotton	1.55
2	Raw cotton treated with 99% EDA, washed with water, and dried	2.0
3	Sample 2 boiled in water and dried	1.75

indicating some permanent change. The lattice transformation which occurs on subsequent repetitive treatments with ethylenediamine has been mentioned in an earlier study.¹¹ It is also seen that on repeated treatments with anhydrous EDA and subsequent washing with D₂O, OD bands characteristic of cellulose II are found on rehydrogenation. It may also be mentioned that the far-infrared region of the cellulose II spectrum shows a relatively strong band at 470 cm⁻¹.

CONCLUSIONS

Highly resolved, resistant OD bands can be obtained in the vibration spectrum of cellulose II by effecting deuterium exchange in the crystalline region by treatment with a strong solution of sodium deuterioxide in D₂O. The OD bands characteristic of cellulose I can be studied by swelling native cotton with anhydrous ethylenediamine and subsequent washing of the complex with D₂O. The observed frequency shifts in the OH-OD bands are in good agreement with the predicted shifts.

Appendix

The frequencies of the OD bands were calculated from those of OH bands according to the OH-OD relationship $1: 1/\sqrt{2}$. A correction factor was applied to these computed OD frequencies since this relationship does not hold well for bonded groups. The corrected values are determined in the following manner. Comparing the OH region of cellulose II spectrum⁸ and the OD region of the NaOD-treated cellulose II, it can be seen that the sharp band at 2560 cm⁻¹ corresponds to the OH band at 3447 cm⁻¹. On calculating the OD frequency from OH according to the above relationship, it can be seen that the observed OD is higher than the calculated OD BY A VALUE OF [2] CM⁻¹/ This value has been used as the correction factor and applied to the computed values. Within the short-frequency range of 2350-2600 cm⁻¹, this correction factor is assumed to be constant.

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