

A Comparative Study of the Swelling Action of Monoamines and Diamines on Cotton Cellulose

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Cotton cellulose was subjected to single and multiple swelling treatments with anhydrous ethylamine and 99% ethylenediamine. The effects of monoamine and diamine treatments on the fine structure of cellulose were found to be similar. The current theory of swelling action of amines on cotton cellulose has been modified. In the light of fresh evidence, the theory of the diamine molecules crosslinking the neighbouring cellulosic chains is found to be untenable.

Swelling studies with amines on cotton cellulose have been made by several workers. Legrand¹ studied the effect of liquid ammonia treatment on the structure of cellulose. Segal *et al.*² and Patil *et al.*³ studied the decrystallization effect of monoamines and diamines respectively. In the case of ethylamine treatment, Segal *et al.*⁴ reported the formation of cellulose III. Such a lattice transformation was not observed so far in the case of ethylenediamine (EDA) treatment. This led the investigators to propose a different mechanism for the swelling action of diamines as compared to that of monoamines. It is postulated that the diamine molecules, due to their difunctional nature, form crosslinks between the cellulose chain molecules and prevent any lattice transformation. In our earlier paper⁵ it was reported that a lattice transformation takes place even with EDA when subjected to multiple swelling where cellulose II is formed. Glegg *et al.*⁶ reported the formation of cellulose II from sulphite wood pulp by repeated treatments with ethylamine. In the present study, it has been shown that basically there is considerable similarity in the swelling actions of monoamines and diamines.

Materials and Methods

Sudan cotton was used. Fibres were subjected to a number of swelling treatments while in a completely slack state. Schematic diagrams of various sequences of the treatments with ethylamine and EDA (99%) are given in Figs 1 and 2 respectively.

X-ray examination—Nickel filtered CuK_α radiation from a Philips 1009 unit was used. The samples were

prepared for powder diffractometry, as in the earlier study⁵. The lateral order in cellulose I structure was estimated by measuring the half-width of the 002 peak.

Infrared analysis—Infrared spectra of the treated samples washed with heavy water, dried and rehydrogenated were taken on Perkin-Elmer model 377 spectrophotometer using KBr pellet technique.

Results and Discussion

Loss in lateral order—The half-widths of the 002 peaks of various treated samples are given in Table 1. It is seen that the half-width of the 002 peak increases as a result of swelling treatments with EDA and ethylamine to the same extent. Further, there is a reduction in half-width when the above treated samples are subjected to boiling water treatment; the magnitude of reduction in the half-widths was found to be the same in both the cases. The half-width for these boiled samples, however, remains larger than that observed for untreated raw cotton sample. This inability of the structure to regain its original lateral order indicates that on boiling with water, while most of the structure reverts back to cellulose I, some of the structure remains in an intermediate state between cellulose I and cellulose II. To see whether this intermediate stage retains the chain conformation of the original lattice, the boiled samples were treated with 7% NaOH (which does not cause any lattice transformation of raw cotton at 0°C for 1 hr) and washed in water and dried. The resultant structure had the same half-width as the untreated cellulose I (Table 1). The X-ray diffractogram of the cotton sample shown in Fig. 3 does not show the presence of cellulose II structure. Thus, it is evident that both EDA and ethylamine behave in a similar fashion as far as

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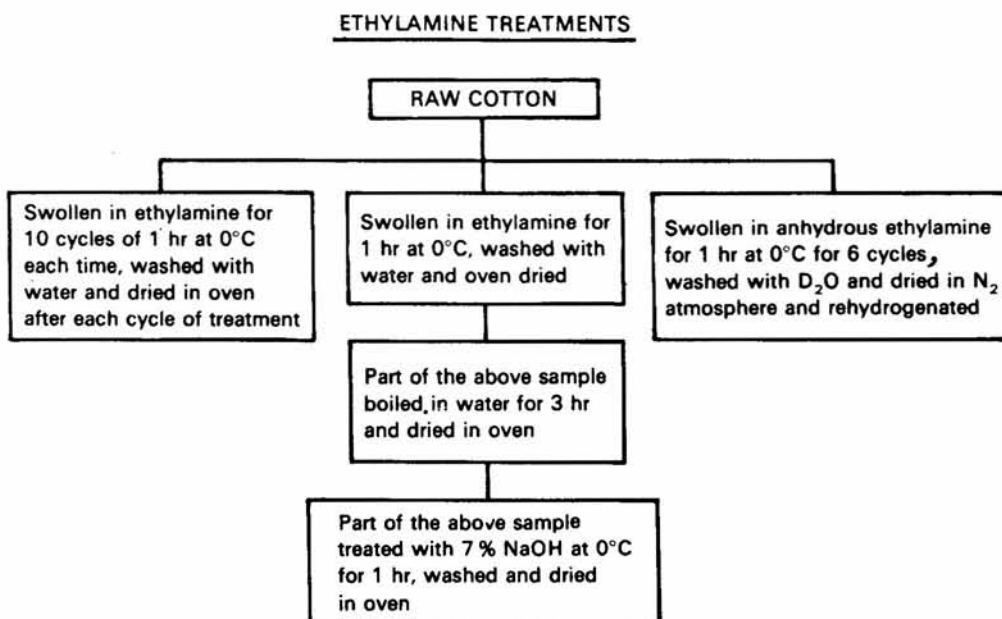


Fig.1—Schematic diagram of various sequences of treatments with ethylamine

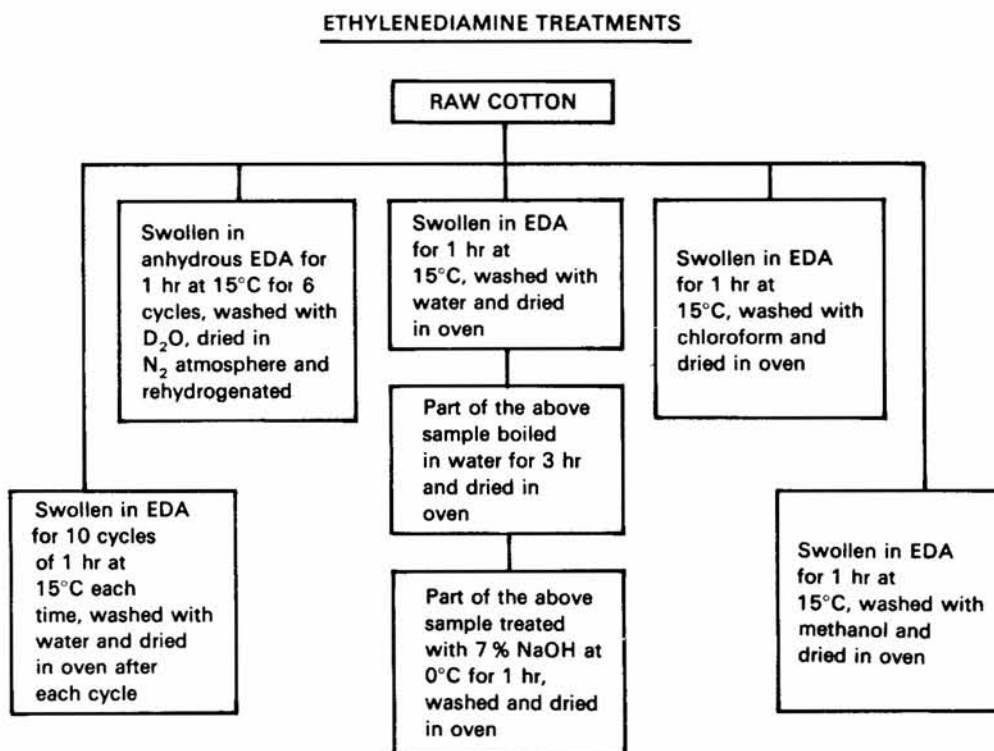


Fig.2—Schematic diagram of various sequences of treatments with ethylenediamine

decrystallization treatment is concerned and that upon single treatment only decrease in the lateral order in cellulose I structure takes place.

Formation of cellulose III—The formation of cellulose III by treatment with ethylamine has been reported by Segal *et al.*⁴ and many other workers.

Similar transformation to cellulose III by EDA was not observed by earlier workers. The slow evaporation method used in the case of ethylamine treated samples which clearly demonstrates the presence of cellulose III could not be used in the case of EDA treated sample, as the boiling point of EDA is very high. This necessitates

Table 1—Half-width of 002 Peak of Treated Samples

Sl No.	Sample	Half-width of 002 peak deg
1	Sudan native cotton	1.55
2	Sudan cotton treated with 99% EDA for 1 hr, washed with water and dried	2.00
3	Sudan cotton treated with anhydrous ethylamine for 1 hr, washed with water and dried	1.95
4	Sample (2) boiled in water for 2 hr	1.75
5	Sample (3) boiled in water for 2 hr	1.70
6	Sample (4) treated with 7% NaOH for 1 hr at 0°C, washed with water and dried	1.55
7	Sample (5) treated with 7% NaOH for 1 hr at 0°C, washed with water and dried	1.55

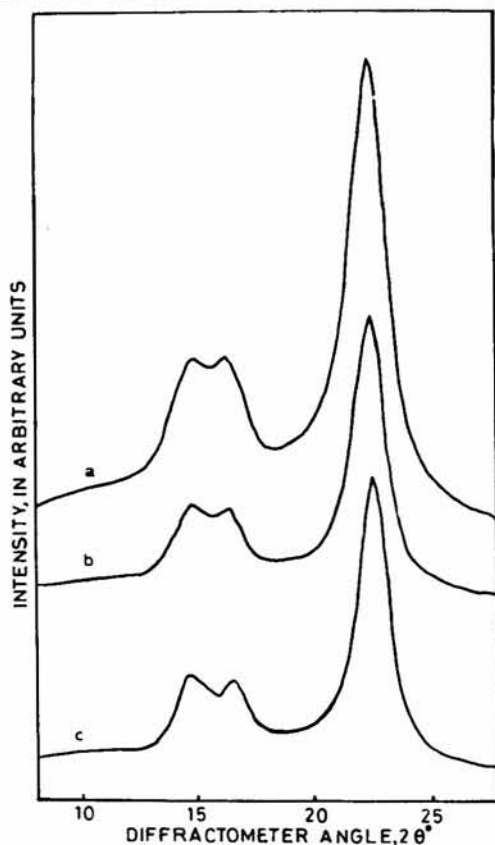


Fig. 3—Diffraction scans for (a) Cotton treated with 99% EDA for 1 hr, (b) Sample (a) boiled in water, and (c) Sample (b) treated with 7% alkali

the use of a solvent to decompose the complex. By washing with water no transformation could be observed. In the present work, non-aqueous solvents, viz. chloroform and methanol, were used to remove EDA. The complete absence of EDA subsequent to such treatment was ascertained by infrared analysis. After thoroughly removing EDA with these solvents, the resultant structure showed the presence of cellulose III, as can be seen from the diffractograms shown in Fig. 4. The appearance of peaks at $2\theta = 11.8^\circ$ and 2θ

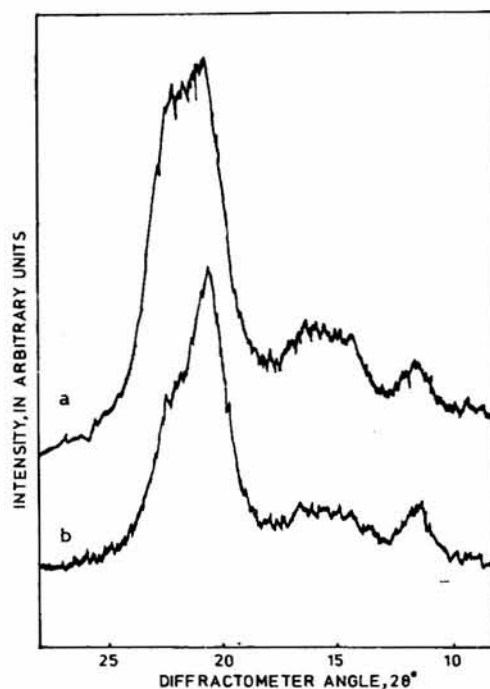


Fig. 4—Diffraction scans of (a) Cotton treated with 99% EDA for 1 hr and washed with methanol, and (b) Cotton treated with 99% EDA for 1 hr and washed with chloroform

$= 20.6^\circ$ shows the presence of cellulose III in the structure. The inability to detect cellulose III by EDA treatment so far has been the principal ground to surmise that the swelling action of EDA is different from that of ethylamine. The formation of cellulose III by EDA treatment, clearly demonstrated in the present work, shows that it is not necessary to postulate two different mechanisms of interactions for ethylamine and EDA with cotton cellulose.

Formation of cellulose II—It has been reported by us earlier^{5,7} that multiple swelling treatment with EDA effects complete lattice transformation from cellulose I to cellulose II. Gregg *et al.*⁶ observed a similar effect on sulphite wood pulp by treatment with ethylamine where solubility in ferric ammonium tartrate solution was used to study the structural change. Figs. 5 and 6 show the diffractograms of cotton repeatedly treated with EDA and anhydrous ethylamine respectively. As in the case of EDA treatment reported earlier⁵⁻⁷, even for ethylamine treatment cellulose II formation is clearly observed.

The infrared spectra of cotton samples treated with anhydrous EDA and anhydrous ethylamine, washed with D_2O , dried in nitrogen atmosphere and rehydrogenated in atmospheric condition are shown in Figs. 7 and 8. The spectra show characteristic bands in the 2500 cm^{-1} region. These well defined bands are due to the systematically arranged deuterium bonds in the crystalline region. Since they are in the crystalline region, they are highly resistant to rehydrogenation.

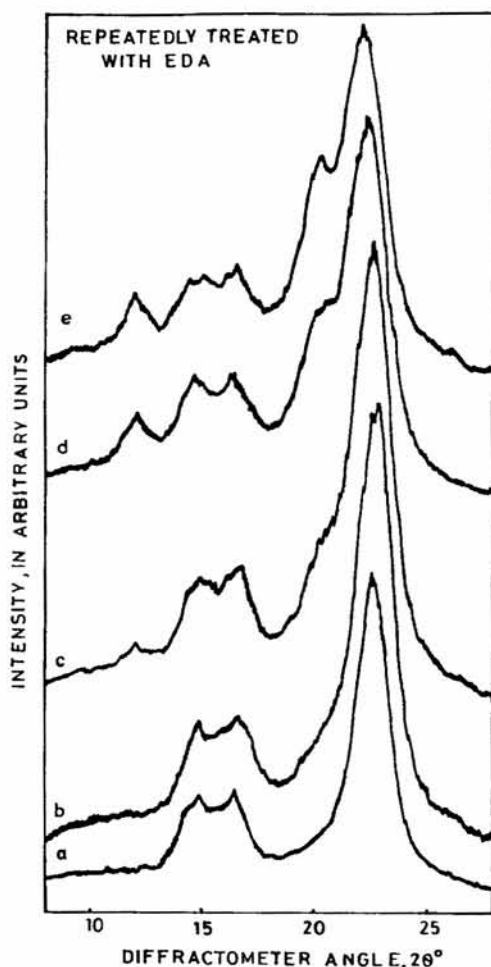


Fig.5—Diffractometer scans of cotton subjected to repeated swelling treatments with anhydrous EDA for various cycles [(a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, (d) 4th cycle, and (e) 5th cycle]

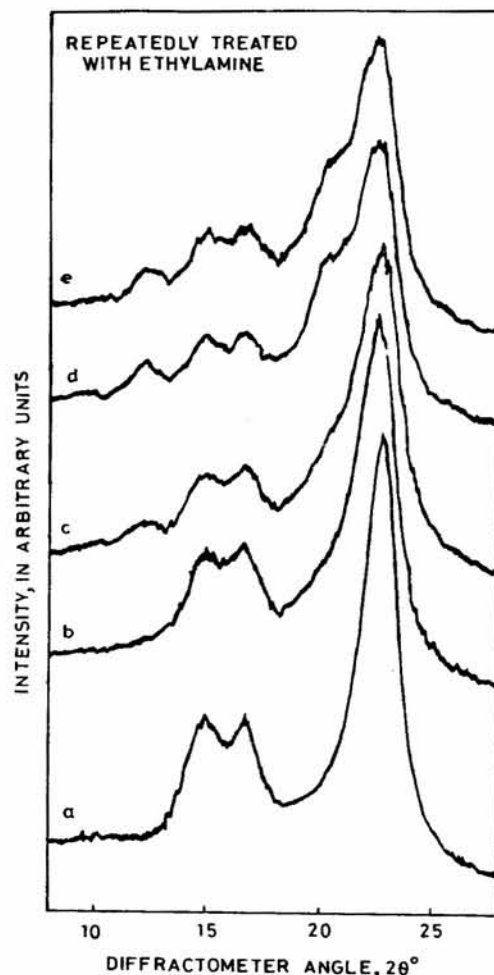


Fig.6—Diffractometer scans of cotton subjected to repeated swelling treatments with anhydrous ethylamine for various cycles [(a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, (d) 4th cycle, and (e) 5th cycle]

The OD bands characteristic of cellulose I and II are discussed in the earlier paper⁸. The bands at 2585, 2560 and 2360 cm^{-1} are characteristic of cellulose II structure. These bands start appearing to observable extent after 3-4 cycles of treatment in the case of both EDA and ethylamine treated samples. This also supports our earlier findings from X-ray study that both EDA and ethylamine convert cellulose I to cellulose II.

It has been reported⁹ that with monofunctional swelling agents (monoamines) the anhydroglucose units are freed from the restraints of interchain hydrogen bondings and rotate around their long axis (b), so that the hydroxyl groups now lie in the 101 plane of the unit cell. The unit cell expands along the 101 direction to make room for the swelling agent molecules to get bonded to the hydroxyl groups. This results in the formation of amine-cellulose complex. The expansion in a direction perpendicular to the 101 direction has been found to be proportional

to the length of the swelling agent molecule¹⁰. It is an established fact that during a single treatment, monoamines fail to break the strong intrachain hydrogen bonding and hence the original cellulose I chain conformation is retained even though the individual chains rotate around their axis. On slow evaporation of amine, the chains tend to form some bonds with their neighbours and get stabilized in their position, giving rise to cellulose III structure. This structure is unstable when treated with water. In the case of EDA treated sample, the slow evaporation of amine is not possible because of the high boiling point of EDA and so it is difficult to decompose the complex without collapsing the structure and forming cellulose III. This necessitates the use of solvents to remove EDA from the complex. On washing with non-polar solvents, traces of cellulose III₁ could be detected from the X-ray scans shown in Fig. 4. But on washing with water, cellulose III formation could not be detected because of the unstable nature of cellulose III₁ in

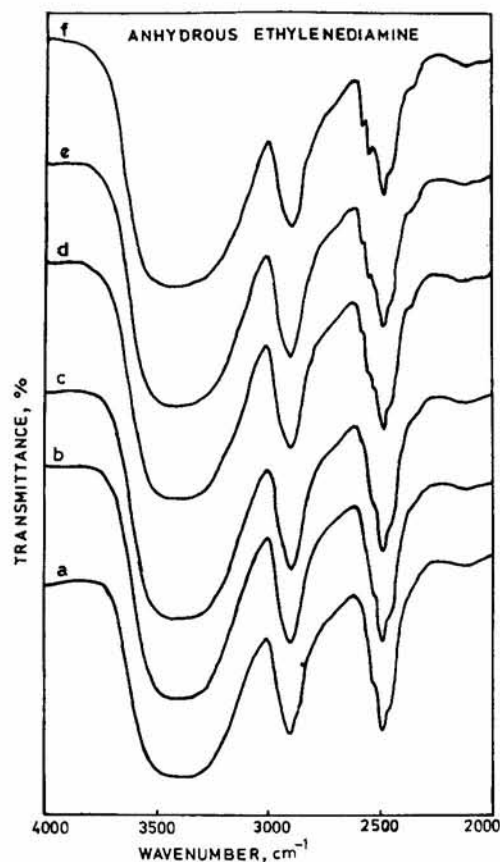


Fig.7—Infrared spectra of cotton treated with anhydrous EDA and washed with D_2O for various cycles [(a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, (d) 4th cycle, (e) 5th cycles, and (f) 6th cycle]

aqueous media. This inability to observe the formation of intermediate cellulose III_1 in the X-ray diffraction pattern perhaps supports the earlier hypothesis that no lattice transformation takes place in raw cotton treated with EDA because of the bifunctional nature of EDA. EDA was thought to be responsible for the formation of weak intermolecular crosslinks which prevented the rotation of individual chains, thus resisting any lattice change. The formation of cellulose II and the detection of cellulose III as intermediate state upon swelling with EDA convincingly show its similarity with the effect of ethylamine treatment. This similarity in the swelling actions of EDA and ethylamine rules out the crosslinking theory, as has been suggested by earlier workers⁹.

Conclusion

The effects of swelling treatment with ethylamine and EDA on the fine structure of cotton cellulose have been found to be similar. It is possible to effect lattice conversion from cellulose I to cellulose II or cellulose III by multiple swelling treatments with anhydrous ethylamine and anhydrous EDA. This similarity in the swelling action rules out the possibility of the crosslinking of diamine molecules which was

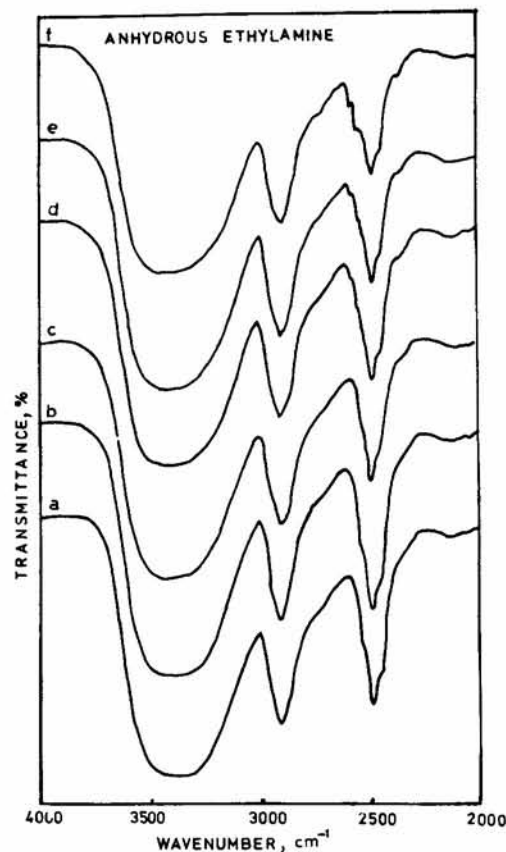


Fig.8—Infrared spectra of cotton treated with anhydrous ethylamine and washed with D_2O for various cycles [(a) 1st cycle, (b) 2nd cycle, (c) 3rd cycle, (d) 4th cycle, (e) 5th cycle, and (f) 6th cycle] considered to be the reason for lack of any lattice change in cellulose on treatment with EDA.

Acknowledgement

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