Swelling of Cotton Fibers in Ethylenediamine–Morpholine Mixtures

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Synopsis

Cotton fibers were treated with anhydrous mixtures of ethylenediamine and morpholine of varying proportions to study the changes in accessibility (X-ray crystallinity index, swelling by propanol-2 retention, formylation, and dyeability) as well as lattice conversions from cellulose I to cellulose II and cellulose III. Positive synergistic influence of the highest order was noticed at 70:30 (molar proportion 3:1) ethylenediamine–morpholine mixture as judged from accessibility and lattice conversion from cellulose I to cellulose II. The same critical proportion was found to give the highest order of negative synergistic effect in the lattice conversion of cellulose I into cellulose III. These opposing trends have been explained on the basis of the different mechanisms associated with the lattice conversions of cellulose I into cellulose II and cellulose III.

INTRODUCTION

Kulkarni and Lokhande[1,2] were the first to report synergistic influence of high order of morpholine during their swelling studies on cotton fibers with aqueous and nonaqueous solutions of ethylenediamine. Lokhande and co-workers[3-5] were also the first to report the cellulose I lattice conversion to cellulose II and cellulose III during washing treatment of ethylenediamine-treated cotton with water and methanol, respectively.

The present communication reports further results of X-ray diffraction studies and physicochemical investigations on cotton fibers treated in nonaqueous mixtures of ethylenediamine and morpholine.

EXPERIMENTAL

Materials

Cotton Cellulose. Long staple Sudanese cotton was purified according to standard procedure.[6] These purified fibers had the following specifications: degree of polymerization 2250; copper number 0.01; carboxyl content 0.335 meq/100 g cotton.

Chemicals. All the chemicals including ethylenediamine and morpholine were of CP grade. These were purified before use. The KBr used in the infrared studies was of spectroscopic grade supplied by Spex Industries, Inc.

Dyes. Procion Brilliant Red M5B (C.I. Reactive Red 2) was used for dyeing after standard purification.

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Methods

Preparation of Swollen Samples

A. Treatment with EDA–Morpholine Mixtures. The purified fibers were subjected to swelling reaction in nonaqueous mixtures of ethylenediamine and morpholine between 0:100 and 100:0 (w/w) proportions, respectively, at 20°C for 1 h. The samples were then squeezed to remove the excess reagents.

B. Washing with Water. The treated samples were dipped in a large volume of distilled water at 30°C. The washing was continued in fresh lots of water until the fibers were free of the traces of swelling mixture. Loosely held water was removed by suction and the sample was air-dried.

C. Washing with Methanol. The treated samples were dipped in a large volume of anhydrous methanol at 30°C. The washing was continued in fresh lots of methanol till the fibers were completely free from the traces of the swelling mixture. The samples were squeezed and finally air-dried.

Determination of Accessibility from Moisture Regain

Moisture regain of the sample was determined at 75% RH and 30°C under conditions of adsorption. Accessibility of the sample to moisture was determined by using Valentine's equation.[7]

Determination of Extent of Swelling

The extent of swelling of cotton fibers was measured by the propanol-2 retention method suggested by Andrews and Oberg.[8] The extent of swelling was expressed in terms of the volume of propanol-2 retained per 100 g fiber.

Determination of Amorphous Fraction

The method of formylation suggested by Marchessault and Howsmon[9] was employed to know the amorphous fraction of the swollen sample.

Determination of X-Ray Crystallinity Index

Ni-filtered CuK_α radiation from a Philips stabilized X-ray generator with diffractometer and recording accessories was used for obtaining X-ray diffraction patterns. Fibers weighing about 150 mg were cut into fine powder, filled in the standard specimen holder, and the patterns recorded using reflection geometry. The X-ray crystallinity was calculated according to Segal et al.[10]

Dyeing of Swollen Samples

Dyeing was carried out using purified reactive dye Procion Brilliant Red M5B (C. I. Reactive Red 2). Standard procedure of exhaust dyeing with reactive dyes was followed. The dye content of substrate was determined spectrophotometrically after dissolving the dyed fibers in 70% (w/w) sulphuric acid in cold.

Specific Conductivity Measurements

The specific conductivity of EDA–morpholine mixtures of varying proportions, as well as those of EDA–morpholine–water and EDA–morpholine–methanol, in which the quantity of EDA was kept constant at 70 g, and morpholine–water and morpholine–methanol, respectively, varied between 0 and 30 g per 100 g of mixture, was measured using "conductivity bridge" type CL01/0 1A (Toshniwal Bros., India).

RESULTS AND DISCUSSION

In our earlier studies on swelling and decrystallization of cotton fibers, maximum synergistic influence was observed when ethylenediamine (EDA) and morpholine were present in the proportion of 70:30 (w/w) (molar proportion 3:1), in which morpholine acted as a solvent for EDA rather than a coswelling agent for cotton fibers.

In the present investigation, the results on influence of the presence of morpholine in the nonaqueous solutions of EDA on the accessibility characteristics of the swollen samples and the conversion of cellulose I into cellulose II and cellulose III have been reported.

Figure 1 gives a plot of X-ray crystallinity index (XRCI) of cotton samples swollen in mixtures with varying proportions of EDA and morpholine. The results indicate that the XRCI of 80.51% for the control remains almost unchanged for pure morpholine (80.59%) and is reduced to a level of 72.00% in case of pure EDA alone. When part of EDA is replaced by morpholine,

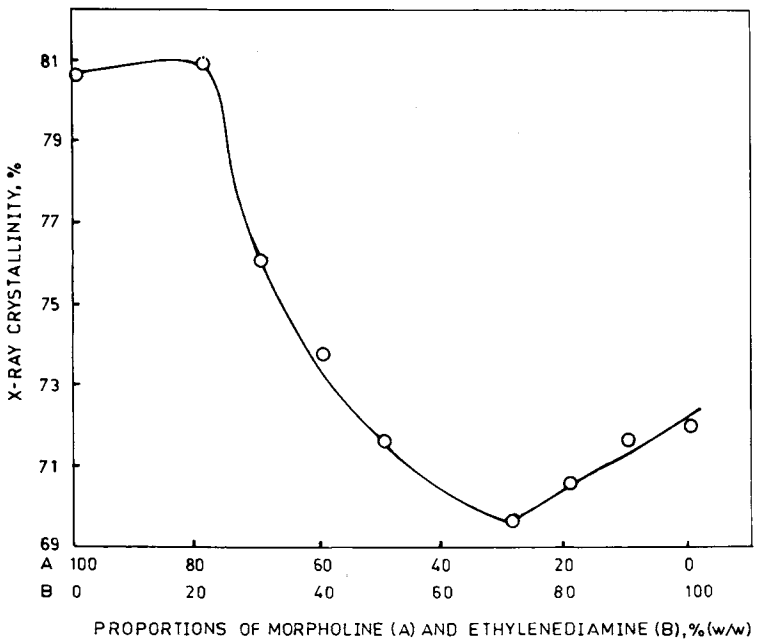

Fig. 1. Relation between X-ray crystallinity index and quantity of EDA and morpholine in the mixtures.

the decrystallization pattern changes depending upon the proportion of morpholine in the mixtures. It is interesting to note that the EDA–morpholine mixture of 70:30, giving a molar proportion of 3:1, brings about enhanced decrystallization of cotton fibers (XRCI 69.66%) even below the level of that produced by pure EDA alone. This indicates the synergistic influence of morpholine in EDA solution in bringing about enhanced decrystallization of cotton fibers.

With a view to study the changes in the accessibility of swollen cotton fibers, the degree of swelling by propanol-2 retention technique, accessibility by formylation and dyeability with reactive dye were studied. These results have been given in Table I. The results indicate that, in general, the above three characteristics improve progressively when the amounts of EDA and morpholine go on increasing and decreasing, respectively, in their mixtures. At a ratio of 70:30 of EDA and morpholine, the influence is pronounced giving a maximum. Thus, the degree of swelling by propanol-2 retention is 44.85 as compared to 30.12 mL/100 g fiber, the accessibility by formylation is 61.71% as compared to 38.13% for control and the dye content is 10.24 as compared to 6.75 g/kg fiber for the control. The respective values for the 70:30 EDA–morpholine swollen cotton samples are not only higher than the control, but they are also quite above the level of those obtained with 100% EDA alone. These results are in confirmity with the earlier findings for moisture regain and other characteristics of the swollen cotton fibers.[1]

In order to study the synergistic effect or otherwise of the presence of morpholine in EDA on the conversion of cellulose I into cellulose II during the swelling and decrystallizing of cotton fibers, four swelling-water washing–drying cycles were carried out on cotton fibers, since the extent of conversion of cellulose I to cellulose II was shown to improve with increase in the number of swelling cycles.[4] The results on the lattice conversion ratio (LCR) are given in Table II. The results indicate that the presence of morpholine in its mixture with EDA has a synergistic influence on the conversion of cellulose I into cellulose II, when EDA and morpholine are present

TABLE I
Changes in the Structural Properties of Cotton Cellulose on Swelling in EDA–Morpholine Mixtures at 20°C for 1 h

EDA:Morpholine	Propanol-2 retention (mL/100 g fiber)	Accessibility by formylation (%)	Dye content (g dye/kg fiber)
0:0	30.12	38.13	6.75
0:100	31.96	41.00	8.17
10:90	32.82	42.71	8.20
20:80	34.57	42.71	8.24
30:70	37.16	44.33	8.30
40:60	38.25	50.15	8.87
50:50	41.36	—	8.37
60:40	43.82	55.25	9.99
70:30	44.85	61.71	10.24
80:20	41.85	60.71	10.06
90:10	40.55	54.32	9.21
100:0	38.94	39.91	8.62

TABLE II
Conversion of Cellulose I into Cellulose II on Swelling in EDA-Morpholine Mixtures at 20°C for 1 h (Four Cycles Repeated)

EDA:Morpholine	LCR
0:0	0.21
0:100	0.21
30:70	0.34
50:50	0.56
60:40	0.64
70:30	0.71
80:20	0.69
90:10	0.58
100:0	0.68

in the critical proportion of 70:30. Thus, the LCR of 0.21 for the control rises progressively with the increase in the amount of EDA accompanied by the proportionate decrease in the amount of morpholine in EDA–morpholine mixtures, up to the critical ratio of the mixture (LCR 0.71). The LCR for 100% EDA alone, however, is only 0.68. This goes to show that morpholine has a synergistic influence, when present with EDA in the above proportion, during the conversion of cellulose I into cellulose II. (Incidently, the LCR for fully mercerized cotton was found as 0.90.) The EDA–monomorpholinate species, which are present to the maximum extent in this mixture, seem to bring about enhanced swelling and decrystallization accompanied by conversion of cellulose I lattice into cellulose II lattice structure.

The conductivity results of EDA–morpholine mixtures, shown in Figure 2, support the above contention. Two breaks are obtained in the curve at 40:60 and 70:30 proportions of EDA and morpholine, at which the molar proportions of the two reagents are 1:1 and 3:1, respectively. This suggests that EDA and morpholine do not form an ideal additive mixture, but their molecules try to acquire a particular type of arrangement depending upon the conditions available in the mixture. Around 1:1 molar proportion and beyond, the effectiveness of the mixture increases. The effectiveness to break the hydrogen bonds and penetration of the 3:1 complex in the crystallites is maximum at the critical 3:1 proportion of EDA and morpholine. After the penetration inside the crystallites, the labile complex between EDA and morpholine molecules may be broken during the strong interaction between free hydroxyl groups of the two neighbouring cellulose chains and the two amino groups of an EDA molecule, thus forming a bridge. As explained in the previous communication[4], some of the EDA molecules may not be able to form a bridge and in such cases, during washing with water, the chains may rotate to give a partial conversion of cellulose I into cellulose II. In this way, the phenomenon of synergism is not only witnessed in terms of swelling and decrystallization of cellulose, but also with respect to the extent of conversion of cellulose I into cellulose II lattice structure.

Figure 3 gives the results of conversion of cellulose I into cellulose III with varying proportions of EDA–morpholine mixtures. The conversion of

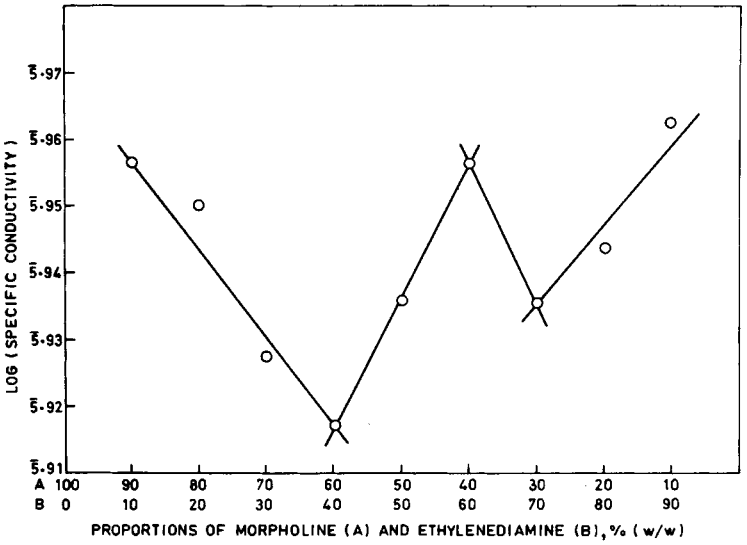

Fig. 2. Relation between log (specific conductivity) and quantity of EDA and morpholine in the mixtures.

cellulose I into cellulose III was obtained by treating the cotton fibers in EDA or mixtures of EDA and morpholine, followed by washing with methanol and air-drying. Four cycles of swelling-methanol washing-drying were repeated in order to ensure full conversion of cellulose I to cellulose III.[5] The results indicate that the conversion of cellulose I into cellulose III is the highest, giving the LCR value of 1.28 for a sample treated with 100% EDA alone. The LCR decreases with the decrease in the proportion of pure EDA and the corresponding increase in the amount of morpholine in the EDA–morpholine mixtures and it is the least at 0.48 for a sample treated with 30:70 EDA:morpholine mixture. It may be noted that the presence of morpholine in the EDA–morpholine mixture hinders the conversion of cellulose I into cellulose III, which may be described as a phenomenon of negative synergism. Earlier, the mechanism of formation of cellulose III was assigned to the possibility that during washing of EDA–cellulose complex with methanol, one end-amino group may be blocked by the methanol molecule while the other end-amino group forms hydrogen bond with the hydroxyl group of a cellulosic chain, thereby causing the rotation of the cellulosic chain to give the cellulose III lattice structure.[5] The presence of morpholine, perhaps, hinders this process, thereby decreasing the efficiency of lattice transformation from cellulose I to cellulose III. The dotted portion in the curve of Figure 3 would have been the expected path of the smooth curve, had there been no other specific factor responsible for reducing the extent of lattice conversion; but it is interesting to note that the curve gives a sharp drop in the lattice transformation at the critical proportion of 70:30 EDA:morpholine mixture, corresponding to the molar proportion of 3:1. Thus, while the LCR of the samples treated in 80:20 and 60:40 EDA–morpholine mixtures are almost identical, i.e., 1.14 and 1.12, respectively, the

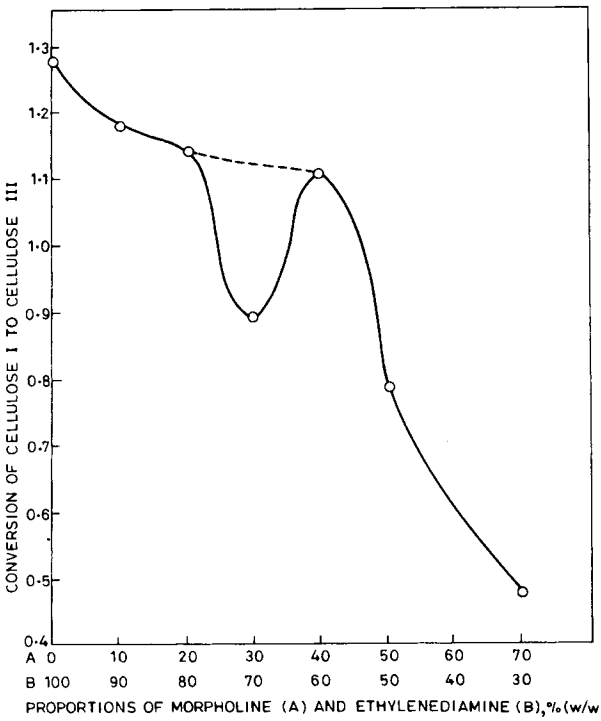

Fig. 3. Relation between LCR for cellulose I to cellulose III and quantity of EDA and morpholine in the mixtures.

LCR value at the intermediate proportion of 70:30 has dropped to 0.89. It seems that the cluster of four molecules, consisting of three molecules of EDA and one molecule of morpholine, although powerful enough to bring about enhanced swelling, actually hinders to the maximum extent the lattice transformation. This may be, perhaps, due to steric hindrance preventing the chains to rotate about their axes. Thus, the critical concentration of 70:30 EDA:morpholine acts in just the opposite way as compared to its role in the extent of swelling and decrystallization of cotton fibers as well as during the lattice transformation from cellulose I to cellulose II.

In conclusion, it seems that the difference in the roles played by the critical concentration of 70:30 of the EDA–morpholine mixture may be due to the different mechanisms by which cellulose II and cellulose III are produced from cellulose I. In the production of cellulose III, it seems that, apart from the steric hindrance factor, the presence of morpholine also hinders the formation of the EDA–methanol complex, an essential precondition for cellulose III formation, during the washing stage with methanol. The steric hindrance of morpholine as well as its hindrance to the formation of EDA-morpholine complex, when eliminated, say in case of 100% EDA alone, the conversion of cellulose I to cellulose III is found to be of the highest order.

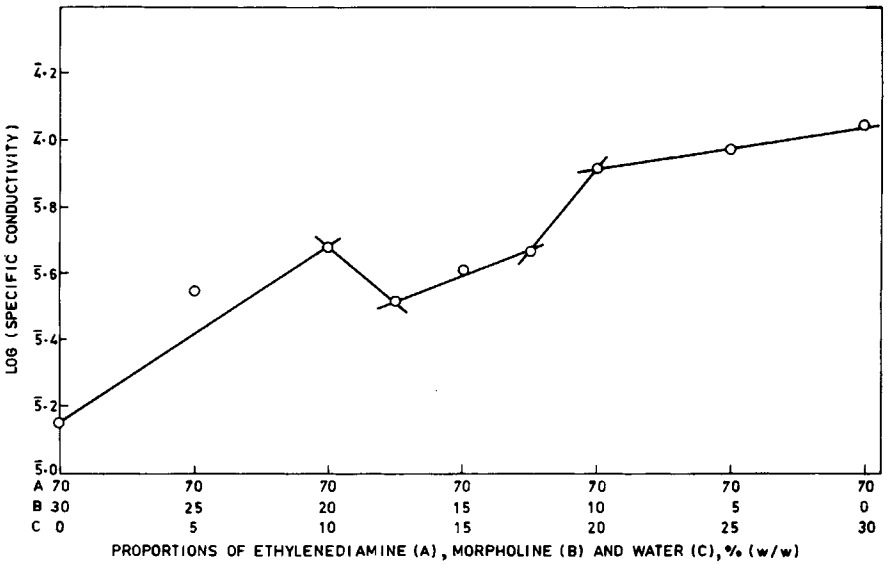

Fig. 4. Relation between log (specific conductivity) and quantity of EDA, morpholine, and water in the mixtures.

These contentions are very well supported by the conductivity studies of 70:30 EDA:morpholine mixtures in presence of water and methanol (Figs. 4 and 5). When 30 g of morpholine in the mixture is progressively replaced by equivalent amounts of water, conductivity of the aqeous mixtures increased progressively, giving a linear plot upto a critical proportion of 70:20:10 EDA:morpholine:water. The break in the conductivity curve around this critical proportion suggests that water, being highly polar sol-

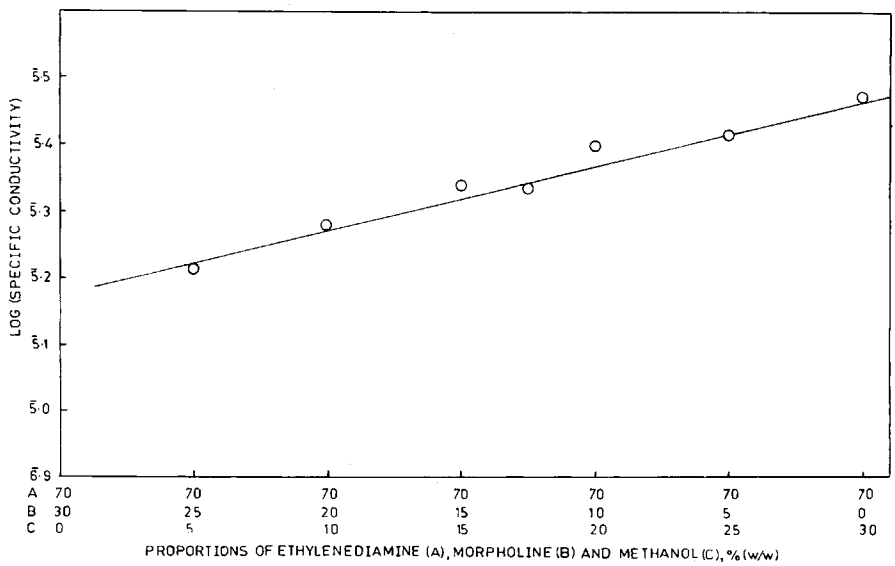

Fig. 5. Relation between log (specific conductivity) and quantity of EDA, morpholine, and methanol in the mixtures.

vent, has an ability to break the EDA–monomorpholinates and form the EDA–monohydrate species, an essential precondition for the enhanced swelling of the cotton fibers and conversion of cellulose I into cellulose II. Similar conductivity studies with respect to the EDA–morpholine–methanol system gave a linear plot in the conductivity curve without any breaks, indicating that the cluster of 3:1 EDA:morpholine and the EDA–monomorpholinate species are practically unaffected and methanol, being a weakly polar solvent, fails to have an interaction with the amino groups of the EDA molecules, an essential precondition for the conversion of cellulose I to cellulose III.

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