Dyeing Behavior of Swollen Cotton Fibers and Swelling Mechanisms of Intra- and Intercrystalline Swelling Agents

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Synopsis

Dyeability was used to study the swelling mechanisms of intra- and intermicellar swelling agents on cotton cellulose. Reactive and direct dyes were used for dyeing, and zinc chloride, ethylenediamine (EDA), and morpholine were used for swelling reactions. Changes taking place in the accessible regions as a result of swelling were determined by moisture regain, acid hydrolysis, formylation, and the lateral order distribution in the fiber structure. The results indicate that the intracrystalline swelling agents, viz., zinc chloride and EDA, induce specific changes in the accessible portions of the fiber. The accessible portion produced by the inorganic swelling agent has a more open structure than the disordered region produced by the EDA treatment. The distinctive nature of the accessible portions in swollen cotton fibers treated with the two reagents was reflected in all the properties studied. This was attributed to the different mechanisms of swelling and decrystallization of cotton fibers by zinc chloride and EDA. Morpholine was shown to bring about considerable changes in the accessible portions of the cotton fiber which were responsible for increased dyeability with reactive dyes, and was also shown to increase the amount of "truly" accessible regions by breaking the "imperfect crystals" in the disordered regions as well as on the surface of crystallites.

INTRODUCTION

Swelling is an inherent property of polymeric substances when they are brought in contact with a suitable liquid or condensable vapor. With cellulosic fiber substances, most of the reactions and chemical modifications usually take place at the hydroxyl groups of the anhydroglucose units, as in the case of dyeing with reactive dyes. In order to achieve significant chemical modifications of the fiber substance, it is necessary to increase the accessibility of the cellulosic hydroxyl groups to the reagent both in the readily accessible region as well as in the difficult-to-reach portions of the fiber. The extent of swelling of cellulose governs its properties, such as moisture sorption, reactivity to various reagents, diffusion of dyes and other chemicals inside the fiber structure, and so on. The nature and extent of dye absorption by the fiber will depend on the nature and extent of open structures of the swollen fiber treated with different swelling agents.

All polymers, including cellulose, are noncompact and contain voids. When cellulose is brought into a fluid environment, for example, when it is totally immersed in a liquid containing a swelling agent, the molecules of the fluid penetrate in the voids of the fiber and are adsorbed on the accessible surface. The opening of these voids depends largely on the nature of the swelling agent. Thus, the mechanism of decrystallization of cellulose is specific for a particular class of

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swelling agents. So far, very little work has been reported in the literature on the mechanism of dye absorption by preswollen substrates.

In recent years morpholine has attracted the attention of many workers because of its unique nature to swell cellulose without any appreciable change in the crystalline regions of the fiber. Lokhande[1,2] and co-workers reported on the behavior of cotton cellulose when treated with aqueous solutions of morpholine and its mixture with ethylenediamine. A high degree of swelling was observed at the microfibrillar level (microfibrillar width and thickness changed from 110 to 205 Å and from 25 to 50 Å, respectively) without any appreciable change in the infrared crystallinity index. The x-ray diffraction patterns were also left unchanged showing that there was no intracrystalline swelling. Morpholine exhibited synergism during swelling of cotton in ethylenediamine–morpholine mixtures and brought about decrystallization of cellulosic fibers in otherwise nondecrystallizing concentrations of ethylenediamine solutions. Paszner[3] also used morpholine as a swelling agent in the study of cellulose degradation by gamma rays and further observed that the morpholine-treated cellulose samples showed improved solubility in EWNN (alkaline iron–tartaric acid sodium complex) solutions even at high D.P. levels.

Aqueous zinc chloride solutions have been found to be intracrystalline swelling agents for cellulose. Smirnov[4] was the first to indicate a peculiar behavior of aqueous zinc chloride solutions at two critical concentrations of 63% and 75% which brought about considerable swelling of cellulose depending upon the temperature of the treatment. Kasbekar and Neale[5] and Patil et al.[6] also studied the swelling behavior of zinc chloride solutions on cotton. These workers, however, did not put forward any explanation regarding such behavior. Lokhande[7] and co-workers made a critical evaluation of the swelling and decrystallizing action of aqueous solutions of zinc chloride of varying concentrations at different temperatures and put forth the mechanism of swelling and decrystallization of cellulose with aqueous zinc chloride solutions by suggesting the formation of specific hydrates of zinc chloride in the aqueous solutions.

Trogus and Hess[8] were first to work on diamines as swelling agents for cellulose. Ethylenediamine caused intracrystalline swelling and decrystallization of cotton cellulose. Subsequently, a number of workers investigated ethylenediamine as a swelling agent for cellulose. The salient features of this voluminous work are that ethylenediamine has been found to be a powerful decrystallizing agent which causes intramolecular swelling of cellulose and forms complex with cellulose by linking two anhydroglucuse units of two cellulose chains, thereby retaining the cellulose I structure intact.[9–11] Recently, however, Lokhande[12] has reported the partial conversion of the cellulose I lattice structure into cellulose II lattice structure as a result of swelling action of ethylenediamine on cotton cellulose. Lokhande[13] and colleagues reported the conversion of cellulose I into cellulose III lattice structure when cotton was swollen and decrystallized with aqueous solution of ethylenediamine followed by washing in dry methanol.

The aim of the present paper is to describe the findings of a systematic investigation in which a swelling agent was a major variable in influencing the dyeing properties of cotton cellulose. Zinc chloride and ethylenediamine represent inorganic and organic intracrystalline swelling agents, respectively, while morpholine is selected as an intercrystalline swelling agent.

EXPERIMENTAL

Materials

Scoured and bleached cotton fabric was used for the investigation. The swelling agents used, viz., zinc chloride (anhydrous), ethylenediamine, and morpholine, were of C.P. grade. Ethylenediamine and morpholine were distilled twice before use. The reactive dyes used were C.I. Reactive Violet 13 and C.I. Reactive Red 76 with dichloro- and monochlorotriazine types of the reactive system, respectively, and the direct dyes used were C.I. Direct Blue 1 (Chlorazol Sky Blue FF) and C.I. Direct Red 2 (Benzopurpurine 4B). All the dyes were carefully purified before use.

Preparation of Swollen Cellulose Samples

Accurately weighed samples of cotton fabric were entered into aqueous solutions of zinc chloride (50%, 65%, 68%, 70%, and 73%), and ethylenediamine (40%, 60%, 65%, 70%, and 80%), keeping the liquor ratio at 20. The swelling treatment was carried out for 1 hr with frequent stirring at 20°C and 35°C. In a few cases the time of treatment was increased to 5 hr at 20°C. The samples were then removed and repeatedly washed first with tap water and then with distilled water until they were free from the swelling agent. Samples were then squeezed and air dried.

Dyeing of Cellulose Samples with Reactive Dyes

C.I. Reactive Violet 13. The cold-brand reactive dye was dissolved by first pasting it with a little cold water followed by dilution with warm water at about 40°C. The dye bath was set in the cold with the quantity of dye required for 2% shade at a liquor ratio of 20. The swollen samples were then entered into the dye bath and worked for about 10 min. An equivalent quantity of aqueous solution of common salt (to give 20 g/l. salt) was added to the dye both in two installments within 20 min. The dyeing was continued for another 20 min after which 7.5 g/l. soda ash was added in two installments within 10 min, and dyeing was further continued for 30 min. Under these conditions no equilibrium dyeing was obtained.

Samples were then taken out, squeezed, rinsed well in cold water, soaped at the boil for 15–20 min to remove the hydrolyzed dye, rinsed repeatedly with cold distilled water, and then air dried.

C.I. Reactive Red 76. This hot-brand dye was first pasted with cold water followed by dilution with hot water at about 80°C. The amount of dye solution required for 2% shade was added to the dye bath set at 65–75°C. Swollen cotton fabric samples were then entered into the dye bath and were worked for 5–10 min. Then, 70 g/l. of common salt was added in two installments within 20 min. Dyeing was further carried out for 20 min. After this, 15 g/l. of trisodium phosphate was added in two installments within 10 min. The dyeing was continued for a further 30 min at 70–80°C. Under these conditions no equilibrium dyeing was obtained. After the dyeing was over, the material was lifted from the bath, squeezed and rinsed well in cold water, soaped at the boil for 15–20 min, washed well, and dried.

Dyeing of Cellulose Samples with Direct Dyes

The amount of the dye required for 3% shade and a pinch of soda ash were pasted first with cold water and then diluted by adding hot water to the paste.

Swollen samples of cotton fabric were entered in the dyebath at 40°C. Temperature was then raised to boil and dyeing was carried out for 30 min. Then 20% glauber salt was added to the dyebath on the weight of the material and dyeing was carried out further 15 min. Samples were then removed, rinsed in water, squeezed and dried. Under these conditions no equilibrium dyeing was obtained.

Measurements

Determination of Moisture Regain and Accessibility of Swollen Cellulose. Moisture regain of the sample was determined at 75% R.H. and 30° ± 1°C under conditions of adsorption. Accessibility of the sample to moisture was determined by using Valentine's equation.[14]

Determination of Extent of Swelling. Extent of swelling of cotton fibers was measured by the propanol-2 retention method suggested by Andrews and Oberg.[15] The extent of swelling was expressed in terms of volume of propanol-2 retained by 100 g of the fiber.

Determination of Fiber Accessibility to Acid Hydrolysis. Accessibility of the swollen fibers to acid hydrolysis was determined by the method suggested by Sharples[16] using mild conditions (1N HCl at 30°C).

Measurement of Lateral-Order Distribution. Lateral-order distribution in swollen samples was obtained from the results of formylation carried out in a temperature range of 5–65°C using the method suggested by Marchessault and Howsmon.[17] The low-order (L) fraction was the one which was accessible at 5°C and is due to crystallite surfaces. The intermediate-order (I) fraction was taken as the portion accessible at temperatures above 5°C but less than 65°C.

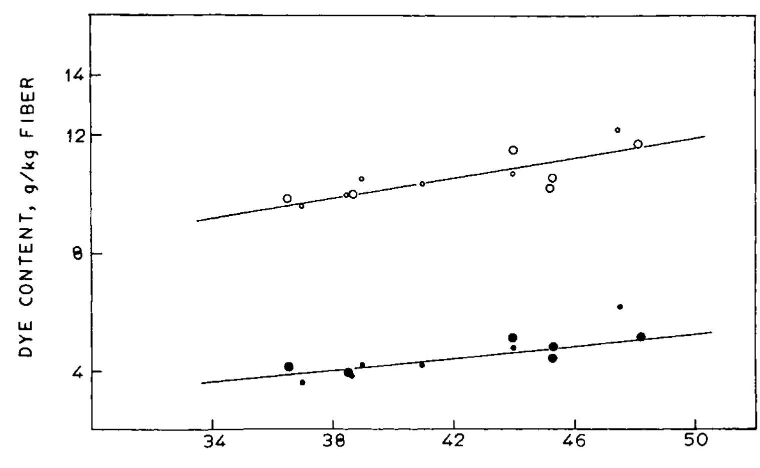

Fig. 1. Reactive dye content of swollen and decrystallized cotton cellulose vs accessibility from moisture regain: (o),(•) zinc chloride; (●),(O) EDA; (•),(●) C.I. Reactive Red 76; (o),(O) C.I. Reactive Violet 13.

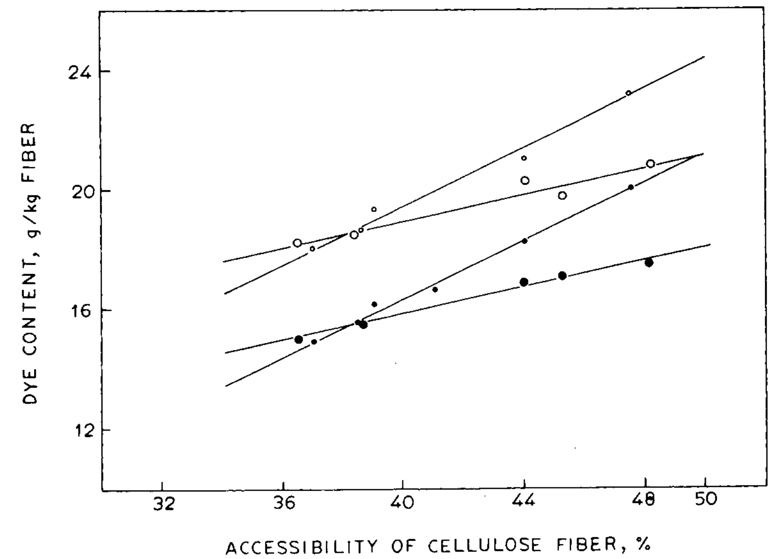

Fig. 2. Direct dye content of swollen and decrystallized cotton cellulose vs accessibility from moisture regain: (•),(o) zinc chloride; (●),(O) EDA; (•),(●) C.I. Direct Blue 1; (o),(O) C.I. Direct Red 2.

The high-order (*H*) fraction was the remaining inaccessible fraction of the fiber.

Determination of Dye Content of Swollen and Subsequently Dyed Cotton Cellulose. Samples dyed with a direct dye were stripped off in 25% aqueous pyridine, and the optical density of the colored solutions was found using a Hilger Spekker Absorptiometer.[18] The absolute value of the dye content was obtained using a previously constructed calibration curve for the particular dye in the pure form. Cellulose samples dyed with a reactive dye were dissolved in 70% sulfuric acid in the cold, and the optical density of the colored solutions was determined on the Absorptiometer. The dye contents in the cotton samples were calculated in the same way as described above for direct dyes.

RESULTS AND DISCUSSION

The results of the present investigation reveal that the characteristics of cotton cellulose, such as moisture regain, accessibility, and dye uptake, change depending on the nature of the swelling agent as well as the concentration of the swelling agent in the solutions used (Figs. 1 and 2).

Effect of Swelling Reaction on Dye Uptake

Two swelling maxima have been observed at 65% and 70% (w/w) concentrations of zinc chloride.[7] Exactly at the same concentrations, a maximum amount of dye uptake has been obtained, the 65% concentration being the more effective of the two. Thus, at this concentration the increase in reactive dye content was as high as 59% for C.I. Reactive Red 76 and 22% for C.I. Reactive Violet 13. Similar results have been obtained with direct dyes, where the dye uptake increased by 28.9% for C.I. Direct Blue 1 and 24.7% C.I. Direct Red 2. The trend with respect to increase in dye uptake is similar when cotton is treated with a

70% solution of zinc chloride, although the corresponding absolute values of increase in dye uptake are lower. With the intermediate concentration of 68% of zinc chloride, there is relatively no change in dye uptake as compared with the control.

An ethylenediamine concentration of 70% (w/w) has been found to be the most effective in enhancing the dye uptake. Thus, the percent increase for C.I. Reactive Red 76 and C.I. Reactive Violet 13 was 35.9% and 17.0%, respectively, while the values were 12.2% and 12.4% for C.I. Direct Blue 1 and C.I. Direct Red 2, respectively.

The changes in accessibility to moisture correspond very well to those in dye uptake of the treated samples in zinc chloride or ethylenediamine solutions, and the two characteristics could be very well correlated with each other (Figs. 1 and 2).

Morpholine or its aqueous solutions do not decrystallize cotton cellulose to an appreciable extent, and hence there is no appreciable increase in the moisture regain values. Earlier, it was noted that morpholine treatment did not affect the rate of acid hydrolysis of cotton but increased propanol-2 retention almost by 100%.[19] It is, however, very interesting to note that there was a considerable increase in dye uptake by morpholine-treated cotton cellulose. The percent increase of C.I. Reactive Red 76, C.I. Reactive Violet 13, C.I. Direct Blue 1, and C.I. Direct Red 2 was 36.0%, 12.0%, 10.9%, and 11.8%, respectively, for cotton fibers treated with morpholine solutions beyond 40% (w/w) for 1 hr.

Mechanisms of Swelling Reactions

In an earlier communication, the mechanism of swelling and decrystallizing action of zinc chloride solutions on cotton had been suggested by attributing the action to specific types of hydrate, viz., trihydrate and tetrahydrate in the solutions.[7] These hydrates bring about swelling and decrystallization of cotton in a specific way, giving greater accessibility. It is likely that the physical state of the accessible portion might be specific to the manner in which it is produced by the zinc chloride solutions.

Aqueous solutions of ethylenediamine above 60% concentration have been shown to be effective in bringing about swelling and decrystallization of cotton, which have been attributed to the monohydrate of ethylenediamine present in the solutions.[10,11] The monohydrate penetrates into the crystallite and breaks the hydrogen bonds, and the EDA molecule forms a bridge between the two hydroxyl groups of cellulose thus set free. When the reagent is washed off, the penetrated portion of the fiber adds to the accessibility. Thus, zinc chloride and ethylenediamine brings about swelling and decrystallization of cotton cellulose, and hence the proportionate increase in the dye uptake.

It seems that the manner in which decrystallization occurred is of considerable importance. The mechanisms of decrystallization in case of the two reagents studied are essentially different; and although equal degrees of accessibility to moisture could be produced by these reagents, the physical states of the accessible regions might be quite different from each other. When accessibility values to moisture were plotted against direct dye content of the samples, two separate straight lines for each dye were obtained in case of the two intracrystalline swelling agents studied, showing that the mechanism of decrystallization is

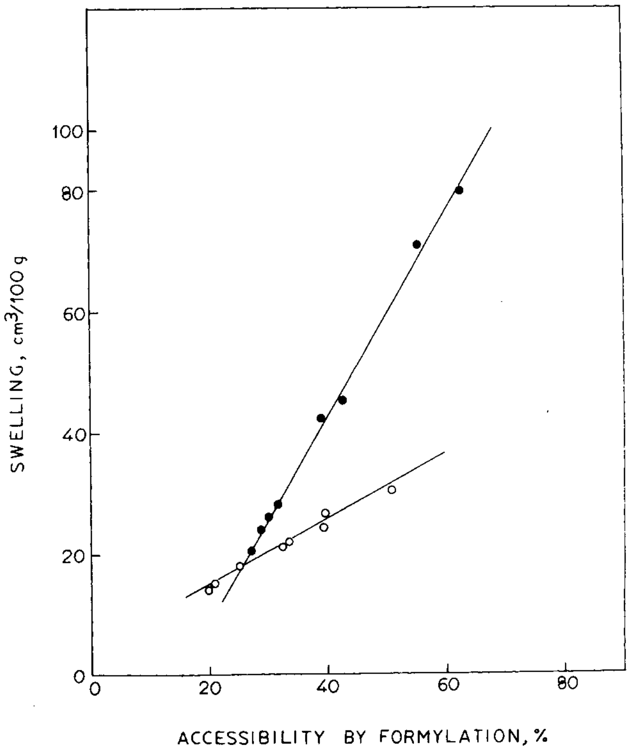

Fig. 3. Extent of swelling vs accessibility of cotton fibers by formylation: (●) zinc chloride; (O) EDA.

different for each of the reagents (Fig. 2). No separate straight lines were, however, obtained for the reactive dyes studied, and all the points for ethylenediamine- and zinc chloride-treated samples fell on the same straight line for each individual reactive dye (Fig. 1). A similar correlation was observed when both the swollen samples were subjected to formylation reaction.[19] Although the physical states of the accessible portions in the two cases are different, the availability of the —OH groups will be equal in both samples, irrespective of the different nature of the physical state. Thus, the probability of reaction between the reactive dye molecule and the accessible hydroxy group of the cellulose remains the same for both ethylenediamine- and zinc chloride-treated cotton cellulose.

Nature of Accessible Portion

Figure 3 shows a correlation between the extent of swelling of cotton fibers as measured by propanol-2 retention and the accessibility to formylation; the former describes mainly the extent of voids in the fiber while the latter gives the accessibility of the same fiber in terms of the number of accessible reaction sites to formic acid molecules. It can be seen that for a given amount of accessibility to isopropyl alcohol, the EDA-treated and zinc chloride-treated samples have different values of accessibility to formylation. Accessibility values of swollen fibers to moisture and HCl also show two separate straight lines for the samples treated with the two swelling agents (Fig. 4).

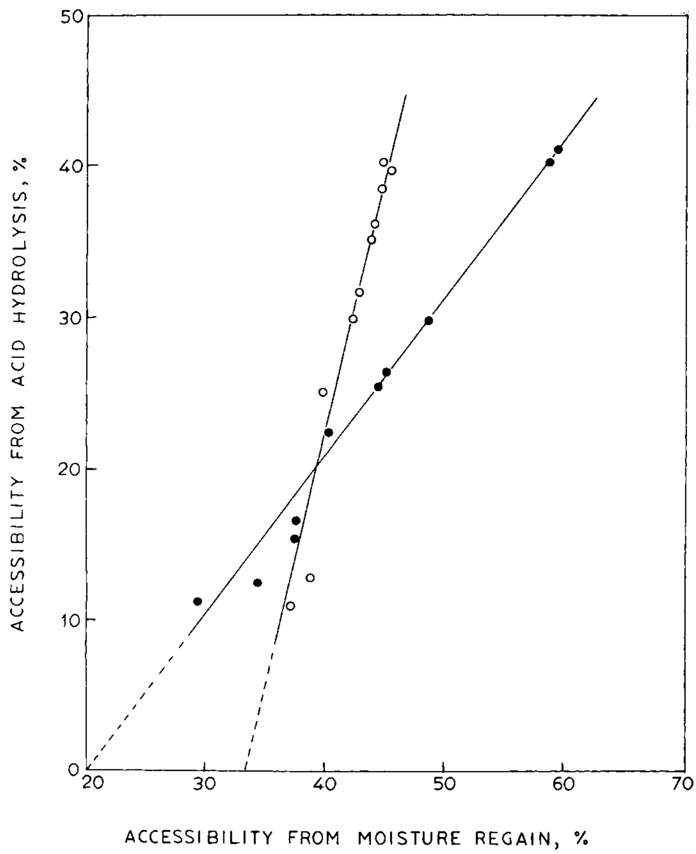

Fig. 4. Accessibility from acid hydrolysis vs accessibility from moisture regain: (●) zinc chloride; (○) EDA.

TABLE I

Changes in Low-Order (L), Intermediate-Order (I), and High-Order (H) Fractions in Swollen Cotton Fibers[a]

Reagent	Concentration, % (w/w)	Fraction L, % Absolute	Fraction L, % Change	Fraction I, % Absolute	Fraction I, % Change	Fraction H, % Absolute	Fraction H, % Change
Control	—	19.04	—	11.55	—	69.41	—
Zinc chloride	65	30.32	+60	24.83	+115	44.85	−35
	70	21.85	+15	17.78	+54	60.37	−13
Ethylene-	75	27.08	+42	20.59	+78	52.33	−25
diamine	100	25.04	+32	19.37	+68	55.59	−20
Morpholine	40	16.10	−15	15.55	+35	68.35	−2
	100	15.53	−18	15.24	+32	69.23	negligible

[a] Accuracy ±1%.

Table I gives the changes occurring in the low-order (L), intermediate-order (I), and high-order (H) fractions in cotton fibers on treatment with effective concentrations of the swelling agents. Although zinc chloride and EDA bring about considerable increases in the L and I fractions, accompanied by decreases in the H fraction; it can be seen that the emphasis of the two is quite different in the two regions. Zinc chloride (65%) brings about an increase in the L region by 60% of the original L fraction, making the fiber more sensitive to absorption of dyes and chemicals by eroding crystal surfaces to a greater extent than EDA (75%), which enhances the same region only by 42% of the original. In case of the I fraction, zinc chloride also brings about an increase by 115% of the original I fraction as compared to an increase of only 78% by EDA. It seems, therefore, that the accessible portions produced by zinc chloride are in a much more loose condition than those obtained by the EDA treatment.

All the above results may be attributed to the basically different modes of swelling and decrystallizing action of tetrahydrate in zinc chloride solutions on the one hand, which is responsible for breaking the hydrogen bonds in the cotton fibers thus setting the cellulose chains free and increasing the disordered region, and of the EDA monohydrate on the other hand, which breaks the hydrogen bond between the two chains but induces almost simultaneously a bridge formation through the EDA molecule across the same two chains and producing accessible portions under controlled freedom of movement for the cellulosic chains in the cotton fiber. In this respect, it is significant that the microfibrillar dimensions of the control (110 × 25 Å) were enlarged to a greater extent in zinc chloride-treated cotton (240 × 120 Å) as compared to those in EDA-treated cotton fibers (160 × 30 Å).[19]

Morpholine has been shown to induce appreciable swelling at the interfibrillar level, and although there is no decrystallization of cotton, the extent of swelling brought about was found to be of the same order of magnitude as that obtained with sodium hydroxide of mercerizing strength.[1] It seems that because of its powerful swelling action, morpholine brings about further opening up of the fiber structure in the accessible region, thus facilitating better dye uptake of the direct dyes.

Although morpholine treatment produces no decrystallization of cotton fibers, it is rather surprising that a considerable increase in the reactive dye uptake was also observed. Table I shows that although the total amount of accessibility remains unaltered in the morpholine-treated cotton fibers, a considerable amount of change does take place in the L and I regions of the fiber. The L region is reduced by about 15% of the original amount of the L region, while the I region is improved by about 35% of the original I fraction. This indicates that the intercrystalline swelling action of the morpholine solution is so powerful that, although the crystallites remain unaffected, the L region on their surface is surely affected in such a way that part of the crystallite surfaces is now covered by truly accessible (I) portions, thus increasing the truly accessible portion. This is to say that the imperfect crystallites present on the true crystals or in the I regions are broken and converted into truly accessible regions. It is therefore likely that the morpholine-treated sample is more easily penetrated, and those —OH groups in the accessible portion which were easily accessible to water vapor but were not available for the bulky molecule of the reactive dye are now made available for this purpose also, thus increasing the reaction sites for the reactive dye molecules. Thus, although there is no increase in accessibility to moisture, a considerable increase in the reactive dye uptake has taken place due to the further opening up of the existing accessible portion of the fiber reflected in the increase in I fraction.

The wash and light fastness properties of the cotton samples treated with all the three reagents studied remained unaltered, although in few cases slight improvement was noted.

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