JOURNAL OF APPLIED POLYMER SCIENCE VOL. 20, 525–542 (1976)

Studies on Chemically Modified Cotton. V. Effect of Zinc Chloride Solutions on Swelling and Other Properties of Cotton*

S. N. PANDEY and PREMA NAIR, *Cotton Technological Research Laboratory, Adenwala Road, Matunga, Bombay 400019, India*

Synopsis

This paper describes the effect of zinc chloride solutions of different molarity at different temperatures, viz., 10°, 25°, 36°, 55°, and 75°C, on various properties of cotton fiber such as degree of swelling, accessibility to water vapor and iodine absorption, infrared ratio, barium activity number (BAN), and leveling-off degree of polymerization (LODP). Zinc chloride solution caused inter- and intrafibrillar swelling in cotton fiber depending on conditions of treatment, viz., concentration of solution and temperature employed. Fibers treated in 10.07 moles/l. (*M*) solution of zinc chloride in slack state showed rapid increase in degree of swelling up to 2 hr, followed by a slow increase, reaching the maximum after 3 hr of treatment. Fibers swollen with fixed ends without allowing shrinkage showed gradual increase with maximum swelling after 6 hr of treatment. Cotton fibers treated in different molar solutions of zinc chloride at 55°C showed varying degrees of swelling (inter- and intrafibrillar) and a somewhat different trend compared to that observed at 10°C. Electron micrographs revealed mostly intercrystalline swelling in case of samples treated with 9.26*M* at 10°C, while the same concentration produced intracrystalline swelling at 55°C. Accessibility to water vapor, iodine absorption, and BAN of treated samples showed specific effect of temperature with regard to effectiveness of concentrations of zinc chloride solutions. Similar effects of temperature with regard to concentrations of reagent were observed on infrared ratio and LODP. Accessibility by iodine absorption and LODP correlate with BAN; also, the accessibility by iodine absorption correlates with the LODP.

INTRODUCTION

Zinc chloride is one of the best known of the inorganic salt swelling agents for cellulose. Mercer[1] included aqueous zinc chloride solutions in his original patent covering the mercerization of cotton, specifying a 50% solution at 65–71°C. Earlier work on zinc chloride has been reviewed recently by Warwicker et al.[2] Considerable swelling in cotton cellulose has been reported by a number of workers employing aqueous solutions of different strengths of zinc chloride.[3–7] Patil et al.[7] studied with x-ray technique the decrystallization of cotton in aqueous solutions of zinc chloride as function of concentrations and time at 20° and 35°C. They reported no appreciable effect below about 50%; between this concentration and saturation, there are two distinct minima in decrystallization. Recently, Betrabet et al.[4] reported swelling and decrystallizing action of aqueous solution of zinc chloride of different concentrations

* Presented at the 15th Technological Conference of ATIRA, BITRA, and SITRA, Bombay, January 1974.

at temperatures of 20° and 35°C. They explained that the intracrystalline swelling and decrystallization of cotton cellulose under different conditions of treatment with zinc chloride solutions is due to the nature and extent of formation of specific hydrates rather than to formation of different types of complex between zinc chloride and cellulose. From the review of literature, it is seen that most of the work reported is in the limited range of temperature of 20° to 35°; and, therefore, it was considered desirable to study the effect of different concentrations of zinc chloride at a wider range of temperature on various properties of cotton fiber.

In this paper, information on swelling cellulose, accessibility by different methods such as water vapor, iodine absorption, and infrared ratio, barium activity number (BAN), and leveling-off degree of polymerization (LODP) of cotton treated with different molar solutions of zinc chloride under different condition of treatment are reported.

EXPERIMENTAL

Materials and Chemical Treatments

Lint samples of cotton MCU.3 were used in this study. The samples were cleaned and purified as described earlier[8] before chemical treatment.

Zinc chloride used was of analytical reagent grade. Aqueous solutions of zinc chloride of different strengths expressed in molarity up to 12.77 moles/l. (*M*) were used for the treatment. Most of the treatments were carried out in slack state of the fiber at different temperatures, i.e., 10°, 25°, 36°, 55°, and 75°C, for 1 hr. At the end of each treatment, the fibers were washed in running tap water and finally with distilled water, and air dried. Fibers were also treated in 10.07M solution of zinc chloride in (i) slack state and (ii) with fixed ends without tension on a glass slide for different periods of time ranging from 10 min to 21 hr at room temperature.

Methods

Degree of swelling was determined by treating cotton fibers in zinc chloride solution of required strength for different periods of time at room temperature. Swollen fibers, ten each, were mounted on microscope slides. These slides were examined under the microscope with a calibrated eye piece scale at room temperature. The width of the central part of each fiber was measured in all the cases. One hundred and fifty fibers were examined this way. Average value is reported in relation to the swelling of cotton fibers in water under similar experimental conditions.

Treatment of cotton fibers with fixed ends without allowing shrinkage was carried out in the same manner as described above, except that straight fibers were mounted on a series of slides with both the ends fixed on slides with "stick fast." After treatment for the required period, measurements were made and the degree of swelling expressed as stated above. Cotton fibers treated for 1 hr with different molar solutions of zinc chloride at 10° and 55°C were also studied for swelling.

Moisture regain at 85% R.H. was determined by the method described earlier.[9] Number of moles of water per anhydroglucose unit is expressed as M.R.% × 162/1800.

Accessibility per cent is calculated by using the constant value 2.29 moles of water per anhydroglucoss unit (AGU) absorbed by completely accessible cellulose at 85% R.H.,[10] using the following formula[11]:

$$\text{accessibility to water vapor } \% = \text{moles of water AGU} \times 100/\text{constant.}$$

Accessibility by iodine absorption was determined by the method of Hessler and Power[12] with slight modifications described earlier.[8]

Barium activity number (BAN) of swollen samples was determined as per the I.S.I. Standard Method.[13] BAN was calculated as the ratio of quantity of barium hydroxide absorbed by swollen cotton to that absorbed by untreated (control) cotton under identical conditions, multiplied by 100.

Infrared crystallinity index was calculated according to the method of O'Connor et al.[14] Infrared spectra were obtained on a Grubb-Parsons Spectrometer Mark II infrared spectrometer by KBr pellet technique. Infrared grade as KBr was employed for disc preparation in which 200 mg of the dry halide and 1 mg of the ground cotton were accurately weighed on a microbalance and thoroughly mixed. Of this mixture, 150 mg was placed in the evacuable die in which a transparent disc was produced.

Leveling-off degree of polymerization[15] (LODP) was determined by refluxing samples for 15 min in 2.5N hydrochloric acid, washing, drying, and determining the viscosities of the resulting hydrocelluloses, in cuprammonium solvent.[16] The LODP was calculated using Kraemar's[17] constant, viz., LODP = 260 × η_{sp}/c, where c equals concentration, in g/100 ml solution, and is 0.5%; and η_{sp} is specific viscosity.

X-Ray diffractograms were obtained (on cotton fibers finely cut and packed in a standard Philip's sample holder) as described below:

The sample mounted in the goniometer of a stabilized Philips x-ray generator was scanned using nickel-filtered CuK_x radiation, ½ divergence slit 0.1 mm receiving slit along with ½° scatter slit. The diffracted intensity was recorded using a strip-chart recorder; x-ray observations were limited to the cotton samples treated with 8.83M and 9.26M zinc chloride at 55°C.

To observe the microfibrillar morphology of zinc chloride-treated cotton, the electron-microscopic observations were made by the modified two-step layer expansion technique of Rollins and Coworkers.[18,19] The observations were limited to cotton treated with zinc chloride at 9.26M concentration at 10° and 55°C. Ultrathin cross sections of embedded fibers were appropriately shadowed with platinum after the removal of the polymerized polymethacrylate and examined under low and high magnification in a Hitachi HU-11 E electron microscope at 75 KV.

RESULTS AND DISCUSSION

Degree of Swelling

The results on the degree of swelling of fibers for different periods of time in 10.07M solution of zinc chloride are shown in Figure 1. Fibers swollen in the slack state showed rapid increase in swelling up to 2 hr, followed by fur-

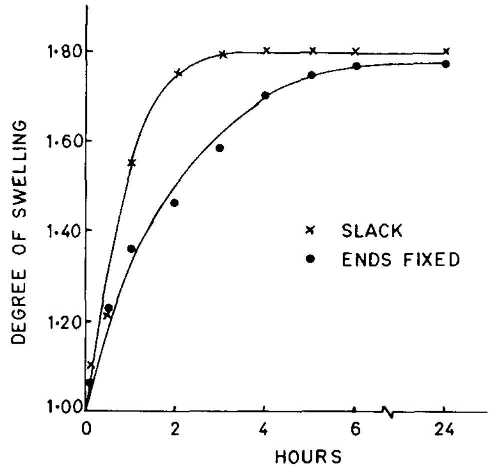


Fig. 1. Degree of swelling of cotton treated with 10.07 moles/l. zinc chloride solution vs. time under different conditions.

ther increase up to 3 hr beyond which there was no further increase. Fibers swollen with fixed ends without tension showed increase in degree of swelling up to 6 hr beyond which there was no further increase. Degree of swelling was almost the same up to ½ hr under both conditions; but beyond ½ hr, swelling was considerably higher in the case of slack samples for the same time.

Fibers swollen in different molar solutions of zinc chloride at 10° and 55°C showed marked differences in degree of swelling at the same concentration. Fibers at 10°C showed a gradual increase in swelling up to 8.83*M* solution, with a sudden decrease in swelling in 9.26*M* solution and again a slight increase in 10.07*M* solution and then a gradual decrease in swelling with higher concentrations (Fig. 2). At 55°C, there was a gradual increase in degree of swelling up to 7.70*M* (122%), followed by a rapid increase up to 9.26*M* (188%) beyond which there was a gradual decrease up to 10.51*M* (180%); and thereaf-

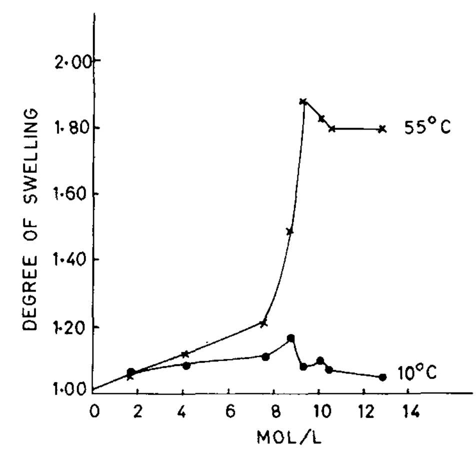


Fig. 2. Degree of swelling of cotton vs. zinc chloride concentrations at different temperatures.

ter, it remained the same for higher concentrations. These results indicate an enormous increase in fiber swelling at 55°C at higher concentrations, while at 10°C, swelling was comparatively much lower.

Moisture Sorption and Related Data

Data with respect to the moisture sorption, moles of water per anhydroglucose unit, and accessibility per cent of cotton fibers treated in different molar solutions of zinc chloride at different temperatures are summarized in Table I. Moisture regain showed gradual increase initially up to a solution of 7.7*M*, followed by a sharp rise at 8.83*M* solution, and then showed rapid decrease at 9.26*M*, followed by slight increase at 10.07*M*, then decreased at 10.5 and remained unchanged thereafter (Fig. 3). A similar trend was obtained at 25° and 36°C, except that the moisture regain values of the samples treated with higher molar solutions, 8.83*M* and above, at higher temperatures were comparatively higher, as may be seen from the respective curves (Fig. 3).

Further, it is observed that a maximum increase in moisture regain is obtained with a solution of 10.07*M* at 36°C, while at 10° and 25°C, the highest values were obtained in samples treated with the 8.83*M* solution. The shape of the curve in the case of samples treated at 55° and 75°C are quite different from those treated at lower temperatures (Fig. 3). At 55°C, a maximum in sorption value was noted with the 9.26*M* solution (16.82%), followed by a slight decrease at 10.07*M* (16.48%) and then a sharp decrease at 10.51*M* (15.1%), with no change thereafter. At 75°C, the trend was similar as at 55°C. Moles of water per anhydroglucose unit and accessibility per cent derived from the same (Table I) showed a similar trend.

From these data it is observed that zinc chloride produces different degrees of swelling (inter- and intrafibrillar) or decrystallization at different temperatures, and the samples treated at higher temperatures showed higher reactivi-

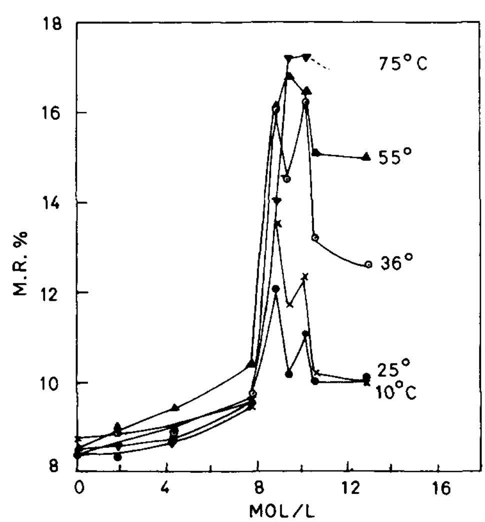


Fig. 3. Moisture regain per cent of cotton vs. zinc chloride concentrations at different temperatures.

TABLE I
Moisture Regain (M.R.) and Accessibility of Cotton Treated with Zinc Chloride Solution at Different Temperatures

Sample no.	$ZnCl_2$ concentration, moles/l.	10°C			25°C			36°C			55°C			75°C		
		M.R., %	Moles of H_2O/AGU	Accessibility, %	M.R., %	Moles of H_2O/AGU	Accessibility, %	M.R., %	Moles of H_2O/AGU	Accessibility, %	M.R., %	Moles of H_2O/AGU	Accessibility, %	M.R., %	Moles of H_2O/AGU	Accessibility, %
1	Control	8.39	0.76	33	8.67	0.78	34	8.39	0.76	33	8.52	0.77	34	8.61	0.78	34
2	1.74	8.29	0.75	33	8.98	0.81	35	8.85	0.80	35	9.00	0.81	35	8.51	0.77	34
3	4.16	8.66	0.78	34	8.89	0.80	35	8.78	0.79	34	9.40	0.95	41	8.63	0.78	34
4	7.70	9.52	0.86	38	9.47	0.85	37	9.73	0.88	38	10.40	0.94	41	9.52	0.86	38
5	8.83	12.04	1.08	47	13.53	1.22	53	16.05	1.44	63	16.10	1.45	63	13.99	1.26	55
6	9.26	10.14	0.91	40	11.73	1.06	46	14.50	1.31	57	16.82	1.51	66	17.18	1.55	68
7	10.07	11.13	1.01	44	12.35	1.11	48	16.24	1.46	64	16.48	1.48	65	17.29	1.56	68
8	10.51	10.00	0.90	39	10.20	0.92	40	13.20	1.19	52	15.10	1.36	59	—	—	—
9	12.77	10.10	0.91	40	10.00	0.90	39	12.60	1.13	49	15.00	1.35	59	—	—	—

ty than those treated at lower temperatures for corresponding molarity, except in a few cases. Further, it is observed that the accessibility values showed only slight improvement with solutions up to 7.70*M* at all the temperatures, beyond which marked increase in accessibility was noted at higher temperatures (25° to 75°C).

The most important observation in this study seems to be the effect of the 9.26*M* solution at higher temperatures (55° to 75°). There was less effect with this solution at 10°C compared to the solution of 8.83*M* and 10.07*M*. There is a gradual increase in accessibility in case of samples treated with 9.26*M* and 10.07*M* solutions with increase in temperature. The 8.83*M* solution, which was more effective than others at 10° and 25°C, showed its maximum effect at 36°C, with an accessibility of 63%, with no further increase in accessibility (63%) at 55°C and a lower value at 75°C with accessibility of 55%.

Specific characteristics of aqueous solutions of zinc chloride at 20° and 35°C were examined by Betrabet et al.[4] using ultraviolet and infrared studies. They indicated that the intracrystalline swelling and decrystallization of cotton cellulose under different conditions of treatment with zinc chloride solutions is due to the nature and extent of formation of specific hydrates in the aqueous solutions.

Barium Activity Number (BAN)

Data on BAN of native and chemically treated samples (Fig. 4) show a similar trend as observed in the case of moisture regain, except in a few cases. There are five distinct stages in BAN curves of 10°, 25°, and 36°C, indicating gradual increases in BAN values at molarity up to 7.70*M* followed by a sharp increase at 8.83*M*. Thereafter, the BAN curves showed a sharp decrease at

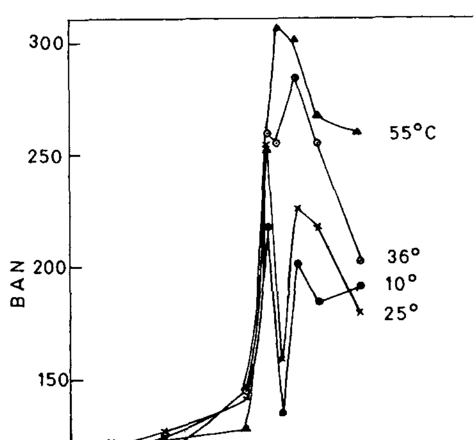


Fig. 4. Barium activity number (BAN) vs. zinc chloride concentrations at different temperatures.

9.26*M* (only a slight decrease at 36°C), followed by a sharp rise again at 10.07*M*, followed by a decrease with higher molarity. The 8.83*M* solution was most effective at 10° and 25°C, while the 10.07*M* solution was so at 36°C. The BAN curve at 55°C showed gradual rise up to 7.70*M*, with a sharp rise up to 9.26*M*, thereafter followed by gradual decrease with higher molarity. It is noteworthy that the BAN curve at 55°C showed a maximum increase in degree of swelling (305) with a solution 9.26*M*, which was less effective at lower temperatures. Therefore, it may be stated that the effect of solutions of zinc chloride on BAN of cellulose is dependent on specific temperature, the curves for 10°, 25°, 36°, and 55°C generally take progressively higher positions, with a few exceptions. And for corresponding treatments, the BAN increases as the temperature increases.

Accessibility by Iodine Absorption

Accessibility data by iodine absorption of native and treated cottons are graphically shown in Figure 5. Accessibility curves at different temperatures (10°, 25°, 36°, 55°, and 75°C) show little effect of solutions up to 7.70*M*. The curve at 10°C showed a marked increase in accessibility, viz., from 11.5% to 28.2% with the 8.83*M* solution. The value decreased to 18.1% with the 9.26*M* solution and again increased to 23.5% with the 10.07*M* solution, then decreased with higher molarity. The curve at 25°C followed a similar trend with higher accessibility values than those of 10°C for corresponding treatments. The curve at 36°C was also similar, except that the highest degree of decrystallization (53%) was observed at the 10.07*M* solution instead of 8.83*M*. The accessibility curve at 55°C showed a somewhat different trend, indicating maximum increase in accessibility (53.3%) with 9.26*M* solution and a decrease thereafter with higher molarity. The curve at 75°C was similar to that

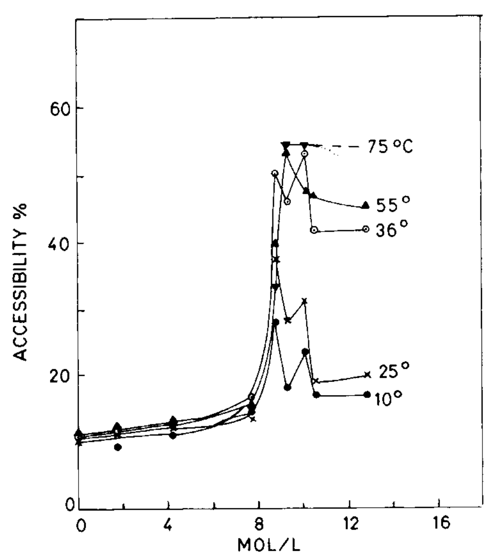


Fig. 5. Accessibility per cent by iodine absorption (I.A.) vs. zinc chloride concentrations at different temperatures.

TABLE II
Infrared Ratio of Cotton Treated with Zinc Chloride Solution at Different Temperatures

Sample no.	$ZnCl_2$ concentration, moles/l.	10°C	25°C	36°C	55°C	75°C
1	Control	2.52	2.52	2.52	2.52	2.52
2	8.83	1.88	1.61	0.90	1.40	1.67
3	9.26	2.44	1.86	0.96	0.77	0.64
4	10.07	2.22	1.65	0.87	0.78	0.66

of 55°C, except that the accessibility remained unchanged after 9.26*M* with increased molarity and the accessibility with the 8.83*M* solution was lower (33.3%) compared to that at 55°C (39.9%).

In general, these data confirm the observations made in the case of moisture sorption and BAN. Further, it may be stated that inter- and intrafibrillar swelling with the same molar solution is evidenced when conditions of treatment, viz., temperature, are changed. In the case of 9.26*M* solution, accessibility at 10°C is only 18.1%, indicating slight interfibrillar swelling, which is increased to 54% indicating intrafibrillar swelling at elevated temperature of 75°C. Similarly, 8.83*M* solution showed maximum decrystallization effect at 36°C.

Infrared Ratio

Infrared ratio data of native and treated cottons at selected molarities are given in Table II. The values of samples treated at 10°C showed marked decreases, viz., from 2.52 to 1.88, with the 8.83*M* solution while in other cases there was slight decrease, and the 9.26*M* solution was least effective. A similar trend was observed at 25°C, except that the values were appreciably lower at 9.26*M* and 10.07*M*. At 36°C, infrared ratio values were further reduced with all the three molarities indicating maximum change with the 10.07*M* solution.

At 55° and 75°C, the trend was somewhat different, indicating least change with 8.83*M* and maximum decrease (0.77 and 0.64) with 9.26*M*, followed by very close values (0.78 and 0.66) with 10.07*M*. It is worth noting that the 8.83*M* solution was most effective and caused maximum intrafibrillar swelling and decrystallization up to 36°C. At higher temperature, it produced the least change in fine structure of cellulose, while solutions 9.26*M* and 10.07*M*, which were less effective at 10° and 25°C, produced greater swelling and decrystallization at elevated temperatures. These results corroborate earlier findings of moisture sorption, BAN, and iodine absorption data.

X-Ray Studies

Figure 6 shows the x-ray diffractograms of control and zinc chloride-treated samples with 8.83*M* and 9.26*M* concentrations at 55°C. Curve A shows the x-ray pattern of native cotton. Curve B is for the sample treated with 8.83*M* solution, and it is decrystallized and shows trace of cellulose II lattice.

Curve C is for the sample treated with 9.26*M* concentration, and it exhibits a highly decrystallized and ill-defined pattern. This is in agreement with the observation made in case of sorption ratio and infrared ratio. The zinc chloride is a powerful swelling and decrystallizing reagent, and the 9.26*M* concentration is more effective than the 8.83*M* concentration at 55°C.

Electron-Microscopic Studies

Figure 7 shows characteristic layers in a normal cotton fiber. Figure 8 also shows profuse layering. This indicates that at 10°C, zinc chloride solution 9.26*M* brings about primarily intercrystalline swelling. Loss of discrete microfibrillar pattern and some fusion of microfibrils along the lamallae is, however, evident at high magnification (Fig. 8b). The intracrystalline nature of swelling brought about by 9.26*M* zinc chloride solution at 55°C is evident in Figure 9. Compactness of the mass as a result of lateral fusion of lamallae and destruction of characteristic layering is evident, particularly at high magnification (Fig. 9b). Betrabet and Rollins[18] have reported complete fusion of lamellae and destruction of microfibrillar pattern in cotton treated with 65% zinc chloride at 20°C.

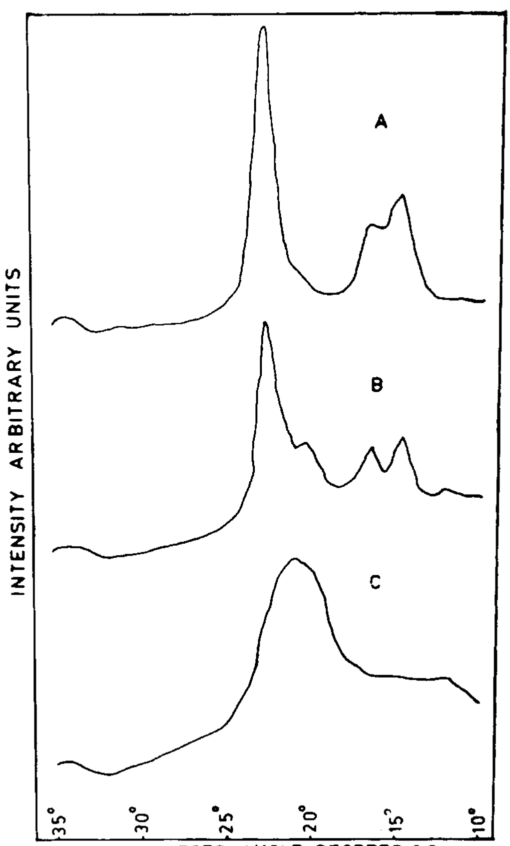
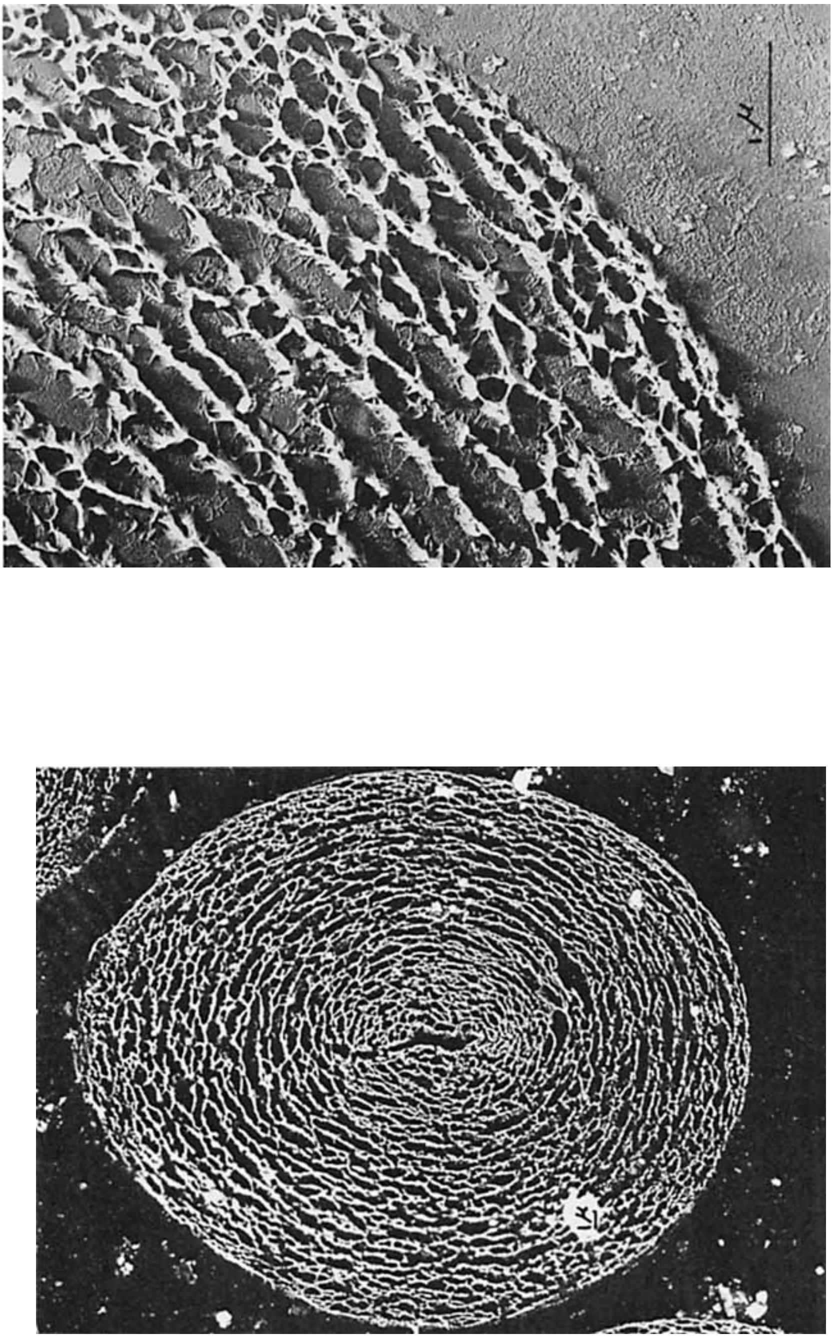
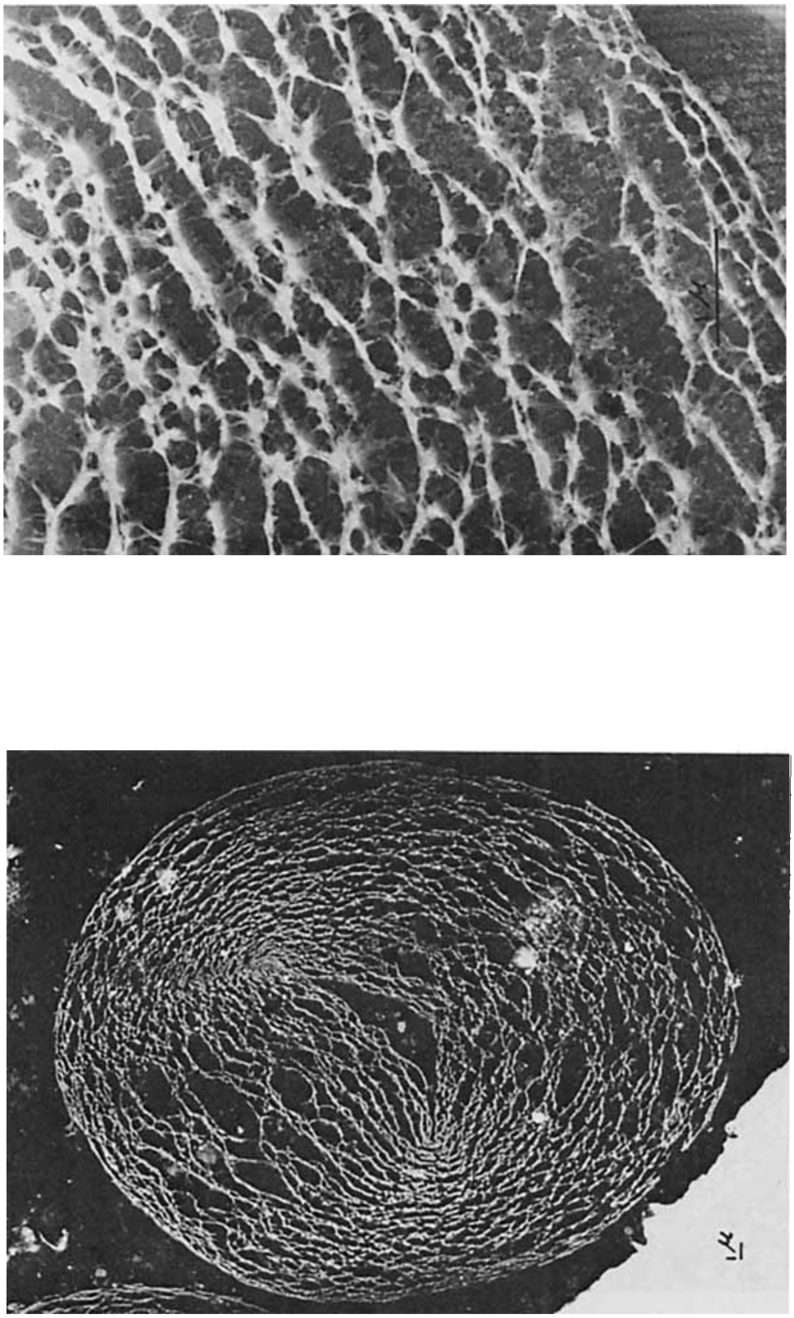


Fig. 6. X-Ray radial tracings of cotton cellulose treated with 8.83*M* and 9.26*M* zinc chloride solution for 1 hr at 55°C.



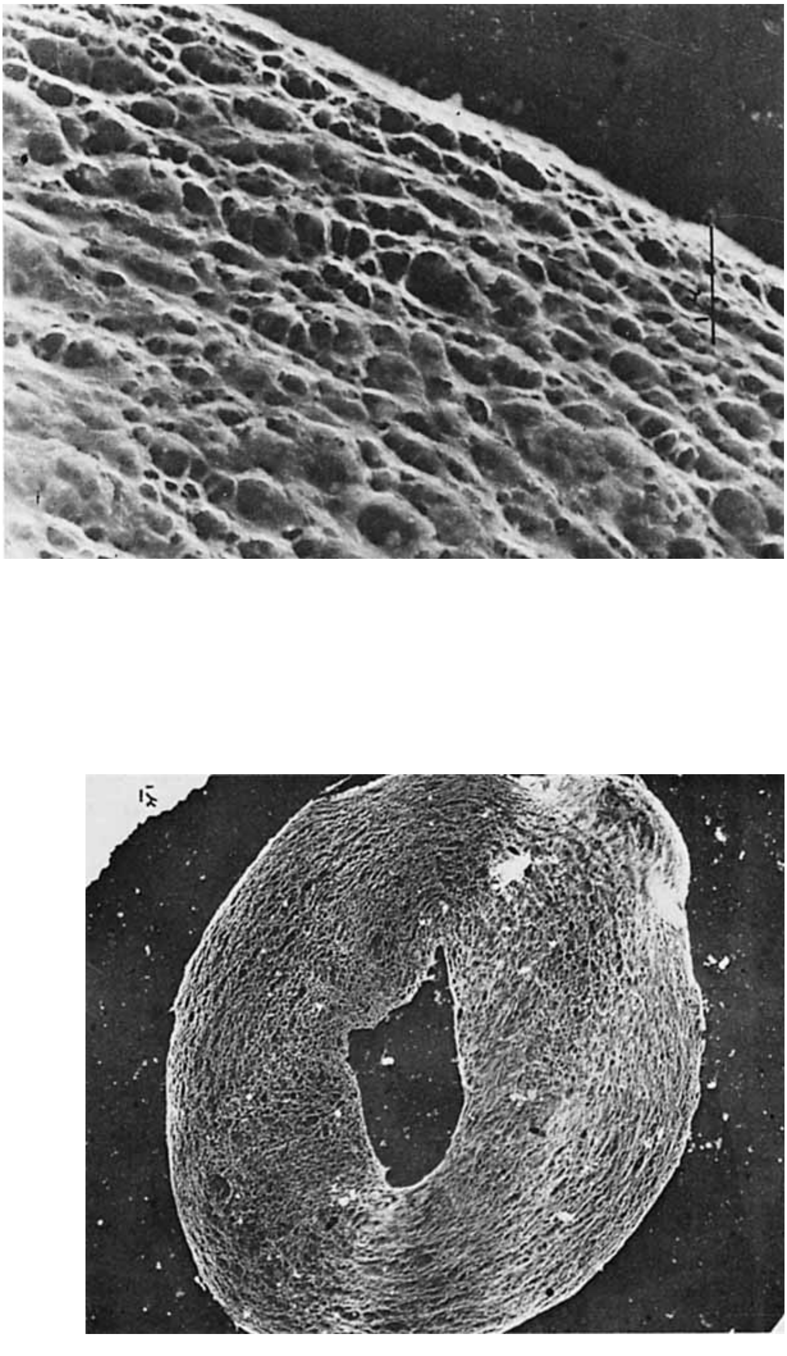
(a) (b)

Fig. 7. Cross section of untreated cotton fiber by layer expansion, showing (a) characteristic layers, and (b) microfibrile. Length of line represents 1 micron.



(a) (b)

Fig. 8. Cross section of zinc chloride-treated cotton, 9.26M, 10°C, 1 hr: (a) profuse layering and (b) lamellae as in Fig. 7 but with some loss of microfibrillar pattern.



(a) (b)

Fig. 9. Cross section of zinc chloride-treated cotton, 9.26*M*, 55°C, 1 hr, by layer expansion showing (a) spongy structure, loss of layering due to lateral disorder; (b) compactness and fusion of microfibrils.

TABLE III
Levelling-Off Degree of Polymerization (LODP) of Cotton Treated with Zinc Chloride Solutions at Different Temperatures

Sample no.	$ZnCl_2$ concentration, moles/l.	10°C	25°C	36°C
1	Control	265	265	255
2	1.74	255	255	242
3	4.16	240	236	230
4	7.70	230	220	210
5	8.83	190	166	125
6	9.26	234	203	177
7	10.07	208	180	115
8	10.51	240	203	180
9	12.77	225	210	185

The electron-microscopic observation by the layer expansion technique illustrate the subtle differences in the morphology of decrystallized cotton brought about by a swelling agent under different conditions of treatment. This is confirmed by these results.

Leveling-Off Degree of Polymerization (LODP)

The leveling-off degree of polymerization of hydrocelluloses is related to crystallite particle length. The average crystallite length of cellulose fibers is affected by swelling treatments and by conditions of solution and treatments. Data on LODP of native and chemically modified cotton are given in Table III. It is seen there that the LODP of samples treated at 10°C showed only a slight decrease with a concentration up to 7.70*M*, i.e., from 265 for control to 230. Like other properties, it showed marked decrease to 190 and 208 with the 8.83*M* and 10.07*M* solutions, respectively, indicating only slight change beyond these concentrations. LODP of samples treated at 25°C showed almost a similar trend, with the values comparatively lower for the corresponding concentrations. Samples treated at 36°C also showed a similar trend, except that the values are comparatively still lower and the maximum change in LODP is noted at the 10.07*M* solution instead of 8.83*M*. These data indicate nearly a similar trend as observed in the case of accessibility values by iodine sorption and moisture sorption, BAN, and infrared ratio values.

Relationship Between Properties of Modified Cellulose

Accessibility values derived from iodine absorption and moisture regain data are closely related, correlation coefficient being 0.95 (significant at the 1 per cent level) as may be expected. These results show that the moisture regain and iodine absorption accessibility values show definite changes in fine structure of cotton after swelling in zinc chloride and that the degree of change is dependent on various factors and conditions of treatment. The foregoing relationship of accessibility by the above methods confirms the earlier findings.[9,20]

Relationship between BAN and accessibility by iodine absorption has been shown in Figure 10. The plot of data and regression line show high positive correlation between the properties, the correlation coefficient being 0.94, which is highly significant at the 1% level. The regression equation between BAN and accessibility by iodine absorption is given below:

$$X_1 = 4.08X_2 + 78.79$$

where X_1 = BAN and X_2 = accessibility by iodine absorption.

The relationship between BAN and LODP is shown in Figure 11. It is observed that the two parameters show a negative but close relationship, the correlation coefficient being −0.91, highly significant at the 1% level. The data show some scatter but fit a straight line, indicating that the higher the degree of swelling and chemical reactivity, the lower the LODP. The regression equation calculated for these data is given below:

$$X_1 = 1.3186X_3 + 454.19$$

where X_1 = BAN and X_3 = LODP. A similarly close relationship between accessibility to water vapor and LODP was reported by Warwicker et al.[21]

BAN was also correlated with infrared ratio, and the correlation coefficient between the two properties was −0.88, which is highly significant at the 1% level. Regression equation was calculated and is given below:

$$X_1 = -98.07X_4 + 379.32$$

where X_1 = BAN and X_4 = infrared ratio.

These data show that the higher the degree of swelling and chemical reactivity in modified cellulose, the lower the infrared ratio.

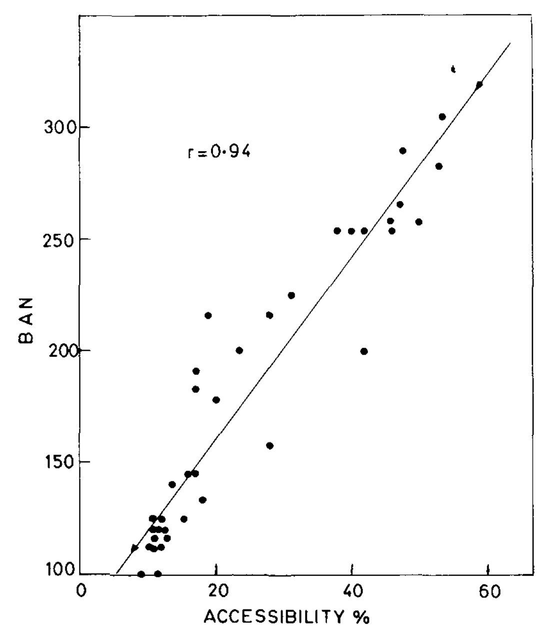


Fig. 10. Correlation between barium activity number (BAN) and accessibility per cent (I.A.) of cotton treated with zinc chloride solutions.

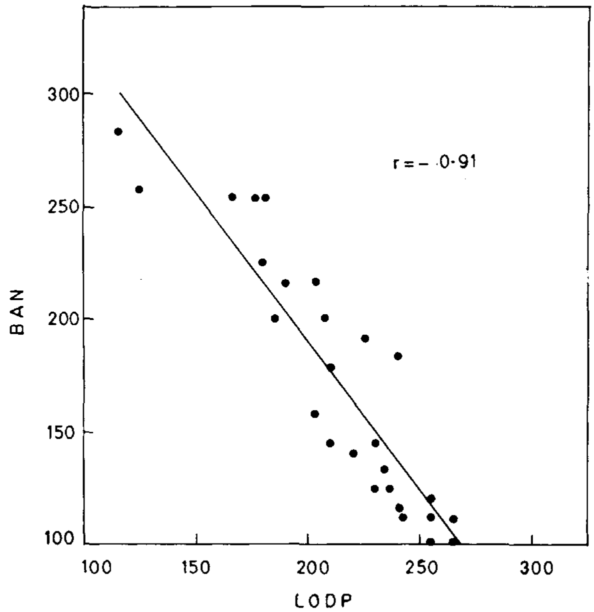


Fig. 11. Correlation between barium activity number (BAN) and leveling-off degree of polymerization (LODP) of cotton treated with zinc chloride solutions.

Relationship between accessibility by iodine absorption and LODP is graphically shown in Figure 12. It will be seen from the figure that there is close negative association between the two properties, correlation coefficient being −0.93, which is highly significant at the 1% level. Regression equation was statistically worked out and is given below:

$$X_2 = -0.3258X_3 + 92.20$$

where X_2 = accessibility by iodine absorption and X_3 = LODP. These results confirm the earlier findings that there is close negative association between accessibility (reactivity) and LODP.

The relationship between accessibility by iodine absorption and infrared ratio was also studied. The two properties showed a close negative correlation, confirming the earlier findings.[22,23] Correlation coefficient was −0.95, highly significant at the 1 per cent level, and the regression equation was as follows:

$$X_2 = -23.54X_4 + 73.02$$

where X_2 = accessibility by iodine absorption and X_4 = infrared ratio. This close association indicates that in these methods, measurements of degree of order are made at the same level of organization of fine structure.

CONCLUSIONS

The following conclusions are drawn from the foregoing discussion:

Zinc chloride is a powerful inter- and intrafibrillar swelling agent of cotton and, depending upon the concentration and the temperature of treatment, it

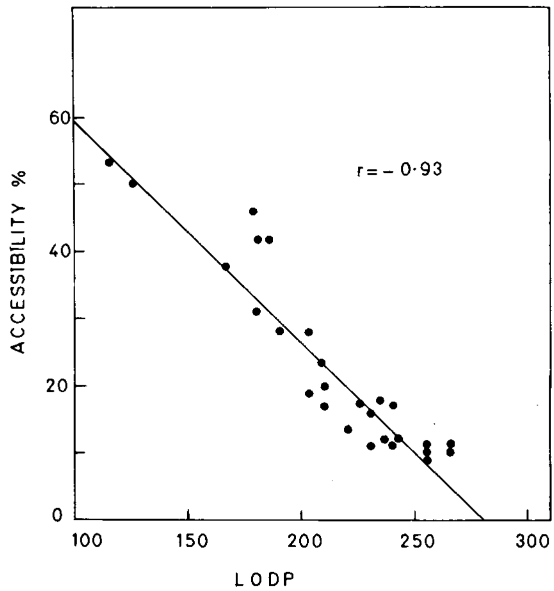


Fig. 12. Correlation between accessibility per cent (I.A.) and LODP of cotton treated with zinc chloride solution.

can modify fine structure and physicochemical properties of cotton. The degree of swelling, BAN, accessibility, and chemical reactivity are generally increased with temperature, but for each temperature level, the optimum conditions are attained in different concentrations of zinc chloride. Solutions up to 7.70*M* caused only slight change in swelling and accessibility of cotton at all the temperatures. At 10° and 25°C, maximum swelling and decrystallization were obtained with the 8.83*M* solution; at 36°C, with 10.07*M*; and at 55° and 75°C, with 9.26*M* and 10.07*M*. Infrared ratio and LODP showed marked decrease at specific molarities, specially where enormous intrafibrillar swelling took place and the values were reduced to a great extent with increase in the temperature of treatment for the corresponding molarities.

X-Ray diffractograms showed decrystallized pattern and trace of cellulose II in samples treated with 8.83*M*, while in samples treated with 9.26*M* at 55°, the sample showed highly decrystallized and ill-defined cellulosic pattern.

Electron micrographs reveal mostly intercrystalline swelling in case of samples treated with 9.26*M* concentrations at 10°C, while the same concentration produced intracrystalline swelling at 55°C.

BAN correlates with accessibility, LODP, and infrared ratio; also accessibility correlates with LODP and infrared ratio.

It is evident that concentrations up to 7.70*M* produce only slight swelling in cotton without any appreciable change in accessibility. Possibly, this is accompanied by interfibrillar swelling. With increase in concentration or temperature, the swelling attains a high maximum (as in the case of treatment at 55°C and 9.26*M* solution). However, it is observed that all such treatments are accompanied by increase in accessibility also. Evidently, these treatments lead to intrafibrillar swelling in addition to interfibrillar swelling seen earlier. Chemical reactions on cellulose depend not only on the amount of swelling but also on the nature of swelling. Since it is possible to have inter- as well as intrafibrillar swelling with zinc chloride solutions of required concentrations and temperature, further chemical processing of cotton at any desired level could be achieved on the industrial side depending upon the end use.

The authors wish to express their thanks to Dr. V. Sundaram, Director, Cotton Technological Research Laboratory, for his permission to publish this paper, to Dr. S. M. Betrabet for the electronmicrographs, to Mr. P. K. Chidambareswaran for the x-ray diffraction, and to Shri D. V. Madgut for carrying out the statistical analysis.

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Received May 14, 1975
Revised June 3, 1975