Studies on the Swelling of Cotton Fibers in Alkali Metal Hydroxides. III. Structure–Property Relations in Fibers Swollen at 0°C

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SYNOPSIS

Cotton fibers were subjected to swelling in various concentrations of LiOH, NaOH, and KOH at 0°C. Swollen fibers were characterized by measurements of physical, mechanical, and fine structural properties. Slack swelling in LiOH and NaOH produced tremendous changes in fiber properties. Clear-cut swelling maxima, disorientation, and subsequent deterioration in tensile properties at and near the swelling maxima were evident in both LiOH and NaOH. On the other hand, KOH swelling did not produce any clear swelling maximum. Fibers swollen in this reagent showed better retention of tensile properties due to conducive changes in the structural parameters resulting from a lower but more uniform swelling. © 1993 John Wiley & Sons, Inc.

INTRODUCTION

Structural investigations[1-7] on cotton fibers swollen in alkali metal hydroxides demonstrated that the swelling power of a given reagent depends on its cationic size, concentration, and temperature. The tenacity of the swollen fibers decreased with an increase in the extent of swelling.

In a recent study[8] on structure–property relations in cotton fibers swollen in LiOH and KOH at ambient temperature, we noted that the cationic size differences among swelling agents influenced the tensile properties. It was further found[9] that when varieties of cotton, widely varying in fiber properties, were compared after alkali swelling, the tensile behavior was influenced not only by the resultant fine structure but also by the radial packing of structural elements.

Lowering the temperature of swelling enhanced the swelling power of a reagent at a given concentration. This increased swelling capability has been attributed to the greater degree of hydration of the alkali ions, particularly in the more dilute solutions. Studies[10-12] on the swelling of cotton fibers using NaOH at 0°C have shown that the excessive swelling could even cause breaking up of the outer protective primary layer, leading to disorientation of the fibrils in the secondary cell-wall. Such detailed studies on swelling at 0°C, using the other alkali metal hydroxides, are not available except that it has been shown[4] that the tenacity of the KOH-treated fibers is higher than that of NaOH- or LiOH-treated fibers.

The present investigation deals with an extensive study made on swelling of cotton fibers in aqueous LiOH and KOH solutions of different concentrations at 0°C. Fibers were simultaneously swollen in NaOH solutions of different concentrations as well, for comparison. The physico–mechanical and fine structural properties of the treated fibers were measured by using appropriate techniques. The results are presented and analyzed on the basis of modern concepts of swelling and structure.

EXPERIMENTAL

Materials

Cotton fibers belonging to the variety Suvin (G. barbadense) were used throughout the study. Fibers

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were kier-boiled under normal conditions prior to treatments.

Slack Swelling

Fibers were swollen in the three alkali metal hydroxides viz. LiOH, NaOH, and KOH in various concentrations in the range 2.0 N–5.0 N. The solutions were cooled to 0°C before introducing the fibers into the liquor; a material-to-liquor ratio of 1 : 50 was used. Fibers were swollen slack for about 15 min and the temperature was maintained at 0°C ± 0.5°C during treatment. The swollen fibers were washed in air.

Slack Swelling and Stretching

Flat bundles of parallelized fibers were prepared and mounted on jaws by means of a special device. These bundles were swollen under slack conditions and were stretched as described in an earlier publication.[13]

Bulk Sliver Treatment

About 10 g of cotton fibers, in sliver form, were treated in selected concentrations of alkali at 0°C. The other conditions of treatment and washing were the same as those described under slack swelling.

Cut Fiber Treatment and Shrinkage

Fibers cut to 1.5 cm in length before treatment were used for shrinkage measurement. After swelling, washing, and drying, the fibers were mounted on a glass slide and the length of each fiber was measured using a travelling microscope. For each treated sample, the length was measured on about 50 fibers and the average length after treatment was ascertained. The percentage of shrinkage was computed, based on the original length as being 1.5 cm.

Water Retention Values

About 1 g of the treated and washed fibers, from which excess water had been removed by squeezing, was transferred to centrifuge tubes containing special wire mesh. Centrifuging was carried out at 2500 rpm for 30 min at 25°C using a "Soraval" ultracentrifuge. After the specified time, the weight of fibers was determined. Untreated fibers were soaked in water overnight before centrifuging. The dry weights were determined after heating the samples for 5 h in an oven maintained at 105°C. The water retention values were computed from the difference between centrifuged and dry weights and were expressed as a percentage of dry weight.

Length and Fineness

The untreated sliver, along with the treated slivers, were used for fiber length measurements with Digital Fibrograph. The fiber fineness was measured using a Micronaire, based on the evaluation of resistance offered to the air-flow through fiber plugs. In addition, the gravimetric fineness was measured using the cut-and-weigh method. The details of the procedure are described elsewhere.[14]

Moisture Regain

The moisture regain for the fibers was measured using the standard procedure.[14]

Tensile Properties

Bundle tenacities, both at nominal zero gauge length (T_0) and at 3.2 mm gauge length ($T_{3.2}$), as well as extension (E %) for the fibers, were measured using a stelometer.

Tensile and Modulus Measurements on Single Fibers

Single fiber breaking tests were carried out using an Instron tensile tester. The test length remained 1 cm and the crosshead speed was adjusted so that all the fibers broke within 20 ± 5 sec. The linear density was measured by the cut-and-weigh method. The tenacity, extension, initial and final moduli, and work of rupture were all computed from the stress–strain diagram.

Crystallinity and Crystallite Dimensions

The radial intensity scans from powder samples were obtained using a Philips stabilized x-ray generator fitted with diffractometer and recording accessories. The cellulose I (CI), Cellulose II (CII), and Amorphous (Am) contents were computed as described earlier.[9] The half-maximum breadths of (200) and (004) reflections were measured to yield an indication of the crystallite breadth and length, respectively.

Crystallite Orientation

The Azimuthal intensity distribution from the well-parallelized bundle of fibers was obtained at 2θ, cor-

responding to (200) reflection. From the distribution, Herman's orientation factor, f_x, was evaluated using well-known methods. For the untreated fibers, the orientation factor was evaluated as per standard formula, $f_x = 1-3 \sin^2\delta$, where δ is the azimuth angle of the (200) reflection. For treated fibers, the f_x values were computed using the modified formula suggested by Shelat et al.,[15] viz. $f_x = 1 - 7/2 \sin^2\beta$, β being the azimuth angle corresponding to the combined (200) and (110) reflection. For swollen fibers having mixed lattices, that is, CI and CII in comparable proportions, the average f_x has been computed using both the equations, giving weightages to the respective polymorphic content.

Infrared Spectra

Infrared spectra of the cut powders from the treated samples were obtained by using a Perkin–Elmer Model 457 Infrared Spectrophotometer, and employing potassium bromide matrix. The intensities of the bands were measured by the baseline technique. The crystallinity index I, proposed by O'Connor et al.,[16] was computed for a few of the treated fibers.

Surface Morphology

The surface morphology of the treated fibers was studied with the scanning electron microscope (Cambridge Stereo Scan 150), as described earlier.[9] Micrographs, showing specific fiber morphology, were photographed.

RESULTS AND DISCUSSION

Shrinkage

Table I shows the shrinkage values of single fibers swollen in LiOH, NaOH, and KOH of selected concentrations. The corresponding measurements on fibers swollen in 4.6 N at ambient temperature are also shown in Table I for comparison.

It can be noted from Table I that at 0°C, the shrinkage is minimal after swelling in KOH. However, there is no marked difference in the shrinkage of fibers swollen in the other two reagents at this temperature. Shrinkage, which generally increases with the extent of swelling, follows the order LiOH > NaOH > KOH. At ambient temperature, shrinkage is less, indicating that the extent of swelling has an inverse relationship with temperature. Table I also contains fibrograph results measured on treated slivers. Both the 2.5% and 50% span lengths decrease after treatment, the decrease being the least after KOH treatment. The average shrinkage values, calculated from both span lengths, agree well with the single fiber shrinkage data shown in Table I. *This agreement indicates the possibility of estimating the extent of swelling using bulk measurements on swollen fibers.* The fiber fineness data, displayed in Table I, also show that the extent of swelling follows the same order as length contraction.

Water Retention Values

The water retention values (WRV), obtained on fibers swollen in LiOH, NaOH, and KOH, are plotted

Table I Length Contraction After Swelling in Alkali Metal Hydroxides

				Sliver			
				Span	Length		
Reagent	Concentration (N)	Temp. (°C)	Single Fiber Shrinkage (%)	2.5% (mm)	50% (mm)	Shrinkage Average[a] (%)	Fiber Fineness (μg/inch)
Nil[b]	Nil[b]	Nil[b]	—	37.3	18.2	—	3.6
LiOH	3.30	0	23.6	29.3	13.9	22.5	5.2
	4.60	30	17.3	—	—	—	—
NaOH	2.90	0	23.9	29.7	14.0	21.7	5.3
	4.60	30	14.6	—	—	—	—
KOH	3.30	0	17.5	31.4	14.5	18.1	4.8
	4.60	30	9.8	—	—	—	—

[a] Average shrinkage for 2.5% and 50%.
[b] Data for control sliver.

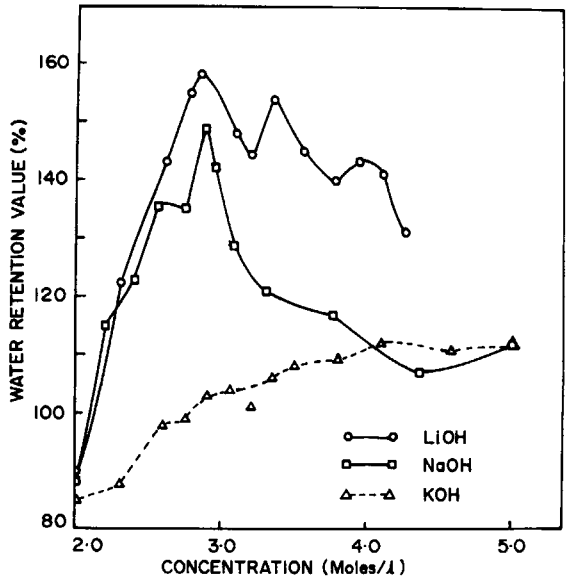

Figure 1 Water retention values (%) against concentration of the swelling agent.

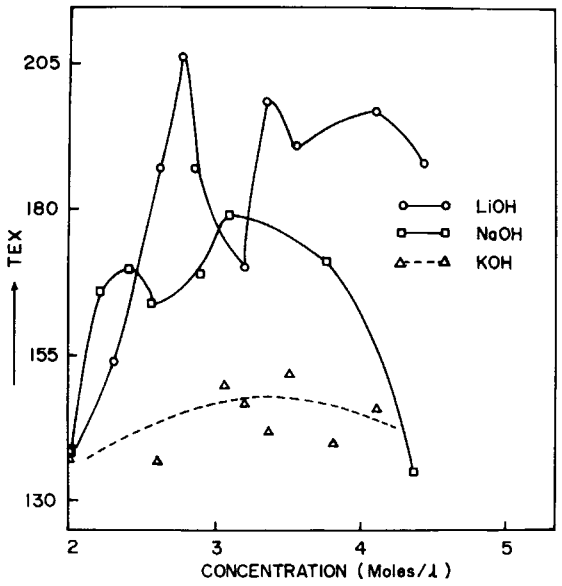

Figure 2 Tex (gravimetric fineness) of swollen fibres against concentration of the swelling agent.

against concentration in Figure 1. The value of WRV is the highest for fibers swollen in 2.85 N LiOH. Investigation of the curves further reveals that there are three maxima for LiOH at concentrations 2.85 N, 3.35 N, and 3.95 N. Although not as well defined, NaOH swollen fibers also show two maxima corresponding to 2.55 N and 2.9 N. As observed elsewhere, such maxima are present in the measurement of tex and moisture regain as well, although peak positions show small variations. However, with fibers swollen in KOH, such distinct transitions are not observed. In this case, WRV gradually increases with concentration and tends to level off after 4 N. The WRV values, measured on wet fibers after removing the swelling agent, follow the order LiOH > NaOH > KOH, in agreement with the shrinkage measurements discussed above.

Fiber Fineness (Gravimetric)

The linear density for treated fibers is plotted against reagent concentration in Figure 2. As discussed elsewhere,[8,9] the fiber tex can be used as an index of swelling retained after drying. From Figure 2, it is clear that the shape of the curves for all three swelling agents are similar to those obtained for WRV (Fig. 1). This further confirms the use of fiber weight as an index of swelling. Here too, LiOH swollen fibers have three maxima at around the same concentrations as found in WRV. Whereas two distinctly defined maxima were obtained for NaOH swollen fibers, KOH swollen fibers show a progressive increase in tex with an increase in concentration up to almost 3.35 N, after which a slight fall is observed. At the swelling maximum, the increase in tex for fibers swollen in LiOH (2.9 N) is 65%. The corresponding figures for fibers swollen in NaOH (2.9 N) and KOH (3.5 N) are 30% and 22%, re-

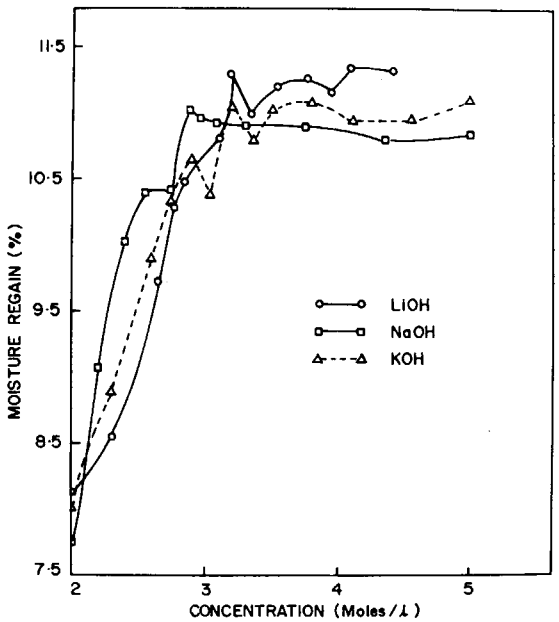

Figure 3 Variation of moisture regain (%) with concentration of the swelling agent.

spectively. However, the gradation of the extent of swelling remains essentially same as that obtained using shrinkage and WRV measurements.

Moisture Regain

The moisture regain data, shown in Figure 3, is mostly in agreement with the swelling measurements obtained earlier for LiOH and NaOH swollen fibers. However, despite the lower extents of swelling, the regain values for KOH swollen fibers are almost at par with those of LiOH and NaOH treated fibers. As moisture is essentially absorbed by the amorphous regions and also by surface of crystallites, it may be inferred that the disorder created by KOH is not commensurate with the lesser swelling suggested by the tex and WRV values. The higher cationic size of KOH leads to a more uniform swelling and disruption of crystallites, leading to higher regain.

Bundle Tenacity and Elongation

Slack Swollen Fibers

Bundle tenacities T_0 and $T_{3.2}$, as a function of the concentration of the reagent, are plotted in Figures 4 and 5, respectively. The bundle elongations at 3.2 mm gauge length are depicted in Figure 6. From Figure 4 it is clear that T_0 decreases on swelling, the decrease being dependent on the swelling agent.

It is interesting to note (Fig. 5) that $T_{3.2}$ also decreases after NaOH and LiOH swelling and the decrease is substantial at the swelling maximum. However, regardless of the concentration, the tenacity of KOH treated fibers is, in general, higher than that of untreated fibers. Swelling normally strengthens weak places in cotton fibers and leads to increased tenacities at higher gauge lengths. However, a reduction in $T_{3.2}$ after LiOH and NaOH

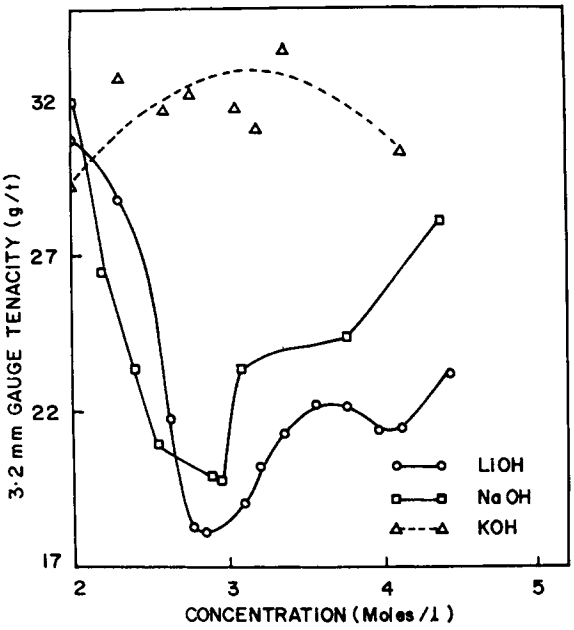

Figure 5 3.2 mm gauge tenacity (g/tex) of the swollen fibers against concentration of the swelling agent.

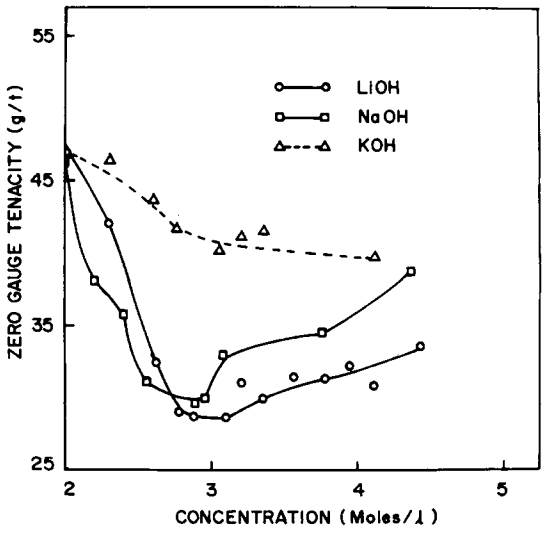

Figure 4 Variation in zero gauge tenacity (g/tex) with concentration of the swelling agent.

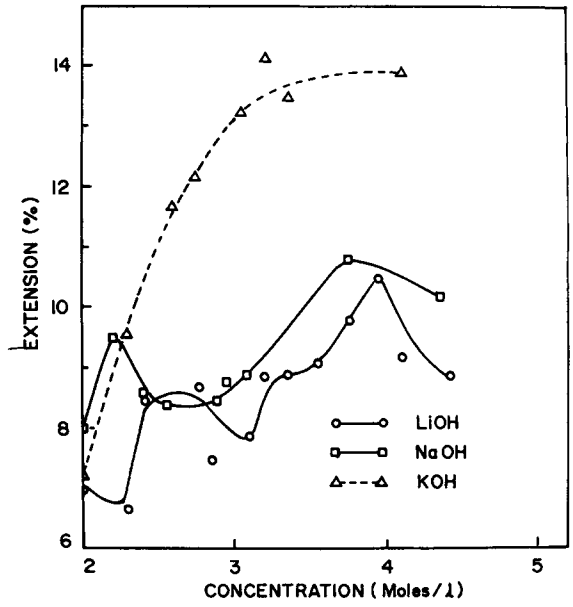

Figure 6 Extension (%) of the swollen fibers as a function of concentration of the swelling agent.

swelling indicates the introduction of structural and morphological nonuniformities, due to excessive swelling. On the other hand, the relatively higher tenacity of KOH swollen fibers also points to the more uniform swelling, specific to KOH, that may be linked to its higher cationic size.

The breaking elongation values plotted in Figure 6 also show that KOH swollen fibers register higher values as compared to fibers swollen in the other two reagents. The concentration vs. elongation curve for KOH swollen fibers smoothly increases with increase in swelling, whereas for the other two fibers, the curve has maxima at positions, which are broadly in agreement with those observed in measurements such as WRV and tex.

The higher elongation for KOH treated fibers might be a result of a uniform swelling of the structural elements despite lower swelling. In the case of NaOH treated fibers at regions near the swelling maxima, because of the excessive swelling, it is likely that some of the interlamellar bonds give way during tensile loading, which resulted in lower breaking load and elongation. In other words, while KOH leads to a lesser but more uniform swelling retaining compactness of the layers, swelling in NaOH is more drastic and nonuniform. This is also evident from the surface morphology, which is discussed in more detail elsewhere in this article.

Swollen and Stretched Fibers

The tensile properties of fibers swollen slack between jaws and also those stretched to original length in the swollen condition are presented in Table II. It is clear that tremendous reduction in both T_0 and $T_{3.2}$ occurs when fibers are swollen slack in LiOH and NaOH at 0°C. Maximum retention in T_0 and a marginal improvement in $T_{3.2}$ are observed after KOH swelling. A greater decrease was observed for fully slack swollen fibers, which was discussed in the previous section. The fibers, though held slack, are between jaws, and hence the decreases in T_0 and $T_{3.2}$ are marginally lower in this case.

Stretched fibers, regardless of their preswelling conditions, show increases in tenacities at all gauge lengths, mainly due to the preferred orientation occasioned by stretch. The tenacities T_0 and $T_{3.2}$ are the highest after KOH swelling. Although the breaking elongation reduces due to stretching, it is the highest after KOH swelling followed by stretch. *Higher tenacities at both gauge lengths coupled with higher extension for fibers swollen and stretched in KOH is of technological importance and points to its potential use as a better pretreating agent prior to finishing.*

Tensile and Modulus Values of Single Fibers

The tenacity and modulus data obtained on single fibers are presented in Table III. The breaking load *per se* improves after swelling in NaOH and KOH, whereas it deteriorates after LiOH swelling. This could mean that the weak places do not get strengthened when swollen in LiOH even at 4.6 N. Note from Table III that at 4.6 N, the breaking load improvement is the highest after KOH swelling, implying a better strengthening of weak places.

The breaking extension considerably improves after swelling, the improvement is much higher after swelling in NaOH and KOH than in LiOH. This improved extension might be due to the additional mobility imparted to the molecular elements due to swelling.

The initial modulus values become reduced after swelling in the alkali metal hydroxides, the reduction being the minimum after KOH swelling. The rela-

Table II Tensile Properties of Swollen and Stretched Fibers

Treatment Conditions				Tenacity (g/t)		Breaking Elongation (%)
Reagent	Concentration (N)	Temp. (°C)		T_0	$T_{3.2}$	
Untreated	—	—	—	55.2	37.5	4.4
LiOH (a)	3.35	0.0	Slack	29.7	23.3	18.6
(b)	3.35	0.0	Str. to OL.[a]	58.9	55.2	5.1
NaOH (a)	2.90	0.0	Slack	34.9	27.8	19.5
(b)	2.90	0.0	Str. to OL.[a]	57.1	51.5	6.1
KOH (a)	3.35	0.0	Slack	43.0	39.5	20.4
(b)	3.35	0.0	Str. to OL.[a]	60.0	56.3	6.9

[a] Swollen slack and stretched to original length

Table III Single Fiber Tensile Data on Swollen Fibers

Treatment Conditions							Modulus Data		Work of Rupture (J/g)
Reagent	Concn (N)	Temp. °C	Breaking Load (g)	Tenacity (g/t)	Extension (%)	Yield Point (g)	Initial (g/t)	Final (g/t)	
Nil	—	—	5.5	42.3	7.9	—	618	648	16.4
LiOH	3.3	0.0	3.6	17.3	15.0	1.55	295	85	12.7
	4.6	0.0	4.6	26.4	16.8	1.71	345	136	13.3
NaOH	3.0	0.0	4.6	23.3	19.0	1.63	313	103	21.7
	4.6	0.0	5.6	33.8	21.3	1.60	338	143	35.3
KOH	2.5	0.0	6.4	39.6	18.1	1.64	412	200	35.1
	4.6	0.0	6.3	39.7	21.5	1.75	396	158	41.9
	10.0	0.0	5.6	31.8	18.6	1.90	370	142	29.0

tively higher initial modulus after KOH swelling would imply that the slippage of molecular segments, which leads to extension, should be minimum for these fibers. In other words, a more compact structure at a molecular level is retained after KOH swelling. The final modulus is also the highest after KOH swelling, as compared to swelling in the other two reagents, and suggests better strengthening of weak places.

Specific work of rupture, which gives the energy required to break a fiber of unit length and unit linear density, is also the highest after KOH swelling. The improved uniformity of the fiber leads to an increase in the rupture load, resulting in higher work of rupture for fibers swollen in KOH, even when the breaking extension is same as in NaOH.

In NaOH and LiOH treated fibers, an increase in the concentration helps in recovering some of the tensile properties, whereas for KOH, an increase in the concentration does not produce any significant difference. This is essentially due to higher swelling in lower concentrations of LiOH and NaOH, as discussed earlier. When the swelling concentration was increased to even 10 N KOH, the breaking load did not deteriorate drastically and was still comparable to fibers treated in 4.6 N NaOH. This means that for a given load, KOH treated fibers extend less due to their compact nature.

X-ray Crystallinity

The percent amorphous content, as a function of concentration of the swelling agent, is shown in Figure 7. It is clear from Figure 7 that, regardless of the concentration, KOH swollen fibers have the highest amorphous content. The amorphous content for fibers swollen in NaOH shows certain maxima at selected concentrations, which almost coincide with other measurements on these fibers. KOH swollen fibers also showed two broad maxima at around 2.9 N and 3.5 N. LiOH swollen fibers had the lowest amorphous contents up to concentrations of about 2.8 N; beyond this their values too approached those corresponding to the other swollen fibers. Maxima appearing at selected concentrations might be due to the presence of different lateral order fractions in untreated cotton fibers, which become swollen at these concentrations. Higher amorphous contents after KOH swelling, despite lower shrink-

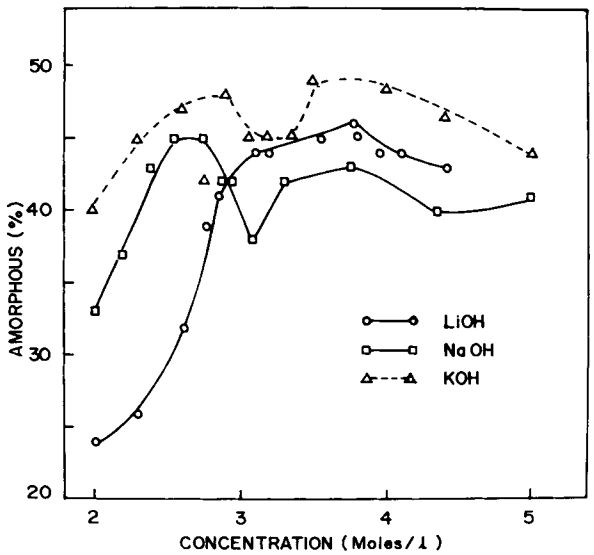

Figure 7 Variation of amorphous (%) with concentration of the swelling agent.

age and WRV values, further substantiate the view that cationic size has a role in the swelling mechanism as noted earlier.[8]

Crystallite Dimensions

Crystallite Breadth

The half breadth of the (200) peak, the inverse of which can be taken as crystallite breadth, has been measured for fibers treated at selected concentrations, and is summarized in Table IV. The half breadth values are the highest after KOH swelling, irrespective of concentration. This implies that the crystallites are reduced in size after KOH swelling. This can contribute to higher flexibility in the crystalline regions of the fibers during application of a tensile load.

Crystallite Length

The crystallite length measured using the refined experimental technique[9] for a few selected swollen fibers is also presented in Table IV. As observed for the (200) peak, the half maximum breadth values for (004) are the highest after KOH swelling. Another important observation is that at a concentration of 3.5 N, LiOH swollen fibers register half maximum breadth of (200) peak that is equal to those of KOH swollen fibers. However, the half maximum breadth of the (004) peak in the former does not increase to the same extent as in the latter. In other words, the crystallite length preferentially reduces to a greater extent in KOH treated fibers. This occurs due to more uniform swelling imparted by KOH, which includes higher ordered regions also. This in turn would lead to better flexibility to crystallites, which are embedded in a more disordered matrix.

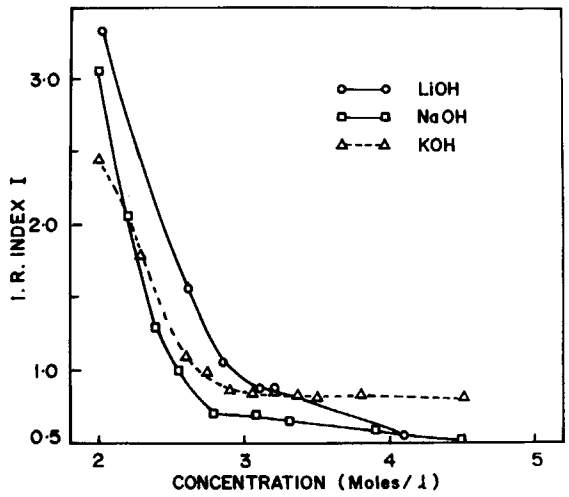

Figure 8 Infrared Crystallinity Index (I) vs. concentration of the swelling agent.

Infrared Crystallinity

Evidence for the disruption of the molecular order at lower concentrations of KOH was obtained from the infrared spectrum. All three crystallinity indices yielded the lowest value for KOH at 2.0 N. On the contrary, as concentration increased, KOH preserved a higher order at the molecular level. This is clear from Figure 8 where the crystallinity index I,[16] calculated for a few swollen fibers, are plotted against their respective concentrations. As discussed earlier,[9] this index is sensitive to decrystallization, conversion to cellulose II, and changes in intramolecular *H*-bonding, all of which take place during swelling.

A point worth noting from Figure 8 is that at concentrations above 3.0 N, the molecular order is

Table IV Half Maximum Breadth of Crystalline Peaks for Swollen Fibers

		Half Maximum Breadth of Peaks (in degrees)[a]					
		LiOH		NaOH		KOH	
Concn (N)	Temp (°C)	(200)	(004)	(200)	(004)	(200)	(004)
2.5	0.0	1.40	—	1.60	—	2.00	0.40
3.0	0.0	1.55	—	2.20	0.37	2.40	—
3.5	0.0	2.45	0.37	2.10	—	2.45	0.42
4.0	0.0	2.20	—	2.00	—	2.65	—
4.5	0.0	2.20	0.34	2.05	0.36	2.40	0.41

[a] Inversely related to the dimension.

Table V Half Maximum Breadth of OH Band for Fibers Swollen at 0°C

Concentration (N)	δ Width at Half Maximum ($d\nu$) in cm^{-1}		
	LiOH	NaOH	KOH
2.0	390	400	415
2.5	460	480	465
3.0	490	490	470
3.5	495	490	480
4.5	490	490	470

higher after swelling in KOH than in NaOH and LiOH, despite higher amorphous contents found by x-ray methods. The δ width at half maximum ($d\nu$) of the OH peak, which may be related to the molecular order in the swollen fibers, for fibers swollen at selected concentrations, is given in Table V. The higher the width, the poorer the organization at the molecular level. Note that at 2.0 N, the width is higher in KOH. This shows that KOH, due to its higher cationic size, is able to penetrate the ordered regions and impart more uniform swelling even at this concentration. The $d\nu$ value is the lowest for fibers swollen in 4.5 N KOH, as compared to those swollen in identical concentrations of NaOH and LiOH. Preservation of a better molecular order in KOH swollen fibers, particularly at higher concentrations, may be partly responsible for the better tensile properties of these fibers as noted earlier.

Crystallite Orientation

The Hermans' orientation factor (f_x) values are graphically presented in Figure 9 against concentration. Fibers swollen in both LiOH and NaOH deteriorate considerably in orientation at the swelling maxima and thereafter they recover to some extent due to lesser swelling. In the case of KOH swollen fibers, the deterioration in crystallite orientation is minimal at all concentrations. Further, the actual orientation is far higher as compared to those in NaOH and LiOH swollen fibers.

While studying the changes in x-ray orientation of cotton fibers, brought about by swelling in NaOH, Warwicker[10] suggested that at a concentration of 3 N at 0°C, where maximum bulging of fibers takes place, the outer protective layer is broken, leading to excessive swelling of the now free secondary cell-wall. This leads to disorientation. At any other concentration below 3 N, the restrictive primary wall exerts an orienting influence on the swollen gel leading to increased orientation. The present results are in line with those obtained by Warwicker[10] at regions of excessive swelling. However, we failed to observe higher orientations than those of untreated fibers at concentrations below 3 N. This disparity could be due to the difference in estimates of orientation used in their study, viz. $(1/\phi_{1/2})$, which generally gives a good account of orientation in normal fibers. However, in excessively swollen and disoriented fibers, f_x seems to be a more realistic measure, as this would take into account other disoriented fractions that are likely to be present in swollen fibers. Warwicker himself has suggested that different disoriented fractions do exist in excessively swollen fibers.

The higher retention of orientation in fibers swollen in KOH would go a long way towards explaining the increased tenacity of these fibers at all gauge lengths.

Surface Morphology

Micrographs showing typical changes in surface morphology of the swollen fibers are reproduced in Figure 10. While swelling in alkalies at 0°C, particularly in LiOH and NaOH, produces nonhomogenities in surface appearance, those swollen in KOH have smooth and uniform surfaces. In an earlier study[9] on fibers swollen in 4.5 N at 0°C, nonhomogeneities were observed in LiOH and NaOH swollen fibers. The appearance of increased ridges and

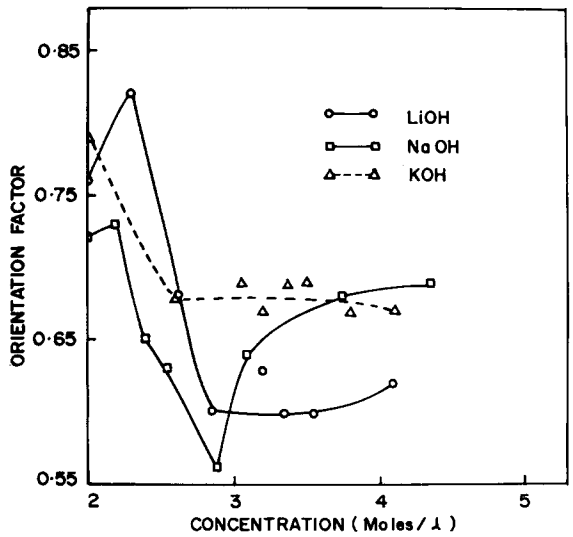

Figure 9 Hermans' orientation factor (f_x) vs. concentration of the swelling agent.

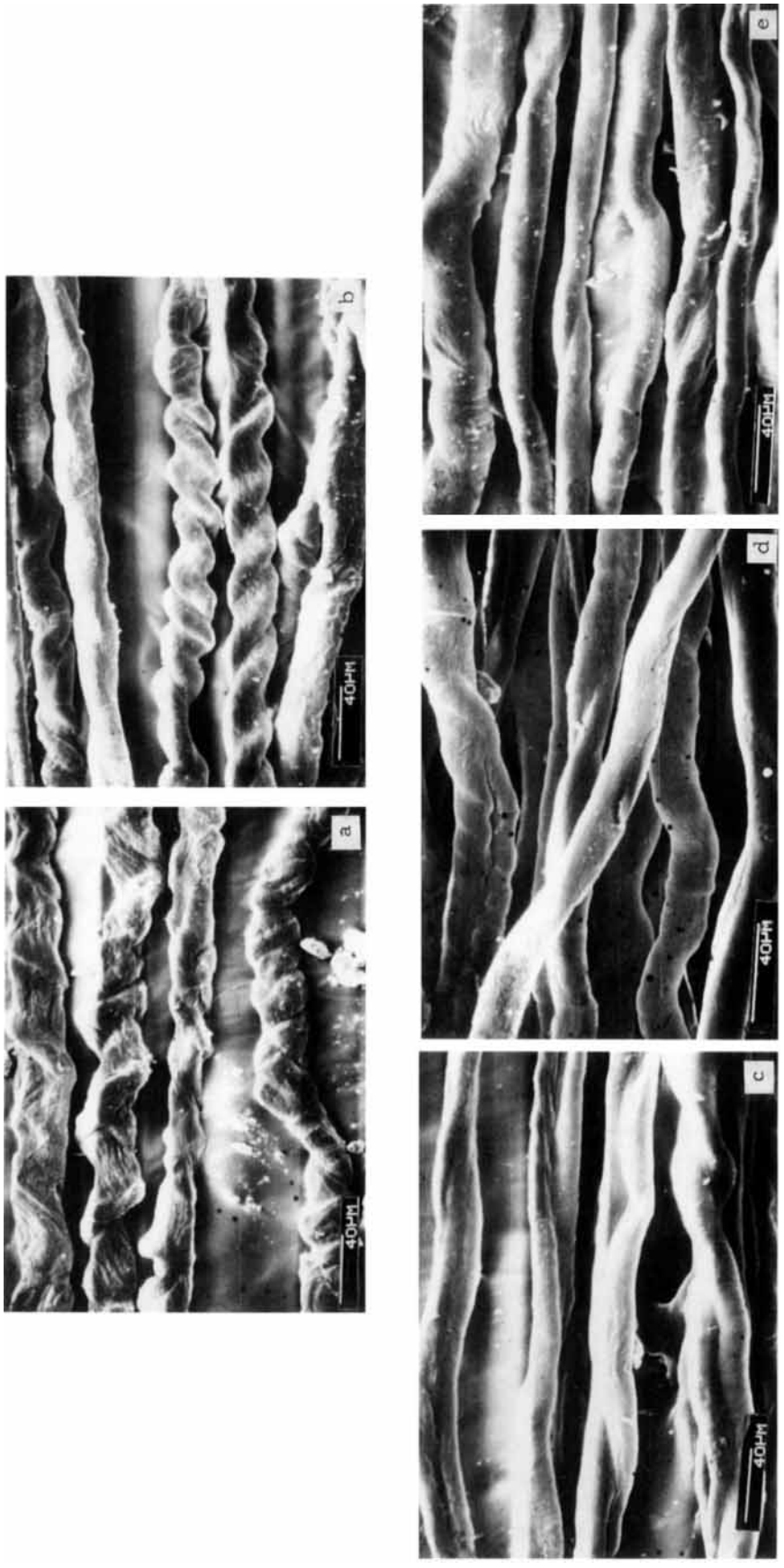

Figure 10 SEM Micrographs for fibers swollen in 0°C of (a) 3.5 N LiOH, (b) 3.0 N NaOH, (c) 2.5 N KOH, (d) 4.6 N KOH, (e) 10.0 N KOH.

Table VI Structure–Property Correlations in Fibers Swollen at 0°C

Parameters	Correlation Coefficients		
	LiOH	NaOH	KOH
$T_{3.2}$, Am	−0.84	−0.80	0.67
$T_{3.2}$, f_x	0.88	0.85	−0.52
$T_{3.2}$, $\beta_{1/2}$ (200)	−0.48	−0.45	0.60
$T_{3.2}$, f_x Am	0.95	0.93	0.76
$T_{3.2}$, f_x Am $\beta_{1/2}$ (200)	0.96	0.93	0.78
E, Am	0.84	0.22	0.67
E, f_x	−0.80	0.32	−0.95
E, f_x Am	0.84	0.60	0.95

nonhomogenities on fiber surface in fibers swollen at low concentrations of LiOH and NaOH at this temperature is in conformity with the excessive swelling. This excessive swelling has introduced additional twists and other nonuniformities, which would act as weak places during tensile loading. On the other hand, fibers swollen in KOH of high concentrations up to 10 N do not possess any nonuniformities and the fiber surface appears smooth and uniform.

Structure–Property Correlations

The structure–property correlations for fibers swollen in the three reagents at selected concentrations are summarized in Table VI.

From the correlation data (Table VI), it is clear that, for LiOH and NaOH swollen fibers, the tenacity depends to a large extent on the increased amorphous content and decreased orientation. The combined effect of decrystallization and disorientation explains (R = 0.95 in LiOH and R = 0.93 in NaOH treated fibers) the tenacity drop during treatment. The crystallite dimensional change does not seem to have a significant influence on tenacity. Including $\beta_{1/2}$ (200), R improves only marginally to 0.96 in LiOH treated fibers and remains 0.93 in fibers treated with NaOH.

The tenacity of KOH treated fibers, on the other hand, depends almost equally on all three parameters, viz. Am, f_x, and $\beta_{1/2}$ (200). This shows that the reduced crystallite breadth has a positive role to play in realizing higher tenacities during mechanical loading. However, it is to be noted that even when all three parameters are taken together, R comes to only 0.76. This means that parameters other than those considered here can influence the tenacity. As already shown, the reduced crystallite length especially found for KOH swollen fibers might influence the tensile behavior of these fibers. As the measurement of crystallite length is carried out only for selected samples, the influence of this parameter on the structure–property correlations could not be quantified. However, from the limited measurements on crystallite length, it would appear that, at least in the case of KOH treated fibers, the flexibility introduced in the crystalline elements, due to reduced crystallite length, contributes to the higher retention of tenacity by these fibers. This observation is in line with the finding by Zeronion et al.[4] who noted that the LODP values (directly related to crystallite length) were the lowest after KOH swelling and helped in retaining the higher breaking load.

The changes in elongation obtained for the various swollen fibers could be explained as being due to the combined effect of increased amorphous fraction and greater disorientation, resulting in the loosening of the fine structure of the fibers. Barring NaOH swollen fibers, the combined correlations R = 0.84 for LiOH treated fibers and R = 0.95 for KOH treated fibers seems to agree with the above explanation. The high amorphous contents, coupled with a small disorientation, helps to realize higher elongations in KOH treated fibers. On the other hand, the excessive swelling at some concentrations could result in the breakdown of some of the interlamellar linkages, particularly in NaOH treated fibers. This takes precedence over the fine structural parameters already discussed and leads to tensile failure before attaining elongation commensurable with shrinkage. As a result, considerably lower elongation is recorded.

Another aspect to be considered in explaining the tensile behavior is the contribution from packing changes in the fibrillar elements due to swelling. As noted in our earlier publication,[9] lower circularity values for cotton fibers belonging to *G. barbadense,* such as the one used in this study, due to their peculiar bean-shaped cross section, leaves them with a high packing density in the untreated state. With moderate swelling achieved by KOH treatment, increased circularity might decrease the packing. But this might be compensated for by the strengthening of weak links, among other things, with the result that the tenacity might still be retained or improved beyond the untreated level. However, with excessive swelling imparted by LiOH and NaOH treatment, particularly at lower concentrations at 0°C, the packing density considerably decreases because of the bulging of the secondary cell-wall. This reduced packing density, resulting from a higher layer separation, leads to poorer interlayer bonding and, upon

strain, might easily give way, realizing poorer tenacity and extension values.

Thus, the superior tensile behavior after KOH swelling is a result of a combination of various factors, such as conducive fine structural features and closer packing of structural elements within the secondary cell wall of the resultant swollen fibers.

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