Alkaline Treatment of Cotton in Different Reagent Mixtures with Reduced Water Content. I. Influence of Alkali Type and Additives

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ABSTRACT: The purpose of this study was to examine the influence of some swelling agents with reduced water content on final properties of cotton fabrics. A single-step swelling of cotton in the reagent was used. There were selected properties generally used to characterize mercerized cotton that are technologically important, such as water retention, shrinkage, stiffness, crease recovery angle, and hand. Water retention method and dyeing with CI Direct Red 81 have been used to compare the degree of swelling for different samples. Correlations have been established between structural changes induced by the swelling agents and final properties of cotton fabric. The mixtures of an alkali solution and an additive produced similar or better end-use properties as compared with classical sodium hydroxide or ammonia treatments, combining the action of a diluted alkali solution (3.13 mol/L NaOH or KOH) and a nonalkali reagent. © 2005 Wiley Periodicals, Inc. J Appl Polym Sci 99: 2848–2855, 2006

Key words: additives; alkali solutions; cotton; stiffness; structure-property relations; swelling

INTRODUCTION

One of the most important treatments performed on cellulosic fabrics to improve properties, such as dimensional stability, tensile strength, luster, and hand, is mercerization. Mercerized cotton is more easily acted upon by chemicals than native cellulose. The process of mercerization is accompanied by important changes in the microscopic appearance of the fiber. Mercerization of yarn or fabric is normally accomplished either in the slack state to obtain, for example, stretch properties, or under tension to improve properties such as strength and luster.

Theoretical and practical importance of cellulose mercerization phenomenon based on intercrystallite and intracrystalline swelling in alkali hydroxide solutions is well known. The study of the interaction between cellulose and alkali hydroxides gave useful information in understanding the cellulose structure and reactivity, resulting in large-scale technical processes.[1] The most commonly used mercerization agents were sodium hydroxide (NaOH) solutions of different concentration, but recently, a lot of attention has been paid to the use of other swelling reagents or mixtures.[2,3]

The swelling of cellulose in alkali solutions causes changes in the crystallinity, accessibility, unit cell structure, and orientation of fibrils in cellulosic fibers. The extent to which mercerization solutions change these properties depend on factors such as the concentration of the solution, the additives mixed with alkalis, the temperature, the degree of polymerization, the source of cellulose, the physical state of the cellulose (i.e. fiber, yarn, or fabric), and the degree of tension employed to restrict fiber shrinkage and swelling.[3] These variables have been effectively controlled for the mercerization of cotton to improve or optimize one or more of the following properties: dimensional stability, affinity for dyes, tensile strength, higher add-on of finishing agents, luster, and fabric smoothness.

Fabric mercerization yields different results as compared to fiber or yarn mercerization. Usually a high degree of nonuniformity is obtained due to the maximum swelling effect at the surface and the limited penetration of the mercerization agent into the interior of yarns and fabric. This behavior will especially the affect mechanical performance of the material.[4]

The interaction between cellulose and aqueous alkali hydroxides resulting in swelling and specific uptake of alkali and water must be considered as a very

complex process comprising destruction of hydrogen bonds within the cellulose moiety as well as the aqueous lye phase, as a decrease in supramolecular order of the polymer, changes in the structure of hydratation shells as well as in the chain conformation of cellulose, and finally as a partial anionization of cellulosic hydroxy groups. Because of the presence of Na^+ ions, which apparently bond with the cellulose hydroxyl groups, almost all of the interchain hydrogen bonds that ordinarily stabilize the cellulose I structure have been broken. New types of interchain bonds were formed by the help of Na^+ ions and water molecules present in system.[5] Usually, the hydroxy anions seem to be responsible for the primary interaction with the cellulosic hydroxy groups in the ordered regions of the structure, while the hydrated cation seems to be responsible for the resulting swelling.[1]

In 1925, Heuser and Bartunek opened up a new and very promising route to understanding cellulose-alkali hydroxide interaction by the so-called "hydrate shell explosion" theory. This concept was focused for the first time on the important role of NaOH hydratation and of the so-called free water on swelling, alkali uptake, and lattice transition of cellulose interacting with aqueous NaOH. Other theories were centered on breaking of defined inter- and intramolecular hydrogen bonds within the solid state structure of cellulose by hydrated NaOH ion dipoles, resulting in conformational changes of the macromolecules, with a preference for twisted conformations at higher lye concentration.

The cellulose II recovered from alkali cellulose by washing and/or neutralization differs from the original cellulose I sample not only with regard to lattice dimensions but also with regard to degree of order, fibrillar morphology, and pore and void structure, as well as with regard to water vapor sorption and liquid water retention.[1]

If Figure 1 (which gives the correlation between the strength of an alkali solution and water content) is analyzed, some specific solutions may be "placed" in different areas of this illustration.

For example, a concentrated NaOH solution is placed on the upper right side. Such solution will contain hydratation water and "free water." Ammonia is a weak base and contains no water ($C_{OH^-} = 0$), as well as glycerin. If NaOH solution is diluted, water content increases and the point moves downwards on line 1 (star points). Trying to approach conditions of ammonia treatment some possibilities to move from line 1 to 2 were looked for. Idea was to replace parts of free water with some other reagent. In a mixture of diluted NaOH and glycerin, some free water was replaced by glycerin. Increasing glycerin content, NaOH concentration was kept constant but free water content decreased, and in this way, the point moved from line 1 to 2. The same result could be obtained using
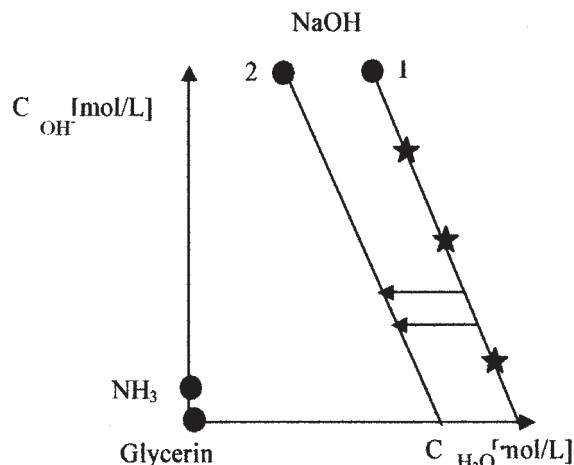

Figure 1 Hypothetical diagram showing correlation between water content and the concentration of an alkali solution.

other reagents such as NaCl, sodium silicate, or sodium gluconate. The problem was to verify how much final properties of textiles are influenced by the use of these alkali mixtures.

If some water in the alkali solution is replaced with ethanol[6] or another alcohol, the beginning of cellulose I to cellulose II transformation shifts to lower alkali concentrations. The alkalization effect obtained with NaOH dissolved in a mixture of water and alcohol resembles that observed with an aqueous lye of much higher concentration, obviously because of the formation of a cellulose/NaOH/water phase with a high alkali concentration at the expense of alkali and water content of the surrounding alcoholic phase. Furthermore, some competition between alcohol molecules and NaOH ion dipoles for H_2O molecules can be assumed, resulting in the decrease of the NaOH hydratation shell and in consequence in the mode of cellulose/NaOH interaction observed with aqueous lye of much higher concentration.[1]

Swelling of a number of cotton samples in NaOH and KOH solutions of different concentrations and in mixtures of these solutions and different additives were studied. The additives were chosen by taking into consideration their chemical structure and their possibilities to influence the amount of water in alkali mixtures. Their concentration was established after some preliminary studies, and it is still a subject for further examination in the future work.

Among the additives used, special attention was paid to glycerin, which exerts a softening action on cellulose fibers by interacting with the hydrogen bond system, and could have a positive effect on further processing of the textile material. Properties of textiles were analyzed and compared with those of ammonia-treated samples (considered as reference samples).

The objective of this work was to compare "mercerizing" effect of alkali solutions (NaOH and KOH) and

TABLE I
Formulations Used for Alkaline Treatment

Sample no.	NaOH (mol/L)	KOH (mol/L)	Sodium silicate (mol/L)	NaCl (mol/L)	Glycerin (mol/L)	Na-gluconate (mol/L)	Water (mol/L)	Label for samples
1	3.13						54.94	A
2	3.75						54.38	
3	5.00						53.83	
4	6.25						53.27	
5	7.50						51.61	
6		3.13					52.44	A
7		3.75					52.16	
8		5.00					50.22	
9		6.25					49.11	
10		7.50					46.61	
11	3.13			1.71			52.16	B
12		3.13		1.71			49.94	
13	3.13				2.17		46.34	C
14		3.13			2.17		44.12	
15	3.13		0.31				51.33	D
16		3.13	0.31				47.84	
17	3.13					0.46	51.33	E
18		3.13				0.46	49.11	
19	7.50			3.42			46.89	F
20		7.50		3.42			47.45	
Blank	Raw material							
A1	Ammonia treated – reference sample							R

different alkali mixtures with reduced water content, to study the effect of these mixtures on final properties of cotton fabrics, and to see to what level the properties of these samples can approach or even overcome those of ammonia-treated textiles.

EXPERIMENTAL

Materials

The fabric used in this study (both for alkali and ammonia treatment) was a 100% cotton plain woven fabric, with 54 ends and 30 picks per cm, and a weight of 112 g/m^2 (F. M. Haemmerle Textilwerke GmbH, Dornbirn, Austria). It was a blue, yarn-dyed, desized, and unbleached material. Chemicals used were as follows: sodium hydroxide (NaOH), solution 50% (K. Deuring, Hoerbranz, Austria), potassium hydroxide (KOH), pellets, (Riedel-de Haen, Seelze, Germany), sodium silicate, (K. Deuring), sodium chloride (NaCl) technical grade (SALIN, Salinen, Austria), glycerin, (Merck, Darmstadt, Germany), and sodium gluconate (Merck).

Methods

Fabric samples(dimensions 30 × 100 cm^2) were padded using solutions described in Table I. The samples were padded through liquor in a one-dip-one-nip operation in an HVF-type horizontal padder, from Mathis AG, at a roller speed of 1.0 m/min and nip pressure of 1.0 bar. All samples were weighed after pad-

ding to determine wet pickup, and the values of which ranged from 50 to 66%.

After padding, all the samples were rolled on glass rods, closed in plastic sheets, and stored for 4 h at room temperature. After this period, the samples were opened, washed with soft water, neutralized in a 1 mL/L acetic acid solution, and dried at 40°C. For the samples used in this part of our study, no type of finishing was used.

Ammonia-treated samples nonresin finished, kindly supplied by F.M. Haemmerle, were analyzed for comparison (reference samples). The influence of alkali reagents on final properties of textiles were studied.

Prior to testing, all samples were conditioned for over 24 h in a standard atmosphere at (20 ± 2)°C and (65 ± 4)% relative humidity, and all the evaluation were performed in the same atmospheric conditions.

Analyses performed in this study were as follows:

1. Shrinkage in process –measuring reduction in length on warp and fill direction and calculation reduction of a definite area. Results were expressed as percentage of the same area in blank samples (raw material).
2. Stiffness –the length needed for the material to produce a 45° angle on warp and fill direction. Results were also expressed as percentage of the corresponding value of the blank sample.
3. The water retention value (WRV) of cellulosic fabrics was determined as difference between weight of the sample dried at 105°C for 2 h and
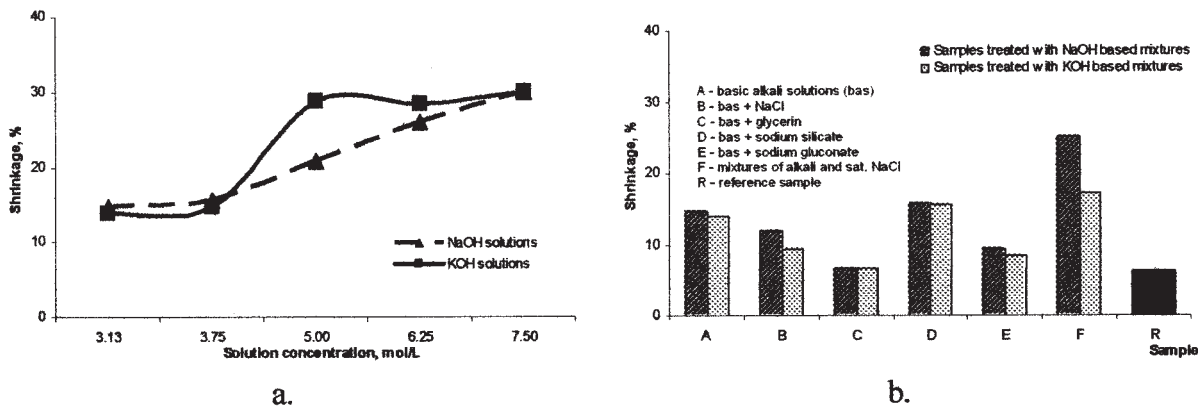
Figure 2 Shrinkage in process: (a) influence of the concentration of alkaline solutions and (b) influence of additive type.

the weight of the same sample after 10 min centrifugation at 4000 × g (Heraeus Labofuge M) multiplied with 100.[7]

4. Determination of crease resistance of textile fabrics by measuring the angle of recovery, method of horizontal fold, and erected free limb on the dry sample (DIN 53890) –five 5 × 2 specimens (each along warp and fill) per sample.

5. Dyeing with CI Direct Red 81 –method used to compare different degrees of mercerization. Fabric (1.2–1.4 g) (only mercerized) was dyed at a material to liquor ratio of 1 : 30 with a solution containing 2.0 g/L CI Direct Red 81 (purchased from Aldrich) and 0.5 g/L technical grade NaCl. The samples were placed in individual dye-pots and dyed simultaneously in one batch in a Mathis Labomat dyeing machine. Dyeing began at ambient temperature and the temperature was raised to 100°C at a rate of 5°C/min, held at 100°C for 30 min, and then cooled to 50°C at a rate of 3.5°C/min. The dyed samples were rinsed in cold soft water until the wash liquor was colorless, and line dried overnight. Reflectance values of the dyed samples were measured at the wavelength of maximum absorbance (525 nm) on a Pye-Unicam spectrophotometer equipped with an integrating sphere. The depth of the shade was estimated from the Kubelka-Munk function, using (K/S) values, which were corrected for reflectance from undyed (initial blue) substrate, using eqs. (1) and (2).

$$\left(\frac{K}{S}\right) = \frac{(1 - R)^2}{2R} \quad (1)$$

$$\left(\frac{K}{S}\right)_{corr} = \left(\frac{K}{S}\right)_D - \left(\frac{K}{S}\right)_U \quad (2)$$

where R is fraction of light reflected at a wavelength of maximum absorbance; $(K/S)_D$ is (K/S) values of the dyed substrate; $(K/S)_U$ is (K/S) values of the undyed substrate; and $(K/S)_{corr}$ is (K/S) values corrected for reflectance from undyed substrate.

RESULTS AND DISCUSSION

Shrinkage in process

Fabric shrinkage is a consequence of increased fiber diameter and decreased fiber length and was characterized by dimensional change on warp and fill direction and by dimensional change of a specific area. The conditions in which shrinkage could be reduced as compared with the blank sample (raw material) were analyzed. Therefore, if specific area shrinkage (as percent of the same area in blank sample) was calculated, the data plotted in the graphs represented (100 − this percentage). Thus, a clear image of how much the shrinkage of a sample differs from blank was obtained (Fig. 2).

As it was expected, an increase in alkali solution concentration determined the increase in shrinkage. Some authors also associate shrinkage and the extent of conversion of cellulose I to cellulose II,[8] thereby indicating the effectiveness of the mercerization. The influence of the cation in alkali solutions is noticeable [Fig. 2(a)]. KOH penetrates into the ordered regions of cellulose at somewhat lower molar concentrations than NaOH, and KOH uptake is higher than that of NaOH up to a lye concentration of about 5 mol/L, while above that concentration NaOH uptake exceeds that of KOH. Probably the different behavior of KOH is caused by its somewhat higher basic strength and its lower tendency to ion dipole formation, resulting in a stronger partial anionization of cellulosic hydroxy groups, in agreement with the stronger ionic character of potassium alcoholate as compared with sodium alcoholate.[1]

Regarding the influence of additives on fabric shrinkage [Fig. 2(b)], it is obvious that almost all mixtures determine an increase in shrinkage as compared with the reference ammonia-treated samples. The only
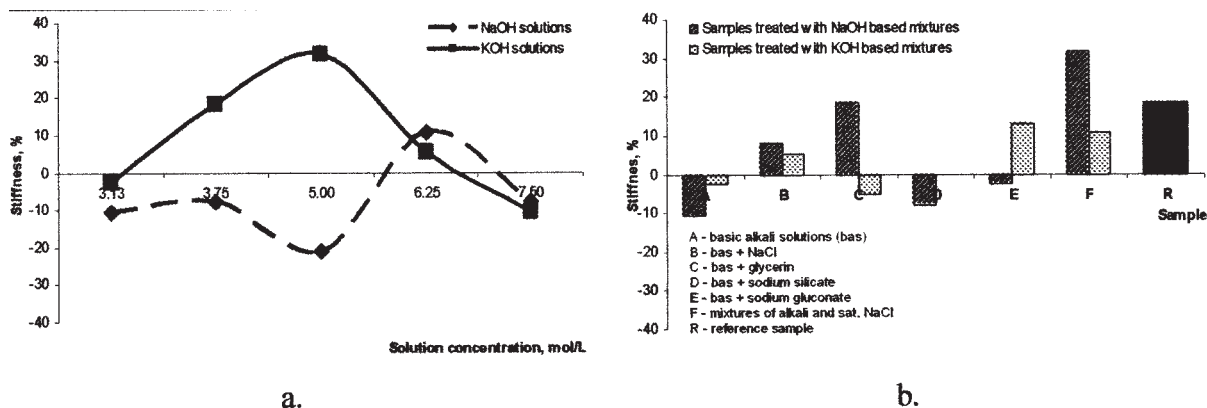
Figure 3 Stiffness: (a) influence of the concentration of alkali solutions and (b) influence of additive type.

exception is represented by samples treated with a mixture of NaOH (or KOH) and glycerin, exhibiting a lower shrinkage, very close to that of reference sample. It is interesting to notice that with almost all mixtures, shrinkage values were reduced to some extent as compared with samples treated only with alkali solutions (labeled A on graphs).

Stiffness

The intramolecular hydrogen bonds are responsible for the considerable stiffness of the cellulose chain and stabilize the twofold helix conformation of crystalline cellulose. Therefore, because the interaction between cellulose and aqueous alkali hydroxides or different mixtures based on them involves destruction of hydrogen bonds within the cellulose moiety as well as the aqueous lye phase, some reduction of stiffness was expected. Stiffness was determined by comparison with blank samples and it was expressed first as percentage of blank sample stiffness. For a better relevance of graphs, stiffness for each sample was calculated as (sample stiffness − 100). So, negative values represent a reduced stiffness compared with blank sample and positive values an increased stiffness.

Our objective was to obtain a soft material, and so we were interested in treatments able to decrease stiffness or, at least, to maintain it to values close to blank sample. A point of interest was not to increase stiffness more then the characteristic value for ammonia-treated sample (reference sample).

After alkali treatments stiffness increased, especially when KOH solutions were used [Fig. 3(a)]. NaOH treatments diminished stiffness in samples for concentrations up to 6 mol/L. Once more, the influence of cation and its hydratation shell in the interaction between alkali hydroxides and cellulose were noticed. In dependence on lye concentration, a rather large number of defined hydratation states have been postulated for sodium hydroxide, while a much smaller one is assumed for KOH. At a lye concentration of 5 mol/L, lattice conversion was found to be completed with both NaOH and KOH, while differences between these alkali hydroxides were observed at lower concentrations.[1]

Almost all mixtures of alkali (NaOH or KOH) and different additives [Fig. 3(b)] produced samples with a reduced stiffness as compared with reference sample (ammonia-treated fabric). Stiffer samples were only obtained with mixtures of NaOH and saturated NaCl solution. However, it has to be noticed that the stiffness of ammonia-treated sample is higher than for samples mercerized with NaOH solutions.

Water retention

When cellulosic fibers are treated in alkali solutions, the crystalline structure of cellulose is modified and the percentage of amorphous or less ordered regions increases. Therefore, as the capacity of cellulose fibers for water absorption depends largely on the availability of free hydroxyl groups, it is generally considered that water absorption occurs almost entirely in the amorphous regions of cellulose. Therefore, these amorphous or noncrystaline regions are also called the accessible regions of cellulose.[9] It has been shown that crystalline areas of cellulose absorb only small amounts of water. The extent of less ordered regions in a fiber or fabric may be estimated by evaluating water absorption. Cellulose fibers with greater amorphous content absorb a greater quantity of water.[9,10] The increase in WRV generally observed after interaction of cellulose with aqueous alkali and subsequent neutralization depends largely on steeping lye concentration and type of alkali employed, as well as on the physical structure of the original sample and the procedures of alkalinization, neutralization, and drying.

Considering that alkali treatments change internal order of cellulose in fabrics, WRVs were determinated to estimate the degree of modification produced. The
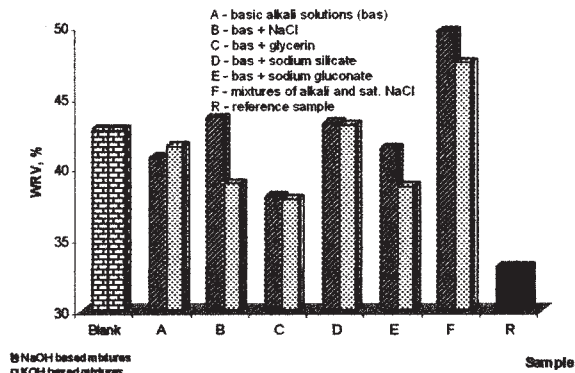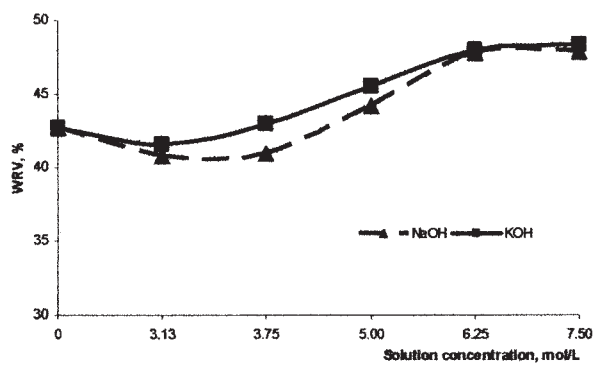
Figure 4 Variation of WRV: (a) with alkali solutions and concentration and (b) with the type of additive.

results for alkali treatments are plotted in Figure 4(a). The higher values proved the efficiency of alkali treatments, and WRV increases for higher solution concentration. No essential differences have been noted for the two alkalis used.

For samples treated with alkali and different additives, the WRVs were compared with those for reference sample [Fig. 4(b)]. A higher affinity for water was remarked. Samples treated with mixtures of alkalis and saturated NaCl showed the highest values for water retention.

Crease recovery angle

Studies proved that the poor crease recovery of cotton-woven fabrics is to a large extent attributable to the poor elastic recovery of cotton fibers. This, in turn, is caused by the rheological flow in the fiber under strain.

Nevertheless, it was also revealed by some studies[11] that moisture generally tends to increase rheological flow, thus decreasing crease recovery. Therefore, an improvement of crease recovery was expected because of the use of mixtures with reduced water content.

For all the samples, the differences between warp and fill direction are generally small. The figures taken into account are the sums of the warp and fill data obtained. Crease recovery angle (CRA) values were measured both for 5 and 30 min, and an increase of about 15° was noticed for CRA at 30 min. Thereby, this discussion refers only to CRA after 5 min, but all conclusions are valid for CRA for 30 min too.

As one may see from Figure 5(a), mercerizing led to a higher CRA, both for NaOH and KOH solutions. CRA increased with increasing solutions concentrations. The differences induced by the nature of cation were higher for lower concentrations. Samples treated with KOH solutions exhibited higher CRA values. As observed with other properties considered in this study, the influence of the cation diminishes at higher concentrations.

As it was expected, the use of mixtures with reduced water content produced an increase of CRA. This effect is more visible because the samples are not crosslinked, and any change in crease recovery properties may be attributed only to the influence of the additive [Fig. 5(b)]. Ammonia-treated fabrics (reference samples) exhibited the lowest values for CRA; all
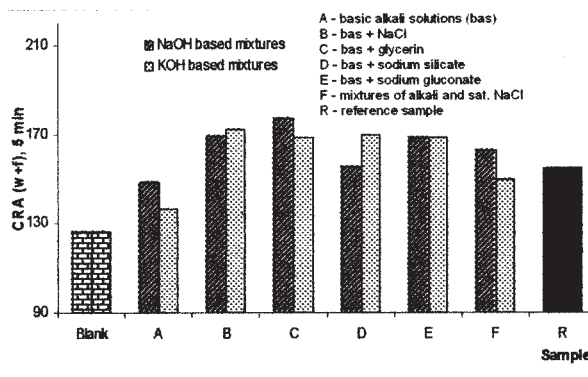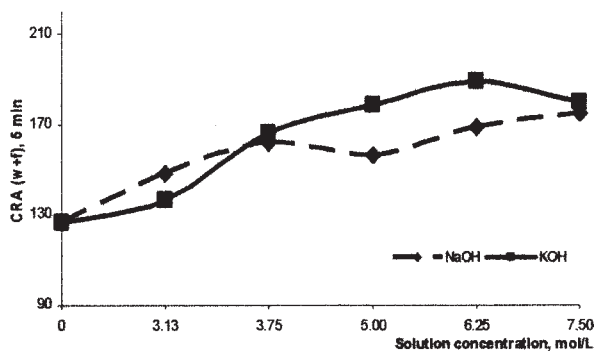

Figure 5 CRA: (a) influence of the concentration of alkali solutions and (b) influence of additive type.
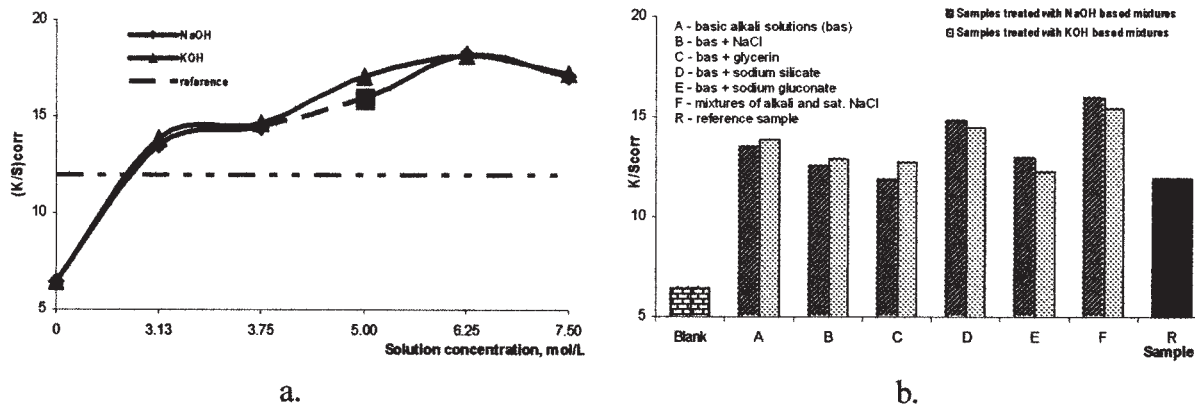
Figure 6 Variation of *K/S* with (a) concentration of alkali solutions and (b) type of additive.

the mixtures used, however, improved this property. Lower the water content, higher the CRA values were. Furthermore, the mixtures with glycerin exhibited useful qualities for processing.

Dyeing with CI Direct Red 81

During mercerization, the microfibrilar nature of native cellulose is strongly affected and in some cases, even partially lost: this denotes a profound modification of the supramolecular arrangement of cellulose during the process. Most aqueous reagents penetrate only the amorphous areas of cellulose fibers. Therefore, the degree of penetration of different reagents into cellulosic fibers allows us to estimate the degree in which the internal structure of cellulose was modified.

The qualitative connection between the depth of shade of dyed fabrics and the degree of reorganizing of cellulose structure during alkali treatments[12] led to the idea of using this method to evaluate and compare the degree in which the structure of cellulosic fibers was changed due to the treatment applied. The principle of the test is based on the observation that higher the degree of reorganizing fiber structure, higher the *K/S* value was, and so *K/S* values are an indication of an easier penetration of dyestuff into fiber. Taking into consideration the results obtained for the samples treated with different concentrations of alkali solutions (NaOH and KOH) [Fig. 6(a)] first, an increase in *K/S* value was noticed (up to about 7 mol/L both for NaOH and KOH solutions), followed by a decrease for more concentrated solutions. From this representation, it is clear that *K/S* value is influenced by solution type and concentration, and this method could be used for a qualitative estimation of the influence that different alkali solutions have on internal order in cellulosic fibers.

It was reported that swelling power of the alkali metal hydroxides depends on the cationic size, in addition to concentration and temperature.[12,13] The extent of amorphous regions were proved always higher for materials swollen in KOH, which also produces more uniform swelling than NaOH.[14] Therefore, the difference between the two curves in Figure 6(a) could be an illustration of this effect.

If observations are extended to the samples treated with mixtures of alkalis and different additives [Fig. 6(b)], it is obvious that, generally, the additive decreases the affinity of fibers for dyestuff as compared with samples mercerized only with alkali solutions. The only exception is sodium silicate both for NaOH- and KOH-based mixtures. Because the samples were treated in the same conditions, differences in color depth may be attributed to differences in the way of action of different mixtures on internal order of cellulosic fibers. Nevertheless, all mixtures improved the penetration of dyestuff into fiber as compared with reference samples.

CONCLUSIONS

It can be summarized that replacing parts of water in alkali solutions with different additives produced a favorable effect on some practical important properties of textiles. According to all the properties investigated, crease recovery, shrinkage, stiffness, and WRV, the alkali mixture treated samples exhibit qualities at least similar as compared with ammonia-treated samples. Water retention method and dyeing with CI Direct Red 81 proved the effectiveness of "mercerizing" effect of these alkali mixtures. The most promising results were obtained when mixtures of NaOH and NaCl or glycerin were used, which are also expected to have favorable effects on further processing of textiles. Furthermore, the effect of different finishings and finishing procedures would be studied in the future.

The results presented may indicate a possible alternative to ammonia treatment without affecting final

quality and end-use properties of fabrics, but this aspect should be further analyzed.

In addition, the use of these mixtures for alkali treatment gave us supplementary degrees of freedom for the development of new materials with special properties.

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