Sodium Cellulose Formation
by Activation Process

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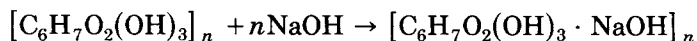*Technical University of Lodz, 90-924 Lodz, Poland*

Synopsis

The formation of sodium cellulose is the first reaction step in some large scale derivatization process of cellulose, e.g., xantation or carboxymethylation, as well as in the mercerization of cotton. It was found that the sodium cellulose formation depends on some activators present in the steeping lye, as well as on the press ratio, steeping temperature, and steeping ley concentration. IR data and X-ray scattering showed that the initial native cellulose was converted into an unoriented cellulose II in the lower concentration of steeping ley with presence of urea, thiourea, and sodium aluminate or zincate as activators. The sodium cellulose formed with activators was more reactive to xanthation than the cellulose from unactivated process.
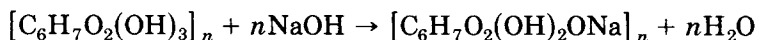
INTRODUCTION

Although the preparation of alkali cellulose has been a commercial process for about 100 years, its mechanism has not been completely explained as yet in spite of the many attempts made.[1-5] From the technological and theoretical points of view, the mercerization of cellulose is of great importance since the properties of alkali cellulose obtained in this process affect the reaction and conditions of preparation of cellulose derivatives, e.g., xanthate or carboxymethylate. Conditions of the cellulose mercerization process affect the chemical composition of the product, and consequently its reactivity. Hence, both the theoretical and industrial significances of this process are still great and unfailing.

Studies on cellulose mercerization are aimed at full elucidation of the chemical structure of alkali cellulose, structural changes taking place during mercerization,[6,7] and understanding the role of activators and mechanism of their action in the mercerization process.[8,9] Solutions of alkali metal hydroxides, depending on concentration and temperature, bring about structural changes in cellulose resulting from different degrees of solvation of hydroxide groups in cellulose macromolecules and their conformation. Therefore, several mutable polymorphs have been found in mercerized cellulose, which show different values of the unit cell parameters as well as different quantitative compositions of the mercerization products obtained. Sodium hydroxide can react with cellulose in two ways:

$$[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow [C_6H_7O_2(OH)_3 \cdot NaOH]_n$$

or

$$[C_6H_7O_2(OH)_3]_n + nNaOH \rightarrow [C_6H_7O_2(OH)_2ONa]_n + nH_2O$$

As follows from the above reactions, cellulose can form with sodium hydroxide either an additive compound or alcoholate. It is assumed[3,10] that, in alkalicellulose, sodium hydroxide is in the form of an adduct being in equilibrium with the alcoholate form:

$$C_6H_{10}O_5 \cdot NaOH \cdot xH_2O \rightleftarrows C_6H_9O_4ONa + (x + 1)H_2O$$
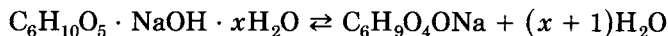
If we assume that the alcoholate is a reactive form with carbon disulfide in xanthation, then, having introduced activators into the mercerizing lye, we should expect the structural changes in alkali cellulose, as well as the alcoholate form concentration to increase, and consequently increased reactivity of cellulose.

The present study was aimed at the examination of structural changes in cellulose mercerized with sodium hydroxide with the addition of activators and of the effect of various activators on the extent of polymorphic transformations in cellulose.

EXPERIMENTAL

Methods and Materials

For the experiments, beech cellulose was used after being mercerized with NaOH and activating agents such as zinc oxide, aluminium hydroxide, urea, and thiourea in amounts 0.5–10% by wt of NaOH contained in the mercerizing lye.

Beech cellulose was mercerized in aqueous NaOH solution at 55°C for 30 min by the mashing method. The ratio of the cellulose mass to lye solution during mercerization was determined by the weight method. Results of cellulose mercerizing was determined by IR spectrophotometry and X-ray radiography. The beech cellulose is characterized by X-ray photographs without well-developed diffraction peaks for particular values of the 2θ angle. Despite this, the X-ray photographs obtained allow to interpret the structural changes taking place in cellulose on mercerization. The basis for interpretation was the peak at the angle $2\theta = 22.6°$ (002), corresponding to cellulose I and the peak at $2\theta = 20°$ (10$\bar{1}$), characteristic for cellulose II. The measurements were taken using CuK$_\alpha$ radiation at a voltage of 32 kW and current intensity of 26 mA, the threshold voltage was 12 V, and the range of $2\theta = 6$–30° at a recording rate of 2°/ min.

As is generally known, the crystallinity degree of polymers determined by X-ray radiography is completely different from the value obtained by spectrophotometry. However, the mercerization process was evaluated by the spectrophotometric method, which is more useful in examining structural changes in beech cellulose. During this examination the degree of crystallinity of cellulose was determined from the relationship

$$C_r D = \frac{A_{1429 \, cm^{-1}}}{A_{893 \, cm^{-1}}}$$

and the mercerization depth from

$$M_D = \frac{A_{1375 \text{ cm}^{-1}}}{A_{1325 \text{ cm}^{-1}}}$$

taking into account values of the ratio of intensities of corresponding wavelength in cm^{-1}, where $C_r D$ is the crystallinity degree and M_D the mercerization depth.

The spectrophotometric measurements were carried out with a Specord 71 spectrophotometer at 4000–700 cm^{-1} wavelength, using samples in the form of KBr tablets.

RESULTS AND DISCUSSION

Mercerization of cellulose is a basic technological process in the manufacture of viscose fibers, aiming at making the cellulose more reactive. As a result of the mercerization, the native cellulose, also called in the literature cellulose I, is changed morphologically into cellulose II, possessing a developed inner surface and good reactivity. On mercerization, many processes take place, e.g., swelling of cellulose with some exothermic effect and dissolution of hemicellulose as a non-fiber-forming components. Because degradation of cellulose occurs to a slight extent, an addition compound of cellulose and NaOH is formed and the intermolecular hydrogen bonds become loose. These phenomena bring about structural changes in cellulose, the extent of which depends on concentration of NaOH used for mercerization and also on other parameters of this process. The effect of mercerization is affected by some inorganic and organic compounds, e.g., zincate, aluminate, urea, or thiourea.

Determination of the Mercerization Depth
by IR Spectrophotometry

In order to determine the mercerization depth precisely, the mercerized cellulose was washed with distilled water to pH 7 and then dried to constant weight. The mercerization effect depends on the mercerization lye concentration. Figure 1 shows a model dependence of structural changes in cellulose, determined by the IR absorption method, on the concentration of mercerizing lye. Tangents of the model experimental curve form angles α_1 and α_2 by intersection of these straight lines. Bisectors of these angles, at the intersections with the experimental curve, form points P_1 and P_2, which determine the beginning and the end of the structural changes, respectively. Perpendiculars to the axis of coordinates from points P_1 and P_2 will determine limiting concentrations C_1 and C_2 of the mercerizing lye, corresponding to the minimum and maximum concentrations, respectively, at which the structural changes in cellulose take place on mercerization at a definite temperature.

Figure 2 illustrates the characteristics of mercerization depth as a function of NaOH concentration for conventional mercerization (curve 1) and mercerization with aqueous NaOH solutions containing activators (curves 2–5). As is seen from Figure 2, the ratio of band intensities $A_{1375 \text{ cm}^{-1}}/A_{1325 \text{ cm}^{-1}}$ within the range of mercerization lye concentration to C_1 practically does not change. When the concentration is higher than C_1, the mercerization depth
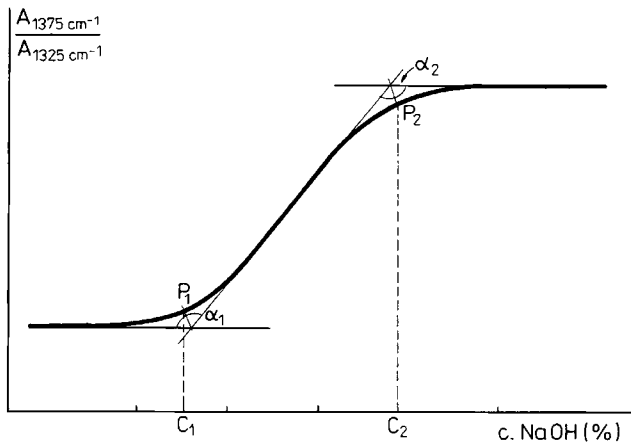
Fig. 1.   Model curve of structural changes in the steeping process of cellulose.

clearly increases and is fixed at C_2. When concentration C_2 is exceeded, the value $A_{1375 \text{ cm}^{-1}}/A_{1325 \text{ cm}^{-1}}$ is practically unchanged. Thus, the curves shown in Figure 2 can be used to determine the structural changes taking place in cellulose on mercerization and to point out the lye concentration at which these changes occur. It was found that the beginning of structural changes takes place at $C_1 = 9$–11% NaOH with the end being at $C_2 = 13$–17% NaOH, depending on the activator used. So, over the range from C_1 to C_2, the crystallographic change of cellulose I to cellulose II takes place.

Table I contains data concerning the mercerization depth. It is seen that the most effective activators are urea and thiourea.

Computer Analysis of the Mercerization Depth

In order to examine more precisely the changes taking place in cellulose on mercerization, a computer analysis was carried out consisting of the determination of approximation function which, at a sufficiently low error, will characterize the mercerization process. The Gauss–Seidl method of square
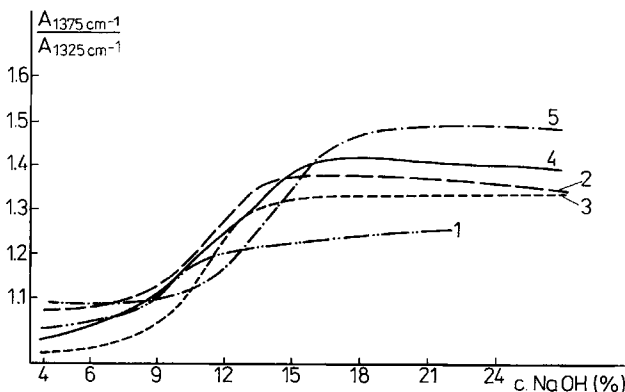

Fig. 2.   Characteristic of the steeping depth. Aqueous sodium hydroxide solution contains: (1) sodium hydroxide only; (2) sodium zincate; (3) sodium aluminate; (5) urea; (6) thiourea.

TABLE I
Characteristics of the Mercerization Depth of Cellulose Mercerized
with the addition of Various Activators

Activator	C_1 (%)	C_2 (%)	Mercerization depth
Zincum oxide	9.3	13.5	1.35
Aluminium hydroxide	9.0	14.0	1.28
Urea	9.0	15.5	1.38
Thiourea	11.0	17.5	1.45
None	9.0	11.0	1.17

approximation was used. Of the analyzed functions, the lowest error was in the case of the function

$$y = a + b \arctan(x - c)$$

from which, on the basis of a developed program, characteristic points of the mercerization depth (Fig. 2), and the relative error of the mercerization depth value, functions for mercerizations with and without activators were determined (Table II) over the mercerizing lye concentration 0–28% NaOH.

Based on the approximation functions, the activation coefficient of beech cellulose mercerized with aqueous NaOH solutions and activators were determined.

Determination of the Cellulose Activation Coefficient

Evaluation of the cellulose reactivity from the reaction with carbon dioxide or from the cellulose solubility in NaOH is an indirect method and does not always provide satisfactory results. In our studies, the determination of mathematical function of the mercerization kinetics allowed for direct evaluation at the cellulose reactivity in terms of activations coefficients of absolute and relative. The results obtained in conventional mercerization were a reference point in this case. The coefficient of absolute activation is expressed by the equation

$$F_{AA} = y(x)_A - y(x)_K$$

TABLE II
Approximation Functions for Mercerization of Cellulose
with Addition of Activators

Activator	Approximation function
Zinc oxide	$y(x) = 1.20110159 + 0.897030265 \arctan(x - 11.3)$
Aluminium hydroxide	$y(x) = 1.14898208 + 0.117387441 \arctan(x - 11.2)$
Urea	$y(x) = 1.23278927 + 0.129227214 \arctan(x - 13.2)$
Thiourea	$y(x) = 1.29573032 + 0.140727007 \arctan(x - 15.0)$
None	$y(x) = 1.10863837 + 0.716846557 \arctan(x - 8.0)$

and the coefficient of relative activation:

$$F_{RA} = \frac{y(x)_A - y(x)_K}{y(x)_K}$$

where $y(x)_A$ = the function describing the mercerization with activator and $y(x)_K$ = the function describing the conventional mercerization. After substitution of the approximation functions from Table II to the above equation, the following expression will be obtained:

$$F_{AA} = [a_1 + b_1 \arctan(x - C_1)] - [a_2 + b_2 \arctan(x - C_2)]$$

$$F_{RA} = \frac{[a_1 + b_1 \arctan(x - C_1)]}{[a_2 + b_2 \arctan(x - C_2)]} - 1$$

These coefficients, calculated from the experimental data, allow us to describe numerically the activity of mercerized cellulose. It is important, first of all, when there is a need to evaluate the activity of cellulose mercerized in various conditions and to select optimal parameters of mercerization. Table III contains values obtained in mercerization of cellulose with various activators at various concentrations of the mercerizing lye.

Activation of the mercerization process with ley with concentration below 10% of NaOH assumes negative values (Table III). This shows that the lye concentration is in this case too low to bring about activation of cellulose and morphological change from cellulose I to cellulose II. When the lye concentration is over 10%, increased values of the activation coefficients are observed. Comparing the values given in Table III, it is seen that thiourea and urea are

TABLE III
Characteristics of the Cellulose Activity after Mercerization
with Lye Containing Various Activators

Activator	Concentration of lye (%)	M_D[a]	F_{AA}[b]	F_{RA}[c]
Zinc oxide	10.21	1.12	−0.06	−5.30
	15.09	1.31	0.10	8.89
	19.21	1.33	0.11	9.54
Aluminium hydroxide	10.21	1.05	−0.13	−11.17
	15.09	1.30	0.09	7.65
	19.21	1.31	0.10	8.56
Urea	10.21	1.07	−0.11	−10.05
	15.09	1.38	0.17	14.58
	19.21	1.43	0.21	17.83
Thiourea	10.21	1.10	−0.08	−7.32
	15.09	1.30	0.09	8.06
	19.21	1.48	0.26	22.15

[a]M_D = mercerization depth
[b]F_{AA} = coefficient of absolute activation of mercerized cellulose.
[c]F_{RA} = coefficient of relative activation of mercerized cellulose.

more effective activators than zinc oxide and aluminium hydroxide, which is in agreement with previous observation, based on IR spectrophotometric measurements and calculated mercerization depth. It follows from the measurements performed that when cellulose is mercerized with 19% NaOH containing thiourea as activator, its activation is increased by 22% as compared with that of cellulose mercerized without activator.

Determination of the Crystallinity Degree of Cellulose by IR Spectrophotometry

To evaluate structural changes taking place in cellulose on mercerization, the IR spectrophotometric method was used. The preparation procedure for cellulose samples to be examined was the same as described previously. It is known from literature that the band at wavelength 1429 cm^{-1} characterizes the crystalline state of cellulose and the intensity of this band is proportional to the content of crystalline in cellulose. The band at wavelength 893 cm^{-1} is characteristic for amorphous regions. Thus, the ratio of intensities of these bands can be used to determine the degree of crystallinity of cellulose.[11,12] In this case, this degree is dependent not only on the content of crystalline phase but also on the state of change of cellulose I into cellulose II. Hence, from the ratio of intensity of the given bands, one can evaluate the structural state of cellulose mercerized both by the conventional method and with mercerizing lye containing activators.[13] The results (Fig. 3) show that cellulose treated with NaOH solutions with concentration below 9% reveals the crystallinity degree only slightly increased. This apparent increase in crystallinity results probably from the fact that low molecular amorphous fractions of cellulose are dissolved during the treatment, which is seen in the case of using activators. In the case of zinc oxide and thiourea used as activators, the increase in the crystallinity degree at low lye concentrations is higher than these obtained with aluminium hydroxide and urea. The structural changes in cellulose mercerized in the presence of activators are particularly considerable within the lye concentration 9–19% NaOH, which confirms the results of the mercerization depth analysis of bands at 1375 and 1325 cm^{-1}.
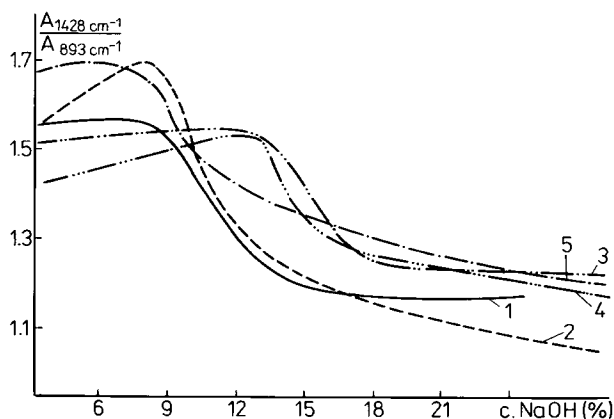

Fig. 3.   Crystallinity degree of steeping cellulose with: (1) sodium hydroxide only; (2) sodium zincate; (3) sodium aluminate; (4) urea; (5) thiourea.
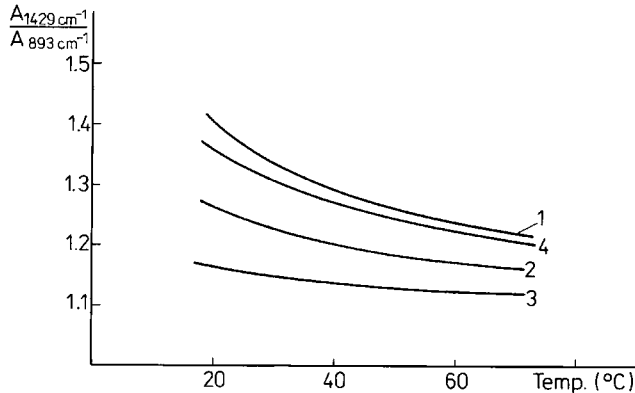
Fig. 4. Crystallinity degree of steeping cellulose vs. time. Steeping lye contained: (1) sodium zincate; (2) sodium aluminate; (3) urea; (4) thiourea.

The crystallinity degree of mercerized cellulose are affected by the conditions of mercerization, and first of all, by temperature and time, which are the main parameters controlling the reactivity of alkalicellulose. In this case, the mercerization was carried out with 17.5% NaOH solution since as was previously found this concentration provides a reactive alkalicellulose. The mercerization was performed by the mashing method at 20–80°C and the cellulose to lye ratio being 1:15.6. The mercerizing lye contained 1% of an activator in relation to the weight of NaOH. The crystallinity degree of mercerized cellulose was evaluated by IR spectrophotometry. It is seen from Figure 4 that increasing the mercerization temperature brings about a decrease in the degree of crystallinity, the lowest value being obtained with aluminium hydroxide and urea used as activator. At temperatures over 60°C, the decrease in the crystallinity degree of cellulose mercerized for 30 min is insignificant. Prolongation of the mercerization time brings about a considerable decrease in the crystallinity degree of beech cellulose (Fig. 5) Also in this case the highest effect of decreasing the crystallinity degree is observed when mercerization is performed with lye containing aluminium hydroxide or urea
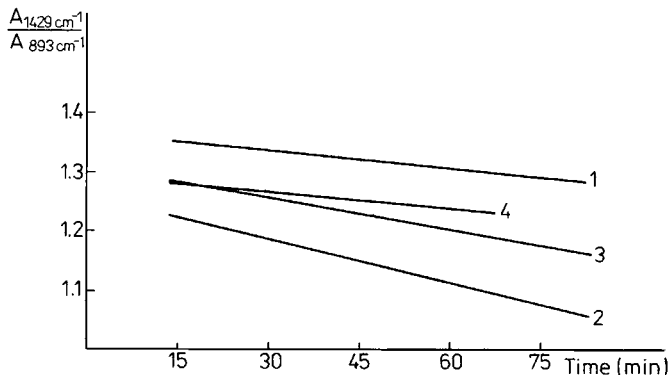

Fig. 5. Steeping time of cellulose vs. crystallinity degree. Steeping lye contained activators as in Figure 4.

as activators. During this examination it was found that the greatest decrease in the crystallinity degree is obtained when 1% of activator in relation to the weight of NaOH is added to the mercerizing lye. With higher percentage of activator, no further decrease in the crystallinity degree was observed.

Evaluation of the Crystallinity Changes in Mercerized Cellulose by X-Ray Radiography

The X-ray radiographic method has a limited use for evaluation of structural changes in beech cellulose since the X-ray patterns have no developed sharp peaks of the scattering intensities for particular values of the angle 2θ. Hence, the X-ray patterns obtained (Fig. 6) are difficult for quantitative interpretation of the changes taking place on mercerization. However, they allow for a general evaluation of the changes, and the results are a supplement for the IR spectrophotometric examination. The diffractogram of unmercerized beech cellulose (Fig. 6) shows two peaks within the 2θ range 21–23° corresponding to crystallographic form of cellulose I and two broadened peaks within the 2θ range 15–19°. The values of the 2θ angles, at which the given peaks are observed, are unchanged during the treatment of cellulose with lye of concentration below 12% NaOH even when the lye contains an activator [in
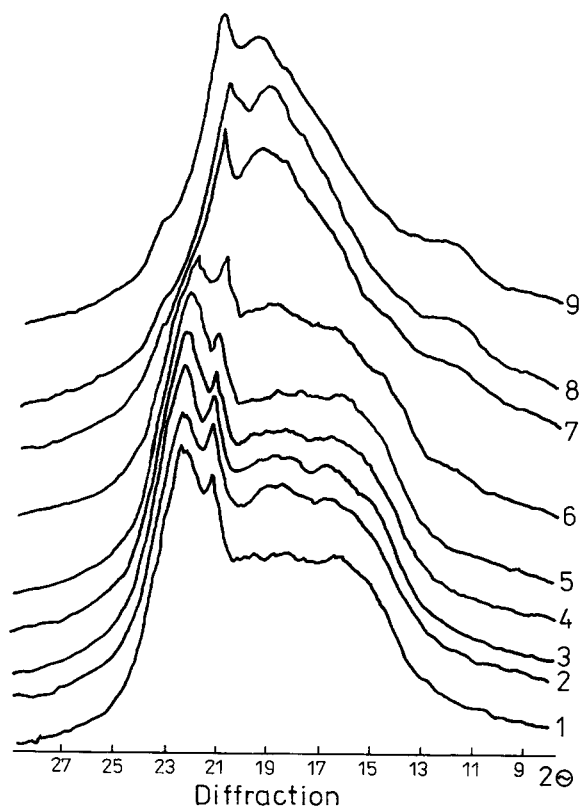

Fig. 6. Diffractogram of steeping cellulose. Steeping lye contained 1% aluminate hydroxide and: (1) 0% NaOH; (2) 4% NaOH; (3) 6% NaOH; (4) 8% NaOH; (5) 9% NaOH; (6) 12% NaOH; (7) 15% NaOH; (8) 17.5% NaOH; (9) 28% NaOH.
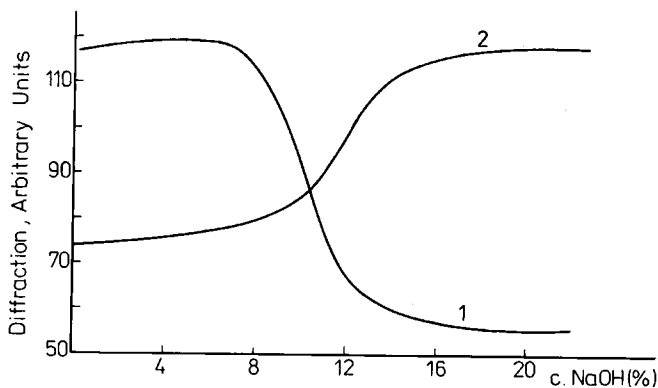
Fig. 7. Diffraction vs. steeping lye concentration measured at $2\theta = 22.6°$ for cellulose I (curve 1) and at $2\theta = 20°$ for cellulose II (curve 2).

this case 1% $Al(OH)_3$]. But when the concentration of lye is over 12% the peaks within the 2θ range 15–19° disappear and a peak at $2\theta = 12°$ appears, which is characteristic for cellulose II. At the same time the sharpness of peak $2\theta = 22.6°$ decreases with its shift to $2\theta = 20°$. This peak is also characteristic for cellulose II. In the evaluation of structural changes taking place in cellulose on the treatment with lye containing activators, the change in intensity of two peaks was taken into account, namely, at $2\theta = 22.6°$ (002) and $2\theta = 20°$ (10$\bar{1}$). These peaks correspond to polymorphic changes of cellulose I into cellulose II. Based on the curves of scattering intensities at both the mentioned angles, the content of cellulose I and cellulose II in the mercerized cellulose mass was determined depending on the lye concentration and type of activator.

Figure 7 shows the changes in the scattering intensities for the cellulose mercerized with lye of various concentration without activator. The changes in the scattering intensity at the angle $2\theta = 22.6°$ (curve 1) characterize the cellulose I content in the mercerized cellulose mass. It follows from the relationship that when the mercerization is performed with lye of a concentration 8% NaOH, there is a fast reduction of the cellulose I content and increase in the cellulose II content (curve 2), which is characterized by the changes in the scattering intensity at the $2\theta = 20°$. The discussed curves of the cellulose I and cellulose II contents in the mercerized cellulose mass are intersected at the lye concentration 10.3%, and this point was called an equilibrium point. The equilibrium point of both polymorphic forms of cellulose shows not only the equilibrium state of cellulose I and cellulose II but also determines the lye concentration at which this state occurs. Thus, the equilibrium point describes the values of effectiveness of an activator. It is worth noting that, with the increase in the activate affectiveness, the equilibrium point shifts higher concentrations of NaOH. For the conventional mercerization, this point appears at 10.3% NaOH, for urea at 11.8% NaOH, and for thiourea at 13.3% NaOH.

In accordance with previous observations, zinc oxide shows lower effectiveness, the equilibrium point occurs at 9.6% NaOH, and aluminium hydroxide,

as an activator with a considerable effectiveness, has the equilibrium point at 12.7% NaOH.

CONCLUSION

The IR spectrophotometric and X-ray radiographic examinations of the mercerization of beech cellulose have shown that thiourea, urea, zinc oxide, and aluminium hydroxide activate the mercerization of cellulose. The cellulose mercerized with lye containing activators shows higher reactivity than that mercerized by the conventional method. The determination of approximation functions for the mercerization process allows us to calculate the coefficients of absolute and relative activations for the activators used in mercerization, which, in turn, makes it possible to evaluate quantitatively this process and to characterize the reactivity or the obtained cellulose II.

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