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The conversion from cellulose I to cellulose II in NaOH mercerization performed in alcohol–water systems: An X-ray powder diffraction study

Paavo Mansikkamäki, Manu Lahtinen, Kari Rissanen *

Department of Chemistry, University of Jyväskylä, P.O. Box 35, FIN-40014 Jyväskylä, Finland

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Abstract

The slurry-mercerization (SM) processes in 2-propanol–water and 2-propanol–ethanol–water and wet-mass-mercerization (WMM) process in ethanol–water solvents are investigated. Based on X-ray diffraction measurements in the earlier reports, we have derived a mathematical method to evaluate more exactly the conversion of cellulose I (CI) to cellulose II (CII) and used it to survey the effects of different alkali treatments on cellulose crystals. This method is very useful when the crystal system changes in a certain set of experiments are compared with each other. The optimal alcohol concentration in SM processes was found to be 80–92 w/w-% in 2-propanol–water solution, 85–90 w/w-% in 2-propanol–ethanol–water solution and 45–55 w/w-% in the WMM process. In the WMM mercerization, the effect of the solvent/cellulose ratio showed that the conversion to CII increased linearly with a decreasing solvent/cellulose ratio. Temperature increase, as well as higher lye concentration, had a positive effect on the conversion of CI to CII. This study confirms also our earlier results that the concentration of soluble lye in the used solvent system is the most important factors in the mercerization of cellulose.

Keywords: Alkalization; Cellulose I; Cellulose II; Mercerization; X-ray diffraction

1. Introduction

Mercerization of cellulose is an important initial step in the production of many cellulose derivatives as cellulose is activated by the mercerization for the main reactions. Our recent studies concentrated in investigating how alcohol and lye concentration and mercerization time and temperature together with the solvent–cellulose ratio influence the mercerization degree of cellulose. Moreover, the influence of different solvents, additives, temperature, time, external pressure and the concentration of alkali on the transformation from CI to CII was studied by X-ray diffraction method (Mansikkamäki, Lahtinen, & Rissanen, 2005). The conversion is usually detected by evaluating the overall intensities of the diffraction peaks originating from the cellulose polymorphs. This method is useful for evaluating the general magnitude of crystal system changes, but observation of smaller changes needs more detailed analysis of the X-ray diffraction patterns, which is presented in this study. Secondly, our studies focus on the mercerization of linter in 2-propanol–water (IPA), 2-propanol–ethanol–water (IPA/EtOH) and ethanol–water (EtOH) solutions as both 2-propanol and ethanol are widely used in the industrial processes. Even though the alkalization of cellulose has been widely investigated during the last decades, many questions still remain open especially about the SM- and WMM-mercerization in solvent-water systems. Particular effort was made to examine the changes in crystal forms of cellulose in different solvent systems using different solvent/cellulose ratios. Our goal in this study is to look deeper at the effect

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* Corresponding author. Tel.: +358 14 260 2672; fax: +358 14 260 2651.
E-mail addresses: pamansik@jyu.fi (P. Mansikkamäki), manu.lahtinen@jyu.fi (M. Lahtinen), kari.rissanen@jyu.fi (K. Rissanen).

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of temperature, time, solvents and lye concentration on the cellulose transformation from CI to CII, since even small changes in the mercerization can be relevant when further derivatization of cellulose is considered. When the characteristic diffraction peaks of cellulose polymorphs are used in the data analysis, the different definitions of the cellulose unit cells in the literature may cause slight uncertainties in the peak designations as reviewed recently by O'Sullivan (O'Sullivan, 1997). The differences are partially due to continually evolving knowledge about the arrangement of the cellulose chains in the unit cell (Gardner & Blackwell, 1974; Honjo & Watanabe, 1958; Langan, Nishiyama, & Chanzy, 1999, 2001; Meyer & Misch, 1937; Sarko & Muggli, 1974; Sugiyama, Vuong, & Chanzy, 1991; Wada, Okano, & Sugiyama, 1997; Woodcock & Sarko, 1980). The uncertainties arise from the fact that native cellulose consists of two polymorphs, the more recently found triclinic form designated as I_α and the monoclinic polymorph designated as I_β (Nishiyama, Sugiyama, Chanzy, & Langan, 2003; VanderHart & Atalla, 1984). In addition the choice of the unique axis in the monoclinic crystal systems of cellulose varies in the literature due to historical reasons (Jensen, Virkola, & Arjas, 1977; Young, 1986). The original choice of the unit cell axes in the monoclinic crystal system was generally performed so that the *b*-axis (fiber axis) was set unique with an acute β angle ($\beta \neq 90°$) following the classical Meyer–Mark–Misch model. Nowadays a unique *c*-axis is generally preferred in the case of cellulose unit cells ($\gamma \neq 90°$). Fink, Hofmann, and Philipp (1995) have presented a comparison of peak designations of two different crystallographic settings of monoclinic unit cells of CI; this was reported earlier by Sugiyama et al. (1991) and Meyer and Misch (1937). Depending on the selection of the monoclinic cell setting, the lattice planes of, for example, diffraction peaks 14.7°, 16.1° and 22.5° (2θ) of polymorph CI can be designated as $(1\bar{1}0)$, (110), (200) according to Sugiyama, while in the Meyer–Mark–Misch system the planes have indices of (101), $(10\bar{1})$ and (002), respectively. Finally, it should be pointed out that the 2θ values of the diffraction peaks vary slightly in the previous publications due to several obvious factors such as the quality of instrumentation, experimental setups, general crystallinity and mixing ratio of the cellulose polymorphs and finally the "biological origin" of the samples analyzed. Measurements of cellulose crystal sizes and shape are also shortly discussed because the changes in crystal forms and crystallinity of cellulose are closely involved in the alkalization process of cellulose.

2. Materials and methods

2.1. Powder diffraction methods for monitoring changes in cellulose crystals

Based on the previous single crystal and powder diffraction studies (Fink et al., 1995; Kolpak & Blackwell, 1976; Langan et al., 1999, Langan, Nishiyama, & Chanzy, 2001; Mansikkamäki et al., 2005; Nishiyama et al., 2003; Okano & Koyanagi, 1986; O'Sullivan, 1997; Raymond, Kvick, & Chanzy, 1995; Stipanovic & Sarko, 1976; Wellard, 1954), two characteristic diffraction peaks ($2\theta = 14.6°$, $16.1°$) of polymorph CI and one diffraction peak ($2\theta = 12.1°$) of CII were selected as probes for the conversion from CI to CII in the mercerization conditions selected. Some analysis methods for monitoring the conversion can already be found in the literature (Ruland, 1961; Rånby, 1952; Sao, Samantaray, & Bhattacherjee, 1994; Zhang, Dongli, Zhang, & Yuguan, 1993). However, in our case, these methods were not applied as such but were used as a basis for the presented method. They are therefore discussed briefly.

Sao et al. (1994) have used the following equation to evaluate the extent of conversion in the mercerization process

$$I_{\mathrm{p}} = \alpha I_1 + (1 - \alpha) I_2, \tag{1}$$

where I_1 and I_2 are measured intensities at 15° (2θ) of CI and CII, respectively. The partially mercerized fraction of CI is indicated by α, and I_{p} represents the intensity of the composite sample also at 15° (2θ). The complete conversion from CI to CII was assumed to be complete within a mercerization time of 1 h, either at room temperature (30% NaOH–water solution), or at 0 °C (12% NaOH–water solution). Sao et al. investigated the crystallinity in ramie fibers by using the equations of Ruland for the calculation of crystallinity of ramie and compared these values with the tensile properties of the fibers (Ruland, 1961).

More suitable formulas for defining the extent of conversion in crystalline areas can be derived from the equations of (Zhang et al., 1993; Rånby, 1952). Even though these two equations are formulated differently, they are mathematically equivalent. In the equation of Rånby, a relative intensity number (I_{r}) is defined as follows:

$$I_{\mathrm{r}} = \frac{2I_{\mathrm{II}}}{I_{\mathrm{I}} + 2I_{\mathrm{II}}}, \tag{2}$$

where according to Rånby, I_{I} and I_{II} ($I_{\mathrm{I}} + I_{\mathrm{II}} = 1.0$) are the estimated intensity ratios of diffraction peaks with Miller indices of (101) and $(10\bar{1})$ of CI to that of (101) of CII. I_{r} is defined as zero for pure native cellulose and one for completely mercerized cellulose, intermediate values of I_{r} indicating partially mercerized cellulose. Intensity of I_{II} is determined from diffraction peak (101) on CII and I_{I} arises from lattice planes (101) and $(10\bar{1})$ on CI. If the equation of Rånby is interpreted so that I_{I} is defined as sum of intensities $I_{14.7} + I_{16.1}$ and I_{II} corresponds to the intensity $I_{12.0}$, the equation is analogous to Eq. (3) which is presented by Zhang et al. (1993) as follows:

$$C_{\mathrm{II}} = \frac{I_{12.0}}{I0_{12.0} + 0.5(I_{14.7} + I_{16.1})}, \tag{3}$$

where $I_{12.0}$, $I_{14.7}$ and $I_{16.1}$ represent the intensities of diffractions peaks 12.0°, 14.7° and 16.1° (2θ), respectively. Thus, the equation of Zhang can be written so that

$(I_{14.7}+I_{16.1})=I_{\mathrm{I}}$ and $I_{12.1}=I_{\mathrm{II}}$ and by multiplying the right side of the equation, the equation of Rånby can be derived:

$$C_{\mathrm{II}}=\frac{I_{\mathrm{II}}}{I_{\mathrm{II}}+0.5I_{\mathrm{I}}}, \tag{4}$$

$$C_{\mathrm{II}}=\frac{2I_{\mathrm{II}}}{2I_{\mathrm{II}}+I_{\mathrm{I}}},\ \text{so evidently } C_{\mathrm{II}}=I_{\mathrm{r}}. \tag{5}$$

In addition, Zhang et al. have defined and calculated the overall percentage of CII in the samples by including the amorphous part of cellulose. First they measured the intensities of the maximum diffraction (I_o) from the baseline of the X-ray pattern and subtracted the base level from this value (I_k). They then calculated the degree of crystallization of cellulose (X) as presented in equation.

$$X=n\frac{I_k}{I_0},\quad n=0.75. \tag{6}$$

The percentage of CII (X_{II}) in the whole cellulose sample according to Zhang is

$$X_{\mathrm{II}}=XC_{\mathrm{II}}. \tag{7}$$

Eq. (6) is a strongly simplified formula for calculating the crystallinity of cellulose. The distribution of crystalline and amorphous parts of cellulose is rather ambiguous. Ruland has presented already 1961 a more exact calculation theory and measurement method for the crystallinity of polymers (Ruland, 1961), but it is not discussed here in more detail. Also Fengel et al. investigated the influence of the alkali concentration on the transformation of bleached cotton from CI to CII (Fengel, Jakob, & Stropel, 1995), as well as the change of crystallinity and crystallite sizes in water solution by alkalizing cotton powder in a water solution for 2 h at room temperature. The samples were further washed and dried carefully and the dried samples were then analyzed by X-ray diffraction (SAXS and WAXS) and FTIR (Fengel et al., 1995). The average size of the crystallites, d_{hkl}, was calculated from the X-ray diffraction data by applying the Scherrer (Langford & Wilson, 1978; Scherrer, 1918) equation

$$d_{hkl}=\frac{2\sqrt{3\ln 2}\cdot\lambda}{\pi w\cdot\cos\theta}, \tag{8}$$

where d_{hkl} = average crystallite dimension; w = full width at half maximum of reflection in radians; λ = wavelength of radiation and θ = diffraction angle. The crystallite dimensions, d_{hkl}, were calculated from the lattice planes (101), $(10\bar{1})$ and (002). According to Fengel et al., the transformation of CI into CII started at room temperature in 12% and was complete in 15% NaOH concentration (Fengel et al., 1995). The degree of the change between these NaOH concentrations was not evaluated, but the variation in the degree of crystallinity and the dimensions of crystallites calculated from the lattice planes (101), $(10\bar{1})$ and (002) were monitored. Both crystallinity (X_{c}) and the crystallite sizes (d_{hkl}) decreased clearly when the NaOH concentration increased from 12% to 15%.

Zhang, Ruan, and Zhou (2001) used a slightly different variation of Scherrer's equation (8) in investigating the structure and properties of regenerated cellulose films by using a definition for apparent crystal size, ACS

$$\mathrm{ACS}=\frac{0.9\lambda}{\beta(\cos\theta)}, \tag{9}$$

where $\beta=(B^2-b^2)^{1/2}$; λ = wavelength of incident X-rays; θ = diffraction angle; B = integral breadth in radians of diffraction angle and b = instrumental integral breadth in radians. Actually, if Eqs. (8) and (9) are examined more carefully, the original so-called shape-dependent Scherrer constant, K, has been changed to an approximate value of $\sim 0.9((2\sqrt{3\ln 2})/\pi\approx 0.91)$, which is a generally accepted value when the shape of the crystallites is assumed to be spherical. In principle, different K values should be used for each lattice plane, as the constant is dependent on the true shape of the crystallites, the definition of the line breadth (either by measuring the full-width at half-maximum of the peak, FWHM or w, or by an integral method where the total area under peak maximum is divided by the peak intensity, β) and the crystallite-size distribution (Langford & Wilson, 1978). But since the variation of the constant is rather modest, a general constant value between 0.9 and 1.0 is commonly used and in this view the Eqs. (8) and (9) are more or less equivalent.

In this study the method used is analogous to the methods discussed above but from a slightly different perspective. At first, the baseline definition and observation of the individual relative intensity values ($I_{\mathrm{r},2\theta}$ according to Eq. (10)) were carried out with Bede ZDS Search/match software (Ondrus, Skala, & Bowen, 2000)

$$I_{\mathrm{r},2\theta}=\frac{I_{2\theta}}{I_{\max}}*100, \tag{10}$$

where $I_{2\theta}$ = measured intensity of a single peak (2θ = 12.1°, 14.6° or 16.1°) and $I_{\max}$ = a maximum intensity value of the measured sample (2θ = 19.5–22.0°). Instead of the Zhang method, the percentage of CII (Eqs. (3) and (7)) was not multiplied by crystallinity parameter X (Eq. (6)), but the intensity values $I_{12.1}$, $I_{14.6}$ and $I_{16.1}$ in Eq. (3) where respectively replaced by relative intensity values $I_{\mathrm{r},2\theta}$. The relative degree of mercerization $\mathrm{CII}_{\mathrm{r}}$ in crystals is then obtained according to the following equation:

$$\mathrm{CII}_{\mathrm{r}}=\frac{I_{\mathrm{r},12,1}}{I_{\mathrm{r},12.1}+0.5(I_{\mathrm{r},14.6}+I_{\mathrm{r},16.1})}, \tag{11}$$

where $I_{\mathrm{r},12.1}$, $I_{\mathrm{r},14.6}$ and $I_{\mathrm{r},16.1}$ = the relative intensity values of measured sample at 2θ of 12.1°, 14.6° and 16.1°, respectively. Next, the total minimum $\mathrm{CII}_{t\min}$ and total maximum $\mathrm{CII}_{t\max}$ intensities from our test results were selected and placed in Eq. (12). The calculated degree of mercerization of cellulose (CII-%) can then be written as follows:

$$\text{CII-\%}=\frac{\mathrm{CII}_{\mathrm{r}}-\mathrm{CII}_{t\min}}{\mathrm{CII}_{t\max}-\mathrm{CII}_{t\min}}*100, \tag{12}$$

where $CII_{t\,\min}$ corresponds to the lowest relative CII_r value in the tested samples and $CII_{t\,\max}$ to the highest relative CII_r value, respectively. The Eq. (12) does not pay attention to the amorphous parts of cellulose but gives the average degree of mercerization in the crystalline part of cellulose. Therefore, the calculated results are comparable only within the same test series. However, this comparability proved to be sufficient for the evaluation of small differences affecting the mercerization process.

2.2. Cellulose

The cellulose used in this study was a high viscosity cotton linter produced by Southern Cellulose Products Inc. (Grade 1059). The cellulose was ground in two steps by a hammer mill type Condux pilot grinder; in the second grinding step the cellulose was passed through a sieve with pore size 2.1 mm.

2.3. Chemicals

All chemicals and solvents used in this study were laboratory grade and the water was deionized by ion exchange column. The supplier and purities of the chemicals and solvents were as follows: sodium hydroxide (Akzo Nobel, purity 98%), 2-propanol (Kebo, purity 98%), ethanol (Primalco, purity 99.5%).

2.4. Alkali treatments

In SM experiments, the alkalization of cellulose was performed in Erlenmeyer flasks and mixed with a magnetic stirrer. The samples were cooled in ice or salt-ice baths and heated with a heating plate. The WMM experiments were carried out in cylindrical glass reaction vessels with a flat flange lid. The mixer was a unique blade-scraper head welded to a round metal staff that was developed to get the best possible mixing in a small cylindrical glass reactor.

In the SM process ground cellulose was first added into an Erlenmeyer flask, followed by the addition of the alcohol–water solvent. After temperature adjustment sodium hydroxide was added into the reaction mixture as a 50%-w/w water solution. In the WMM process cellulose was first disintegrated by mixing for 5 min before the alcohol–water solvent was added. After the homogenization and temperature adjustment, sodium hydroxide solution was added slowly to the alcohol–cellulose mass. After mercerization, all samples were washed with water to neutral (pH 7.00). Laboratory sheets (100 g/m^2) were made in a Büchner funnel and the sheets were dried by pressing gently with a heating plate at 120–150 °C.

2.5. Wide angle X-ray scattering

The X-ray powder diffraction data were obtained at room temperature with a Huber imaging-plate Guinier camera 670. The sealed-tube X-ray generator system was operated at 45 kV and 25 mA and pure line-focused Cu $K_{\alpha 1}$ radiation ($\lambda = 1.5406$ Å) was produced by a primary beam curved germanium monochromator. The measurements were carried out in Guinier-type transmission geometry with the angle of incidence 45° to the sample normal. The measurements were made directly from the laboratory sheets by attaching them to the sample holder. Some of the sample sheets were so fragile that they were first placed between two Mylar foils before attaching to the sample holder. The vertical sample holder oscillated horizontally with amplitude of 10 mm to improve the statistics of the measurements. The X-ray diffraction data were recorded using the curved imaging plate in the 2θ angle range from 4° to 100° with recording time of 20 min and resolution step of 0.005°. The calibration of the equipment was achieved with mixture of LaB_6 and Si standards (SRM660 and SRM640b, National Institute of Standards and Technology).

3. Results and discussion

3.1. Effect of alcohol concentration

The percentage of CII (CII-%) as a function of the alcohol concentration from SM and WMM processes are presented in Fig. 1. In the SM process the lye concentration of the total solvent amount was 1.8 w/w-% and in the WMM process 8.4 w/w-%. The solvent–cellulose ratio in the SM processes was 30 v/w and in the WMM process 6 v/w (v/w = volume/weight). In the 2-propanol–ethanol–water solution the ratio of alcohols was 50/50 w/w-% and in all the figures the abbreviations IPA for 2-propanol and EtOH for ethanol are used.

As can be seen in Fig. 1, the optimal alcohol concentration varies from case to case depending on the alcohol–water mixture. The transformation from CI to CII

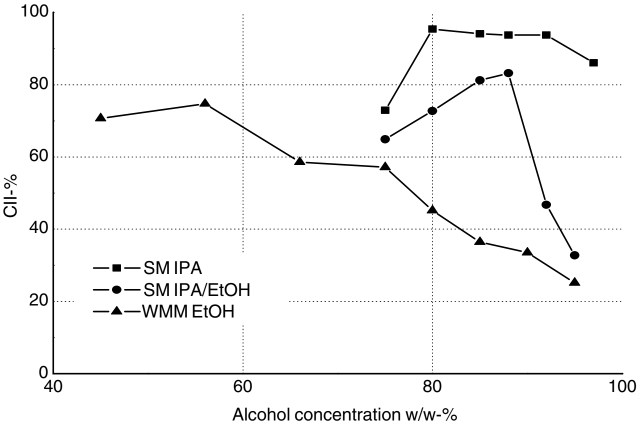

Fig. 1. The degree of mercerization (CII-%) presented as a function of alcohol concentration. (temperature in IPA and IPA/EtOH SM process = 25 °C and in EtOH WMM process = 30 °C, mercerization time 60 min).

was highest in the IPA–water solution. The optimal IPA concentration region is quite broad varying from 80 to 92 w/w-% and the highest CII-% value is 95.3%. In the IPA/EtOH–water mixture the optimal transformation was found between 85 and 90 w/w-% with a maximum CII-% value of 83.2%. In the WMM process the EtOH concentration varied from 45 to 95 w/w-% and the solvent–cellulose ratio was 6 v/w, while in the SM processes the corresponding ratio was 30 v/w. The highest transformation in this test set from CI to CII (CII-% 74.5%) was achieved when an ethanol concentration of 56 w/w-% was used.

Based on our previous studies the sodium hydroxide tends to precipitate easily from ethanol–water solvent systems (Mansikkamäki et al., 2005), but in IPA–water and IPA/EtOH–water solvents two clear phases are formed and the lye remains mainly in the lower water-rich phase. It was also found that the most important lye concentration in the mercerization of cellulose is the amount of lye in the water-rich phase, which should exceed 7–8% (w/w). The mercerization degree of CII (CII-%) as a function of NaOH concentration calculated from the total water amount is shown in Fig. 2.

The maximum transformation from CI to CII was achieved in all solvent systems when the lye concentrations remained between 8 and 20 w/w-% as calculated from the total water amount. The transformation decreased when the alcohol concentrations were increased further. As expected, the decrease of transformation was lowest in the IPA–water solutions because of the easy formation of two phases after adding the NaOH–water solution. The CII-% was found to be lowest in the WMM process, but it must be pointed out that some experimental conditions were not optimized. This will be discussed later on.

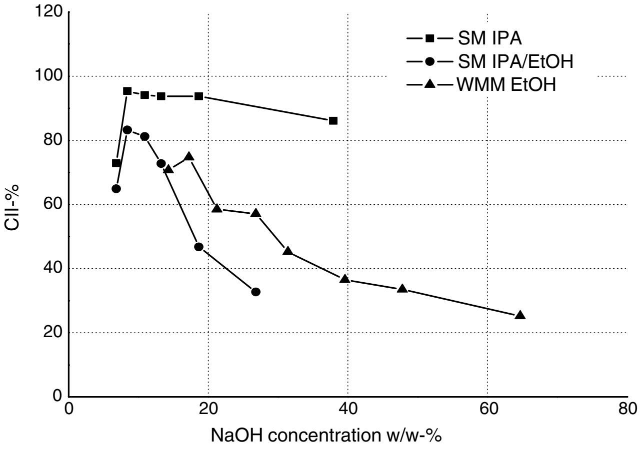

Fig. 2. Degree of mercerization (CII-%) as a function of the NaOH-concentration calculated from the total water amount (alcohol concentration in IPA–water SM process = between 75 and 97 w/w%, in IPA/EtOH–water SM process = 80–95 w/w-% and in EtOH–water WMM process = 45–95 w/w-%).

3.2. Effect of mercerization temperature

The degree of mercerization (CII-%) in SM and WMM processes is presented in Fig. 3 as a function of the mercerization temperature. In the SM processes, the lye concentration calculated from the total solvent amount was 1.8 w/w-% and that calculated from the total water amount 15.5 w/w-%. Similarly, the lye concentration in the WMM process was 8.4 w/w-% and 15.5 w/w-%, respectively. In these experiments, the cellulose-solvent ratio was 30 v/w in the SM process, and 6 v/w in the WMM process.

A temperature increase had a positive effect on the mercerisation of cellulose in all test sets. Based on the experiments, the effect of temperature increase is not quite linear in all SM processes (IPA/EtOH) as the observed increase of CII-% from 10 to 50 °C is somewhat slower than between −5 and +10 °C and at temperatures over 50 °C. However, this conclusion is not statistically reliable because the number of experiments was too small and the variations in test conditions may have some effect on the results. Nevertheless, it can be stated that in these test sets a 2-propanol–water solution had the best effect on transformation of CI to CII and that the temperature increase clearly favours the crystal transformation to CII.

3.3. Effect of NaOH concentration

As previously discussed, the most significant matter in alcohol–water solutions is the optimum water concentration and the solubility of lye in the solvent system used. The effect of the NaOH concentration in SM and WMM is shown in Fig. 4. The alcohol concentration in solvents was 90 w/w-% in the SM processes, and in the WMM process the ethanol concentration was 50 w/w-%. The cellulose-solvent ratio in the SM process was 30 v/w, and in the WMM process 6 v/w.

The highest degree of mercerization was achieved in all solvent systems when the concentration of sodium

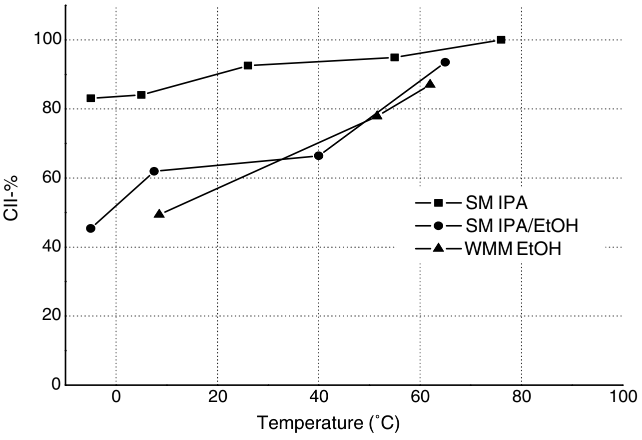

Fig. 3. Degree of mercerization (CII-%) as a function of temperature (alcohol concentration in IPA–water and IPA/EtOH–water SM processes = 90 w/w-%, and in EtOH WMM process = 50 w/w-%).

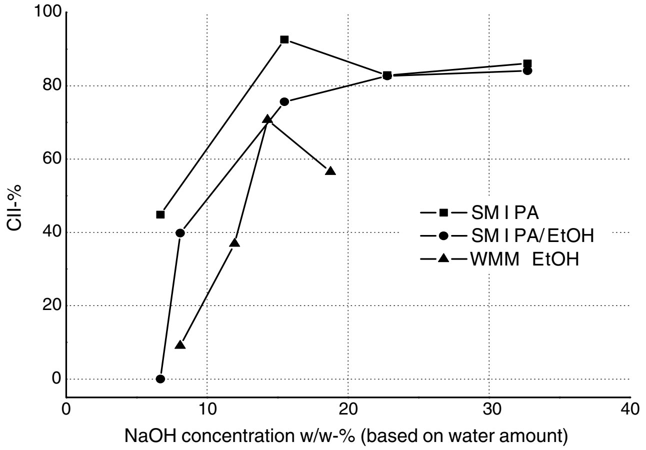

Fig. 4. Degree of mercerization (CII-%) as a function of NaOH concentration calculated from the total water amount (alcohol concentration in IPA–water and IPA/EtOH–water SM processes = 90 w/w-% and in EtOH–water WMM process = 50 w/w-%).

hydroxide was at least 12 w/w-%. In the WMM process the degree of mercerization clearly decreased in higher lye concentrations; this is probably caused by the precipitation of sodium hydroxide in the ethanol–water solution. The results of the above experiments support our earlier conclusions (Mansikkamäki et al., 2005) that a good solubility and proper concentration of sodium hydroxide in the solvent system used are the most important matters in the mercerization of cellulose. These observations are consistent with the literature studied as a minor discrepancy was reported by Nishiyama, Kuga, and Okano (2000). In the report, results show that, Na-cellulose I is formed at room temperature in water solution in 3–5 M lye concentration, but Na-cellulose II is not formed until NaOH concentration is higher than 7 M at 60–100 °C. According to our experiments, the regenerated CII is completed at NaOH concentration 3 M (12 w/w-%) or higher, when calculated from the water phase. This difference can be a partially resulted by the accuracy of analytical methods used in our study. Secondly, Nishiyama et al. mainly analyzed unwashed-samples of Na-cellulose forms while we have analyzed the washed regenerated samples. It is likely, that in normal conditions, the major part of Na-cellulose I transforms to CII during the washing process when NaOH concentration is 3 M or more which is also indirectly mentioned by the Nishiyama et al.

3.4. *Effect of mercerization time and solvent–cellulose ratio in the WMM process*

Based on our previous studies, the process time of 60 min is normally sufficient for the mercerization of cellulose in IPA–water and IPA/EtOH–water slurry systems (Mansikkamäki et al., 2005). Therefore, the effect of time was investigated only in WMM processes where low alcohol–cellulose ratios were used in the ethanol–water solution (ethanol–cellulose ratio 1–10 v/w). Even though WMM processes have been used for a long time in chemical industry, it is still difficult to find relevant studies concerning the optimal mercerization conditions. The degree of mercerization as a function of mercerization time in the WMM processes is shown in Fig. 5. The solvent–cellulose ratio in these tests was 6 v/w and the concentration of sodium hydroxide was 15.5 w/w-% as calculated from the total water amount.

In Fig. 6 the degree of mercerization is presented as a function of the solvent–cellulose ratio. In Fig. 7 the degree of mercerization is shown as a function of the NaOH concentration calculated from the total water amount in the WMM process. Both curves (Figs. 6 and 7) have calculated from the same test results.

Unlike the SM processes, the degree of mercerization increased in the WMM process up to 240 min and it showed a still increasing trend even above that (Fig. 5). However, the degree of mercerization (CII-%) increased to 92% even with mercerization times of 60 min when the solvent–cellulose ratio was changed from 10 to 1 (Fig. 6).

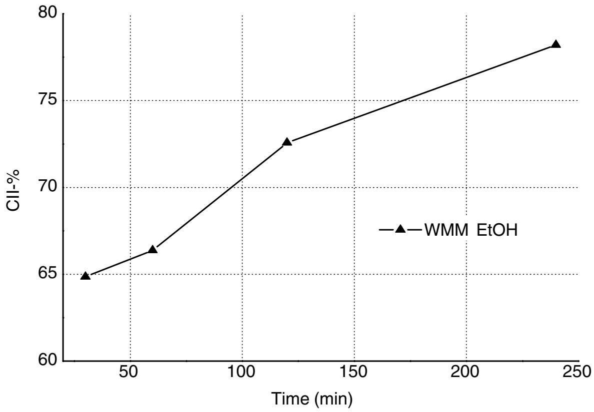

Fig. 5. Degree of mercerization (CII-%) as a function of mercerization time. (EtOH–cellulose ratio = 6 v/w and alcohol concentration 50 w/w-%).

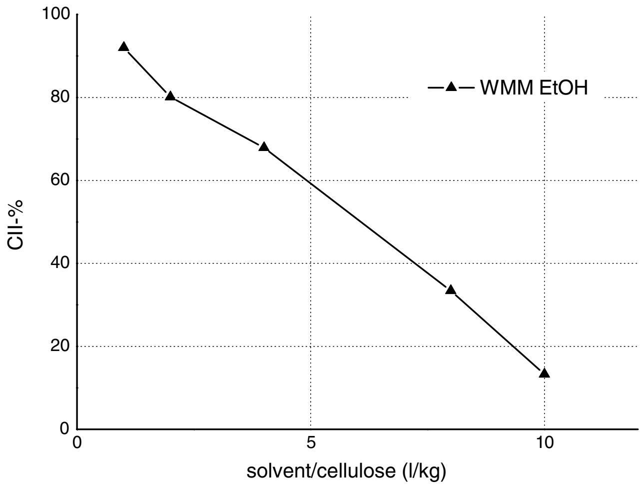

Fig. 6. Degree of mercerization (CII-%) as a function of the solvent–cellulose ratio (alcohol concentration in EtOH–water system = 50 w/w-%).

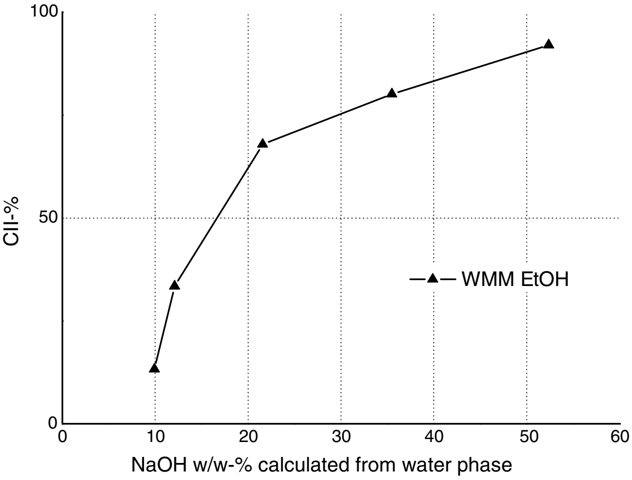

Fig. 7. Degree of mercerization (CII-%) as a function of the NaOH concentration calculated from the total water amount (alcohol concentration in EtOH–water system = 50 w/w-%).

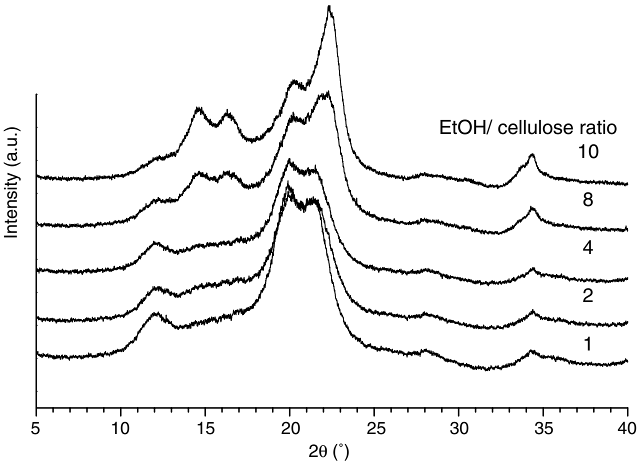

Fig. 8. X-ray powder diffraction data of the WMM process whit EtOH/ cellulose ratios from 1 to 10 v/w (EtOH–water system, alcohol concentration 50 w/w-%).

Certainly one reason for this is the increase of water-based lye concentration while the total solvent–cellulose ratio decreased. Furthermore, the increase of lye concentration cannot be the only explanation; according to our earlier studies in ethanol–water solution the mercerization of cellulose is poor due to the precipitation of sodium hydroxide in SM processes with a solvent–cellulose ratio higher than 10%. The degree of mercerization increased with increasing NaOH concentration despite the fact that concentrations up to 35 w/w-% (calculated from total solvent amount) and 52.4 w/w-% (calculated from total water amount) were used, as can be seen in Fig. 7. These observations suggest that the lye precipitation that occurs in SM processes is not occurring in WMM processes.

3.5. Estimate of accuracy of used analyzing method

The calculation of the degree of cellulose mercerization derived from the equations of Rånby and Zhang proved to be useful for detecting small changes in the cellulose crystallites. The differences between our equation with those presented by the Rånby and Zhang are only modest (Eqs. (10) and (12)). An example of diffraction patterns is presented in Fig. 8, from which the degrees of mercerization (CII-%) shown in Fig. 6 were obtained.

If the powder patterns are examined visually they are easy to arrange in order according to the increasing CII-%, except for two of the patterns. The diffraction data originated from mercerization test with EtOH–cellulose ratio 2 and 4 seem to be quite similar but the calculations still showed logical and clear differences in the degrees of CII (CII-%). Similar observations can be made from the other test sets, although the smallest differences still cannot be explained by these test results. This means that the smallest crystal changes are not discovered in cases where the changes have been evaluated only visually from the X-ray diffraction patterns. Generally, it can be stated that all the results were logical and most of tests behaved as expected.

The only problem in our calculations was the powder pattern of untreated cellulose, as it gave a clearly higher value for the relative degree of mercerization (CII_s in Eq. (12)) than was obtained for the samples mercerized in a dilute NaOH solution. The exact reason for this is not proven but it can be suggested that the dilute lye is actually not mercerizing cellulose but merely dissolving smaller molecules, like hemicelluloses, from the samples. Hemicelluloses make up a part of the amorphous material in cellulose and they affect the backgrounds shape of the powder pattern. The comparison of powder patterns measured from original untreated cellulose and the celluloses mercerized with low lye concentrations are shown in Fig. 9. The untreated cellulose gave a clearly higher relative degree of

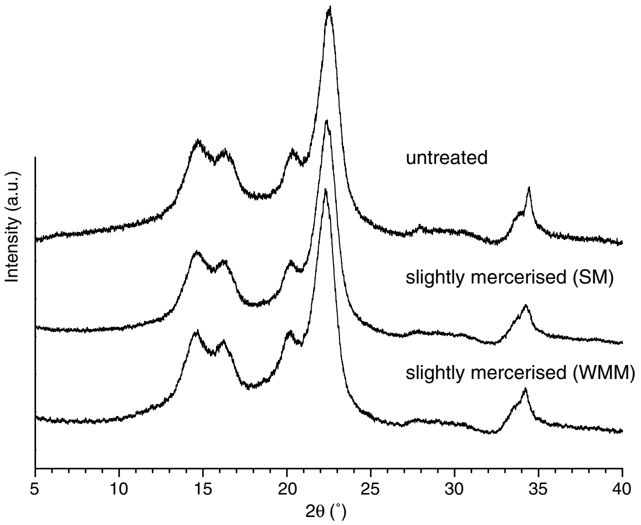

Fig. 9. Powder data of untreated cellulose and cellulose treated in the SM and WMM processes with dilute NaOH. (EtOH–water system, alcohol concentration 50 w/w-%).

mercerization ($CII_r = 0.139$) than a slightly mercerized celluloses ($CII_r = 0.079$ and 0.123). The lye concentrations used in these cases were less than 9 w/w-% calculated from the total water amount.

It can be concluded that amorphous hemicelluloses were washed out in the mercerization process and the best diffraction pattern for CI can be achieved after washing with a diluted alkali solution. As can be seen, the overall shape of all diffraction patterns is quite similar but in the case of untreated cellulose the baseline of the diffraction pattern is clearly higher, suggesting a higher content of amorphous material in the sample. Accordingly, the lowest relative intensity value from our test results was defined as $CII_{r\min}$ in Eq. (12).

Another method since 1980 (Atalla, Gast, Sindorf, Bartuska, & Maciel, 1980; Earl & VanderHart, 1980), namely ^{13}C-CP/MAS NMR spectroscopy, offers a slightly different point of view from X-ray diffraction by giving information of the changes in the chemical environments of each carbon atom between different crystal forms. Recently Kunze and Fink (Kunze & Fink, 2005) analyzed the crystal changes of different celluloses that were activated by caustic soda and urea solutions by using ^{13}C-CP/MAS NMR spectroscopy. This report emphasizes that ^{13}C solid state NMR spectroscopy is also an effective method for monitoring minor changes in cellulose crystals and it seems that X-ray and NMR spectroscopic methods can be used to complement each other.

4. Conclusions

Both 2-propanol, and the mixture of 2-propanol–ethanol work very well in slurry mercerization when the total alcohol concentration is between 80 and 90 w/w-%. A 2-propanol–water solution was found to be somewhat better than a 2-propanol–ethanol–water mixture.

As already stated, an ethanol–water solution is not suitable for slurry mercerization due to the precipitation of lye when the alcohol–water/cellulose ratio and the alcohol concentration are too high (Mansikkamäki et al., 2005). On the contrary, decreasing the alcohol–water/cellulose ratio linearly increases the degree of mercerization and the optimum alcohol concentration seems to be between 45 and 55 w/w-%. The exact reasons are not known, but based on our results it can be assumed that at low solvent/cellulose ratios, the solvent properties on the surface, of fibers change so that sodium hydroxide does not precipitate so readily but instead penetrates through the fiber walls up to the crystallites of the micro fibrils. In addition it seems that once the mercerization process is optimized, cellulose can be mercerized even with the same lye concentration both in the WMM as well as in the best SM processes. The total water amount is important because the solubility of sodium hydroxide decreases also in solvents where two phases can be formed. This effect can be seen when Figs. 2 and 4 are compared. In both figures the degrees of mercerization (CII-%) are shown as a function of the NaOH concentration calculated from the total water amount, but in Fig. 2 the mercerization degrees decrease after optimum points because, unlike in Fig. 4, the total water amount decreases with an increasing alcohol concentration. The alcohol concentration in experiments described in Fig. 4 was 90% in the SM processes and 50% in the WMM process. Furthermore, the WMM process is technically more challenging as a good distribution and homogeneity of solvents and lye are more difficult to achieve than in the SM process. Secondly, mercerization times need to be longer in the WMM process due to a slower diffusion in some process conditions; this comes up especially when the solvent/cellulose ratio is increased.

Increasing the temperature has a positive effect on the mercerization of cellulose in all the solvent systems tested. Based on these experiments, the dependence of CII-% on temperature seems to be linear also in the WMM process.

Increasing the concentration of sodium hydroxide has, as expected, a positive effect on the conversion of CI to CII as long as the lye does not start to precipitate. The most interesting results indicate that good mercerization results can be achieved also in ethanol–water solution when the solvent/cellulose ratio and the solvent concentration are optimized. Even though new information was obtained about slurry (SM) and wet-mass-mercerization (WMM) in the present study, some of the conditions in SM and WMM processes performed in 2-propanol–water, 2-propanol–ethanol–water and ethanol–water systems still wait for further optimization. After this investigation the most interesting question is: Why is the activity of lye in the ethanol–water system higher at low solvent/cellulose ratios?

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