# DISSOLUTION OF CELLULOSE IN AQUEOUS ALKALINE SOLUTIONS WITH ADDED UREA AND THIOUREA

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*The solubility of wood cellulose of various molecular weights in aqueous NaOH solutions with added urea and thiourea was studied with variable temperature, solvent composition, and sequence of dissolution stages. It was shown that cellulose of average degree of polymerization up to 500-600 dissolved. Thermally reversible gels formed in solutions held at 20°C for 2 d. The structural organization of cellulose-hydrate films prepared from the solutions was studied using IR spectroscopy and x-ray diffraction.*

A crucial problem in the chemistry and physical chemistry of natural polymers is the development of ecologically friendly and safe technologies for processing cellulose into finished products. The method that was used until the middle of the 1980s to produce cellulose-hydrate fibers from cellulose xanthogenate required the use of highly toxic $CS_2$.

Cellulose-hydrate fibers are currently produced by the viscose process and by a technology that uses methylmorpholine-*N*-oxide as the solvent for cellulose (MMO-process) [1, 2]. Ionic liquids, in which natural and synthetic polymers are soluble, have been the subject of extensive studies in the last few decades and are promising for producing composite films and fibers with new functional properties [3-5]. The usefulness of ionic liquids on industrial scales is limited by their cost.

The search for relatively inexpensive, ecologically safe, and technically acceptable solvents for cellulose remains today a critical problem. Many publications are focused on the dissolution of cellulose in aqueous NaOH solutions with added urea (U), thiourea (TU), and polyethyleneglycol (PEG) and without added $CS_2$.

Cellulose dissolves in aqueous NaOH solution even with cooling (up to freezing), in contrast with the viscose process. The molecular weight of cellulose, its degree of crystallinity and polymorphic form, and the presence of impurities can affect its solubility [6, 7]. Solutions of cellulose in aqueous NaOH solution with polymer concentrations up to 5 mass% are suitable for forming cellulose-hydrate films. However, such a solution concentration is too low for fiber production.

Three-component systems ($H_2O$/NaOH/additive) in which U, TU, and PEG were used as additives were proposed for improving the solubilizing capability of aqueous NaOH solutions for cellulose [8]. Furthermore, the use of four-component systems such as $H_2O$/NaOH/U/TU was also proposed [9]. Cellulose solutions with concentrations up to 7.3 mass% [10] from which fibers could be spun [11] were produced by adding the aforementioned additives to the working mixture. According to the literature [12], cellulose is very soluble in an aqueous mixture with a component ratio NaOH/U = 7/15 mass%. A mixture with NaOH/TU = 9.5/4.5 mass% is considered optimal if U is replaced by TU [10]. The component ratio for the NaOH/U/TU mixture was 8/8.5/6.5 mass% [9]. Various temperature regimes for the dissolution and sequences of solution preparation steps were described in different publications [8-14].

It is noteworthy that such dissolving systems are relatively inexpensive and that the same process equipment that is used for the viscose process but without $CS_2$ can be used to prepare the cellulose working solutions and to spin

fibers and prepare films from them. The various temperature regimes for dissolving cellulose in aqueous alkaline solutions, the sequences of steps for preparing the polysaccharide solutions, and the durations of the processes that are described in the literature suggest that additional research is needed to find the optimum conditions for preparing the cellulose solutions.

The goal of the present work was to compare the conditions for dissolving cellulose in aqueous alkaline solutions with added U and TU and to study the structural organization of the resulting films.

Industrial samples of whitened deciduous cellulose with degree of polymerization (DP) 250, 500, 750, and 900 were investigated. The DP of the polysaccharide was determined by viscometry from the viscosity of its solutions in cadoxen using the Mark—Kuhn—Houwink equation $[\eta] = 7.0"10^{-3}"DP^{0.9}$ [15].

Two aqueous alkaline mixtures of different composition were used to dissolve the cellulose, i.e., one containing NaOH (7 mass%) and U (12%) [12] and one with NaOH (8%), U (8%), and TU (6.5%) [9]. Doubly distilled $H_2O$, NaOH (chemically pure), and U and TU (pure grade) were used to prepare the mixtures.

Cellulose solubility was studied for 1 mass% solutions. Polymer samples were prepared by drying at 105°C to constant mass. Solutions were prepared as follows.

1. A weighed portion of cellulose (0.5 g) was placed into solvent (49.5 g) that was cooled beforehand to –12.5°C and stirred vigorously for 1 h as the temperature was gradually raised to 20°C.

2. A weighed portion of cellulose (0.5 g) was placed into solvent (49.5 g), stirred vigorously mechanically for 1 h at room temperature, and stored at –12.5°C for 12 h. The resulting solution was stirred vigorously for 1 h as the temperature was gradually raised to 20°C.

3. A weighed portion of cellulose was placed into aqueous NaOH solution, stirred at room temperature for 1 h, treated with the calculated amount of U and TU, stirred for 1 h, and stored at –12.5°C for 12 h. Then, the solution was stirred again for 1 h as the temperature was gradually raised to 20°C.

4. A weighed portion of cellulose was placed into the solvent, stirred at room temperature for 0.5 h, irradiated by ultrasound for 5 min, and stored at –12.5°C for 12 h. Then, the solution was stirred for 1 h as the temperature was gradually raised to 20°C.

5. A weighed portion of cellulose was placed into the solvent, stirred at room temperature for 0.5 h, quickly cooled by liquid $N_2$ to –25°C, and stored for 0.5 h. The resulting solution was stirred for 1 h as the temperature was gradually raised to 20°C.

6. A weighed portion of cellulose was placed into the solvent, stirred at room temperature for 0.5 h, quickly cooled by liquid $N_2$ to –25°C, and stored at –12.5°C for 12 h. Then, the solution was stirred for 1 h as the temperature was gradually raised to 20°C.

All solutions were centrifuged for 0.5 h at 4500 rpm to remove undissolved cellulose. The resulting precipitate was rinsed on the filter with distilled $H_2O$ until the rinsings were neutral (pH = 7) (monitoring with phenolphthalein paper) and dried at 105°C to constant mass. Cellulose was precipitated from the solution by adding $H_2SO_4$ solution (5%). The precipitate was also rinsed on the filter with distilled $H_2O$ until the rinsings were neutral and dried at 105°C to constant mass. The cellulose solubility (S, %) was calculated using the formula

$$S = \frac{M_1 - M_2}{M_1} \cdot 100,$$

where $M_1$ is the mass of the weighed cellulose and $M_2$, the mass of undissolved cellulose.

Solutions were irradiated by ultrasound in an IL 100-6 ultrasonic bath (Russia) at room temperature.

Cellulose-hydrate films were prepared by wet spinning of the solution at 20°C through a spinneret with a controlled gap onto glass plates that then were immersed into a precipitating bath. The precipitating bath contained aqueous $Na_2SO_4$ solution (5 mass%). Spun films were rinsed with distilled $H_2O$ until neutral (pH = 7).

The structural organization of the films was studied using x-ray diffraction analysis and Fourier-IR spectroscopy. IR spectra of films were taken on a Vertex-70 spectrometer (Bruker) using a Pike ATR micro-accessory. The obtained samples were studied by x-ray diffraction on a Dron-2.0 instrument using Cu Kα-radiation and a Ni-filter monochromator. Samples were prepared as sets of films of thickness 1-2 mm. Starting cellulose powder was pressed into a pellet. Exposures were taken in transmission mode.

Table 1 presents results for the solubility of deciduous cellulose in aqueous alkaline mixtures with added U and TU. Cellulose with DP 250 dissolved fully when prepared by the first three methods. This agreed well with previous

Table 1. Solubility of Cellulose for Various Solution Preparation Methods and Degree of Polymerization of Dissolved Polysaccharide and Insoluble Residue

| Method No. | Cellulose DP | Solvent composition | Solubility, % | DP S/IS* |
|---|---|---|---|---|
| 1 | 250 | 7% NaOH / 12% U | 98 | – |
| | | 8% NaOH / 8% U / 6.5% TU | 95 | – |
| | 900 | 7% NaOH / 12% U | 25 | 230/1150 |
| | | 8% NaOH / 8% U / 6.5% TU | 25 | 245/1160 |
| 2 | 250 | 7% NaOH / 12% U | 100 | – |
| | | 8% NaOH / 8% U / 6.5% TU | 100 | – |
| | 750 | 7% NaOH / 12% U | 35 | – |
| | | 8% NaOH / 8% U / 6.5% TU | 35 | – |
| | 900 | 7% NaOH / 12% U | Up to 35 | 275/1140 |
| | | 8% NaOH / 8% U / 6.5% TU | 30 | 330/1240 |
| 3 | 250 | 7% NaOH / 12% U | 95 | – |
| | | 8% NaOH / 8% U / 6.5% TU | 65 | – |
| | 900 | 7% NaOH / 12% U | 40 | 255/1165 |
| | | 8% NaOH / 8% U / 6.5% TU | 30 | 275/1190 |
| 4 | 900 | 7% NaOH / 12% U | 45 | 270/1230 |
| | | 8% NaOH / 8% U / 6.5% TU | 40 | 320/1250 |
| 5 | 250 | 7% NaOH / 12% U | 85 | – |
| | | 8% NaOH / 8% U / 6.5% TU | Up to 85 | – |
| | 750 | 7% NaOH / 12% U | 60 | – |
| | | 8% NaOH / 8% U / 6.5% TU | 80 | – |
| | 900 | 7% NaOH / 12% U | > 50 | 440/1020 |
| | | 8% NaOH / 8% U / 6.5% TU | 70 | 550/1070 |
| 6 | 900 | 7% NaOH / 12% U | 50 | 390/1100 |
| | | 8% NaOH / 8% U / 6.5% TU | 40 | 410/1120 |

*DP S/IS is the degree of polymerization of soluble and insoluble (insoluble residue) cellulose.

results of other researchers [7, 9]. The cellulose solubility was 85% if the solution was rapidly frozen to –25°C without storing it at reduced temperature for a long time (method 5). Storage of the cellulose solution at low temperature (e.g., –12°C) was probably important. It was supposed that the components of the mixed solvent diffused further into the cellulose fiber crystallites during this stage although the diffusion rate of the solvent molecules was extremely slow because of the low temperature.

Cellulose with a high DP (750 and 900) was only partially soluble. The influence of storing the mixture at low temperature became evident. Thus, 25% of the polymer dissolved upon rapid dissolution in solvent that was cooled beforehand to –12.5°C (method 1). The solubility increased to 35% if cellulose was stored in the complex solvent for 12 h at this same temperature (method 2). The solubility of the polysaccharide increased by another 5-10%, up to 40-45%, if the cellulose was irradiated beforehand with ultrasound and then stored at –12.5°C for 12 h (method 4). It is noteworthy that adding the other components (U or TU, method 3) to the cellulose suspension in aqueous NaOH solution did not substantially increase the cellulose solubility compared with method 2. The highest solubility of cellulose with DP 900 was attained after freezing the mixtures to –25°C (method 5). Then, storing the mixture at reduced temperature for 12 h (method 6) did not increase its solubility.

It was shown before [9] that cellulose was more soluble in the ternary mixture NaOH/U/TU than in binary mixtures NaOH/U or NaOH/TU. Clearly improved solubility on going from the binary to the ternary system was not observed in the present experiments.

The DP of the polysaccharide that did and did not dissolve was found because all samples of the used cellulose had different molecular-weight distributions. It can be seen that cellulose with an average DP up to 550 dissolved (method 5). Other researchers showed that cellulose with DP up to 500-800 dissolved depending on the dissolution conditions and the mixture component compositions [10, 12, 16-18]. Cellulose with DP up to 700-800 is usually used in the viscose process to produce cellulose-hydrate fibers. An analysis of the data in Table 1 showed that the optimum
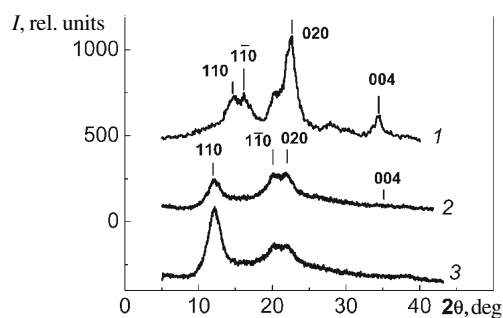
Fig. 1. X-ray diffraction patterns of starting cellulose (1) and cellulose-hydrate films formed from cellulose solutions in NaOH/U prepared without ultrasound treatment (2) and with ultrasound treatment for 2 min (3).
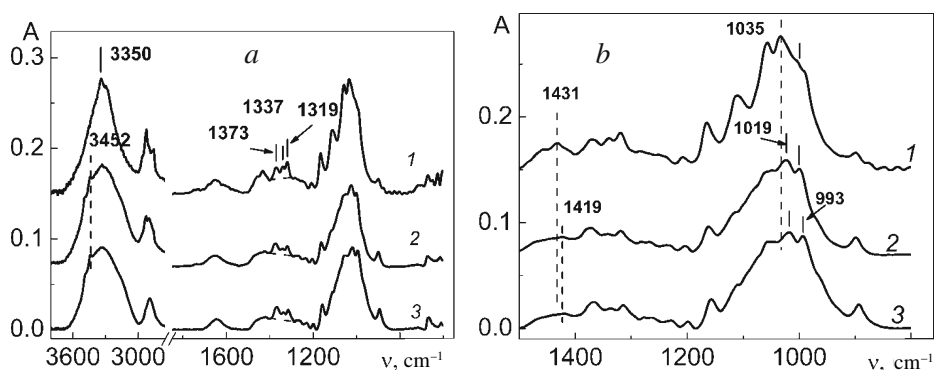


Fig. 2. General IR spectra of starting cellulose (1), industrial cellulose-hydrate film (2), and film prepared from aqueous NaOH/U solution (3) (*a*) and IR spectra in the range 800-1500 cm⁻¹ (*b*).

conditions for dissolving cellulose were methods 5 and 6 with the mixtures frozen to –25°C. However, these methods can also be the most energy-intensive with respect to technology and production. Analogously, introducing the ultrasound irradiation step (method 4), although providing increased solubility, requires additional equipment.

Therefore, in our opinion, the optimum system is method 2. Cellulose with DP 500 was fully dissolved by this method. Solutions with concentrations from 1 to 5 mass% were obtained. Cellulose with this DP was produced by hydrolysis of cellulose with DP 900 using the literature method [19]. Slight turbidity was observed visually after storing the cellulose solution at –12.5°C for 12 h. The prepared solutions were completely transparent after additional treatment with ultrasound for 2 min followed by vigorous stirring as the temperature was gradually raised to 20°C. Further studies were conducted using these solutions. It is noteworthy that thermally reversible gels formed during storage of all obtained solutions at room temperature for 2 d.

Wet spinning of the obtained solutions produced transparent cellulose-hydrate films, the structural organization of which was studied. As expected, polymorphous structure C II was observed in the films using x-ray scattering and IR spectroscopy.

Figure 1 shows x-ray diffraction patterns of starting cellulose and cellulose-hydrate films obtained from aqueous alkaline solutions prepared by two methods without ultrasound irradiation and with it for 2 min.

The x-ray diffraction pattern of starting cellulose showed typical reflections characteristic of polymorphous structure C I at 2θ = 14.5, 16.5, 22.4, and 34.5° that belonged to planes [110], [1$\overline{1}$0], [020], and [004], respectively (Fig. 1, curve 1) [20]. X-ray diffraction patterns of cellulose-hydrate films prepared from the solutions contained characteristic reflections of polymorphous structure C II at 2θ = 12, 20, and 22° that belonged to planes [110] and [020], respectively (curves 2 and 3). A similar pattern was observed for cellulose-hydrate films that were regenerated from

cellulose dissolved in alkali [6] and fibers obtained from aqueous alkaline solutions with added U and TU [11, 21, 22]. It is noteworthy that a strong reflection with $2\theta = 12°$ was observed in the x-ray diffraction pattern of a film obtained from a cellulose solution after treatment with ultrasound. This could have been due to orientation effects as the film dried.

IR spectra of starting cellulose and cellulose-hydrate films showed that the spectrum of cellulose-hydrate film regenerated from aqueous alkaline solution was identical to that of commercial cellulose-hydrate film (Fig. 2). Natural cellulose (C I) is characterized by absorption bands in the range 3000-3700 cm$^{-1}$ (broad) for free and bound intra- and intermolecular H-bonds of OH groups, a band at 2900 cm$^{-1}$ for CH stretching vibrations, and a series of bands at 800-1400 cm$^{-1}$ (Fig. 2a) [23, 24].

The transition of cellulose from polymorphous form C I to polymorphous form C II is associated with changes in the shapes of the OH absorption bands, where a band appears at 3452 cm$^{-1}$ in addition to the band at 3350 cm$^{-1}$, and the band at 2900 cm$^{-1}$. The intensities of the absorption bands at 1373, 1337, and 1319 cm$^{-1}$ also change (Fig. 2a) [23].

The CH$_2$ absorption bands (shift from 1431 to 1419 cm$^{-1}$) and the C$_6$ C–O band (shift from 1035 to 1019 cm$^{-1}$ and increased intensity of the absorption band at 993 cm$^{-1}$) are more obvious and sensitive to the polymorphous transition (Fig. 2b) [23, 24]. The IR spectroscopic results agreed well with those from x-ray diffraction.

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