CELLULOSE CHEMISTRY AND TECHNOLOGY

SWELLING AND DISSOLUTION OF CELLULOSE IN NaOH AQUEOUS SOLVENT SYSTEMS

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As a fundamental step towards creating a new class of cellulose engineering materials, the proposed research investigated swelling and dissolution of cellulose in NaOH aqueous solvent systems (NaOH/H_2O, NaOH/thiourea/H_2O and NaOH/thiourea/urea/H_2O). The dependence of swelling and dissolution behavior of cellulose fibers on the quality of the solvent was investigated in detail. For the two cellulose samples – cotton linter and spruce wood fibers – the swelling and dissolution mechanisms in NaOH-water and NaOH-water-additives stayed the same. Adding thiourea to NaOH-water produced the same ballooning mechanism, but with a larger expansion of the balloons, indicating a better solvent. The cotton fiber could not completely dissolve in NaOH/H_2O and NaOH/thiourea/H_2O. However, the cotton fiber swelled evidently showing no balloon formation and then disintegrated into rod-like fragments in NaOH/thiourea/urea/H_2O, which was an indication of the best solvent of all the NaOH aqueous solutions used.

Keywords: cellulose, swelling, dissolution, NaOH, urea, thiourea

INTRODUCTION

Cellulose is the primary product of photosynthesis in terrestrial environments, and the most abundant renewable polymer produced in the biosphere (e.g. 100 billion dry tons/year). Because of the un-moldable identity, wood and cotton fibers are difficult to be refabricated as other thermosetting and thermoplastic polymers are.[1] Therefore, fundamental understanding of the cellulose dissolution chemistry in aqueous solution is of particular interest to cellulose chemists. If an effective, economic and environmentally friendly cellulose dissolution method can be developed, a new platform for producing moldable cellulosic intermediate materials will be created to provide new opportunities for using cellulosic materials as renewable and sustainable engineering polymers.[2]

Swelling and dissolution of cellulose in non-derivating solvents and the description of the achieved dissolution state are important tasks and are a matter of both scientific and technical interest.[3] Cellulose swelling and cellulose dissolution are two completely different processes. The cellulose swelling process maintains the gross structure of cellulose as a moiety of particles, fibers, or a film (i.e., solid cellulosic phase), despite significant changes of physical properties and an increase in sample volume due to uptake of the swelling agent. Cellulose dissolution is a transition from a two-phase system to a one-phase system (clear solution), in which the original supramolecular structure of cellulose is destroyed.[4]

However, cellulose swelling and dissolution have a common feature, namely, the disruption of its supramolecular structure. Both processes are, therefore, controlled by the same solvent-biopolymer interactions.[5-8] So there is no clear-cut borderline between a swelling process and a dissolution process: the same system can act either as a swelling agent or as a dissolution agent, depending on the properties of cellulose and operation conditions.

The most spectacular effect of the heterogeneous swelling and dissolution of cellulose fiber is the ballooning phenomenon. The swelling can take place in some selected zones along the fibers. This heterogeneous ballooning swelling was observed a long time ago, first by Nageli in 1864,[9] then by Pennetier in 1883,[10] Fleming and Thaysen in 1919,[11] Marsh *et al.* in 1941,[12] Hock in 1950,[13] or Rollins and Tripp in 1952.[14,15] In 1954, Ott *et al.*[16] proposed an explanation of this phenomenon. It must be noted that similar explanations were suggested in all the preceding references. For a wide range of cellulose fibers, the microfibrils of the secondary wall are aligned in a helical manner with respect to the long axis of the fiber. Ott *et al.* deduced that the swelling is greater transversely than lengthwise (as it is generally for fibers where the orientation of the cellulose chains is mainly in the fiber direction). Consequently, they proposed that "when raw cotton fibers are placed in a certain swelling agent, the radial expansion of the cellulose in the secondary wall causes the primary wall to burst. As the expanding swollen cellulose pushes its way through these tears in the primary wall, the latter rolls up in such a way as to form collars, rings or spirals, which restrict the uniform expansion of the fiber and forms balloons". Navard *et al.* described the state of cellulose swelling into balloons and the swelling and dissolution mechanisms of the different walls (primary wall, secondary wall composed of S1 wall and S2 wall, as well as the lumen) by means of high resolution observations.[17,18] The mechanisms leading to the dissolution of other than cotton and wood have never been studied as a function of the solvent quality, with the exception of the work of Chanzy *et al.*[19] They observed by optical microscopy the swelling and dissolution of ramie fibers in (N-methylmorpholine-N-oxide (NMMO)–water with various contents of water at 80 ºC. They observed that at low water content, the fibers fully dissolved as rod-like segments. Based on the previous study, Navard *et al.*[17,18] performed observations by optical microscopy of free floating fibers between two glass plates for a wide range of solvent qualities. They identified five main dissolution modes for wood and cotton fibers as a function of the quality of the solvent:

- Mode 1: Fast dissolution by disintegration into rod-like fragments;
- Mode 2: Large swelling by ballooning and then dissolution of the whole fiber;
- Mode 3: Large swelling by ballooning and partial dissolution of the fiber, still keeping its fiber shape;
- Mode 4: Homogeneous swelling and no dissolution of any part of the fiber;
- Mode 5: No swelling and no dissolution (case of a non-solvent).

These modes reflect the quality of the solvents, which decreases from mode 1 to mode 5.

These mechanisms have been observed with ionic liquid solvent, NMMO solution,[2] for a wide range of plant fibers[3] and some cellulose derivatives if the derivatization occurred without dissolution.[4] These studies have shown that the dissolving mechanism proceeds as follows: the solvent penetrates inside the fibers through the primary wall of the fibers, which acts as a semi-permeable membrane; the cellulose chains of the secondary wall dissolve and swell, breaking the primary wall, which cannot expand.

Recently, a new exciting method that involves a low-energy, extremely simple and relatively safe process has been developed and seems to be grandly expanding, judged by the number of publications on the topic: NaOH aqueous solution systems at low temperature. NaOH complex solvent systems can dissolve cellulose without any pretreatment and/or derivatization. The first traces of this method found in the literature involve the placement of a modified – but non-derivatized – form of cellulose in an aqueous solution of sodium hydroxide at low temperatures,[20-23] while cellulose I with a higher than leveling-off DP (200) can only be partially dissolved in NaOH/H_2O. In the last three years, however, some authors have made significant progress in making this method a lot more efficient by adding urea or thiourea in the mixture of NaOH and water.[24-27] Similarly, however, both Zhang's and Isogai's works suggest that there exists an upper DP limit of cellulose for these two solution systems, the cellulose with a higher DP value (>800) that is beyond the corresponding upper limit can not be dissolved in the solution.[26,28,29] Most commercial wood pulps and original cotton linters have DP values of about 800, this may partially explain why these celluloses cannot be easily dissolved in aqueous NaOH/urea or NaOH/thiourea solutions.

In a recent publication, we reported the use of urea and thiourea in combination. It was believed that the combination produces a solvent with the capacity to fully dissolve more cellulose and cellulose with higher DP (>1200) than any of the NaOH/urea or NaOH/thiourea formulations on their own.[30]

However, the lack of sufficient understanding of the NaOH aqueous solutions dissolution process significantly constrains its applications. In order to fully understand the cellulose dissolution in alkali solvent systems, there are several aspects of problems that need to be addressed. The focus of this paper is to study the swelling and dissolution mechanisms of cellulose fibers in varied NaOH solvent systems. The swelling and dissolution mechanisms of three kinds of cellulose fibers are studied here in aqueous solvents (NaOH solution with or without urea and/or thiourea).

EXPERIMENTAL

Materials

Three native fibers and their characteristics are given in Table 1. The crystallinity is measured by wide-angle X-ray diffraction (WAXD). The (average) degree of polymerization (DP) was determined by a standard procedure, as follows: the cellulose was dissolved in cadoxen, and the intrinsic viscosity of a dilute solution was measured on an Ubbelodhe capillary viscometer. The viscosity-average molecular weight ($\overline{M}_\eta$) can be calculated with the following equation:

$$[\eta] = 3.85\times 10^{-2}\times \overline{M}_\eta^{\,0.76} \qquad (1)$$

where the DP of cellulose can be obtained from equation 2:

$$\overline{M}_\eta = DP\times \mathrm{M} \qquad (2)$$

where M is the molecular weight of the glucopyranosyl unit of cellulose. Prior to their use, all cellulose samples were dried in a vacuum oven at 70 °C for 24 h.

Table 1
Properties of the cellulose samples

Cellulose fiber	DP	Crystallinity (%)	α-cellulose content (%)
Cotton linter (C620)	620	78.6	96.2
Spruce wood (W800)	800	64.8	94.6
Absorbent cotton (C1400)	1400	91.7	98.5

Preparation of NaOH solvent systems

The swelling and dissolution treatments were performed with mixtures of sodium hydroxide (NaOH) and water, with or without additives. NaOH–water is a mixture containing 8% (in weight) of NaOH. Two types of mixtures containing additives were prepared with 8% NaOH-water:

- thiourea: mixtures (in w/w) with thiourea as an additive were tested: NaOH (8%), thiourea (6.5%), water (85.5%).
- urea and thiourea: mixtures (in w/w) with thiourea and urea as additives were tested: NaOH (8%), urea (8%), thiourea (6.5%), water (77.5%).

Preparation and observation of the solutions

The solutions were prepared by mixing cellulose and the given solvent mixture in a container made of two glass plates, suitable for optical microscopy observations. About ten fibers were placed on glass plates where solvent had been introduced. The fibers could move freely on the plates. Only one extremity of cellulose fibers was attached by adhesive tape onto the plate in order to avoid the fiber to be too much affected by the solvent convection, which could cause difficulties for optical observations. The swelling and dissolution of cellulose fibers were observed by optical microscopy (Olympus BX51) equipped with a Linkam LTS350 hot/cooling stage. The samples were investigated in transmission mode. The swelling and dissolution experiments were performed between -10 ºC and +5 ºC.

RESULTS AND DISCUSSION

Swelling of cellulose in aqueous NaOH

It has been found that the solvents based on NaOH/H_2O do not swell the balloons so much, and they do not make balloons burst (Fig. 1). The balloons reach a certain maximum expansion, smaller than the one of mode 2, and the process stops. The fiber stays like this without dissolving completely.

This will be the case for NaOH aqueous solution at -10 ºC, similar to NMMO/H_2O at 90 ºC, with water contents between 25 and 30%.[2] The swelling mechanism of cellulose fibers in NaOH/H_2O shows that the solvent is not very good. Only cellulose of low DP, like microcrystalline cellulose, can be nearly fully dissolved, with very few insoluble particles present. As soon as cellulose fibers of larger DP that have kept their original structure are put in contact with this solvent, only the cellulose present in the balloons is dissolved. The cellulose solution can be collected when the balloons are mechanically broken during mixing, which is not the case in the type of experiments that are performed here under the microscope. The membrane and the non-swollen sections cannot dissolve, that is, the cellulose fiber is a mixture of dissolved (inside of the balloon) and non-dissolved (non-swollen section and membrane) cellulose parts.

It can be deduced from the POM (polarized optical microscope) image of the swollen fiber that the balloons of the fiber were in amorphous state, while the connection areas were still undissolved and in crystalline state (Fig. 2).

Moreover, at ambient temperature (>0 ºC), cotton and wood fibers swell homogeneously with no balloon. This seems to indicate that decreasing the temperature below 0 ºC increases the quality of the solvent. It can be concluded that NaOH on its own does not seem to be the best solvent and it certainly cannot replace powerful organic solvents.[31] It can only partially dissolve celluloses with low DP.

Swelling and dissolution of cellulose in aqueous NaOH/thiourea

In order to enhance the dissolving ability of NaOH aqueous solution, scientists have tried to use this first approach and have refined it by bringing into play some additives. Urea and thiourea were found to be a successful candidate from practical, environmental and simplicity standpoints. A few methods that deal with the addition of thiourea or urea to NaOH are available in the literature.[31-35] Studies also show that thiourea is a better additive to NaOH than urea. It can be found from Fig. 4 that the behavior of cellulose fibers dissolving in NaOH/thiourea/H_2O is a four step process (mode 2):

– Phase 1: balloon formation
– Phase 2: balloon dissolution
– Phase 3: dissolution of the unswollen sections
– Phase 4: dissolution of the balloon membrane scraps.

This will be the case, for NaOH/thiourea aqueous solution at -10 ºC. The zones where the swelling starts increase their size and the fiber has a series of swollen transparent balloons. These balloons grow until they reach a maximum size at which they burst. The balloon will burst when the membrane is not able to sustain the pressure inside the balloon. The whole fiber will then dissolve. This is similar to NMMO/water at 90 ºC, with water contents between 19 and 24%.[2,17-19] These features are a clear indication that the addition of thiourea in NaOH/water increases the quality of the solvent. However, only a small part of C1400 (14%) can be dissolved in this solvent. The solvent molecules can penetrate the fiber, but cannot break the intermolecular hydrogen bonding network of cellulose. In accordance with the conditions described by Zhang *et al*., the solvent does not necessarily completely dissolve cellulose. A 1.5M NaOH/0.65M thiourea composition could dissolve ~22% of cotton linter with a DP of ~1070 and ~77% of cellulose with a DP of ~540; it could however totally dissolve a cellulose II sample with a DP of ~670.[27]

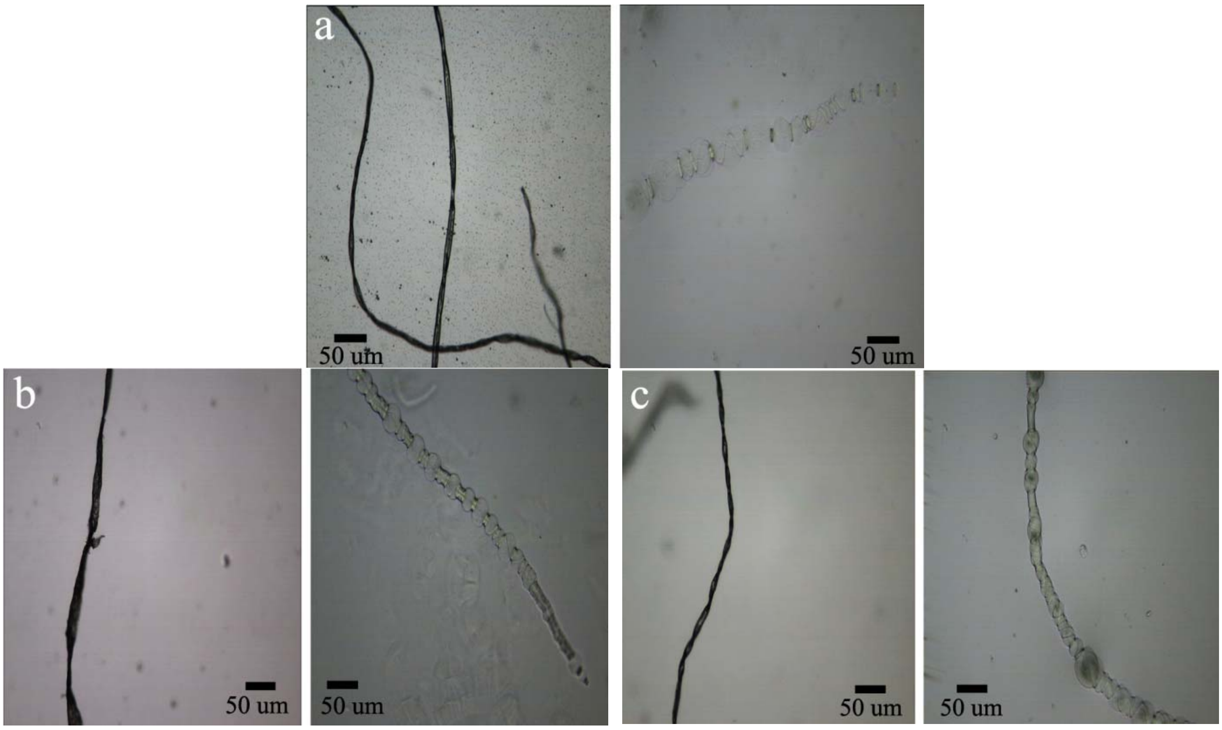


Figure 1: (a) C620, (b) W800 and (c) C1400 swollen in 8% NaOH aqueous solution at -8 ºC (optical microscopy in transmitted light)

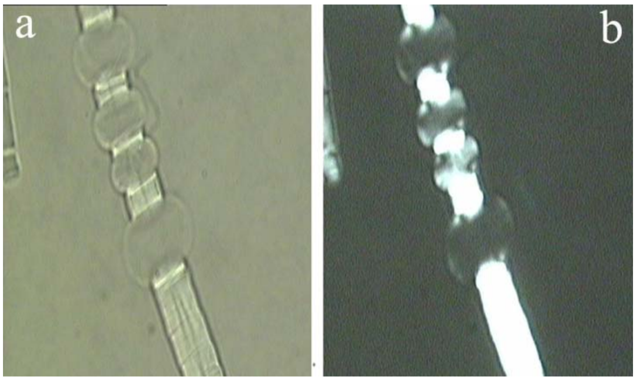


Figure 2: Swollen fibers observed in a non-agitated solution of C620 in 8% NaOH aqueous solution, (a) direct light transmission, (b) between cross-polarizer

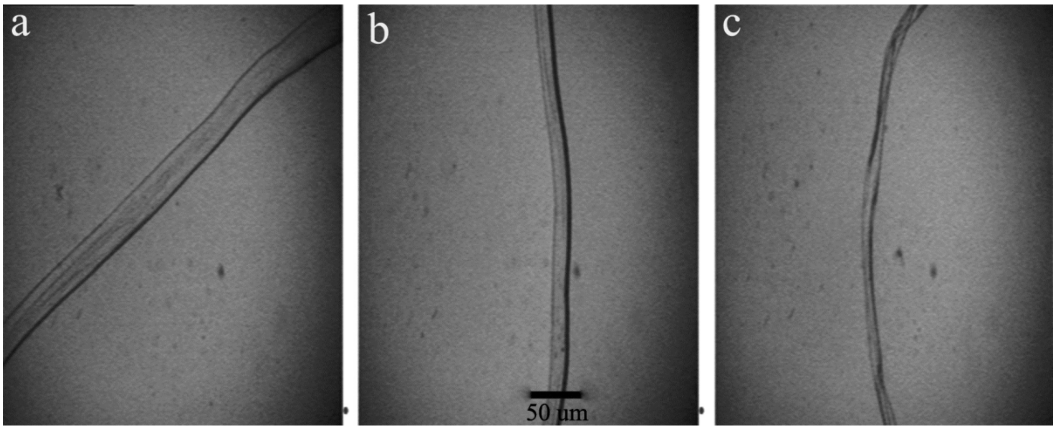
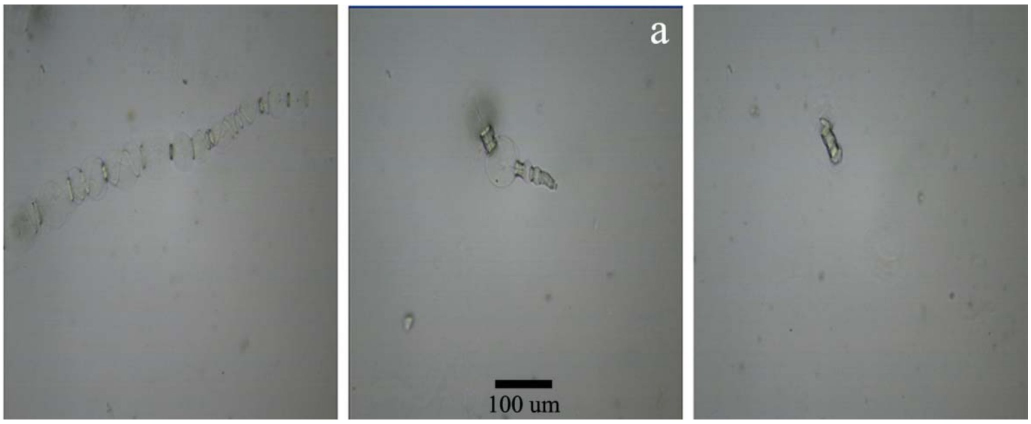


Figure 3: (a) C620, (b) W800 and (c) C1400 swollen in 8% NaOH aqueous solution at ambient temperature (optical microscopy in transmitted light)



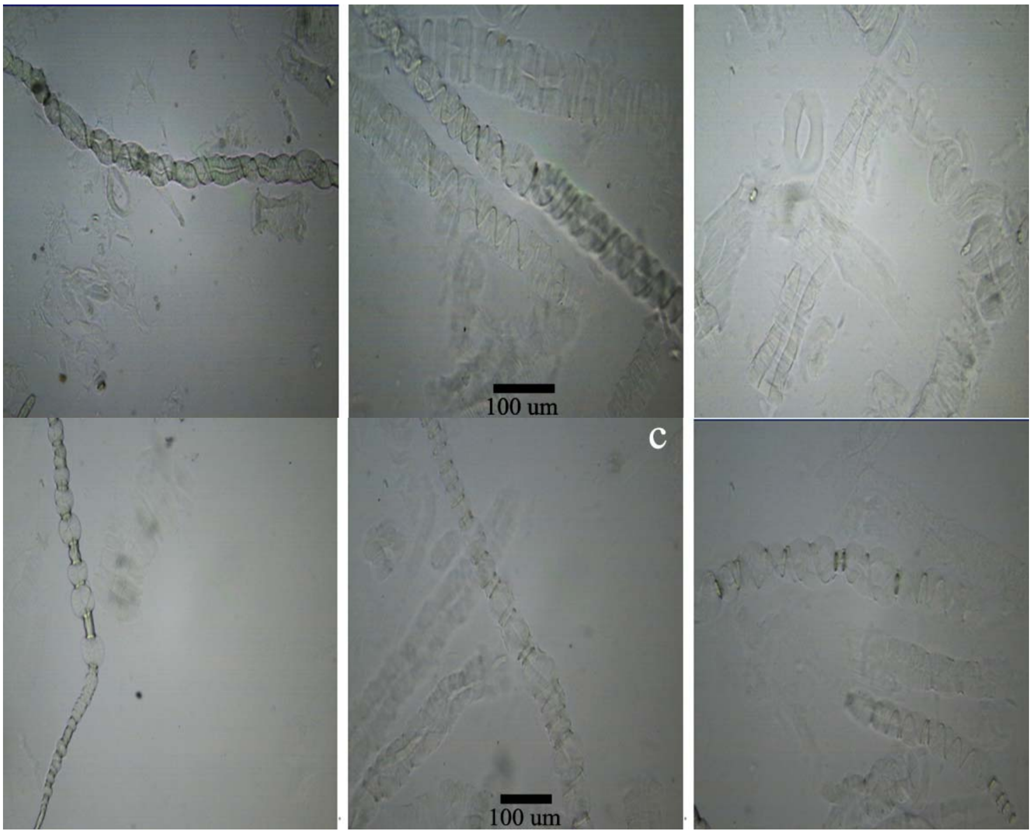


Figure 4: (a) C620, (b) W800 and (c) C1400 dissolving in 8% NaOH/6.5% thiourea aqueous solution (optical microscopy in transmitted light)

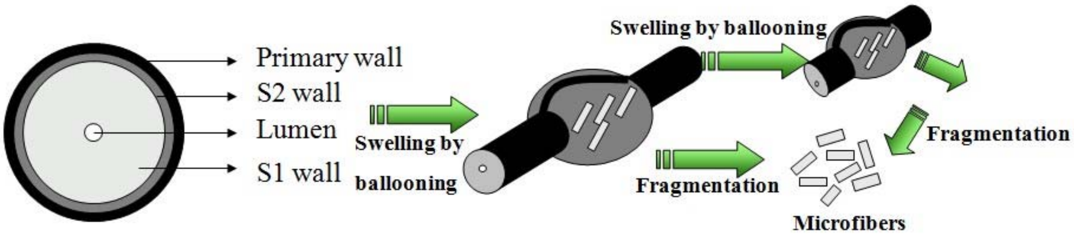


Figure 5: Schematic representation of the S2, S1 and primary wall behaviour in NaOH/thiourea aqueous solution

Swelling and dissolution of cellulose in aqueous NaOH/thiourea/urea

As soon as contacting with the NaOH/thiourea/urea aqueous solution, three kinds of cellulose fibers were directly broken along all their length, producing large rod-like pieces of cellulose fibers, which will dissolve shortly after. No visible swelling occurs before the disintegration of the fiber structure in rod-like fragments (Fig. 6). From the NMMO monohydrate (13%) to 17% of water in NMMO/water mixtures or in ($[C4mim]^+Cl^-$), the cotton fibers were also readily dissolved.[2-4,17-19] This mode of dissolution is called mode 1.

The fiber fragmentation is due to an easier penetration of the solvent in weak zones (amorphous regions or pores). A breaking in longitudinal fragments, much longer than they are wide, expresses the fact that there are long, connected paths that extend all along the fiber, deep inside the secondary wall and over quite long distances, where the solvent will quickly diffuse and dissolve cellulose chains. The mechanisms of swelling and dissolution are schematically represented in Fig. 7 as a function of the solvent quality.

The dissolution process of varied cellulose in three kinds of NaOH aqueous solvent systems was summarized in Fig. 8. From this study, it can be concluded that the dissolution mechanisms are similar for wood and cotton fibers, the solvent quality driving the type of mechanism that will occur for a given fiber type.

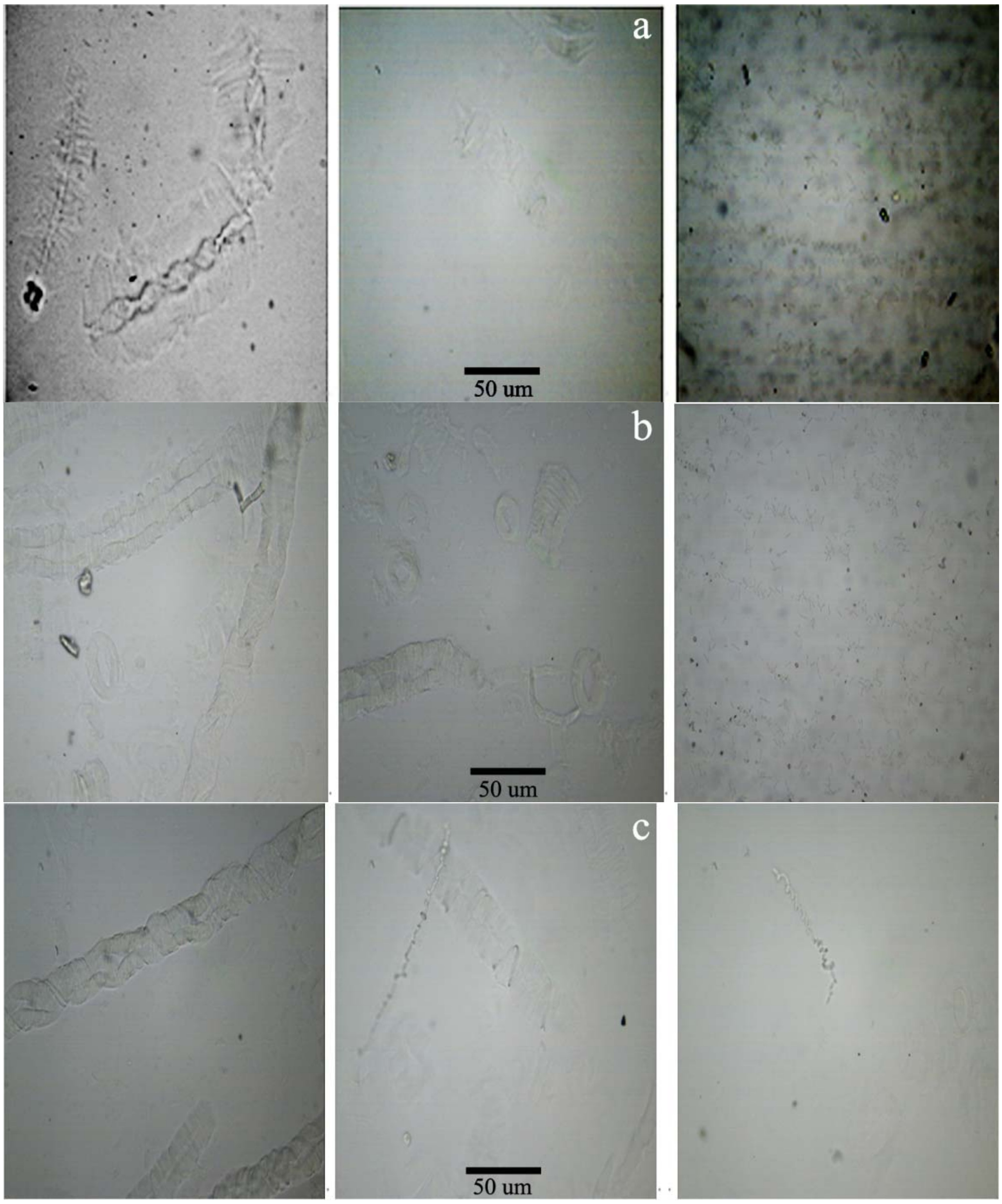


Figure 6: (a) C620, (b) W800 and (c) C1400 dissolving in 8% NaOH/8% urea/6.5% thiourea aqueous solution (optical microscopy in transmitted light)

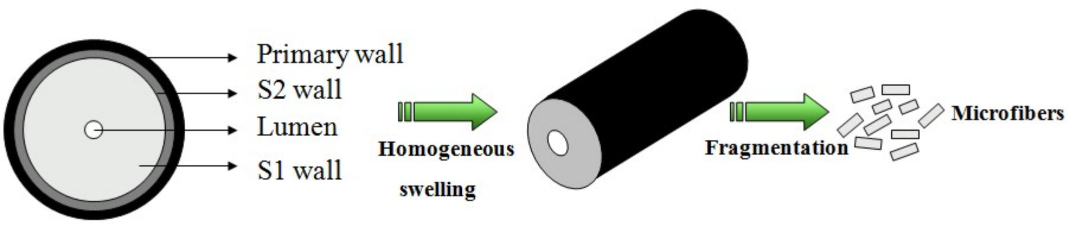


Figure 7: Schematic representation of S2, S1 and primary wall behaviour in NaOH/thiourea/urea aqueous solution

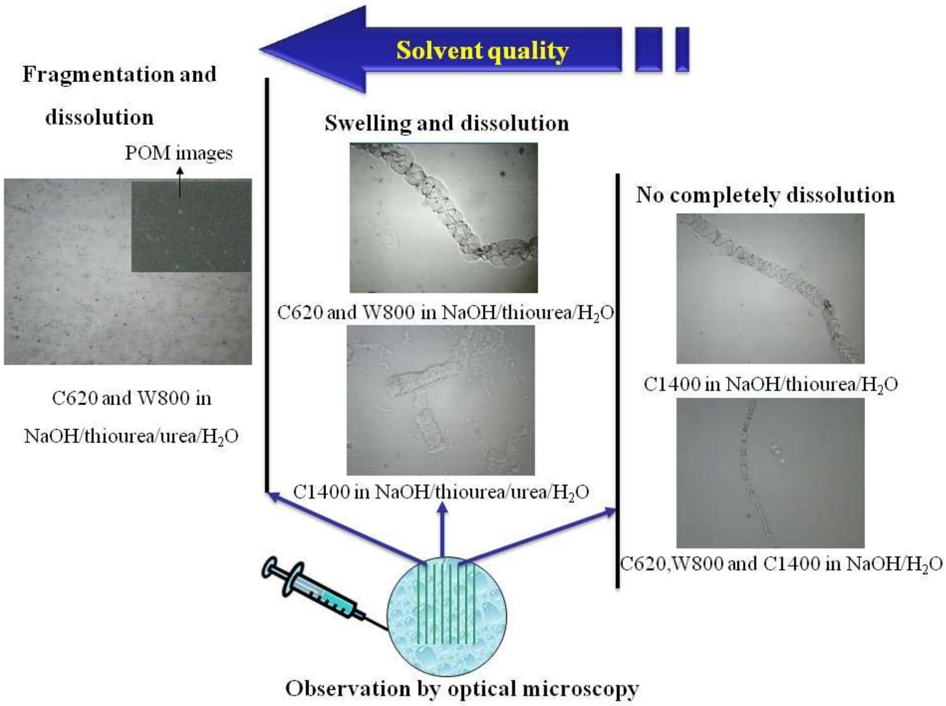


Figure 8: Swelling and dissolution mechanisms of wood and cotton fibers as a function of solvent quality

CONCLUSION

In summary, we have gained new insights into the mechanism of cellulose dissolution in alkali solution with or without urea and/or thiourea, and demonstrated its dependency on solvent composition. NaOH/thiourea/urea aqueous solution disintegrates the cellulose fiber into long needles (for all three cellulose pulps) that are then dissolved. The NaOH/thiourea aqueous solution first swells the fiber into balloons, which may be dissolved completely (cotton linter and spruce wood) or not dissolved. NaOH/H_2O can swell homogeneously the fibers without dissolution (for all three cellulose pulps). So it can be concluded that the swelling and dissolution mechanisms of cellulose fiber are strongly influenced by the solvent quality and NaOH/thiourea/urea aqueous solution is the best solvent of the three kinds of NaOH aqueous solutions.

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