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Swelling and Dissolution of Cellulose Part II: Free Floating Cotton and Wood Fibres in NaOH–Water–Additives Systems

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Summary: The swelling and dissolution mechanisms of native cotton and wood cellulose fibres in NaOH–water are studied. The cellulose fibres exhibit a heterogeneous swelling by ballooning in the best dissolving conditions (−5 °C, 7.6% of NaOH). This corresponds to the mode 3 of the swelling-dissolution (see companion paper). In this region of the mixture phase diagram, cellulose is only dissolved inside the balloons. A lot of insoluble parts are present. Increasing the temperature and/or the content of NaOH decreases the quality of the solvent. In this case, the cellulose fibres do not show ballooning, but only a homogeneous swelling (mode 4). Three components are tested as additives: urea, zinc oxide and *N*-methylmorpholine–*N*–oxide (NMMO). The swelling and dissolution mechanisms in NaOH-water and NaOH–water–additives stay the same. Adding urea to NaOH-water (−5 °C, 7.6% of NaOH) gives the same ballooning mechanisms, but with a larger expansion of the balloons, indicating that the solvent is better. Zinc oxide does not increase the expansion of the balloons, but the kinetics of swelling is faster. NMMO acts as a dissolution inhibitor.

Keywords: cellulose; cotton; dissolution; sodium hydroxide; swelling; urea; zinc oxide

Introduction

As the most important skeletal component in plants, cellulose is an almost inexhaustible polymeric raw material with fascinating structure and properties. Formed by the repeated connection of D-glucose building blocks, the highly functionalized, linear stiff–chain homopolymer is characterised by its chirality, biodegradability, broad chemical modifying capacity, and its formation of versatile semi-crystalline fibre morphology. Cellulose does not melt before thermal degradation because of strong intra- and intermolecular hydrogen bonding. In order to fulfil the various demands for its industrial use, it is often modified by physical, chemical, enzymatic, or genetic means. Modification leads to changes in the solubility, properties and behaviour of the polymer.[1]

It is generally admitted that cellulose is difficult to dissolve due to a tight array of inter and intra hydrogen bonds that are hard to break to free individual cellulose chains. For this reason, cellulose needs to be "activated" or "accessible" to be dissolved, even if these notions are covering different mechanisms. It is usually stated that cellulose crystals are difficult to dissolve, being a limiting point for dissolution. For many decades, the manufacture of cotton and wood celluloses in the form of fibres and film has been based on dissolution. These last decades, there has been an intensive search for new solvents being environmentally friendly and able to produce new materials, opening new markets

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for cellulosic products. Among the many aqueous and non aqueous cellulose solvent systems reported in the past three decades, only *N*-methylmorpholine–*N*–oxide (NMMO) has been successful for the production of regenerated cellulose textile fibres.

In the first paper of this series[2], it was shown that the dissolution of cellulose fibres in mixtures of NMMO and water is complex, depending on the quality of the solvent. Five modes of dissolution were identified:

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

In order to assess the universality of this classification, another aqueous solvent has been studied. The mixture of NaOH and water was chosen due to its strong potential for commercial use, despite the reported difficulties to dissolve cellulose. The interactions between cellulose and NaOH has been the subject of numerous studies and publications after the discovery of Mercer in 1851 that, under specific conditions, the properties of cotton can be drastically improved after a dipping in an NaOH-water mixture.[3] It was first recognised by Sobue[4] that there exists specific interactions between cellulose and NaOH-water in a limited range of NaOH concentration (from 7 to 9%) and temperature (from –7 to –3 °C). The result of dipping cellulose in this region of the NaOH-water phase diagram was called cellulose Q region.[4–7] In the 1980's, Japanese scientists [5, 8–11] found that cellulose can be dissolved in the Q region and even processed. In 1984, Kamide and his co-workers[5] discovered that cellulose regenerated from cuprammonium cellulose solution in aqueous sulphuric acid, after partially and slowly evaporating ammonia from the cast solution in the air, could be dissolved completely in aqueous hydroxide within a limited range of alkaline concentration. Yamashiki and his co-workers[8–9] succeeded in preparing alkali-soluble steam exploded cellulose with cellulose I crystal form of cellulose I. Although the range for reaching a complete solution of cellulose is limited (i.e. aqueous NaOH between 8 and 9 wt% at 4°), these cellulose samples are defined as "alkali-soluble" celluloses. Kamide[10] established for alkali-soluble regenerated cellulose some empirical relations between the solubility towards aqueous NaOH with a concentration between 8 and 9% and the degree of breakdown of the intramolecular hydrogen bonds at C_3 originally existing in soluble natural cellulose. Further on, Kamide[11] showed by using NMR that cellulose is dissolved without any chemical reaction with alkali in aqueous alkaline solution.

More recently, there was a strong increase of research to find ways to solve the dissolution difficulties and reach an acceptable solubility state, compatible with processing. An extensive study on the dissolution of cellulose using a novel solvent, namely NaOH/urea, or NaOH/thiourea aqueous solution has been carried out.[12–16] These solvents are reported to have a strong power to dissolve cotton linters and other natural cellulose, showing significant advantages including non – pollution, simple and safe dissolution procedure. The authors showed that a moderate addition of urea to the NaOH solution significantly improved the solubility of cellulose. They suggest that NaOH (6%) – urea (4%) aqueous solution (w/w) or thiourea is a new and cheap solvent class of cellulose, having strong potential applications. For example, novel microporous membranes from cellulose in NaOH/thiourea aqueous solution were obtained by coagulation with ammonium sulphate aqueous solution. The mean pore size and water permeability of the membranes are significantly larger than those from viscose and cuprammonium rayon process as well as NaOH/urea aqueous solution.

A thermodynamic study has been carried out these last years in our laboratory. The latest results [17–18] show that microcrystalline cellulose can be fully dissolved in the Q region. NaOH-water has a eutectic behaviour in this region, with a eutectic mixture melting at –33 °C. Addition of cellulose decreases the capability of forming the eutectic mixture without changing the amount of free water formed. From this finding, it was possible to deduce that the cellulose chains interact with NaOH hydrates: when $C_{cell}(\%)/C_{NaOH}(\%) > 0.5$, four NaOH are linked to each anhydroglucose corresponds to the limit of cellulose dissolution. Thus, for microcrystalline cellulose, the maximum concentration of cellulose by weight is equal to the amount of NaOH in the solvent mixture (i.e. for a 8%NaOH-water mixture, the maximum cellulose concentration will be 8%). It was also shown[19] that cellulose of high DP is not easily dissolvable. A lot of insoluble parts are present in the solution. In order to increase the solvent power of NaOH-water, additives have been searched. Among the ones tried, ZnO[20–21], urea and thiourea[12–16] seem to have some efficiency.

Fink[16] have reported investigations on the activation of cellulose by mixed solutions of caustic soda and urea. The concentration of NaOH was varied in a range from 0 to 8% and the urea concentration in a range from 15% to 40% at ambient temperature and –25 °C. The results obtained by ^{13}C-CP/MAS-NMR show that the cellulose activation the NaOH concentration of the caustic soda could be remarkably improved by adding urea. The spectra of the samples treated with urea containing lye is similar, but not identical, to the spectra of the sodium celluloses I or II, suggesting a specific urea-NaOH–cellulose complex. This complex is also formed by treating sodium cellulose I with concentrated urea solutions.

The effect of urea has also been understood as a breaking of the clustered water structure enhancing the content of free monomolecular water with cellulose, promoting swelling and dissolution of the polymer. The increase in solubility by lowering the temperature of the system is in agreement with an exothermic heat of dissolution, and has been investigated thoroughly in recent years with regards to a possible fibre spinning from cellulose – NaOH solutions at low temperatures.[22] Zinc oxide shows some efficiency for delaying gelation. Addition of zinc oxide was supposed to lead to an in-situ formation of a zincate complex facilitating dissolution of cellulose chains up to a DP of about 200, even at room temperature.

The purpose of this paper is to show that the dissolution of cellulose in NaOH-water can be understood with the help of the results obtained in NMMO-water. In particular, we will study the way cellulose dissolves, its importance for a possible use as a commercial solvent, and the influence of the addition of ZnO and urea, known to increase the solubility. Another additive (NMMO), decreasing the solvent power, has also been used for the sake of comparison.

Experimental Part

Cellulose Samples

Three native fibres, one bleached cotton and two wood fibres, Buckeye VFC (pine wood pulp obtained after a treatment by vapour hydrolysis, the cooking having occurred in a sodium sulfite and soda solution) and Borregaard VHF (fir tree pulp obtained by an acid process with calcium bisulfite) have been used. The characteristics of the samples investigated are given in Table 1. The crystallinity is measured by Fourier transform infrared spectrometry.[23] The values of Mn, Mw or Mz are determined by gel permeation chromatography (GPC).

Table 1.
Properties of the Cellulose Samples.

	Bleached cotton	Buckeye VFC	Borregaard VHF
Crystallinity (%)	55	46	43
Mn (* 1000) (g/mol)	262.9	63.9	152.6
Mw (*1000) (g/mol)	606.3	121.1	766.7
Mz (* 1000) (g/mol)	998.4	215.2	1600.5
w ($DP < 50$)	0.1	0.3	0.3
w ($DP < 200$)	1.1	9.3	4.7
w ($DP > 2000$)	68.1	4.7	63.1

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 7.6 or 15% (in weight) of NaOH. The NaOH powder comes from Fisher and is pure to about 97%. Three types of mixtures containing additives were prepared with 7.6%NaOH-water:

- urea: mixtures with urea (Fisher) were prepared with the following composition (w/w): NaOH (7.6%), urea (12%), water (80.4%).
- N-methylmorpholine-*N*-oxide (NMMO): NMMO with 3% water (w/w) was obtained from Sigma Aldrich (powder). Two mixtures (in w/w) with NMMO as an additive were tested: NaOH (7.6%), NMMO (2%), water (90.4%) and NaOH (7.6%), NMMO (10%), water (82.4%).
- zinc oxide (ZnO): this product (powder pure at 98%) is supplied by Prolabo. The composition (w/w) is NaOH (7.6%), water (90.9%) and ZnO (1.5%).

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. The procedure is as described in companion paper.[2]

The swelling and dissolution of cellulose fibres were observed by optical microscopy with a METALLUX 3 (LEITZ), in transmission mode. The optical microscopy is equipped with a LINKAM TMS 91 cooling stage.

The swelling and dissolution experiments were performed between $-10\,^{\circ}C$ and $+5\,^{\circ}C$.

Studied Parameters

As was seen before[2], cotton and wood cellulose fibres can swell and dissolve with different mechanisms. The studied parameters are the same than those describing in the companion paper.[2]

Results and Discussion

The swelling and dissolution of wood and cotton fibres in various mixtures based on 7.6 or 15% NaOH-water are described below. As it will be evident, these NaOH-water mixtures, with or without additives, are not very good solvents for cellulose. They are unable to dissolve completely the cellulose fibre. This is what is causing difficulties for using them in commercial applications.

Swelling and Dissolution in 7.6% NaOH-water at $-5\,^{\circ}C$

According to literature[4], the best dissolution conditions are obtained at a temperature of $-5\,^{\circ}C$ for solvents having 5–10% of NaOH in water. A concentration of.7.6% of NaOH at $-5\,^{\circ}C$ was chosen as the standard condition for dissolution. The three studied native fibres (bleached cotton, Buckeye, Borregaard) are strongly swelling in this solvent through a ballooning

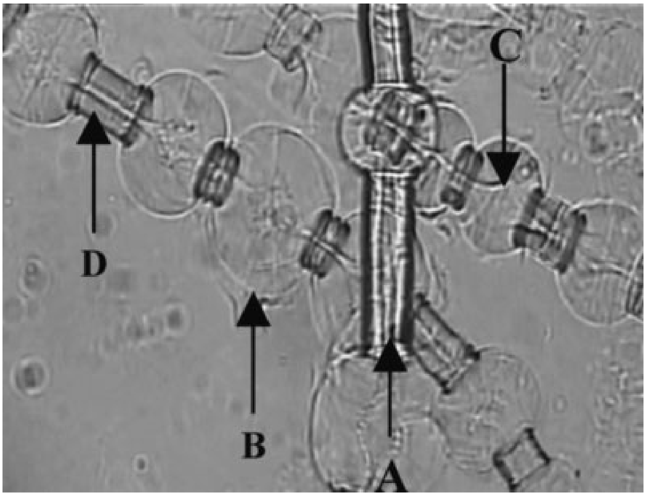


Figure 1.
Swelling by ballooning in NaOH–water solutions (Borregaard fibre swollen in 7.6% NaOH–water, T = −5 °C, optical microscopy in transmitted light): a non-swollen fibre (A), a balloon (B) surrounded by a membrane (C) and a section (D).

mechanism. An example of such ballooning is seen in Figure 1. The fibres, having a rather regular diameter in a dry state, start to swell at given isolated points along the fibre. The zones where the swelling starts increase their size, which leads to the appearance of the balloons seen in Figure 1. These balloons are growing until they reach a maximum diameter (called D_{sm}) from which a stable situation is attained. Without shaking the fibres, the fibres and the balloons are staying as they are. This is the case of the mode 3 of swelling-dissolution that was described for NMMO-water.[2] As in the case of balloons seen in NMMO-water solvents, we can distinguish the same three different zones within one fibre during the ballooning (seen in Figure 1). These various zones are non-swollen fibre parts (A), balloons (B) surrounded by a membrane (C) and non-swollen sections (D). An non-swollen fibre (A) is the part of one fibre, or a full fibre, that did not start yet the swelling process, but that will swell later as balloons.

All these features are exactly similar to what was seen for NMMO-water in some concentration range of water. At some random intervals along the cellulose fibres, localised zones of about the same length L_b start to swell. The zones between the balloons seem to keep their original diameter. The non-swollen sections between balloons do not swell. The balloons have the aspect of a beaded structure. The balloons do not appear at the same time along cotton or wood fibres and have various growing speeds. The balloons are not spherical, their size is larger perpendicularly than along the fibre and they do not have symmetry of revolution, having a complicated shape around the fibre axis. The repartition of balloons seems to be made at random. In the case of bleached cotton, the balloons distribution is more or less regular. Each balloon is separated by an non-swollen section which length is between 10 and 20 μm. In the case of wood fibres (Borregaard and Buckeye), the swollen zones are distributed per group (between 2 and 6 balloons per group).

Helical ribbons are clearly observed at the balloons surface (Figure 2). This helical membrane can be seen as a line surrounded the balloons from one non-swollen section to another. This helical membrane surrounding the balloons has always been observed with the NMMO–water mixtures[2], when the swelling occurs by ballooning. It seems to be a general feature,

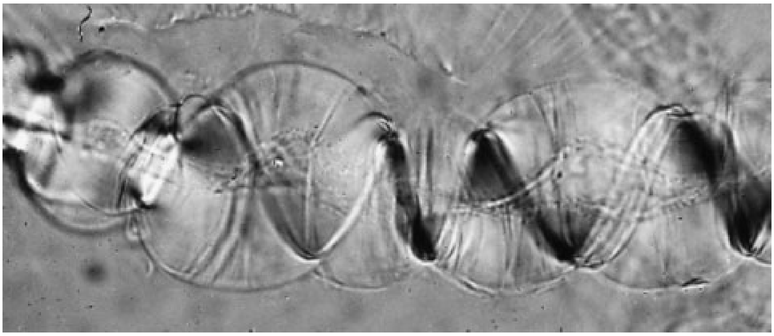


Figure 2.
Helical ribbons at the balloons surface (Buckeye fibre swollen in 7.6% NaOH–water, T = −5 °C, optical microscopy with transmitted light).

also observed by many observers.[24] The influence and role of this helical feature will be examined in a forthcoming paper.

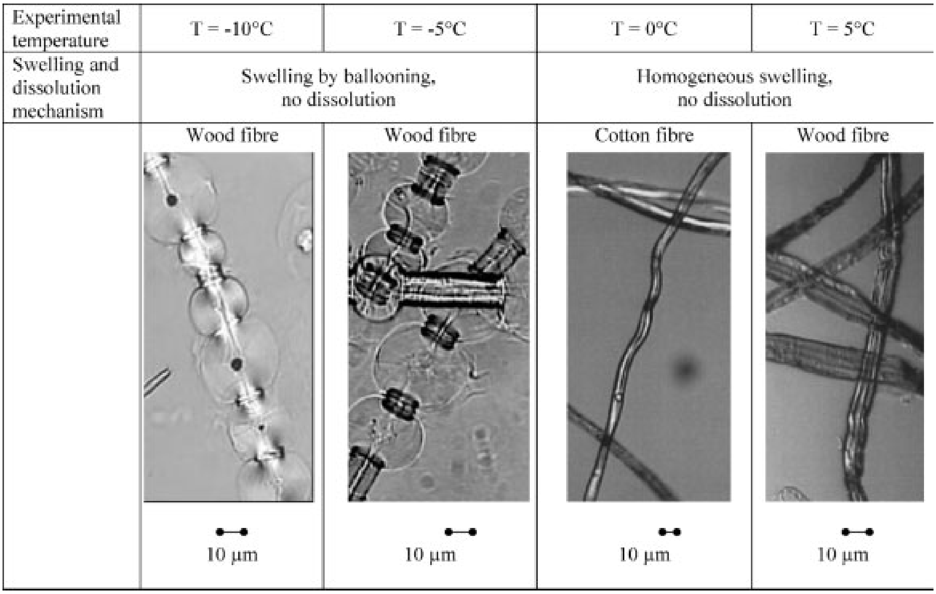
The swelling mechanism of cellulose fibres in NaOH-water at 7.6% and –5 °C shows that the solvent is not very good. This is what has been already found. Only cellulose of low DP like microcrystalline cellulose can be nearly fully dissolves, with very few insoluble particles present. As soon as cellulose fibres of larger DP and having kept their original structure are put in contact with this solvent, it behaves in the mode 3 of swelling-dissolution. Only cellulose present in the balloons is dissolved. The membrane and the non-swollen sections cannot dissolve. The balloons never burst since the osmotic pressure inside the balloons is smaller than the breaking resistance of the membrane. When mechanically broken, the inside of the balloon can flow out and it was shown to be a cellulose solution.[25] This is indeed what is occurring when cellulose is mixed in a mechanical mixer. Cellulose solutions prepared in this way have a lot of insoluble particles that are easy to recognise as remains of membranes and non-swollen sections.

NaOH Solution at 7.6% at Various Temperatures

The aim is to explore the swelling and dissolution mechanisms of native cellulose in NaOH solution at 7.6% at different temperatures, from −10 °C to 5 °C. Two main domains of temperature (Figure 3) are found, looking at the observed mechanisms: one from −10 to –5 °C, another one from 0 to 5 °C.

At –10 °C and –5 °C, cotton and wood fibres swell heterogeneously by ballooning and the total dissolution of the fibres is not reached. Decreasing the temperature does not influence the swelling and dissolution mechanism, still in mode 3. However, $D_{sm}/D_{i,}$ expressing the extent of swelling of the balloon, is lower at −10 °C than at −5 °C. D_{sm}/D_i is a good indicator of the quality of the solvent, since the better the solvent is, the larger the osmotic pressure is and thus the larger the balloons are. Table 2 gives the values of D_{sm}/D_i for various solvent systems: NMMO-water at 20% of water (solvent in mode 2, which can be considered as a reference because the balloons reach their maximum size at burst), NMMO-water at 30% of water which is in mode 3 (the maximum size of the balloons is smaller that the size at which they will explode), NaOH–water at 7.6% at −5 °C, and NaOH–water at 7.6% at –10 °C. The D_{sm}/D_i value of cotton and wood fibres in NaOH–water system at –5 and 10 °C are lower than the values obtained in mode 2 (NMMO-water at 20% of water) and in the same range as the values for NMMO-water at 30% (mode 3).

This is fully in agreement with the idea that the quality of the solvent decreases from mode 2 to mode 3 and that the



Experimental temperature	T = -10°C	T = -5°C	T = 0°C	T = 5°C
Swelling and dissolution mechanism	Swelling by ballooning, no dissolution		Homogeneous swelling, no dissolution	
	Wood fibre 10 µm	Wood fibre 10 µm	Cotton fibre 10 µm	Wood fibre 10 µm

Figure 3.
Swelling and dissolution mechanisms in NaOH-water solutions at 7.6%, at various temperatures (−10 °C, −5 °C, 0 °C and 5 °C).

maximum expansion of the balloons is a good indicator of the quality of a solvent. The value D_{sm}/D_i of cotton and wood fibres in NaOH–water system at −10 °C are slightly lower than the values obtained at −5 °C. This seems to indicate that decreasing the temperature below −5 °C is decreasing the quality of the solvent. This is in agreement with the authors that defined this small Q range of dissolution.[4,10,11]

At 0 °C and 5 °C, cotton and wood fibres swell homogeneously as seen in Figure 3. The value D_{sm}/D_i varies between 1.3 and 1.5, which is about the value found in pure water. 7.6%NaOH-water solutions at 0 °C and 5 °C cannot dissolve cellulose.

These experiments at different temperatures confirm that the temperature dissolution window is very narrow. What will be explored in the following paragraph is the case where the NaOH concentration is increased.

NaOH Solution at 15% at Various Temperatures

Outside the Q dissolution region, it is well known that NaOH has a dramatic effect on cellulose. When increasing the NaOH concentration, the area of the phase diagram where mercerisation occurs is reached (between 10 to 30% NaOH-water mixtures, at 18–20 °C. We will explore the behaviour

Table 2.
Final Over Initial Diameter Ratio in the Case of Native Fibres Swollen in NaOH–Water Solutions at 7.6%, at Various Temperature (−10 °C and −5 °C), in NMMO – Water (at 20% and 30% of Water, T = 90 °C).

	Bleached cotton	Borregaard	Buckeye
Crystallinity	55	43	46
D_{sm}/D_i in NaOH (7.6%)–water, $T = -5\,^{\circ}C$	3.2	3.6	3.6
D_{sm}/D_i in NaOH (7.6%)–water, $T = -10\,^{\circ}C$	3.0	3.5	3.4
D_{sm}/D_i in NMMO–water (20% of water), $T = 90\,^{\circ}C$	4.8	5.9	5.2
D_{sm}/D_i in NMMO–water (30% of water), $T = 90\,^{\circ}C$	3.9	4.1	4.1

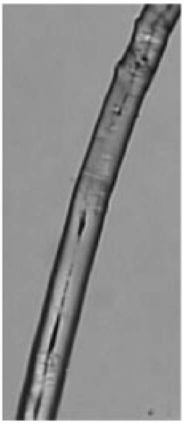
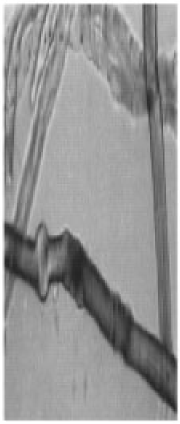
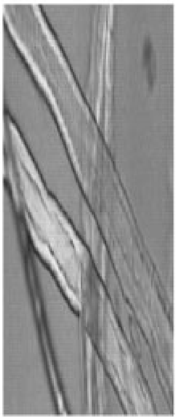
Experimental temperature	T = -10°C	T = -5°C	T = 0°C	T = 5°C
Swelling and dissolution mechanism	Homogeneous swelling, no dissolution	Few balloons appear + homogeneous swelling, no dissolution	Homogeneous swelling, no dissolution	Homogeneous swelling (low), no dissolution
15 µm	Wood fibre 	Wood fibre 	Wood fibre 	Cotton fibre 

Figure 4.
Swelling and dissolution mechanisms in NaOH-water solutions at 15% at various temperatures (−10 °C, −5 °C, 0 °C and 5 °C).

for a NaOH concentration of 15% at three temperatures, −5 °C, 0 °C and +5 °C.

At 0 °C and +5 °C, the cotton and wood fibres swell homogeneously, in mode 4 (Figure 4). The swelling is larger at 0 °C than at 5 °C, as shown by the values D_{sm}/D_i (Table 3). The swelling is significant at 0 °C since D_{sm}/D_i is rather large (2.2–2.6). At +5 °C, the NaOH solution at 15% is a very poor solvent with D_{sm}/D_i values are similar to the NaOH solution at 7.6% at +5 °C.

Cellulose in 15% NaOH-water at –5 °C shows in most of the cases a homogeneous swelling of mode 4, with rather large D_{sm}/D_i values. A very interesting point shown on Figure 4 is the presence of few balloons at this temperature. This is not always seen. It could mean that in some cases, cellulose may dissolve inside the balloons, as in mode 2.

NaOH–Water–Urea System

The three native fibres have been tested at −5 °C with NaOH (7.6%)–urea (12%). The swelling still occurs by ballooning as in the case without urea. Non-swollen sections, balloons and its membrane are seen by optical microscopy (Figure 5). The balloons appear more rapidly with the presence of urea and the final to initial diameter D_{sm}/D_i ratio values are greater to those obtained in the same conditions with pure NaOH–water solutions (Table 4). These features are a clear indication that the addition of

Table 3.
Final Over Initial Diameter Ratio in the Case of Native Fibres Swollen in NaOH–Water Solutions at 7.6% and 15% (T = −5 °C, 0 °C or 5 °C), in NMMO–Water (at Content of Water > 35%, T = 90 °C).

	NaOH at 7.6% T = −10 °C	NaOH at 15% T = +5 °C	NaOH at 15% T = 0 °C	NaOH at 15% T = −5 °C	NaOH at 15% T = −10 °C	NMMO–water (water content > 35%)
D_{sm}/D_i for cotton and wood fibres	1.3–1.5	1.3–1.6	2.2–2.6	2.2–2.6	1.8–2.8	2.3–2.6

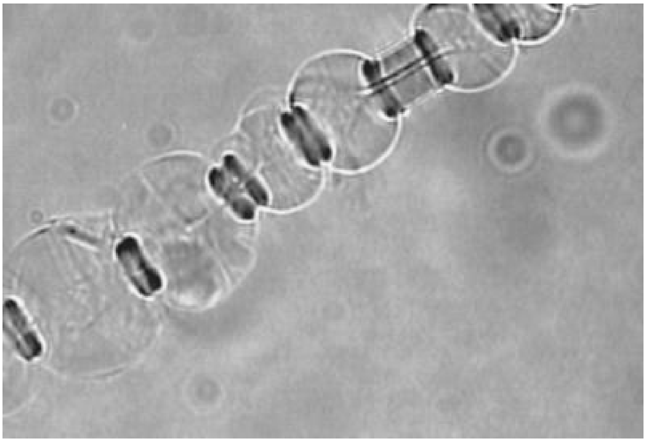


Figure 5.
Swelling by ballooning in NaOH–water-urea solutions (Buckeye fibre swollen in NaOH (7.6%)–water–urea (12%) solution, T = −5 °C, optical microscopy in transmitted light).

urea in NaOH–water increases the quality of the solvent.

NaOH–Water–ZnO System

The studied system is composed by NaOH at 7.6%, water at 90.9% and ZnO at 1.5% (w/w). As seen on the Figure 6, the cotton and wood fibres swell by ballooning. The helical membrane surrounding the balloons is clearly observed on this picture. ZnO is increasing the swelling kinetic. The balloons appear as soon as the solvent is in contact with the fibres. However, the balloon expansion decreases with the addition of ZnO with values of D_{sm}/D_i being lower than without ZnO (Table 4). Such behaviour should indicate that the solvent quality is decreased with the addition of ZnO, a feature which seems in contradiction with the faster swelling kinetics.

NaOH–Water–NMMO System

Two amounts of NMMO were added to NaOH–water solution: 2 and 10% (w/w). In the case of NaOH (7.6%)–water–NMMO (2%); the fibres swell by ballooning (Figure 7). The balloons are always surrounded by a helical membrane and separated by non-swollen sections. However the balloon formation is very slow. The values D_{sm}/D_i is strongly decreased by adding only 2% of NMMO in NaOH–water solution (Table 4). Adding 10% of NMMO has a very strong effect on NaOH–water mixtures: the fibres show a very weak swelling (Figure 8), the mean diameter increasing by less than 10%. Most probably,

Table 4.
Final Over Initial Diameter Ratio of Native Fibres Swollen in NaOH (7.6%)–Water Mixtures with or Without Additives (urea, ZnO or NMMO).

	Bleached cotton	Borregaard	Buckeye
Crystallinity	55	43	46
D_{sm}/D_i in NaOH (7.6%)–water, T = −5 °C	3.2	3.6	3.6
D_{sm}/D_i in NaOH (7.6%)–water–urea (12%), T = −5 °C	3.9	3.7	3.7
D_{sm}/D_i in NaOH (7.6%)–water–ZnO (1.5%), T = −5 °C	2.8	2.8	2.3
D_{sm}/D_i in NaOH (7.6%)–water–NMMO (2%), T = −5 °C	1.6	2.3	2.2

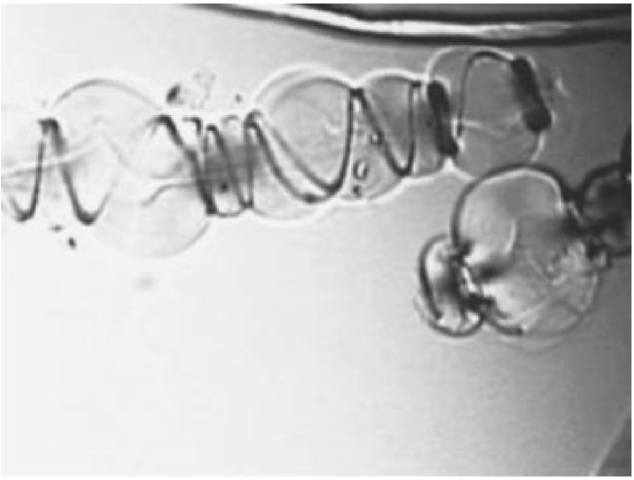


Figure 6.
Swelling by ballooning in NaOH–water-ZnO solutions (Borregard fibre swollen in NaOH (7.6%)–water–ZnO (1.5%) solution, T = −5 °C, optical microscopy in transmitted light).

the sodium hydroxide hydrates that are acting in dissolving cellulose are not anymore formed in the presence of NMMO that is itself attracting strongly water.

Conclusions

Observing the way a cellulose fibre is swelling and/or dissolving is a good way to assess the quality of a solvent. The observations performed with NMMO-water showed that five modes can be identified. Two of these modes (mode 3: ballooning without total dissolution, mode 4: homogeneous swelling) can be seen with the different NaOH-water systems.

The results confirm that the best dissolution conditions are obtained in a narrow range of temperatures and concentrations (around −5 °C and with 7–9% of NaOH). In these conditions, a cellulose fibre swells by ballooning, with cellulose

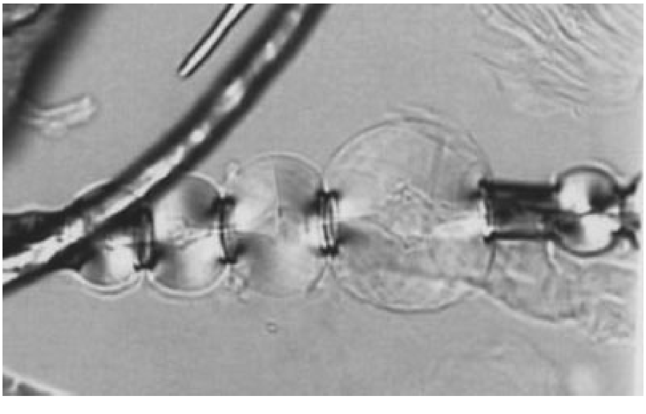


Figure 7.
Swelling by ballooning in NaOH–water-NMMO solutions (Buckeye fibre swollen in NaOH (7.6%)–water–NMMO (2%) solution, T = −5 °C, optical microscopy in transmitted light).

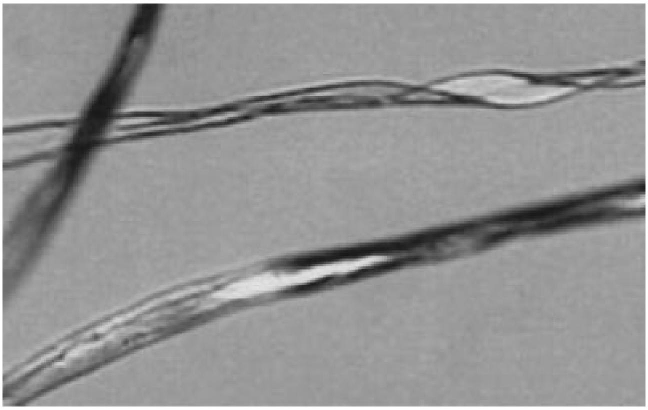


Figure 8.

Swelling by ballooning in NaOH–water-NMMO solutions (Cotton fibre swollen in NaOH (7.6%)–water–NMMO (10%) solution, T = −5 °C, optical microscopy in transmitted light).

being dissolved inside the balloons. The morphology of the fibre swollen in NaOH-water and their evolution mechanisms are similar to the case of NMMO-water, showing the universality of the classification by these five modes (this will be also shown for non aqueous solvents, for other types of fibres and for some cellulose derivatives, in forthcoming papers).

When increasing temperature, the solvent quality of 7.6% NaOH-water decreases strongly. Adding urea is clearly increasing the quality of the solvent, with ballooning occurring faster and with a larger expansion. Adding ZnO gives a mixed result, with balloons being smaller, which should indicate a smaller osmotic pressure inside them, and thus a worse

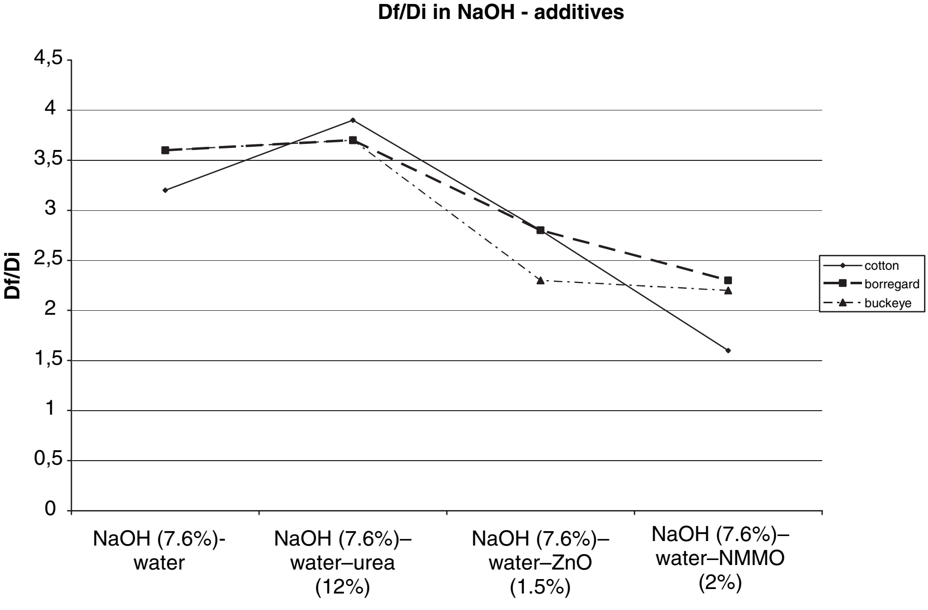


Figure 9.

Values D_f/D_i for cotton, Borregaard or Buckeye fibres swollen in NaOH–water systems and NaOH–water–additives systems (additives = urea, ZnO or NMMO).

Table 5.
Comparison of the Additives Influence (urea, ZnO, and NMMO) on NaOH–Water System.

	Urea (12%)	ZnO (1.5%)	NMMO (2%)
Balloons size	+	–	–
Kinetic of balloons formation	+	+	–

quality solvent, but with a swelling kinetic being faster, which should indicate a better solvent.

Adding NMMO strongly decreases the quality of the NaOH-water solvent. Adding more than 10% (w/w) of NMMO on NaOH-water systems seems to prevent cellulose fibres from interacting with the solvent.

Figure 9 summarizes the results concerning the balloon size and the kinetics of balloon formation. A comparison between the three additives on these two points is given in Table 5.

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