

Swelling and dissolution of cellulose. Part IV: Free floating cotton and wood fibres in ionic liquids

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Abstract

The objective of this paper is to investigate if the swelling and dissolution mechanisms found for aqueous solvents are valid for non-aqueous ones. Three different ionic liquids were used and the swelling and dissolution mechanisms were investigated by optical methods. Native and enzymatically treated cellulose fibres (cotton and wood fibres) are dipped into three ionic liquids (1-*N*-butyl-3-methylimidazolium chloride ([C4mim]⁺Cl[−])/DMSO, allylmethylimidazolium bromide ([Amim]⁺Br[−]) and butenylmethylimidazolium bromide ([Bmim]⁺Br[−]). ([C4mim]⁺Cl[−])/DMSO shows a swelling of cellulose by ballooning and then dissolution. ([Amim]⁺Br[−]) and ([Bmim]⁺Br[−]) show a homogeneous swelling but no dissolution. The swelling and dissolution mechanisms of cellulose in ionic liquids are similar to those observed in aqueous solvents. It indicates that the swelling and dissolution mechanisms are entirely due to the way cellulose fibres are structured, not depending on the type of solvent. The quality of the solvent is giving the type of mechanism.

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1. Introduction

Cellulose is a polydisperse linear polyglucan which forms hydrogen-bonded supramolecular structures. Cellulose is insoluble in water and a lot of common organic liquids. The growing willingness to develop new cellulosic material results from the fact that cellulose is a renewable resource, although many of the technologies currently used in cellulose processing are not environmentally desirable. For example, viscose rayon is prepared from cellulose xanthate (production over 3,000,000 tons per year) utilising carbon disulfite as both reagent and solvent. Most recently, processing using more environmentally acceptable non-

derivatizing solvents (*N*-methylmorpholine-*N*-oxide, NMMO) has been used industrially. With increasing governmental regulations restricting the use of current cellulose solvents, the need to replace them is becoming more important. Among the potential new solvents, ionic liquids have gained considerable attention. Ionic liquids (Adams, Dyson, & Taverner, 2004) are composed of an organic cation and an inorganic anion. Ionic liquids are very effective solvents for a wide variety of solutes, ranging from organic to inorganic and from small molecules to polymers. There are numerous ways in which ionic liquid can be defined, and perhaps the most widely accepted definition is: a material that is composed of ions, and has a melting point below 100 °C. The notable characteristics of ionic liquids are their thermal stability, wide liquid temperature range, and good solvating properties for various kinds of materials. Another important feature of ionic liquids is their miscibility with water or organic solvents, which can be tuned through side chain lengths on the cation and choice of

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anion. Furthermore, they can be functionalised to act as acids, bases or ligands. Because of their properties, ionic liquids attract great attention in many fields, including organic, chemistry, electrochemistry, and engineering. In addition, their non-volatility results in a low impact on the environment and human health.

Graenacher (Graenacher C., 1934) first suggested in 1934 that molten *N*-ethylpyridinium chloride in the presence of nitrogen-containing bases could be used to dissolve cellulose. However this seems to have been treated as a novelty of little practical value since the molten salt system was, at this time, somewhat esoteric and has a relatively high melting point (118 °C). The availability of a wide and varied range of ionic liquids, coupled with the current understanding of their solvent properties, should allow the tailoring and control of dissolution, processing and the final properties. The ability of ionic liquids to dissolve cellulose fibres could be explained by studying the behaviour of non-derivatizing solvents for cellulose (Swatloski, Spear, Holbrey, & Rogers, 2002). These cellulose solvents affect dissolution by disrupting and breaking the intermolecular hydrogen-bonding network. For *N,N*-dimethylacetamide (DMAC)/LiCl solvents, complex of lithium ions with DMAC mobilises chloride ions which interact with cellulose hydroxyl groups. In a typical 10 wt% LiCl/DMAC solution, free chloride ion concentration is about 6.7 mol%. In contrast, ([C4mim]+Cl[−]), which is an ionic liquid, has a chloride concentration almost three times higher, (approximately 20 mol%). In all these cases, the chloride ions are non-hydrated. The assumption is that the high chloride concentration and activity in ([C4mim]+Cl[−]) is very effective in breaking the extensive hydrogen-bonding network present, thus bringing a much quicker dissolution, and dissolving higher concentration of cellulose than the traditional solvent systems. The ionic liquids can also be applied as reaction media for the synthesis of cellulose derivatives like carboxymethyl cellulose and cellulose acetate (Barthel & Heinze, 2006; Heinze, Schwikal, & Barthel, 2005; Schluter, Schmauder, Dorn, & Heinze, 2006).

As we have seen in the preceding papers of this series (Cuissinat & Navard, 2006a, 2006b), five modes describing the behaviour cellulose fibres dipped into NMMO–water or NaOH–water agents have been identified:

- Mode 1: fast dissolution by disintegration into fragments
- Mode 2: large swelling by ballooning, and dissolution
- Mode 3: large swelling by ballooning, and no dissolution
- Mode 4: homogeneous swelling, and no dissolution
- Mode 5: no swelling, and no dissolution

These modes reflect the quality of the solvents, decreasing from mode 1 to mode 5. Very good solvents disintegrate the cellulose fibre into long needles (mode 1) that are then dissolve. Moderate to bad solvent swells first the fibre into balloons that are then bursting (mod-

erate solvent quality, mode 2) or not (bad solvents as NaOH at 7.6%, mode 3). In both cases, at least part of the fibre (inside the balloons) has been dissolved. Non-solvents can either swell homogeneously the fibres without dissolution (mode 4) or not interact at all with cellulose (mode 5).

The objective of this paper is to investigate if the above five-mode description found for aqueous solvents is also valid for non-aqueous ones. This is an important piece of information for the understanding of cellulose solubility, since the mechanisms can be due either only to the structure of the cellulose fibre or to the way solvents are interacting with cellulose (in this latter case, aqueous and non-aqueous solvents should have a very different behaviour). To discriminate between these two hypotheses, three different ionic liquids will be used and the swelling and dissolution mechanisms will be investigated in the same way as described by Cuissinat & Navard, 2006a, 2006b.

2. Experimental

2.1. Samples

Three fibres, one bleached cotton and two wood fibres, Buckeye VFC (pine wood pulp obtained after a treatment by vapour hydrolysis, cooking in a sodium sulfite and soda solution) and Borregaard VHF (fir tree pulp obtained by an acid process with calcium bisulfite) were used either as received or after an enzymatic peeling treatment. When used without an enzymatic treatment, they are called untreated samples.

The enzymatic treatments were performed in the research laboratory of Lenzing AG, (Austria) to obtain cotton and wood cellulosic fibres without outer layers. The samples (bleached cotton, Borregaard and Buckeye) were treated with a mixture of cellulase and xylanase enzymes. The hypothesis is that the enzymes remove layer after layer of the fibre, peeling the primary wall first, attacking the secondary layer after. The results of Kassenbeck (1970) suggest that this peeling may not be uniform all around the fibre. Enzyme treatments were performed with a gentle shaking, leading to very low mechanical forces on the fibres. The enzymatic reaction was stopped by washing in cold water and heating 30 min at 40 °C. The extent of the peeling was characterised by the “peeling rate”, the percentage of solubilised sugars analysed in the supernatant by capillary electrophoresis per fibre weight. Nine different enzymatically treated cotton and wood fibres were prepared, with various peeling rates. We will particularly consider samples which peeling rate is around 10%. At this rate, only the primary and part of the secondary wall are put out. The characteristics of the samples having a peeling rate of around 10% are given in Table 1. Crystallinity is measured by Fourier transform infrared spectrometry (Baldinger, Moosbauer, & Sixta, 2000).

Table 1
Properties of the cellulose samples

	Bleached cotton		Buckeye VFC		Borregaard VHF	
Peeling rate (%)	0	10.00	0	9.41	0	11.26
Cristallinity (%)	55	57	46	47	43	48
Mn (*1000) (g/mol)	262.9	172.1	63.9	53.8	152.6	115.8
Mw (*1000) (g/mol)	606.3	512.3	121.1	114.1	766.7	449
Mz (*1000) (g/mol)	998.4	907.8	215.2	216.1	1600.5	1411.5

A peeling rate of 0% indicates cellulose sample without enzymatic treatment (untreated samples).

2.2. Solvent

Three ionic liquids were used:

1-*N*-butyl-3-methylimidazolium chloride, noted ([C4mim]⁺Cl[−]),

1-*N*-allyl-3-methylimidazolium bromide, noted ([Amim]⁺Br[−]),

butenylmethylimidazolium bromide, noted ([Bmim]⁺Br[−]).

The ionic liquid 1-*N*-butyl-3-methylimidazolium chloride ([C4mim]⁺Cl[−]), Mp 73 °C was employed as received from Solvent Innovation, Köln, Germany. The *N*-allyl-3-methylimidazolium bromide (noted ([Amim]⁺Br[−])), butenylmethylimidazolium bromide (noted ([Bmim]⁺Br[−])) are both room temperature ionic liquids. The melting points are 17 °C for ([Amim]⁺Br[−]) and 20 °C for ([Bmim]⁺Br[−]). Both are synthesized by Dr. Anne Stark, Institute for Technical Chemistry and Environmental Chemistry, Friedrich Schiller University of Jena. The molecular structures of ([C4mim]⁺Cl[−]), ([Amim]⁺Br[−]) and ([Bmim]⁺Br[−]) are, respectively, given in Figs. 1–3. The dissolution experiments are performed at 80 °C with ([Amim]⁺Br[−]) and ([Bmim]⁺Br[−]), at 100 °C with ([C4mim]⁺Cl[−]).

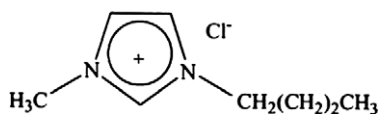


Fig. 1. Molecular of ionic liquid ([C4mim]⁺Cl[−]).

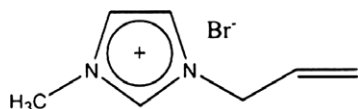


Fig. 2. Molecular structure of ionic liquid ([Amim]⁺Br[−]).

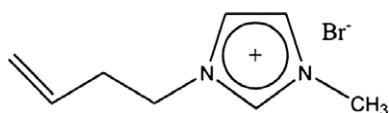


Fig. 3. Molecular structure of ionic liquid ([Bmim]⁺Br[−]).

([C4mim]⁺Cl[−]) is a very good solvent for cellulose. As a consequence, the swelling and dissolution of cellulose are very rapid. Since we were interested in varying the solvent quality, we first tried to decrease the kinetics of swelling and dissolution by adding a small amount of water. However, the presence of water in the ionic liquid was shown to significantly decrease the solubility of cellulose, presumably through competitive hydrogen-bonding to the cellulose microfibrils (Swatloski et al., 2002). When water was added to the ionic liquid at concentrations greater than 1 wt%, cellulose was no longer soluble. Adding DMSO in ([C4mim]⁺Cl[−]) slowed down the kinetics of dissolution by decreasing the ionic strength of cation and anion. The proportion in weight is ([C4mim]⁺Cl[−]) (75%) + DMSO (25%). DMSO is not a solvent for cellulose, only a swelling agent. DMSO molecules solvate the cation of the ionic liquid. As the dissolution of cellulose in ionic liquids depends on the interaction between the anion and the cation, with the hydrogen bonds at the level of cellulose structure, the solvating action of ([C4mim]⁺Cl[−]) is decreased.

2.3. Preparation

The solutions were prepared by mixing cellulose and solvent in a container made of two glass plates. No agitation was applied. About 10 fibres were placed between the two glass plates. The fibres can move freely between the two plates except that one end of the fibres was attached by adhesive tape to one plate in order to avoid the fibre to limit movement by solvent convection, which caused difficulties in optical observations. The solvent contained in a pipette was introduced by capillary forces between the two plates. Due to the method employed for studying the swelling and dissolution, the cellulose concentration between the two glass plates is not well controlled. This will not allow obtaining quantitative kinetic data to be obtained.

The swelling and dissolution of cellulose fibres were observed by transmission optical microscopy with a Metalux3 (Leitz) equipped with a Linkam TMS 91 hot stage.

3. Results and discussion

The swelling and dissolution of cotton and wood fibres in three ionic liquids, ([C4mim]⁺Cl[−]) + DMSO, ([Amim]⁺Br[−]) and ([Bmim]⁺Br[−]), is described. A com-

parison with aqueous solvents (NMMO–water mixtures, and NaOH solutions) is given. The behaviour of untreated and enzymatically treated fibres in $([C4mim]+Cl^-) + DMSO$ is described first, followed by the results with $([Amim]+Br^-)$ and $([Bmim]+Br^-)$.

3.1. Swelling and dissolution mechanism in $([C4mim]+Cl^-)$

Cotton and wood samples dissolves very quickly in $([C4mim]+Cl^-)$ at 100 °C, with a mechanism that is the one found for very good aqueous solvents, called mode 1 (Cuissinat & Navard, 2006a, 2006b).

3.2. Swelling and dissolution mechanism in $([C4mim]+Cl^-) + DMSO$

3.2.1. Cotton and wood fibres

Cotton and wood samples swell by ballooning in $([C4mim]+Cl^-) + DMSO$ system at 100 °C, before being dissolved. Dipping native cellulose fibres in an ionic liquid as $([C4mim]+Cl^-) + DMSO$ induces a swelling and dissolution mechanism defined as mode 2 (Cuissinat & Navard, 2006a, 2006b).

Native cellulose fibres start to swell in isolated points along the fibre, forming balloons. The balloons increase their size, which leads to the appearance of a beaded structure (Fig. 4). The fibre has thus a series of swollen transparent parts, of a rounded shape. The balloon diameter increase up to the point where the balloons burst.

As for the aqueous solvents (Cuissinat & Navard, 2006a, 2006b), the structure of a swelling fibre consists on several well defined zones: unswollen section fibre along a fibre

(A), unswollen part between two balloons (D), balloon (B) surrounded by a helical membrane (C), as seen in Fig. 4. Each of these zones has a specific way of swelling and dissolving. Cotton and wood fibres, in ionic liquid $([C4mim]+Cl^-) + DMSO$, are following the same sequence of the four phases leading to the full dissolution as described previously for aqueous solvents:

Phase 1: balloon formation

Phase 2: balloon bursting

Phase 3: dissolution of the unswollen sections

Phase 4: dissolution of the balloon membrane scraps

The mechanism is the same as for aqueous solvents. The outside of the fibre acts as a semi-permeable membrane, allowing the solvent to penetrate inside the fibre to dissolve cellulose. But the cellulose chains remain inside the fibre and cannot go out. This phenomenon occurs only at some zones along the fibre, called balloons. The solvent penetration increases the volume of the balloons, and expands the membrane that is holding it (phase 1). They are held by a membrane that is bursting when the expansion of the balloon reaches a certain diameter (phase 2) and the liquid cellulose solution inside flows out. After the balloon bursting, only two parts remain in the solvent agent: the unswollen sections that were between the balloons and the scraps of the membrane. The next parts to be dissolved are the unswollen sections (phase 3). No swelling occurs during the dissolution of this part, which begins at the outer surface of the unswollen section. The last parts to be dissolved are the scraps of the balloon membrane (phase 4).

These experiments show that $([C4mim]+Cl^-) + DMSO$ is not a good solvent for cotton and wood fibres. The described swelling and dissolution mechanisms are similar to what was found for aqueous solvents of bad dissolution quality (Cuissinat & Navard, 2006a, 2006b). It clearly shows that the swelling and dissolution mechanisms through ballooning (called mode 2) is due to the structure of the cellulose fibres, not to a specific solvent.

Another comparison between behaviour of native cellulose fibres in aqueous solvents and ionic liquids $([C4mim]+Cl^-)$ can be performed with regard to swelling ratio $D_{\text{swelling}}/D_{\text{dried}}$. D_{swelling} is the diameter of the balloons, before bursting, D_{dried} is the diameter of cellulose fibre before being penetrated by a solvent systems. The values of $D_{\text{swelling}}/D_{\text{dried}}$ are indicated in Table 2.

The swelling ratio $D_{\text{swelling}}/D_{\text{dried}}$ of cotton or wood fibres in $([C4mim]+Cl^-) + DMSO$ is slightly above 4. These values remain lower than those observed in the case of NMMO–water mixtures, but are higher than those observed with NaOH solutions. The swelling ratio indicates the ability of solvent to penetrate the cellulose fibres and to swell them. It can be seen as a first indicator of solvent quality since the swelling is directly linked to the osmotic pressure generated inside the cellulose fibre by the penetration of the solvent and the dissolution of the cellulose chains. All the NMMO–water mixtures at water

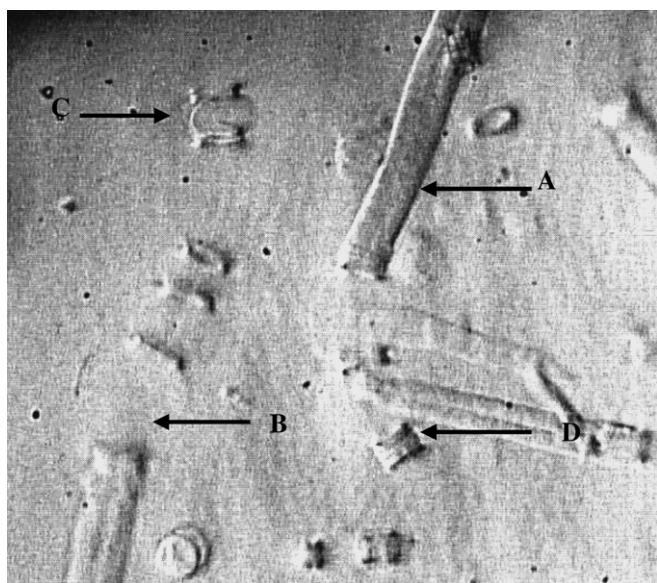


Fig. 4. Borregaard wood fibres in $([C4mim]+Cl^-) + DMSO$ seen by optical microscopy in transmitted light ($T = 100$ °C). (A) unswollen fibre, (B) balloon, (C) membrane and (D) unswollen section between two balloons.

Table 2

Swelling ratio $D_{\text{swelling}}/D_{\text{dried}}$ for untreated cotton and wood fibres (Borregaard, Buckeye and bleached cotton) in aqueous solvents and ionic liquid ([C4mim]+Cl[−])/DMSO

	Untreated Borregaard VHF	Untreated Buckeye VFC	Untreated bleached cotton
<i>Aqueous solvents</i>			
NMMO–water (19%)	5.3	5.3	4.8
NMMO–water (20%)	5.2	5.2	4.7
NMMO–water (23.5%)	4.8	4.8	4.9
NaOH (at 7.6%)	3.6	3.6	3.2
NaOH (at 7.6%) with 12% urea	3.7	3.7	3.9
<i>Ionic liquid</i>			
([C4mim]+Cl [−]) – DMSO	4.1	4.7	4.2

D_{swelling} is the maximum diameter during the swelling by ballooning. D_{dried} is the fibre diameter without solvent. The values in bold indicate that the balloon is swelling up to burst.

content between 19% and 23.5% induces a swelling and dissolution mechanisms referred as mode 2 where the balloons are swelling so much that they burst. On the contrary, solvents based on NaOH are not swelling the balloons so much, and they do not burst. Only the cellulose inside the balloons is dissolved. The cellulose solution can be collected when the balloons are mechanically broken during mixing, which is not occurring in the type of experiments that are performed here under the microscope. This is what was called mode 3 of dissolution. ([C4mim]+Cl[−]) + DMSO has a swelling and dissolution mechanism described as mode 2. An interesting factor is the swelling ratio at which the balloons burst. Table 2 suggests that the better is the solvent in this mode 2, the larger is the swelling ratio at burst. This may be due to the kinetics of the dissolution. The better the solvent, the faster is the swelling of the balloon. The balloon will burst when the membrane is not able to sustain the pressure inside the balloon. This resistance of the membrane is directly linked to its thickness. We can imagine that the thickness of the membrane is smaller when the swelling is slow, which leads to a burst at a lower swelling ratio. ([C4mim]+Cl[−]) + DMSO is a solvent of cotton and wood fibres, better than NaOH solution at 7.6% but not as good as than NMMO–water mixtures with water content between 19% and 23.5%.

3.2.2. Enzymatically treated cotton and wood fibres

It is shown that treated cotton and wood fibres swell homogeneously and then dissolve in aqueous solvents (Cuissinat 2006) due to the removal of the outer layer, which composes the balloon membrane (primary wall plus some part of secondary wall). Without a membrane, there is no balloon and the dissolution proceeds through a homogeneous swelling. The same effect is found with ([C4mim]+Cl[−]) + DMSO. No balloons appear during the swelling step. A balloon membrane composed of pri-

mary wall plus some part of secondary wall resists dissolution and is responsible for the formation of the balloons. As the enzymatic treatment destroys the outer layers of cellulose fibres, the treated cotton and wood samples swell homogeneously and dissolve. The detailed description of swelling and dissolution mechanisms is as follows. The mechanism of dissolution for the treated cotton and wood fibres shows three steps. The first step is a homogeneous swelling. Then, an unwinding of the cellulose fibres occurs. The cotton and wood fibres without outer layer turn on themselves, from right to left. This untwisting induces the separation of each fibre into two sub fibres. Then in a third step these sub fibres dissolve by fragmentation (Fig. 5). The first step of swelling is very low (swelling ratio of about 1.5). Then the unwinding of the fibres occurs. Comparatively with the NMMO–water mixtures (at water content between 19% and 23.5%), the unwinding is slower. The division of fibres into sub fibres appears before the total unwinding of the fibres. The pitch of the helical structure for treated cotton and wood fibres is multiplied by about two during the unwinding in NMMO–water (20%) mixtures. In the case of ([C4mim]+Cl[−]) + DMSO, the treated samples have not enough time to become totally untwisted before the dissolution begins.

Thus the same three steps are present in aqueous solvent and ([C4mim]+Cl[−]) + DMSO, even if the last two steps follow one another more rapidly in the case of this ionic liquid.

3.3. Swelling and dissolution mechanism in ([Amim]+Br[−]) and ([Bmim]+Br[−])

3.3.1. Cotton and wood fibres

The cotton and wood fibres dipped in ([Amim]+Br[−]) and ([Bmim]+Br[−]) swell homogeneously. No dissolution occurs after the swelling step. This swelling and dissolution mechanism is defined as mode 4. The two ionic liquids

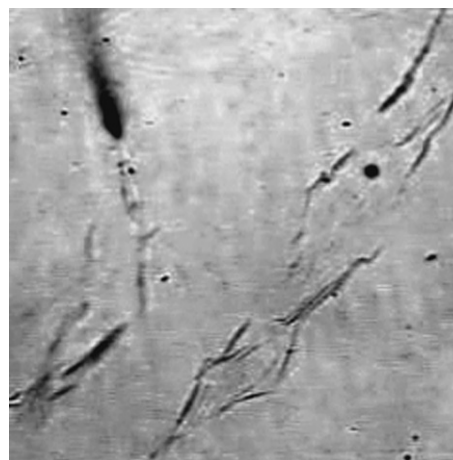


Fig. 5. Treated Buckeye sample in ([C4mim]+Cl[−]) + DMSO seen by optical microscopy in transmitted light, $T = 100\text{ }^{\circ}\text{C}$.

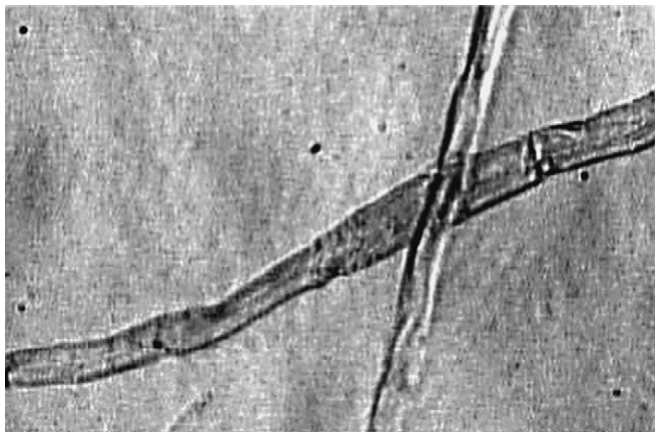


Fig. 6. Borregaard sample in ionic liquid ([Bmim]+Br[−]) seen by optical microscopy in transmitted light, $T = 80\text{ }^{\circ}\text{C}$.

([Amim]+Br[−]) and ([Bmim]+Br[−]) are swelling agents for our cotton and wood samples. The fibres stay without change in a swollen state (Fig. 6).

The maximum diameter of fibre is reached very quickly after the contact with the ionic liquids. Thus, the penetration and the diffusion of these agents is fast. The absence of balloons, as in mode 2 with ([C4mim]+Cl[−]) + DMSO, is due to the very low ability of the ionic liquids ([Amim]+Br[−]) and ([Bmim]+Br[−]) to dissolve cellulose. The molecules can penetrate the fibre, but cannot break the intermolecular hydrogen bonding network of cellulose.

3.3.2. Treated cotton and wood fibres

The treated cotton and wood fibres are tested in ([Amim]+Br[−]) and ([Bmim]+Br[−]). ([Amim]+Br[−]) and ([Bmim]+Br[−]) are only swelling agents for untreated cotton and wood fibres. In the same way, enzymatically treated cotton and wood fibres in ([Amim]+Br[−]) and ([Bmim]+Br[−]) ionic liquids swell homogeneously, but no dissolution occurs (Fig. 7).

This swelling and dissolution mechanism is compared with those observed with the same fibres in ([C4mim]+Cl[−]) + DMSO which induces a homogeneous swelling and dissolution. This phenomenon is divided in three steps: homogeneous swelling, untwisting of fibres and dissolution. In the case of ([Amim]+Br[−]) and ([Bmim]+Br[−]), only the first step of homogeneous swelling is observed. ([Amim]+Br[−]) and ([Bmim]+Br[−]) are less efficient than ([C4mim]+Cl[−]) + DMSO for dissolving cellulose in the case of untreated cotton and wood fibres. The same is occurring for the treated samples, as ([Amim]+Br[−]) and ([Bmim]+Br[−]) are not able to dissolve cellulose. The values of swelling ratio are given in the Table 3. The ability to swell in ([Amim]+Br[−]) and ([Bmim]+Br[−]) ionic liquids is not linked to the presence of outer layers. The values of swelling ratio of treated or not cotton and wood fibres is the same ($D_{\text{swelling}}/D_{\text{dried}} = \text{about } 1.2$) in ([Amim]+Br[−]) and ([Bmim]+Br[−]).



Fig. 7. Treated cotton sample in ionic liquid ([Bmim]+Br[−]) seen by optical microscopy in transmitted light, $T = 80\text{ }^{\circ}\text{C}$.

Table 3

Average of $D_{\text{swelling}}/D_{\text{dried}}$ ratio for cotton and wood fibres (Borregaard, Buckeye and bleached cotton) in ionic liquids ([Amim]+Br[−]) and ([Bmim]+Br[−])

		Swelling ratio $D_{\text{swelling}}/D_{\text{dried}}$
Enzym. treated cotton and wood fibres	([Amim]+Br [−]), ([Bmim]+Br [−])	1.2
Untreated cotton and wood samples	([Amim]+Br [−]), ([Bmim]+Br [−])	1.2

D_{swelling} is the reached maximum diameter during the homogeneous swelling. D_{dried} is the fibre diameter without solvent.

4. Conclusion

Three ionic liquids have been used in order to study the swelling and dissolution behaviour of non-aqueous solvents. A comparison can be made with the five modes identified with aqueous solvents. ([C4mim]+Cl[−]) is a very good solvent, dissolving cellulose very quickly, as in mode 1 found for aqueous solvents. Adding DMSO is strongly decreasing its solvent capability and the swelling and dissolution occur as in mode 2 found for aqueous solvents, i.e. through a ballooning step followed by dissolution with a sequence of events being the same as in aqueous solvents. ([Amim]+Br[−]) and ([Bmim]+Br[−]) are not solvents for cellulose and they swell cellulose fibres without ballooning, as in mode 4. When the cellulose fibres are enzymatically treated, the same results are found with aqueous and ionic liquids with no ballooning and similar sequences of events.

The conclusion is that untreated and enzymatically treated cotton and wood fibres behaves in the same way in these ionic liquids and in aqueous solvents. The complex swelling and dissolutions mechanisms that are observed do not seem to be linked to the nature of the solvent, but are fully controlled by the physical and chemical organisations of the cellulose fibres. A chemical agent will act on a cellulose fibre with a swelling and dissolution mode that is selected by its solvent quality.

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