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REVIEW PAPER

Cellulose in NaOH–water based solvents: a review

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Abstract The article is a critical review of all aspects of the dissolution of cellulose in NaOH-based aqueous solutions: from the background properties of the solvent itself, to the mechanisms of cellulose fibre swelling and dissolution, solution structure and properties and influence of additives and, finally, to the properties of various materials (fibres, films, aerogels, composites and interpenetrated networks) prepared from these solutions. A historical evolution of the research on this topic is presented. The pros and cons of NaOH-based aqueous solvent for cellulose are summarised and some prospects are suggested.

Keywords Cellulose · Solutions · Alkali · Sodium hydroxide

Introduction

Cellulose is a linear, semi-flexible polymer that is self-organised in crystalline and non-crystalline phases. This is the case when cellulose is bio-synthesised in plants or other organisms or when it is coagulated or regenerated from a solution. As such, it is following the general rules that are applicable to long chain molecules. For example, non-crystalline phases (so-called amorphous phases) have different degrees of order and organisation; long chains are more difficult to dissolve than short ones for thermodynamic reasons and chains can entangle at high enough molar mass and concentration.

Since cellulose cannot melt, dissolution is a major issue. Many reviews have been devoted to cellulose dissolution (e.g. Warwicker et al. 1966; Liebert 2010). Cellulose solutions are used for processing cellulose in the form of fibres, films, membranes or other not too bulky objects such as sponges or aerogels, or for performing chemical derivatisation. Since cellulose chains have no specific features, dissolving cellulose should then happen as it is occurring for any other flexible or semi-flexible polymer, and solutions should behave as normal polymer solutions. This is indeed almost the case with one major difference from most synthetic polymers: cellulose is "synthesised" by nature in a complex environment where many other compounds (lignin, hemicellulose, fats, proteins, pectins) are present and interacting more or less

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strongly with cellulose chains. It is thus important to distinguish cellulose as a polymer and native cellulose fibres. In addition, due to the bio-synthesis mechanisms, the organisation of chains is usually complex, like in the secondary plant cell walls, where cellulose chains are forming a sort of composite with many differently oriented layers.

Due to the importance of polymer dissolution in materials engineering where dissolution is used in many industrial areas (drug delivery, pulp and paper, membranes, recycling, etc.), there is a good knowledge of the mechanisms at stake when a solid polymer is placed in contact with a solvent (Miller-Chou and Koenig 2003). As a general basis, polymer chains will go into solution through the interface between the solid polymer and the solvent and will pass several phases. When the solid phase is placed in contact with the solvent, the solvent is swelling the solid phase at the interface, which goes above the glass transition temperature, and this swelling is increasing up to the point of chain disentanglement. Chains can then move out of the swollen phase to the solvent phase and the solubilisation front can advance inside the solid material. Such a scheme is indeed what is occurring when a man-made cellulose fibre is placed in a solvent (Chaudemanche and Navard 2011). In this case, cellulose is behaving as a normal polymer. This is not what is happening when a native cellulose fibre is dissolving. When placed in a swelling agent or a solvent, natural cellulose fibres show a heterogeneous swelling. The most spectacular effect of this inhomogeneous swelling is the ballooning phenomenon, where swelling takes place in some selected zones along the fibres. This type of swelling was observed and discussed a long time ago (Nägeli 1864; Pennetier 1883). One explanation for this phenomenon is that the swelling of the cellulose chains present in the secondary wall is causing the primary wall to extend and burst. According to this view, the expanding swollen cellulose pushes its way through tears in the primary wall. This wall rolls up in such a way as to form collars, rings or spirals, which restrict the uniform expansion of the fibre, and forms balloons as described by Ott et al. (1954). This explanation assumes that cellulose is in a swollen state in each of the balloons. Further studies of Chanzy et al. (1983), Cuissinat and Navard (2006a, b, 2008) and Cuissinat et al. (2008a) have shown that the dissolution mechanism is strongly dependent on the solvent quality. Cuissinat and Navard performed observations by optical microscopy of free floating fibres between two glass plates for a wide range of solvent quality (as an example, *N*-methylmorpholine-*N*-oxide with various amounts of water). They identified four main dissolution modes for wood and cotton fibres as a function of the quality of the solvent.

It is usually said that cellulose is difficult to dissolve and that a rather limited number of solvents is available. However, this is the case for nearly all polymers. Dissolution is favoured since the entropy will increase in a solution state through the contributions of several entropic factors such as the entropy of mixing, the entropy of conformation mobility and, if applicable, the entropy gain due to counter ions. This is counterbalanced by the very large decrease of entropy if the polymer is compared to its parent monomer because of the polymer long chain. All these thermodynamic considerations apply to cellulose, with two additional difficulties. One is chain rigidity, which hampers the entropy increase when the chain is going into solution (degrees of freedom for a chain undergoing conformational changes are very limited for a cellulose chain that can only turn around its 1.4 links). A second difficulty is the large number of intra- and inter-hydrogen bonds present in cellulose, thus compelling the solvent to break them and prevent chains' self-aggregation in solution. The existence of hydrophobic interactions has been recently advocated as a reason for cellulose not to be soluble in water (Lindman et al. 2010; Glasser et al. 2012a, b). A recent molecular dynamic simulation shows that the cellulose dissolution in supercritical water is driven by the entropy gain upon the chain dissociation and is hindered by the loss of solvent entropy. Water molecules increase their density around chains in the solution with supercritical water, the opposite being found in ambient water situation (Tolonen et al. 2015). Aside from thermodynamics, kinetic effects are also playing a major role, which is recognised in the cellulose field as a need to "activate" cellulose, in other words, to find methods to accelerate fibre swelling and dissolution.

Cellulose being not soluble in classical organic solvents, the search for solubilisation has been a major field of research since the isolation of cellulose. The most active time was in the 1930s when four major classes of solvents, still studied now, were discovered: phosphoric acid, NaOH–water, ionic liquids and amine oxides. Many chemical compounds used to prepare solutions are derivatising or complexing cellulose (Liebert 2010), implying it reverts (or regenerates) to cellulose after/during processing. The Fortisan process uses cellulose acetate-acetone solutions for producing cellulose acetate fibres that are saponified in caustic soda to revert to cellulose fibres (Segal and Eggerton 1961). Cellulose carbamate is obtained by the reaction of cellulose with urea and then regenerated in acid (Hill and Jacobsen 1938; Sprague and Noether 1961; Kunze and Fink 2005). The viscose process is based on cellulose xanthate dissolution in caustic soda followed by regeneration in acid (Russler et al. 2005, 2006; Musatova et al. 1972).

Many aqueous-based compounds are complexing cellulose. They are not leading to a real solution, i.e. a dispersion of cellulose chains at the molecular level in a solvent. The first such agent was discovered by Schweitzer in the middle of the 1800s. He found that it is possible to prepare clear solutions when cellulose is dissolved in mixtures of copper salts and ammonia (the cuprammonium process, with low production today). This class of compounds is very interesting in the sense that these cellulose complexes can be easily studied. Two compounds of this class, cuoxen ($[Cu(NH_2(CH_2)2NH_2)_2[HO]_2$) and cadoxen ($[Cd(NH_2(CH_2)2\text{-}NH_2)_2[HO]_2$), are widely used to give an indication of the cellulose molar mass through the measurement of the intrinsic viscosity [these methods being normalised as ASTM D1795 (2013) and ASTM D4243 (2009)]. These metal complexes dissolve cellulose by deprotonating and coordinatively binding hydroxyl groups in C2 and C3 positions (Liebert 2010). Many other inorganic salt hydrates combined or not with water were also found to dissolve cellulose while complexing it. A list of aqueous salts is given in Liebert (2010). As an example (Hattori et al. 2004), ethylenediamine/thiocyanate salts can solubilise cellulose of DP = 210 up to 16 wt%, leading to the formation of a mesophase for the highest concentrations.

Not many classes of compounds are leading to more or less well dispersed but non-derivatised and non-complexed cellulose solutions. The most important ones are phosphoric acid-based solvents, LiCl-based solvents, *N*-methylmorpholine *N*-oxyde/water, ionic liquids and NaOH–water. The possibility to dissolve cellulose in phosphoric acid has been known for a long time, starting with a patent of British Celanese in 1925 (British Celanese 1925). Boerstel et al. (2001) and Northolt et al. (2001) showed that concentrated cellulose–phosphoric acid solutions are anisotropic at rest and that their spinning gives high modulus (44 GPa) and high strength (1.7 GPa) cellulose fibres. The possibility to dissolve cellulose in a non-aqueous mixture of *N,N*-dimethylacetamide (DMAc) and LiCl was first published in 1979 by Charles McCormick (McCormick and Lichatowich 1979). It is a widely used method to analyse cellulose chains in solution or to perform derivatisation at the laboratory scale. None of these solvents are commercially exploited to produce cellulose materials.

Graenacher and Salman (1939) obtained a patent in which they described the possibility to dissolve cellulose in amine oxides with aliphatic and cycloaliphatic amine oxides in up to 7–10 % solutions of cellulose at 50–90 °C. This discovery was not exploited until 1960–1980 when a series of patents (Johnson 1969; Franks and Varga 1979; McCorsley III and Varga 1979) disclosed that one member of this series of compounds, *N*-methylmorpholine *N*-oxide (NMMO) mixed with water, is able to dissolve cellulose. It is only within a rather limited range of compositions and temperatures that NMMO–water can dissolve cellulose. Fibres spun from these solutions are industrially produced under the generic term of Lyocell and mainly used in the textile industry.

Ionic liquids are now entering a very active phase of research. Here again, the dissolution of cellulose in “liquefied quaternary ammonium salts” was patented a long time ago, in 1934 (Graenacher 1934). In 2002, imidazolium-based ionic liquids were suggested to be promising cellulose solvents (Swatloski et al. 2002): cellulose can be dissolved up to rather high concentrations [up to 25–27 % (Le et al. 2014)] without any activation. 1-Butyl-3-methylimidazolium chloride (BMIMCl), 1-ethyl-3-methylimidazolium acetate (EMIMAc) and 1-allyl-3-methylimidazolium chloride (AMIMCl) have been used for making films and fibres and performing homogeneous esterification of cellulose as well (Zhang et al. 2005b; Heinze et al. 2005; Turner et al. 2004; Kosan et al. 2008). The advantages of ionic liquids are their negligible vapour pressure, nonflammability, high thermal and electrochemical stability, and ability to tailor their physical properties through changes in cation and anion chemical structures. One of the problems remaining to be solved is ionic liquid recycling.

The last major cellulose solvent family is based on aqueous sodium hydroxide solutions. Preparing cellulose solutions in NaOH–water is very attractive. It is rather simple, with reagents that are easy to recycle and cheap, and the solvent itself is well known and widely used in the pulp industry. It is thus not surprising that it attracted attention. The history of the "relations" between cellulose and sodium hydroxide dates back to the nineteenth century. It was the discovery of mercerisation and the viscose process in which a cellulose derivative is dissolved in NaOH–water that gave the real start to using NaOH in the cellulose industry, in particular for making films (cellophane) and fibres (viscose). In the 1930s, it was found that cellulose is soluble in NaOH–water solutions in a certain limited range of low NaOH concentrations and low temperatures (Davidson 1934, 1936). However, the dissolution of most untreated cellulose samples was only partial. Due to these difficulties, the effects of adding other chemicals to NaOH–water to help dissolution were looked for. Already at that time, it was found that the addition of compounds such as ZnO or urea helped the dissolution (Davidson 1937). This discovery was not used until the 1980s when scientists from Asahi Chemicals in Japan found that steam-exploded cellulose was readily soluble in NaOH–water. These researchers made most of the basic physical and chemical studies of cellulose–NaOH solutions, but they did not manage to bring their process to industrialisation. More recently, processes based on enzymatically treated pulps and on the use of additives were developed, but with no industrial production up to now. Difficulties such as use of low temperatures for dissolution, low stability of the mixtures (gelation), low maximum concentration of cellulose (7–8 wt%) and moderate mechanical properties of the fibres were the main factors explaining why this dissolution method is not used. Other methods such as *N*-methylmorpholine *N*-oxyde or ionic liquids are favoured over NaOH–water at the present time.

The purpose of this article is to review the history of the dissolution of cellulose in NaOH–water with or without additives, the various hypotheses made for explaining the way dissolution occurs and the attempts to process cellulose fibres, films, membranes and highly porous objects.

Structure and properties of aqueous NaOH systems

Anhydrous NaOH is a crystalline compound that strongly interacts with several chemicals of interest here, including water. Upon interaction with water, a series of hydrates are formed after the destruction of the NaOH crystalline structure. The first to draw the water–NaOH phase diagram was Pickering (1893). He found a complex binary phase diagram, with multiple melting temperatures, ascribed to various hydrate structures. He identifed eight hydrates. The phase diagram was completed by Antropoff and Sommer (1926). Later, a comprehensive study using thermal analyses and solubility was performed by Cohen-Adad et al. (1960). They built the NaOH–water phase diagram based on crystallised hydrates; it is the most complete to date (Fig. 1).

Both ends of the phase diagram show rather simple behaviour. In the concentrated NaOH solutions, there is only one stable hydrate formed by one molecule of water and one molecule of NaOH. On the side of water concentrated solutions (the one of interest for dissolving cellulose), a stable crystalline hydrate is formed with seven water molecules and a metastable one with five water molecules. Between 25 and 70 % of NaOH, the phase diagram is very complex, with several hydrates being stable or even metastable like (NaOH, $4H_2O$) and (NaOH, $3H_2O$) located between 30 and 45 % of NaOH. The most complex region is where the NaOH concentration is between 20 and 40 %. Table 1

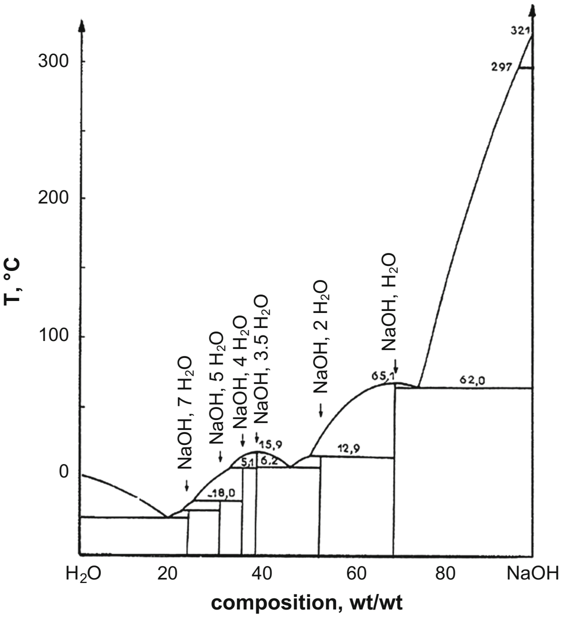


Fig. 1 Binary phase diagram of NaOH and water. Adapted from Cohen-Adad et al. (1960)

Table 1 Composition and temperature range of various NaOH–water hydrates

Hydrates	NaOH concentration (wt/wt, %)	Temperature range °C
NaOH, 1 H_2O	69	12.9 to 62
NaOH, 2 H_2O	52.6	6.2 to 12.9
NaOH, 3.5 H_2O	38–38.8	5.1 to 6.2
NaOH, 4 H_2O	34.8–35.7	−18 to 5.1
NaOH, 5 H_2O	30.2–30.9	−24 to −18
NaOH, 7 H_2O	22.8–24.1	−28 to −24

Adapted from Roy (2002) and Rollet and Cohen-Adad (1964)

shows the various identified hydrates with their composition and temperature.

In the region of low NaOH concentration, two hydrates can be present. According to Rollet and Cohen-Adad (1964), a stable hydrate with composition (NaOH, $7H_2O$) is obtained after a rapid drop in temperature, in liquid air or dry ice, followed by an isothermal step. A metastable hydrate can also be formed, with composition (NaOH, $5H_2O$), when the temperature decreases relatively slowly. The region of interest for cellulose dissolution is below 20 % of NaOH. This has been recently studied by Roy et al. (2001), Roy (2002), Egal (2006) and Egal et al. (2007). The phase diagram in this region is reported in Fig. 2.

A classical eutectic mixture is found. The composition of the eutectic mixture was proposed to be (NaOH, $5H_2O$; $4H_2O$). It gives 20 % NaOH and 80 % H_2O. The melting temperature of this eutectic compound is ~33.4 °C with a melting enthalpy of the pure eutectic of 187 J g^{-1} (Egal et al. 2007).

The structure of these hydrates is of importance regarding cellulose dissolution. When ions are in solution, they can have different solvated forms depending on their concentration and temperature (Fig. 3). The strongly bonded water forms the primary cage. In this region, ions and solvent molecules are moving together. The less bonded part is forming the secondary cage. These cages are organised in several possible manners, as shown in Fig. 3.

In the case of sodium hydroxide in water, Van Geet (1972) and Yamashiki et al. (1988) observed separated ion pairs for NaOH concentration around 9 % while Bartunek (1955) favoured the hypothesis of hydrated ion pairs.

Another important aspect is the measurement of the number of solvated water molecules present in these cages, which determines the size of these hydrates. Different techniques (NMR, ultrasonic velocity, ion mobility) can be used to measure the number of water molecules in the different cages. Yamashiki et al. (1988) found that the primary cage contains 8 water molecules per NaOH at +4 °C for a 10 wt% NaOH solution. For a 9 % solution, at 30 °C, Kunze et al.

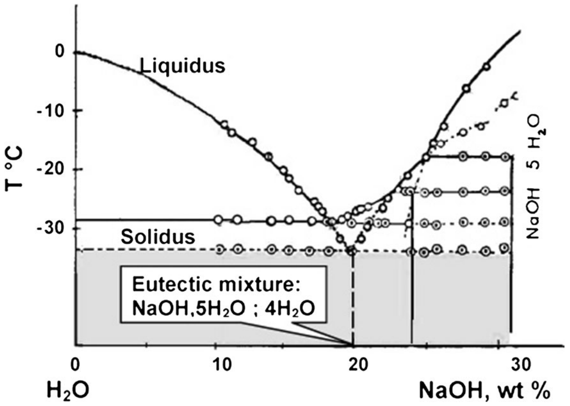
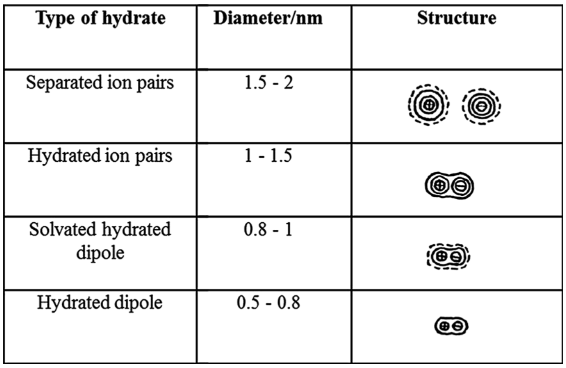


Fig. 2 Binary phase diagram of NaOH and water in the region of low NaOH concentration. Reprinted with permission from Egal et al. (2007) American Chemical Society



Type of hydrate	Diameter/nm	Structure
Separated ion pairs	1.5 - 2	
Hydrated ion pairs	1 - 1.5	
Solvated hydrated dipole	0.8 - 1	
Hydrated dipole	0.5 - 0.8	

Fig. 3 General structures of alkali hydrates, adapted from Bartunek (1955)

(1985) found by ^{23}Na NMR that four moles of water per Na^+ form the primary cage. A similar result was found by Van Geet (1972). This is fully compatible with what was reported by Yamashiki et al. (1988) if considering that OH^- and Na^+ have the same number of water molecules in their primary cages. An interesting point is that the number of solvated water molecules per Na^+ does not seem to depend on temperature. There is no indication on how the structure of the weakly bounded secondary cage is changing with temperature. Yamashiki et al. (1988) found that about 23 water molecules per NaOH are freely moving in the secondary cage.

Yamashiki et al. (1988) proposed a model given in Fig. 4 where four water molecules are around each ion to form the primary solvation cage (in grey on Fig. 4). The secondary cage is around the primary, composed of 23 water molecules split between the two ions.

Cellulose mercerisation

The fact that alkaline aqueous solutions have an effect on cellulose has been known since the nineteenth century with the discovery of mercerisation and the viscose process. Mercerisation is a process named after its inventor, John Mercer. Patented in 1850 (Mercer 1850), mercerisation is the treatment of native cellulose fibres by concentrated aqueous sodium hydroxide solution. After immersion in a NaOH solution and then washing, the initial cotton fabric has improved properties such as better lustre and smoothness, improved dye intake, improved mechanical properties and dimension stability, especially after the discovery by Horace Lowe in the 1890s that mercerisation under tension prevented shrinkage.

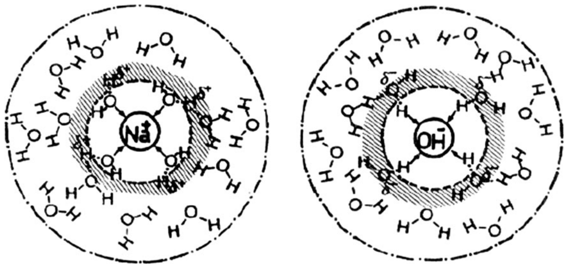


Fig. 4 Tentative representation of the organisation of water molecules around ions for a NaOH–water solution with 9 wt% NaOH. Reprinted by permission from Macmillan Publishers Ltd.: Yamashiki et al. (1988)

Mercerisation has been an industrial process from the the end of the nineteenth century up to now. It has been defined in various standards like ASTM D1695 (2012) as a treatment in strong alkali conditions able to induce cellulose fibre irreversible swelling. One important effect is the transformation of cellulose from its native form (i.e. with Cell I crystalline structure) to cellulose with a Cell II crystalline structure via the intermediate crystalline species called Na–Cell.

Mercerisation is strongly acting on the cell wall morphology of cellulose fibre, changing, for example, the crystalline structure from the native cellulose I to cellulose II (Okano and Sarko 1985). Mercerisation is not fibre dissolution but a change in the morphology and crystalline structure that occurs in a highly swollen state during the formation of various alkali-cellulose complexes. The accessibility of –OH groups on the cellulose chain depends on the crystallinity of cellulose (Tasker et al. 1994), the highly crystalline cellulose being more difficult to mercerise (Chanzy and Roche 1976). During the first mercerisation step, the alkali solution penetrates amorphous regions, leading to cellulose fibre swelling (Okano and Sarko 1984). The polymer chains in these swollen areas are more mobile and they can diffuse laterally to form an alkali complex (Okano and Sarko 1985). Alkali then penetrates into the crystalline regions to ultimately form an antiparallel crystalline soda–cellulose complex called Na–Cell II (Petitpas 1948; Nishimura and Sarko 1987), departing from the parallel arrangement found in native cellulose crystal. The fact that the number of amorphous regions does not increase during mercerisation led many authors to conclude that there is a solid–solid phase transition between crystals of cellulose I to Na–cell II crystals. This suggests that this phase transition occurs through translation diffusion mechanisms, even if this mechanism is not clearly understood. Experiments performed by Nishiyama et al. (2000) showed that once Na–cellulose I or Na–cellulose II species are formed (depending on the initial NaOH concentration), they are stable when changing the NaOH concentration, suggesting the parallel-to-antiparallel conversion cannot take place in the crystalline regions of Na–cellulose. Yokota and coworkers (Yokota et al. 1990) found from the ^{13}C NMR results that both crystalline and noncrystalline components of cellulose decrease their resonance intensities in the transition process from cellulose to the first stage of the transition (Na–Cell I), suggesting that the noncrystalline and the crystalline regions of cellulose are converted to Na–Cell simultaneously. These authors suggest that the crystalline part imposes some restriction on the swelling of the noncrystalline part of cellulose, but the conversion of both parts to Na–Cell may be possible when the swelling prevails in the whole microfibril as a result of the penetration of the alkaline solution into the crystalline part. Na–Cell I has one NaOH molecule per anhydroglucose unit and has a twofold helical chain conformation with a repeat unit of 10.1 Å.

There are conflicting views regarding the exact interaction mechanisms of NaOH with cellulose and even more contradicting opinions when it comes to explaining how cellulose goes from Cell I (parallel configuration) to Cell II (antiparallel configuration) without going through a dissolved state. Crystallogaphy suggests it is a solid–solid transition while polymer physics suggest that chains cannot change their direction because of the lack of mobility. This contradiction has not yet been resolved.

A two-phase model based on “reactive structural fractions” where crystalline and non-crystalline fractions have different compositions, with more NaOH penetrating into the amorphous phases, was proposed in 1986 (Fink et al. 1986). This model is able to explain the differences between the alkali uptake measured by chemical methods and the composition of the crystalline phase.

Many authors (Kamide et al. 1985; Nishimura and Sarko 1991; Takahashi et al. 1991; Fink et al. 1995; Isogai 1997) agree that Na^+ breaks the intermolecular hydrogen bonds O2–H…O6′ and that the most probable location of the Na^+ ion is at C2. The carbon C3 seems to be the most resistant to a complexation with sodium hydroxide.

The classical mercerisation conditions are 18–32 % NaOH concentrations at 25–40 °C and the treatment time is very short, a few tens of minutes depending on the cellulose origin and process details. Mercerisation is a term used for the process of treating fibres and fabrics to change their properties in the above conditions, but it also sometimes refers to contacts between cellulose and NaOH–water, regardless of the concentration and conditions, leading to some confusion. It was noticed that temperature plays a complex role, changing the mercerisation efficiency (Sameii et al. 2008).

Macroscopic mechanisms of cellulose fibre dissolution and cellulose fibre treatments to improve the dissolution in NaOH water

Mechanisms of cellulose fibre dissolution

When placed in a swelling agent or a solvent, natural cellulose fibres show a nonhomogeneous swelling. The most spectacular effect of this nonhomogeneous swelling is the ballooning phenomenon where swelling takes place in some selected zones along the fibres (Fig. 5a). Figure 5b shows these balloons as observed by scanning electron microscopy. The balloon surface is very smooth. This heterogeneous swelling was observed and discussed long ago by Nägeli (1864), Pennetier (1883), Flemming and Thaysen (1919), Marsh (1941), Hock (1950) and Tripp and Rollins (1952).

One explanation of ballooning is that the swelling of the cellulose present in the secondary wall is causing the primary wall to extend and burst. According to this view, the expanding swollen cellulose pushes its way through the tears in the primary wall, which rolls up in such a way that it form “collars”, rings or spirals (Fig. 5c, d), restricting the uniform expansion of the fibre and forming balloons as described by Ott et al. (1954). Further studies of Cuissinat and Navard (2006a, b, 2008) and Cuissinat et al. (2008a, b) showed that the typology of dissolution mechanisms is universal, depending only on solvent quality. This also applies to NaOH–water with or without additives (Cuissinat and Navard 2006b). In all these studies, it is shown that the key parameter in the dissolution mechanism is the morphology of the fibre and, more precisely, the presence or not of the primary wall. Indeed, as long as the original wall structure of the native fibre is preserved, the dissolution mechanisms are similar for wood, cotton, other plant fibres and even some cellulose derivatives. Ballooning, often observed when cellulose native fibres are dissolving, originates from the specific cut of the primary wall followed by its rolling (Le Moigne and Navard 2010).

The study of dissolution of cotton fibres with different maturities (Le Moigne 2008) shows that there is a gradient of dissolution capacity from the inside to the outside of the fibre. The cellulose inside the secondary wall is the easiest part to dissolve. Ballooning appears only in fibres having the secondary

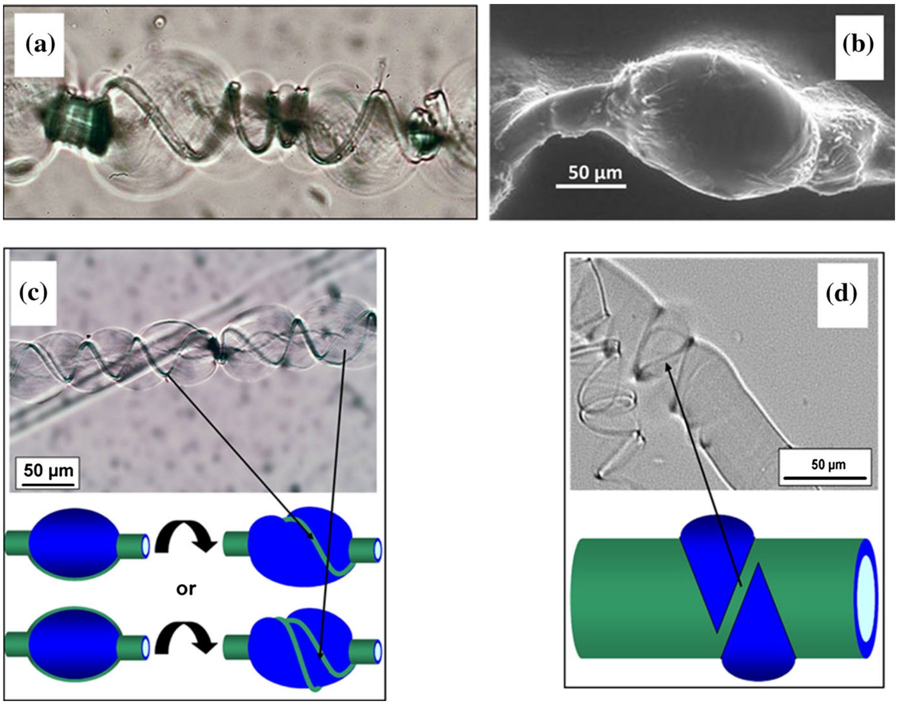


Fig. 5 Ballooning effect seen with a cotton fibre placed in *N*-methylmorpholine *N*-oxyde–water (**a**) and the corresponding SEM image (**b**). Successive balloons can be seen along the fibre (**a**). They are surrounded by a primary wall "thread" (**c**) running all along the swollen fibre. Balloons are constrained on each side by a "collar" made of the rolled primary wall. (**d**) Cuts in the primary wall allowing secondary wall expansion. Adapted from Le Moigne (2008)

wall. When the secondary wall is swelling, the primary wall breaks in localised places, rolls up to form helices and surrounds fibre sections that cannot be swollen (Fig. 5a). When a cut of the primary wall occurs on the whole circumference of the fibre, the primary wall rolls up along the fibre direction in the two opposite directions and forms "collars". If the cut is more local and directed along the fibre axis, the primary wall rolls up perpendicularly to the fibre axis and forms one or more threads attached to two collars (Fig. 5c, d).

The primary wall does not dissolve easily and even sometimes does not dissolve at all as it occurs in thermodynamically bad solvents such as NaOH–water.

This rather complex swelling mechanism with balloons and "collars" is the one at stake when dissolving native cellulose in NaOH–water.

Pre-treatments of native cellulose fibres

Pre-treating cellulose fibres prior to use is a very common action. It is usually called activation and is thought to favour the interactions of all or at least a large fraction of the cellulose chains with a given reagent. Since reacting with this reagent is possible from a thermodynamic point of view (otherwise there would be no point to do it), it means that pre-treatment or activation has the role of speeding up the reaction. Activation is increasing the kinetics of dissolution. In many cases, it is difficult to dissolve or access all the cellulose fractions in the fibre. This is particularly the case when using NaOH-based solvents, but the same difficulty, usually called accessibility, is also present when wanting to transform cellulose into glucose. Cellulose-based materials are thus "activated" in order to help dissolution or degradation.

Many methods have been used for activating cellulose. Of course, thermodynamic actions such as decreasing molar mass are efficient, but they are not the only possibility. As far as dissolution is concerned, one way to activate it is to increase the number of accessible paths inside the cell wall structure that will bring reagents close to cellulose chains. Activation methods are numerous: mechanical, physical, chemical and enzymatic methods have been explored in order to facilitate the dissolution in NaOH–water. The main difficulty with activation, as will be demonstrated further, is that its efficiency is usually very difficult to assess unambiguously and thus to understand and predict the action of activation. Selected examples pertaining to the dissolution of cellulose on NaOH–water will be given for three classes of activation, mechanical/physical, chemical and enzymatic.

Mechanical/physical methods

Ball milling. Hermans and Weidinger (1946) used ball-milled cellulose to help cellulose dissolution in 1 *N* sodium hydroxide. Kamide et al. (1984) reported that regenerated cellulose from a cupramonium solution and ball-milled amorphous cellulose where intramolecular hydrogen bonds are completely broken or weakened dissolves in aqueous alkali and that the solution is stable over a long period of time. It seems unlikely that all hydrogen bonds would be broken by ball milling, which mainly has the effect of strongly decreasing the crystal size such that the X-ray scattering pattern looks amorphous.

Steam explosion. Steam explosion consists of placing the cellulosic material under pressure in a mixture of water steam with other chemicals, waiting for their impregnation and inducing a sudden decompression. Steam explosion has the dual effect of degrading materials other than cellulose while creating many physical paths into the initially compact cell wall structure, thus increasing accessibility (Schultz et al. 1983). Steam explosion was used to obtain a solution of soft wood pulp in NaOH–water with a cellulose concentration high enough to perform spinning and produce cellulose fibres on industrial pilot equipment (Yamashiki et al. 1990a, b, c). These authors performed a complete characterisation of the effects of steam explosion. The resulting pulp was able to dissolve easily in NaOH–water, making a gel-like material ("gelanized state"). Later, Kihlman et al. (2011) used steam explosion to prepare solutions of dissolving pulps in NaOH–water with different additives (urea/thiourea, ZnO, PEG). The authors mentioned that the steam explosion treatment was strongly decreasing fibre length and cellulose DP. In one example, DP is decreased from about 650 to about 150, leading to a good dissolution yield, above 80 %, reaching 94 % in NaOH/urea/thiourea/water.

Hydrothermal treatment. A pulp is submitted to a soaking in water mixed with a very small amount of ascorbic acid at elevated temperature (170 °C). Struszczyk et al. (1991) and Wawro et al. (2009) showed that such a treatment strongly enhances the dissolution in NaOH–water, allowing the production of manufactured goods. Such thermal treatments in hot water under pressure are known to decrease molar mass (Sasaki et al. 1998), which could explain the efficiency of such treatment.

Steam explosion followed by grinding. Yamane et al. (2015) used a sequence of steam exlosion and grinding treatment, a procedure used for preparing cellulose nanofibres. The study compared steam explosion and grinding treatment, concluding that grinding was superior to the steam explosion in terms of increase of solubility.

Chemical methods

Chemical methods usually aim at removing chemicals and polymers, which are possibly hampering dissolution. Lignin and some hemicellulose clearly fall in this category of species that are present in most cellulose materials coming from plants such as wood pulps. Kihlman et al. (2012) looked at the effect of the composition of wood pulp on its dissolution in NaOH/urea/thiourea and in NaOH/ZnO. They found that the solubility was not influenced by the fibre dimensions but that two parameters were important, DP and the composition of the hemicelluloses. The influence of DP clearly comes from a simple thermodynamic consideration. The influence of hemicellulose is more complicated to describe since most, if not all of these hemicelluloses, are soluble in NaOH–water-based solvents. It seems, however, to be important to remove hemicelluloses, which may act as a shield against solvent penetration when they are linked to cellulose (Le Moigne and Navard 2010; Le Moigne et al. 2010). As noted by Kihlman et al. (2012), "solubility of cellulose is not determined by macrocopic properties (e.g.; dimension of the fibres) but rather by properties prevaling at micro- and nano-levels, i.e. in regions close to the molecular and supramolecular architecture of the cellulose in the cell wall within fibrils and fibril aggregates".

One of the most popular techniques is a treatment with alkali solutions. Cellulosic materials will swell and hemicellulose will be mostly dissolved, changing the structure of the material such as the pore structure (Kasahara et al. 2004; Bredereck et al. 2003), fibrillation tendency (Zhang et al. 2005c) or crystallinity (Colom and Carrillo 2002). Such treatments thus strongly influence the accessibility of cellulose chains to small solvent molecules, influencing subsequent chemical treatments (Tatarova et al. 2012). An interesting phenomenon, which can further enhance accessibility, is the fact that parts of the fibres can swell more than others, creating stress inside the fibres (Öztürk and Bechtold 2008) and helping further dissolution.

Other methods have been studied in order to enhance the capability of cellulose fibres to dissolve in NaOH–water. As an attempt to decrease the amount of residual xylan present in fibres, Dos Santos et al. (2013) treated various wood pulps with nitren. Although efficient in removing xylan, this method also decreases the cellulose molar mass (Fig. 6). It was not possible to determine which of the two phenomena (removal of xylan and decrese of DP, or both) was responsible for increasing the solubility in NaOH–water.

Trygg and Fardim (2011) used an ethanol–HCl pretreatment to increase the “accessibility” of cellulose and help its dissolution in NaOH–water based solutions. It was shown that it removes the primary cell wall and also decreases molar mass, but the mechanisms behind the effects of such treatment are not very clear. The solutions of treated pulp were used to prepare cellulose beads (Trygg et al. 2013, 2014).

The effect of lignin on the dissolution in NaOH–urea/water was studied by Shi et al. (2014). The result is not easy to interpret, with a positive effect of lignin on dissolution in some cases and an adverse effect in others. The same positive or negative effects were found regarding the amount of hemicellulose. As stated by the authors, other factors than the lignin and hemicellulose contents control dissolution.

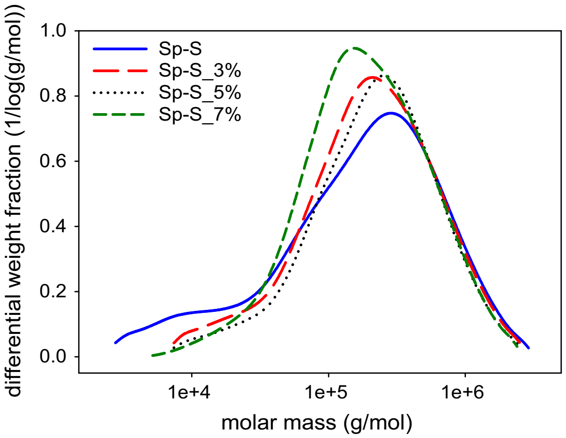


Fig. 6 Effect of nitren treatments at three nitren concentrations *x* of 3, 5 and 7 % on the molar mass distribution: “Sp-S” is untreated and “Sp-S_*x* %” treated spruce bleached sulphite pulps. Reprinted with permission from Dos Santos (2013)

Enzymatic treatments. Enzymatic treatments have been extensively used as a pre-treatment of wood fibres. Several groups investigated the effect of cellulase treatments for improving dissolution in NaOH–water (Struszczyk et al. 1995; Struszczyk and Ciechanska 1998; Rahkamo et al. 1998; Wang et al. 2008; Le Moigne et al. 2010). The main result is that enzymatic treatments do increase the dissolution of cellulose in NaOH–water-based mixtures. However, as shown by Le Moigne et al. (2010), the reduction of molar mass cannot explain everything since the reduction to the same DP of two different pulps does not give the same solubility for these two pulps. As shown for the other treatments, there are deep intermolecular interactions preventing or favouring dissolution. A very clear manifestation of such phenomena is reported in the PhD dissertation of Dos Santos (2013), who used pulps without any detectable presence of pectins and treated them with a pure pectinase. Surprisingly, several pulps showed a very significant increase in solubility. Although the author was not able to give an explanation for this phenomenon, it was clearly shown that touching the molecular and supramolecular arrangement in the native cellulose fibres drastically changes their ability to dissolve. This implies that thermodynamics is not the major player. Other phenomena, more related to the kinetics of the phase change, are important.

Structure, properties and thermodynamics of cellulose–NaOH–water without additives

First investigations of the dissolution in NaOH–water

Davidson (1934, 1936) studied cellulose dissolution and is, to our knowledge, the first to report the dissolution and not swelling as in the mercerisation process. He looked for optimal conditions to dissolve modified cotton, called “hydrocellulose”, which was cellulose hydrolysed in strongly acidic conditions, which decreased its molar mass. Such a product would be called microcrystalline cellulose now. Davidson showed that a decrease in temperature improves cellulose dissolution, as illustrated in Fig. 7.

Davidson found a maximum solubility of 80 % of the initial hydrolysed cellulose, probably due to its low molar mass. This dissolution occurred in a narrow range of NaOH–water concentration (Davidson reported 10 wt% of NaOH) and at low temperature (–5 °C). Davidson noticed that solubility increases when the chain length decreases, leading him to deduce that it would not be possible to dissolve unmodified (i.e. high molar mass) cellulose. With these results, we must consider that Davidson was the real inventor of cellulose dissolution in NaOH–water mixtures. However, it is often Sobue (Sobue et al. 1939) who is cited when cellulose dissolution in NaOH–water is discussed. The reason is that Sobue explored the whole ramie cellulose–NaOH–water ternary phase diagram based on the work of his group and previously published data on cellulose-alkali mixtures by Saito (1939). He noticed that in a narrow range of NaOH concentrations and temperatures, cellulose can be dissolved. The dissolution range was NaOH concentrations of 7–10 wt% and the temperature range −5 to +1 °C. He referred to this region and cellulose state with the term “Q-state”. This phase diagram, reported in all reviews, is shown in Fig. 8.

Figure 8 shows the presence of five different forms of alkali celluloses, or Na–Cell (I, II, III, IV or Q and V). The Na–Cell type depends on the temperature and NaOH concentration. The region of interest for dissolution, below 0 °C and at about 8 wt% NaOH concentration, is the location of what the authors called the alkali cellulose Na–Cell Q, Q as in Quellung (“swelling” in German). Sobue et al. (1939) also investigated the composition of alkali celluloses from molecular volume considerations. Later, Marsh (1941) reported cellulose swelling in aqueous solutions of different alkaline hydroxides (lithium, sodium, potassium, rubidium and caesium). All alkaline hydroxides can act on cotton, with a maximum swelling at a given hydroxide concentration depending on the nature of the metal ion, in the order Li > Na > K > Rb > Cs in terms of efficiency, measured by looking at the lowest concentration able to swell cellulose. Swelling (dissolution was apparently not an issue at this time) was explained in terms of the size of the hydrated ion. The larger is the ion, the more difficult it is to penetrate cellulose (Petitpas 1948). Such explanations are still considered today (Freytag and Donzé 1983). At very low alkaline hydroxide concentrations, hydrated ion pairs may be too large to separate cellulose chains effectively (Fig. 3). When the ion concentration increases, the number of water molecules decreases to form solvated dipole hydrates. Their hydrodynamic diameter decreases and ions can penetrate into

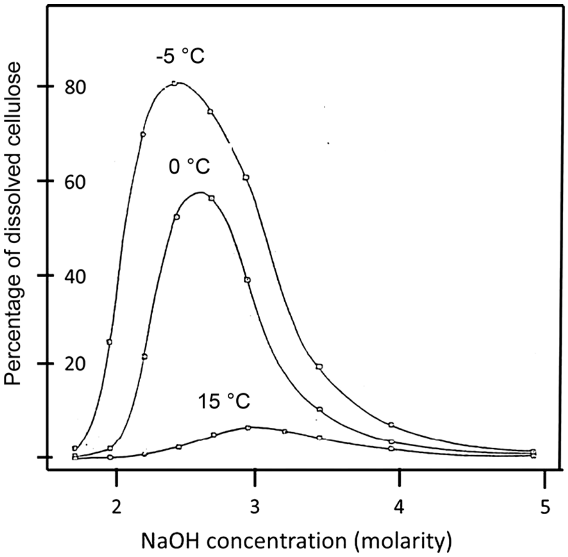


Fig. 7 Hydrocellulose solubility versus NaOH concentration and solution temperature. Adapted from Davidson (1934)

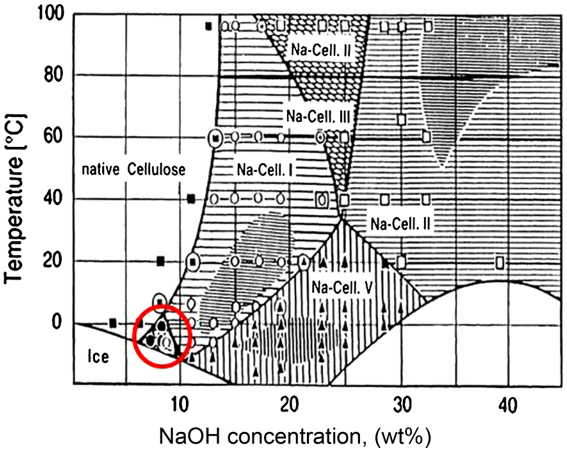


Fig. 8 NaOH–water–cellulose phase diagram, adapted from Sobue et al. (1939). The circle indicates the dissolution range

amorphous areas of cellulose fibre and then in well-organised domains. Another explanation of the influence of alkali concentration is that water is needed to swell cellulose. Na ions must bring water close to the cellulose chain to first swell it (Legrand and Grund 1952). A last hypothesis is that if the NaOH concentration is too high, the hydration of alkali ions is insufficient to break hydrogen bonding (Kuo and Hong 2005).

Staudinger and Mohr (1941) found that cotton dissolves in a 10 wt% NaOH solution if the cellulose DP is lower than 400. Hermans and Weidinger (1946) studied ball milling of cellulose. They confirmed that ball milling produced amorphous cellulose. They found this amorphous cellulose to be soluble in 1 *N* sodium hydroxide without specifying the temperature. After the pioneering work of Keller (1957, 1968) showing that polymers could crystallise via a chain-folding mechanism, Maeda et al. (1970a, b) studied cellulose crystallisation from solutions in NaOH. Maeda et al. (1970b) attempted to dissolve cellulose in the Q-state [unspecified "cold" temperature, low cellulose concentration (0.02–0.5 wt%) at a low alkali concentration (2–6 wt%)]. They report dissolution and subsequent slow recrystallisation upon heating at temperatures in the range 25–50 °C. Maeda et al. (1970a) discussed this method for dissolution and also proposed another one that leads to faster crystallisation kinetics, where cellulose is dissolved in similar conditions with the addition of an equal amount of methanol. Crystallisation occurred in this case in less than 24 h.

Dissolution of cellulose in NaOH–water: research in Japan in the 1980s

A revival of interest in cellulose dissolution in NaOH–water came in the middle of the 1980s. A team of researchers from Asahi Chemical Industry Co. made a breakthrough in the dissolution of cellulose in dilute aqueous solutions of sodium hydroxide. In a series of papers (Kamide et al. 1984, 1987; Yamashiki et al. 1988, 1990a, b, c, 1992; Kamide et al. 1990, 1992; Yamada et al. 1992; Matsui et al.1995; Yamane et al. 1996a, b, c, d), they extensively studied dissolution mechanisms using different approaches, focussing their efforts on finding dissolution methods able to produce materials, mainly fibres and films. The first paper by Kamide et al. (1984) reported that regenerated cellulose from a cupramonium solution and ball-milled amorphous cellulose, where intramolecular hydrogen bonds are completely broken or weakened, dissolved in aqueous alkali and that the solution was stable over a long period of time. They identified the intramolecular hydrogen bond (O_3–H……O_5') to be weakened for the ensuring dissolution. The authors found that although crystallinity has a role, the more crystalline cellulose being the more difficult to dissolve (as found already by Davidson in 1934), it is by far not the only factor governing dissolution. The authors concluded that "in other words, the solubility behaviour cannot be explained by only the concepts of crystal-amorphous" *or* "accessible–inaccessible". The lack of a strong correlation between the amount of amorphous phase and solubility was confirmed later (Kamide et al. 1992). Wang et al. (2008) used enzymes to tailor the molar mass and crystallinity of cotton linters and dissolve them in NaOH–urea. Their conclusion is that the decrease in molar mass strongly decreases the dissolution time but that high crystallinity does not result in low solubility; "at least crystallinity alone could not explain the difficulty of cellulose dissolution". This issue of crystallinity where some authors found an influence on solubility and some others did not is probably linked to the difficulty of separating the crystallinity and crystal size. For example, ball milling strongly decreases the crystal size, which results in a solubility increase (Kamide et al. 1984). Being able to prepare stable cellulose–NaOH solutions, the same Asahi research group studied some of the solution properties. Regenerated cellulose (M_w of 8×10^4), using the same protocol as in Kamide et al. (1984), was dissolved in 8 % NaOH–water. The molar mass as measured by light scattering did not change in the temperature range 10–45 °C and was similar to the one measured in cadoxen, showing that no aggregation was taking place in this solution. The authors deduced that their solutions were molecularly dispersed. The solvent was found to be a theta solvent at 40 °C. Cellulose has the behaviour of a semi-rigid chain (flexibility in NaOH–water lying between those in cadoxen and iron sodium tartarate) having a partially free draining behaviour. The unperturbed dimensions decreased with temperature.

A detailed study of cellobiose–NaOH interactions was conducted by Yamashiki et al. (1988). Based on ^1H and ^{23}Na NMR results, they proposed a model for explaining NaOH–cellulose interactions. The number of water molecules solvated to a NaOH molecule is maximal at 4 °C in the range 0–15 wt% of NaOH, decreasing at this temperature from 11 water molecules at very low concentration to 8 water molecules at 15 wt% of NaOH. The authors concluded that provided that the proper intermolecular hydrogen bonds have been broken, the factor that controls dissolution is the structure of the alkali. Cellobiose takes part in hydrogen bond formation with the cations and anions strongly solvated with water. Na cations do not show a specific interaction with the OH groups of cellulose. A tentative model of the structure of cellobiose in NaOH–water was given by the authors (Fig. 9).

Because the weakening intermolecular hydrogen bonds were supposed to be a pre-requisite for good solubility of cellulose in NaOH–water, the same group of authors turned towards steam-explosion treatment in order to avoid using regenerated cellulose. The solubility of steam-exploded pulp was found to be very high, always with a maximum solubility in the temperature-NaOH concentration window found by the first investigators (Davidson and Sobue), as shown in Fig. 10. As far as the influence of temperature on cellulose dissolution in NaOH–water is concerned, Fig. 10 shows that the dissolution is slightly better at 4 °C than at −5 °C and shows a non-monotonous temperature dependence. However, Fig. 7 shows that the dissolution is better at −5 °C than at 0 °C. As will be shown later, some researchers prefer to use a solvent (NaOH–urea–water) cooled to −12 °C (Qi et al. 2008a) and others report the best dissolution after solution freezing at −20 °C and thawing (Isogai and Atalla 1998). The exact influence of temperature on cellulose dissolution is thus not well established. What is now accepted is that the dissolution must be performed below 0 °C.

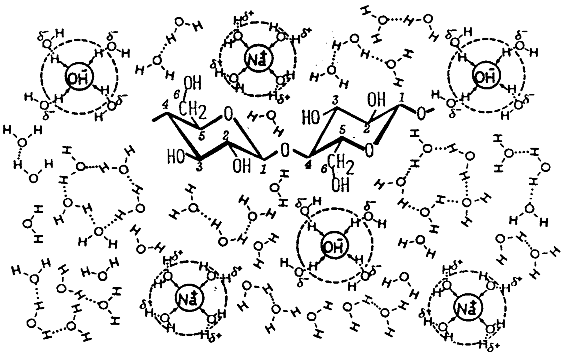


Fig. 9 Schematic representation of the tentative structure of the dissolved cellobiose in NaOH–water. Reprinted with permission from Macmillan Publishers Ltd.: Yamashiki et al. (1988)

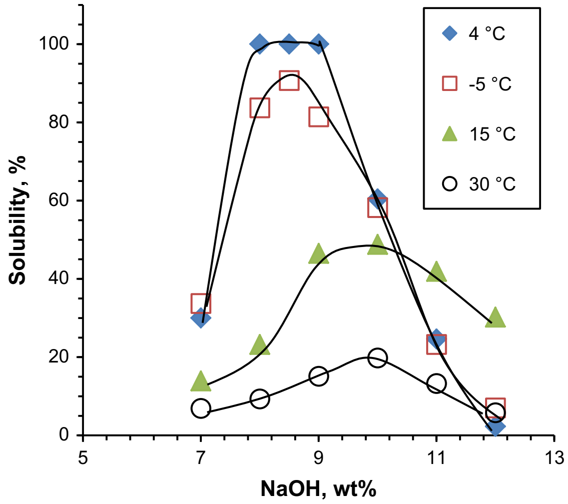


Fig. 10 Dependence of solubility of alkali-soluble cellulose as a function of NaOH concentration at four temperatures (−5, 4, 15 and 30 °C). Lines are given to guide the eye. Replotted from Kamide et al. (1990)

X-ray studies showed that dissolution occurs in 8–9 wt% of NaOH in water at low temperature without any conversion of cellulose into Na–cell I and that dissolution may start first in the amorphous parts, resulting in a transparent, molecularly dispersed solution (Kamide et al. 1990). Steam explosion proved to be a very efficient way to produce stable solutions, at least as claimed by the authors, with a molecular weight of the dissolved cellulose high enough to lead to spinnable solutions and fibres with good mechanical properties (Zhang et al. 2005a). The solubility of steam-exploded soft wood pulps was greatly enhanced for degrees of polymerisation lower than 400. It was found that despite crystallinity increasing after steam explosion, the solubility increased. The degree of intramolecular hydrogen bond breakdown at the C3 and C6 positions was correlated with the increase of solubility. Solid-state ^{13}C NMR confirmed the destruction of intermolecular O_3–H…O_5' hydrogen bonds and O_2–H…O_6' hydrogen bonds (Takahashi et al. 1991; Kamide et al. 1992). Molecular weight is a normal factor influencing solubility. Figure 11 shows that very large differences in solubility can be seen for cellulose of a similar molecular weight.

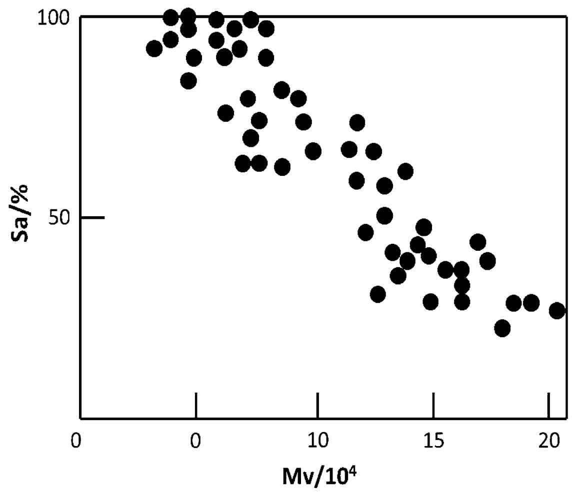


Fig. 11 Solubility S_a versus the average molecular weight of native cellulose, replotted from Kamide et al. (1992)

Up to this point, only regenerated cellulose and steam exploded softwood pulp were used for preparing solutions. Isogai (1997) studied the interactions between solid or swollen cellulose with Na^+ and OH^- ions by NMR using low molar mass cellulose (DP 15). His conclusions were that all C–H protons undergo an electron-shielding effect by NaOH. The shielding effect of carbons by NaOH was found to be varied, with C1 and C4 showing a shielding effect while C2, C3, C5 and C6 show an electron-deshielding effect. Experiments with NaOD-D_2O suggest that C3–OH has the highest resistance to dissociation in NaOH among the three hydroxyl groups on the anydroglucose unit. Isogai and Atalla (1998) had difficulties in dissolving microcrystalline cellulose using the procedure developed by the Asahi group. They found that dissolution of a large variety of cellulose origins (microcrystalline cellulose, cotton linter, softwood bleached and unbleached kraft pulp, groundwood pulp) and treatments (mercerised, regenerated) can be better performed if the cellulose solution in 8.5 wt% NaOH is frozen at −20 °C before thawing at room temperature while adding water to reach 5 wt% NaOH in the solvent. With this procedure, solutions of microcrystalline cellulose were stable at room temperature. Other cellulose samples were partially soluble. The authors found that the presence of hemicellulose did not seem to be a factor influencing dissolution since most hemicellulose fractions were soluble in NaOH–water mixtures. Molar mass was supposed to be the key point for explaining solubility, the higher masses being more difficult to dissolve, a fact explained by the authors through the concept of cellulose chain-coherent domains (and, surprisingly, not through simple entropic effects).

Structure and properties of cellulose–NaOH solutions (without additives)

Not many results have been reported in the literature regarding the possible mechanisms of dissolution of cellulose in NaOH–water without additives. A set of experiments carried out by Roy et al. (2001) and Egal et al. (2007) using thermal analysis as a main tool allowed better understanding the interations between NaOH and cellulose. The analysis is based on the fact that NaOH–water in the region of low NaOH concentration has a eutectic behaviour (see Fig. 2).

NaOH–water and the ternary microcrystalline cellulose–NaOH–water phase diagrams were studied by DSC. DSC melting thermograms of NaOH–H_2O solutions at $T < 0$ °C and a concentration of NaOH between 0 and 20 wt% show two peaks, characteristic of a eutectic phase diagram. The melting peak at low temperature, around −33/−34 °C, is independent on the NaOH concentration and is the classical trace of the melting of the crystalline eutectic mixture, which was found to be composed of one metastable sodium pentahydrate and four water molecules ($NaOH{\cdot}5H_2O$; $4H_2O$). Its melting enthalpy is 187 J g^{-1}, measured at the eutectic position (Egal et al. 2007). The high temperature peak corresponds to the melting of ice. An interesting feature shown in Fig. 12 is that the enthalpy of melting of the eutectic peak depends on the cellulose concentration. However, the melting temperature is constant.

Two conclusions can be drawn from these experiments. The first is that the eutectic mixture is still present when cellulose is added. The second is that the presence of cellulose drastically decreases the amount of this eutectic mixture. The higher the cellulose concentration, the smaller the amount of eutectic compound is. Since NaOH is only present in the eutectic compound, the decrease in its melting enthalpy allows the calculation of the number of NaOH molecules linked to cellulose and thus is not able to participate in the $NaOH{\cdot}5H_2O$ crystal fraction of the eutectic mixture. The fact that the eutectic peak vanishes at a certain cellulose concentration means

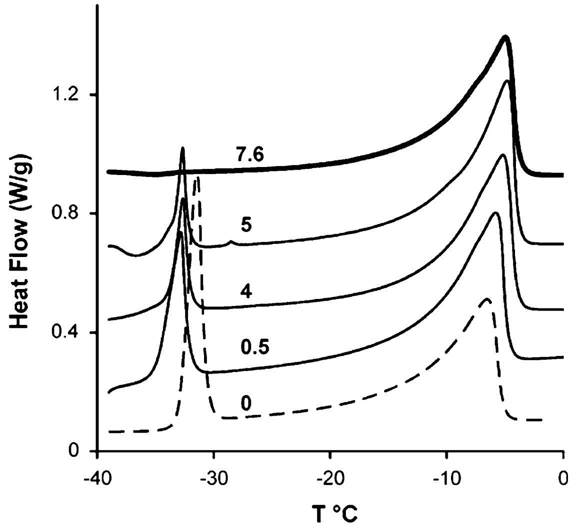


Fig. 12 DSC melting thermograms of X Avicel–7.6NaOH–water solutions with $X = 0, 0.5, 4, 5$ and 7.6 g in 100 g solution. *Dashed line* corresponds to $X = 0$ (solution without cellulose). *Curves* are shifted vertically for clarity. Reprinted with permission from Egal et al. (2007) American Chemical Society

that at this cellulose concentration all sodium hydroxide molecules have been "trapped" by the cellulose chains. This corresponds to the dissolution limit since no more NaOH molecules are able to solvate any additional cellulose chains that could be brought in the solution. This concentration corresponds to four moles of NaOH per mole of anhydroglucose unit. Calculations showed that at very low cellulose concentrations, up to 20 NaOH molecules are linked to one anhydroglucose unit, but as soon as the concentration increases, there is a stable number of four NaOH molecules trapped by each anhydroglucose unit. Such a value, which roughly equals a maximum solubility of 7–8 wt% of cellulose in 7–8 wt% NaOH–water solution, corresponds to what is experimentally found when willing to prepare the highest possible concentrated solutions.

Wang and Deng (2009) looked at the dissolution kinetics of a cotton linter sample of DP 850 in static conditions, i.e. without stirring, varying the temperature and NaOH concentration, at a 2.5 wt% cellulose concentration. They measured two main parameters, solubility and the change between Cell I to Cell II crystal structure of the undissolved part. Without stirring, the authors show a very large influence of temperature. Almost no dissolution occurred above −11 °C while dissolution started to be effective at −15 and −20 °C, with up to 30 wt% of the cotton linters dissolved. The undissolved fraction kept its Cell I structure when the cooling bath was above −11 °C. However, a gradual change of the cellulose crystal structure from cellulose I to cellulose II as a function of time was clearly observed for the undissolved fraction when the cooling bath was at −15 °C. At this temperature, the authors showed that the fraction of Cell I crystals was quickly reduced in the first 10 min of dissolution before the appearance of Cell II. They noted that this quick disappearance of cellulose I in the first 10 min has a similar trend as in the solubility measurement. The authors suggest that the dissolution of cellulose in alkaline solution is closely related to the transformation of cellulose I into cellulose II. Considering the NaOH–water phase diagram as the one plotted in Fig. 2, the authors calculated the amount of ice formed when cooling. They suggest that the ice formation in the free water present in the solution during cooling induced a higher liquid NaOH concentration (this is the classical eutectic behaviour described above in "Structure and properties of aqueous NaOH systems" section) in the immediate environment of solid cellulose, resulting in higher absorption of NaOH on cellulose, leading to its solubility. The higher the NaOH concentration is, the higher the solubility, according to Wang and Deng (2009). The fact that the NaOH concentration reaches 14 wt% at −15 °C is considered a major contribution to the solubility. However, the fact that cellulose is not dissolving in NaOH concentrations above about 10 wt% is in contradiction with this hypothesis. The interest of this work is to show that without stirring cellulose of DP 850 cannot dissolve at temperatures above −11 °C while Avicell of DP about 200 can be nearly fully dissolved at −6 °C. This illustrates the influence of molar mass in the thermodynamics of the dissolution process (the higher the molar mass, the more difficult it is to dissolve for entropic reasons) and clearly shows that the lower the temperature is, the better the enthalpic factors favouring dissolutions are.

Another approach to understanding cellulose dissolution in NaOH–water was recently suggested by Lindman and coworkers (Lindman et al. 2010; Medronho et al. 2012, 2015; Medronho and Lindman 2014a, b). They revisited the amphiphilic property of cellulose in order to show that the hydrophobic character of cellulose was not considered enough among the mechanisms operating during cellulose dissolution. Their main point is that owing to the strongly hydrophilic character of cellulose, it should be easily soluble in water-based solvents able to make hydrogen bonds with cellulose. The fact that in some cases the additives that are used (like urea) are known to disrupt hydrophobic interactions pushed them to dispute the "all-hydrogen bond" attitude advocated widely for explaining why a given chemical is a solvent or not. This approach helps to explain why cellulose solubility has an inverse temperature dependence.

The amphiphilic character of cellulose is evident, aliphatic carbons being present on the edges of the pyranose rings together with highly polar groups on the side of the chain. Dissolution in NaOH–water at low NaOH concentrations means that a lot of water is present around the cellulose chains. A recent Monte Carlo simulation suggests that, as could be expected, the concentration of water is higher around the hydroxyl groups than around the hydrophobic moieties (Stenqvist et al. 2015). These authors concluded that the mutual polarisation between water and hydroxyl groups of cellulose is important and may induce orientation correlations of species close to the cellulose chain, influencing how cellulose interacts with co-solutes such as NaOH. If correct, polarisability effects could explain in part the influence of the temperature of dissolution reported in all studies because of the possible varying structure of the hydrated ions in contact with the cellulose chains. A recent simulation also confirms the presence of well-ordered, tightly coordinated water structures at the cellulose surface (Hadden et al. 2013). Finally, an NMR spectroscopic study of the interactions between water, KOH, LiOH and NaOH with cellobiose and cellulose (Xiong et al. 2013) showed that the dissolution behaviour seems to be very affected by the type of hydration shell alkali forms with water. The authors note that LiOH and NaOH are solvents for cellulose while KOH is not. The only difference they saw was that Li^+ and Na^+ are able to form two hydration shells, while K^+ only has a "loose hydration shell". They deduce that the key point is the ability of the alkali ions to form a stable complex with cellulose in order to dissolve it.

The structure of cellulose chains in water-based media is not well understood, with possible stacks of glucopyranose rings, a hypothesis supported by X-ray scattering experiments during cellulose regeneration (Isobe et al. 2012) and simulation of the first stages of aggregation after chains exit from the plasma membrane during cell wall formation (Haigler et al. 2014). The organisation and conformation of chains, the structure of the hydrated ions, the coordination and polarisability of water around the hydroxyl groups and the way the hydrophobic planes escape polar regions must be better described in order to understand cellulose solubility in NaOH–water. In particular, the existence or not of molecularly dispersed solutions is still an open question.

The measurements of the viscosity of cellulose in NaOH–water give indications of possible aggregations in dilute solutions. In NaOH–water, cellulose intrinsic viscosity decreases with temperature increase (Kamide et al. 1987; Roy et al. 2003). However, the cellulose apparent average molecular weight remains constant with a temperature increase in 8 % NaOH–water (Kamide et al. 1987). The decrease in the intrinsic viscosity with the temperature increase cannot be the consequence of a gelation process since viscosity should increase with gelation and dilute solutions do not gel (Roy et al. 2003). Cellulose degradation was not the reason for this decrease either.

One way to explain the intrinsic viscosity decrease with temperature is the decrease of cellulose solvent thermodynamic quality, which seems to be a general phenomenon not only for dissolved cellulose (in any solvent), but also for solutions of cellulose derivatives. For example, the same dependence was reported for microcrystalline cellulose of DP 300 dissolved in EMIMAc ionic liquid (Gericke et al. 2009). The decrease in the intrinsic viscosity with a temperature increase is known for cellulose esters: for example, for cellulose acetate dissolved in EMIMAc (Rudaz and Budtova 2013), in m-cresol or dimethylformamide (Flory et al. 1958) or in acetone (Suzuki et al. 1980). The influence of temperature on the intrinsic viscosity was attributed to changes in the unperturbed chain dimensions.

Roy et al. (2003) explain that the decrease of the intrinsic viscosity with temperature is due the increasing role of the hydrophobic interactions with temperature increase. They assume that two mechanisms leading to the intrinsic viscosity decrease have to be considered. On one side, cellulose agglomerates become increasingly compact because of the interchain hydrophobic interactions with temperature increase. On the other side, because of interagglomerate interactions, new compact agglomerates are formed with a hydrodynamic volume smaller than the additive sum of volumes of the initial agglomerates (like the formation of interpolymer complexes between oppositely charged macromolecules). Thus, in the dilute region, the increasing role of inter- and intrachain hydrophobic interactions with temperature increase (above 20 °C) leads to aggregate compactisation. This is the same reason that has been advocated to describe the solution behaviour in semi-dilute states. In this state, solutions gel quickly without any additive. Gelation is faster if the concentration or temperature is increased (Roy et al. 2003; Egal 2006; Gavillon and Budtova 2008). The evolutions of storage and elastic moduli at various cellulose concentrations and temperatures were used to correlate the gelation time with solution temperature and cellulose concentration. Gelation time was approximated as the time where G' and G'' cross, as shown in Fig. 13. Whatever the temperature is, the gelation of semidilute cellulose–NaOH solutions takes place, being faster at higher temperatures. Cellulose–9 % NaOH solutions behave in a similar way as aqueous methylcellulose solutions with a lower critical solution temperature and temperature-increase-induced gelation. However, contrary to methylcellulose solutions, gels formed from cellulose–9 % NaOH solutions are not thermoreversible: after cooling to any temperature including the temperature of cellulose dissolution (−6 °C), they do not re-dissolve.

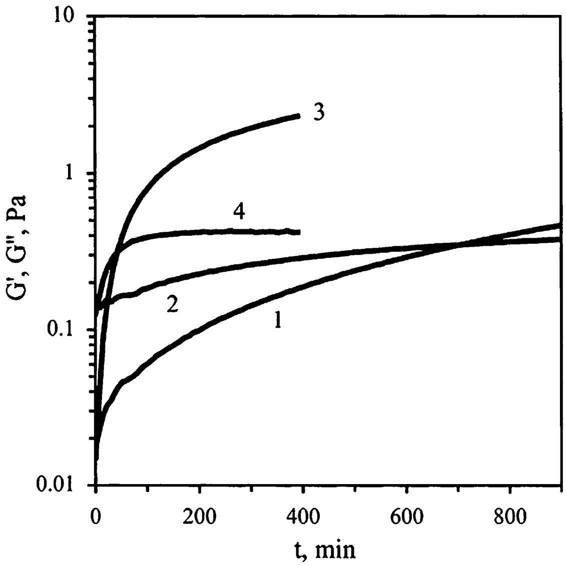


Fig. 13 G' and G'' of a 5 % cellulose–9 % NaOH–water as a function of time at 20 °C: G' (*1*) and G'' (*2*) and at 25 °C: G' (*3*) and G'' (*4*). Reprinted with permission from Roy et al. (2003) American Chemical Society

With time, at a fixed temperature, the solution gradually transforms from a viscous liquid to an elastic, solid-like network. Both hydrogen bonding and hydrophobic association may lead to gelation, each being more or less pronounced at a certain temperature. Because all cellulose–NaOH gels are slightly turbid, a phase separation with local chain segregation could be a possible mechanism governing thermo-induced changes. The formed gel becomes opaque as a sign of a phase separation, which becomes more evident with long times where syneresis occurs. The overall picture of temperature-induced changes in the cellulose coil in dilute and semi-dilute solutions is shown in Fig. 14.

Influence of additives on cellulose dissolution and solution properties in aqueous NaOH

Since the discovery of mercerisation, various low-molecular-weight components were added to cellulose or cellulose derivative solutions with the aim to improve either viscose processing (to lower the consumption of carbon disulphide, to ease filtration) or the properties of final materials. Urea, thiourea and different metal oxides were shown to increase the swelling of cellulose fibres and "fluidity" of viscose solutions. As will be demonstrated later, these experimental findings were mainly due to the increase of the cellulose soluble fraction, this fraction being of low molecular weight. At the same time, the dissolution of cellulose in 7–10 wt% NaOH at low temperatures was

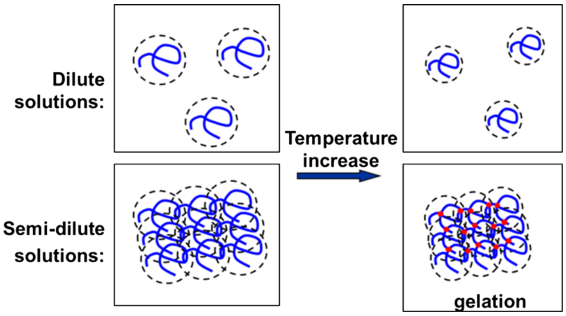


Fig. 14 Schematic presentation of the cellulose coil dimension changes with a temperature increase in dilute and semi-dilute solutions

discovered and the correlation between the swelling of cellulose fibres and cellulose dissolution was understood. The next logical step was to study whether the additives that influence the swelling of cellulose fibres could improve cellulose dissolution in aqueous NaOH.

Davidson in the late 1930s (1937) and then Laszkiewicz at the beginning of 1990s demonstrated the influence of metal oxides and urea or thiourea on cellulose dissolution in NaOH–water (Laszkiewicz and Wcislo 1990; Laszkiewicz and Cuculo 1993). Acrylamide, acrylic acid, acrylonitrile and later polyethylene glycol were also tested for improving cellulose solubility in aqueous sodium hydroxide. In the last 10–15 years, studies concentrated on ZnO, urea and thiourea added to NaOH–water for dissolving cellulose, the main goal being to understand the mechanisms of cellulose dissolution, the role of additives, the solution properties and making films and fibres.

In this section, we first give an overview of the influence of metal oxides, mainly ZnO, on cellulose dissolution and solution properties. Then the role of urea and/or thiourea are discussed. Finally all "other" additives to NaOH–water will be briefly presented.

Influence of ZnO and other metal oxides

The main facts and figures characterising cellulose dissolution in NaOH–water solutions with various metal oxides (MeO) such as zinc, beryllium and aluminium were obtained by Davidson (1937). In his work, the NaOH concentration, solution temperature and molar ratio MeO/NaOH were varied. Cotton and activated celluloses (so-called "oxycellulose" prepared from cotton linters treated first in sodium hypochlorite solution of pH 8.4 and then alkaline boiled) were examined in terms of the percentage of dissolved cellulose. The main results summarising the influence of ZnO are as follows:

- It was confirmed that the lower the solution temperature (−5 vs. 15 °C), the better the cellulose dissolution is, whatever the concentration of ZnO.
- At −5 °C the highest dissolution is achieved at a NaOH concentration of about 2.5 mol l^{-1}.
- The maximum dissolution yield, 100 %, was reached for "oxycellulose" dissolved in NaOH–water of 2–4 mol and a ZnO/NaOH ratio of 0.178; the increase of the ZnO concentration led to the appearance of precipitated ZnO particles.
- Cellulose pre-treatment ("oxycellulose") improves the dissolution to the point that even cotton linters can be dissolved to a yield of about 85 %.
- It was also noticed that except being dissolved at the optimal NaOH concentration, the solutions were gelling.

Potassium hydroxide, mixed with ZnO or not, was also tested for improving cellulose solubility. The addition of ZnO increased the dissolution in KOH, but NaOH was shown to be more efficient: for the same oxycellulose, the best dissolution yield was of 70 % at 2 mol of KOH and ZnO/KOH molar ratio of 0.14 and 100 % in NaOH in the same conditions.

The addition of beryllium oxide to NaOH–water had a slightly lower but similar effect as ZnO. It is interesting to note that with beryllium oxide, the highest cellulose dissolution was obtained at 15 °C and not at −5 °C. However, for the same oxycellulose sample dissolved in sodium berrylate solution, the dissolution never reached a yield of 100 %.

Unlike zinc oxide and beryllium oxide, aluminium oxide decreases cellulose solubility in NaOH–water. Increasing the Al_2O_3 concentration decreased the cellulose solubility and shifted the maximum solubility towards higher NaOH values.

Until cellulose dissolution in NaOH–water was used to make materials in the late 1980s by a group of researchers from Asahi Chemical Industry, the dissolution of cellulose in aqueous NaOH and sodium zincate was used to fractionate cellulose. For example, Kleinert (1958) correlates the wt% of dissolved cellulose and % of low DP cellulose (below DP = 200) in various pulps. In other words, it was suggested that by measuring cellulose solubility in certain conditions (12 wt% NaOH, 2 wt% ZnO, at 20 °C), the amount of low-molecular-weight cellulose could be determined.

The next step was to understand the role of ZnO in increasing cellulose dissolution in aqueous NaOH. The question asked was whether Zn or sodium zincate is chemically bound to cellulose or not. Using radioactive-labelled Zn^{65} and following its diffusion during cellulose coagulation, it was demonstrated that Zn is not bound to cellulose in any form (Borgin and Stamm 1950).

For more than 30 years, additives for dissolving cellulose in aqueous alkali seem to have been forgotten, at least from what is known in scientific publications. In 2002 a patent filed by Polish researchers from the Institute of Chemical Fibres from Łódź mentions the use of urea and ZnO in processing cellulose from NaOH–water solutions to increase the stability and spinnability of solutions (Struszczyk et al. 2002). The Polish group continued to work on the improvement of cellulose processing from aqueous NaOH together with Finnish scientists from VTT and Tampere University and the Biocelsol process was developed: cellulose was treated with a commercial endoglucanase-rich enzyme, dissolved in 7.8 % NaOH–0.84 % ZnO and coagulated in 5–15 % sulphuric acid with 10 % sodium sulphate (Vehviläinen et al. 2008, 2010, 2015). Fibres were spun with the best tenacity of 1.8 cN dtex^{-1}. At the same time, in her PhD thesis, M. Egal studied the structure of NaOH–ZnO–water and cellulose–NaOH–ZnO–water solutions and reported that gelation of the cellulose solution is significantly delayed in the presence of 0.5–2 wt% of ZnO (Egal 2006).

Finally, in 2011 three articles appeared simultaneously describing the properties of cellulose–NaOH–ZnO–water solutions and the corresponding films (Yang et al. 2011a, b; Liu et al. 2011a). In both articles from the L. Zhang group (Yang et al. 2011a, b), ZnO was added to 7 wt% NaOH–12 wt% urea–water and the solvent was cooled to −13 °C. The maximal dissolution yield was reported to occur at 0.5 wt% ZnO. The findings of Davidson (1937) concerning the influence of temperature and molecular weight on cellulose dissolution were confirmed: solubility increased with a cellulose molecular weight decrease but did not surpass 8 wt% cellulose for the lowest molecular weight used (6×10^4) and the temperature increase strongly decreased the solubility. Yang et al. (2011a) claimed that inclusion complexes are formed: without ZnO, NaOH hydrates are attached to cellulose and urea self-assembled on the surface of NaOH hydrogen bonded to cellulose helping in dispersing cellulose. With ZnO, the interactions between $\mathrm{Zn(OH)_4^{2-}}$ and cellulose were said to be stronger than between cellulose and NaOH. The role of ZnO was supposed to "break the intermolecular hydrogen bonds of cellulose and keeping the cellulose chains further apart from each other" (Yang et al. 2011a).

The influence of ZnO on the rheological properties of cellulose–NaOH solutions was studied in various works (Egal 2006; Yang et al. 2011b; Liu et al. 2011a). All articles report that the addition of ZnO delays solution gelation. Egal (2006) and Liu et al. (2011a) report an exponential dependence of the gelation time on temperature in the range of 10–50 °C in 8 wt% NaOH–water with various amounts of ZnO added (from 0 to 1.5 wt% ZnO) while no gelation over several days was observed in the temperature range −5 to 10 °C with 0.7–1.5 wt% ZnO. Gelation in less than 1 day in the same low-temperatue range was reported for a cellulose solution with 0.5 wt% ZnO added to 7 wt% NaOH–12 wt% urea–water (Yang et al. 2011b); the same was reported for cellulose in 7 wt% NaOH–12 wt% urea without ZnO (Cai and Zhang 2006). In these two latter cases, a peak in gelation time versus temperature dependence was reported at 0 °C and a strong decrease in gelation time (quick gelation) was reported around −5 °C. Fast gelation of cellulose–NaOH–water solutions between − 5 and −10 °C is somehow surprising as it is at these low temperatures that the best cellulose dissolution is observed. It was suggested by Liu et al. (2011a) that the reason for the quick gelation in this temperature range reported in Yang et al. (2011b) and Cai and Zhang (2006) is due to the viscosity increase because of the water crystallisation below −5 °C, as demonstrated in Egal et al. (2007).

Despite the fact that the increase of ZnO concentration above 0.5 wt% in 8 wt% NaOH leads to partial ZnO precipitation and formation of undissolved particles, the increase of ZnO concentration above 0.5 wt% still delays gelation (Liu et al. 2011a). The shape of gelation time versus temperature curves for various ZnO concentrations does not depend on the ZnO concentration and a master plot can be obtained, as shown on Fig. 15. Gelation time t_{gel} increases exponentially with ZnO concentration C_{ZnO} (Liu et al. 2011a):

$$t_{\mathrm{gel}} = t_0 + B \times C_{\mathrm{ZnO}}^{m}$$

where t_0 is the gelation time at $C_{\mathrm{ZnO}} = 0$, B is a constant and m is an exponent indicating the influence of ZnO.

The cellulose intrinsic viscosity in 8 wt% NaOH–water with 0.7 % ZnO and without ZnO was measured at different temperatures (Liu et al. 2011a). At a given temperature, the values of intrinsic viscosity coincide, and for both cases, the intrinsic viscosity decreases with temperature increase indicating the decrease of

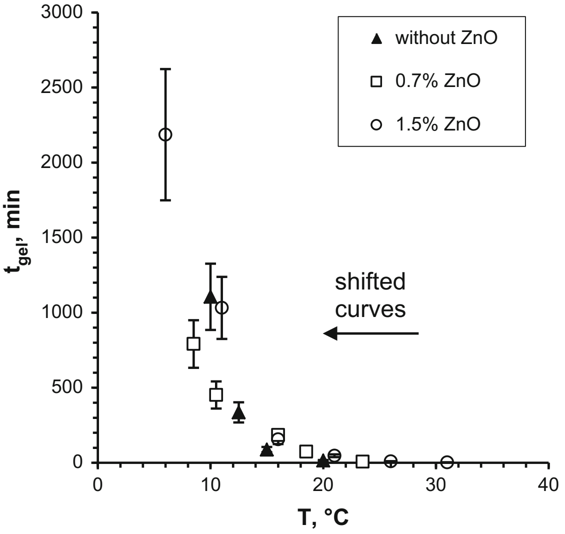


Fig. 15 Master plot of gelation time versus temperature for 6 wt% cellulose–8 wt% NaOH–water solutions with 0, 0.7 and 1.5 wt% ZnO: the curves are shifted towards 0 wt% ZnO by 6.5 °C for 0.7 wt% ZnO and by 14 °C for 1.5 wt% ZnO. With kind permission from Springer Science + Business Media: Liu et al. (2011b, Figure 6)

solvent thermodynamic quality. The presence of ZnO did not bring any noticeable change to the intrinsic viscosity of cellulose. In cellulose–8 wt% NaOH–0.7 wt% ZnO–water solution, only part of ZnO is dissolved. The unaffected value of the intrinsic viscosity indicates that neither dissolved nor suspended ZnO influences polymer conformation and the behaviour of chains at the molecular level in the dilute region.

The role of ZnO was proposed to be as follows (Liu et al. 2011a). During the dissolution process, the NaOH hydrates break inter-chain hydrogen bonds between cellulose macromolecules and links to cellulose chains. As was already mentioned in the "Structure, properties and thermodynamics of cellulose–NaOH–water without additives" section, at least four NaOHs per one anhydroglucose unit are needed to dissolve cellulose (Egal et al. 2007). It was assumed that there is an unstable equilibrium between NaOH hydrates bound to cellulose chains. When the temperature is raised, cellulose–cellulose interactions become more favoured compared to cellulose–NaOH interactions, leading to the shrinkage of cellulose coils in dilute solution and decrease of intrinsic viscosity. In semi-dilute solutions, this leads to the inter-chain connection of cellulose coils and gelation happens. When ZnO is suspended in NaOH–water solutions, a "network" of tiny particles is formed. The surface of particles is hydrolysed, attracting water molecules. When dissolved, zincate complexes with water and $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ are formed. Thus ZnO may play the role of water "binder", strongly decreasing the amount of free water around the cellulose chains that may drive chain aggregation. This could explain why ZnO only delays the gelation but does not change cellulose dissolution, solvent quality and gelation kinetics in NaOH–water solutions.

Influence of urea and thiourea

Additives like urea and thiourea have also been studied and used for a long time for improving the viscose process or understanding Na–cell formation (see for example Harrison 1928). It was thus rather straightforward to investigate whether the addition of these compounds would improve the solubility of cellulose in NaOH. Laszkiewicz and Wcislo (1990) demonstrated, using IR and X-ray analysis, that in the presence of urea, thiourea, sodium aluminate and zincate, cellulose is "more reactive to xanthation" than cellulose without these additives, and the formation of cellulose II was confirmed. In a subsequent publication, Laszkiewicz and Cuculo (1993) reported that the highest cellulose solubility in 5 wt% NaOH–water was achieved with the addition of thiourea and of acrylamide as compared with the addition of acrylic acid or acrylonitrile or without any additive. They also emphasised that freezing-thawing of cellulose solutions strongly increased cellulose solubility. Later, Laszkiewicz (1998) reported that the addition of 1 wt% urea in 8.5 wt% NaOH at −5 °C improves the solubility of bacterial cellulose having an initial DP of 680. The fraction of dissolved cellulose was 48.6 % with 1 wt% urea and 17.8 % without it.

The influence of urea and thiourea on cellulose dissolution in NaOH–water and solution properties was then studied in detail by the group of L. Zhang from Wuhan University, China. They confirmed that urea–NaOH–water is a direct cellulose solvent and demonstrated that the addition of 2–6 wt% of urea to 6–8 wt% NaOH–water improves cellulose dissolution (cellulose with viscosity-average molecular weight of 6.7×10^4 was completely dissolved in 4 wt% urea–6 wt% NaOH–water). They measured the Mark-Houwink constants for cellulose dissolved in 4 wt% urea–6 wt% NaOH at 25 °C as $K = 2.45 \times 10^{-2}$ ml g^{-1} and a = 0.815 for cellulose of $M_w = (3–13)\ 10^4$ (Zhou and Zhang 2000; Zhou et al. 2004a, c). When comparing with the constants reported for other cellulose solvents such as cadoxen ($K = 3–5 \times 10^{-2}$ and a = 0.75–0.77), 0.5 M cupriethylenediamine hydroxide or CED ($K = 1–3 \times 10^{-2}$ and a = 0.8–0.9) and LiCl/DMAc ($K = 1.3 \times 10^{-4}$ and a = 1.19) [data taken from Table 1 of Kasai (2002)], the values found for cellulose dissolved in urea–NaOH appear to be close to those of CED.

A rather complicated and somehow contradictory influence of urea on cotton cellulose dissolution in NaOH–water was found in Wang and Deng (2009). At low urea concentrations (4 wt%), practically no influence on solubility was recorded while at a higher urea concentration (12 wt%), a strong decrease of cellulose solubility in 10 wt% NaOH–water was observed. It should be noted that cellulose dissolution was performed without stirring, which may strongly influence the kinetics of dissolution.

While urea improves cellulose dissolution in aqueous NaOH, as found by most researchers, the dissolution yield strongly decreases with the increase of dissolution temperature and cellulose molecular weight (Qi et al. 2008a). The same trends were reported earlier for NaOH–water solvent without additives and with ZnO (Davidson 1937). The best dissolution was achieved in 7 wt% NaOH–12 wt% urea–water at −12 to 10 °C and the highest cellulose concentration dissolved was 8 wt% of $M_\eta = 3 \times 10^4$ (Qi et al. 2008a). As explained in "Structure, properties and thermodynamics of cellulose–NaOH–water without additives" section for cellulose dissolved in (8–9) wt% NaOH–water, at least four NaOH molecules are needed to dissolve one AGU giving an approximately equal cellulose/NaOH weight per cent ratio. This ratio does not change with the addition of urea: the decrease of the enthalpy of the eutectic peak of NaOH–water (i.e. amount of free NaOH hydrates not bound to cellulose) with the increase of cellulose concentration is absolutely the same with or without urea; see Fig. 16 (Egal et al. 2008). By carefully analysing the DSC thermograms of urea–water, NaOH–urea–water and cellulose–NaOH–urea–water and keeping in mind the results obtained for NaOH–water and cellulose–NaOH–water (Egal et al. 2007), it was concluded that urea does not interact with either NaOH or cellulose. The same result, i.e. the absence of any interactions between cellulose and urea, was obtained later using ^{13}C, ^{15}N and ^{1}H NMR (Cai et al. 2008a, b). No direct interactions between urea and cellulose were demonstrated in a recent detailed study of cellulose–LiOH–urea–water solutions (Isobe et al. 2013): it was suggested that urea may promote the decrease of cellulose crystallinity and stabilise alkali-swollen cellulose. The increase of the dissolved fraction of cellulose in the presence of urea was reported in 4.6 wt% LiOH at 0 °C (15 vs. 6 g l^{-1} with 15 wt% urea vs. 0 % urea, respectively), but cellulose solubility strongly decreased with temperature increase and became the same with and without urea above 10 °C.

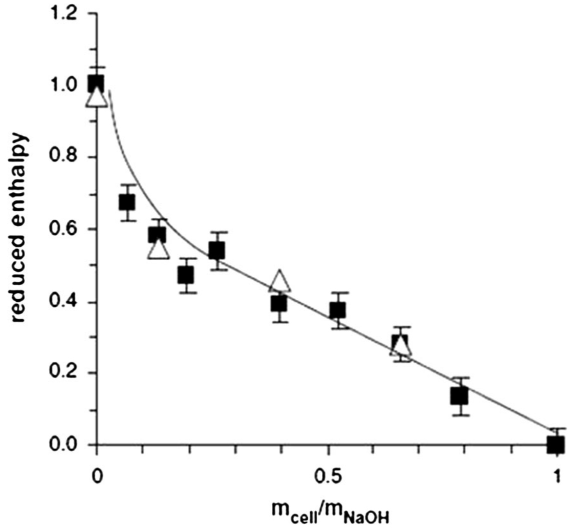


Fig. 16 Reduced melting enthalpy of the NaOH–water eutectic versus reduced cellulose/NaOH mass ratio. *Dark points* are for cellulose–7.6 wt% NaOH–water without urea and *open points* are for cellulose–7.6 wt% NaOH–6 wt% urea–water. The *line* is given to guide the eyes. With kind permission from Springer Science + Business Media: Egal et al. (2008, Figure 6)

Despite the agreement in the main experimental findings, scientists propose different and sometimes contradictory explanations regarding the role of urea. Based on NMR, FT-IR, SANS, TEM and WAXS, Cai et al. (2008a, b) found that low temperatures promote the formation of hydrogen-bonded networks of NaOH, urea and water and that their formation is favoured at low temperatures. The chemical shifts of carbon atoms are similar in NaOH–urea–water and NaOH–water environments, showing that urea does not interact with cellulose, a result in agreement with Egal et al.'s (2008) findings. Cai et al. (2008a, b) suggest a model where NaOH hydrates are hydrogen-bonded to

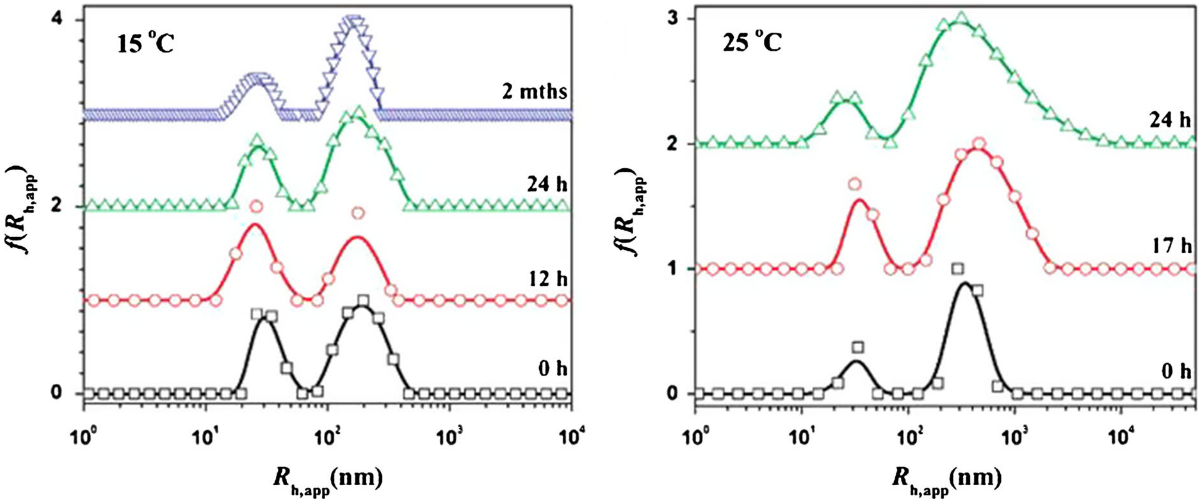


Fig. 17 Time dependence of particle size distribution in solution of 0.470 g l^{-1} cellulose in 7 wt% NaOH–12 wt% urea at 15 and 25 °C. Reprinted with permission from Lu et al. (2011) American Chemical Society

cellulose molecules and urea hydrates are bonded to NaOH hydrates on the surface of cellulose–NaOH complex. This is making a sort of "envelope" preventing cellulose chains to aggregate. These authors claim that this arrangement, called the inclusion complex, is metastable and is slowly displaced with time and temperature increases, leading to the formation of large cellulose complex aggregates with radii of gyration larger than 200 nm (Lu et al. 2011; Lue et al. 2007). The same was reported by Jiang et al. (2014). However, in a recent publication, Xiong et al. (2014) suggest that the cellulose conformation in NaOH–urea–water solution is nearly a rigid rod with a length of 300 nm and diameter of 3.6 nm. Those results were based on cryo-TEM observations and should be confirmed by other methods. The same authors (Xiong et al. 2014) report that urea has no "strong direct interaction" with either cellulose or NaOH and suggest that urea "accumulates on the cellulose hydrophobic region", thus preventing the cellulose chain from agglomeration.

Another interpretation of the role of urea was proposed by Egal et al. (2008): urea "stabilises" cellulose in aqueous NaOH by binding water in the same way as ZnO does (Liu et al. 2011a).

As demonstrated in the "Structure, properties and thermodynamics of cellulose–NaOH–water without additives" section, the properties of cellulose–NaOH–water solutions change with time and temperature. Ageing also occurs when urea or thiourea is added. Static and dynamic light scattering of dilute solutions showed that large aggregates grow in cellulose–7 wt% NaOH–12 wt% urea–water with time and temperature, Fig. 17 (Cai et al. 2008a, b; Lu et al. 2011). Solution instability was interpreted by the "*imperfection*" of the urea "*shell*" and "*reconstruction*" of hydrogen bonds between cellulose macromolecules.

Another point of view on the behaviour of dilute cellulose–NaOH–water solutions with and without urea was proposed based on the measurements of cellulose intrinsic viscosity. The intrinsic viscosity of cellulose dissolved in NaOH–urea–water decreases with temperature increase (Egal 2006) in the same way as demonstrated for pure NaOH–water solvents (Kamide et al. 1987; Roy et al. 2003) or when ZnO is added (Liu et al. 2011a). The reason for cellulose intrinsic viscosity's negative temperature dependence in NaOH–water in the presence of urea can thus also be the same as for cellulose dissolved in ionic liquids or for many cellulose derivatives: it is due to the decrease of solvent thermodynamic quality. The contradictory results, i.e. growth of aggregates against the intrinsic viscosity decrease with temperature increase, are probably caused by the different experimental techniques used, static versus dynamic: aggregates, detected with the light-scattering technique, may be destroyed when the solution is flowing.

In the semi-dilute state, cellulose–NaOH–water solutions gel with time and temperature increase (Roy et al. 2003), and the same happens when urea or thiourea is added (Cai and Zhang 2006; Lue and Zhang 2008; Ruan et al. 2008). Similar to the ZnO case, gelation is delayed in the presence of urea or thiourea as compared with cellulose dissolved in pure NaOH–water solvent (Egal 2006).

Some authors claimed that using both urea and thiourea further improves dissolution (Jin et al. 2007). ^{13}C NMR showed that this mixture is a direct solvent and the authors state that NaOH, urea and thiourea are all bound to cellulose, which “brings cellulose molecules into aqueous solution to a certain extent” and prevents gelation. The structure of the solvent does not change with the introduction of cellulose. The authors suggest that NaOH hydrates are bound to cellulose to form a protective layer preventing cellulose chain aggregation. This solvent was also studied by Zhang et al. (2011) and Kihlman et al. (2011). Overall, the urea + thiourea mixture in NaOH–water does not seem to bring more advantages as compared with urea–NaOH or thiourea–NaOH solvents.

It should be noted that one has to be very careful with the interpretation of the interactions between cellulose and urea. The composition of the solvent and dissolution conditions are very important and will drastically influence the “interactions”. The same is observed for the case of sodium hydroxide–cellulose system: NaOH may or may not transform cellulose from a I to II polymorph. In certain conditions, urea does strongly interact with cellulose, the best example of this interaction being the formation of cellulose carbamate. The latter can be prepared, for example, by heating the cellulose–urea mixture above the urea melting temperature or by heating urea and cellulose “activated” with aqueous sodium hydroxide or by dispersing cellulose in xylene, adding urea and caustic soda and heating (Kunze and Fink 2005). A formation of cellulose–urea–NaOH complexes was reported for cellulose treated with 7 wt% NaOH–(30–40) wt% urea at room temperature (Kunze and Fink 2005). This treatment with high-concentrated urea in the presence of sodium hydroxide allowed obtaining cellulose carbamate at lower temperatures and with higher degrees of substitution. Cellulose carbamation at reducing end groups was reported for cellulose treated with 7 g l^{-1} urea–20 g l^{-1} NaOH at 160 °C (Ershova et al. 2012). It was thus not surprising to find another confirmation that urea molecules “interact directly” with cellulose in concentrated aqueous urea solutions, 3 mol l^{-1} (Bergenstrahle-Wohlert et al. 2012). The result was obtained when comparing CP/MAS ^{13}C spectra and molecular dynamics of cellulose in aqueous 3 M urea and in pure water.

What still remains as an open question is why urea improves cellulose dissolution in (7–10) wt% NaOH–water at urea concentrations below 12 wt% while there is a confirmed absence of any interactions between urea and cellulose. The same question holds for thiourea for which less research has been performed.

Influence of “other” additives

Aside from metal oxides and urea-based components, some other low-molecular-weight compounds were tested for the improvement and/or stabilisation of cellulose in aqueous alkali solutions. Among acrylamide, acrylic acid and acrylonitrile, acrylamide was found to be the most efficient in improving cellulose dissolution in 8.5 wt% NaOH–water (Laszkiewicz and Cuculo 1993). The fraction of dissolved cellulose was the same as that obtained in 8.5 wt% NaOH–5 wt% thiourea–water and higher than that in 8.5 wt% NaOH–water. Acrylic acid and acrylonitrile did not improve cellulose dissolution in NaOH–water.

The influence of 1 wt% polyethylene glycol (PEG) on cellulose ($M = 132{,}000$ g mol^{-1}) dissolution in 9 wt% NaOH–water was also studied (Yan and Gao 2008). Solutions were prepared via the freezing-thawing process. Authors reported that cellulose–PEG–NaOH–water was still flowing after 11 days of solution storage at room temperature. This result is very interesting but should be taken with care as far as their cellulose–6 wt% NaOH–4 wt% urea–water solutions were not gelled after 4 days of storage at room temperature, contrary to what is reported by Cai and Zhang (2006). A “new complex” with PEG was suggested and maximum cellulose solubility in this new solvent was reported to be 13 wt%, which is higher than any known ones in alkali solvents, with or without additives.

Betaine derivative (neither the exact composition nor concentration given) was reported to increase the gelation temperature (Medronho et al. 2012) by 10 °C as compared with 3.5 wt% cellulose–10 wt% NaOH–water. It was suggested that it is the amphiphilic nature of the additive that prevents hydrophobic interactions between cellulose chains. Unfortunately no more details were reported to confirm this hypothesis.

Processing of cellulose from NaOH aqueous solutions and material properties

Cellulose coagulation kinetics from NaOH–water solutions

For cellulose materials that are made via direct cellulose dissolution, coagulation (sometimes called regeneration) is an inevitable step in cellulose processing. During coagulation, cellulose is phase separated from the solvent. Most cellulose products, fibres and films are made through wet or dry–wet spinning or film casting. Coagulation conditions (cellulose concentration and solvent type, composition of the non-solvent, temperature) determine the material morphology in the wet (coagulated) state and also control process kinetics. The latter plays an important role as soon as processing up-scaling is considered. In case of NaOH–water solvents, cellulose solutions gel with time and temperature. Thus the state of cellulose before coagulation should also be taken into account to understand the coagulation kinetics.

The kinetics of cellulose coagulation from cellulose–NaOH–water gels was first described by Gavillon and Budtova (2007): the release of NaOH from cellulose–NaOH–water gel into a water bath was monitored over time as a function of cellulose concentration and bath temperature; see the example in Fig. 18. Microcrystalline cellulose of DP 180 was used. First, it was demonstrated that the Fick diffusion law can be applied to describe the kinetics of the evolution of the NaOH concentration in the coagulating bath. Then, mean diffusion coefficients were determined and compared with those of NMMO obtained during cellulose coagulating in water from solid cellulose–NMMO solutions: as expected, D_{NaOH} is slightly higher than D_{NMMO} and D_{NaOH} varies from 2.1×10^{-10} to 1.1×10^{-10} $\mathrm{m^2\ s^{-1}}$ for cellulose concentrations from 3 to 7 wt%, respectively, at 25 °C.

The influence of the cellulose concentration on the value of diffusion coefficients was analysed in details using various theories developed for homogeneous and heterogeneous gels (solute diffusing in a gel) and for polymer membranes. It was demonstrated that hydrodynamic and free volume approaches fit the experimental data well, indicating that a "membrane" and not "hydrogel" approach should be used to describe NaOH diffusion during cellulose coagulation from a gelled solution. There are several reasons explaining this finding. First, when solution is gelling, a micro-phase separation between cellulose and NaOH occurs: the resulting gel is opaque and syneresis was observed when keeping the solution for a long time at slightly elevated temperatures, around 50 °C (Gavillon and Budtova 2008). NaOH thus diffuses in a highly heterogeneous medium with pore sizes much larger than the dimensions of the solute. Second, during coagulation, cellulose undergoes a phase separation with the solvent and a 3D network of coagulated cellulose "fibrils" is formed. Coagulated cellulose containing water or any other non-solvent fluid in the pores of the network is often called a "hydrogel" or "gel". This term is not appropriate here: by definition, the polymer gel or hydrogel results from physical or chemical gelation of a dissolved polymer and thus is based on dissolved (and cross-linked) macromolecules. In the coagulated state, cellulose is not dissolved anymore and there is no physical or chemical cross-linking.

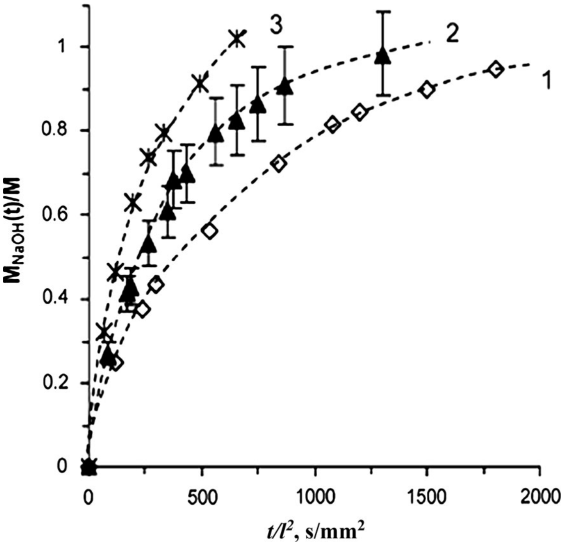


Fig. 18 Diffusion of NaOH from 5 wt% cellulose–7.6 wt% NaOH–water gels into the water coagulation bath at (*1*) 25, (*2*) 50 and (*3*) 80 °C. $M_{\mathrm{NaOH}}(t)$ is the mass of NaOH released at time *t* into coagulation bath, *M* is the total amount of NaOH in the system and *l* is the sample (disk) half thickness; the *lines* are drawn to guide the eye. Adapted with permission from Gavillon and Budtova (2007) American Chemical Society

The influence of the state of cellulose, dissolved or gelled, and of gelation time and temperature on coagulation kinetics was studied by Sescousse and Budtova (2009). It was shown that diffusion of NaOH from the sample into 0.1 mol l^{-1} acetic acid from the cellulose–NaOH gel is three times faster as compared with non-gelled solution of the same cellulose concentration. This interesting result, which may look unexpected, is due to different local cellulose concentrations in a solution and in a gel. As mentioned above, cellulose–NaOH–water gels are highly heterogeneous with polymer-rich and polymer-poor regions (Fig. 19). The viscosity in the "pores" of the gel is thus lower than that in cellulose solutions (macroscopic viscosity) leading to a higher mobility of NaOH. Cellulose coagulation from cellulose–NaOH–water solution will thus take more time than from the gel of the same concentration and geometry. As soon as gel is formed, gelation conditions do not influence NaOH diffusion during cellulose coagulation. Coagulation bath acidity, from 0 to 0.1 mol l^{-1} acetic acid, also did not influence the NaOH diffusion coefficient.

As shown in Fig. 18, the higher the bath temperature, the quicker the release of NaOH is into the coagulation bath (Gavillon and Budtova 2007). As far as coagulation is a diffusion-driven process, NaOH diffusion coefficients obtained for various bath temperatures obey Arrhenius law. The activation energy was calculated to be within 16–19 kJ mol^{-1} for a cellulose concentration of 5 wt% (Gavillon and Budtova 2007; Sescousse and Budtova 2009).

In order to study the influence of the bath composition on cellulose coagulation from cellulose–NaOH–water gels, different alcohols (ethanol, isopropanol, butanol, panthenol and hexanol) were used and compared with coagulation in water (Gavillon and Budtova 2007). It turned out that samples strongly contract in alcohols making the calculation of the diffusion coefficient rather difficult. It was suggested that contraction is governed, at least partly, by the solubility parameter δ, which indicates polymer–solvent affinity and thus polymer dissolution or swelling in a given solvent. In the first approximation, the closer the cellulose and bath fluid solubility parameters are, the lower the sample contraction should be during coagulation. This indeed was what was obtained for the change in sample volume when placed in water and alcohol baths, as shown in Fig. 20, where the sample reduced volume at equilibrium $(V/V_0)_{eq}$ is plotted against the difference between the cellulose and bath fluid solubility parameters $\Delta\delta$. The smallest $\Delta\delta$ corresponds to the cellulose/water system: the larger $\Delta\delta$ is, the higher the cellulose sample volume reduction is.

Films and membranes

The easiest way to prepare an object from a cellulose solution and test its properties is to coagulate cellulose in the form of a film or a thin disk. Cellulose films from aqueous NaOH solutions with and without additives have been widely studied and characterised. Many parameters can be varied: the cellulose molecular weight and concentration in the solution, solvent composition (NaOH–water, NaOH–water with urea, thiourea, ZnO and their mixtures), coagulation conditions (for aqueous solutions, it is the type of acid and its concentration, temperature, type of coagulation

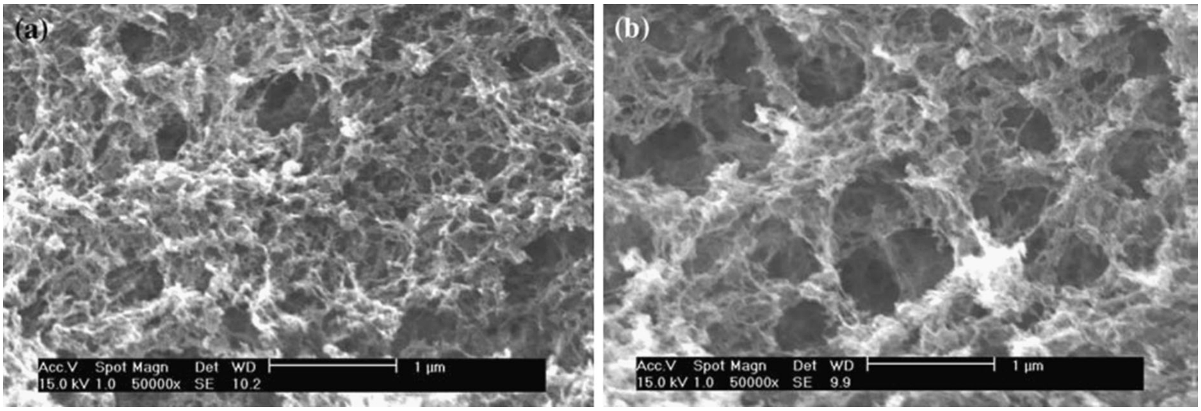


Fig. 19 SEM images of aerocellulose from not gelled (**a**) and gelled at 50 °C for 20 h (**b**) 5 wt% cellulose–NaOH–water solution coagulated at 22 °C in 0.1 mol l^{-1} acetic acid. With kind permission from Springer Science + Business Media: Sescousse and Budtova (2009, Figure 8)

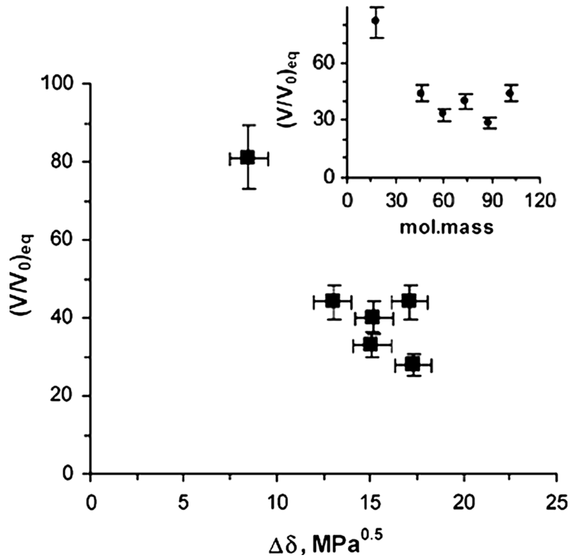


Fig. 20 Contraction of a 5 wt% cellulose–7.6 wt% NaOH–water gel at equilibrium as a function of the solubility parameter difference. *Inset* the same as a function of coagulating liquid molecular mass. Reprinted with permission from Gavillon and Budtova (2007) American Chemical Society

fluid such water, ethanol or their mixture), method used for casting/film drawing, use of plasticisers and way of drying. The mechanical properties of the obtained films are also controlled by the experimental conditions: film conditioning and thus the moisture content in the film, deformation rate, etc.

Detailed studies of the influence of coagulation parameters on cellulose crystallinity and film morphology and mechanical properties were performed in Japan, for cellulose I and cellulose II dissolved in 9 wt% NaOH–water (Matsui et al. 1995; Yang et al. 2007). It was shown that most of the films have a skin-core morphology that is typical for membrane formation because of the phase inversion (Matsui et al. 1995). The size of the pores in wet coagulated cellulose, after freeze drying, was around several tens of nanometres in the skin and several hundreds of nanometres, up to a few microns, in the core (Matsui et al. 1995). The higher the coagulation bath temperature was, the larger the pores (Matsui et al. 1995). The increase of the H_2SO_4 concentration in the coagulation bath first slightly decreased the size of the pores in wet coagulated cellulose, but above 60 wt% of acid, large pores were observed because of the cellulose degradation (Matsui et al. 1995). As a consequence, the crystallinity and mechanical properties also strongly decreased when the sulphuric acid concentration was higher than 60 wt% (Yang et al. 2007).

The influence of coagulation conditions was investigated for cellulose films prepared from cellulose–NaOH–urea or thiourea solutions (Zhang et al. 2002a, 2005a; Liang et al. 2007; Mao et al. 2006; Ruan et al. 2004b, c; Zhou et al. 2002). The opposite morphology, as compared to that described above for cellulose coagulated from 9 wt% NaOH–water, was observed: a denser core and a porous skin, for both the NaOH–urea and NaOH–thiourea solvent systems. This particular morphology was explained by a "pre-gelation" step used before cellulose coagulation. Pore size increased with the increase of coagulation bath temperature for films coagulated from NaOH–urea solvent (Cai et al. 2007b), similar to what was previously observed for cellulose coagulated from NaOH–water solvent. The influence of the acid type and concentration and presence of salts on pore size in wet coagulated cellulose will be discussed below when analysing the permeability properties of wet cellulose films.

One of the main characteristics of films is their mechanical properties: tensile strength and elongation at break. They are summarised in Table 2 for NaOH–water-based solvents with different additives and cellulose pre-treatments; Innovia Films (UK) cellophane properties are also added for comparison. Overall, the mechanical properties of films made from aqueous NaOH-based solvents, whatever the additives and pre-treatments are, are slightly lower than those of cellophane.

If willing to use wet cellulose films as separation membranes, permeability is then the key parameter. Aside from the intrinsic membrane properties, experimental conditions used to study permeability, such as applied pressure, also have to be taken into account. For example, it was shown that wet cellulose is compressible and thus permeability depends on the applied pressure (Liu and Budtova 2012). Water flux through wet coagulated cellulose prepared from 4–5 wt% cellulose dissolved in NaOH–urea or NaOH–thiourea was measured under 0.1 MPa pressure (Mao et al. 2006; Ruan et al. 2004a; Cai et al. 2007b; Zhou et al. 2002). Permeability strongly depends on coagulation conditions and may vary from 6 to 8 ml (h m^2 mmHg)$^{-1}$ for cellulose coagulated in an aqueous $(NH_4)_2SO_4$ bath (Ruan et al. 2004a) or 10–15 ml (h m^2 mmHg)$^{-1}$ for 5 wt% H_2SO_4–10 wt% Na_2SO_4 bath (Cai et al. 2007b) to 70–80 ml (h m^2 mmHg)$^{-1}$ for 1–10 wt% $CaCl_2$–3

Table 2 Mechanical properties of films from cellulose–NaOH solutions with various additives and of cellophane

Solvent composition	Cellulose DP and treatment	Tensile strength (MPa)	Elongation (%)	References
Cellophane P25 from Innovia Films (viscose process)		130 in machine direction (MD), dry; 80 in transverse direction (TD), dry	22 (MD) 70 (TD)	Innovia Films (2015)
9 wt% NaOH	360	From 100 to 40 with the increase of H_2SO_4 from 0 to 70 wt% in coagulation bath		Yang et al. (2007)
NaOH–urea–ZnO	250–350, hydrothermal treatment	50–65 Casing: 58	5–15 Casing: 33	Struszczyk et al. (2002)
NaOH–urea–ZnO	350–450 Biocelsol	40–60	5–7	Struszczyk et al. (2001)
7.5 wt% NaOH–1 wt% urea	600	15–25 (wet) 65–90 (dry)	15–35 (wet) 7–15 (dry)	Zhang et al. (2005a)
9.5 wt% NaOH–4.5 wt% thiourea	600	1–2 (wet)	100–190 (wet)	Liang et al. (2007),
6 wt% NaOH–5 wt% thiourea	600	From 90 to 10 (dry) with the increase of H_2SO_4 from 0 to 50 wt% in coagulation bath	From 15 to 1, respectively	Zhang et al. (2002b)
		From 95 to 80 (dry) with the increase of $(NH_4)_2SO_4$ from 0 to 20 wt% in coagulation bath	From 11 to 6, respectively	Ruan et al. (2004a)
7 wt% NaOH–12 wt% urea	600	From 100 to 70 (dry) and from 1 to 1.5 (wet) with temperature of coagulation bath from 10 to 60 °C	From 10 to 3 (dry) and from 70 to 30 (wet), respectively	Cai et al. (2007b)
6 wt% NaOH–4 wt% urea	600	From 80 to 110 (dry) with the increase of $CaCl_2$ in coagulation bath from 1 to 10 wt%	10–11	Zhou et al. (2002)
5 % cellulose in 7 % NaOH	540 from cellulose nanofibres	130	31	Yamane et al. (2015)

wt% HCl bath (Zhou et al. 2002). The lowest values are somewhat comparable to the permeability of wet cellulose films coagulated from cuprammonium (Abe and Mochizuki 2003) and the highest values with permeability of wet cellulose coagulated from NMMO monohydrate (Abe and Mochizuki 2002) and from ionic liquid (Liu and Budtova 2012). It can be concluded that wet cellulose coagulated from NaOH-based solvent systems can be used for separation of undissolved solid particles (i.e. in microfiltration).

Fibres

The processing and properties of fibres spun from cellulose–NaOH solutions were studied and reported in several papers (Yamashiki et al. 1990a, 1992; Yamane et al. 1994, 1996a, b, c, d; Okajima and Yamane 1997). Some authors used steam-exploded cellulose pulps (Yamashiki et al. 1990a, 1992) combined, in some cases, with wet pulverisation to increase the surface of cellulose particles for better dissolution, followed by a pre-treatment in 2–5 wt% NaOH at −2 °C and high-speed mixing (Yamane et al. 1994, 1996a, b). The dissolution was performed in 7–9 wt% NaOH–water at −2 to 4 °C at cellulose concentrations around 5 wt% (Yamashiki et al. 1990c, 1992, 1994, 1996a, b, c, d; Okajima and Yamane 1997). Cellulose DP suitable for spinning was found to be 200–300. Spinning followed by coagulation in sulphuric acid gave filaments with good mechanical properties (Table 3). The orientation degree measured by X-ray scattering increases slightly from 0.76 to 0.8

Table 3 Summary of the tensile properties of cellulose fibres spun from various NaOH–water solutions and comparison with other cellulose fibres

Solvent/process	Initial DP	Modulus (GPa)	Tenacity, dry (MPa)	Elongation at break (%)	References
NaOH–water		6.6–9.3 (50–70 g d^{-1})	70–110 (0.5–0.8 g d^{-1})	1–8	Yamashiki et al. (1990c)
	330		200–240 (1.5–1.8 g d^{-1})	7	Yamashiki et al. (1992)
	1060	0.06 wet (0.45 g d^{-1})	170–240 (1.3–1.8 g d^{-1})	15–21	Yamane et al. (1994)
		10.5–14.5 (80–110 g d^{-1}) for H_2SO_4 from 20 to 70 wt%	190–200 (1.4–2.2 g d^{-1})	10–17	Yamane et al. (1996c)
		19.3 (146 g d^{-1})	250 (1.9 g d^{-1})	15	Okajima and Yamane (1997)
NaOH–ZnO (Biocelsol)	580		190 (12.6 cN tex^{-1})	15	Struszczyk et al. (2001)
	270 fibre		180–270 (1.2–1.8 cN dtex^{-1})	15	Vehviläinen et al. (2008)
NaOH–urea–ZnO (Biocelsol)	620		230–240 (15–16 cN tex^{-1})	15–16	Struszczyk et al. (2002)
NaOH–urea	600		150–300 (1–2 cN dtex^{-1})	9–21	Cai et al. (2004)
	440 and 620		190–270 (1.3–1.8 cN dtex^{-1})	2–18	Cai et al. (2007a)
	490		150–300 (1–2 cN dtex^{-1}	1–2.8	Qi et al. (2008b)
NaOH–urea–thiourea	330 and 620		150 (1 cN dtex^{-1})	15–18	Ruan et al. (2004b)
Viscose			190 (1.44 g d^{-1})	18	Yamashiki et al. (1992)
		9.3	260	23	Northolt et al. (2001)
			330–390 (22–26 cN tex^{-1})	20–25	Fink et al. (2001a)
		11	340	15	Adusumali et al. (2006)
		11	423	19	Gindl et al. (2008)
	300 fibre	5.4 (36 cN dtex^{-1})	320 (2.15 cN dtex^{-1})	23	Jiang et al. (2012)
Modal		13	440	10	Adusumali et al. (2006)
Rayon tirecord		22	780	11	Adusumali et al. (2006)
Lyocell		23.4	560	9	Adusumali et al. (2006)
		30	620	7	Gindl et al. (2008)
	(550 fibre)	13.2 (88 cN dtex^{-1})	650 (4.3 cN dtex^{-1})	13	Jiang et al. (2012)

Table 3 continued

Solvent/process	Initial DP	Modulus (GPa)	Tenacity, dry (MPa)	Elongation at break (%)	References
Alceru	570 (520 fibre)	14.1 (942 cN tex^{-1})	650 (43.6 cN tex^{-1})	17	Kosan et al. (2008)
Cupramonium	380		260 (2 g d^{-1})	9	Yamashiki et al. (1992)
		1–2 wet (8–15 g d^{-1})	360 (2.7 g d^{-1})	11	Yamane et al. (1994)
		16 (121 g d^{-1})	370 (2.8 g d^{-1})	13	Okajima and Yamane (1997)
Ionic liquid BMIMCl	570 (520 fibre)	10.2 (682 cN tex^{-1})	800 (53.4 cN tex^{-1})	13	Kosan et al. (2008)
	(540 fibre)	11.3 (75 cN $dtex^{-1}$)	530 (3.5 cN $dtex^{-1}$)	7	Jiang et al. (2012)
Ionic liquid EmimAc	570 (520 fibre)	10.2 (682 cN tex^{-1})	680 (45.6 cN tex^{-1})	11	Kosan et al. (2008)
CarbaCell			200–390 (13–26 cN $dtex^{-1}$)	8–27	Fink et al. (2001a)
cellulose acetate-saponified in caustic soda (Fortisan)		32	1000	6.8	Northolt et al. (2001)
			170 (1.3 g d^{-1})	36	Kim et al. (2006)
Phosphoric acid	800 (620 fibre)	45	1700	5.1	Northolt et al. (2001)
LiCl/DMAc		0.19 wet (1.4 g d^{-1})	500 (3.74 g d^{-1})	6.2	Turbak et al. (1981)

In some cases, the cellulose initial DP was not reported, but that of cellulose in the fibre was determined; in this case it is indicated as the DP of "fibre". The density of cellulose fibre is taken as equal to 1.5 g cm^{-3} to calculate the values in SI units. In brackets we show the original values as given in the literature

and Young's modulus increases from 10.5 to 14.5 GPa (80–110 g d^{-1}) with an increase of the sulphuric acid concentration in the coagulation bath from 20 to 70 wt%. The authors interpret this phenomenon by the "shrinking stress due to the dehydration effect" of sulphuric acid (Yamane et al. 1996c). The degree of crystallinity was around 45 % and the elongation at break was high, about 20 % (Yamashiki et al. 1990b, 1992; Okajima and Yamane 1997; Yamane et al. 1996c, d).

Fibres were also prepared from solutions in NaOH–water–urea (Cai et al. 2004; Cai et al. 2007a; Qi et al. 2008b; Chen et al. 2007) and NaOH–water–thiourea (Ruan et al. 2004b; Chen et al. 2006). The cellulose concentration in the solution was usually about 4–5 wt%, probably to avoid gelation and also partly for viscosity reasons. The total crystallinity of spun fibres was around 60 %, higher than that of viscose, and the orientation parameter was around 0.8. Overall, the tensile strength was 150–300 MPa (1–2 cN $dtex^{-1}$) and elongation at break 10–20 %. These values are very similar to those obtained with cellulose dissolved in NaOH–water without additives (Table 3).

The overall comparison between the mechanical properties of fibres prepared in the 1990s in Japan and in the 2000s in China by the group of Zhang and in Poland using the Biocelsol process is given in Table 3 together with the fibre properties from other solvents. Table 3 shows that cellulose fibres from NaOH–water solvent have properties comparable to those of viscose (a similar tensile strength and modulus but lower elongation) and lower (modulus and tensile strength) when compared with Lyocell. One of the reasons is that cellulose solubility is low, with the maximum cellulose concentration being of the order of 7–8 wt% and in reality, in order to avoid quick gelation, the cellulose concentration in the solution for spinning should not be higher than 5 wt%. Gelation of the solutions with time and temperature causes problems. These features do not help to prepare a good spinning dope with a high enough cellulose molecular weight and concentration to produce fibres with good mechanical properties. The fact that a cooling at negative temperature is needed for cellulose dissolution hampers the industrial use of this process.

Cellulose aerogels or “aerocellulose”

Aqueous NaOH solutions can be used to make high added-value cellulose materials such as cellulose aerogels or aerocelluloses. Aerocellulose is lightweight and highly porous and has a high specific surface area and thus offers a wide range of potential applications inspired by organic and inorganic aerogels: from bio-medical and cosmetic products (delivery systems, scaffolds), catalyst supports, gas filters and gas and energy storage to thermal insulation and electrochemical applications when pyrolysed.

There are two classes of cellulose aerogels (Wendler et al. 2012): (1) based on cellulose I such as bacterial cellulose (Maeda et al. 2006; Liebner et al. 2010) and nano- or micro-fibrillated cellulose (Pääkko et al. 2008) and (2) based on cellulose II (aerocellulose), which can be obtained via cellulose dissolution-coagulation (Jin et al. 2004; Innerlohinger et al. 2006; Gavillon and Budtova 2008; Liebner et al. 2008, 2009; Tsioptsias et al. 2008; Sescousse and Budtova 2009; Deng et al. 2009; Aaltonen and Jauhiainen 2009; Duchemin et al. 2010; Sescousse et al. 2011a). In all cases, a wet cellulose aerogel precursor is dried in such a way that the porosity is preserved and the pores remain open, i.e. via freeze-drying or drying under supercritical conditions. In the latter case carbon dioxide is used. It is one of the most commonly used supercritical fluids in polymer chemistry and technology because of its non-inflammability, low cost and low critical point pressure and temperature.

The preparation of aerocellulose is inspired by the route of making classical aerogels: the sol–gel process followed by drying in supercritical CO_2. However, no cellulose chemical cross-linking is involved. Aside from aqueous NaOH (Gavillon and Budtova 2008; Cai et al. 2008b; Sescousse and Budtova 2009; Sescousse et al. 2011b, Demilecamps et al. 2014), aerocelluloses can be obtained via cellulose dissolution in any solvent, for example, in *N*-methylmorpholine *N*-oxyde (NMMO) monohydrate (Innerlohinger et al. 2006; Liebner et al. 2008, 2009), LiCl/DMAc (Duchemin et al. 2010), calcium thiocyanate (Jin et al. 2004) or ionic liquid (Tsioptsias et al. 2008; Deng et al. 2009; Aaltonen and Jauhiainen 2009; Sescousse et al. 2011a, Demilecamps et al. 2015). Cellulose is then coagulated in a non-solvent (water, alcohols) and dried either via freeze-drying or with supercritical CO_2. When coagulated in water, the latter must be replaced by an organic solvent miscible with CO_2 (ethanol, acetone) before supercritical drying. A general preparation scheme is given in Fig. 21.

If dissolving cellulose in aqueous NaOH, solution gelation can be an advantage since three-dimensional objects of various sizes and shapes can be prepared. The solution is poured into a mould and gelled and the shape of the mould determines the final aerocellulose shape. It is also possible to prepare aerocellulose beads of different shapes, from flat plates to spherical, by dropping cellulose–NaOH–water solutions into water, exchanging water to acetone or ethanol and drying in supercritical CO_2 (Sescousse et al. 2011b).

Depending on cellulose solvent used, two types of aerocellulose morphologies can be obtained: a “network”-like and “globular”-like. A network-like morphology is obtained from gelled (in NaOH–water) and solidified (NMMO monohydrate) cellulose solutions (Fig. 22a). A globular morphology is obtained when solutions are coagulated directly from the fluid state such as in hot NMMO monohydrate and ionic liquid 1-ethyl-3-methylimidazolium acetate (EMIMAc) (Fig. 22b). The development of different morphologies is supposed to be driven by different mechanisms of phase separation. If solutions are gelled or solidified before coagulation (network-like morphology), two phases exist in solution: free solvent (NaOH–water hydrates or crystals of NMMO monohydrate) and cellulose + bound solvent. Coagulation then takes place in two steps: first, non-solvent dilutes regions with “free” solvent and then removes the rest of the solvent bound to cellulose. In the liquid solution, cellulose–EMIMAc and hot cellulose–NMMO monohydrate, cellulose is homogeneously distributed all over the solution and phase separation occurs in one

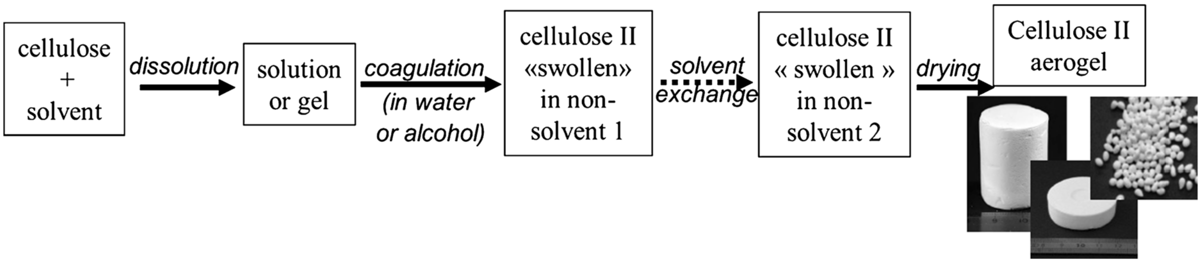


Fig. 21 Scheme of aerocellulose preparation

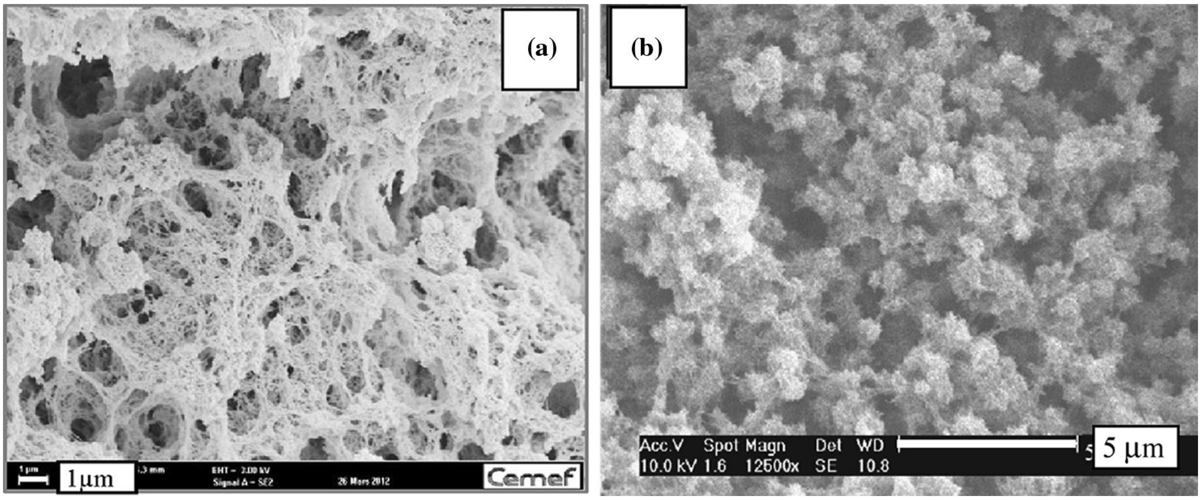


Fig. 22 Aerocellulose morphology: **a** from 5 wt% cellulose–8 % NaOH–water solution, with kind permission from Springer Science + Business Media: Demilecamps (2014, Figure 8a, and b) from 3 wt% cellulose–EMIMAc solution (reprinted from Sescousse et al. 2011a), with permission from Elsevier

step, via spinodal decomposition, creating regular micron-size spheres (Fig. 22b).

The density of aerocellulose depends on the initial cellulose concentration in solution. For aerocelluloses prepared from cellulose of the same molecular weight (DP around 200) and in the same drying conditions, density is directly proportional to the initial cellulose concentration (Fig. 23). Density can be strongly reduced if the solution is “foamed” with a surfactant (Gavillon and Budtova 2008): for example, the addition of 1 % Simulsol SL 8 (alkyl polyglucoside) to 5 wt% microcrystalline cellulose dissolved in 8 wt% NaOH–water reduced more than twice the aerocellulose density.

The pore size distribution in aerocellulose is very wide, from a few tens of nanometres to several microns, as can be seen in Fig. 22. Because of the fragility of the cellulose pore walls, the mercury

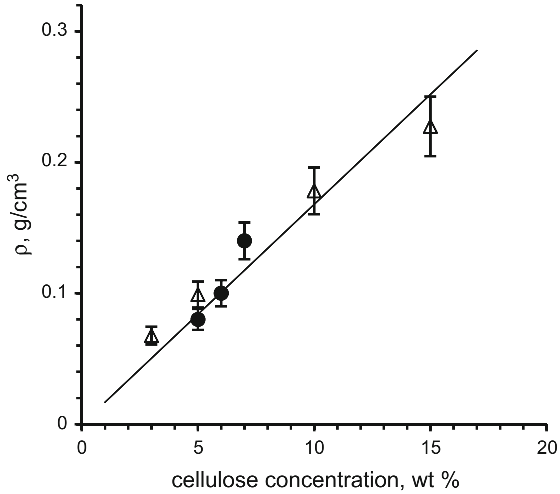


Fig. 23 Density of aerocellulose obtained from cellulose dissolved in ionic liquids (*open points*) and in 8 wt% NaOH–water (*dark points*) as a function of the cellulose concentration in solution. Data taken from Sescousse et al. (2011a)

intrusion method does not work since pore walls collapse under the applied pressure, preventing mercury penetration. Nitrogen adsorption method shows pores sizes of a few tens of nanometres, but it is only a fraction of total pore volume. The BET-specific surface area obtained from nitrogen adsorption is from 200 to 400 $m^2\ g^{-1}$.

A detailed study of the influence of the coagulation bath type, concentration and temperature on aerocellulose morphology was performed by Trygg et al. (2013). Contrary to Cai et al. (2008b) who did not observe an influence of temperature on the aerocellulose-specific surface area, Trygg et al. (2013) found that the specific surface area decreases with the increase of bath temperature and is lower when the coagulation fluid is a salt solution (10 wt% NaCl) as compared to nitric acid (Fig. 24). This result was explained by different coagulation kinetics, which are influenced by bath temperature and acidity: for example, slow coagulation (due to slower diffusion at lower temperature) leads to looser structures.

The mechanical properties of aerocellulose were determined from compression experiments. Figure 25 shows Young's modulus of aerocelluloses obtained from microcrystalline cellulose that was dissolved in either EMIMAc or 8 wt% NaOH–water. Young's modulus was found to be proportional to the aerocellulose density to the power three (Fig. 25) (Sescousse et al. 2011a). This is a typical scaling obtained for classical aerogels, but not for the open-cell regular foam model, which predicts square-law dependence. Structural defects appearing during cellulose coagulation can be at the origin of the similarity between aerocellulose and classical aerogels formed via the sol–gel process.

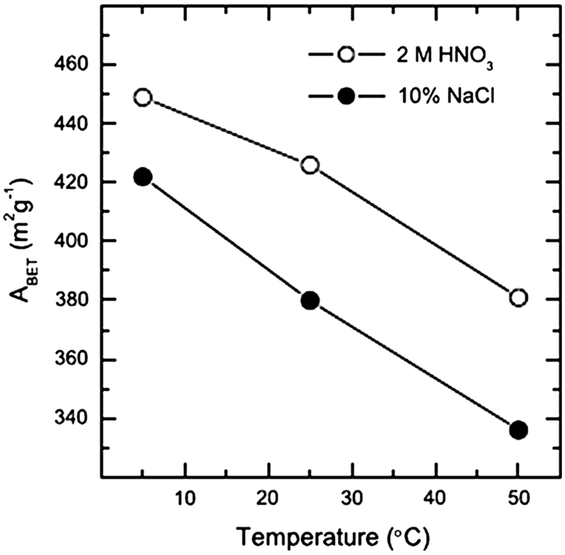


Fig. 24 Specific surface area of aerocellulose beads prepared from ethanol–hydrochloric acid pre-treated cellulose dissolved in 7 wt% NaOH–12 wt% urea as a function of coagulation bath temperature. Reprinted from Trygg et al. (2013), with permission from Elsevier

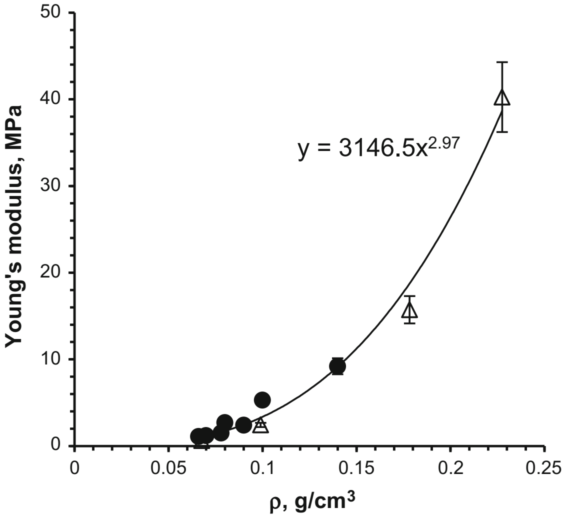


Fig. 25 Young's modulus of aerocelluloses from 8 wt% NaOH–water (*dark points*) and from EMIMAc (*open points*). The *line* is the power-law approximation. Data taken from Sescousse et al. (2011a)

New nano-structured carbons with interesting properties for electro-chemical applications were obtained after pyrolysing aerocellulose (Guilminot et al. 2008; Rooke et al. 2011, 2012). By varying the cellulose concentrations, coagulation conditions and pyrolysis parameters, monolith carbons with controlled shape and porosity were obtained from cellulose dissolved in 8 wt% NaOH–water (see Fig. 26). As compared with the non-carbonised aerocellulose, the obtained carbons

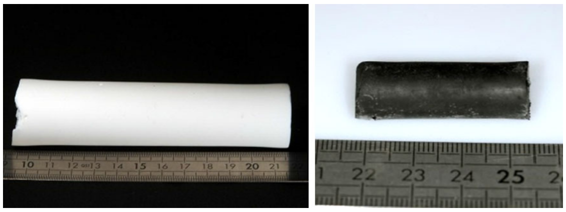


Fig. 26 Aerocellulose and its carbon counterpart

are of higher density, 0.2–0.3 cm^3 g^{-1}. The volume of mesopores is from 2 to 4 cm^3 g^{-1}, the pore size is around 70–90 nm and the specific surface area is from 250 to 350 m^2 g^{-1}. The capacity tested by the French company SAFT in Li/$SOCl_2$ primary (button type) batteries is 20 % higher than that used as their industrial reference (Rooke et al. 2012). In the single proton exchange membrane fuel cell test bench, the texture of the new carbon allowed improving the mass transfer at the cathode (Rooke et al. 2011).

The results presented above show a great potential of cellulose aerogels. Because of the presence of OH groups on the cellulose backbone, aerocelluloses can also be functionalised for targeted applications. Aqueous sodium hydroxide solvent can play an important role here in the development of these new materials. Gelation of cellulose–NaOH solutions can be an advantage for making aerocelluloses and their carbons of various shapes.

Blending cellulose with other polymers in aqueous NaOH and making materials

This section gives an overview on how aqueous NaOH can be used for making “hybrid” or composite cellulose-based materials, i.e. various materials where another compound, in addition to cellulose, is present. Chemical reactions involving cellulose–NaOH solutions will also be considered. The section is divided into three parts:

- mixing cellulose with another polymer in aqueous NaOH as a common solvent;
- mixing cellulose–NaOH–water solutions with “fillers”, i.e. when aqueous NaOH is a solvent only for cellulose, but does not dissolve the other component;
- aqueous NaOH as a reaction medium for cellulose cross-linking or performing derivatisation.

Mixing cellulose with another polymer in aqueous NaOH as a common solvent

Because cellulose cannot melt, homogeneous mixing on the molecular level with other polymers can be performed only via dissolution and mixing in a common solvent. To find such a polymer is a rather challenging task because of the specific solvents needed to dissolve cellulose. Some were used in the 1980s and beginning of the 1990s for mixing cellulose with various synthetic polymers: for example, LiCl-dimethylacetamide for mixing with nylon and polycaprolactone (Nishio and Manley 1990), polyethylene oxide (Nishio et al. 1989a), polyvinyl alcohol (Nishio et al. 1989b) and polyacrylonitrile (Nishio et al. 1987); paraformaldehyde-DMSO for mixing with polyvinylpyrrolidone (Masson and Manley 1991a) and polyvinylpirridine (Masson and Manley 1991b); NMMO monohydrate for mixing with polyamide (Garcia-Ramirez et al. 1994) and NO_2-DMF for mixing with cellulose triacetate and polyacrylonitrile (Jolan and Prudhomme 1978). In the beginning of the twenty-first century, the re-discovery of ionic liquids allowed mixing cellulose with synthetic polymers such as polyacrylonitrile (Wendler et al. 2009; Ingildeev et al. 2012) and polyamides (Ingildeev et al. 2012), but this research direction still remains rather unexplored.

In the view of making fully biomass-based (and biodegradable) materials from cellulose mixed with polysaccharides, an attempt on using environmentally friendly solvents was made: aside from mixing in aqueous NaOH, which will be overviewed in the next paragraphs, NMMO monohydrate and ionic liquids were also used. For example, it was recently demonstrated that it is possible to use NMMO monohydrate for mixing cellulose with xanthane and tragacanth gum (Wendler et al. 2011), chitosan (Twu et al. 2003) and silk fibroin (Marsano et al. 2008). In imidazolium ionic liquids, cellulose was mixed with starch (Wu et al. 2009; Kadokawa et al. 2009; Liu and Budtova 2012), chitin and chitosan (Kadokawa et al. 2012; Ma et al. 2011; Park et al. 2011), natural wool (Hameed and Guo 2010), konjac glucomannan (Yi et al. 2009) and guar gum, tragacanth gum and locust bean gum (Wendler et al. 2011).

There are several problems in using aqueous sodium hydroxide as a common solvent for a homogeneous mixing of cellulose with another polymer and making materials. The main one is that for cellulose to be dissolved, the NaOH concentration should be around 1.5–2 mol l^{-1}, which gives a pH of around 14–14.5. Not many polymers, synthetic or natural, can be dissolved at the molecular level at such high pH. The literature does not always report whether indeed the second polymer is dissolved in 1.5–2 mol l^{-1} NaOH or whether it is a sort of a suspension that is mixed with aqueous cellulose–NaOH. The second problem is that aqueous cellulose–NaOH solutions are unstable (gelation in time is accelerated with temperature increase): mixing should be performed below room temperature and better below 0 °C. It should also be kept in mind that if willing to make a material containing both polymers, the second one should not be washed out during the coagulation and washing steps, i.e. should not be soluble in fluids that are used to coagulate cellulose (usually water or acidic water or ethanol). As will be shown later, this constraint can be used as an advantage: it may allow varying pore size in the obtained materials by controlling the amount of the second phase that is washed out. The question then is the recovery of the second polymer that is washed out.

Most of the work on using aqueous NaOH (sometimes with urea or thiourea) as a common solvent was performed for cellulose mixed with another natural polymer, mainly a polysaccharide: starch (Miyamoto et al. 2009), alginate (Zhou and Zhang 2001; Chang et al. 2009a; Wendler et al. 2010), chitin (Wendler et al. 2010; Zhou et al. 2004b; Zhang et al. 2002a), chitosan (Wendler et al. 2010; Morgado et al. 2011; Almeida et al. 2010), konjac glucomannan (Yang et al. 2002), xanthan and tragacanth gum (Wendler et al. 2010, 2011). A few other biomass-based polymers were also mixed with cellulose in aqueous NaOH: casein (Yang et al. 2001), soy protein (Chen et al. 2004), and organosolv lignin (Sescousse et al. 2010). In most of these cases, mixtures were used to prepare films via wet casting. Wendler et al. (2010, 2011) describe fibres obtained with wet-spinning technology and Sescousse et al. (2010) use NaOH to make aerogels based on cellulose and lignin.

When two polymers are mixed in a common solvent, various scenarios are possible. The first is when macromolecules coexist in the solvent without any special interactions, and this is the most typical case. If there is no competition for the solvent between the macromolecules of different types, i.e. the polymer concentration is not high and no phase separation occurs, this "simple" coexistence will be reflected by following the mixing rule in terms of the density, viscosity, refractive index, etc. When coagulated in a fluid that is a non-solvent for both components, or if solvent is evaporated, the two polymers will phase separate and form either co-continuous solid phases in the case of comparable volume fractions or a continuous phase of the major component with the inclusions of the second one. Unless any special treatment is used, such solid materials keep the characteristics of the initial components. Mechanical properties can even degrade.

The second scenario is when the two polymers interact in the common solvent. This is the case when interpolymer complexes are formed either via ionic interactions (case of aqueous solutions of oppositely charged polyelectrolytes) or via hydrogen bonding (a typical example is low-charged polyacrylic acid complexing with polyvinyl alcohol). In both cases a new compound is formed. If complexes are formed via the "zip" mechanism and the proportion between the components is stoechiometric, they become insoluble and precipitate, which is reflected by a significant change (decrease) in the mixture viscosity and change in solution pH. If the proportion is not stoechiometric, a gel-like structure may be formed and the mixture viscosity will not follow the mixing rule, being higher than the additive sum of the viscosities of the neat solutions. All these phenomena are reflected by the change in the chemical structure and hydrodynamic size of the new compound as compared with the initial ones and can be detected not only by viscosity and light scattering, but also by the change in mixture pH, chain mobility, light transmittance, etc. Obviously IR and NMR spectra will also show the formation of a new compound. However, making such a conclusion concerning mixed polysaccharides as far as similar spectra are superimposed is precarious.

It is somehow difficult to imagine the formation of interpolymer complexes in such a strong basic environment as 2 mol l^{-1} aqueous NaOH. Indeed, no interpolymer complexes between cellulose and the second polymer, both dissolved in aqueous NaOH, have been reported. In most of the articles, partial "leaching out" of the second component was observed during the coagulation and washing step, because the second polymer is soluble or at least very well dispersable in coagulation and washing fluid; this is the case for konjac glucomannan (Yang et al. 2002), alginate (Zhou and Zhang 2001), soy protein (Chen et al. 2004), organosolv lignin (Sescousse et al. 2010) and starch (Miyamoto et al. 2009). The release of the second component leads to the formation of pores and channels in coagulated cellulose. The obtained films are highly macroporous: pore diameters usually vary from hundreds of nanometres to a few microns. The increase of the second polymer concentration in the mixture usually leads to an increase in pore size in the obtained material (Yang et al. 2002; Chen et al. 2004; Sescousse et al. 2010; Miyamoto et al. 2009). The fact that the second component can be easily removed from the cellulose matrix is a clear indication of the absence of any special interaction between the two polymers. The main questions here are: what is the concentration of the second component in the final material? How does its presence influence the material properties? Can it be released during the application? The usual approach taken is to test the film's permeability and mechanical properties. As compared with coagulated pure cellulose, the increase in the concentration of the second polymer usually leads to an increase in the permeability and a decrease in the Young's modulus.

The second component may not leach out during the coagulation and washing steps if the fluid used is also a non-solvent for the second polymer. It is thus trapped in the pores of the "network" of coagulated cellulose. However, this does not mean that cellulose and the second polymer are bound by any links. This is the case for non-hydrolysed soy protein (Chen et al. 2004), chitin and chitosan (Zhou et al. 2004b; Zhang et al. 2002a; Morgado et al. 2011), alginate when coagulated in calcium salt solution (Zhou and Zhang 2001) and organosolv lignin when coagulated in a concentrated acid bath (Sescousse et al. 2010). For the last example, the following demonstration experiment was performed. It is known that organosolv lignin is soluble at high and neutral pH and that its solubility decreases with pH decrease. Cellulose-lignin mixtures in 8 wt% NaOH–water were coagulated in 0.1 and 1 mol l^{-1} acetic acid aqueous solutions. The amount of lignin "lost" in the first bath was 82 and 65 % in the second one. The higher the bath acidity was, the darker the samples obtained because of the larger amount of lignin trapped in coagulated cellulose. Another example is the weight loss of soy protein as compared with the "hydrolysed" sample (additional NaOH treatment), shown in Fig. 27 (Chen et al. 2004). Practically all soy proteins (closed points in Fig. 27) are washed out from cellulose, and "hydrolysed" soy protein (open points) remains in cellulose. Soy proteins here were initially in the form of slurry (not in the dissolved state) in NaOH–thiourea solvent. Surprisingly, the pore size in both types of films is reported to be the same and the water permeability in "hydrolysed" membranes (soy protein not leached out) is even higher than that of the non-treated one (Chen et al. 2004). Correlating the interactions between the two polymers and final film properties is rather delicate.

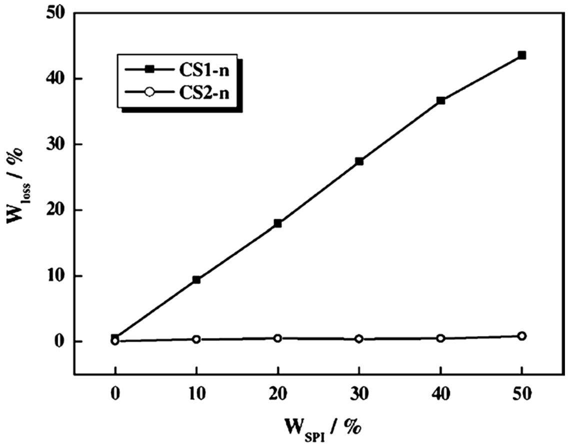


Fig. 27 Weight loss (W_{loss}) in membranes made from cellulose and non-hydrolysed (CS1-n) and hydrolysed (CS2-n) soy protein as a function of the initial concentration of soy protein W_{SPI} in the mixture. Reprinted from Chen et al. (2004), with permission from Elsevier

The application of porous films based on cellulose mixed with another polymer (which is more or less present in the material) may be in the area of microfiltration. However, because of the phase separation occurring between two polymers and formation of large voids, the mechanical properties of such membranes are lower than for industrially used ones. Probably more promising is the use of "mixed" porous cellulose-based films in bio-medical applications as matrices for growing various cultures or tissue engineering.

Of special interest are materials based on cellulose mixed with chitin or chitosan. Chitin and its derivatives are known to have antibacterial properties and to adsorb oppositely charged molecules; however, their mechanical properties are poor. Mixing with cellulose could help to overcome this drawback. Films and beads were prepared from cellulose–chitin and cellulose–chitosan dissolved in NaOH–thiourea solution. It is not clear whether chitin and chitosan are well dissolved in aqueous NaOH in as far as Wendler et al. (2010) report their insolubility in 8 wt% NaOH. Zhou et al. (2004b), Zhang et al. (2002b), Morgado et al. (2011) and Almeida et al. (2010) discuss mixing and making materials in (5–6) wt% NaOH–(6–5) wt% thiourea solvent. It was shown that chitin–cellulose beads can be used for the adsorption of heavy metals

(Zhou et al. 2004b). Chitosan–cellulose films were prepared and characterised (crystallinity, roughness, water absorption, thermal degradation, biodegradability) by Morgado et al. (2011) and Almeida et al. (2010). The thermal properties and crystallinity of mixed films were in between the corresponding characteristics of the initial components and film roughness increased with the increase in chitosan content. Unfortunately, the authors were not able to measure the mechanical properties of cellulose film made from dissolved linters and so the comparison with mixed films is difficult. It was reported that both tensile strength and elongation at break increased with the increase of chitosan content.

Finally, an interesting application of cellulose–sodium alginate mixtures was suggested by Kim et al. (2007). Films made from this mixture were used as soft electro-sensitive actuators. Mixtures were prepared in NaOH–urea and coagulated in water; glycerol was added and dried. A displacement of a few millimetres of 10 × 30-mm film under AC voltage was recorded. The displacement increased with the increase of alginate content and relative humidity. It should be noted that even without alginate, the film bent under the applied voltage. The results obtained are similar to what is known for electro- and chemo-mechanical actuators based on cross-linked synthetic polyelectrolytes. Cellulose, as a natural biocompatible polymer, may be used as a reinforcing matrix for polyelectrolyte gels.

To the best of our knowledge, rather few attempts were made to use aqueous NaOH as a common solvent to mix cellulose and a synthetic polymer: polyethylene-co-acrylic acid (PE-co-AA) (Lipponen et al. 2012; Saarikoski et al. 2012), polyvinyl alcohol (PVA) (Chang et al. 2008) and polyaniline (PANI) (Shi et al. 2011). Except PVA, aqueous NaOH was not a solvent of the synthetic polymer. For example, aqueous 6.5 wt% NaOH–1.3 wt% ZnO used as cellulose solvent (Lipponen et al. 2012; Saarikoski et al. 2012) is not a solvent of PE-co-AA, as far as the latter solution was of pH 10, much lower than for 6.5 wt% NaOH (pH ~14). When mixing with cellulose, a suspension was obtained either due to partial cellulose coagulation or partial PE-co-AA coagulation or both. Here the approach taken was different from what was described above: the goal was to make mixtures with cellulose as the minor phase to obtain an injectable thermoplastic composite material reinforced with dispersed cellulose. After mixing, coagulation, washing and drying, a powder was obtained. It was possible to use the injection moulding technique for compositions with less that 20 wt% of the cellulose phase. The size of cellulose inclusions was of a few microns at low cellulose concentrations. The crystallisation temperature of PE-co-AA slightly increased with the addition of cellulose but the melting and glass transition temperature did not change. The storage modulus of the composite material increased with the increase of the cellulose content. In order to conclude about the influence of cellulosic inclusions on PE-co-AA material, it could be interesting to compare the mechanical properties of the material obtained with those composed of the same matrix but reinforced with natural fibres.

In cellulose–PANI mixtures (Shi et al. 2011) cellulose acts as a sort of PANI "stabiliser" in aqueous NaOH–urea solution: hydrogen-bonded supramolecular complexes formed between cellulose and PANI were reported. Dark-green films were prepared with their crystallinity decreasing and conductivity increasing with the increase of PANI content.

Cellulose and PVA seemed to be miscible in aqueous NaOH–urea (Chang et al. 2008). These mixtures were either coagulated in water after several cycles of freezing-thawing (7 times) or cross-linked with epichlorohydrin (ECH) and then coagulated. In the first case it was not clear whether PVA leached out or not. As for the second case, after the thermal treatments used, PVA might not be very soluble in cold water and thus coagulated cellulose was probably "filled" with highly swollen PVA. After vacuum drying and reswelling in water, the higher PVA concentration in the initial mixture resulted in a higher degree of swelling. When chemically cross-linked, an interpenetrated network was most probably formed. After immersing in water, the cellulose coagulated and PVA remained as a gel. These samples showed much higher swelling degrees than their counterparts without cross-linking. After drying and reswelling in water, a higher PVA content induced lower water uptake.

Composite materials with cellulose matrix from cellulose–NaOH aqueous solutions

Various composite cellulose materials, films and beads, were prepared from aqueous cellulose–NaOH solutions (sometimes with thiourea or urea added) mixed with organic or inorganic fillers. One of the most common goals for making composite materials is to improve the mechanical properties compared to the initial components. To do this, fibres are often used and, in this case, material reinforcement requires having good adhesion between the fibre and matrix, homogeneous fibre distribution, reasonably high fibre volume fraction and high fibre aspect ratio (ratio between fibre length L and diameter D). In some cases, fillers are used to bring new properties to material such as sensitivity to electric or magnetic fields, change of colour or transparency or antibacterial properties.

Let us first consider the mechanical reinforcement of films made from aqueous cellulose–NaOH solutions. Up to now, only organic fibres were used. Cellulose fibres (all-cellulose composites) and (nano)whiskers (all-cellulose nanocomposites) from cellulose and chitin were used. The choice of polysaccharide fibres is explained by an expected good adhesion with cellulose matrix (cellulose fibres can swell and be impregnated by aqueous NaOH solvent) and also by keeping the same "bio"-properties as the matrix.

To prepare all-cellulose composites, cellulose "macro" fibres, ramie and regenerated fibres were randomly dispersed in aqueous NaOH–urea, and films were prepared via wet casting (Nadhan et al. 2012; Yang et al. 2010). As compared to a non-reinforced cellulose film made from the same solution, light transmittance slightly decreased (by 10–20 %) and the mechanical properties increased in terms of Young's modulus (from 4 to 6 GPa) and tensile strength (from 100 to 120 MPa) and decreased for elongation at break (from 7 to 2–3 %); see Table 4. Similar work on making all-cellulose composites was performed slightly earlier for cellulose dissolved in LiCl/DMAc with incorporated ramie fibres (Nishino et al. 2004), beech pulp (Gindl et al. 2006) and filter paper (Nishino and Arimoto 2007). The best obtained mechanical properties of all-cellulose composites are summarised in Table 4. As compared with composites made from NaOH–urea, slightly better results were obtained when cellulose was dissolved in LiCl/DMAc and reinforced with randomly dispersed beech pulp (Gindl et al. 2006) and filter paper (Nishino and Arimoto 2007), and very high reinforcement was obtained with aligned ramie fibres (Nishino et al. 2004; Qin et al. 2008; Soykeabkaew et al. 2008). Such a difference was due to the fibre orientation and volume fraction, although the cellulose matrix DP and processing conditions also play an important role. As far as all composites were prepared in different conditions and with different starting materials, making a comparison between the results reported is rather difficult.

When nano-scale fibres such as cellulose or chitin whiskers were used, the properties of films prepared via whisker dispersions in cellulose–NaOH–urea solution and wet casting turned out to be very similar to the ones obtained with "macro" fibres obtained via the NaOH–urea process as described above (Qi et al. 2009a; Huang et al. 2013): compare the first two lines in Table 4 and first two lines in Table 5. One could have expected much better results for nano-composites as compared to cellulose films reinforced by "macro"-fibres.

To understand these results, several parameters influencing the reinforcement have to be taken into account: the fibre aspect ratio and their volume fraction. The aspect ratio of both types of whiskers was around 15 but the aspect ratio of macro-fibres was not reported and thus the comparison is difficult. The concentration of macro-fibres was much higher than that of whiskers: the weight ratio between ramie and dissolved cellulose was 3:1, between regenerated fibres and cellulose 1:1, while the ratio between chitin whiskers and cellulose was 1:10 and between cellulose whiskers and cellulose 1:4.

In order to obtain a good reinforcing effect, fibres should form a percolating network and this is possible when fibres are in the concentrated regime. The transition from a semi-dilute to concentrated regime occurs when the fibre volume fraction (in the final material) is roughly higher than $(L/D)^{-1}$. For the aspect ratio of whiskers used, their volume fraction should thus be above 7 vol%. If considering the maximal concentrations of whiskers reported, cellulose whiskers are in the concentrated state (Qi et al. 2009a) and chitin whiskers in the transition region from semi-dilute to concentrated (Huang et al. 2013); composites with cellulose whiskers should thus give an increase of mechanical properties. The moderate reinforcement obtained may be explained by (1) whisker agglomeration and thus a decrease of the real L/D and (2) inhomogeneous distribution in the matrix: indeed Qi et al. (2009a) point out a decrease in the film optical transmittance from 90 % for the neat cellulose film to 50 % for maximum reinforced film because of the formation of whisker aggregates.

In terms of making all-cellulose nano-composites, interesting results were obtained for films made from

Table 4 Mechanical properties (best values) of all-cellulose composites

Reinforcing fibre	Solvent	Dissolved cellulose DP	Vol% of fibres	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break (%)	References
Ramie	7 wt% NaOH–12 wt% urea	610	8 g cellulose with 15 g ramie	130	5.3	∼3	Yang et al. (2010)
			8 g cellulose with 25 g ramie	80	6	∼3	
Regenerated fibres (spun from the solution used as matrix)	7 wt% NaOH–12 wt% urea	620	4 wt% solution with 5 wt% fibres	76	7	2.9	Nadhan et al. (2012)
Beech pulp	LiCl/DMA			154	12		Gindl et al. (2006)
Filter paper	LiCl/DMA			211	8		Nishino and Arimoto (2007)
Ramie (aligned)	LiCl/DMA	"Craft pulp"	80 %	480	45	3–4	Nishino et al. (2004)
Ramie (aligned)	LiCl/DMA			540			Qin et al. (2008)
Ramie (aligned)	LiCl/DMA			460			Soykeabkaew et al. (2008)
Cotton fabric (impregnated)	BMIMCl			21	0.140	25	Shibata et al. (2013)
Hinoki cypress lumber (impregnated)	BMIMCl			51	6.3	14	Shibata et al. (2013)
Microfibrillated cellulose (impregnated)	BMIMCl	1000 (initial) 720 (in composite)		120	10	3–4	Duchemin et al. (2009b)
Filter paper (impregnated)		1240 (initial) 590 (in composite)		92	5	3–4	

partially dissolved microcrystalline cellulose in LCl/DMAc (Gindl and Keckes 2005) because of a homogeneous dispersion of highly crystalline cellulose nano-fillers of 1–3 nm that are, in fact, non-dissolved "remains" of microcrystalline cellulose. Young's modulus increased more than twice, to 15 GPa, with a tensile strength of 200–250 MPa. As expected, the elongation at break decreased drastically, from 18 to 4 %. Because of the nano-size of the filler, the optical transmittance did not decrease. A similar work on a partial dissolution of microcrystalline cellulose in LiCl/DMAc was performed later (Duchemin et al. 2009a), but less impressive results were obtained (Table 5). The moderate results obtained were interpreted by the use of different processing conditions (use or not of compression before solvent extraction, various coagulation conditions). It could be interesting to check whether this approach on partial dissolution can give good mechanical reinforcement when using aqueous NaOH solvent.

A second class of cellulose composites consists of dispersing particles and pigments in the cellulose matrix. The goal is to add special properties to the matrix. Two main approaches were taken: (1) dispersing particles, or their suspension, directly in aqueous cellulose–NaOH (with urea or thiourea) solution and then making materials via coagulation-drying (Ruan et al. 2004c, 2005; Sescousse et al. 2011b; Chang et al.

Table 5 Mechanical properties (best values) of all-cellulose nano-composites

Reinforcing fibre	Solvent	Dissolved cellulose DP	Vol% of fibres	Tensile strength (MPa)	Young's modulus (GPa)	Elongation at break	References
Cellulose whiskers	7 wt% NaOH–12 wt% urea	500	200 g solvent +8 g cellulose with 10 ml 10 wt% whiskers	124	5	n/a	Qi et al. (2009b)
Chitin whiskers	7 wt% NaOH–12 wt% urea	610	200 g solvent +8 g cellulose with 20 ml 3 wt% whiskers	117	13.5	4	Huang et al. (2013)
MC cellulose (partial dissolution)	LiCl/DMAc	MC cellulose from Aldrich	3 g cellulose in 100 ml	240	13	8.6	Gindl and Keckes (2005)
MC cellulose (partial dissolution)	LiCl/DMAc	163	20 wt% initial solution	106	7	3.3	Duchemin et al. (2009a)

2009b) or (2) impregnating wet coagulated cellulose (obtained via dissolution in aqueous NaOH–urea or LiOH–urea) with an inorganic solution and then gelling or precipitating the inorganic matter inside the cellulose matrix (Liu et al. 2006, 2008, 2011b, c; Cai et al. 2012; Liu et al. 2013; Demilecamps et al. 2014). The impregnation approach can be applied on cellulose coagulated from any solvent (Demilecamps et al. 2015). Whatever the route chosen, the result was a cellulosic material with embedded particles or a continuous inorganic network.

The incorporation of iron induced magnetic properties (Liu et al. 2006, 2011b; Sescousse et al. 2011a, b), of cadmium photoluminescence and photocatalytic activity (Ruan et al. 2005; Liu et al. 2011c), of tourmaline antibacterial properties (Ruan et al. 2004c), and of pigments and of CdSe/ZnS quantum dots fluorescent and photoluminescent properties (Qi et al. 2009b; Chang et al. 2009b).

Different options of particle incorporation and various types of impregnating liquids that can be used open many ways of making cellulose-based organic–inorganic hybrid or composite materials. For example, wet coagulated cellulose obtained from cellulose–NaOH–urea solution was impregnated with tetraethyl orthosilicate dissolved in ethanol (Cai et al. 2012). The latter was then converted into gel using ammonia as catalyser. The samples were dried under super-critical CO_2 to form a composite aerogel based on interpenetrated cellulose–silica networks. Pore sizes obtained with nitrogen adsorption were in the range of a few tens of nanometres. The presence of silica aerogel inside the cellulose matrix resulted in lower mechanical properties as compared with the pure cellulose counterpart (compressive modulus of 7.9 MPa for composite vs. 12 MPa for cellulose aerogel) and higher ones than that of classical silica-based aerogels. The increase of silica concentration increased the composite thermal conductivity as compared with pure cellulose aerogel (23–27 mWK^{-1} m^{-1}). However, the values of 30–40 mWK^{-1} m^{-1} remain in the domain of interesting thermal-insulating properties (Fig. 28). The applications can be extended not only to cellulose II-based matrices, but also to calcinated (Liu et al. 2008) and pyrolysed cellulose.

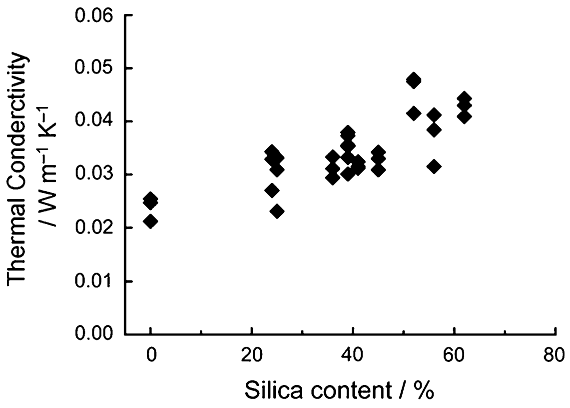


Fig. 28 Thermal conductivity of cellulose–silica composite aerogels as a function of silica volume concentration. With acknowledgements to Wiley Materials, Cai et al. (2012)

A very similar approach was taken by Liu et al. (2013): coagulated cellulose obtained from cellulose dissolved in NaOH–urea was impregnated with sodium silicate solution and dried with super-critical CO_2. The specific surface area of composite aerogels slightly decreased compared to the neat cellulose aerogels, and the mechanical properties of composite aerogels were improved. SEM images suggest that distinct silica particles and not silica aerogels were formed in the pores of the cellulose matrix.

Another way to prepare cellulose–silica composite aerogels with silica particles incorporated in a cellulose matrix was suggested in a "one-pot" approach by Demilecamps et al. (2014). Cellulose–NaOH aqueous solution was mixed with sodium silicate solution of the same pH. The gelation time of the mixture was strongly reduced as compared to that of cellulose–NaOH, which was interpreted by cellulose self-aggregation inducing partial coagulation because of competition for the solvent with sodium silicate. A similar phenomenon, i.e. "accelerated" cellulose gelation, was reported when mixing cellulose and organosolv lignin in NaOH–water (Sescousse et al. 2010). The gelled cellulose/sodium silicate samples were placed in aqueous acid solution, which terminated cellulose coagulation and led to in situ formation of sub-micronic silica particles trapped in a porous cellulose matrix (Fig. 29). After drying with super-critical CO_2, an organic–inorganic aerogel composite was formed. The specific surface area of composite aerogels was decreased as compared to the neat aerocellulose, but the silica phase had a reinforcing effect on the cellulose aerogel.

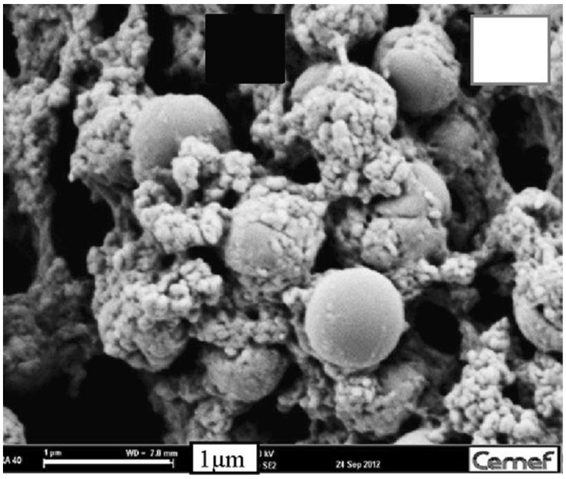


Fig. 29 SEM image of silica particles embedded in cellulose aerogel, with kind permission from Springer Science + Business Media: Demilecamps et al. (2014, Figure 8d)

Coagulated wet cellulose can be impregnated not only with inorganic solutions or suspensions, but also with polymer solutions to make composite films. For example, cellulose coagulated from LiOH–urea solution was impregnated with polymethylmethacrylate-acetone and polystyrene-toluene solutions (Isobe et al. 2011). After drying in ambient conditions transparent films were obtained. Their mechanical properties were lower than those of neat cellulose and decreased with the increase of the second phase concentration. The tensile modulus was found to be 50 % of that of pure cellulose film only for a few films with low contents of polystyrene. The same approach was taken by Li et al. (2014): coagulated wet (in chloroform) cellulose obtained from cellulose dissolved in NaOH–urea was impregnated by ε-caprolactone, which was subsequently polymerised. The storage modulus of cellulose–polycaprolactone interpenetrating polymer network (IPN) at 100 °C (above glass transition temperature of polycaprolactone) increased from 10 to 10^8 Pa but stress at break at room temperature strongly decreased in the presence of cellulose. These examples show various possibilities of making cellulose-organic and cellulose-inorganic composite materials by impregnating coagulated cellulose matrix, as far as its dimensions practically do not change whatever the non-solvent fluid is inside.

Using the same impregnation route, the surface of coagulated cellulose can be modified by "partial impregnation" by dipping wet coagulated cellulose in a solution containing a substance that can be then chemically cross-linked. The goal here is to modify surface properties (hydrophobisation) and permeability. As a result, the biodegradability and mechanical properties are also changed (Cao et al. 2006; Lu et al. 2004; Lu and Zhang 2002). The approach taken is to use biomass-based polyurethane pre-polymer from castor oil, mix it with a modified polysaccharide (benzyl konjac glucomannan or benzyl starch) in THF or DMF, coat the coagulated cellulose with the mixture and then cure it to perform cross-linking. This procedure can be applied to any cellulose material as far as surface modification is performed on coagulated and air-dried films as, for example, cellulose films made from dissolution in cuoxam (Zhang et al. 1997, 1999).

Depending on the polysaccharide used, the tensile strength and elongation at break of dry coated cellulose films increased with the addition of the second polysaccharide (case of benzyl starch (Cao et al. 2006)) while for benzyl konjac glucomannan the tensile strength increased but elongation at break decreased (Lu and Zhang 2002). The latter finding was explained by the increase of solid content in the film, as expected. Biodegradation kinetics were slower for coated films as compared with pure cellulose and the water permeability decreased (Cao et al. 2006; Lu et al. 2004).

Aqueous NaOH as a reaction medium for performing cellulose modifications

Aqueous NaOH can be used to dissolve cellulose and then to perform various chemical reactions in homogeneous conditions. Several examples of the synthesis of cellulose ethers such as hydroxyethyl cellulose (HEC), hydroxypropyl cellulose (HPC) and methyl cellulose (MC) in aqueous NaOH–urea have been reported (Zhou et al. 2004c, 2005, 2006). In all cases, a homogeneous substitution of hydroxyl groups of anhydroglucose units was achieved. The degree of substitution (DS) varied from 0.5 to 2, and water-soluble samples of HEC with DS = 0.5 and higher and of HPC with DS = 0.85 and MC with DS = 1.5 were obtained. A higher gelation temperature of the MC solution as compared with industrial samples was recorded, 67 °C, and 2 wt% HPC aqueous solutions with DS = 0.85, 0.93 and 1.18 remained transparent when heated up to 95 °C. These properties were attributed to a uniform distribution of substituted groups over the anhydroglucose unit.

Hydroxyethyl cellulose with low degrees of substitution was also synthesised in heterogeneous conditions using cellulose treatment in 21 wt% NaOH and ethylene oxide (Wang et al. 2013). The obtained low-substituted HECs were soluble in 8 wt% NaOH–water at higher polymer concentrations and solution gelation was strongly delayed as compared to non-substituted cellulose in the same solvent (Wang et al. 2015). Cellulose fibres were successfully spun from these HEC solutions showing properties similar to those of viscose (Wang et al. 2013).

Cellulose-based polyelectrolytes were obtained by performing a chemical reaction in aqueous NaOH–urea with acrylamide (Song et al. 2008). Various degrees of substitution were obtained. Saponification of amide groups transferred them into carboxyl groups, which became charged in neutral and basic medium. The new macromolecule showed polyelectrolyte properties typical for polymers having charged carboxylic groups: reduced viscosity $(\eta - \eta_0)/\eta_0 C$ (where η and η_0 are the solution and solvent viscosity, respectively, and C is the polymer concentration) increased with dilution and decreased in salted medium. This can be an alternative way of making cellulose-based polyelectrolytes.

Cellulose chemical cross-linking with epichlorohydrin in aqueous NaOH was performed (Zhou et al. 2007; Chang et al. 2010a; Qin et al. 2013). Zhou et al. (2007) reported a cross-linking reaction in NaOH–urea with heating the reaction solution at 50 °C for 20 h and Chang et al. (2010a) reported the same gel synthesis with heating in the same conditions and also with freezing. Freezing gave slightly lower water retention after coagulation as compared to the heating procedure. Cellulose gels were coagulated in water and washed and a swollen cellulose network obtained. It was somehow similar to "simply" coagulated cellulose but cross-linked swollen cellulose was reported to be transparent contrary to classical opaque coagulated wet cellulose. Two reasons explaining this difference can be given: (1) a cross-linked cellulose network is more homogeneous than coagulated cellulose or (2) cross-linked cellulose is absorbing much more water and thus the polymer concentration in the swollen sample is much lower. It is not very clear if cross-linked coagulated cellulose keeps more water than coagulated cellulose prepared from the solution of the same concentration. Simple calculations show that it seems that the water retention should be similar, but no direct comparison was performed. If water retention is the same, then the structure of the cross-linked cellulose network is more homogeneous than the one of coagulated cellulose. This is most probably true as far as epichlorohydrin was always taken in excess towards cellulose and thus the degree of cross-linking should be high.

Qin et al. (2013) studied gelation of cellulose–7 % NaOH–12 % urea solutions in the presence of epichlorohydrin. They demonstrated that with the increase of the concentration of the cross-linker from 5 to 15 wt% the gelation time decreases. They also showed that the increase of the epichlorohydrin content from 5 to 15 wt% leads to the decrease of the coagulated cellulose swelling degree in water, from 3000 to 2000 % for 4 wt% cellulose in the initial solution.

Cross-linking with epichlorohydrin allows making hybrid networks if mixing cellulose with another polymer in the same solvent and then cross-linking both at the same time, or cross-linking cellulose and then impregnating the obtained gel with a solution of another polymer and then cross-linking the second one leading to the formation of an IPN structure. The first strategy was used to prepare cellulose/carboxymethyl cellulose (CMC) gels (Chang et al. 2010b), cellulose–sodium alginate gels (Chang et al. 2009a) and cellulose–lignin gels (Ciolacu et al. 2012); the second was used to synthesise cellulose/poly(*N*-isopropyl acrylamide) IPN (Chang et al. 2011). In the cases of cellulose–CMC, cellulose–alginate and cellulose–polyNIPAm, samples were washed in water after the cross-linking reaction had been completed: cellulose was thus in a coagulated state and the second polymer, being soluble in water but cross-linked, formed a hydrogel. When mixed with carboxymethyl cellulose, the sample swelling ratio decreased in monovalent salt solutions and the sample collapsed in polyvalent metal ones. This was because CMC is a polyelectrolyte. Cellulose/CMC samples kept the properties of the water-soluble component. When mixed with poly(isopropyl acrylamide), the samples became temperature sensitive. When mixed with alginate, the size of pores in the freeze-dried cellulose–alginate gel increased with an increase of alginate content, swelling increased and mechanical properties decreased. More studies are needed to understand the influence of the second component on IPN properties and several questions remain: are the cellulose and second component cross-linked separately or with each other? What is the degree of cross-linking and is it the same for both components? It could be very interesting to know more about the influence of cellulose in the IPN as compared with the hydrogel based only on the second cross-linked polymer.

Making hybrid gels using cellulose dissolution in aqueous NaOH can be interesting for controlled release applications. This is what was tested by following the kinetics of polyphenol release from epichlorohydrin cross-linked cellulose–lignin (Ciolacu et al. 2012). Swelling and release were performed in water:ethanol = 19:1 medium. Samples were swollen to 2000–3000 wt%. Higher swelling, higher porosity and quicker release were for matrices containing larger amounts of lignin. While all the data correlate, the reason for the higher solvent uptake and thus higher porosity in the presence of lignin is not very clear; the affinity of each component towards the water–ethanol mixture should be evaluated as well as the cross-linking degree.

The aqueous-alcoholic (isopropyl alcohol)–NaOH system used in CMC synthesis was applied for cellulose alkalisation (Yokota 1985). This article describes the distribution of sodium hydroxide between cellulose and the medium as well as how the solvent separates in layers. X-ray results showed that alkali-cellulose can partly revert to cellulose I. The authors deduce that isopropanol acts as a kind of swelling restrictive agent of cellulose.

Conclusions

Since the 1930s, many efforts were made to understand cellulose dissolution in aqueous NaOH solvent in view of making cellulose fibres and films. This solvent is very attractive because of its price, availability and ease in recovery. Particularly interest increased at the end of the twentieth century because of the search for direct cellulose solvents that could replace the viscose process and result in the same or better material properties. However, currently there is no industrial production of cellulose fibres or films using this solvent. Several reasons can be given:

- The need for low temperatures (around −5 °C) for the dissolution, which generates high processing costs;
- Low stability of the solutions (irreversible gelation with time and temperature);
- Need for additives to slow down gelation, which does not facilitate solvent recovery;
- Low maximum concentration of cellulose possible to dissolve in any NaOH-based solvent, with or without additives (the theoretical maximum is around 8 wt% but practically it is around 5 wt% because of very quick gelation of "concentrated" solutions);
- Difficulty in dissolving cellulose of high molecular weight.

The last two points result in medium mechanical properties, similar to or lower than those of viscose and lower than those from the Lyocell process, and thus not enough to replace well-established industrial routes. In addition, the lower polymer concentration as compared to other wet-spinning processes results in very low economic efficiency of the NaOH process.

As the review of pre-treatments shows, the only clear factor influencing dissolution is the decrease of cellulose molar mass. This is easy to understand with classical thermodynamic considerations: the lower the molar mass is, the higher the degree of freedom, and the higher the entropy gain of the dissolved chains, decreasing the free energy of the solution towards the undissolved situation. All the other activation effects are linked to subtle physical and chemical changes in the internal structure of the fibres, usually called accessibility. A much better understanding of the nature of these changes would enormously help cellulose dissolution, derivatisation or sugar production.

One of the potential ways to use aqueous NaOH solvent is to make high added-value materials, such as cellulose hybrids or composites with organic or inorganic compounds and also aerogels and their carbon counterparts. When the mechanical properties are not of primary practical importance (for example, in highly porous materials such as cellulose aerogels), aqueous sodium hydroxide can be a suitable solvent for cellulose. Aerocelluloses can be used as matrices for controlled release, for catalysis, for specific adsorption and separation and in electro-chemical applications when pyrolysed. A low dissolution limit and gelation are not negative features anymore. On the contrary, gelation helps make aerocellulose of a predefined shape and facilitates handling and coagulation.

Despite the long research history of aqueous cellulose–NaOH, several points still remain to be clarified from the scientific point of view. For example, the organisation and conformation of cellulose chains in solution, the structure of the hydrated ions close to cellulose, the coordination and polarisability of water around the hydroxyl groups and the existence or not of molecularly dispersed chains must be better described in order to understand cellulose solubility in NaOH–water. The role of additives and why they delay gelation are also not clear.

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