

Chapter 2

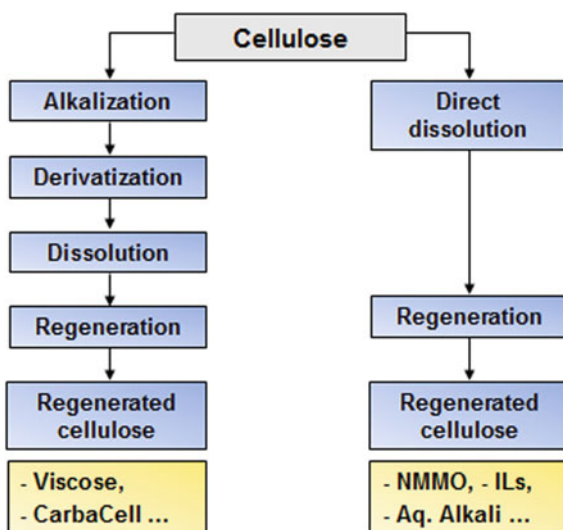
Platforms for Functionalization of Cellulose

Abstract The shaping, chemical modification, and functionalization of cellulose are largely depended on the process of dissolution in an efficient solvent. Viscose process as the most important method for production of cellulose-regenerated materials was introduced. The dissolution of cellulose in several other most frequently used eco-friendly solvents was also discussed, including cellulose carbamate, N-methylmorpholine-N-oxide, aqueous alkali system, and ionic liquids. These processes provide efficient platforms for development of new regenerated materials and other products based on cellulose.

Keywords Cellulose solvents • Viscose process • Carbamate • NMMO • Aqueous alkali system • Ionic liquids

Due to its large proportion of intra- and intermolecular hydrogen bonding, cellulose is difficult to process as a melt or solution. That is, the reason that only around 200 million tons of the 40 billion tons renewed annually are used as raw materials (pulp) in the manufacture of materials and goods such as textile fibers, packaging, paper, and body care products [1]. Normally, the processing of regenerated cellulose includes two ways: chemical derivatization and direct physical dissolution in a suitable solvent, as shown in Fig. 2.1. The viscose process is the oldest and most important derivate methods for producing cellulose fibers and films. An alternate derivatization method without the use of sulfur-containing compounds is the CarbaCell process, which retains the viscose spinning technology. Compared to derivatization, the direct dissolution and shaping of cellulose is much simpler. However, cellulose is not soluble in water or conventional organic solvents. As a very early direct spinning route of cellulose (Cupro silk, Cuprophane), copper ammonia technology is rarely used anymore for posing environmental hazards. Some solvents such as DMA/LiCl, zinc chloride, and phosphoric acid are also reported as direct solvents. More recently, new eco-friendly direct solvents, such as N-methylmorpholine-N-oxide (NMMO), ionic liquids, and aqueous alkali system, are developed and show great potential to shape cellulose or to produce functional celluloses by chemical modification.

Fig. 2.1 Process principles in regenerated cellulose technologies: *left*, derivate methods; *right*, direct methods



2.1 Derivate Methods

2.1.1 Viscose Process

Although Anselme Paven discovered cellulose in 1838, the first cellulose-based thermoplastic material was produced in 1870 by the Hyatt Manufacturing Company. This material was manufactured by treating cellulose with nitric acid to form cellulose nitrate and commercialized under the trade name “celluloid” [2]. In 1892, the viscose process as a new process to regenerate cellulose fibers in a larger scale was developed [3]. As shown in Fig. 2.2, this process mainly involves a derivatization process of cellulose with sodium hydroxide and CS_2 to cellulose xanthogenate.

Generally, cellulose used in the manufacture of viscose process is alpha cellulose, which is obtained from pulping of wood (or cotton linters and bamboo), where

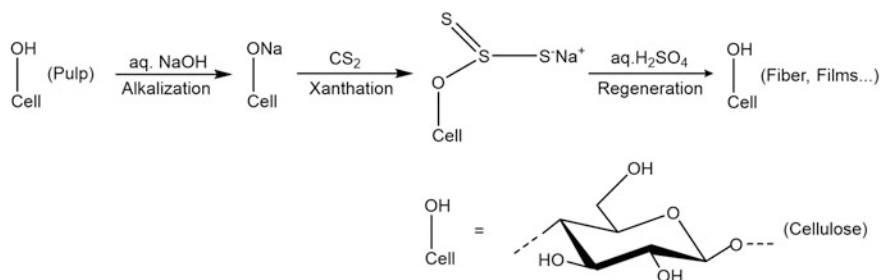


Fig. 2.2 Viscose solution is formed during dissolution of cellulose xanthogenate

special care is taken in pulping and bleaching so that the pulp is of higher strength with high cellulose content. Rayon is one of the most common and popular uses of viscose, which is used for many types of clothing and other textile products. The process of manufacturing viscose rayon consists of several steps, such as steeping, pressing, shredding, aging, xanthation, dissolving, ripening, filtering, degassing, spinning, and washing. Viscose fibers have excellent properties for a broad product range, from wet-strength cotton like textile fibers (Modal fibers) to technical fibers in the form of cord (Rayon) for use in high-performance tires. Besides the application in textile industry, viscose technology is still in use today for film (cellophane) production, which is particularly important for food casing products. In addition, viscose process also rendered possible the utilization of cellulose in different fields such as construction, ceramics, paints, cosmetics, etc.

The viscose process has developed more than 100 years, and still dominates the regenerated cellulose products market with an annual world production of about 2.2 million tons (2002) [2]. However, viscose process causes environmental pollution and damage to human health due to the use of heavy metal salts (in the precipitation process), CS_2 , and other harmful chemical substances. In addition, the viscose route is technologically complex, and one produce cycle would last for more than one week. Despite continuous improvement in the past decades, waste water and exhaust air treatment is complex owing to tough environmental requirements. The increased cost of viscose technology incurred by the purification of exhaust gas and waste water is also a disadvantage. Due to the economic and ecological drawbacks of the viscose process, scientists have long been engaged in efforts to make cellulose-based materials production more cost effective and eco-friendly.

2.1.2 Cellulose Carbamate Process

As an alternate method to viscose process, the cellulose carbamate (CC) process employs urea instead of CS_2 to react with cellulose (Fig. 2.3) [4]. The obtained product calls cellulose carbamate, which is soluble and shapeable in sodium hydroxide solution. The patented CarbaCell process is a specific carbamate technology using a novel synthesis route for CC with xylene as the transfer medium. As shown in Fig. 2.4, the technical sequence of the CC process is similar to the viscose technology [5]. Thus the regenerated cellulose products based on CC can be processed on the existing viscose wet-spinning systems. It should be noted that, there are no zinc or other heavy metals in the spin-bath. An important advantage of the cellulose carbamate is the relatively high stability at room temperature allowing storage for over a year. Thus, the synthesis of cellulose carbamate can be carried out on a large scale in a central location, from which products can then be shipped to decentralized facilities for processing (such as spinning factories) [2, 5].

Although there are several advantages over the viscose process, the CarbaCell process has not yet been industrially established until now. It is mainly due to certain requirements such as a catalyst, organic solvents, long reaction times, and

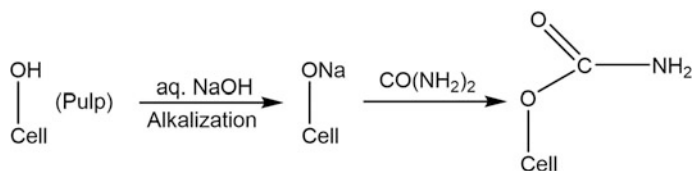


Fig. 2.3 Formation of cellulose carbamate by transformation of cellulose with urea

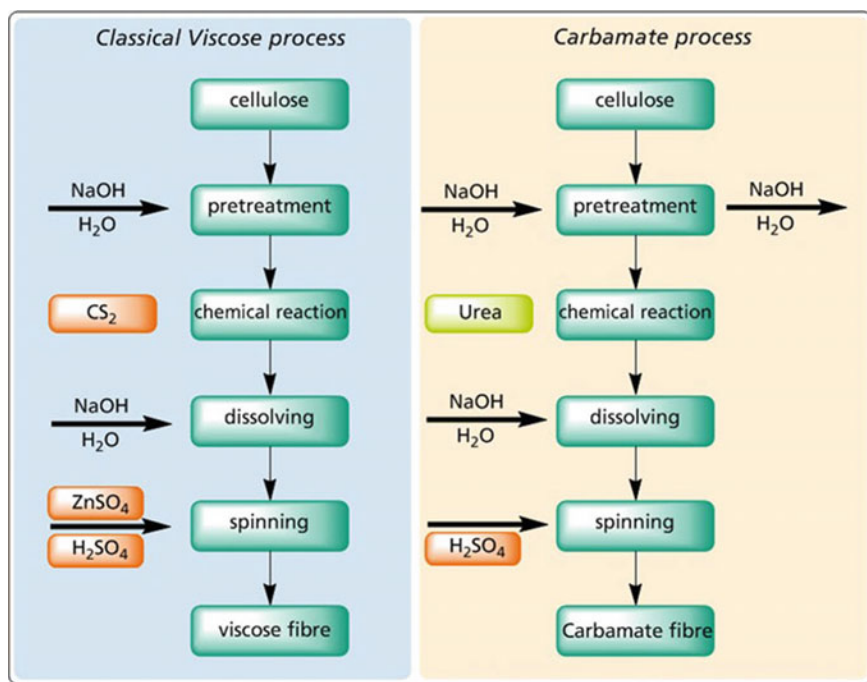


Fig. 2.4 Comparison of the viscose and carbamate process steps. Images taken with permission from [5]

high temperatures. It was reported that CC could be synthesized by supercritical CO₂-assisted impregnation [6]. More recently, Zhou et al. presented a novel process for the synthesis of CC by using microwave irradiation [7]. Due to a well controllable heating process, conversion of the cellulose is successful within a few minutes under catalyst-free and solvent-free conditions. This efficient synthesis process is greatly significant for the commercialization of the carbamate process. In addition, the microwave-assisted process is highly ecological, especially since side products and harmful waste are avoided and no raw material is lost. They found that the solubility of CC could be significantly improved with the addition of a small amount of ZnO to the NaOH solution [8–10].

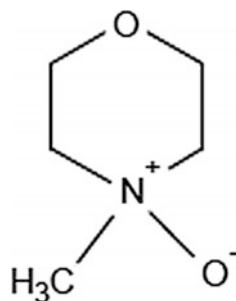
2.2 Direct Solvents

2.2.1 NMMO System

Many attempts have been made to invent new solvents to directly dissolve cellulose; and some successful results have been reported. Indisputably, the most industrially successful of all non-derivatizing solvents for cellulose is N-methylmorpholine-N-oxide, commonly known as NMMO. This particular organic solvent has proven to be a viable commercial solvent system, mainly due to its ability to dissolve high concentrations of cellulose directly and without alteration of the chemical properties of the cellulose chain. The first patent involved the dissolution of cellulose in tertiary amine oxides was issued to Greanacher and Sallmann in 1936 [11]. About 30 years later, Johnson et al. filed patents describing solutions of different synthetic and natural polymers in different cyclic tertiary amine oxides, including NMMO [12]. These compounds are better solvents than tertiary amine oxides, since they can dissolve not only cellulose but also other polymers. Nowadays, the NMMO process has ripened technically and has made its technical breakthrough, leading to a new class of man-made cellulose fibers [13].

Well known as an oxidizing agent in organic chemistry, NMMO is extremely hygroscopic and completely soluble in water. NMMO in combination with water can dissolve cellulose without prior activation or derivatization, mainly due to its strong N–O dipoles (Fig. 2.5). There is not a very clear mechanism for dissolution of cellulose and the structure of cellulose–water–NMMO solutions. Commonly, it is agreed upon that the solvation power of NMMO originates in its ability to disrupt the hydrogen bonding networks of cellulose, and to form solvent complexes by establishing new hydrogen bonds between the polymer and the solvent [14]. There are two stable hydrates of NMMO, the monohydrate (NMMO·H₂O) and the 2.5-hydrate (NMMO·2.5H₂O). The oxygen in NMMO is able to form hydrogen bonds with nearby hydroxyl groups that in water or cellulose [15]. The competition of water and cellulose for these hydrogen bonds thus determine the state of dissolution and precipitation of cellulose in the NMMO system. Figure 2.6 shows the solubility of cellulose in the binary NMMO–water [13]. Cellulose is soluble all the

Fig. 2.5 Structure of N-methylmorpholine-N-oxide



way up to $\text{NMMO} \cdot 1.2\text{H}_2\text{O}$, and can be easily regenerated by precipitation for higher amounts of water. Hence, the monohydrate can dissolve cellulose while the 2.5-hydrate cannot.

The dissolution procedure of cellulose in NMMO is much simpler comparing with viscose process. Solutions with cellulose content of up to 23% can be produced starting with the dispersion of conventional cellulose in NMMO with a large excess of water (such as 50%) [2]. As indicated in the phase diagram (Fig. 2.6), cellulose can only be dissolved completely in a relatively small region. The excess water provides low viscosity and thereby superior mixing. Surplus water is then removed by heat between 100 and 120 °C and reduced pressure until the point of complete cellulose dissolution is reached. After dissolution, the cellulose/NMMO/water solution can be used for production of various cellulose materials, such as cellulose fibers, films, food casings, membranes, sponges, beads, and others without hazardous by-products [13].

Compared with conventional viscose process, many steps in NMMO process may be left out since NMMO is non-derivatizing. Fibers (such as Lyocell) spun from NMMO solution have outstanding properties in certain respects, such as strength in both wet and dry states, modulus of elasticity, sorption behavior, wearing properties, gloss, and touch. In addition, the industrial recovery of NMMO is 99.6–99.7% from the precipitation bath in a closed circle, with its upgrade and cleaning by an ion-exchange process [2]. These clear advantages make NMMO a serious competition to the viscose process. NMMO is now successfully applied as a direct cellulose solvent on industrial scale. Besides the man-made fibers with generic name Lyocell mentioned above, several other commercial cellulose fibers based on NMMO were developed till now, such as Tencel, Alceru, and Cocol.

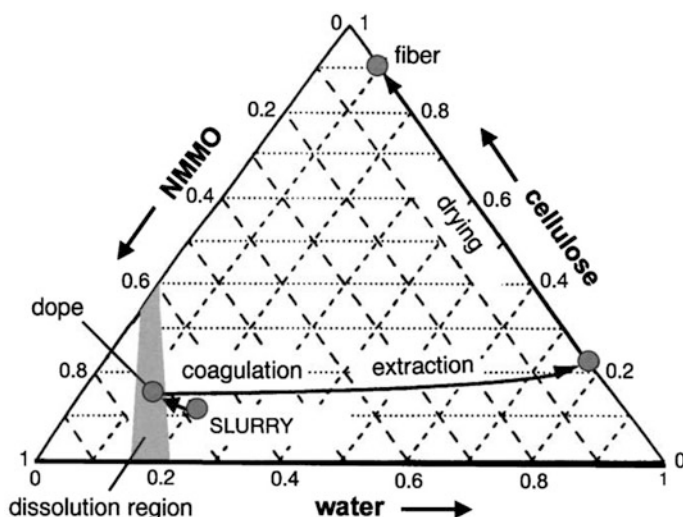


Fig. 2.6 Phase diagram of cellulose/NMMO/water. Images taken with permission from [13]

However, the NMMO process also has some shortcomings, which hinder it from the replacement of the viscose process to date. For example, NMMO is thermally unstable, which can cause deconstruct of the solvent molecule at high temperature. Although the stabilizers were added, there are no guarantees of avoiding dangerous runaway reactions [14, 16]. Another reason is the severe fibrillation of the fibers manufactured and the fiber profile which is closer to cotton. In addition, the high viscosity of the cellulose solution in NMMO system sets limits in both the process economy and the strength properties of the fibers. Therefore, the extension of the NMMO to direct cellulose solvents of high thermal and chemical stability comprising lower solution viscosity is very attractive from a safety, environmental, and economic point of view.

2.2.2 Aqueous Alkali System

In recent years, aqueous alkali systems have attracted much attention because they can serve as eco-friendly and low-cost solvents for cellulose. Sodium hydroxide (NaOH) as a common strong base is largely used in the pulp and paper industry. NaOH can cause cellulose to swell and in a narrow range of the phase diagram, even can dissolve cellulose. The earliest cellulose-NaOH-water phase diagram was plotted by Sobue [17]. Cellulose would interact with NaOH in different way to form different complex depended on the NaOH concentration and temperature. In the region of NaOH concentration between 6 and 10% and temperature from -10 to 4 °C, cellulose is highly swollen and form so-called “cellulose Q”.

Normally, cellulose can only be dissolved in NaOH aqueous solution (7–10% NaOH) below room temperature. NaOH can penetrate the amorphous area of cellulose, then solvate to cellulose and destruct the neighboring crystalline regions. The amount of cellulose that is soluble in NaOH/H₂O depends on DP, the concentration and the crystallinity of cellulose [18]. Some treated cellulose (such as regenerated cellulose and steam-exploded cellulose) and microcrystalline cellulose (MCC) can be dissolved in NaOH/H₂O directly or by the method of freezing–thaw (Table 2.1) [18–21]. It is found that cellulose with DP lower than 200 could easily be dissolved completely in the NaOH solution, while that with higher DP might only be partially dissolved. Cellulose fibers were also prepared based on NaOH/H₂O. However, the quality of these fibers is poor [19]. Consequently, aqueous NaOH solutions are not suitable for technical applications.

More recently, Zhang and coworkers found that NaOH/urea can dissolve cellulose more efficiently than the binary NaOH/H₂O system itself [22, 23]. For example, 7 wt% NaOH/12 wt% urea aqueous system can dissolve cellulose within 2 min after precooled to -12 °C. The main advantage of this method is its rapid dissolution, relative simplicity, and cost effectiveness; and it is an eco-friendly process [24]. Especially, this solvent can dissolve cellulose with relatively high DP (DP = 500 – 900) completely, which render it a good platform for fabrication of cellulose materials with high performance. In addition, some other additives such as

Table 2.1 Dissolution Cellulose in NaOH-based aqueous systems

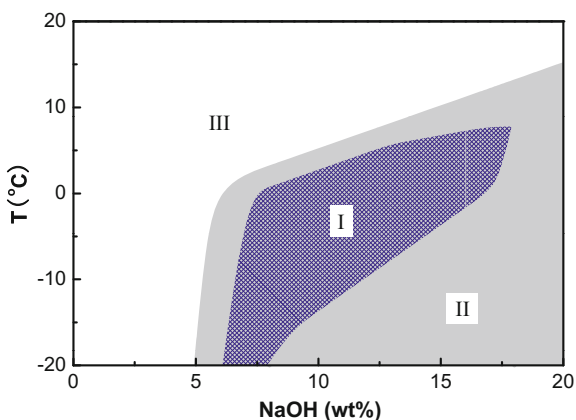
Solvents	Method	Cellulose	Ref.
8–10 wt% NaOH	Direct dissolution	Treated cellulose	[18]
7–9 wt% NaOH	Direct dissolution	Treated cellulose	[19]
8–9 wt% NaOH	Freezing–thaw	MCC	[20]
7.9–14.9 wt% NaOH	Freezing–thaw	MCC	[21]
6 wt% NaOH/4 wt% urea	Freezing–thaw	Cotton linter	[22]
7 wt% NaOH/12 wt% urea	Direct dissolution –10 °C	Cotton linter	[23]
9.5 wt% NaOH/4.5 wt% thiourea	Direct dissolution –4 to –5 °C	Cotton linter	[25]
9 wt% NaOH/1 wt% PEG	Freezing–thaw	Cellulose powder	[26]
12–18 wt% NaOH, 16–28 wt% urea	Two-step, –2 to 5 °C	Cotton linter, Avicel	[27]

Table derived with permission from [27]

thiourea and poly(ethylene glycol) (PEG) were also used to enhance the solubility of aqueous NaOH solutions for cellulose [25, 26]. Lithium hydroxide and potassium hydroxide are expected to have a similar effect as sodium hydroxide. A strong impact of the choice of salt has been observed, and the dissolution power of the different systems is in the order $\text{LiOH/urea} > \text{NaOH/urea} \gg \text{KOH/urea}$. Both LiOH and NaOH in combination with urea are able to rapidly dissolve cellulose, while KOH is not [23].

It should be noted that there are mainly three processes for dissolution of cellulose in NaOH-based aqueous system (Table 2.1): (1) freezing–thaw; (2) direct dissolution in solvents; (3) two-step dissolution process. Although the compositions and dissolution conditions are different, furthermore, all NaOH-based aqueous systems mentioned previously have similar NaOH concentrations (ranging from 6 to 10 wt%) and can only dissolve cellulose at low temperatures [27]. Figure 2.7 shows a schematic diagram of the solubility of cellulose in NaOH-based aqueous

Fig. 2.7 Schematic diagram of the solubility of cellulose in NaOH-based aqueous systems depending on NaOH concentration and temperature: I, complete dissolution area; II, partial dissolution area; III, non-dissolution area. Images taken with permission from [27]



systems depending on NaOH concentration and temperature. It exhibits that cellulose can be dissolved completely in wide range of NaOH concentration (from 6 to 18%, area I), through three dissolution processes. Cellulose can only dissolve partially in area II, while can not dissolve in area III. Furthermore, the proper method for cellulose dissolution is determined by the NaOH concentration: (1) 6–10 wt% NaOH for freezing–thaw; (2) 6.5–10 wt% NaOH for direct dissolution; and (3) 10–18 wt% NaOH for two-step process. Whatever process being used, however, the NaOH concentration in the final cellulose solution must keep in a range of from 6 to 10% to maintain the stability of the solution [27].

It was suggested that the dissolution mechanism is based on that the hydrates of NaOH in low temperatures are able to form hydrogen bonds with the cellulose chain, while the urea molecules surrounds the cellulose/NaOH/H₂O inclusion complex, screening it from other cellulose molecules and thereby prevent cellulose aggregation [28]. Regeneration takes place by precipitation in non-solvents, e.g., dilute H₂SO₄, ethanol, butanol, or acetone. From the cellulose dope based on this solvent, a series of regenerated cellulose products have been fabricated, including novel cellulose fibers, films, and aerogels [24, 25, 29]. Therefore, aqueous alkali systems provide a novel eco-friendly and economic platform for shaping and functionalization of cellulose. However, there exists an upper DP limit of cellulose for these aqueous alkali systems. The resulting cellulose solutions are also sensitive to temperature, cellulose content, and DP of cellulose. In addition, the existence of lignin in cellulose pulp will reduce the solubility.

2.2.3 *Ionic Liquids*

In the past decade, ionic liquids (ILs) have emerged as effective and green solvents, mainly due to their high thermal and chemical stability, nonflammable nature, and miscibility with many other solvent systems [30]. Liquids consisting only of ions are called ILs. In the broader sense, this term includes all kind of salt melts, like sodium chloride at temperatures above its melting point of 800 °C. Today, the term “ionic liquid” refers particularly to salts composed of organic nitrogen inorganic cations and inorganic anions, with a melting point below 100 °C. Salts with a melting point below 25 °C are called “room-temperature ionic liquids” (RTILs) [31].

In 1934, Graenacher found that liquefied quaternary ammonium salts, alone or diluted in suitable solvents, could dissolve cellulose. In 2002, Swatoski et al. discovered the ability of some ILs, in particular 1-N-butyl-3-methylimidazolium ([C4mim]⁺) combined with different anions, to dissolve cellulose, which opened new paths for the shaping of polysaccharides and provoked a high interest in this area [32]. In the following years, more ILs for dissolution of cellulose have been reported, such as imidazolium salts (including 1-ethyl-3-methylimidazolium salts, 1-butyl-3-methylimidazolium salt, 1-allyl-3-methylimidazolium salt, etc) pyridinium salts, and ammonium salts [33]. Among them, compounds based on

dialkylimidazolium cations are the majority; while chloride and acetate are the most frequently reported anions.

ILs appear to be highly polar due to their ionic character, resulting in their enhanced biopolymer dissolving capacity [34]. It is thought that both anions and cations are involved in the dissolution process. Figure 2.8 shows the proposed dissolution mechanism of cellulose in ionic liquid ([BMIM]Cl) [35]. The oxygen and hydrogen atoms of the cellulose form electron donor–electron acceptor complexes with the charged species of the IL. The anion acts as a hydrogen bond acceptor and the cation as a hydrogen bond donor. This interaction causes the disruption of the hydrogen bonding networks in cellulose, leading to dissolution of cellulose in IL.

A number of factors influence the cellulose dissolution, such as temperature, time, cellulose source, DP, and the structure of ILs. Microwave was also applied as a heating method instead of pretreatment to improve cellulose dissolution. This internal heating may be responsible for the more effective breakdown of the H-bond network between the microfibrils, although care must be taken because heating occurs rapidly and can easily lead to cellulose pyrolysis. Sonication-assisted dissolution, however, seems only to have little benign influence on the dissolution [34]. The number of reported low melting organic salts for cellulose dissolution is growing rapidly. More recently, a new generation of ILs as cellulose solvents has been developed by conjugation of the organic acids and organic super-base (1,1,3,3-tetramethylguanidine). It can be technically “distillable” to high purity (>99% purity, >99% yield), not yet observed for earlier generations of ILs for cellulose [36]. Furthermore, tetrabutylphosphonium hydroxides containing 30–50 wt% water are capable of dissolving cellulose rapidly at ambient temperature without derivation or degradation. In particular, tetrabutylphosphonium hydroxides containing 40 wt% water can dissolve cellulose and remain stable throughout the process, treating a natural biomass containing a considerable amount of water [37].

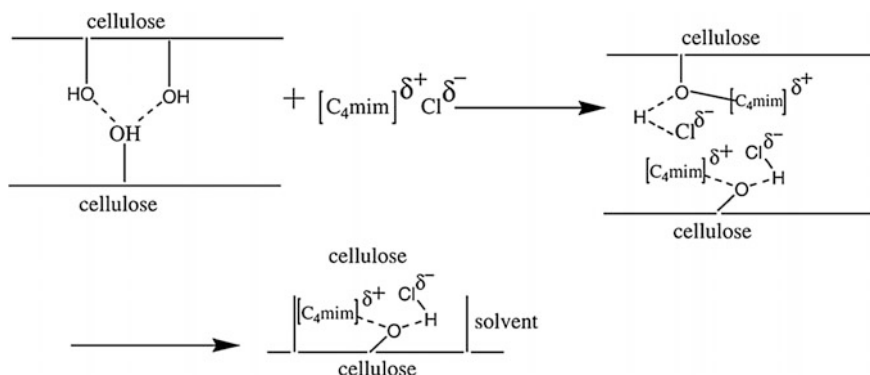


Fig. 2.8 Proposed dissolution mechanism of cellulose in ionic liquid ([BMIM]Cl). Images taken with permission from [35]

This relatively new class of solvent has already shown great versatility in the field of cellulose technology, including cellulose-regenerated materials, homogeneous derivatization, and biomass processing [38–40]. However, ILs also possess various disadvantages for a commercial application, such as side products and recycling of solvents [1]. Thus, further research and development is needed for both economic and environmental sustainability, including the design of a “next generation” of cellulose dissolving ILs as well as the more conscious use of established ones, based on their specific advantages and disadvantages [33].

2.3 Summary

By using the two main approaches, chemical derivatization and direct dissolution, native cellulose can be converted into various regenerated cellulose products which are used in our ordinary life. As the oldest and most important commercial method, viscose process mainly involves a derivatization process of cellulose with sodium hydroxide and CS_2 to cellulose xanthogenate. However, viscose process causes environmental pollution and damage to human health. CarbaCell process is an eco-friendly derivatization method, which was developed recently as an alternate process for viscose and can retain the viscose spinning technology. Compared with the chemical derivatization methods, the direct solvents are much simpler in dissolution and shaping of cellulose. Especially, three new eco-friendly direct solvents, e.g., NMMO, aqueous alkali system, and ILs, are developed more recently and attracted much attention over the past decades. The dissolution mechanism and regeneration process of these solvents were investigated by many researchers. Although having the great potential to shape cellulose, these solvents also have some challenges, which must be addressed before the final replacement of the viscose process. On the other hand, the development of other new efficient and “green” solvents for cellulose is still an important issue in field of cellulose science and technology.

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