Gelatine sizing of paper and its impact on the degradation of cellulose during aging: a study using size-exclusion chromatography

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Chapter 2. Review of most commonly used methods for the dissolution and the characterisation of cellulose

Abstract

The techniques available to date for the analysis and the characterisation of cellulose, such as viscometry and size-exclusion chromatography (SEC), are evaluated in terms of the quality of the information obtained, as well as their overall advantages and drawbacks. The solvents most currently associated with these methods and their potential effects on the degradation of cellulose are reviewed. In order to understand the choices made in this study, the advantages of the solvent lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) and its action on cellulose are detailed.

2.1 Molar mass averages

The polymerisation process is inherently random; therefore most natural and synthetic polymers are composed of a mixture of molecules of different size. Proteins can be considered as a special type of polymer in that their biosynthesis is a complex biochemical process, which results in identical molecules at all structural levels, from the amino acid assembly to the three-dimensional arrangement. This spatial conformation of a native protein is a key factor to its bioactivity.

Most of the analytical techniques commonly used to evaluate polymerisation, such as batch light scattering, fractionation, sedimentation, osmometry and viscometry, each provide average values for only one of the molar mass averages of a polymer.

The different molar mass averages are the number-average molar mass $M_n$, the weight-average molar mass $M_w$ and the z-average molar mass $M_z$. For ease throughout the text we will hereafter and in the following chapters omit the bar ($\bar{M}$), and refer to the molar mass averages as $M_n$, $M_w$ and $M_z$.

The molar mass averages are expressed as follows:

$$M_n = \frac{\sum n_i M_i}{\sum n_i}$$
$$M_w = \frac{\sum n_i M_i^2}{\sum n_i M_i}$$
$$M_z = \frac{\sum n_i M_i^3}{\sum n_i M_i^2}$$
Where \( n_i \) is the number of molecules with molar mass \( M_i \).

An additional molar mass average that is sometimes used when working with very high-\( M_i \) polymers is \( M_{z+1} \).

\[
M_{z+1} = \frac{\sum n_i M_i^4}{\sum n_i M_i^3}
\]

From these expressions, it can be derived that the impact of high molar mass (\( M_i \)) molecules on these molar mass averages is in decreasing order: \( M_{z+1} > M_z > M_w > M_n \).

Specifically, if upon degradation cleavage occurs preferentially in the high-\( M_i \) molecules, the relative decrease in the values of \( M_z \) and \( M_{z+1} \) will be larger than the relative decrease in \( M_n \). Conversely, if the low-\( M_i \) molecules are preferentially degraded, the relative decrease in \( M_n \) will be larger than the relative decrease in \( M_w \) and \( M_z \). This concept of course has its limitations since high-\( M_i \) molecules are statistically more likely to undergo random cleavage than low-\( M_i \) molecules.

The polydispersity index (PD) is expressed by the ratio \( \frac{M_w}{M_n} \).

\( M_n \) is usually determined by end-group analysis or by osmometry, \( M_w \) by light scattering - which also provides the root mean square radius (rms or \( r_g \)), and \( M_z \) by ultracentrifugation (\( z \) stands for the German word “zentrifuge”).

In terms of physical properties, there is a direct relationship between \( M_i \) averages and processing characteristics of polymers. \( M_z \) relates to elongation and flexibility. \( M_n \) relates to brittleness, flow properties and compression set. \( M_w \) relates to strength properties such as tensile strength and impact resistance.

Molar mass can also be expressed relative to intrinsic viscosity. The viscosity-average molar mass \( M_v \) is usually determined in batch or capillary viscometry and relates to extrudability and molding properties.

\[
M_v = \left[ \frac{\sum n_i M_i^{1+\alpha}}{\sum n_i M_i} \right]^{\frac{1}{\alpha}}
\]

Where \( \alpha \) is the exponent in the Mark-Houwink-Sakurada (MHS) equation:

\[
[\eta] = K' M_v^a
\]

[\( \eta \)] is the intrinsic viscosity, determined by viscometry. \( K' \) and \( a \) are constants for a given polymer-solvent system, temperature and molar mass range. These constants are tabulated for a wide range of polymer-solvent systems [1]. \( M_v \) depends on a number of factors, including the solvent and the molar mass distribution (MMD), i.e. chain size distribution, of the polymer in solution. Viscosity measurements are generally more affected by the high-\( M_i \) components of the polymer reflected in \( M_w \), and practically, \( M_i \) is usually closer to \( M_w \) than to \( M_n \) [2]. In the specific case where \( \alpha \) is equal to unity, \( M_v \) is equal to \( M_w \).
2.2 Methods of dissolution and analysis of cellulose

2.2.1 Viscometry: solvents and methods

Viscometry measurements allow the calculation of the polymer's intrinsic viscosity $[\eta]$. The intrinsic viscosity is determined by extrapolation towards concentration zero of the viscosity of solutions of the polymer in the solvent at different concentrations:

$$[\eta] = \lim_{c \to 0} \left[ \frac{(\eta - \eta_{solv})}{\eta_{solv} \times c} \right]$$

Where $\eta$ is the viscosity of the polymer solution at concentration $c$ in the solvent, and $\eta_{solv}$ is the solvent viscosity.

The relationship between intrinsic viscosity and $M_r$ in dilute solutions is given by the MHS equation described in section 2.1.

There are different viscometry methods used for cellulose analysis. The method with copper di-ethylene diamine dihydroxide (called CED or CuEn) [Cu(En)$_2$(OH)$_2$] (with En = H$_2$N(CH$_2$)$_2$NH$_2$) gained considerable acceptance because of the wide range of papers that this solvent system is capable of dissolving.

Most standard viscometry methods for cellulose are based on dissolution in CED: ASTM D539-51 [3], ISO 5351/1 [4], TAPPI T 230 om-89 [5], AFNOR NF T12-005 [6], and SCAN-CMM 15:88 [7]. The advantage of these standard methods is that no sophisticated equipment is required; the measurements are done with a capillary glass viscometer. There are nonetheless major drawbacks, as these methods provide information on only one $M_r$ average ($M_r$), and not on the molar mass distribution (MMD) of the cellulose, which is critical in relation to the mechanical strength and expected longevity of a cellulosic material. Furthermore, when the MMD of a polymer changes upon aging, it is difficult to relate $M_r$ with the real bond scission rate since $M_r$ varies with a number of factors, among which is MMD. In this case it is necessary to know $M_n$. Viscometry methods also have limitations as to the type of paper they can be applied to. In addition, the presence of mineral fillers and sizes can modify the solution viscosity and hence lead to erroneous values of $M_v$.

An additional drawback of these methods resides in the fact that the solvents used in viscometry are fairly alkaline. The pH of CED is 11, and the pH of Cadoxen (see next paragraph) is 13. This inevitably leads to degradation of the cellulose by atmospheric oxygen [8]. Jerosch [9] showed that the temperature and age of cellulose solutions in CED played an important role in the extent of the degradation. The author reported that the DP$_v$ of a softwood pulp of high-$M_r$ ($5.8 \times 10^5$ g mol$^{-1}$) decreased by 13% after 8 days in solution when kept at room temperature, and by 8% when kept at 4°C. Strlič et al. [10] showed that degradation of oxidised cellulose in CED was pronounced; leading to a
systematic error of up to 56% in \( M_c \). Santucci and Plossi Zappala [11] also reported the sensitivity of oxidised cellulose to CED. This is probably due to the fact that oxycelluloses are easily hydrolysed in alkaline medium through a process called \( \beta \)-alkoxy elimination. It has been shown that cellulose that was reduced with sodium borohydride prior to dissolution underwent less solvent-induced degradation [10,12,13].

Cadoxen is sometimes used as an alternative to CED because it is colourless and was shown to be less degrading than CED [14,15] in addition to being stable at room temperature [8]. Cadoxen, an aqueous solution of cadmium tri-ethylene diamine dihydroxide \([\text{Cd(En)}_3](\text{OH})_2\) \((\text{En} = \text{H}_2\text{N(CH}_2\text{)}_2\text{NH}_2)\), was first described by Jayme [16,17], and shortly after the first viscometric studies were carried out [18,19]. Cadoxen makes more stable solutions with cellulose, and is less prone to oxidation than CED solutions [20]. However, the use of Cadoxen is limited because no standard method of viscometry in this solvent exists, and because it is not commercially available. The solvent has to be prepared in the laboratory, which often results in poor repeatability in batch-to-batch quality.

In Cadoxen and similar solvents, hydrogen bonding occurs between the amino groups of the ethylenediamine and the two equatorial hydroxyl groups of cellulose on C3 and C6 [21]. \(^{13}\text{C}\) and \(^{113}\text{Cd}\) Nuclear Magnetic Resonance (NMR) showed that enhanced hydrogen bonding takes place arising from a combination of steric and electronic factors due to the presence of the metal ions.

In the MHS equation, typical values for the coefficient \( a \) of cellulose are in the range of 0.8 to 1.0 for most solvent systems [22]. Donetzhuber [23] and Henley [24] were the first researchers to study the system cellulose/Cadoxen using cotton linters. The first found \( K' = 3.85 \times 10^4 \text{ dL g}^{-1} \) and \( a = 0.76 \) at 30°C; and the second, \( K' = 5.4 \times 10^4 \text{ dL g}^{-1} \) and \( a = 0.735 \). Other values reported in the literature for cellulose in Cadoxen are \( K' = 3.15 \times 10^5 \text{ dL g}^{-1} \) and \( a = 0.93 \) at 25°C [25].

Experiments of viscometry in lithium chloride/\(N,N\)-dimethylacetamide (LiCl/DMAc) have also been reported. McCormick et al. [26] determined \( K' = 1.278 \times 10^4 \text{ dL g}^{-1} \) and \( a = 1.19 \) for cellulose in 9%LiCl/DMAc at 30°C. Such a high value of \( a \) indicated rod-like rigid conformation of cellulose in LiCl/DMAc. This was later confirmed by light scattering measurements by Dawsey and McCormick [27]. It can be noted at this point that the experiments carried out in the present work (see section 4.2.4 of Chapter 4) allowed to determine the coefficient \( a \) for cellulose in 0.5%LiCl/DMAc as 0.81, using size-exclusion chromatography with multiangle light scattering detection (SEC/MALS).

For cellulose tricarbanilates - the structure of which can be found in Appendix 5-2- in THF at 25°C, \( K' \) was found equal to 5.3\times10^5 \text{ dL g}^{-1} [25] and 4.3\times10^5 \text{ dL g}^{-1} [28], and \( a \) to 0.84 [25,28]; at 20°C, the value of \( K' \) found was 2.01\times10^5 \text{ dL g}^{-1}, and the value of \( a \) was 0.92 [29].
Paraformaldehyde with dimethylsulfoxide (PF/DMSO) was acknowledged as a good solvent for cellulose by Johnson [8] and by Minor [30], who reported it as a fast and simple dissolution process, non-degrading for cellulose. More recently, He and Wang [31] studied solutions of cellulose in PF/DMSO using viscometry and confirmed the solvent was non-degrading, showing negligible drop in DP after 2 years in solution. However, it must be noted that the authors used low-$M_r$ cellulose, with which a depolymerisation effect is less noticeable. The authors found that PF/DMSO was a better solvent than Cadoxen and FeTNa (iron sodium tartrate), but that LiCl/DMAc had better solvation capacity.

It has to be noted that intrinsic viscosity [$\eta$] as well as $a$ and $K'$ parameters in the MHS equation can also be obtained with a capillary viscosity detector that has a flow cell allowing its use on-line in size-exclusion chromatography. In this case, as explained in the next section, information such as the various $M_r$ averages defined earlier can be obtained.

### 2.2.2 Size-exclusion chromatography (SEC) and dissolution methods compatible with SEC

#### 2.2.2.1 Principle of SEC

Knowing only one $M_r$ average of a polymer is sometimes sufficient. However, in order to assess polymer properties and characterise degradation it is important to obtain the MMD. Size-exclusion chromatography (SEC) is the technique of choice to evaluate composition and MMD of polymers. The separation mechanism in SEC is based on differences in size, i.e. differences in the hydrodynamic volume of solutes. Polymer molecules travel with the mobile phase through porous particles, which constitute the packing material of the column (the solid phase). The small molecules can penetrate smaller pores than the large molecules. As a result the smaller molecules travel longer through the packing material and elute from the column in higher volumes than the larger molecules (Figure 2-1). SEC hence results in a separation of the polymers according to their molar mass, and more precisely to their hydrodynamic volume in solution. The number $n_i$ of molecules of molar mass $M_i$ in each slice of a chromatogram can be calculated and yields $M_{n_i}, M_{w}, M_{z}$ and $M_{z+1}$. Although $M_r$ values can be determined by SEC if the MHS coefficient $a$ is (accurately) known, $M_r$ is usually only determined when on-line viscosity detectors are used.
SEC has been widely used to determine cellulose MMD and to monitor degradation arising from the pulping, bleaching and viscoso processes. Valuable information can be found in publications originating from the pulp and paper industry, and from the electrical engineering sector since paper is, still to date, used as the main insulation material in electrical transformers. Developments in new column packings technology and in detection systems for molecular size and MMD have increased the range of information on molecular characteristics that can be obtained from SEC measurements [32,33,34,35].

Solvents used for SEC must allow polymer chains to open up into their most relaxed conformation: from solid state (crystalline or semi-crystalline) to liquid state, and they must be compatible with the column packing material.

For the study of a protein such as gelatine, which is soluble in water under moderate heat, aqueous SEC with mobile phases such as buffers and salt solutions can be applied. For a biopolymer such as cellulose, which has a limited solubility in most common solvents used in chromatography, the use of SEC is conditional to overcoming the solubility/system compatibility difficulty. For example solvents used for viscosity are incompatible with most SEC columns packings. Emsley et al. [36] reported Cadoxen was too aggressive and rapidly dissolved the poly (styrene-divinyl benzene) (PSDVB) column packing. Nevertheless, Schwald et al. [37] and Geresh et al. [38] used Cadoxen as SEC eluent and reported no column problem. The first used columns packed with Fractogel TSK (Merck), and the second, with a hydrophilic gel material, PSS Suprema (Jasco). Minor [30] successfully did SEC of methylol cellulose with DMSO as mobile phase on PSDVB columns, and Agg and Yorke [39] used iron sodium tartrate as cellulose solvent and mobile phase on Sepharose columns.

The following section presents the two methods that were tested in the frame of this study for characterisation of cellulose.
Dissolution and characterisation of cellulose

2.2.2.2 Cellulose tricarbanilate (CTC) and dissolution in THF

The first processes that were used to analyse cellulose by SEC involved "derivatising" the polymer in order to be able to dissolve it in organic solvents that are compatible with SEC column packings.

The very first methods were based on the modification of cellulose into nitrate [40,41] and acetate derivatives [42,43,44]. Cellulose nitrate has a relatively small refractive index difference with tetrahydrofuran (THF), the preferred solvent, which limited the sensitivity of the method and the precision (mostly baseline instability) [44]. More importantly, the poor stability of the cellulose nitrate, the significant chain scission of the polymer induced during the derivatisation, and the difficulty in obtaining uniform and consistent degrees of substitution (DS) - which introduced additional uncertainty in the results - were major drawbacks and the methods employing nitrate and acetate derivatives were rapidly abandoned.

Research into less degrading derivatisation methods led to other cellulose derivatives such as methylol cellulose [45] and cellulose tricarbanilate (CTC). The latter appeared as the most viable solution.

The suitability of CTC derivatives for SEC was first advocated in the mid-1970s [25,29]. The methods were widely used and further improved through the 1980s [28,46,47,48]. CTC proved to be a good alternative to cellulose acetate, showing fairly reproducible DS, and inducing no apparent degradation of the cellulose [25,49]. Hemicelluloses could also be carbanilated, which extended the applicability of the method to holocelluloses (i.e. cellulose and hemicelluloses) that are present in wood pulps. The CTC was shown to more readily dissolve in organic solvents than trinitrate, and THF was found to be the best solvent and SEC mobile phase [25]. The development of the first low-angle light scattering detectors in the early 1980s set ideal conditions for the development of methods of characterisation of cellulose using tricarbanilation.

CTC are prepared in DMSO or in pyridine, and are re-dissolved in THF for the SEC run. With cotton linters, faster reaction rates were reached in DMSO than in pyridine, but partial degradation of high-$M_r$ cellulose fractions during derivatisation was observed [50]. For softwood Kraft pulps, DMSO was a better solvent for carbanilation than pyridine.

With the latter solvent aggregation occurred in THF [51]. Hill et al. [52] showed that under specific reaction conditions, substitution was complete (DS = 3). Shroeder and Haigh [53] showed that no degradation occurred when the reaction was performed at 80°C but that higher temperatures induced depolymerisation within the first hours.

The effectiveness of the procedure for analysing CTC in THF was found to vary depending on the source of cellulose. Complete delignification is necessary prior to derivatisation. Therefore, certain lignin-containing pulps and papers cannot be derivatised [53]. Additionally, low-$M_r$ cellulose may be lost during the precipitation step with methanol or ethanol [50,54], which makes hemicelluloses very vulnerable.
Chapte rr  2

2.2.2.3 Direct dissolution of cellulose in lithium chloride/$N,N$-dimethylacetamide

Due to the problems associated with the derivatising methods, research into new direct solvent systems continued in parallel, and led to the development of the solvent system lithium chloride / $N,N$-dimethylacetamide (LiCl/DMAc).

LiCl/DMAc was first discovered to dissolve polyamides and chitin in 1972 [55,56,57,58,59]. The use of LiCl/DMAc quickly spread and it was applied for the first time for cellulose dissolution almost concomitantly by McCormick [60] and Turbak [61], who both patented a similar dissolution process. Other non-derivatising solvent systems for cellulose, such as amine oxide and liquid ammonia/ammonium salt systems, were developed around the same time under the economic pressure of the textile industry [62]. However, the use of LiCl/DMAc grew more rapidly and the methods initially proposed were quickly adapted to suit the cellulose source and the sample characteristics. For instance, it appeared that bimodal or multimodal SEC MMD profiles obtained for certain types of wood pulps yielded information on the hemicelluloses content [63,64].

The popularity of LiCl/DMAc is linked to the clear advantage that a direct dissolution method has over derivatisation by being faster, easier and more reproducible. Additionally, none of the common solvents for cellulose allows as wide a range of organic reactions with polysaccharides as does LiCl/DMAc, yielding a number of cellulose derivatives of industrial interest such as esters, ethers, carbamates and sulfonates [27]. LiCl/DMAc is also currently used for a number of other non-water-soluble polysaccharides of commercial interest, such as chitin, amylose, amylopectin, arabinogalactan, dextrans and pullulans, which differ from cellulose only in the extent of branching, type of linkages and anomeric configuration [65].

The major advantage of LiCl/DMAc is that it can be used as mobile phase in SEC with column packings such as PSDVB. The solvent and mobile phase being identical simplifies the procedure. The SEC of cellulose in LiCl/DMAc was applied for the first time by Ekmanis [66,67].

2.2.2.3.1 The dissolution mechanism

The first studies by McCormick [60], Turbak [61] and Mc Cormick and Dawsey [27] showed the unique characteristics of LiCl/DMAc as solvent system.

However, after two decades of use, a generally accepted mechanism still remains to be revealed in order to fully explain the solvation of cellulose in LiCl/DMAc, in particular the solvent-lithium interaction, and the crucial role of the chloride ion. Slightly different interpretations on the structure of LiCl/DMAc were found in the literature, but all emphasise as basic principle that the polar aprotic nature of DMAc allows ionic compounds to readily dissolve. LiCl forms ion pairs, held together by electrostatic rather
than covalent bonds. Unable to form hydrogen bonds, DMAc does not solvate anions to any appreciable extent while cations are strongly solvated. The lithium ions are more tightly linked with the carbonyl group of DMAc, while the chloride ions are left unencumbered and thereby highly active as nucleophilic bases.

Many models have been proposed, all are based on this special structure of the ion pair \([\text{Li} \cdot \text{n(DMAc)}]^+ \text{Cl}^-\) (Figure 2-2). The concept of the formation of \([\text{Li} \cdot \text{(DMAc)}]^+\) as a macrocation where \(\text{Li}^+\) is located adjacent to the carbonyl of DMAc in a mesomeric equilibrium (Figure 2-2 (a)) emerged as the most likely to occur after infrared spectroscopy studies [68]. The latter showed the appearance of a different absorbance spectrum upon adding LiCl to DMAc. In addition it was demonstrated that an increase in viscosity of DMAc occurred when LiCl was added. According to McCormick et al. [26], the complexation involves one \(\text{Li}^+\) with the carbonyl oxygen atom of up to four DMAc molecules. The cation \([\text{Li} \cdot \text{n(DMAc)}]^+ (n = 4)\) formed is only loosely associated with Cl\(^-\). This likely forms a tetrahedral-like structure [69]. The stability of this complex is paramount for the dissolution of cellulose. If too stable or too weak, the solvent power is affected. Figure 2-2 (b) represents a model proposed by Turbak of a cation complex where the \(\text{Li}^+\) interacts simultaneously with both electronegative atoms O and N of the DMAc [70]. In Figure 2-2 (c) the lithium moiety of LiCl interacts with the amide oxygen and the complex stability is due to electron transfer from the amide on the LiCl ion pair. Figure 2-2 (d) represents a possible nucleophilic addition of a lithium halogenide to DMAc eventually resulting in a covalent complex. [27].

\[\text{(a)} \quad \text{R} \quad \text{C} \quad \text{O} \quad \cdots \quad \text{Li}^+ \quad \text{R} \quad \text{C} \quad \text{O} \quad \text{Li} \quad \text{R} = \text{H}, \text{CH}_3\]

\[\text{(b)} \quad \text{CH}_3 \quad \text{C} \quad \text{O} \quad \text{Li}^+ \quad \text{R} = \text{H}, \text{CH}_3\]

\[\text{(c)} \quad \text{CH}_3 \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{Li} \quad \text{R} = \text{H}, \text{CH}_3\]

\[\text{(d)} \quad \text{CH}_3 \quad \text{N} \quad \text{C} \quad \text{O} \quad \text{Li} \quad \text{X} = \text{Cl}, \text{Br}\]

Figure 2-2. Proposed structures of the LiCl/DMAc complexes [69].

\(^1\text{H}, ^7\text{Li}\) and \(^{13}\text{C-NMR}\) [58,71,72,73,74] yielded important information for the understanding of the dissolution process of cellulose in LiCl/DMAc. The solvent was shown to be a true non-derivatising solvent, \(i.e.\) one that does not form chemical bonds with the cellulose molecule [22].

A number of structural models for solvation and complexes formed have been proposed, which place the emphasis on the chloride anion being highly active as a nucleophile towards cellulose. Cl\(^-\) enters in competitive hydrogen bond formation with hydroxyl
protons of cellulose, thereby disrupting the existing intermolecular hydrogen-bonded structure, ultimately leading to dissolution [26,69,70,72] (Figure 2-3 (a) to (c)).

The lithium cation was shown to play an important role in the dissolution process. Using $^7$Li-NMR, Morgenstern and Kammer showed that the solvated lithium strongly interacted with the hydroxyl groups of cellulose (Figure 2-3 (d)) [69]. Using $^{13}$C-NMR, Davé et al. [75] also observed that strong ionic interactions existed between the carbonyl oxygens of DMAc and cellulose acetate butyrate with Li$^+$, and postulated the formation of electrostatic bonds between the cation and the molecule backbone. Interactions between Li$^+$ and cellulose were recently studied by Brendler et al. [76] with celllobiose as model molecule, using $^7$Li-NMR and $^7$Li-$^1$H HOESY NMR (Heteronuclear Overhauser Effect Spectroscopy). The authors showed that celllobiose was part of the coordination sphere of Li$^+$, and therefore expected cellulose also taking part in the solvation of lithium ions, this being one of the driving forces for the dissolution of the polymer.

![Figure 2-3. Models of the cellulose –LiCl-DMAc complexes. (a): proposed by Mc Cormick et al [26], (b): proposed by El-Kafrawy [72], (c): proposed by Turbak [70], (d): proposed by Morgenstern et al [69].](image)

Since the addition of cellulose in LiCl/DMAc displaces a DMAc molecule by a cellulosic hydroxyl group, as expressed by the equilibrium shown in Figure 2-4, steric considerations are paramount in the dissolution process of cellulose in LiCl/DMAc. The latter can be visualised as an exchange of ligands that can occur if the solvent complex has an adequate spatial configuration, so that steric hindrance cannot prevent solvation.

![Figure 2-4. Ligand exchange reaction in the cellulose-LiCl-DMAc solutions.](image)
Dissolution and characterisation of cellulose

Considering the cellulose chain in its entire length, accumulated associations of Cl\(^-\) along the chain produce a negatively charged polymer with the macrocation [Li-DMAc\(^+\)] as counter-ion. It is assumed that each hydroxyl of the anhydroglucose may be approached by a single LiCl/DMAc complex [26]. The molecules of cellulose are therefore also forced apart by charge repulsion [27].

Studies with Scanning and Transmission Electron Microscopy (SEM and TEM) on the morphological changes of cellulose during the dissolution in LiCl/DMAc showed that there was no degradation occurring at the supramolecular level [77]. Firstly, the solvent penetrates into the fibre wall and then into the fibres and fibrils structure, starting preferentially in the less ordered regions. Displaced fragments appear gradually, and progressively, fibrils are separated to a greater extent and isolated to finally result in dissolution of the fibrils structure.

2.2.2.3.2 The solvent complex specificity

Investigation into the suitability of other polar aprotic solvents showed among a wide array of solvents tested (dimethyl sulfoxide, dimethyl formamide, formamide, ethanolamine) that very few could achieve dissolution of cellulose, and those that did induced degradation. Apart from DMAc, only N-methylpyrrolidinone (NMP), the cyclic analogue of DMAc was found effective (albeit less than the former). This was attributed to the greater polarisability of DMAc and NMP as compared with the other solvents [72].

Lithium halides other than LiCl were inefficient [22]. The order of nucleophilicity of nonsolvated halide ions is the same as that of the electronegativity of the halogen atoms, with Cl\(^-\) > Br\(^-\) > I\(^-\). Bromide (Br\(^-\)) and iodide (I\(^-\)) are larger ions than Cl\(^-\). They are more tightly bound to DMAc and less available to break inter- and intramolecular cellulose hydrogen bonds [22,27,78]. Under such consideration it could be hypothesised that LiF would provide even more efficient ion pairing than LiCl. However, there is no practical organic solvent for LiF [78]. Furuhata et al. [79] achieved dissolution of microcrystalline cellulose in LiBr/DMAc, but found that the concentration of LiBr needed to be larger than LiCl in order to achieve comparable dissolution.

Nitrate and sulfate lithium salts were also inefficient along with other alkali and alkali-earth chlorides such as sodium, potassium, barium, calcium, magnesium and zinc chlorides [22]. With alkali chlorides, in the range of alkali cations Li, Na, K and Cs, the solvation by DMAc decreased as the ionic radii increased, because they provided a smaller charge to radius ratio and weaker ion dipole interactions [22].
References