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

Dupont, C.

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Chapter 3. Dissolution of cellulose in the solvent system lithium chloride / N,N-dimethylacetamide (LiCl/DMAc)

Abstract

Activation and dissolution methods of cellulose in lithium chloride/N,N-dimethylacetamide (LiCl/DMAc) are studied. A literature review shows the importance of the multiple parameters involved such as salt concentration, sample source and preparation. The experiments carried out in order to perfect the activation and dissolution method to be used throughout the present study are presented and the suitability and efficiency obtained in the different trials is evaluated. The final procedure involves as a first step the activation by solvent exchange, with a water/methanol/DMAc sequence, followed in a second step by dissolution in 8% LiCl/DMAc at 4°C. A study of the stability of the cellulose solutions in the actual experimental conditions showed that no degradation occurred during the solvation process and confirmed the non-aggressiveness of LiCl/DMAc.

3.1 Literature review

3.1.1 Dissolution of cellulose in LiCl/DMAc

3.1.1.1 Activation procedure

As explained in chapter 1, the activation step is crucial for opening up the polymer chains into the most relaxed conformation in order to enhance the diffusion kinetics of the solvent to the tightly packed crystalline regions that are less accessible. For most polymers, this means mainly allowing sufficient time for chains to unfold. The larger the molar mass ($M_t$) and crystallinity are, the longer is the time needed to obtain a true solution.

The most effective activation methods prior to dissolution in LiCl/DMAc as described in the two US patents No. 4,302,252 [1] and No. 4,278,790 [2] and by Dawsey and McCormick [3] are:

- Polar medium swelling and DMAC exchange

This can be achieved by either of the following:
- Water activation followed by DMAc exchange. Water swells and opens the structure; inter- and intramolecular hydrogen bonds are replaced by hydrogen bonds with H$_2$O. DMAc introduced subsequently impedes the inter- and intra-hydrogen bonds to re-form (shown in Figure 1-7 (A) and (C) of Chapter 1)\(^1\).

- Steam activation followed by DMAc exchange, which works with a similar mechanism as water activation but at a higher vapour pressure, where the efficiency of penetration of water is enhanced.

- Water activation in LiCl/DMAc/H$_2$O by fractional distillation to less than 4% water.

- Liquid ammonia activation followed by DMAc exchange.

- **Heat activation with DMAc**

This method first proposed by Ekmanis [4,5] is based upon the fact that at or near its boiling point, the amide has sufficiently high vapour pressure to penetrate in the fibre and swell it. In heat activation, DMAc is therefore allowed to reflux with the cellulose at a temperature close to the solvent boiling point [6,7]. This procedure was reported as more advantageous over polar medium activation because it requires less LiCl in the subsequent dissolution phase but foremost because it is a one-step procedure thereby allowing easier handling of a large number of samples [8].

Recovered cellulose from heat activated solutions were found to have lost 10% in intrinsic viscosity, which indicated a slight but non significant polymer degradation [1]. Dawsey and McCormick [3], and Terbojevich *et al.* [9] observed that solutions prepared via heat activation were slightly coloured, which they attributed to oxidative degradation of the polymer at high temperature. They found that flushing nitrogen in the solutions minimised this oxidation and resulted in clear solutions. More recently Potthast *et al.* [10] showed that heat activation indeed resulted in the depolymerisation of cellulose, which was more or less pronounced depending on the pulp type and the time of activation. The authors demonstrated that this degradation occurred via endwise peeling reactions and random cleavage. The first reactions take place through the formation of $N,N$-dimethylacetoacetamide, a condensation product of DMAc. The second reactions occur through the formation of $N,N$-dimethylketeniminium ions at temperatures above 80°C, which are extremely reactive electrophilic ions able to cleave glycosidic bonds.

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\(^1\) In the papermaking industry, the fabrication of handsheets designated for the physical testing involves an aqueous impregnation of the pulp which is carried out before the disintegration. One hour in hot water or 24 hours in cold water are usually considered necessary in order to obtain a good hydration state of the fibres and even swelling that will allow optimal intra-fibre cohesion and reproducible inter-fibre linking in the subsequent drying phase of the handsheets. This step ensures stable and reproducible physical characteristics of the testing material.
3.1.1.2 Proportion of LiCl in DMAc

After the activation phase, the cellulose substrate is ready to dissolve in LiCl/DMAc. The thorough literature review by Dawsey and McCormick [3] of the experimental conditions tested by different authors showed that the relative proportions of LiCl and cellulose were critical for optimal dissolution. “Ideal” concentrations of LiCl by weight of cellulose were reported ranging between 2 and 12% [1,2]. For cotton fibres [7,8] and for a wide variety of wood fibres such as softwood and hardwood in Kraft pulps [7], 8% LiCl was found the least amount necessary to achieve complete dissolution. Using heat activation, even high-$M_r$ cotton celluloses appeared to completely dissolve at lower LiCl concentrations [8,11]. Nevertheless this could be an experimental error due to the degradation occurring at high temperature. According to McCormick et al. [12] a critical number of complexed sites seem to be required and concentrations greater than 6% are necessary for a complete dissolution of low-$M_r$ celluloses. Reportedly, at LiCl concentration above 12% [7] to above 15% [1], the DMAc becomes supersaturated with the salt and the cellulose tends to precipitate out of solution.

Aggregate free solutions of polymers are in general difficult to prepare [13]. Sjöholm et al. [14] found the concentration of LiCl to be critical in the formation of aggregates upon dissolution of wood pulp and cotton linter, independently of the sample concentration. For hardwood Kraft pulp, the proportion of aggregates increased when the concentration of LiCl increased from 6% to 8% and from 8% to 10%.

Strlić et al. [15] recently reported the important role of the LiCl concentration. They showed that after dissolution of cellulose in 8% LiCl/DMAc, and further dilution for size-exclusion chromatography (SEC) analysis, 3% LiCl in the sample resulted in lower $M_r$ than 1%. The authors attributed this to a decrease in the intermolecular interactions and extent of aggregation during sample preparation thereby pointing sample preparation prior to injection as a decisive process.

3.1.1.3 Sample source and composition, sample preparation

Other parameters in the dissolution process such as the cellulose concentration as well as the supramolecular structure of the polymer (which depends on the cellulose source), and the sample preparation for the activation step greatly influence the dissolution process.

In paper substrates, the access of the activation liquids to the cellulose molecules has to be facilitated. Grinding until a good defibrillation is achieved is necessary in order to reduce surface heterogeneity (see section 1.4.2 of Chapter 1). Native and chopped or cut fibres have been reported to result in incomplete and inconsistent dissolution [8,16]. This could be confirmed experimentally in the present chapter (section 3.2.1.2).
McCormick [2] reported that complete solutions of 1 to 5% cellulose powder could be achieved in less than one hour, while it took 24 to 48 hours for solutions of 6 to 15% cellulose. Turbak [17] reported that upon activation by water swelling and solvent exchange, up to 12-15% cellulose of relatively low-$M_r$ ($9 \times 10^4$ g mol$^{-1}$) could be solubilised in 10% LiCl/DMAc in 4-6 hours. However with higher $M_r$ ($3 \times 10^5$ g mol$^{-1}$), solutions up to about only 4% cellulose could be prepared. According to Silva and Laver [7], among solutions ranging from 0.8% to 1.6% cellulose, the concentration resulting in ideal dissolution was 1.2%. Similarly, Timpa [8] found the ideal cellulose concentration also being 1.2%.

Molar mass and presence of lignin [18] are also described as important parameters in the dissolution process. Ekmanis [4] noted that the higher the $M_r$, the more difficult the dissolution. But while most of the early studies focussed on concentrated solutions of low-$M_r$ cellulose, Striegel and Timpa chose to study the dissolution and characterisation of high-$M_r$ cellulose [11]. Kennedy et al. [19] reported that in 10% LiCl/DMAc the maximum concentration of cotton cellulose for complete dissolution was 0.075% as compared with 0.15% for softwood and hardwood cellulose. The author suggested this was due to the higher crystallinity of the cotton cellulose, and to the difference in composition and processing of the pulps. This referred especially to the treatment used to remove lignins in wood pulps, which creates voids and a wide distribution of pores. Such a microporous structure eases the penetration by activation liquids and solvent.

After water activation, sulphite pulp was reported to dissolve faster than cotton linters, which in turn dissolved faster than partially hydrolysed cotton linters [20]. Again, this was attributed to the high crystallinity of cotton cellulose.

According to Silva and Laver [7], depending on the cellulose source (pulp from softwood, hardwood, Kraft, sulphite, bleached or unbleached), the necessary time required for the different steps (activation, dissolution) in order to achieve clear solutions varied widely. Here also, the author suggested that, for higher $M_r$, crystallinity, $\alpha$-cellulose and lignins contents, longer times were required in each step leading to dissolution. According to Sjöholm et al. [18], the high lignins content in softwood pulps was responsible for a decrease in the ability to swell the fibres, and therefore a decrease in solubility.

Despite these observations, inconsistencies were noted about the role of crystallinity in the solubilisation process. Hardwood Kraft pulp (low crystallinity) was reported to dissolve much more slowly than cotton (high crystallinity) [7]. Recent publications also confirmed that the degree of crystallinity is not responsible for the difference in solubility between cellulose substrates [21].

In wood pulps, differences were reported between softwood and hardwood, the former showing slower dissolution [19] or lower solubility [22]. Softwood Kraft pulp dissolved in LiCl/DMAc was shown to lead to the formation of gel-like structures consisting of mannans and lignins, which could not be related to the crystallinity [18]. In that case two hypotheses were submitted, the first being that lignins content was more probably
involved in the long solubilisation times required, and the second being the formation of a gel constituted of glucomannans hemicelluloses, which quickly covered the fibres and hindered the progress of further dissolution.

Other studies confirmed the presence of aggregates under specific conditions [9]. Aggregates and associates that were shown to form in solutions of cellulose from diverse sources (micro-crystalline cellulose and cellulose from softwood Kraft pulp and hardwood sulphite pulp) in 6% and 9% LiCl/DMAC could be disintegrated by a dilution to 2.6% LiCl (i.e. SEC concentration). But this was only possible within certain limits of cellulose versus salt concentration [23]. A maximum concentration of 1% cellulose in 9% LiCl/DMAC was required to form a true (disaggregated) solution upon dilution to 0.9% LiCl. Cellulose often forms so-called fringe-micelles in solution. These large associates or aggregates were proven to be highly swollen parts of the former crystalline regions of the cellulose. In a solution with too low LiCl concentration and/or too high cellulose concentration, the solvent is unable to completely rupture the strong hydrogen bonds in the cellulose [24].

Recently, Schult et al. [25] published a modified polar medium activation process that reportedly allowed them to obtain the complete dissolution of high-$M_c$ cellulose from sulphite pulp in 8% LiCl/DMAC. The procedure involves first a swelling, in 0.1 M LiCl instead of water, and subsequent steps of washing with chelating agents such as EDTA (ethylene diamine tetraacetic acid), DTPA (diethylene triamine pentaacetic acid) and citric acid. These washings allow to remove any remaining ion in the pulp, as these are thought to interfere in the association of the cellulose with the solvent complex, thereby hindering the dissolution process. Following, a second swelling in LiCl ensures that all the ions associated with the cellulose are Li$^+$. Then a Soxhlet extraction in acetone removes any possible extractive left in the pulp and acts as first stage in the solvent exchange, which proceeds with methanol and DMAC.

However, probably the most difficult situation remains that of mechanical wood pulp because of the strong interactions between cellulose, hemicelluloses and lignins. Heat activation was reported to be more efficient than polar medium activation in allowing dissolution of a higher proportion of groundwood pulp. However, total dissolution of mechanical pulp in LiCl/DMAC has never been reported.

It is noteworthy that very few authors have included sized papers in their studies. Concerning residual presence of non-fibrous components, only one small mention could be found in the literature, reportedly that small amounts (<2%) of pectins and waxes should not interfere in the dissolution process [8].

### 3.1.2 Stability of solutions of cellulose in LiCl/DMAC

The solutions of cellulose in LiCl/DMAC are reported to be extremely stable [26]. Some researchers found no degradation of the cellulose after several months in solution [9] and
even years at room temperature [1,27]. High LiCl concentrations (above 10%) were reported to have no degradation effect on cellulose over time [19]. McCormick et al. [12] noted a slight decrease of 2% in relative viscosity of cellulose solutions in 9% LiCl/DMAC over 30 days, which they attributed to changes in inter and intra-molecular hydrogen bonding.

Strlič et al. [28] showed that cellulose from linters powder that were submitted to an oxidation treatment, in order to increase the sensitivity to solvent-induced degradation, did not undergo further degradation in 8% LiCl/DMAC. In a more recent study, the authors found for cellulose in 1% LiCl/DMAC at room temperature a constant $k$ of random glycosidic bond cleavage (derived from the Ekamstam equation described in Appendix 6-3) of $6.9 \times 10^{-8}$ mol mol$^{-1}$ monomer day$^{-1}$, i.e. a decrease in $M_t$ of 47 g mol$^{-1}$ per day [15].

In contrast, a recent study by Jerosch [29] found LiCl/DMAC had some degrading action on cellulose in specific cases. When cellulose was kept in 8% LiCl/DMAC at 40°C over 5 days, $M_t$ was stable for 2 weeks only, and fell with a decrease of 23% after 22 days. The initial degradation state of cellulose and the temperature-time history was found paramount in the stability of cellulose solutions. However, with softwood bleached Kraft pulp paper and cotton linters paper, no decrease in $M_t$ was found when dissolution was carried out at 4°C. With papers that had been subjected to accelerated aging, including either heat/humidity or pollution, the stability of the solutions was lower as the $M_t$ started dropping slightly after one week.

### 3.2 Development of the method for the dissolution of cellulose in LiCl/DMAC

#### 3.2.1 Experimental

##### 3.2.1.1 Solvent and mobile phase preparation

As outlined in Chapter 1, water has to be excluded from the solvent system since its presence hinders the complexation with cellulose [1]. The amount of water has to be kept to less than 5% in the final solution. As both LiCl and DMAC are hygroscopic, special care has to be taken in the preparation of the solvent. LiCl was oven-dried and stored in a desiccator over drierite (CaSO$_4$). Aliquots of LiCl were weighted swiftly when needed and placed back in the desiccator until dry before use.

For drying DMAC two methods were tested: the first was heating at 100-110°C for 10 minutes in order to drive off the residual moisture, and the second was adding aluminium sodium silicate molecular sieve (0.4 nm effective pore size) to the solvent bottle. Both
Dissolution of cellulose in LiCl/DMAc

methods worked equally well; therefore the method of drying with molecular sieve was chosen because it was feared that the heating method could lead to some oxidation of the DMAc.

When dry, DMAc was filtered through 0.5 μm pore, 25 mm diameter Millex LCR filters (Millipore) with a hydrophilised polytetrafluoroethylene (PTFE) membrane. If not used immediately, the solvent was stored under nitrogen at 4°C until use within the same week.

In the trials of high temperature activation/dissolution, the appropriate amount of LiCl was added directly in the reacti-vials (Pierce) containing the activating cellulose in the appropriate volume of DMAc (see section 3.2.1.3.1).

In the procedure of dissolution following solvent exchange activation, LiCl/DMAc was prepared in stock solution by adding the required amount of dry LiCl (8%) to warm DMAc (40°C) under magnetic stirring. LiCl dissolved within about one hour. Warm DMAc allowed for the best dissolution of the salt over room temperature DMAc and DMAc heated to 100°C (Table 3-2).

Samples of 200 mL of this stock solution were prepared at a time. Only 50 mL was used as dissolution solvent and the rest made the size-exclusion chromatography (SEC) mobile phase (0.5% LiCl/DMAc) by diluting with anhydrous DMAc, in order to have the same batch of solvent for the dissolution and the SEC run. When not used immediately, the LiCl/DMAc solutions were flushed with nitrogen and stored at 4°C to limit any possible degradation.

3.2.1.2 Sample preparation

The necessity of defibrillating the paper in order to ease the solvent access was verified by a trial of heat activation/dissolution of paper cut in small pieces (2 mm x 2 mm) which did result in very incomplete dissolution. Under the same experimental conditions paper defibrillated as described hereafter, resulted in complete dissolution.

Two to 2.5 g of paper were taken out of four different samples of Whatman No.1 paper in different part of the sheets (150 mm x 190 mm), left, middle and right portions. The paper was ground during five minutes in a small two-blade blender (50 mL volume capacity). The samples were then placed in a controlled environment chamber at 50% relative humidity (rH) and 23°C, conditions corresponding to TAPPI standard T 412 om-94 [30], in order to equilibrate for at least 2 days. The reason for equilibrating the samples was mainly because it ensured the reproducibility of the weighting. About 5×10⁻² g (±0.02%) was weighted for activation/dissolution.

3.2.1.3 Optimisation of activation and dissolution

Two methods were tested to obtain an appropriate and efficient dissolution.
The first method was heat activation/dissolution as proposed by Timpa [8,31], adapted from the ‘one-pot’ procedure developed by Ekmanis [5]. This procedure was tried in the first place since the activation phase was reported to be faster and less work intensive than the solvent exchange activation method. The latter procedure was tried afterwards and was derived from the original method as proposed by Turbak [1] and McCormick [2]. In all cases, the activation was done in conical bottom 10 mL reacti-vials (Pierce) capped with Teflon lined screw caps, under constant stirring in a heating/stirring unit (Pierce), using V-shaped Teflon-coated magnetic stirrers.

3.2.1.3.1 High temperature activation and dissolution

3.2.1.3.1.1 High temperature activation

Several conditions were tested by varying the activation time and the concentration of LiCl, which are listed in Table 3-1. In all the trials, 5 mL of anhydrous DMAc was heated to 150°C, just below boiling temperature (boiling point =164-166°C) in the reacti-vial left uncapped for 10 minutes in order to drive residual moisture out. Fifty milligrams (±1×10⁻⁵ g) of defibrillated paper was added, and the reacti-vial was then tightly capped. The activation proceeded at 150°C with refluxing DMAc.

3.2.1.3.1.2 High temperature dissolution

After activation, the temperature was lowered from 150°C to 100°C and allowed to stabilise for 20 minutes. Then LiCl was added directly in the reacti-vial. The temperature was either kept at 100°C or lowered to 50°C.

In the different trials, the amounts of dry LiCl added in the DMAc activation mixture were: 5%, 8%, 10%, 12% and 13% (0.25 g, 0.4 g, 0.5 g, 0.6 g and 0.7 g in 5 mL DMAc). The sample was left heating/stirring until maximum dissolution stage was reached, which took from 3 to 4 days. Assuming dissolution was complete, the cellulose solution was then 10 mg mL⁻¹, i.e. 1% (wt/v). Table 3-1 reports the experimental conditions in the different trials.

3.2.1.3.2 Polar medium swelling activation followed by warm, ambient or cold dissolution

Table 3-2 lists the trials of solvent preparation, polar medium activation, dissolution time, cellulose concentration and LiCl concentration in order to optimise the dissolution conditions.
3.2.1.3.2.1 Polar medium swelling and solvent exchange

Polar medium swelling and solvent exchange activation consisted in a thorough swelling in water followed by exchange first with methanol and second with DMAc. Activation volumes were 8 to 10 mL. The time and the number of exchanges varied in the different trials.

The extra step of methanol exchange was added compared to the methods described in the literature in order to help expel the residual water, thus avoiding a collapse of the fibres and pores structure, and thereby enhancing further penetration of DMAc.

Two methods were tested for the elimination of the swelling liquid after each of the exchanges: centrifugation and filtration. Centrifugation at 2500 rpm during 20 minutes was unsatisfactory as the liquid was not eliminated and a non-negligible amount of fibres was lost after several centrifugation steps. Filtration under vacuum was found more appropriate, with almost no fibre loss and a satisfactory elimination of the liquids. Filtration was therefore adopted and was carried out with a 25 mm glass microanalysis vacuum filter holder and fritted glass 15 mL funnel capacity (Millipore), using 0.5 μm pore Millex LCR filters.

3.2.1.3.2.2 Dissolution

Dissolution took place after filtering out the last DMAc exchange volume, by adding 5 mL of the stock solution 8% LiCl/DMAc to the paper fibres in the reacti-vial. Solutions with lower salt concentrations were achieved by diluting this stock solution with dry DMAc. The reacti-vial was tightly capped and left stirring. Different dissolution temperatures (warm, ambient and cold) were tested. The different conditions are reported in Table 3-2.

3.2.2 Results

3.2.2.1 High temperature activation and dissolution

Table 3-1 reports the results of the different trials carried out. The hot DMAc procedure often resulted in yellow cellulose solutions. This discoloration was present regardless of the state of degradation (unaged, artificially aged) and composition of the samples (plain Whatman No.1, with/without alum, and with/without gelatine). This is consistent with the results from Terbojevitch et al. [9]. Complete dissolution was not achieved in any case.

It was found that long activation time (22 hours) was detrimental, resulting in significant yellowing and lack of improved dissolution, and that one-hour activation was found
Chapter 3

sufficient. Maximum dissolution was usually reached within 3 to 4 days and did not proceed further even upon prolonged periods of up to 11 days.

The concentration of LiCl appeared to be critical. The best - yet incomplete - dissolution of plain Whatman No.1 paper (unsized unaged) was achieved in 3 days with exactly 8% LiCl. No yellowing of the solution occurred. This corresponded to a ratio of cellulose to LiCl of 1/8. Less or more LiCl resulted in a poorer dissolution and/or yellowing.

After activation and upon adding LiCl it was found that if temperature was lowered from 100°C to 50°C, the yellowing of the solution could be avoided. The yellowing was believed to arise from degradation of the cellulose in the solvent at high temperature. Indeed, it was expected that prolonged activation times at 150°C, as well as a dissolution at 100°C in the presence of lithium salts, would most likely partially degrade the paper constituents. This effect would increase in the case of partially oxidised (oxicelluloses) or hydrolysed cellulose. Additionally, at such temperatures, any residual oxygen present in the reacti-vial would contribute to the oxidative degradation of the polysaccharides.

Residual moisture present in the paper that would not have been totally eliminated during the activation in the anhydrous DMAc could also play a role in the low efficiency of the dissolution.

According to the results, a gelatine content of 0.5% (wt/wt) did not seem to hinder the dissolution (sample No. 5c) but with higher gelatine content in the paper, such as 12.5% (wt/wt), a precipitation of the gelatine out of solution occurred (sample No. 4). However, the visual examination did not allow to determine whether the precipitate was gelatine alone or a co-precipitate of gelatine and cellulose.

3.2.2.2 Polar medium/solvent exchange activation and dissolution in warm, ambient or low temperature

3.2.2.2.1 Polar medium/solvent exchange activation

Given the unsatisfying results obtained with the high temperature activation/dissolution method reported in the previous section, namely of irreproducible efficiency yet incomplete dissolution, and yellowing associated with potential degradation at high temperature, it was decided to test activation and dissolution at lower temperature. The extra step of the exchange from water to methanol prior to the exchange with anhydrous DMAc was done in order to ensure the total elimination of water from the paper substrate and eliminate the suspected negative effect of residual moisture.
# Dissolution of cellulose in LiCl/DMAc

## Table 3-1. High temperature activation and dissolution experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>sample</th>
<th>activation</th>
<th>LiCl concentration</th>
<th>dissolution time and efficiency</th>
<th>yellowing</th>
</tr>
</thead>
<tbody>
<tr>
<td>1a</td>
<td>W (^1) unsized unaged RC (^3)</td>
<td>1h DMAc 150°C</td>
<td>1) 5% - 100°C - 3 days 2) after 3 days, added to 10% -100°C</td>
<td>1) 3 days, no dissolution 2) 5 days, mostly dissolved</td>
<td><strong>-</strong></td>
</tr>
<tr>
<td>1b</td>
<td>W / A5 aged 4 days (^4) RC</td>
<td>1h DMAc 150°C</td>
<td>1) 5% - 100°C - 3 days</td>
<td>1) 3 days, no dissolution 2) 11 days, mostly diss., crystalline deposit</td>
<td><strong>+</strong></td>
</tr>
<tr>
<td>1c</td>
<td>W / A5 aged 13 days (^4) RC</td>
<td>1h DMAc 150°C</td>
<td>1) 5% - 100°C - 3 days</td>
<td>1) 3 days, no dissolution 2. 2) 11 days, mostly diss., crystalline deposit</td>
<td><strong>+</strong></td>
</tr>
<tr>
<td>2</td>
<td>W unsized unaged RC</td>
<td>22 h DMAc 150°C</td>
<td>1) 8% - 100°C - 6 days</td>
<td>1) 6 days, no dissolution 2) after 6 days, added to 12% - 100°C 2) 9 days, little dissolved</td>
<td><strong>+</strong></td>
</tr>
<tr>
<td>3</td>
<td>W unsized unaged, RC</td>
<td>1h DMAc 150°C</td>
<td>10% - 100°C</td>
<td>5 days, mostly dissolved</td>
<td><strong>+/—</strong></td>
</tr>
<tr>
<td>4</td>
<td>W / 12.5% K(^{5}), RC</td>
<td>1h DMAc 150°C</td>
<td>13% - 100°C</td>
<td>8 days, mostly diss., gelatin precipitated</td>
<td><strong>+</strong></td>
</tr>
<tr>
<td>5a</td>
<td>W unsized unaged, C (^6)</td>
<td>1h DMAc 150°C</td>
<td>1) 8% - 100°C 2) T immediately lowered to 50°C</td>
<td>3 days, mostly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>5b</td>
<td>W unsized aged 91 days, C</td>
<td>1h DMAc 150°C</td>
<td>1) 8% - 100°C - 2) T (\downarrow) 50°C</td>
<td>3 days, mostly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>5c</td>
<td>W / K0.5 aged 91 days (^7), C</td>
<td>1h DMAc 150°C</td>
<td>1) 8% - 100°C - 2) T (\downarrow) 50°C</td>
<td>3 days, mostly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>6a</td>
<td>W unsized unaged, C</td>
<td>1h DMAc 150°C</td>
<td>1) 12% - 100°C - 2) T (\downarrow) 50°C</td>
<td>1) 3 days, partly dissolved 2) no further dissolution with (\uparrow) time</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>6b</td>
<td>W unsized unaged, RC</td>
<td>1h DMAc 150°C</td>
<td>1) 12% - 100°C - 2) T (\downarrow) 50°C</td>
<td>1) 3 days, partly dissolved 2) no further dissolution with (\uparrow) time</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>7a</td>
<td>W unsized unaged, C</td>
<td>1h DMAc 150°C</td>
<td>1) 5% - 100°C - 2) T (\downarrow) 50°C</td>
<td>11 days, partly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>7a'</td>
<td>W unsized unaged C</td>
<td>1h DMAc 150°C</td>
<td>1) 8% - 100°C - 2) T (\downarrow) 50°C</td>
<td>11 days, partly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>7b</td>
<td>W unsized unaged, dry (^8)</td>
<td>1h DMAc 150°C</td>
<td>1) 5% - 100°C - 2) T (\downarrow) 50°C</td>
<td>11 days, partly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>7b'</td>
<td>W unsized unaged, dry</td>
<td>1h DMAc 150°C</td>
<td>1) 8% - 100°C - 2) T (\downarrow) 50°C</td>
<td>11 days, partly dissolved</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>8a</td>
<td>W / N0.5 aged 91 days (^9), C</td>
<td>1h DMAc 150°C</td>
<td>1) 10% - 100°C - 2) T (\downarrow) 50°C</td>
<td>4 days, little dissolved, no further dissol.</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>8b</td>
<td>W / N2 aged 91 days (^9), C</td>
<td>1h DMAc 150°C</td>
<td>1) 10% - 100°C - 2) T (\downarrow) 50°C</td>
<td>4 days, little dissolved, no further dissol.</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>8c</td>
<td>W / K0.5 aged 91 days (^9), C</td>
<td>1h DMAc 150°C</td>
<td>1) 10% - 100°C - 2) T (\downarrow) 50°C</td>
<td>4 days, little dissolved, no further dissol.</td>
<td><strong>—</strong></td>
</tr>
<tr>
<td>8d</td>
<td>W / K2 aged 91 days (^9), C</td>
<td>1h DMAc 150°C</td>
<td>1) 10% - 100°C - 2) T (\downarrow) 50°C</td>
<td>4 days, little dissolved, no further dissol.</td>
<td><strong>—</strong></td>
</tr>
</tbody>
</table>

---

1 Whatman No.1 paper.
2 "—" = no yellowing; "+" = yellowing.
3 room environment conditions.
4 A5 = sample immersed in 5% aqueous alum solution (wt/v), accelerated aging conditions of 80°C and 50% rH.
5 K12.5 = sample sized with Kind and Knox gelatine 12.5% uptake (wt/wt).
6 C = conditioned to TAPPi standard conditions [30] (23°C and 50% rH).
7 K0.5 = sample sized with Kind and Knox gelatine, 0.5% uptake (wt/wt); accelerated aging conditions of 80°C and 50% rH.
8 sample dried in a desiccator over drierite for 7 days.
9 N0.5, N2, K0.5 and N2 = samples sized with Norland and Kind and Knox gelatines, 0.5% and 2% uptake (wt/wt), accelerated aging conditions of 80°C and 50% rH.
The trials reported in Table 3-2, carried out in order to optimise time and efficiency of dissolution allowed to conclude that:

- Thorough swelling in water was crucial and was more efficient when done at 40°C than at room temperature.
- One water exchange at 40°C was sufficient for unsized papers, but for sized papers the operation was more efficient if repeated twice. The water helped wash out part of the gelatine, which eased dissolution in the next step.
- One hour for the water exchange was enough; prolonging swelling beyond that was not necessary.
- Thorough “drying” by two consecutive exchanges in methanol and in DMAc resulted in faster and more efficient subsequent dissolution.
- Two DMAc exchanges of 45 minutes proved sufficient but for convenience of a one-day work, the second exchange was prolonged overnight.

3.2.2.2 Warm, ambient or low temperature dissolution

Water and solvent exchange activation allowed for better subsequent dissolution and turned out much less aggressive for the cellulose than high temperature activation/dissolution. The different trials reported in Table 3-2 allowed to conclude that:

- Complete dissolution could be achieved, as opposed to high temperature activation/dissolution.
- Complete dissolution was fast, as in most cases it took 48 hours and in some cases even less (samples No. 4a, 4b, 5a, 5b).
- No yellowing of the solutions occurred.
- Concentrations of LiCl in DMAc below 8% were not sufficient for complete dissolution.
- A concentration of 1% cellulose was suitable.
- After initial dissolution at room temperature for 15 to 16 hours, completion of the dissolution could be achieved at 4°C.

3.2.3 Conclusion of the activation and dissolution study

Polar medium swelling and solvent exchange activation although more labour intensive than the one-pot method at high temperature, allowed to achieve better, faster and more reproducible subsequent dissolution. Therefore this activation method was preferred for the following experiments over heat activation. Additionally, degradation of cellulose when submitted to high temperatures was a major concern. Also, the possibility of Maillard reactions (see Appendix 3-1) leading to browning of the samples where residual gelatine was present could not be ruled out when performing heat activation.
Activation with warm water (40°C) and exchange with solvents at ambient conditions was therefore less aggressive and allowed to carry out subsequent dissolution at ambient temperature for 15 hours (first) and completion at 4°C in about 30 additional hours. Ideal dissolution conditions were obtained with 8% LiCl/DMAc and 1% cellulose.

Table 3-2. Polar medium/solvent exchange activation and warm, ambient or cold temperature dissolution experiments.

<table>
<thead>
<tr>
<th>No.</th>
<th>sample type</th>
<th>activation phase</th>
<th>solvent preparation</th>
<th>dissolution phase</th>
<th>cellul conc</th>
<th>dissolution time and efficiency</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>W unsized unaged</td>
<td>1) 60 min H2O room T°</td>
<td>LiCl added to DMAc room T°</td>
<td>8 % LiCl/DMAc room T°</td>
<td>2 ) 30 min MeOH room T°</td>
<td>3 ) 1h DMAc room T°</td>
</tr>
<tr>
<td>2</td>
<td>W unsized unaged</td>
<td>1) 30 min H2O room T°</td>
<td>LiCl added to hot DMAc</td>
<td>6.7 % LiCl/DMAc room T°</td>
<td>2 ) 30 min MeOH room T°</td>
<td>2x</td>
</tr>
<tr>
<td>3</td>
<td>W unsized unaged</td>
<td>same as sample &quot;2&quot;</td>
<td>LiCl added to hot DMAc</td>
<td>6.7 % LiCl/DMAc at 40°C</td>
<td>0.83 % diss. incomplete after 9 days</td>
<td></td>
</tr>
<tr>
<td>4a</td>
<td>W unsized unaged</td>
<td>1) 60 min H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % diss. in less than 48 h both</td>
<td></td>
</tr>
<tr>
<td>4b</td>
<td>W unsized aged</td>
<td>1) 60 min H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % diss. in less than 48 h both</td>
<td></td>
</tr>
<tr>
<td>5a</td>
<td>W / K2 unaged</td>
<td>1) 30 min H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % diss. in less than 48 h both</td>
<td></td>
</tr>
<tr>
<td>5b</td>
<td>W / K0.5 aged</td>
<td>1) 30 min H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % diss. in less than 48 h both</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>W unsized unaged</td>
<td>1) 3 h H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % dissolution in 48 h</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>W unsized unaged</td>
<td>1) 16 h H2O 40°C</td>
<td>LiCl added to cooled DMAc</td>
<td>8 % LiCl/DMAc room T°</td>
<td>1 % dissolution in 48 h</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>W unsized unaged</td>
<td>1) 60 min H2O 40°C</td>
<td>LiCl added to dry DMAc</td>
<td>1 ) 8 % LiCl/DMAc room T°</td>
<td>2 ) placed at 4°C after 16 h</td>
<td>1 % dissolution in 48 h</td>
</tr>
</tbody>
</table>

1 DMAc is heated to 100-110°C for 10 minutes to drive off the moisture.
2 6.7% LiCl/DMAc was achieved by adding 5 mL 8%LiCl/DMAc and 1 mL of DMAc to the cellulose sample.
3 Accelerated aging conditions: 94 days at 80°C and 50% rH.
4 K2 = sample sized with Kind & Knox gelatine, 2% uptake (wt/wt).
5 K0.5 = sample sized with Kind & Knox gelatine, 0.5% uptake (wt/wt).
6 DMAc was dried with molecular sieve.
3.2.4 Final procedure for activation and dissolution

3.2.4.1 Final procedure for activation

This section summarises the final conditions chosen for activation and dissolution of cellulose in LiCl/DMAc according to the different trials carried out. Figure 3-1 shows a schematic representation of the process.

Defibrillated paper samples were swelled during one hour in 10 mL deionised water at 40°C (milli-Q, Millipore) twice consecutively.

Two consecutive exchanges of 45 minutes each with 8 mL methanol were carried out subsequently, followed by two consecutive exchanges with 8 mL anhydrous DMAc (prepared as described in section 3.2.1.1). The first DMAc exchange lasted for 45 minutes and the second was prolonged overnight.

After each exchange, the activation liquids were filtered under vacuum through 0.5 μm pore Millex LCR filters (Millipore) and the paper fibres were carefully removed with tweezers from the filter and placed back in the reacti-rial for the next liquid exchange. For each sample, the same filter was kept through the whole activation procedure in order to minimise fibre loss, to the exception of the heavily sized papers, which tended to clog the filters.

3.2.4.2 Final procedure for dissolution

The dissolution solvent was a solution of 8% LiCl/DMAc, and was prepared by adding the required amount of dry LiCl to dry warm DMAc (40°C) (see section 3.2.1.1) previously filtered through 0.5 μm pore, 25 mm diameter Millex LCR filters with a hydrophilised PTFE membrane. The solvent was freshly made every week, and if not used immediately, was stored under nitrogen at 4°C until use.

Dissolution took place under magnetic stirring after filtering out the second DMAc exchange, by adding 5 mL of the stock 8% LiCl/DMAc to the fibres.

The sample was stirred at room temperature for 24 hours and the reacti-rial, still capped, was placed at 4°C to complete dissolution. In all cases, the solutions were clear in a reasonable period of time with no visible residue or cloudiness, no gel formation, and no yellowing. The Whatman No.1 samples dissolved totally within 2 to 6 days, depending on the presence or absence of sizing (and on the gelatine content of the samples), and on the state of degradation (aging). Other paper types tested such as softwood chemical pulp paper dissolved totally in 30 minutes. It was noted that if the sample was not totally dissolved within 7 days, the dissolution did not progress further. In the stock sample solution, the concentration of cellulose was about 10 mg mL⁻¹, i.e. 1% (wt/v), assuming no fibre loss during the procedure.
Right after dissolution was achieved, the samples were diluted for size-exclusion chromatography with multiangle light scattering detection (SEC/MALS) experiments to 0.5% LiCl/DMAc with anhydrous DMAc, *i.e.* to a sample concentration of about 0.625 mg mL\(^{-1}\) (0.0625% wt/v). They were filtered through 0.5 μm Millex LCR filters before injection on the SEC columns. The remaining cellulose solutions were stored at 4°C under nitrogen.

![Diagram](image)

Figure 3-1. Diagram of the activation and dissolution procedure chosen for cellulose in LiCl/DMAc

### 3.3 Stability of cellulose/LiCl/DMAc solutions

Good stability of cellulose solutions in LiCl/DMAc over time is generally, but not unanimously, reported in the literature (see section 3.1.2). However, fewer mentions could be found of the stability of cellulose/LiCl/DMAc at low temperature [29]. In the present study it was important to investigate this stability under the experimental conditions chosen.

#### 3.3.1 Experimental

Two samples of Whatman paper No.1 unaged were dissolved in LiCl/DMAc according to the final procedure (section 3.2.4). After completing dissolution, one sample was left in 8% LiCl/DMAc (sample denoted C\(_t_0\) 8%LiCl 10m) and the second sample was diluted \(\frac{1}{4}\) to 2% LiCl/DMAc (sample denoted C\(_t_0\) 2%LiCl 10m). Both were left standing at 4°C for a period of 10 months (10m), after which they were diluted to 0.5% LiCl/DMAc for analysis by SEC/MALS. Each sample was run twice. The values of molar mass (\(M_r\)) obtained were averaged.
Three other samples of Whatman paper No.1 unaged were dissolved in the same manner and immediately diluted to 0.5% LiCl/DMAc to be analysed right after completion of the dissolution (Ct0 ref). Each sample was run in two to three replicates for a total of seven runs, and the values of $M_r$ obtained were again averaged.

At this stage, the method of SEC with MALS detection used has not been described but in order to alleviate the text of redundant descriptions, the reader is referred to Chapter 4. The theory of light scattering measurements is described in section 4.1.2.2 and the analytical method applied for cellulose characterisation is in section 4.2.3.

### 3.3.2 Results

Table 3-3 reports the average values of $M_0$, $M_w$ and $M_z$ of each sample. The molar mass distribution (MMD) profiles of Ct0 ref, Ct0 2%LiCl 10m and Ct0 8%LiCl 10m are represented in Figure 3-2 which shows overlaid differential molar mass graphs.

![Differential Molar Mass](image)

**Figure 3-2. Overlaid differential molar mass graphs of Ct0 ref, Ct0 2%LiCl 10m and Ct0 8%LiCl 10m.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_0 \times 10^5$ (g mol$^{-1}$)</th>
<th>$M_w \times 10^5$ (g mol$^{-1}$)</th>
<th>$M_z \times 10^5$ (g mol$^{-1}$)</th>
<th>PD</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ct0 ref (± RSD %)</td>
<td>3.96 (± 7.8%)</td>
<td>6.68 (± 2.0%)</td>
<td>10.09 (± 4.6%)</td>
<td>1.70 (± 7.1%)</td>
</tr>
<tr>
<td>Ct0 2%LiCl 10m</td>
<td>3.66</td>
<td>6.50</td>
<td>10.29</td>
<td>1.78</td>
</tr>
<tr>
<td>Ct0 8%LiCl 10m</td>
<td>3.51</td>
<td>6.68</td>
<td>10.80</td>
<td>1.91</td>
</tr>
</tbody>
</table>

Table 3-3. Average $M_r$ values and polydispersity (PD) of the cellulose samples in fresh and long-standing solutions.
The MMD profiles look almost identical, and only a 2.7% difference in the average $M_w$ was found between the three samples, which falls within the calculated relative standard deviation (RSD). Therefore we can conclude that no degradation of the cellulose seems to have occurred in 10 months at 4°C.

A slight difference between the samples was observed in the value of the polydispersity PD ($M_w/M_n$). PD was a little larger for the two 10-months old solutions, but while this slight increase falls within the RSD for $C_t0 2\% LiCl$ 10m compared to $C_t0$ ref, it falls just outside the RSD for $C_t0 8\% LiCl$ 10m. The broader MMD was due to a slightly lower $M_n$ and slightly higher $M_w$.

The somewhat higher proportion of low-$M_t$ and high-$M_t$ fractions in $C_t0 8\% LiCl$ 10m may be due to variations in the hydrogen bonding, and for the high-$M_t$ specifically, to association of the cellulose molecules upon standing at high concentration.

In conclusion, despite minute changes occurring over a period of 10 months, the solutions of cellulose/LiCl/DMAc exhibited remarkable stability at 4°C.

Chemicals and materials

Lithium chloride (LiCl), methanol and N,N-Dimethylacetamide (DMAc) were purchased from Acros Organics (Springfield, NJ, USA). Aluminium sodium silicate molecular sieve (0.4 nm effective pore size), Drierite and Whatman No.1 filter paper were obtained from Fisher Scientific (Springfield, NJ, USA). Millex LCR filters (0.5 μm, 25 mm diameter) and the vacuum filter holder, adapted fritted glass and 15 mL funnel were from Millipore (Bedford, MA, USA) and purchased through Fisher Scientific.

Instruments

Multiangle light scattering detector Dawn EOS and interferometric differential refractometer Optilab DSP were from Wyatt Technologies Corp. (Santa Barbara, CA, USA). The four-channel HPLC solvent degasser Degassit™ was obtained from Metachem Technologies Int. (Torrance, CA, USA) and HP 1100 isocratic pump G1310A was from Hewlett Packard, now Agilent Technologies (Palo Alto, CA, USA). Injector model 7725i was from Rheodyne L.P. (Cotati, CA, USA). The heating/stirring unit was from Pierce (Rockford, IL, USA).

References


