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The Effect of Water on Cellulose Solutions in DMAc/LiCl

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SUMMARY: The solution state of cellulose in the system *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) depends on various factors such as cellulose concentration, provenience (cotton, hardwood, softwood) and chemical history (pulping, pretreatment, bleaching) of cellulose, LiCl concentration, activation method, dissolution conditions (time, shaking), and water content. In particular the influencing of the latter has been intensively investigated in our present studies. Working in anhydrous conditions is not practicable for routine size exclusion chromatography (SEC) analysis. Especially in solutions diluted to SEC levels (0.9 wt% LiCl), an aggregation induced by water was observed. Depending on the time of dissolution and on the amount of water, changes in the solution state were observed. In some cases the amount of aggregates increases within a few minutes. This is reflected by a time-dependent increase in the scattering intensity and quantitatively proved by an increase in the aggregation peak in the calculated intensity distributions. With less soluble pulps, traces of water (lower than 0.01 M) can already suffice to induce and promote aggregation. To disturb a "good" stock solution, the concentration of water must be higher than 0.05 M. The aggregates formed correspond to the model of the fringed micelle.

Introduction

The solvent system *N,N*-dimethylacetamide/lithium chloride (DMAc/LiCl) is commonly used for the determination of the molecular weight distribution of cellulosic substrates by size exclusion chromatography (SEC)[1-4].

As the mixture is able to effect dissolution of cellulose within a certain concentration range of LiCl and cellulose, it is widely used for analytical purposes, *e.g.*, SEC measurements, and in organic synthesis, *e.g.*, for homogeneous derivatization reactions[5]. The published solubility limits of LiCl in "dry" DMAc range from 9 to even 13 wt%. The procedures proposed for drying DMAc and LiCl to obtain a water-free mixture are similarly inconsistent: different distillation protocols and various azeotropic distillation procedures with different water-trapping agents have been proposed to remove traces of water from DMAc. Drying at

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different temperatures, flame drying and even melting are suggested to remove residual water from LiCl. Therefore, also the literature values of the limiting solubility of defined celluloses disagree with each other. More serious, however, SEC data of celluloses dissolved in DMAc/LiCl, which were obtained by different groups under seemingly identical conditions, show strong deviations(6), which might, among other reasons(7), be also a result of differing water contents in the solvents used(8). Therefore the SEC-relevant solutions were investigated in this study with respect to water content and time stability. Dynamic light scattering (DLS) is a very fast and sensitive method to gain information about the solution state.

Since SEC in DMAc/LiCl is the most frequently used method for characterization of pulps in research and industry, our results have a bearing on scientific research as well as industrial purposes.

Experimental

Materials and cellulose dissolution: Chemicals were obtained from commercial sources and of the highest purity available. For dynamic light scattering (DLS) experiments, LiCl was dried 6 h at 200 °C *in vacuo*. Absolute DMAc as used in the experiments was obtained by refluxing commercial DMAc over CaH_2 for 2 h, followed by distillation onto CaH_2. In some cases, refluxing and distillation was preceded by stirring for two days at room temperature. The dry DMAc was stored over CaH_2 and handled according to standard protocols in organometallic synthesis. For the solubility measurements, defined amounts of distilled water were added to the dry DMAc with syringe to obtain H_2O concentrations in the range 0.1 - 10 M. A beech sulfite pulp (Lenzing AG, Austria) with a degree of polymerization of 1500 was used as cellulose sample (KZO_3 - ozone-bleached). For a better dissolution in DMAc/LiCl, the pulp was activated by solvent exchange (H_2O, acetone, DMAc). Completely dry samples were produced by freeze-drying the activated samples.

Light scattering measurements: Viscosities (Table 1) were measured with a SR-5000-NF stress rheometer (Rheometric Scientific, Munich, Germany). Refractive indices were determined with an Atago RX-5000 digital refractometer (Japan).

Table 1: Viscosities and refractive indices for the used solvents at 20 °C

[LiCl] in DMAc (wt%)	Viscosity (Pa s)	Refractive index
2.6	0.0034	1.4443
0.9	0.0013	1.4360

The DLS experiments were performed on a laboratory-built goniometer equipped with a 5-W argon ion laser (λ_0 = 514.5 nm, Spectra Physics, USA). The scattering cells (10-mm cylindrical cuvettes, Hellma, Germany) were immersed in a thermostatted index-matching bath (decalin). The scattering angle was set to 90°. The q-dependence of the correlation time was proved for one example.

Detection was performed *via* a single-mode fiber (OZ from GMP, Zurich, Switzerland) with a grin lens coupled to a Thorn-Emi photomultiplier (type B2FBK/RFI), the output of which was analyzed by an ALV-5000 digital multiple-τ correlator (ALV, Langen, Germany) with 256 quasi-exponentially spaced channels9). In the case of depolarized (VH) measurements, the laser power was set to 1 W. For depolarized dynamic light scattering (DDLS) measurements (VH), the primary beam and the scattered light passed through Glan-Thomson polarizers (Halle, Berlin, Germany) with an extinction coefficient better than 10^{-6}. The first polarizer guaranteed that only vertically polarized light meets the sample; the orientation of the second polarizer (analyzer) was carefully adjusted to crossed position with minimum scattering intensity.

Sample preparation: All measurements were performed at 20 °C. The activated pulp samples were dissolved and filtered through an 0.45-µm PTFE filter prior to measurement. For dissolution of the pulp, a stock solution with 8 wt% LiCl in carefully dried DMAc was prepared. Another stock solution, containing 9 wt% LiCl in commercially available DMAc with 0.03 wt% of water, was prepared by the SCAN-CM 15:99 method. The latter stock solution corresponded to traditionally used methods, and was used to obtain results comparable with those in common practice6). For DLS measurements, the stock solutions were diluted with DMAc to a LiCl content of 2.6 wt% (injection concentration in SEC) and 0.9 wt% (detector concentration in SEC), respectively. The DMAc used for dilution had the same water concentration as that used for the stock solutions.

Theoretical background

Dynamic light scattering (DLS) was employed to examine the effect of water in the solvent system DMAc/LiCl on the solution state of cellulose. This topic is of special interest with regard to SEC measurements that use this solvent system. The possible occurrence of large particles or solvent aggregates in DMAc/LiCl/water was investigated, and the influence of trace amounts of water on the particle size distribution of dissolved cellulose was studied.

The quantity measured in DLS is the angular-dependent auto-correlation function $g_2(q,t)$ of the coherently scattered light; $g_2(q,t)$ is related to the autocorrelation function of the electric field $g_1(q,t)$ in a homodyne experiment by Eq. (1):

$$g_2(q,t)=A\left(1+B\left|g_1(q,t)\right|^2\right) \tag{1}$$

A is the base line and B is the coherence factor. For a polydisperse system and at a constant scattering angle, $g_1(t)$ may be expressed as superposition of the contributions of all particle sizes present to the field correlation function:

$$g_1(t)=\int G(\Gamma_i)\exp(-\Gamma_i t)\,\mathrm{d}\Gamma \tag{2}$$

Equation (2) represents the Laplace transformation of the probability density function $G(\Gamma)$ of the translational diffusion coefficients D_i. With $\Gamma_i = q^2 D_i$, the diffusion coefficient D can be related to the hydrodynamic radius R_H with the Stokes-Einstein relation $D = k_B T / 6\pi\eta_o R_H$, where η_o is the dynamic viscosity of the solvent, T the temperature, and k_B Boltzmann's constant. By inverse Laplace transformation of Eq. (2), the intensity-weighted size distribution of the hydrodynamic radii of the particles present in the solution can be estimated[10]. This graphic representation accentuates larger particle populations by the intensity - radius relationship ($I \propto R_H^6$ for globular particles).

The DLS method is an appropriate tool to gain qualitative information about the distribution of the sizes of particles in dilute solutions on the basis of measurement of only one sample solution. Absolute analysis of concentrated solutions is more complicated; however, solutions of equal concentrations (i.e., of equal viscosities) can be compared with each other. As a result, apparent hydrodynamic radii of the particles are obtained.

Results and discussion

Dilution of the stock solutions to 2.6 wt% and 0.9 wt% LiCl and adjustment of the water content was performed as described in the Experimental Section. Two time frames are important for SEC measurements in the system cellulose/DMAc/LiCl: 1 h - the maximum elution time for the SEC solutions (0.9 wt% LiCl) and 5 days - the maximum storage time for the injected solutions (2.6 wt% LiCl).

The influence of water and aggregation time on the size distribution of cellulose particles in solutions of 2.6 wt% LiCl as a function of the apparent radius is shown in Fig. 1. One hour after diluting the stock solution to SEC injection concentration (2.6 wt% LiCl), no significant differences between completely dry solutions (filled triangles) and solutions 0.05 M in water (filled circle) were detected. However, while the dry solution (empty triangles) remained nearly unaltered over longer periods of time (5 days in this measurement), the moist solution (empty circles) showed pronounced aggregation to larger particles.

Also for cellulose solutions at the SEC detection concentration (0.9 wt% LiCl), the solution in dry DMAc (filled triangles) was stable over time, whereas the solution in moist DMAc showed a distinct tendency to aggregation (fresh: filled circle, 1 day: half-filled circle, 5 days: empty circle). The aggregation process was largely complete after one day. At longer times of standing, the aggregates grew even larger, as demonstrated by the peak broadening at high R_H in Fig. 2. The two maxima around 15 and 40 nm should be interpreted as one polydisperse particle population.

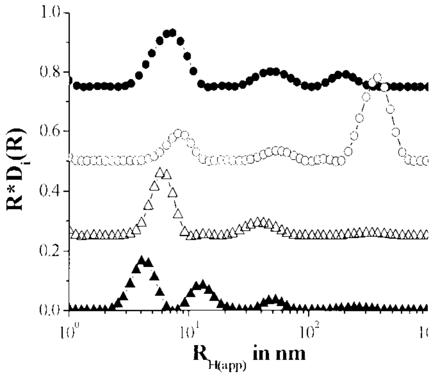


Fig. 1: DLS intensity-weighted size distribution of dissolved cellulose as a function of the apparent radius: the influence of water on the size and number of cellulose particles (2.6 wt% LiCl and 0.325 wt% pulp).

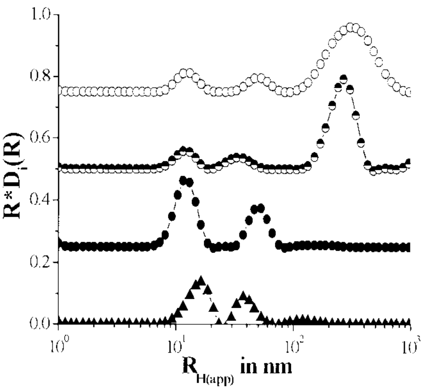
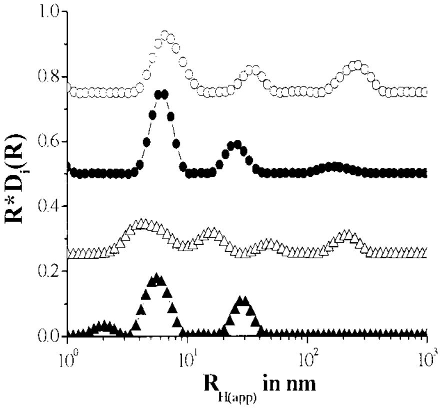


Fig. 2: DLS intensity-weighted size distribution of dissolved cellulose as a function of the apparent radius: the influence of water on the size and number of cellulose particles (0.9 wt% LiCl and 0.028 wt% pulp).

(8 wt% LiCl stock solution with 1 wt% of pulp in dry DMAc; scattering angle 90°.)

Figure 3 shows the results for solutions with 2.6 wt% LiCl, prepared from the 9 wt% LiCl solution in commercial DMAc; they are less unambiguous than those for solutions prepared from dried DMAc stock solutions. Nevertheless, the instability of the solutions can clearly be seen. Not only prolonged times of storage, but also additional water will decrease the quality of the solution state, and lead to the formation of larger aggregates. However, storage time, LiCl content, water content, and cellulose content are important factors for the stability of the solutions.

Solutions with 0.9 wt% LiCl were prepared by diluting the stock solutions with 9 wt% LiCl (commercial DMAc). While the solutions without additional water (regular) showed no signs of aggregation, already the freshly prepared solution with 0.05 M did so (cf. peaks around R_H of 100-200 nm; Fig. 4). The very fast aggregation process was already complete during the dilution of the stock solution, so that a time dependence of the aggregation was not observed. By filtration through 0.45-μm filters, the cellulose aggregates formed in solution are either permanently destroyed or completely retained. Re-aggregation after filtration was not observed, which favours the interpretation of a complete removal of larger particles over a temporary destruction. SEC measurements of the unfiltered solution showed an increased high-molecular-weight portion, while experiments with the unfiltered solution gave a decreased recovery rate.



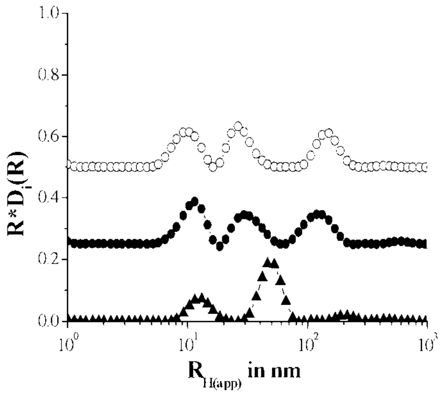


Fig. 3: DLS intensity-weighted size distribution of dissolved cellulose as a function of the apparent radius: the influence of water on the size and number of cellulose particles (2.6 wt% LiCl and 0.346 wt% pulp).

Fig. 4: DLS intensity-weighted size distribution of dissolved cellulose as a function of the apparent radius: the influence of water on the size and number of cellulose particles (0.9 wt% LiCl and 0.028 wt% pulp) .

● 0.05 M in water (fresh), ○ 0.05 M in water (5 days), △ regular (5 days), ▲ regular (fresh).
(9 wt% LiCl stock solution with 1 wt% of pulp in commercial DMAc; scattering angle 90°.)

Influence of dissolution time, an example of what can happen under unfavorable conditions: The stock solutions used before were produced using a laboratory shaker overnight. To demonstrate the influence of the stock solution quality on the SEC measurements, the dissolution time was reduced to 2 h. After this time, the solutions were optically clear. Figure 5 shows the scattering intensity at 90° as a function of time in the SEC solutions with 0.9 wt% LiCl. A few minutes after dissolution, a steady rise in intensity was already observed for solutions containing water. In contrast, the measurements of the dry solution do not show any changes in intensity with time.

The quality of the stock solution was profoundly disturbed by water. However, it was not possible to reproduce the aggregation times. In some cases, aggregation starts after 3 h or even later. The system is obviously rather complex, and the aggregation behavior is dependent on many factors.

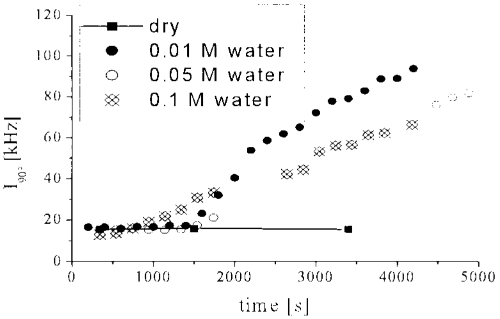


Fig. 5: Time dependence of the scattering intensity of SEC cellulose solutions in DMAc with 0.9 wt% LiCl, 0.028 wt% KZO_3 (freeze-dried) and with various water contents; scattering angle 90°.

Nevertheless, the results represent the solution conditions quite well. As an example, the solution with 0.05 M water content was chosen. Approximately 25 min after dissolution to SEC level, a displacement of the correlation function $g_2(t)$ to longer times occurred (Fig. 6). The scattering intensity of such highly dilute solutions is very low resulting in a low intercept. This intercept increases with increasing aggregation. This effect has no essential influence on the principles of the analysis, only a slight shift in the size distribution by factor 2 is possible. Twenty-five minutes after dilution, a second population of particles around 100 nm is formed (Fig. 7).

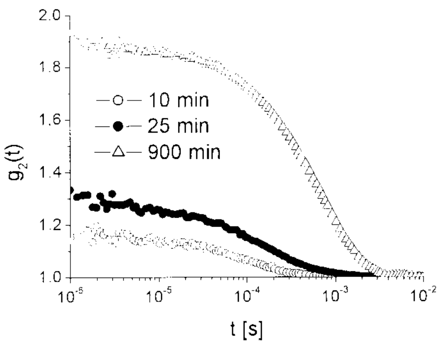


Fig. 6: Time dependence of the intensity autocorrelation function for cellulose (0.028 wt%) in 0.9 wt% DMAc/LiCl with 0.05 M water.

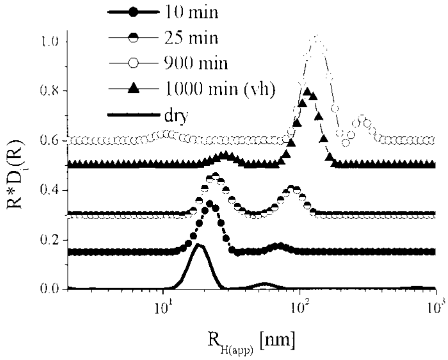


Fig. 7: Time dependence of the intensity-weighted size distribution of dissolved cellulose as a function of the apparent radius (for details, see Fig. 6).

Almost one day later, the radius of the second fraction showed a distribution from 80 to 200 nm. By depolarized dynamic light scattering (DDLS) measurements of the same solution with crossed polarizers, a correlation function was measured which indicated the existence of optically anisotropic particles. The apparent radii of particles range between 70 and 180 nm. Assuming the model of the fringed micelles (a relatively hard and well oriented swollen core with flexible fringes like a hedgehog with soft spines) for the cellulose particles, the DDLS measurements showed the core and the DLS measurements the whole particle. Quantitative estimation of the dimensions failed due to the instability of the system over long times, but the result is yet another indication of the formation and presence of fringed micelles in cellulose solutions[11,12].

Conclusions

An insufficiently long dissolution time and a water content of ≥ 0.01 M can result in cellulose aggregation in the SEC solutions (0.9 wt%) during the regular time window of SEC measurements. All measurements in this study were performed with a standard sample, for which normally no aggregation is observed. Nevertheless, aggregation phenomena were induced. To disturb a "good" stock solution, i.e., well soluble pulps, the concentration of water must be higher than 0.05 M. For pulps with less than optimum solubility, already traces of water (lower than 0.01 M) can suffice to induce and promote aggregation.

Long storage times of the injected solution sometimes result in lower retrieval rates in SEC. Aggregation in the DMAc/LiCl /cellulose system is a very complex process, the influence of water is one factor and should be regarded if SEC problems occur. The following general rules should be considered:

(1) the water content of the used DMAc should be below 0.9 wt%;
(2) sufficient time of dissolution (overnight) is necessary;
(3) freeze-drying of cellulose is not absolutely necessary, but it has no negative effect;
(4) the higher the LiCl amount, the longer the possible storage time before aggregation sets in.

If aggregation problems occur in SEC analysis, reduction of the storage time of the solutions with injection concentration (if possible), or reduction of the cellulose content (probably resulting in lower resolution) are worth considering.

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