Polarized and depolarized light scattering on solutions of cellulose in *N,N*-dimethylacetamide / lithium chloride

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SUMMARY: In the present work, the common solvent system N,N-dimethylacetamide (DMAc)/ LiCl was studied which is used, *e.g.*, for the determination of the molecular weight distribution of cellulosic substrates by size exclusion chromatography (SEC).
Results of dynamic light scattering (DLS) experiments in the concentration range employed in SEC are presented, and discussed in terms of the solution state. A molecular dispersion of cellulose was found. The influence of the salt concentration on the solution state was shown.
In solutions of higher concentrations (> 2% pulp, 6% LiCl) anisotropic particles were found which were further investigated by depolarized dynamic light scattering (DDLS). The particle size was determined by estimating the translational and rotational part of diffusion. These particles can be described as oblate rotational ellipsoids. The axial ratio ρ was found to be 5/4. The half axis *a* was found to be 425 nm and the half axis *b* 530 nm.

Introduction

In polymer chemistry, size exclusion chromatography (SEC) is used to characterize various kinds of macromolecules by means of their molecular weight distribution. Since unsubstituted cellulose is soluble only in few solvent systems, cellulose derivatives are usually synthesized which are soluble in a common solvent. However, degradation of the cellulose molecules during derivatization can occur and distort the results. True cellulose solvents are often multi-component systems with special properties.

The dissolution of cellulose in a mixture of DMAc and LiCl has been known since 1979[1)]. Aggregates or single chains could be found dependent on the salt content, on the cellulose concentration, and on the pulp properties. DMAc itself merely causes intercrystalline swelling. The optimal concentration of LiCl is reported to range from 5 to 9 wt%[2)]. Before dissolution, the activation of cellulose is required. Later it was found that LiCl/DMAc is a suitable eluent for the SEC-analysis of cellulose. For that purpose, DMAc with 0.9 wt% LiCl is used. The injected LiCl concentration can be higher and is normally ranging from 2 to 3 wt% LiCl. The sample molecules are separated according to differences in their effective

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molecular size in solution. LiCl can penetrate all the pores of the column material, and is thus retained on the column to elute last because of its small size. The cellulose molecules penetrate the pore system dependent on their effective molecular size: larger particles elute earlier, smaller later[3].

It was shown that large particles were found in solutions with 1 wt% cellulose and 9 wt% LiCl[4]. After the dilution to one tenth of the LiCl concentration (SEC level with 0.1 wt% cellulose and 0.9 wt% LiCl) most of the large particles were dissolved - the associates were disintegrated. Cellulose is a semi-crystalline polymer consisting of crystalline and amorphous regions. If the solvent is not able to crack the hydrogen bonds of the solid cellulose completely, larger particles could be found in the solution. In the present study we prove the hypothesis that these particles are highly swollen parts of the former crystalline regions of the cellulose. Therefore solutions of a micro-crystalline sample (Avicel) with a large cellulose to LiCl content ratio were investigated. Solutions with a large amount of cellulose are very viscous depending on their degree of polymerization (DP) and on the LiCl content. Avicel (low DP) in a LiCl concentration of 6 wt% was used to get solutions with a large cellulose to LiCl content ratio with a relatively low viscosity.

Experimental

Materials: The cellulose sample used was the micro crystalline cellulose Avicel from Fluka (Vienna, Austria). The DP was determined by intrinsic viscosity measurements in CUEN (copper ethylendiamine complex)[5] was found to be 285. LiCl (p. a., Merck, Darmstadt, Germany) was dried at 200°C. DMAc (HPLC grade, water content < 0.03 %, Fluka, Vienna, Austria) was used without further purification.

Cellulose activation and dissolution: Water swelling followed by a solvent exchange was used for the cellulose activation. Small pieces of pulp were dispersed in deionized water with a lab mixer. The water was then drained, the swollen cellulose was washed twice with acetone and dried through filtration under reduced pressure. This was followed by a solvent exchange with DMAc. Aliquotes of the activated pulp were added to the desired DMAc/LiCl solution (with 9 wt% or 6 wt% LiCl). By using a shaking device the dissolution process occurs overnight at room temperature. This method is described in detail in[6]. The stock solutions were carefully diluted with pure DMAc to prepare the solutions for the scattering experiments. The solutions were pressed through 0.2 μm or 0.45 μm membrane filters into

dust-free sample cells. At high LiCl concentrations (>6%) and high pulp concentrations (>1%) a filtration was not possible.

Light scattering measurements: The refractive indices were estimated with an Atago RX-5000 digital refractometer (Japan). The viscosities were measured with a SR-5000-NF stress rheometer from Rheometric Scientific (Munich, Germany). The values are given in Table 1.

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

[LiCl] in DMAc / %	Viscosity / Pas	Refractive index
9	0.01	1.4607
6	0.0064	1.4522
1	0.0014	1.4365

For the solution of 3.5 wt% Avicel in DMAc with 6% LiCl the viscosity was estimated to 0.49 Pas.

All measurements were done at 20°C. The experiments were performed on a laboratory-built goniometer equipped with a 5W Argon ion laser (λ = 514.5 nm, Spectra Physics, Germany). The scattering cells (10 mm cylindrical cuvettes, Hellma, Germany) were immersed in a thermostated index matching bath (decaline). The typical laser power for the polarized (VV) DLS measurements was 200 mW and the scattering angle was set to 90°. In the case of depolarized (VH) measurements the laser power was set to 1 W and the scattering angle was varied. For DDLS measurements (VH) the primary beam and the scattered light passed through Glan-Thomson (Halle, Berlin, Germany) polarizers 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. Detection was performed via a single mode fiber with 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 channels.[7)]

Results and Discussion

Dilution to SEC level (0.9 wt% LiCl):

In the present study the SEC stock solutions (9 wt% LiCl or 6 wt% LiCl) with 1 wt% Avicel, were diluted in the same way with pure DMAc up to the tenth LiCl concentration of about 0.9 wt% with 0.1 wt% and 0.15 wt% cellulose, respectively. The intensity distributions were calculated by an inverse Laplace transformation with the program ORT[8] and show two particle populations for the higher Avicel concentration (Fig. 1). Measurements[4] on solutions with a cellulose sample of higher DP with 0.2 wt% cellulose and 0.9 wt% LiCl (diluted from 2 wt% cellulose and 9 wt% LiCl) did not show more than one particle population. However, the LiCl concentration of about 6 wt% was not sufficient to guarantee a molecularly dispersed solution after dilution to the SEC level under the described conditions.

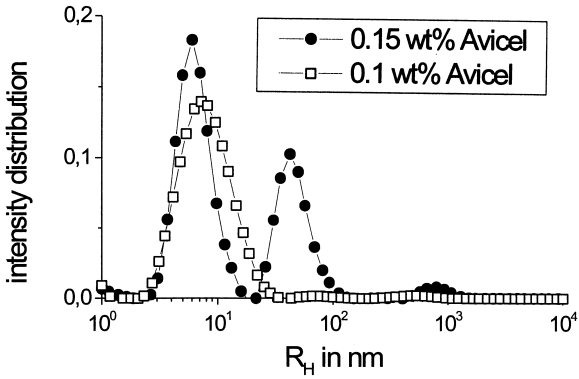

Fig. 1: Intensity distribution for the SEC solutions with 0.1 wt% Avicel (diluted from 1 wt% Avicel and 9 wt% LiCl) and 0.15 wt% Avicel (diluted from 1 wt% Avicel and 6 wt% LiCl) in DMAc with 0.9 wt% LiCl

Concentrated solutions in LiCl-DMAc: Avicel was dissolved in DMAc with 6 wt% LiCl with a cellulose content between 1 wt% and 3.5 wt% with water swelling activation. The correlation function of the solution with 1 wt% Avicel showed a small content of large particles (Fig. 2a, area for t between 0.001 and 0.1 s). Size and amount of large associates or aggregates increased dependent on the cellulose content. At higher concentrations of cellulose a depolarized intensity correlation function could be detected. This indicates the existence of optically anisotropic particles (see Appendix). For a detailed study the solution of 3.5 wt%

Avicel in DMAc with 6wt% LiCl was choosen. From the angular dependence of the reciprocal correlation time the translational diffusion coefficient can be calculated to $6.3 \cdot 10^{-12}$ $cm^2 \cdot s^{-1}$ and the rotational diffusion coefficient to $8.9 \cdot 10^{-3}$ s^{-1}.

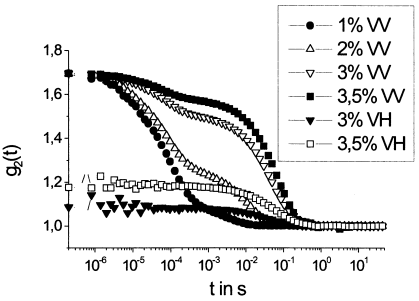

Fig. 2a: Intensity autocorrelation function for various amounts of the Avicel sample (activated with water) in DMAc with 6 wt% LiCl

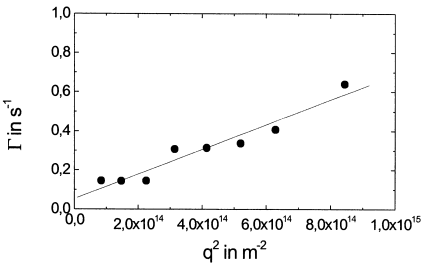

Fig. 2b: q^2-dependency of the reciprocal relaxation time for 3.5 wt% Avicel in DMAc with 6 wt% LiCl with VH-geometry

The anisotropic particles can be described as oblate rotational ellipsoids. The axial ratio ρ was found to be 5/4, the half axis *a* (symmetry axis*)* to be 425 nm and the half axis *b* to be 530 nm (mean values). The proposed structure of these particles is shown in Fig. 3. Cellulose often forms so called "fringed micelles" in solution[9)]. Those fringed micelles are highly swollen parts of the former crystalline regions of the cellulose. The solvent DMAc with 6 wt% LiCl is not able to crack the strong hydrogen bonds in the cellulose completely.

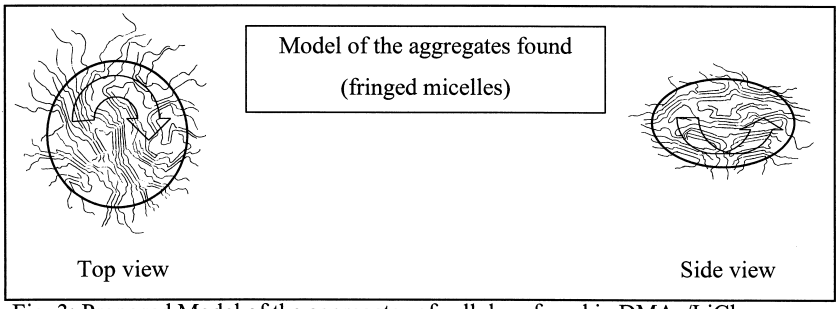

Fig. 3: Proposed Model of the aggregates of cellulose found in DMAc/LiCl

Conclusions

The higher the LiCl concentration in the stock solution, the smaller the particles in the solutions diluted to 0.9 wt% LiCl (SEC level). After dilution with pure DMAc from 9% to 0.9% LiCl the large particles were disintegrated. This usually results in a molecularly dispersed solution. With 6 wt% LiCl and 1 wt% cellulose the LiCl amount is not sufficient to form a molecularly dispersed solution after the dilution to the SEC level.

The existence of large anisotropic particles was found in concentrated solutions with 6 wt% LiCl. These particles can be described as highly swollen fringed micelles and are probably parts of the former crystalline regions of the cellulose.

Appendix

Anisotropic particles - homogeneous elongated particles or inhomogeneous globular particles - can be analyzed by DDLS measurements if an autocorrelation function is detected in the depolarized experiment.

The plot of the reciprocal correlation time Γ versus the square of the scattering vector q (Fig. 2b) should result in a straight line with the intercept zero for VV experiments. In this case only the translational diffusion coefficient (D_T) can be determined. Otherwise, (VH), also a rotational part of diffusion can be measured. The intersection of the ordinate axes gives the rotational diffusion coefficient θ_{ROT}:

$$\Gamma = D_T q^2 + 1/\tau_0 \text{ with } 1/\tau_0 = 6\theta_{ROT} \tag{1}$$

In 1934 Perrin[10] proposed a model for molecular rotational movements of ellipsoids. The following is needed for the mathematical description[11]:

$$\theta_{ROT} = \frac{3k_B T}{16\pi\eta a^3}\left\{\frac{(2-\rho)G(\rho)-1}{(1-\rho^2)}\right\} \tag{2}$$

for elongate ellipsoids with the axial ratio ρ=b/a where a is the axis of rotation and η the shear viscosity of the solution. $G(\rho)$ is a function of the axial ratio. Two different cases have to be considered:

1. prolate ellipsoid (ρ<1) with

$$G(\rho) = (1-\rho^2)^{-1/2} \ln\left\{\frac{1+(1-\rho^2)^{1/2}}{\rho}\right\} \tag{3}$$

2. oblate ellipsoid (ρ>1) with

$$G(\rho) = (\rho^2 - 1)^{1/2}\,\rho \arctan\left\{(\rho^2 - 1)^{1/2}\right\} \tag{4}$$

The translational diffusion coefficient for ellipsoids is defined by:

$$D_{Trans} = \frac{k_B T}{6\pi\eta a} G(\rho) \tag{5}$$

A function F(ρ) results from (2) and (5):

$$F(\rho) = \frac{\theta_{ROT}}{D_{Trans}^3} \cdot \frac{(k_B T)^2}{40{,}5(\pi\eta)^2} = \left\{\frac{(2-\rho)G(\rho) - 1}{G^3(\rho)(1-\rho^2)}\right\} \tag{6}$$

All values on the left side of F(ρ) are known, all values on the right side are unknown. The function F(ρ) can be calculated for various values of ρ with (3) and (4). The equation has a unique solution, i. e. it holds only for one value of ρ.

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