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Solutions of cellulose in *N*,*N*-dimethylacetamide/lithium chloride studied by light scattering methods

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Abstract

The solution state of cellulose dissolved in the solvent system *N*,*N*-dimethylacetamide/lithium chloride (DMAc/LiCl) has been investigated by static and dynamic light scattering. Emphasis has been placed on the influence of the dissolution conditions, such as type of cellulose activation and concentrations of cellulose or LiCl, respectively. Dependent on these conditions, a molecular dispersion of cellulose molecules have been found in diluted solutions. Solutions with a high cellulose concentration (>2 wt%) and a low LiCl concentration (e.g. 6 wt%) have shown a noticeable amount of optically anisotropic particles, the properties of which have been determined by depolarized dynamic light scattering experiments. Dilution of such cellulose solutions did not result in a complete disintegration of these supermolecular structures.

Keywords: Cellulose; Solution state; Light scattering

1. Introduction

In polymer chemistry, size exclusion chromatography (SEC) is used to characterize synthetic and natural polymers by means of their molecular weight distribution (MWD). As cellulose, the most abundant natural polymer, is not soluble in common solvents due to its system of strong inter- and intramolecular hydrogen bonds, usually cellulose derivatives are synthesized, which, in turn, are soluble in a common solvent. However, degradation can occur upon derivatization which might distort the SEC results. Mixtures which are capable of directly dissolving cellulose are in most cases multi-component systems with special properties: they must be able to destroy the hydrogen bond system of the cellulose without any derivatization or degradation of the material.

Mixtures of *N*,*N*-dimethylacetamide (DMAc) and lithium chloride are well-known solvent systems for cellulose [1]. DMAc itself merely causes intercrystalline swelling of cellulose. However, DMAc containing LiCl is able to dissolve cellulose, if the cellulose was 'activated' before. This activation procedure causes a partial breaking of the hydrogen bonds in cellulose, resulting in a better accessibility of the sample.

The optimum concentration of LiCl in the solvent mixture is reported to range between 5 and 9 wt% [2]. Depending on the conditions of the dissolution process, e.g. salt and cellulose concentration as well as pulp provenience, different supermolecular structures of the cellulose molecules (smaller and larger aggregates, single molecules, and fringed micelles) have been found in solution [3–5]. Terbojevich et al. [3] found stable aggregates consisting of seven cellulose molecules when they used 5 wt% of LiCl. Solutions free of aggregates were only obtained with regenerated cellulose or at a minimum LiCl content of 7 wt% with cellulose concentrations up to 1 wt%. However, at moderate cellulose concentrations (<10 g/l) aggregates and associates occurred. An increasing mass of the dissolved cellulose particles in LiCl/DMAc with increasing LiCl content was reported by Fellmann [5].

Later, LiCl/DMAc was found to be a suitable eluent for the SEC-analysis of cellulose [6–10]. A LiCl concentration of 0.9 wt%, which is normally employed, has two advantages. First, the viscosity of the eluent is low (~1 mPas), in contrast to higher LiCl concentrations. Second, after dilution of the stock solution down to 0.9 wt% LiCl, a

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Table 1
Provenience and degree of polymerization (DP) of the cellulose samples investigated

Pulp	Provenience	DP
Avicel	Micro-crystalline cellulose (Fluka, Austria)	285
Buckeye V5	Soft wood, prehydrolysis-kraft (Buckeye, USA)	1360
KZO3	Beech magnesium bisulfite pulp (Lenzing AG, Austria)	1500
n-viscose	Regular viscose (Lenzing AG, Austria)	470

molecularly disperse solution state is obtained. The dilution procedure is necessary since cellulose is initially insoluble in DMAc with less than 5 wt% LiCl. Therefore, it is useful to prepare stock solutions with 9 wt% LiCl, which are then diluted to a LiCl amount of 0.9 wt% for SEC measurements.

In the SEC-column the cellulose molecules are separated according to their hydrodynamic volume, this is, their effective size in solution. Larger molecules — and of course aggregates — elute more quickly than smaller molecules. The presence of a solution of individual cellulose molecules, free of any supermolecular or gel-like structures, is an absolute prerequisite for correct SEC measurements. This problem was not sufficiently covered in the literature.

The aim of our study was to investigate under which conditions molecularly disperse solutions of cellulose in DMAc with 0.9 wt% LiCl (at SEC level) can be prepared. Four concentrations of LiCl are important for SEC in the system DMAc/LiCl/Cellulose:

1. Standard stock solutions prepared with 9 wt% LiCl.
2. Stock solutions prepared with 6 wt% LiCl (near the lower limiting solubility).
3. Diluted inject solutions with 2.6 wt% LiCl.
4. Diluted SEC solutions with 0.9 wt% LiCl.

The investigations were based on static (SLS), dynamic (DLS), and depolarized dynamic light scattering (DDLS) experiments.

2. Experimental

2.1. Materials

The different celluloses used are listed in Table 1. The degree of polymerization (DP) of the samples was determined by intrinsic viscosity measurements in cuen (copper ethylendiamine complex) [11]. LiCl (p.a. Merck, Darmstadt, Germany) was dried at 200°C. DMAc (HPLC grade, water content <0.03%, Promochem, YMC-Europe, Schernbeck, Germany) was used without further purification.

2.1.1. Cellulose activation and dissolution

Two methods were used for the cellulose activation: water swelling followed by a solvent exchange and the activation with liquid ammonia. In the case of swelling in water, small pieces of pulp were dispersed in deionized water using 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. The respective DMAc/LiCl solution, containing 9 or 6 wt% LiCl, was added to aliquots of the activated pulp. By using a shaker, the dissolution occurred overnight at room temperature. This method is described in detail in Ref. [9].

Cellulose dissolution after activation by liquid ammonia was carried out as described previously [12]. A definite amount of fibrous cellulose was placed in a three-neck flask under inert gas (argon). Ammonia was condensed into the flask until the sample was completely immersed. After 1 h the ammonia was allowed to evaporate slowly. When the sample was still just covered by liquid ammonia, a small definite amount of DMAc (2–4 ml) was added. It is important that the sample never becomes dry during this process. The remaining ammonia was completely evaporated under moderate vacuum. A separately prepared solution consisting of the required amounts of DMAc and LiCl was then added to the activated cellulose under rigorous stirring. The dissolution occurred within a few minutes.

Stock solutions, prepared in this manner, were carefully diluted with DMAc/LiCl or pure DMAc to obtain the diluted solutions. Aliquots of both stock solutions and diluted solutions were used to prepare the concentration series for the SLS experiments. Prior to the light scattering measurements all cellulose solutions were filtered through 0.2 or 0.45 μm PTFE-membrane filters directly into dust-free sample cells. At high LiCl concentrations (>6 wt% LiCl) and high cellulose concentrations (>1 wt% cellulose) a filtration was not possible.

2.1.2. Light scattering measurements

Refractive indices were determined with an Atago RX-5000 digital refractometer (Japan). Viscosities were measured with a SR-5000-NF stress rheometer (Rheometric Scientific, Munich, Germany). Refractive index increments were taken from the literature, measured with an RI detector (Erma Inc., ERC-7511), or interpolated from both literature values and measurements. As membranes for dialyse will be swollen or dissolved by LiCl–DMAc, the values were not determined from dialyzed solutions. Data are given in Table 2. For the solution of 3.5 wt% Avicel in DMAc with 6 wt% LiCl, the viscosity was estimated to 0.49 Pas.

A SLS-2 goniometer (SLS Systemtechnik, Haussen, Germany) equipped with a 5 mW He–Ne-laser ($\lambda_0 = 632.8$ nm) was used for SLS measurements. The DLS experiments were performed on a laboratory-built goniometer equipped with a 5 W Argon ion laser ($\lambda_0 = 514.5$ nm, Spectra Physics, USA). The scattering cells (10 mm cylindrical cuvettes, Hellma, Germany) were immersed in a thermostated index matching bath (decaline).

Table 2
Viscosities, refractive indices and refractive index increment for the solvents (20°C)

(LiCl) in DMAc (wt%)	Viscosity (Pas)	Refractive index (n_o)	(dn/dc) (cm^3/g)
9	0.01	1.4607	0.055 [4]
6	0.0064	1.4522	0.08 [3]
2.6	0.0034	1.4443	0.11
1	0.0014	1.4365	0.12 [13]

The typical laser power for polarized (VV) DLS measurements was 200 mW, the scattering angle was set to 90°. The q-dependence of the correlation time was proved for one example. In the case of depolarized (VH) measurements the laser power was set to 1 W. For DDLS measurements the primary beam and the scattered light passed through Glan-Thomson polarizers (Glan Thomson, 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. Detection was performed via a single mode fiber (OZ from GMP, Zürich, Switzerland) 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 [14]. All measurements were performed at 20°C.

3. Results and discussion

3.1. Static light scattering measurements

Two cellulose samples — Avicel and Buckeye V5 with DPs of 285 and 1360, respectively — were chosen for the investigation of the solution state by means of SLS. The samples were activated by the water swelling method. Two types of solutions, differing in their LiCl content, were measured: stock solutions containing 9 or 6 wt% LiCl and the diluted solutions, which were obtained by dilution of stock solutions with pure DMAc resulting in a LiCl content of 2.6 or 1 wt%. The data obtained were evaluated by Zimm [15] or Guinier–Zimm [16] plots, using the method with the best data fit (see Appendix A). As an example, the Guinier–Zimm plot for the sample Buckeye V5 in DMAc with 9 wt% LiCl is shown in Fig. 1. The results are summarized in Table 3.

Buckeye V5. For the stock solutions of Buckeye V5 weight-average molecular weights M_w were obtained (9.09×10^5 and 1.23×10^6 g/mol) which were 4–6 times larger than the values determined viscosimetrically in cuen ($M_{cuen} = 162$ g/mol DP). Also the radii of gyration R_G were very large (170 and 203 nm). According to Terbojevich et al. [3] both facts could be attributed to the presence of a certain fraction of supermolecular structures (large particles, aggregates, or associates) in the stock solutions. This was also indicated by the non-linear angular dependence of the scattering curves $\ln (Kc/R_\theta)_{q,c=\text{const}}$ (see Fig. 1). This curvature could be caused by two different effects: first, the cellulose sample might have a very broad MWD; or second, at least two populations of cellulose particles of different size exist in solution. It was evident from the behaviour of both — stock and diluted — solutions that the application of 9 wt% LiCl instead of 6 wt% LiCl in the

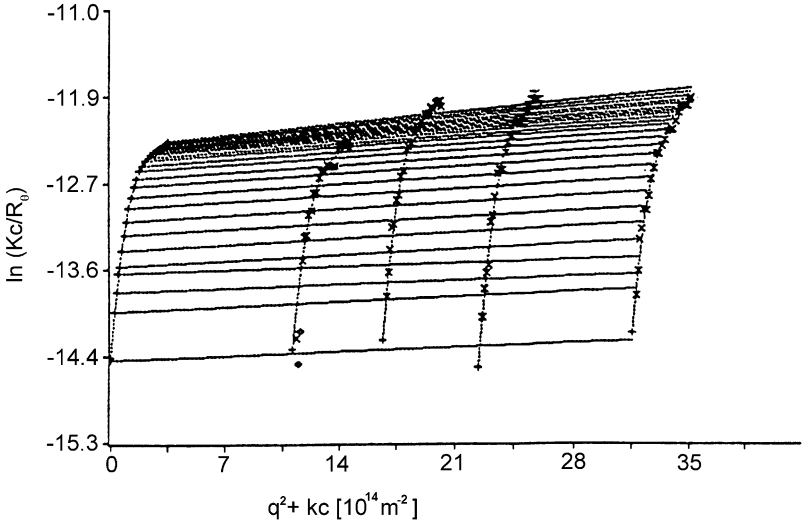

Fig. 1. Guinier–Zimm plot of Buckey V5 dissolved in DMAc with 9 wt% LiCl.

Table 3
Results of static light scattering measurements on cellulose dissolved in DMAc/LiCl

Sample	$(Pulp)_{stock}$ (wt%)	$(Pulp)_{meas.}$ (wt%)	$(LiCl)_{stock}$ (wt%)	$(LiCl)_{meas.}$ (wt%)	M_W (g/mol)	n_W	R_G (nm)	A_2 (molml/g^2)
Avicel	7	0.9	8	1	1,500,000	31	139	< 0
Avicel	3	1.3	6	2.6	258,000	5	105	0.0003
Avicel	3	0.5	6	1	85,000	2	56	0.0006
Buckeye	1	1	9	9	909,000	4	170	0.00001
Buckeye	1	0.3	9	2.6	300,000	1.5	61	0.0015
Buckeye	1	0.2	6	6	1,230,000	6	203	0.00004
Buckeye	1	0.4	6	2.6	509,000	2.5	169	0.0001

dissolution process of sample V5 resulted in lower values of M_w and R_g and in a somewhat smaller fraction of large particles.

Smaller values of M_w and R_g were obtained after dilution of the stock solutions to 2.6 wt% LiCl. In the case of a stock solution with 9 wt% LiCl diluted to 2.6 wt% LiCl, we found $M_w = 300{,}000$ g/mol and $R_g = 61$ nm. Comparing these values with $M_w(DP) = DP \times 162$ g/mol $= 220{,}000$ g/mol, it can be concluded that the diluted solution contains essentially single cellulose chains besides a small fraction of larger cellulose particles. Most of the large particles present in the stock solution were dissolved by dilution. This leads to a better solution state which is indicated by the higher second virial coefficient in the diluted solutions. However, a solution state which is characterized by the exclusive existence of single cellulose molecules was not found.

Avicel. The same behaviour was found for the Avicel sample, which was diluted from 6 to 1 wt% LiCl. Furthermore, if the initial cellulose concentration was high (e.g. 7 wt%), a very large value for M_w (1.5×10^6 g/mol) was obtained after dilution to 1 wt% LiCl. The cellulose was probably not completely dissolved under these conditions, which is supported by the negative second virial coefficient A_2.

However, measurements on cellulose solutions with 1 wt% LiCl (the stock solution for the dilution series of the SLS experiment was prepared from initial solutions having 9 wt% LiCl and 1 wt% pulp) — now the solution composition is comparable with that used in SEC — could not be evaluated properly. This was due to the strong concentration dependence of the RI increment of the DMAc/LiCl solution $\{(\partial n/\partial c) = 0.324$ cm^3/g [5]$\}$. Therefore, the dilution error in the SLS measurements can be very large. We carried out DLS measurements to avoid this problem.

3.2. Dynamic light scattering measurements

SEC stock solutions. Pulps with large differences in their provenience (growing conditions of the plant, cotton or wood type, sulfate or sulfite pulp, chemical/physical conditions during the pulping process) and in their MWDs were investigated.

Viscose. First, the dependence of the solution state on the activation process was examined (Fig. 2). SEC stock solutions with 1 wt% cellulose (regular viscose) and 9 wt% LiCl were used. The intensity-weighted size distribution ($RD_i(R)$) was calculated from the autocorrelation function (ACF) $g_2(t)$ by an inverse Laplace transformation with the ORT program [17]. The resulting radii for the concentrated solutions represent effective hydrodynamic radii and can be compared for samples under equal conditions: concentrations of LiCl and cellulose, cellulose type, scattering angle, and temperature must be the same for different samples.

For cellulose, which was activated either by swelling in

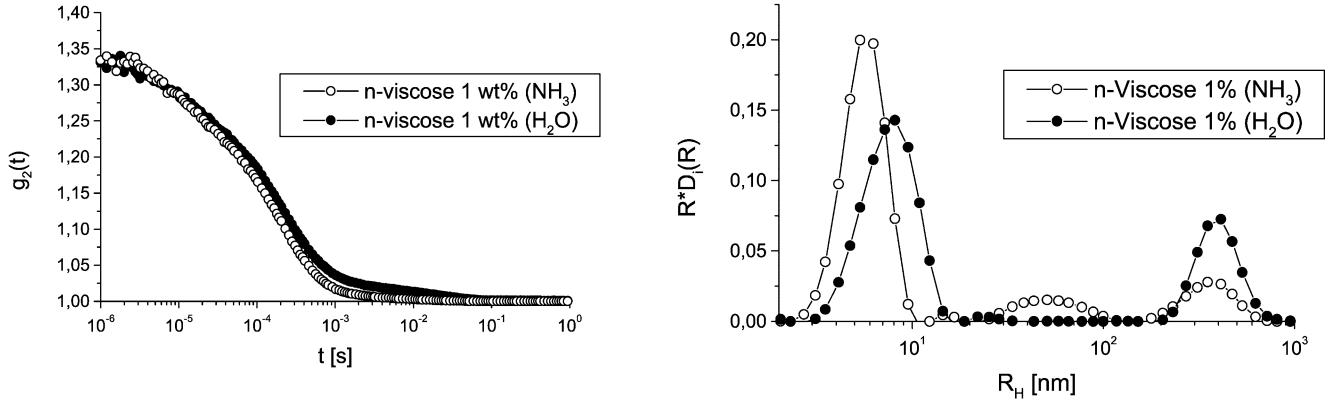

Fig. 2. Intensity autocorrelation function and intensity distribution of 1 wt% viscose in DMAc with 9 wt% LiCl activated by water or ammonia.

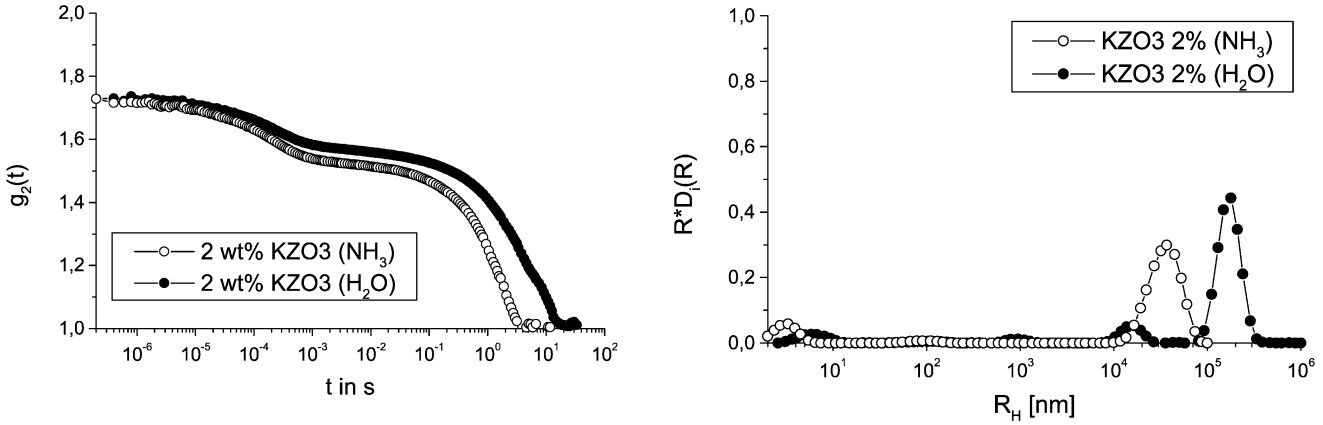

Fig. 3. Intensity autocorrelation function and intensity distribution of 2 wt% KZO3 in DMAc with 9 wt% LiCl activated by water or ammonia.

water or by a pre-treatment with liquid ammonia, the $g_2(t)$ functions did not deviate from each other significantly. There were two maxima found in the intensity distribution of R_H: below 10 nm and at about 400 nm. The peak height is proportional to the scattering intensity of the particle population, due to the calculation of $RD_i(R)$. For globular particles the scattering intensity is proportional to R_H^6. Therefore, the fraction of the large particles is very small as compared to the number of the smaller particles (cellulose molecules). This observation does not depend on the activation method used. One can therefore assume that most of the cellulose molecules exist as single chains.

KZO3. The results of DLS measurements on stock solutions with 9 wt% LiCl and 2 wt% of sample KZO3 are shown in Fig. 3. The autocorrelation functions show two main relaxation times, similar to Avicel at 3 wt% (with 6 wt% LiCl, Fig. 6). The pattern of $g_2(t)$ depended slightly on the activation method. The resulting plot $RD_i(R)$-distribution vs. relaxation time appeared also bimodal. To prove this conclusively, the correlation function was fitted by a double stretched-exponential function (Kohlrausch–Williams–Watts) [18] (Table 4). The calculated relaxation times of the fast motion t_1 correspond to the first maxima of the $RD_i(R)$-distribution. The parameter a describes the part of the motion on the whole correlation function. β is the polydispersity index, for $\beta = 1$, particles are monodisperse. Therefore, the second particle fraction (slow motion) was more unified than the first one. Supermolecular structures (associates or aggregates) of cellulose were present at this concentration. Furthermore, the activation with liquid ammonia favored formation of somewhat smaller supermolecular structures. These results indicated that stock solutions with 2 wt% cellulose or more do not contain only single cellulose molecules, but also an essential amount of aggregates. This effect did not depend on the special type of cellulose.

Dilution to the SEC level. The SEC stock solutions containing 9 wt% LiCl with 1 or 2 wt% cellulose, respectively, were diluted with pure DMAc to one tenth of the LiCl concentration. Fig. 4 shows the effect of this dilution for KZO3 as an example. The $g_2(t)$ curve has a single step, and there is only one maximum in the size distribution curve. Large particles in the stock solution were consequently disintegrated simply by dilution. This is in good

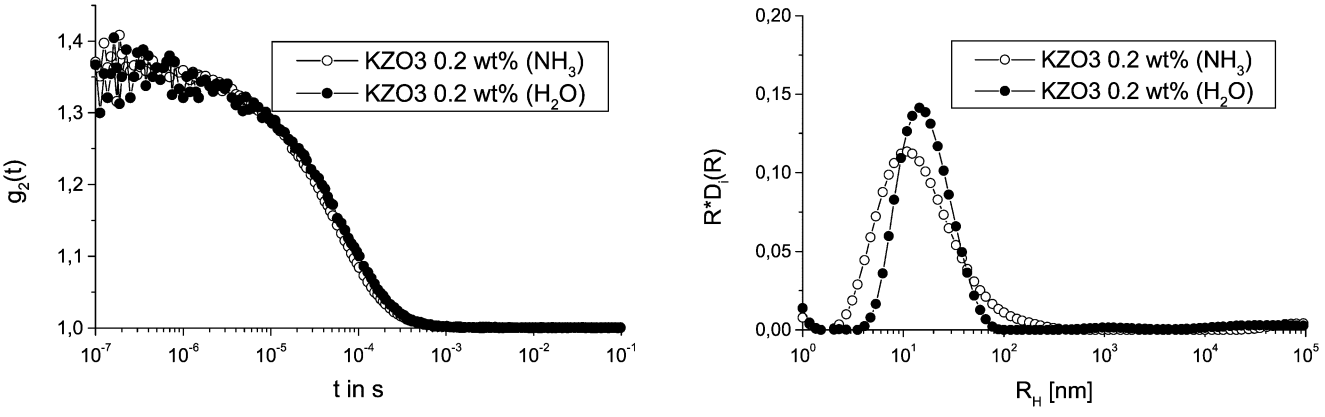

Fig. 4. Intensity autocorrelation function and intensity distribution of 0.2 wt% KZO3 in DMAc with 0.9 wt% LiCl activated by water or ammonia (after dilution from stock solutions in Fig. 3).

Table 4
Dynamic light scattering results for KZO3 pulp (2 wt%) in DMAc/LiCl (9 wt%). Kohlrausch–Williams–Watts analysis of the correlation function

Parameter	2 wt% KZO3		Maxima of $RD_i(R)$	
	(NH_3)	(H_2O)	(NH_3)	(H_2O)
a_1	0.14 ± 0.004	0.16 ± 0.007	2.2×10^{-4}	2.1×10^{-4}
β_1	0.51 ± 0.035	0.54 ± 0.054		
t_1 (s)	$2.1 \times 10^{-4} \pm 2 \times 10^{-5}$	$2.2 \times 10^{-4} \pm 3 \times 10^{-5}$		
a_2	0.37 ± 0.017	0.57 ± 0.0025	2.4	1 and 10
β_2	0.9 ± 0.018	0.8 ± 0.017		
t_2 (s)	1.33 ± 0.02	4.96 ± 0.09		

agreement with the results obtained by SLS. Thus, the large particles are probably associated cellulose molecules. Effects attributed to the different activation methods were negligible. Nevertheless, a different behavior was observed in the case of viscose fibres when activated by the water swelling method (Fig. 5). While all the other samples gave molecularly disperse solutions at 0.9 wt% LiCl, the water-swollen viscose still formed larger structures. However, such differences were not detectable by SEC measurements [9]. It should be mentioned that the cellulose concentration is reduced to about 0.001 wt% during the chromatographic process. In this range, the cellulose solution is molecularly disperse.

3.3. Polarized and depolarized dynamic light scattering

The optimal concentration of LiCl for the dissolution process is reported to range from 5 to 9 wt% [2]. Solutions with a large amount of cellulose are very viscous depending on the DP of the cellulose and on the LiCl content. Avicel, a micro-crystalline cellulose with the lowest DP of all samples used, at a LiCl concentration of 6 wt% was used to obtain solutions with a large cellulose to LiCl ratio and a relatively low viscosity. Avicel was chosen based on the hypothesis that large particles could be swollen parts of the former crystalline regions of the solid cellulose. By using high concentrations of a micro-crystalline sample together with a low concentration of LiCl the solution should consist of such swollen particles.

Fig. 6 gives the autocorrelation functions $g_2(t)$ of the Avicel solutions in DMAc with 6 wt% LiCl at cellulose concentrations ranging from 1 to 3.5 wt%. The cellulose was activated by the water swelling method. At 1 wt% Avicel, $g_2(t)$ showed a large step at a relaxation time of about 0.1 ms and only a small step between 1 and 10 ms. This corresponds to a main fraction of small particles and a very small fraction of larger particles. The amount and size of the large particles increased with the cellulose concentration as indicated by the progressive increase of the height of the second step and its shift to a longer correlation time. This concentration dependence was also found by the SLS measurements.

After dilution of the stock solutions to a LiCl concentration of 0.9 wt% a different behaviour was found. Fig. 7 presents the distributions of the apparent hydrodynamic radii of the diluted Avicel solutions presented in Fig. 6. At least two populations can be distinguished even after dilution. Certain amounts of supermolecular structures exist in these solutions which are probably smaller aggregates. This implies that the dissolution process of cellulose materials in DMAc with 6 wt% LiCl could be incomplete even with only 1 wt% of cellulose. This is caused by the decreasing thermodynamic driving force with decreasing LiCl content in the solvent system.

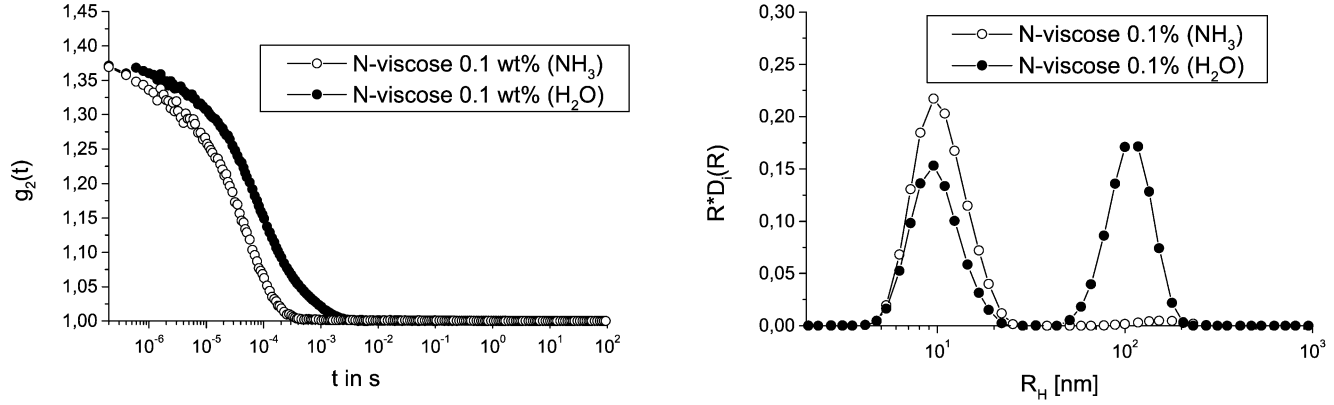

Fig. 5. Intensity autocorrelation function and intensity distribution of 0.1 wt% viscose in DMAc with 0.9 wt% LiCl activated with water or ammonia (after dilution from stock solutions in Fig. 2).

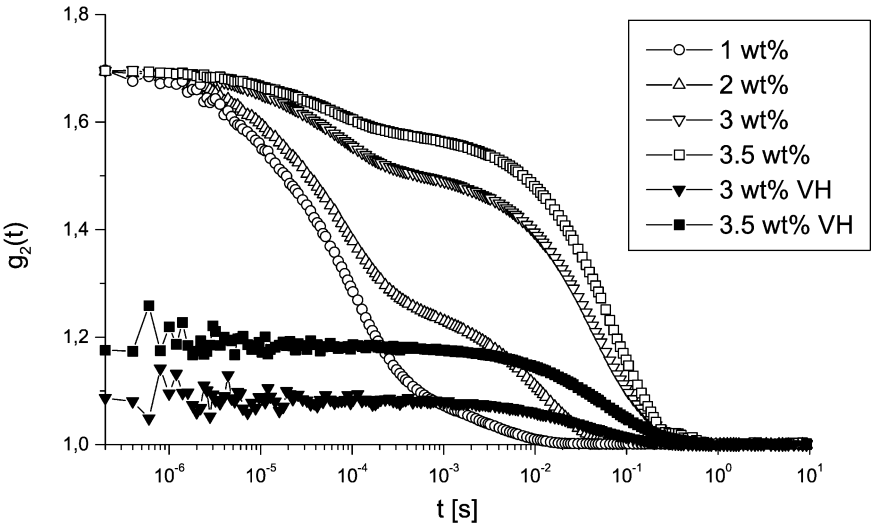

Fig. 6. Intensity autocorrelation functions of Avicel dissolved in DMAc with 6 wt% LiCl.

In the case of an incomplete dissolution, the aggregates probably represent highly swollen parts of formerly crystalline regions of cellulose, so-called fringed micelles [19]. Anisotropic particles — optically homogeneous elongated particles or optically inhomogeneous particles — can be analyzed by DDLS measurements if an autocorrelation function is detected in the depolarized (VH) experiment [14]. DDLS measurements showed that anisotropic particles were present in solutions with 6 wt% LiCl and more than 3 wt% Avicel.

4. Conclusions

The solution state in cellulose/LiCl/DMAc solutions is influenced by the process of the cellulose dissolution, especially by cellulose concentration, LiCl concentration, and activation method used. Stock solutions with 9 wt% LiCl and a cellulose concentration higher than 1 wt% exhibit a bimodal distribution of the particle sizes. After dilution to 0.9 wt% LiCl and 0.1 wt% cellulose the large particles are disintegrated, and — in most of the cases — these solutions contain almost exclusively single cellulose chains. Usually a cellulose activation by swelling in water followed by a solvent exchange is sufficient to dissolve most of the samples in LiCl–DMAc. However, for some samples, such as viscose fibres, an activation with liquid ammonia is more effective.

When stock solutions were prepared with a LiCl content of 6 wt%, the formation of large particles is favored. This behavior was found especially for high cellulose concentrations, and it depends on the DP of the cellulose. Evidently, the amount of reacting solvent complexes is not sufficient to break all the hydrogen bonds between the cellulose molecules [1]. In concentrated solutions (up to 1 wt% cellulose) the existence of large anisotropic particles could be

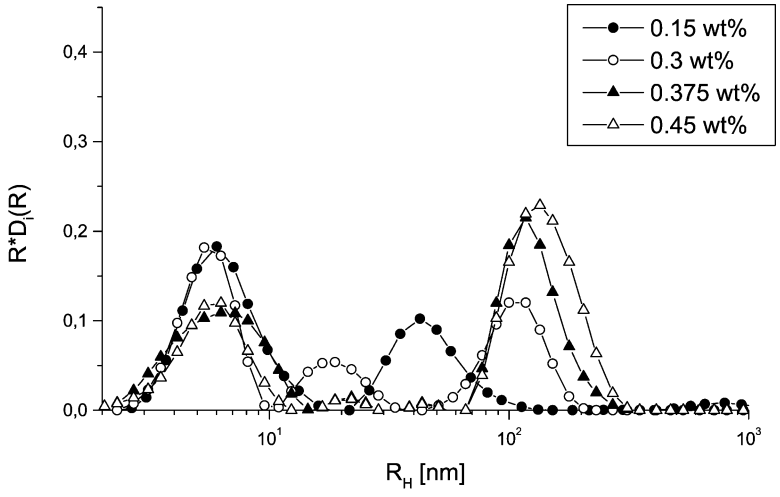

Fig. 7. Intensity distributions for 0.15–0.45 wt% Avicel in DMAc with 0.9 wt% LiCl (after dilution from stock solutions in Fig. 6).

confirmed. After dilution to 0.9 wt% LiCl a significant fraction of large cellulose particles, which can be regarded as swollen fringed micelles, was detected in addition to single cellulose chains. Therefore, the use of a LiCl concentration of 9 wt% should be preferred for the preparation of stock solutions of cellulose. Molecularly dispersed cellulose solutions required for SEC measurements can be obtained under the following conditions:

1. Activation by the water swelling method followed by a solvent exchange. For samples with a higher DP a pretreatment with liquid ammonia is necessary.
2. Stock solutions with 9 wt% LiCl and a maximum of 1 wt% cellulose.

It should be noted that solutions of 9 wt% LiCl in DMAc cannot be obtained with absolutely dry DMAc, but only if DMAc contains some amount of water. The limiting solubility in dry DMAc is 8.46 wt%. The effect of water on the physicochemical properties of the system DMAc/LiCl and the cellulose dissolution process has been discussed elsewhere [20].

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Appendix.

A.1. Static light scattering

For a dilute polymer solution the well-known equation for SLS reads

$$\frac{Kc}{R_\theta} = \frac{1}{M_w P(q)} + 2A_2 c, \tag{A1}$$

where the terms of higher virial coefficients are neglected. R_θ is the difference of the Rayleigh ratios between the polymer solution and the solvent at the scattering angle θ, c is the polymer mass concentration, and $K = 4\pi^2 n_0^2 (\partial n/\partial c)^2 / N_A \lambda_0^4$ is the optical constant for the vertically polarized incident light beam; with n_0, λ_0, $(\partial n/\partial c)$ and N_A being the solvent refractive index, the wavelength of light in vacuum, the specific refractive index increment of the polymer solution and Avogadro's constant, respectively. A_2 is the second virial coefficient and M_w is the weight-average molecular weight of the polymer. The form factor $P(q)$ may be expanded for small particles in good approximation in terms of the scattering vector $q = (4\pi n_0/\lambda_0)\sin(\theta/2)$ for $q \ll 1$ as

$$P(q)^{-1} = 1 + \tfrac{1}{3} q^2 R_g^2, \tag{A2}$$

where R_g is the radius of gyration [21]. The evaluation of the light scattering measurements required two extrapolations, one for an interaction free condition ($c \rightarrow 0$) as well as the other for an interference free condition ($q \rightarrow 0$), e.g. according to Zimm [15], Berry [22] and Wesslau [16]. The method choice has been discussed by Burchard [23].

In the Guinier–Zimm plot [16] $\ln(Kc/R_\theta)$ is plotted against $(q^2 + kc)$, where k is an arbitrary constant. From the intercept and slope of the extrapolation curve $\ln(Kc/R_\theta)_{c,q=0}$ the weight-average molecular weight and the second virial coefficient, respectively, can be estimated. The radius of gyration can be obtained from the initial slope of the extrapolation curve $\ln(Kc/R_\theta)_{q,c=0}$.

A.2. Dynamic light-scattering

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 auto-correlation function of the electric field $g_1(q,t)$ in a homodyne experiment [24] by

$$g_2(q,t) = A(1 + B|g_1(q,t)|^2), \tag{A3}$$

where 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:

$$g_1(t) = \int G(\Gamma_i) \exp(-\Gamma_i t)\, \mathrm{d}\Gamma. \tag{A4}$$

Eq. (A4) 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 $D = k_B T/6\pi\eta_0 R_H$, where η_0 is the dynamic viscosity of the solvent, T the temperature and k_B is the Boltzmann constant. By inverting Eq. (A4) the intensity-weighted size distribution of the hydrodynamic radii of the particles present in the solution can be estimated [17]. Due to the intensity–radius relationship $I \propto R_H^6$ for globular particles, even a very small fraction of large particles could be distinctly identified. This method is a simple tool to gain qualitative information about the size distribution of cellulose particles in concentrated and highly diluted cellulose solutions on the basis of a measurement of only one sample solution.

Another method is the Kohlrausch–Williams–Watts [18] analysis. The correlation function can often be described as a sum of so-called stretched exponential functions:

$$g_1(c,q,t) = \sum a_i \exp(-t/b_i)^{\beta_i}. \tag{A5}$$

References

[1] Morgenstern B, Kammer H-W. Trends Polym Sci (TRIP) 1996;4:87.
[2] Dawsey TR, McCormick CL. J Macromol Sci, Rev Macromol Chem Phys 1990;C30:405.
[3] Terbojevich M, Cosani A, Conio G, Ciferri A, Bianchi E. Macromolecules 1985;18:640.
[4] McCormick CL, Callais PA, Hutchinson Jr. BH. Macromolecules 1985;18:2394.
[5] Fellmann E. Doctoral thesis Dresden: Technische Universität, 1991.
[6] Kvernheim AL, Lystad E. Acta Chem Scand 1989;43:209.
[7] Timpa JD, Ramey Jr. HH. Textile Res J 1989;59:661.
[8] Silva AA, Laver ML. Tappi J 1997;80:173.
[9] Schelosky N, Röder T, Baldinger T. Das Papier (Darmstadt) 1999;53:728.
[10] Ekmanis JL. Polym Notes, Waters 1986:1.
[11] SCAN-CM 15:99.
[12] Morgenstern B, Berger W. Acta Polymerica 1993;44:100.
[13] Schelosky N, Millacher W. Personal communication.
[14] Lehner D, Lindner H, Glatter O. Langmuir 2000;16:1689.
[15] Zimm BH. J Chem Phys 1948;16:1093.
[16] Wesslau H. Makromol Chem 1963;69:213.
[17] Schnablegger H, Glatter O. Appl Opt 1991;30:4889.
[18] Lindsay CP, Patterson GD. J Chem Phys 1980;73:3348.
[19] Burchard W. Adv Colloid Interface Sci 1996;64:45.
[20] Potthast A, Rosenau T, Buchner R, Ebner G, Röder T, Kosma P. Cellulose 2001 (in press).
[21] Guinier A, Fournet G. Small-angle scattering of X-rays. New York: Wiley, 1955.
[22] Berry CG. J Chem Phys 1966;44:4550.
[23] Burchard W. Adv Polym Sci 1983;48:1.
[24] Siegert FJA. MIT Rad Lab Report No. 665, 1943.