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Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 3. Aggregation of Cellulose in *N*,*N*-Dimethylacetamide–Lithium Chloride

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ABSTRACT: Light scattering and viscosity measurements on diluted and moderately concentrated solutions of several cellulose samples dissolved in *N*,*N*-dimethylacetamide (DMAc) containing 5% or 7.8% (w/w) LiCl are reported. Cellulose samples include regenerated cellulose, sulfate pulps, and HCl hydrolyzates having DP between 60 and 760. Solubilization without chain degradation was achieved by using a method reported in the patent literature involving activation of cellulose by DMAc at the reflux temperature followed by addition of LiCl. Cellulose was dissolved either as a molecular dispersion (I) or as stable aggregates (II) consisting of ca. 7 fully extended cellulose molecules with a side-by-side organization. Concentration-dependent association equilibria (III) involving single molecules or aggregates were also observed. The occurrence of said situations depends upon the concentration, C_p, of stock solutions prepared with the method indicated above, the concentration, c, to which stock solutions are diluted, the LiCl concentration, the DP, and the treatment performed by the producer. In particular, acid hydrolysis favors situation II. This complex situation is considered in the accompanying paper in order to establish a relationship between the size of polymer particles and the critical concentration for mesophase formation.

In preceding papers of this series we investigated the relationship between chain rigidity and mesophase formation for (hydroxypropyl)cellulose (HPC) in *N*,*N*-dimethylacetamide (DMAc)[1] and in dichloroacetic acid (DCA).[2] The persistence length q was used to evaluate the axial ratio of the Kuhn segment. The latter was used for testing the prediction of a theory[3] for mesophase formation by semirigid mesogens. Satisfactory agreement between experiment and theory was verified in the high molecular weight range when the Kuhn chain model more likely applies and provided both hard and soft interactions contribute to mesophase formation.

A recurring problem in the above, and in most other studies with polymer liquid crystals,[4] has been the proper evaluation of the axial ratio of the rigid segment, which is inversely related[2] to the critical concentration at which the mesophase appears. In fact, the persistence length can only be determined from dilute solution studies. The chain diameter is often affected by a significant indetermination, which also poses limitations to a test of the various theories.[2] Moreover, the possibility has been considered that *aggregated* polymer species, and not molecularly dispersed entities, occur in the concentrated solutions at which mesophases are observed. In such a case, it would be extremely difficult to assess the length and diameter of the unit related to the critical concentration.

Table I
Characteristics of Samples Investigated[a]

sample	producer	$[\eta]_{\mathrm{CED}}$, dL/g	DP[b]	M_w[b]
A	Snia Fibre (regenerated cellulose II)	1.61	288	46 700
B	Snia Fibre (prehydrolyzed Kraft pulp)	2.52	474	76 800
C	Buckeye Corp. V68 (prehydrolyzed Kraft pulp)	2.40	449	72 800
D	Avicel (microcrystalline for TLC hydrolyzed)	0.92_5	155	25 100
E	Mischia Latifoglia Snia (Kraft pulp, not hydrolyzed)	3.85	760	123 100
F	obtained by hydrolysis of sample E	0.94	159	25 700
G	obtained by hydrolysis of sample E	0.63	102	16 500
H	obtained by hydrolysis of sample E	0.41_5	64	10 400
I	SSCC, Milan, (regenerated cellulose II)	2.45	460	74 500
L	Snia Fibre (regenerated cellulose II)	1.62	290	47 000

[a] "Hydrolyzed" refers to HCl treatments. [b] Determined from $[\eta]_{\mathrm{CED}}$ (M_0 = 162) using eq 1.

In the studies so far reported,[1,2,4] no definite proof has been given for the absence of aggregation in concentrated solutions. On the other hand, no evidence of such an aggregation was suggested by dilute solution studies. Due to the difficulties in solubilizing cellulose and to other features of its phase diagram in DMAc + LiCl prelimi-

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narily observed,[5] there are sound reasons for suspecting aggregation in the latter system. In the present paper, we investigate the occurrence of aggregation for cellulose dissolved in DMAc + LiCl by light scattering and viscosity techniques. These techniques allow the study of diluted and moderately concentrated solutions. It will be shown that aggregation does occur in these solutions and, therefore, its role must be considered in the more concentrated systems in which the mesophase appears.

Experimental Section

Materials. Several cellulose samples obtained from various sources were investigated. Sample origin and characteristics are listed in Table I. Molecular weights (M_w) and degree of polymerization (DP) were evaluated from intrinsic viscosity measurements in 0.5 M cupriethylenediamine (CED) at 25 °C using the relationship reported by Marx[6]

$$[\eta] = 1.01 \times 10^{-4} M_w^{0.9} \qquad (1)$$

which gives values of DP close to the average values obtained from expressions reported by others.[6] CED was purchased from Carlo Erba as a 1 M solution in H_2O and was diluted to 0.5 M. Solutions in CED were obtained by stirring for 24 h small pieces of cellulose which had been dried overnight under vacuum at 80 °C. The flow time of solutions did not vary even after 1 day. Hydrolysis of samples F–H was performed by treating chips of sample E with 20% NaOH at 35 °C for 5 h, followed by neutralization and treatment with 0.5 N HCl at 90 °C for 60 (F), 90 (G), 240 min (H) and washing to neutralization.

Stock Solutions. Stock solutions of cellulose in DMAc containing 5% or 7.8% (w/w) LiCl were prepared by the method described by Turbak et al.[7] with which complete dissolution was better achieved than with the method reported by McCormick and Shen.[8] A weighed amount of DMAc was added to a weighed amount of cellulose which had been dried overnight, under vacuum, at 80 °C. The mixture is heated to the reflux temperature (~165 °C) for 20–30 min, stirring under a N_2 atmosphere. The mixture is allowed to cool to ~100 °C, and a weighed amount of LiCl is added under steady stirring. At variance with Turbak, we continued to stir the mixture at 80 °C for a length of time which varied between 10 and 40 min. The latter precaution ensured complete dissolution in most cases. The cooled solution is clear and slightly brown. Polymer concentration of stock solution, C_p, given as grams of cellulose per 100 g of ternary solution, varied between 0.2% and ~7.2%. Salt concentration, C_s, is given as grams of LiCl per 100 g of binary (LiCl + DMAc) solution. In the few instances in which complete dissolution was not achieved or when a check of C_p was needed, the concentration of dissolved cellulose was determined by precipitating the polymer with H_2O. Following centrifugation, the precipitate was washed several times with H_2O, lyophilized, and dried. The absence of significant degradation of cellulose resulting from the dissolution process was confirmed by measuring the intrinsic viscosity in CED for samples which had been precipitated with water and dried. The observed value of $[\eta]$ was within 5% of that of the original polymer.

Intrinsic Viscosity and Light Scattering. Solutions to be used for light scattering and instrinsic viscosity measurement in DMAc + LiCl were prepared by weighing the required amount of stock solution and of the DMAc/LiCl diluent. Only in the case of viscosity measurements subsequent dilutions were made by volume, directly in the bulb of the viscometer. Following dilution, solutions were shaken for about 1 h to ensure complete homogenization. The latter step was also applied to the viscometer, taking care to carefully close the openings to avoid moisture uptake. The latter precaution was mandatory in order to obtain reproducible results. The concentration, c, of solutions used for intrinsic viscosity and light scattering is given as g/100 mL. Although concentration for light scattering measurements is usually expressed as g/mL, we have used the former unit to facilitate comparison between the concentration of stock solution and phase diagram (C_p) given as g/100 g of solution. Since the density of DMAc + 5% LiCl is 0.982 g/mL, the difference between concentrations expressed on a weight or volume basis is a very small. Viscosities were determined with suspended-level Ubbelohde viscometers at 25 ± 0.1 °C having flow times for the solvent greater than 150 s and relative viscosities between 1.1 and 1.6. The stability of the solution was excellent; neither $[\eta]$ nor the scattered intensity varied even after months following preparation. Newtonian behavior of solutions was observed. Light scattering measurements were performed at 25 °C with a Sofica Model 42000 photometer with cylindrical cells immersed in toluene. Nonpolarized light with λ = 546 nm was used covering scattering angles θ between 30° and 150° (measurements at λ = 436 nm were not performed due to the slight coloration of the solution). Data in the literature[9] indicate that the usual determination of the scattered intensity of solution (I) and solvent (I_0) between 30° and 150° is accurate for M_w up to ~6×10^6 and radius of gyration $\langle R_G^2 \rangle_z^{1/2}$ ~ 2600 Å. A Rayleigh ratio[10] $R_{90} = 15.8 \times 10^{-6}$ cm^{-1} was used for the calibration of the instrument with benzene. Solutions and solvents were clarified by centrifugation at 16 000 rpm for 2 h or at 17 000 rpm for 6 h. The dissymetry of the solvent z ($=I_{45°}/I_{135°}$) was between 1.10 and 1.00 (the latter value obtained with the more extensive centrifugation). Proper evaluation of M_w and $\langle R_G^2 \rangle_z$ by light scattering in a multicomponent diluent requires dilution with a diluent brought to dialysis equilibrium with the solution.[11] This is especially important for the determination of the refractive index increment dn/dc. Unfortunately, our attempts to find a suitable and stable membrane were unsuccessful. Values of dn/dc were determined without equilibrium dialysis by using a Brice-Phoenix differential refractometer at λ = 546 nm. The value obtained in DMAc + 5% LiCl is 0.08 mL/g, which appears too small to reproduce the molecular weight expected on the basis of the viscosity in CED.

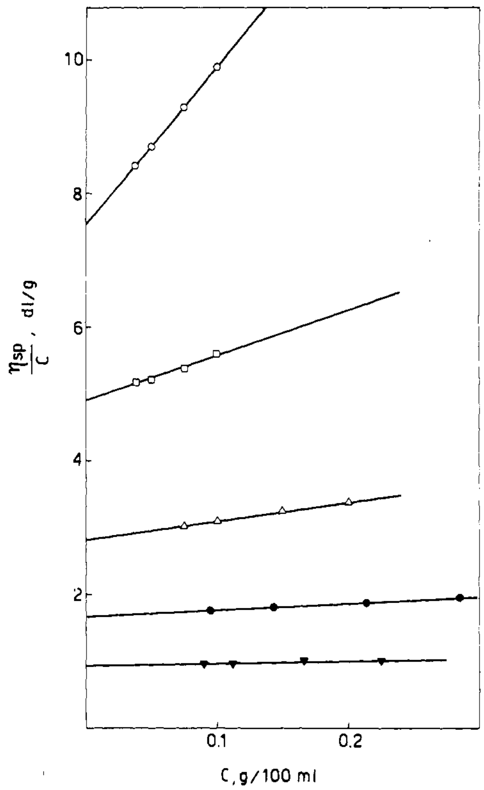


Figure 1. Typical viscosity–concentration data for cellulose in DMAc–5% LiCl at 25 °C: (○) sample E; (□) sample C, C_p = 0.3%; (△) sample A, C_p = 0.3%; (●) sample D; (▼) sample G.

Results and Discussion

Viscosity. The concentration, C_p, of stock solutions directly prepared from various samples by the dissolution procedure of Turbak et al.[7] is indicated in Table II.

Selected η_{sp}/c vs. c data in DMAc–5% LiCl are illustrated in Figure 1. Within the concentration range of most viscosity determinations, 0.05 < c < 0.3 g/100 mL, these plots were linear, with Huggins constants between 0.3 and 0.4. In a few instances, however, below c ~ 0.1 g/100 mL an upturn was observed, but the data were not reprodu-

Table II
Stock Solutions, Viscosity, and Light Scattering Data in DMAc-LiCl

sample (DP)	C_p, %	$[\eta]$, dL/g	$(c/H)_{c=0,\theta=0} \times 10^3$	c range, g/100 mL	$d(c/H_0)/dc$	z	aggr	assoc
				$C_s = 5\%$				
H (64)	0.67	0.65						
G (102)	0.53	0.94	~1.0	0.08–0.24	–	1.38–1.68	+	
F (159)	0.53	1.65	~2.0	0.10–0.21	0	1.24–1.31	+	
D (155)	2.86	1.68	1.2	0.05–2.86	0 → –	1.18–2.21	+	+
A (288)	0.30	2.77		0.3		<1.1	–	–
A (288)	3.00	2.82	3.1	0.11–1.0	+	1.0–1.1	–	–
A (288)	5.00	3.00	3.9	1.0–3.0	0 → –	1.2–3.3	–	+
A (288)	7.20	2.53	3.3					
L (290)	3.00	3.00						
C (449)	0.30	4.90	1.9	0.03–0.12	+	1.2–1.3	–	–
C (449)	3.00	3.40	0.3	0.03–1.5	+	1.6–2.0	+	–
I (460)	3.00	5.00	2.3	0.03–0.11	+	1.2–1.3	–	–
B (474)	0.20	5.63	0.25	0.04–0.20	0	1.6–2.0	+	+
E (760)	0.20	7.54	1.0	0.01–0.12	+	1.2–1.4	–	–
				$C_s = 7.8\%$				
A (288)	3.00	2.77		0.6–2.32	–	1.34–3.74	–	+
C (449)	0.30	4.77	1.9	0.02–0.3	–	1.16–2.00	–	+
C (449)	3.00	5.04	2.3	0.04–0.16 0.4–1.4	+ 0 → –	1.15–1.16 1.17–1.94	– –	– +

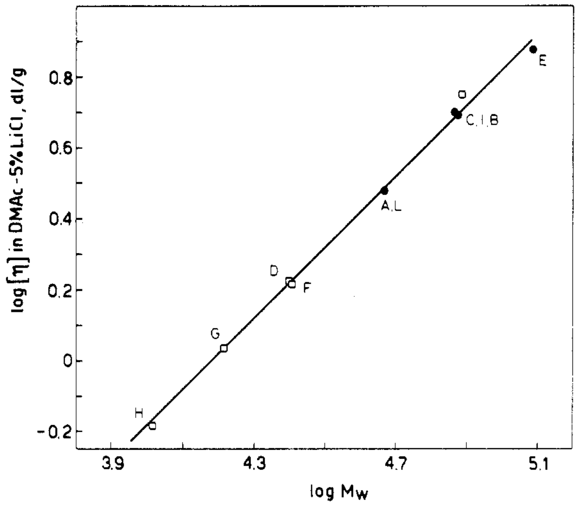


Figure 2. Intrinsic viscosity in DMAc–5% LiCl vs. molecular weight determined from the intrinsic viscosity in CED (eq 1). Data for the cellulose samples indicated are from Tables I and II. For sample A, $C_p = 5\%$; for sample C, $C_p = 0.3\%$.

cible. Extrapolated values of intrinsic viscosity are included in the third column of Table II. $[\eta]$ increases with DP and does not show large variations with the concentration C_p of the stock solution in the case of sample A (DP = 288). However, in the case of sample C (DP = 449), $[\eta]$ is smaller when the concentration of the stock solution is larger.

Apart from the latter effect observed with sample C, the viscosity results do not show direct evidence of aggregation. A logaritmic plot of $[\eta]$ in DMAc–5% LiCl vs. molecular weight is shown in Figure 2. The molecular weight was determined from the viscosity in CED (reported in Table I). Solutions in CED are molecularly dispersed.[6,12] The plot shows a regular trend. Since, as shown below, aggregation does occur for several of the samples included in Figure 2, it appears that the intrinsic viscosity in DMAc/LiCl would be a very misleading tool for assessing the occurrence of aggregation even in dilute solutions.

We point out the large increase of $[\eta]$ in DMAc/LiCl with respect to $[\eta]$ in CED. As recalled elsewhere,[1] the dimensions of cellulosic chains are not largely affected by excluded volume effects. Thus, the larger values of $[\eta]$ in DMAc/LiCl likely reflect specific effects on the unperturbed dimensions. McCormick and Shen[8] observed an increase of $[\eta]$ for cellulose in DMAc/LiCl as a function of ionic strength up to $C_s \sim 4\%$ and suggested a polyelectrolyte effect due to binding of Cl^- to hydroxyl protons. However, at the still higher C_s considered here, any polyelectrolyte effect should be screened out. Consideration of the chemical shifts of the C-2 and C-3 carbons for cellulose dissolved in DMAc/LiCl[13] and of the carbon atoms of DMAc[14] suggests the formation of interactions of the type[13]

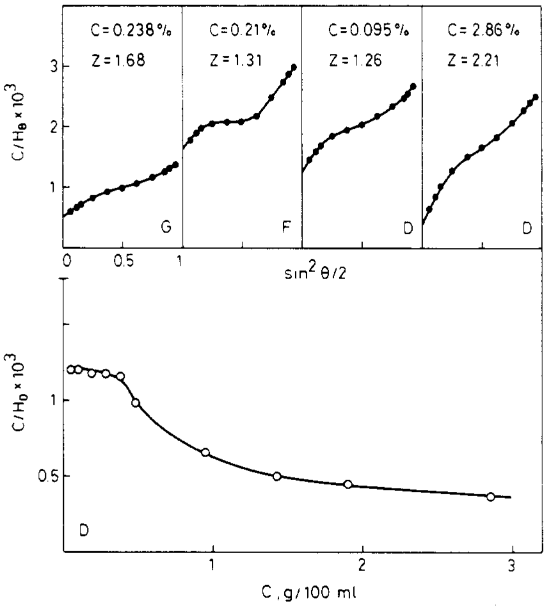
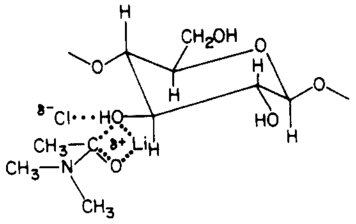


Figure 3. Light scattering data for samples G, F, and D. 5% LiCl.



which could stabilize extended conformers of the glycosidic linkage.

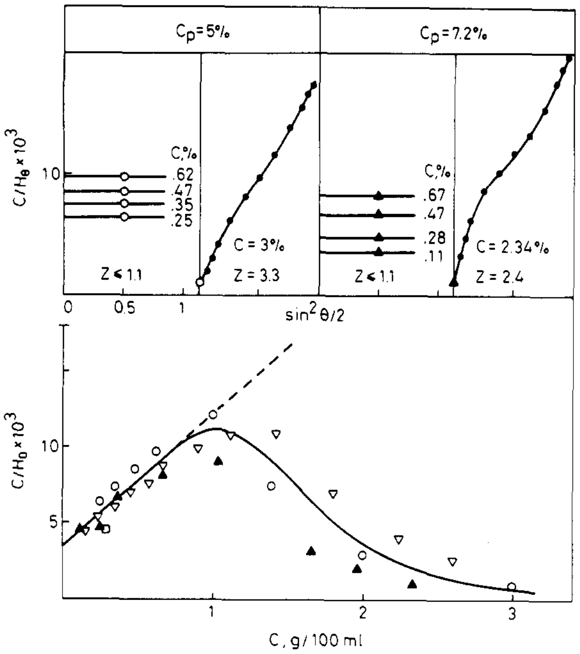


Figure 4. Light scattering data for sample A corresponding to different values of the concentration, C_p, of stock solution. 5% LiCl. (□) $C_p = 0.3\%$; (▽) $C_p = 3\%$; (○) $C_p = 5\%$; (▲) $C_p = 7.2\%$.

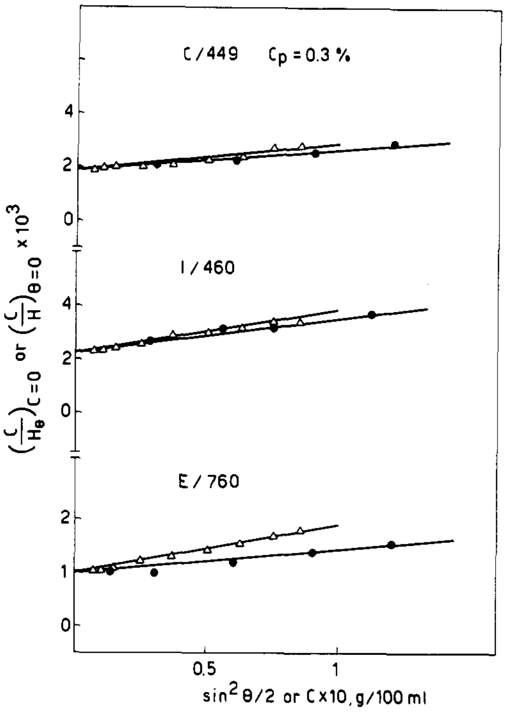


Figure 5. Plots of $(c/H_\theta)_{c=0}$ vs. $\sin^2 \theta/2$ (△) and $(c/H)_{\theta=0}$ vs. c (●) for samples C, I, and E. 5% LiCl.

Light Scattering. The light scattering data are summarized in Tables II and III and are plotted in Figures 3–8 as c/H_θ vs. $\sin^2 \theta/2$ at given c and/or as c/H_θ vs. c at $\theta = 0°$. H_θ is defined as

$$H_\theta = \frac{(I - I_0) \sin \theta}{1 + \cos^2 \theta} \tag{2}$$

The molecular weight was calculated from the relationship

$$\frac{1}{M_w} = \frac{2\pi^2 n_B{}^2}{\lambda^4 N R_B}\left(\frac{dn}{dc}\right)^2 I_B\left(\frac{c}{H_\theta}\right)_{c=0,H=0} = 0.491\left(\frac{dn}{dc}\right)^2 I_B\left(\frac{c}{H_\theta}\right)_{c=0,\theta=0} \tag{3}$$

Table III
Light Scattering Parameters in DMAc-LiCl

sample (M_w)	C_p %	$\bar{M}_w{}^a$	B,^{b} mol·mL·g^{-2}	$\langle R_G{}^2\rangle^{1/2}$, Å
		$C_s = 5\%$		
G (16 500)	0.53	~150 000		
F (25 700)	0.53	~75 000		
D (25 100)	2.86	125 700	0.0×10^{-3}	550 ± 100
A (46 700)	0.30	43 100	2.9×10^{-3}	
A (46 700)	3.00			
A (46 700)	5.00			
A (46 700)	7.20			
C (72 800)	0.30	79 400	2.6×10^{-3}	375 ± 100
C (72 800)	3.00	502 900	8.3×10^{-4}	1160 ± 200
I (74 500)	3.00	65 600	4×10^{-3}	400 ± 100
B (76 800)	0.20	604 000	0.0×10^{-3}	1400 ± 200
E (123 100)	0.20	150 800	1.5×10^{-3}	490 ± 50
		$C_s = 7.8\%$		
C (72 800)	3.0	65 600	6.0×10^{-3}	470 ± 100

^{a} Calculated with assumed $dn/dc = 0.150$ mL/g.

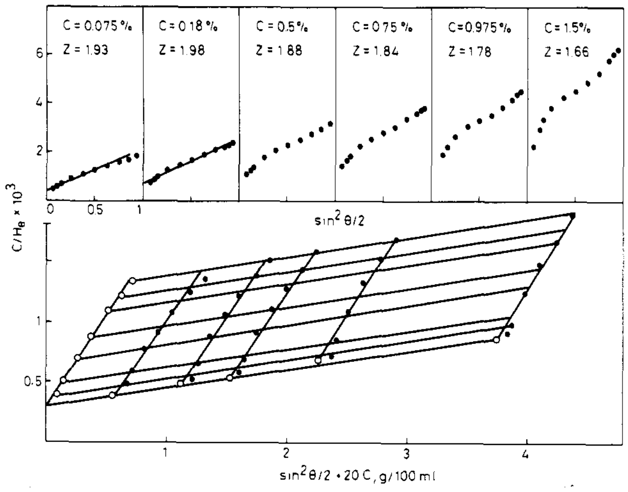


Figure 6. Zimm plot for sample C when $C_p = 3\%$ and $c = 0.05–0.18$ g/100 mL. The upper part shows c/H_θ vs. $\sin^2 \theta/2$ including data obtained when $c > 0.3$ g/100 mL. 5% LiCl.

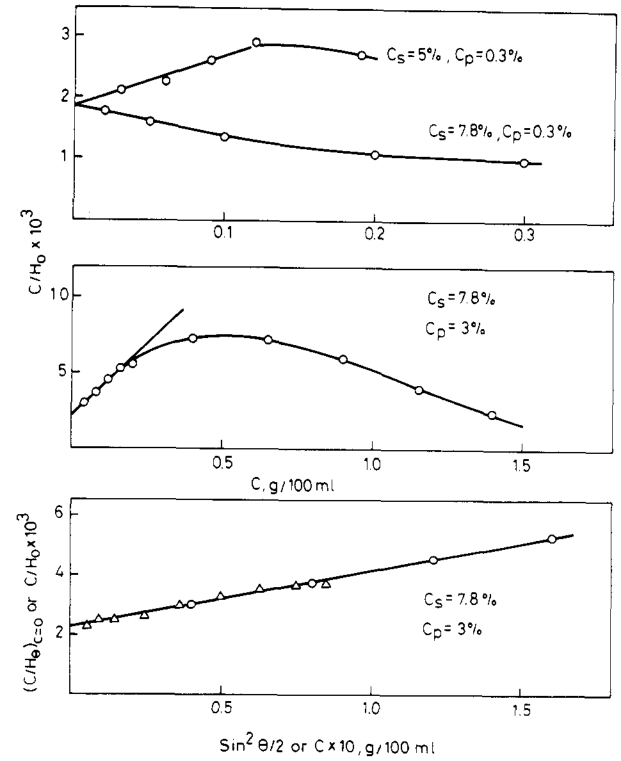


Figure 7. Plots of $(c/H)_{\theta=0}$ vs. C (○) and of $(c/H_\theta)_{c=0}$ vs. $\sin^2 \theta/2$ (△) for sample C at the indicated values of C_s and C_p.

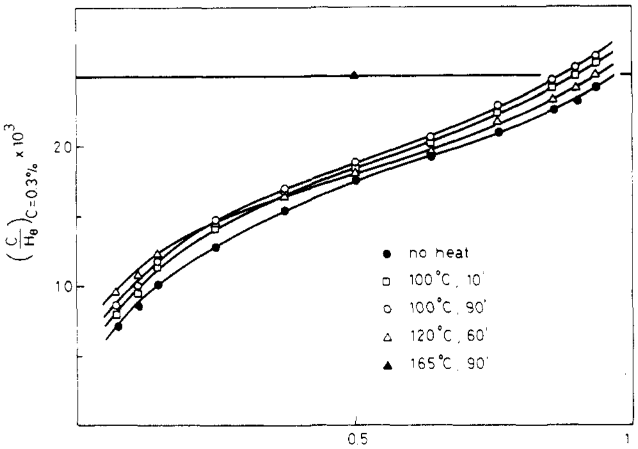


Figure 8. Effect of temperature on the c/H_θ vs. $\sin^2\theta/2$ plot at 25 °C for sample C (stock $C_p = 3\%$) having $c = 0.3$ g/100 mL exposed to the indicated (increasing) temperatures for the indicated length of time.

where n_B, R_B, and I_B are, respectively, the refractive index, the Rayleigh ratio, and the scattered intensity (at 90°) of benzene. The virial coefficient can be determined, once M_w is known, from the slope of the $(c/H_\theta)_{\theta=0}$ vs. c line

$$B = \frac{1}{2M_w} \frac{[(c/H_0)c_1 - (c/H_0)_{c=0}]/(c/H_0)_{c=0}}{c_1} \qquad (4)$$

while the radius of gyration $\langle R_G^2\rangle_z$ is determined, without knowledge of M_w, from the slope/intercept ratio of the $(c/H_\theta)_{c=0}$ vs. $\sin^2\theta/2$ line

$$\langle R_G^2\rangle_z = \frac{3\lambda^2}{16n^2\pi^2} \frac{(c/H)_{\theta=180} - (c/H)_{\theta=0}}{(c/H)_{\theta=0}} \qquad (5)$$

Equation 3 shows that M_w can be calculated from $(c/H_\theta)_{c=0,\theta=0}$, once the refractive index increment is known. As indicated in the Experimental Section, lack of a stable dialysis membrane prevented the determination of a correct value of dn/dc. From the point of view of determining the aggregation of cellulose in DMAc/LiCl, a knowledge of $(c/H_\theta)_{\theta=0,c=0}$ is sufficient. In fact, the latter values are listed in Table II. In order to obtain an estimate of M_w and B, we have derived dn/dc by fitting the molecular weight calculated from the viscosity in CED (eq 1) to the corresponding experimental values of $(c/H_\theta)_{c=0,\theta=0}$ for samples A, I, and E. Rather similar values of dn/dc were obtained, respectively 0.144, 0.140, and 0.166 mL/g. This strengthens our confidence in the average value of dn/dc = 0.150 mL/g which we have used for calculating the other data in Table III.

Often, the c/H_θ vs. $\sin^2\theta/2$ plots were not linear. In some cases, however, the linearity of the plots was improved by extensive centrifugation of the solutions (cf. Experimental Section). Complete elimination of dust (possibly microgels) thus resulted in lower $\langle R_G^2\rangle$ values.

Samples G, F, and D. Typical c/H_θ vs. $\sin^2\theta/2$ plots for different concentrations in the range 0.05–2.9 g/100 mL for samples G, F, and D, having the lowest DP, are included in Figure 3. The indicated values of z reveal considerable dissymetry, increasing with polymer concentration. The c/H_0 vs. c plot for sample D reveals a plateau followed by a negative slope at higher concentrations. Absolute values of $(c/H_0)_{c=0}$ (Table II) converted to molecular weights (Table III, third column) indicate M_w values larger by a factor from 3 to 8 than those determined in CED (first column in Table III). Thus, association occurs in the concentration range investigated and stable aggregates appear to persist to $c \rightarrow 0$. This effect appears to be larger for sample G, which has a lower DP. (The term "aggregation" will be used when no dissociation equilibrium is evident, and "association" when the opposite is observed.[15]) Note that the viscosity data do not reveal such an effect. The value of $\langle R_G^2\rangle^{1/2}$ for sample D appears larger (by a factor ~2.3) than expected for a rod having a length equal to the contour length L of an extended chain with DP = 155 ($L = 155 \times 5.14$ Å, the latter figure being the projection of the residue along the axis of the 2_1 chain occurring in the various polymorphic forms of crystalline cellulose[16]). For a rod, the following relationship applies:[17]

$$\langle R_G^2\rangle = L^2/12 \qquad (6)$$

Sample A. Typical data for sample A, which was examined by using a series of stock solutions having different C_p, are included in Figure 4. The range of C_p is 0.3–7.2% and the range of concentration investigated by light scattering (Table II) is ~0.1–3.0 g/100 mL. For all values of C_p investigated, at low enough concentration ($c \leq 1$ g/100 mL) there is a region where c/H_θ does not greatly vary with θ, with negligible dissymetry ($z \leq 1.1$). The extrapolation of c/H_θ to $c \rightarrow 0$ yields an average value of 3.5×10^{-5}, irrespective of C_p, indicating a much smaller M_w than for samples G, F, and D in spite of the larger DP of sample A. The observed value of M_w is similar (Tables II and III) to that deduced from $[\eta]$ in CED. In this region the virial coefficient is positive and the overall data indicate the absence of association or aggregation. Above c ~1.0 g/100 mL, association sets in, as revealed by the increase of dissymetry and the downward trend of c/H_0 vs. c.

Sample C. The data for sample C are shown in Figures 5 and 6. This sample exhibits dissymetry even at $c \rightarrow 0$, and moreover, there is now evidence of an effect of the concentration, C_p, of the stock solution on the occurrence of aggregation. When $C_p = 0.3\%$ the light scattering data included in Figure 5 reveal no aggregation or association (in Figure 5 $(c/H_\theta)_{c=0}$ is plotted vs. $\sin^2\theta/2$, and (c/H_0) is plotted vs. c). In the concentration range 0.03–0.12 g/100 mL, the virial coefficient is positive and M_w (Table III) is consistent with the value deduced from $[\eta]$ in CED. The radius of gyration (~375 Å) is smaller than the value (~670 Å) predicted by eq 6 for a rod having DP = 449. It allows a determination of a persistence length $q \simeq 180$ Å ($q = 3\langle R_G^2\rangle/L$) which is comparable with that deduced from measurement of $[\eta]$ for nonaggregated samples.[18]

When $C_p = 3\%$, the Zimm plot in Figure 6, which includes data in the concentration range up to ~0.2 g/100 mL, reveals the occurrence of stable aggregated species not influenced by the concentration (cf. the positive B value). The light scattering molecular weight (Table III) suggests an average of ~7 molecules per aggregated particle. The observed radius of gyration (1160 ± 200 Å) is within a factor of 1.7 from that deduced with eq 6 ($\langle R_G^2\rangle^{1/2} \simeq 670$ Å) corresponding to an extended chain with DP = 449. (Evaluation of DP from alternative forms[6] of eq 1 could result in DP larger than those reported by up to 20%. Correspondingly, the calculated $\langle R_G^2\rangle^{1/2}$ for sample C could be as high as ~800 Å, reducing to a factor of ~1.3 the discrepancy with the lowest figure obtained from experiment.) When $C_p = 3\%$ and the light scattering measurements are performed in the concentration range above ~0.3%, the linearity of the Zimm plot breaks down. However, the apparent R_G, the dissymetry, and the apparent M_w do not change, and d(c/H_0)/dc remains positive, suggesting only a limited increase of the degree of association. Thus, sample C at $C_p = 3\%$ offers a clear case of aggregation not superimposed on association. Note that the reduction of intrinsic viscosity for sample C when C_p is increased from 0.3% to 3% is in line with the formation of compact aggregates.[19]

Samples I, B, and E. There are two other samples (I and B) which have DP similar to that of sample C. The data of Figure 5 and Table II show that in the concentration range below 0.11 g/100 mL, sample I prepared at C_p = 3% is molecularly dispersed as sample C was when prepared at C_p = 0.3%. Sample B, instead, prepared at C_p = 0.2%, shows the same type of stable aggregation (superimposed, however, on some association) as sample C prepared at C_p) = 3%. While the concordance of the M_w and $\langle R_G^2 \rangle$ values for the molecularly dispersed and the aggregated species of samples C, I, and B is gratifying, it is surprising to note the different extent of aggregation in these samples. Also surprising is the observations that sample E (Figure 5 and Table III), which has the largest DP of all samples investigated, yielded molecular dispersion when prepared at C_p = 0.2% in the concentration range 0.01–0.12 g/100 mL. Note, in fact, its low dissymetry, a M_w in line with the DP deduced from $[\eta]$ in CED, a positive virial coefficient, and a radius of gyration (~500 Å) smaller than that calculated (~1100 Å) from eq 6. Note, however, that sample E could not be completely dissolved when we attempted to use higher C_p.

These surprising effects indicate that, in addition to DP, there is at least another factor which controls dissolution of cellulose. All the data discussed above point to a significant role of the acid hydrolysis (often performed by the producer) in the case of samples G, F, D, C, and B. All samples which were exposed to acid hydrolysis exhibited aggregation persisting even at $c \rightarrow 0$, the effect being larger the lower the DP (and thus the extent of hydrolysis). A possible interpretation of this effect may be related to the increase of the degree of crystallinity which has been reported upon acid hydrolysis.[20] Hydrolysis occurring at bonds located in regions of relative disorder may facilitate dissolution due to a reduction of DP, leaving largely undisturbed the strong intermolecular contacts responsible for aggregation. Other treatments (those involved in the preparation of Kraft pulps and, particularly, of rayon) appear instead to promote disruption of the latter forces unless DP, or C_p, is too large. When achieved, molecular dispersion appears to be followed by association when concentration is increased.

The evaluation of the extent of association from parameters measured at $c > 0$ is of a limited significance. For sample A, the large dissymetry and the linearity of the c/H_θ vs. $\sin^2 \theta/2$ plot observed at high concentration (c = 3.0 and 2.4 g/100 mL at C_p = 5% and 7.2%, respectively; cf. Figure 4) allow a tentative evaluation of the apparent radius of gyration corresponding to the associated species at $c > 0$. We obtain $\langle R_G^2 \rangle_{app}^{1/2} \sim 1600$ Å. Similarly from the extrapolation to $\theta = 0$ of c/H_θ vs. $\sin^2 \theta/2$, we obtain an apparent M_w of the associated species of ~150 000. The data could suggest rather irregular patterns of association with molecules not in registry along the chain axis. For sample D at c = 2.86 g/100 mL we obtain $\langle R_G \rangle_{app}^{1/2} \sim$ 1400 Å and $(M_w)_{app} \sim 400\,000$.

Effect of LiCl and Temperature. The remaining data illustrate the role of LiCl concentration and temperature on the stability of the aggregates. The solution of sample A with C_p = 3% and C_s = 7.8% exhibits (cf. Table II) dissymetry values larger than those corresponding to the same solution at C_s = 5%. The effect is particularly large at high c, when z values up to 3.7 are observed with 7.8% LiCl. The c/H_0 vs. c plot (Figure 7) for sample C prepared at C_P = 0.3% shows a more pronounced downtrend at high c when C_s is larger. These effects reveal an increased association when LiCl is increased between 5% and 7.8%.

The most dramatic effect of the salt concentration is that exhibited in the two lower sections of Figure 7. It will be recalled that sample C prepared at C_p = 3% showed stable aggregation down to $c \rightarrow 0$, and negligible interaggregate association, when C_s = 5%. The data in Figure 7 illustrate that, at C_s = 7.8%, sample C (C_p = 3%) is, instead, molecularly dispersed. The value of $[\eta]$ (Table II) and the values of M_w, B, and $\langle R_G^2 \rangle$ (Table III) are comparable with the values obtained for the same sample prepared at C_p = 0.3% and C_s = 5%. Thus, it appears that increasing LiCl concentration has the unexpected effect of promoting disaggregation and favoring association.

The effect of temperature on the stability of the aggregates stable to $c \rightarrow 0$ was investigated for sample C having C_p = 3%. The results are illustrated in Figure 8 for a solution having c = 0.3 g/100 mL. A given solution was exposed to higher and higher temperatures up to 120 °C. The solution was maintained to each temperature for lengths of time up to 2h, allowed to slowly cool overnight, and then subjected to light scattering measurements at 25 °C. The results indicate that the size of the aggregates is essentially unchanged by temperature variations in the range 25–120 °C. Degradation explains the results obtained at 165 °C with a fresh solution.

Concluding Remarks

Particularly in the case of sample C prepared at C_p = 3% and C_s = 5%, the data reveal the occurrence of aggregates which act as entities stable to $c \rightarrow 0$, with negligible interaggregate association. The aggregated species appear to be composed of about 7 cellulose chains. Considering the relatively small difference between the measured $\langle R_G^2 \rangle$ and that expected for a fully stretched molecule (consider also the effect of increasing clarification on reducing $\langle R_G^2 \rangle$), the chains in the aggregated particle may be packed side-by-side in the fully extended conformation. The strength of the forces responsible of this aggregation is well documented by the stability of these particles up to temperatures close to degradation. These aggregates are probably survivors of the native structure (where a larger fibril with a 35-Å diameter is often observed[16]).

Stable aggregation of the above type is common with samples which were subjected to acid hydrolysis and may be accompanied by interaggregate association. With samples which received other treatments (particularly regenerated cellulose), molecular dispersion occurs even at C_s = 5%, but only if the DP is not too large and very dilute solutions are considered. In these cases, intermolecular association occurs at intermediate concentrations. However, it is not simple to obtain a measure of the size of associated species which do not persist at $c \rightarrow 0$. Apparent values of M_w and $\langle R_G^2 \rangle$ suggest more irregular patterns of interchain contacts than observed with the stable aggregates.

LiCl promotes the destabilization of the stable aggregates through specific interactions resulting in the formation of pseudocomplexes involving DMAc, but no net charge. However, increasing LiCl concentration also favors the association of solvated cellulose.

The evaluation of the persistence length of molecularly dispersed cellulose and the correlation between chain rigidity, aggregation, and mesophase formation are presented in the accompanying paper.[18]

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Registry No. Cellulose, 9004-34-6; LiCl, 7447-41-8; DMAc, 127-19-5.

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Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 4. Cellulose in *N,N*-Dimethylacetamide–Lithium Chloride

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ABSTRACT: A study of the solubility and mesophase formation of cellulose in *N,N*-dimethylacetamide (DMAc) containing from 2% to 10% LiCl is reported. The cellulose samples and the method of preparation of the solutions are those described in the preceding paper where a study of dilute solution parameters and of aggregation was reported. The solubility of all samples increases with LiCl concentration. However, for several samples the solubility is too low to allow the attainment of the critical concentration for mesophase formation. Aggregated samples prepared by acid hydrolysis never attain the mesophase. The possibility of observing the latter at high LiCl content is confined to samples which show molecular dispersion in dilute solution and DP below ~600. Even in these cases the cholesteric phase is often metastable with respect to the crystal. The critical concentration increases with LiCl content. From the preceding paper we know that irregular patterns of association occur at these concentrations. The interpretation of this complex situation in terms of independent or associated particles is discussed.

In the first two papers of this series we investigated the liquid crystallinity of (hydroxypropyl)cellulose (HPC) in *N,N*-dimethylacetamide (DMAc)[1] and in dichloroacetic acid (DCA).[2] The results could be interpreted in terms of existing theories for semiflexible chains composed of rigid segments connected by flexible joints.[3] Basically, the HPC/DMAc system approached the behavior expected for independent and monodisperse rods[3] having an axial ratio corresponding to the Kuhn statistical link. The occurrence of a small degree of soft interaction[4] had to be postulated in order to obtain complete agreement between the theoretical and experimental values of the critical volume fraction.

In the accompanying paper[5] (part 3) we reported a light scattering and viscosity study of unsubstituted cellulose dissolved in DMAc + LiCl. Cellulose does not present the problems associated with the nonuniform substitution of HPC and also appears to be a somewhat more rigid polymer than the latter. However, the above results show that considerable aggregation occurs depending, in a nonanticipated manner, upon sample preparation, molecular weight, LiCl concentration, and polymer concentration.

Studies with cellulose, particularly with its concentrated solutions, have been hampered by its poor solubility. Exotic solvents such as *N*-methylmorpholine *N*-oxide,[6,7] trifluoroacetic acid + chlorinated alkanes,[8] liquid ammonia + NH_4SCN,[9] and DMAc + LiCl[10] have been reported to dissolve cellulose at concentrations at which the mesophase may be formed. For some of the above solvents, however, degradation is appreciable, while for others the occurrence of a true mesophase was not fully investigated. In no case was an attempt made to correlate the critical volume fraction with dilute solution data obtained in the same solvent. In this paper we report a study of mesophase formation of cellulose in DMAc + LiCl and discuss the problems associated with the occurrence of aggregation.

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