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Solution Studies of Cellulose in Lithium Chloride and *N*,*N*-Dimethylacetamide

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ABSTRACT: The dissolution process and some solution properties of cellulose in mixtures of lithium chloride (LiCl) and *N*,*N*-dimethylacetamide (DMAc) are discussed. Dilute solution properties were measured by viscometry, low-angle laser light scattering and quasi-elastic light scattering. The following Mark–Houwink–Sakurada (MHS) equation and the relationship between the intrinsic viscosity and the *z*-average radius of gyration $\langle S^2\rangle_z^{1/2}$ were established: $[\eta] = (1.278 \times 10^{-4})M_w^{1.19}$ (cm^3/g) and $\langle S^2\rangle_z^{1/2} = (6.48 \times 10^{-10})M_w^{0.74}$ (cm) for cellulose in 9% LiCl/DMAc at 30 °C. On the basis of the light-scattering and viscosity data, the conformation parameter $\sigma = 6.71$, the characteristic ratio $C_\infty = 91.9$, and the persistence length $q = 252 \times 10^{-8}$ (cm) were calculated. Estimations of the MHS equation and the chain dimensions reveal that the LiCl/DMAc solvent greatly enhances the stiffness of the cellulose backbone. Liquid crystalline behavior is observed for solutions at the solubility limit (~15%) by the appearance of an anisotropic phase induced by shearing.

Introduction

In the past, facile characterization and derivatization of unmodified cellulose has been hampered by the lack of suitable nondegrading solvents. The initial discovery in our laboratories of cellulose solubility in lithium chloride/*N*,*N*-dimethylacetamide (LiCl/DMAc) solutions led to the preparation of a number of derivatives[1-4] and the study of the mechanism of dissolution.[5] Recently, we reported evidence for lyotropic mesomorphicity at concentrations approaching the solubility limit.[6] In this work, we present details of solution behavior, an estimation of the molecular dimensions, and additional evidence for a lyotropic liquid crystalline phase in this solvent system.

While a number of cellulose derivatives form lyotropic mesophases,[7] unmodified cellulose has been less suitable due to its poor solubility. Cellulose apparently requires highly interactive solvents for complete dissolution. Mesomorphic solutions of cellulose have been reported by Chanzy and Peguy[8] utilizing a water/*N*-methylmorpholine *N*-oxide solvent system and by Patel and Gilbert[9] in mixtures of trifluoroacetic acid and chlorinated alkanes. By comparison, LiCl/DMAc is apparently nondegrading to cellulose and could be of significance in future commercial developments.

The LiCl/DMAc solvent has been utilized to form films and fibers of chitin,[10] cellulose,[11,12] and aromatic polyamides.[13-18] The implications of enhanced physical properties of cellulose films and fibers formed from liquid crystalline solutions, applications of a variety of cellulose characterization techniques, and the demonstrated utility for homogeneous solution reactions have prompted our continuing investigations.

Experimental Section

Cellulose Sources. The cellulose samples used in this study were from several different sources and representative of a large molecular weight range. PC-1 and PC-3 are catalog no. 0230 and 4853 from Polysciences, Inc. PC-2, PC-5, and PC-6 are catalog no. 1529, 1525, and 1528, respectively, from the J. T. Baker Chemical Co. PC-4 is cellulose powder CF1 from Whitman, Ltd. PC-7 is a regenerated viscose cellulose yarn. PC-8 and PC-9 are buckeye cotton 505 and buckeye cotton ER-6500 from the James River Corp. All samples are unfractionated, and no information

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about the polydispersity is available.

Solvents. Nine percent (w/w) solutions of lithium chloride (LiCl), no. 2370 reagent grade from the J. T. Baker Chemical Co., and *N,N*-dimethylacetamide (DMAc), no. 18 588-4 from Aldrich and distilled over CaH_2, were made by dissolving the appropriate amount of LiCl in DMAc at 100 °C. The solvent was allowed to cool to room temperature before use. Reagent-grade methanol was distilled over anhydrous calcium sulfate before use. Reagent-grade 1-methyl-2-pyrrolidinone (NMP), no. RO53 from the J. T. Baker Chemical Co., was used with no further purification.

Cellulose Dissolution. Since dried cellulose does not go into LiCl/DMAc solutions at room temperature, two dissolution techniques have been developed in our laboratory. The first was previously described by McCormick.[1] Cellulose soltuions were prepared by suspending cellulose (~1–3%) in 3–9% LiCl/DMAc. The mixture was heated to 150 °C and allowed to slowly cool to room temperature. The second technique involved a swelling procedure followed by solvent exchange. Twenty to fifty grams of cellulose powder or cotton linters were suspended overnight in 500 mL of deionized water. The mixture was placed in a crucible filter, and the excess water was removed. Four hundred mL of dried methanol were added for 30 min and then removed. Four such exchanges were done with dried methanol and, finally, five exchanges with DMAc. After the DMAc treatment, the sample was dried by a stream of nitrogen overnight.

The swollen cellulose sample (0.1–30.0 g, approximately 0.05–15.0 g actual cellulose weight) was added to 100-mL 9% LiCl/DMAc. The swollen cellulose went into solution at room temperature, and concentrations of up to 15% have been achieved. Complete solutions of 1–5% have been achieved in less than 1 h, while high concentrations of 6–15% take 24–48 h. The actual concentration of cellulose in the swollen material was determined by drying several 1-g samples in a vacuum oven at 60 °C for 48 h.

Light Scattering. A Chromatix Model KMX-6 low-angle laser photometer was used for both classical and quasi-elastic light-scattering (QLS) measurements. The KMX-6 has a helium–neon laser light source with an incident beam of 633 nm. For classical light-scattering measurements, data were collected at a forward angle of 6°–7° and a 0.2-mm-diameter aperture. At small forward scattering angles and low solute concentration, the relationship between the Rayleigh factor and the weight-average molecular weight is

$$Kc/R_\theta = 1/M_w + 2A_2c \qquad (1)$$

where c is the solute concentration in g/mL, A_2 is the second virial coefficient, R_θ is the excess Rayleigh factor, and K is the polymer optical constant defined as

$$K = (2\pi^2n^2/\lambda^4N)(dn/dc)^2(1 + \cos^2\theta) \qquad (2)$$

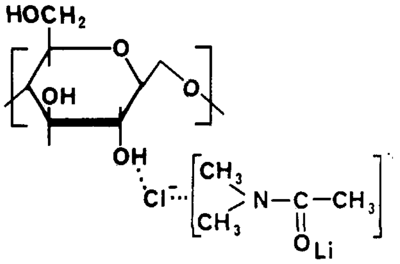
where n is the refractive index of the solution, λ is the incident beam wavelength, N is Avogadro's number, θ is the angle of scattered light collection, and dn/dc is the specific refractive index increment. A Chromatix Model KMX-16 differential refractometer was used to measure the specific refractive index increment.

A 64-channel Langley-Ford Model LFI-64 digital correlator was used to produce an autocorrelation function that was analyzed to yield a value for the diffusion coefficient. The data were collected at a forward angle of 6°–7° and a 0.05-mm-diameter aperture. A sample time of 0.5 ms and a data acquisition time of 500 s were typical analysis conditions. All light-scattering measurements were made at 30 °C and an incident wavelength of 633 nm.

Solution Viscosity. The intrinsic viscosity was determined by using a Cannon-Ubbelohde 4-bulb shear dilution viscometer. All measurements were made in LiCl/DMAc solvent system at 30 °C. Relative viscosities of the concentrated solutions were determined with a Brookfield Model LVT viscometer.

Nuclear Magnetic Resonance. All ^1H and ^{13}C NMR spectra were measured with a JEOL FX 90Q spectrometer with a magnet operating at 21 100 G. The spectrometer has a C/H dual probe system operating at 89.55 MHz for ^1H and 22.5 MHz for ^{13}C. Tube sizes were 5-mm o.d. and 10-mm o.d. for ^1H and ^{13}C, respectively. Spin–lattice relaxation times were determined through an inversion recovery technique with an exponential fit. TMS was used as a standard.

Chart I
Proposed Mechanism for the Dissolution of Cellulose in the LiCl/DMAc Solvent System



Microscopy. The optical textures of the polymer solutions were studied on a Leitz polarizing microscope at a magnification of 320×.

Results and Discussion

Mechanism of Dissolution. The dissolution of cellulose in *N,N*-dimethylacetamide and its cyclic analogue 1-methyl-2-pyrrolidinone, appears to be highly specific, requiring the addition of lithium chloride. In previous experiments we found other lithium salts including bromide, iodide, nitrate, and sulfate to be ineffective. Likewise, the cations sodium, potassium, barium, calcium, and zinc were ineffective as chloride salts. Additionally, *N,N*-dimethylformamide, despite its similarity in structure and solubility parameter, failed to produce cellulose solutions with added LiCl.

The mechanism we believe to be operative for cellulose dissolution is shown in Chart I. The hydroxyl protons of the anhydroglucose units are associated with the chloride anion by hydrogen bonding. The chloride ion is associated with a $Li^+(DMAc)_x$ macrocation. The resulting charge–charge repulsions[19,20] or a bulking effect[21] would tend to allow further solvent penetration into the polymer structure. The rate at which cellulose dissolves appears to be highly dependent on the number of intermolecular hydrogen bonds present in the initial sample. Disruption of hydrogen bonds (by swelling in polar or hydrogen bonding solvents or by heating) increases dramatically the rate of dissolution.

Evidence for the proposed mechanism comes from NMR analysis of model alcohols in LiCl/DMAc solutions and comparison with an analogous mechanism proposed by Panar and Beste[22] for dissolution of poly(1,4-benzamide). For that system the amide hydrogens (rather than the hydroxyl hydrogens, in our case) were shown to hydrogen bond to the chloride–macrocation complex of DMAc with Li^+.

The formation of the $Li^+(DMAc)_x$ macrocation is well documented by evidence from ^{13}C NMR studies,[5,23,24] crystallographic studies,[25,26] and thermodynamic measurements.[26,27] Other cations apparently do not complex as strongly; for example, the carbonyl carbon of DMAc shows little change in its chemical shift in the presence of added $ZnCl_2$ but experiences a downfield shift of 1.0 ppm in the presence of LiCl. The failure of other salts of lithium such as LiBr and LiI to induce dissolution of cellulose in DMAc seems to suggest the important bonding role specifically played by the chloride anion in Chart I and apparently eliminates an alternative proposal of cation binding to the hydroxyl oxygen.

To investigate the mechanism further, ^1H NMR chemical shift studies were conducted on a series of model hydroxyl-containing compounds in DMAc and in its cyclic analogue, NMP, in order to note the effect of added LiCl and LiBr. The chemical shift values of the proton on the hydroxyl group of C-4 of glucose in a 0.3 M solution (Figure

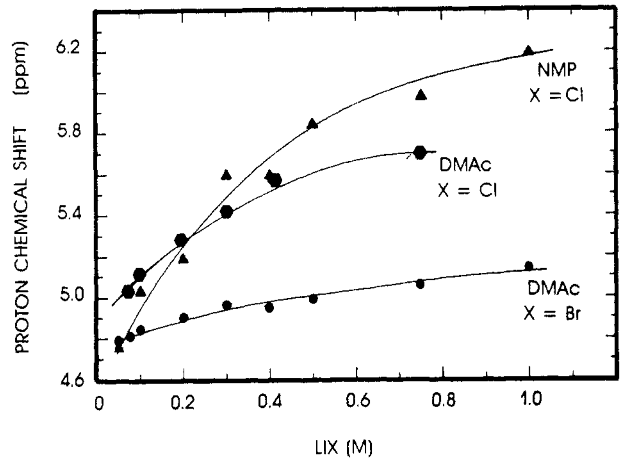


Figure 1. Effect of lithium salt concentration on the chemical shift of the C-4 hydroxyl proton of glucose in DMAc and NMP.

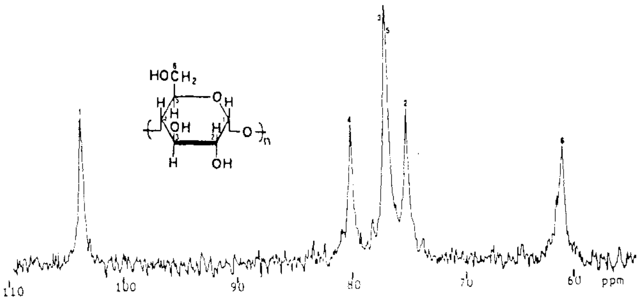


Figure 2. Proton-decoupled ^{13}C NMR spectra of a 3% (w/v) solution of cellulose in 5% LiCl/DMAc with 1-s pulse repetition, 90° pulse angle, and 8000 transients, obtained at 90 °C.

Table I
Spin-Lattice Relaxation Times and NOE for Cellulose[a] in LiCl/DMAc

carbon	T_1[b]	NOE[c]
1	0.78	1.4
2	0.72	1.4
3, 5	0.81	1.4
4	0.72	1.4
6	0.44	1.5

[a] Polymer concentration is 5% (w/v) in 5% LiCl/DMAc at 90 °C. [b] 10%. [c] 0.2 unit.

Table II
Intrinsic Viscosity [η] and Huggins Constant *k'* of the Various Cellulose Samples in 9% LiCl/DMAc at 30 °C

sample	[η], cm^3/g	*k'*
PC-1	148	0.35
PC-2	167	0.36
PC-3	175	0.31
PC-4	221	0.37
PC-5	226	0.32
PC-6	399	0.47
PC-7	545	0.51
PC-8	713	0.45
PC-9	1164	0.52

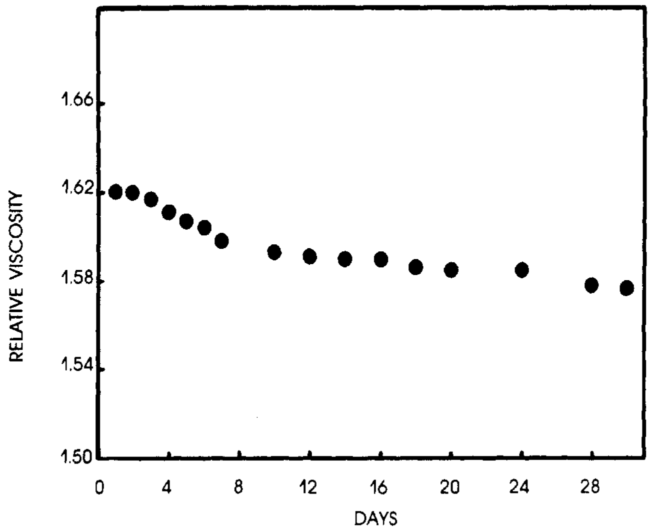


Figure 3. Relative viscosity vs. time of cellulose (PC-5) in 9% LiCl/DMAc at 30 °C.

1) changed 1.3 ppm in NMP and 0.7 ppm in DMAc as the LiCl concentration was changed from 0 to 1.0 and to 0.75 M, respectively. Distinct resonance signal shifts were observed for each of the other hydroxyl protons, indicating that the complex is acting equally on all of them and the complex occurs at the three available hydroxyls of cellulose. Similar behavior was also observed for hydroxyl protons of poly(vinyl alcohol) and ethanol. The magnitude of these downfield shifts is consistent with the proposed hydrogen bonding of the chloride anion with the hydroxyl protons. The smaller chemical shift changes for the LiBr solutions indicate a much reduced tendency for this type of association with the bromide anion. It might be argued that a dilution effect during titration could be responsible for the observed downfield shifts. However, our observation of no change in chemical shift for the anomeric hydroxyl proton of glucose seems to rule out that possibility.

Figure 2 is the proton-decoupled ^{13}C NMR spectra of a 3% cellulose solution in 5% LiCl/DMAc at 90 °C first reported by our laboratories.[5] Later El-Kafrawy[28] reported a similar spectra. Five major peaks are readily identified. Their apparent sharpness indicates that the LiCl/DMAc solution is indeed a "true" solution for cellulose. The five cellulose peaks can be assigned by comparing them with other cellulose solutions[29] and to solid-state spectra.[30-32] The C-1 carbon, the most deshielded, is assigned to the peak at 103.5 ppm. The other easily assignable peak is the C-6 carbon at 60.7 ppm. The three interior peaks from the low to high field have been assigned to the C-2, the C-3 and the C-5 overlap, and the C-4 carbon, respectively.

The measured spin-lattice relaxation times and the NOE values for the five cellulose peaks are given in Table I. All of the methine carbons give the same T_1 within experimental error. The methylene T_1 is approximately one-half of the values for the methine carbons, indicating highly restrained isotropic motion. Since this polymer is likely relaxed entirely through dipole-dipole relaxation, the reduced NOE values denote a violation in the extreme narrowing condition.[33] Studies of the effect of LiCl concentration on the spin-lattice relaxation times of cellulose indicate that the T_1's decrease with increasing LiCl concentration. This is a result of increased solvent viscosity shown by the LiCl/DMAc system.[34]

Dilute Solution Studies. The aging effects of cellulose solutions have been studied by monitoring the relative viscosity as a function of time (Figure 3). Only a 2–3% loss in viscosity was observed after 30 days for a 0.005 g/cm^3 solution maintained at 30 °C. It is likely that these slight changes are due to changes in inter- and intramolecular hydrogen bonding rather than to chain degradation. This stability is in direct contrast to a number of cellulose solvents that rapidly degrade the macromolecular backbone.

Values of intrinsic viscosity [η] and the Huggins constant, *k'*, were determined for each cellulose sample by plotting reduced viscosity vs. concentration (Table II). A typical Flory–Huggins plot is shown in Figure 4 for sample

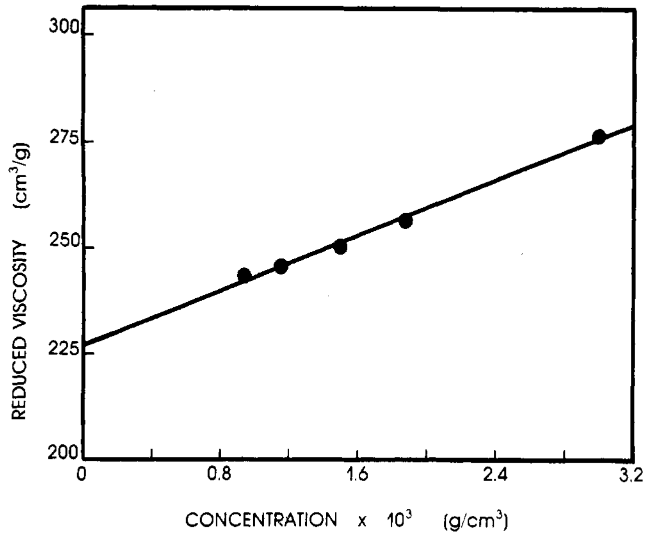


Figure 4. Reduced viscosity vs. concentration of PC-5 in 9% LiCl/DMAc at 30 °C ($[\eta] = 226$ cm³/g).

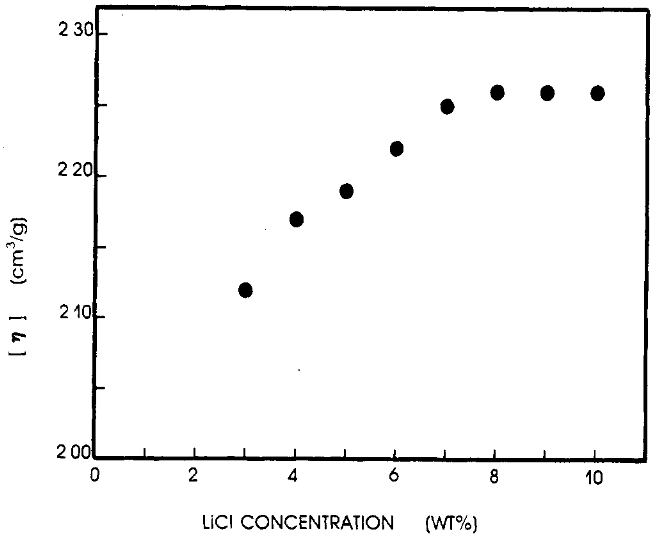


Figure 5. Intrinsic viscosity vs. lithium chloride concentration (w/w) for PC-5 at 3–10% salt concentration.

PC-5 in 9% LiCl/DMAc at 30 °C. Values obtained in 9% LiCl/DMAc indicate k' values ranging from 0.3 to 0.5 and $[\eta]$ values from 148 to 1164 cm³/g. For dilute cellulose solutions containing from 3% to 11% (saturation) LiCl such plots are linear. The magnitudes of $[\eta]$ seem to reflect the relative order of molecular weights expected on the basis of source and pretreatment. For example, the cotton samples PC-8 and PC-9 have intrinsic viscosities of 713 and 1164 cm³/g as compared to wood pulp and rayon which are substantially lower.

A plot of intrinsic viscosity vs. weight percent LiCl in DMAc is shown in Figure 5. At LiCl concentrations of less than 3%, insoluble particles appear to be suspended in the solvent even at low concentrations of cellulose (~ 0.005 g/cm³). There is a slight increase in intrinsic viscosity from 3% to 6% LiCl concentration. This could be due to further dissolution of gel particles. At LiCl concentrations of greater than 6%, complete dissolution of cellulose occurs. Apparently a critical number of complexed sites are required for dissolution.

Light Scattering and Second Virial Coefficient. Figure 6 shows a typical plot of Kc/R_θ vs. concentration of PC-5. Data were analyzed by least-squares straight-line fit; M_w was calculated from the intercept and A_2 from the slope. Generally, five or six concentrations of each polymer were used. Reproducibility for M_w and A_2 for the same polymer was approximately 10%. Table III gives a list of the experimental results for cellulose in 9% LiCl/DMAc. The weight-average molecular weights determined are consistent with those expected from the various sources. Samples PC-8 and PC-9 from cotton exhibited the highest molecular weights of 4.6×10^5 and 7.0×10^5, respectively. The pulp cellulose and rayon samples had lower values in the $1.2–3.5 \times 10^5$ range. Values of A_2 ranged from 5.3 to 3.7×10^{-3}, indicating an extended or a semirigid nature of the molecular backbone.

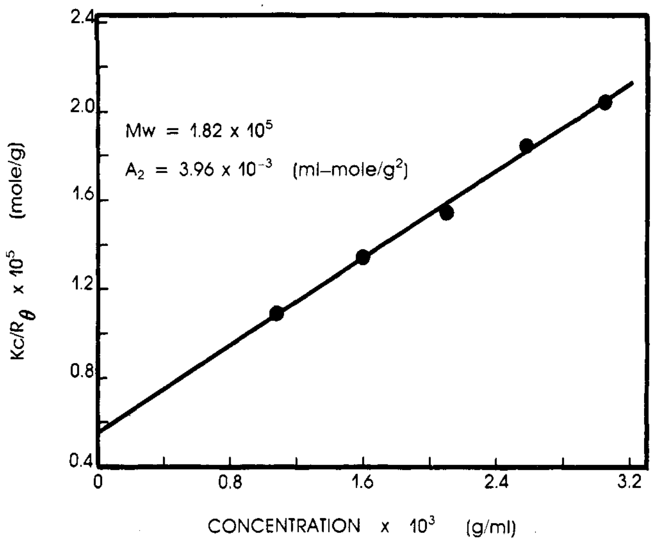


Figure 6. Kc/R_θ vs. concentration for cellulose (PC-5) in 9% LiCl/DMAc.

Table III
Specific Refractive Index Increment dn/dc, Weight-Average Molecular Weight M_w, and Second Virial Coefficient A_2 of the Various Cellulose Samples in 9% LiCl/DMAc

sample	dn/dc	$A_2 \times 10^3$, cm³ mol g⁻²	M_w
PC-1	0.0403	5.34	125 000
PC-2	0.0698	4.92	152 000
PC-3	0.0559	4.77	162 000
PC-4	0.0550	4.20	178 000
PC-5	0.0607	3.96	182 000
PC-6	0.0537	3.93	320 000
PC-7	0.0478	3.60	354 000
PC-8	0.0560	3.51	463 000
PC-9	0.0575	3.69	700 000

We should point out that the specific refractive index increment, dn/dc, of these solutions did show some variance. Repeated determinations confirmed these differences. It is not clear whether these differences are due to structural defects along the backbone resulting from the past history of the cellulose sample or from experimental difficulties due to incomplete sample equilibration. The latter is especially difficult to assess since most conventional membranes used for dialysis prior to dn/dc measurements are soluble in the LiCl/DMAc solvent system.

Mark–Houwink–Sakurada Equation. Figure 7 shows a log–log plot of $[\eta]$ vs. M_w for cellulose in 9% LiCl/DMAc at 30 °C. The plot represented by a straight line suggested that the MHS equation

$$[\eta] = KM_w^{a} \qquad (3)$$

may be well established over the entire M_w range.

The parameters K and a were evaluated for the nine cellulose samples by using the least-squares method and gave a relationship of

$$[\eta] = (1.278 \times 10^{-4})M_w^{1.19} \qquad (4)$$

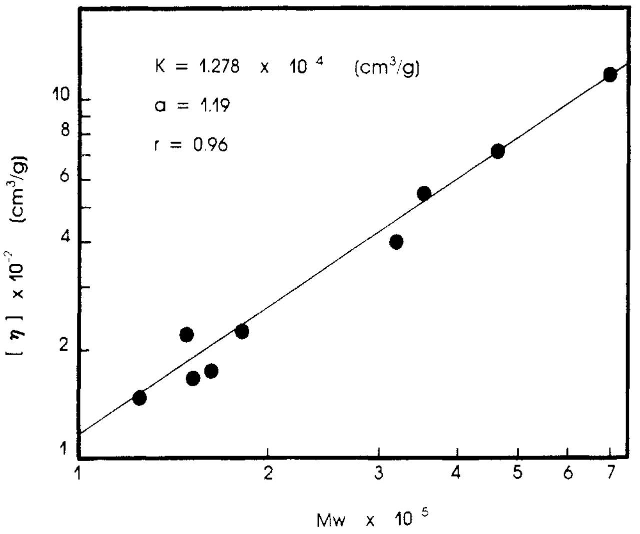


Figure 7. Intrinsic viscosity vs. weight-average molecular weight for cellulose in 9% LiCl/DMAc at 30 °C.

Typically, a values lie between 0.8 and 1.0 for cellulose and cellulose derivatives. The high a value is consistent with the proposed mechanism of dissolution. The cellulose chain should expand due to repulsive interactions of the chloride anions associated with the backbone.

Quasi-Elastic Light Scattering and Radius of Gyration. Diffusion coefficients were obtained from the autocorrelation function generated for each concentration of polymer used. Diffusion coefficients were extrapolated to 0 concentration of polymer to give the infinite diffusion coefficient D_0. The radius of gyration $\langle S^2\rangle_z^{1/2}$ was calculated by using the Stokes–Einstein relationship

$$D_0 = k_B T/6\pi\eta_0 R_H \tag{5}$$

where

$$R_H = \xi_f\langle S^2\rangle_z^{1/2} \tag{6}$$

k_B is Boltzmann's constant, T is the absolute temperature, η_0 is the viscosity of the pure solvent, R_H is the hydrodynamic radius, and ξ_f is a proportionality constant that relates the hydrodynamic radius to the radius of gyration (eq 6). ξ_f was determined via a modified analysis procedure proposed by Kok and Rudin[35] where D_0 can be expressed as

$$D_0 = (k_B T/6\pi\eta_0\xi_f)(\Phi'/M_w[\eta])^{1/3} \tag{7}$$

and $\Phi' = \Phi 6^{3/2}$. Flory's viscosity constant Φ and Φ' were determined by using the relationship derived by Ptitsyn and Eizner[36]

$$\Phi' = \Phi_0(1 - 2.63\epsilon + 2.86\epsilon^2)6^{3/2} \tag{8}$$

where Φ_0 is a universal constant equal to 2.86×10^{23}, $\epsilon = (2a - 1)/3$, and a is obtained from the Mark–Houwink relationship. The Flory constant is assumed to show no significant change with the molecular weight. Figure 8 is a plot of D_0 vs. $(k_B T/6\pi\eta_0)(M_w[\eta])^{-1/3}$ for cellulose in 9% LiCl/DMAc. The least-squares slope through these data in conjunction with a value of (1.13×10^{23}) mol^{-1} for Φ produced a value of 0.336 for ξ_f. Table IV gives a list of the measured diffusion coefficient at infinite dilution and the calculated radius of gyration for each cellulose sample. Figure 9 is a log–log plot of radius of gyration vs. molecular weight. The least-squares analysis gave the following relationship for the molecular weight dependence of the z-average radius of gyration:

$$\langle S^2\rangle_z^{1/2} = (6.48 \times 10^{-10})M_w^{0.74} \text{ (cm)}$$

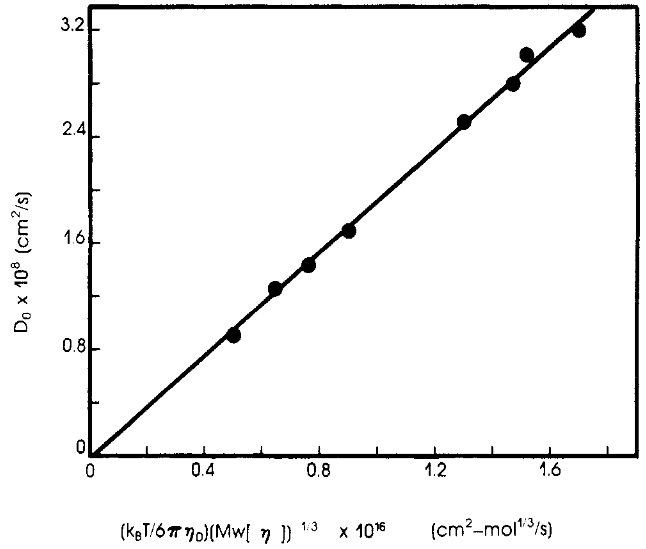


Figure 8. Diffusion coefficient at infinite dilution D_0 vs. $(k_B T/6\pi\eta_0)(M_w[\eta])^{-1/3}$.

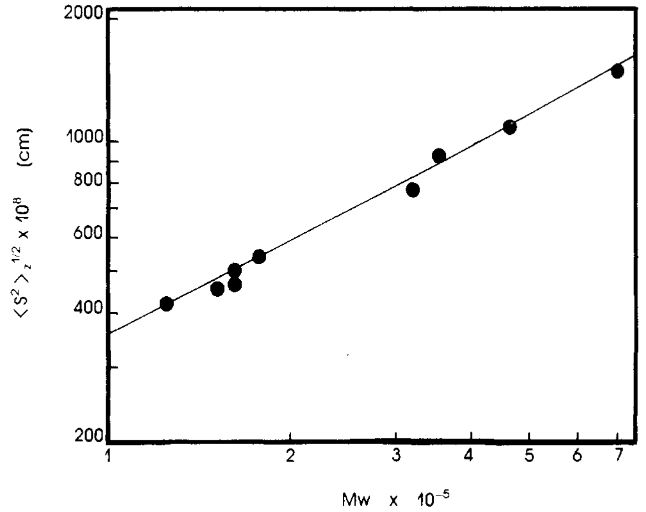


Figure 9. Z-average radius of gyration vs. weight-average molecular weight for cellulose in 9% LiCl/DMAc.

Table IV
Diffusion Coefficient at Infinite Dilution D_0 and Z-Average Radius of Gyration $\langle S^2\rangle_z^{1/2}$ Measured by QLS for Cellulose in 9% LiCl/DMAc

sample	$D_0 \times 10^8$, cm^2/s	$\langle S^2\rangle_z^{1/2} \times 10^8$, cm
PC-1	3.18	420
PC-2	2.93	455
PC-3	2.87	467
PC-4	2.48	539
PC-5	2.50	533
PC-6	1.75	768
PC-7	1.45	925
PC-8	1.24	1074
PC-9	0.92	1449

Unperturbed Chain Dimension. The unperturbed chain dimension, $A = (\langle R^2\rangle_0/M)^{1/2}$, $\langle R^2\rangle_0$ being the mean-square end-to-end distance in the unperturbed state, was estimated by using method 2B proposed by Kamide and Miyazaki[37] and other authors.[38-44] This method relates the linear expansion factor α_s to the radius of gyration in the unperturbed state $\langle S^2\rangle_0^{1/2}$:

$$\langle S^2\rangle_0^{1/2} = \langle S^2\rangle^{1/2}/\alpha_s \tag{9}$$

The linear expansion factor is obtained from M_w, A_2, and $\langle S^2\rangle_z^{1/2}$ data (assuming $\langle S^2\rangle_z^{1/2} = \langle S^2\rangle_w^{1/2}$) through use

Table V
Linear Expansion Factor α_s, Unperturbed Radius of Gyration $\langle S^2\rangle_0^{1/2}$, and Unperturbed Chain Dimensions A Calculated by Method 2B for Cellulose in 9% LiCl/DMAc

sample	α_s	$\langle S^2\rangle_0^{1/2} \times 10^8$, cm	$A \times 10^8$, cm
PC-1	1.06	396	2.74
PC-2	1.07	425	2.67
PC-3	1.07	436	2.65
PC-4	1.04	518	3.01
PC-5	1.04	512	2.94
PC-6	1.05	732	3.16
PC-7	1.03	898	3.70
PC-8	1.03	1043	3.75
PC-9	1.03	1407	4.12

Table VI
Conformation Parameter σ and Characteristic Ratio C_∞ of Cellulose in Various Solvents

polymer	solvent	σ	C_∞
cellulose	cadoxen	2.78	15.8
	FeTNa	4.70	45.2
	9% LiCl/DMAc	6.71	91.9

of a penetration function ψ derived by the Kurata–Fukatsu–Sotobayashi–Yamakawa theory[45]

$$\psi = zh_0(z) = (0.746 \times 10^{-25})A_2M^2/\langle S^2\rangle^{3/2} \quad (10)$$

where

$$zh_0(z) = 1 - (1 + 3.903z)^{-0.468}/1.828 \quad (11)$$

$$\alpha_s^3 = 1 + 1.78z \quad (12)$$

$$A = (6\langle S^2\rangle_0/M)^{1/2} \quad (13)$$

Table V lists the linear expansion, α_s, the radius of gyration in the unperturbed state, $\langle S^2\rangle_0^{1/2}$, and the unperturbed chain dimension, A, calculated by this method. The A values obtained were found to be higher than those of other cellulose and cellulose derivative solvent systems.

To further illustrate this, the conformation parameter σ and characteristic ratio C_∞ were determined by eq 14 and 15, respectively

$$\sigma = \langle R^2\rangle_0/\langle R^2\rangle_{0,\mathrm{f}} = A/A_\mathrm{f} \quad (14)$$

$$C_\infty = (\langle R^2\rangle/nl^2)_\infty \quad (15)$$

where A_f is the unperturbed chain dimensions of a freely rotating chain (A_f = (0.614 × 10^{-8}) cm when a bond length of (5.47 × 10^{-8}) cm and a bond angle of 110° are used),[37] A is the unperturbed chain dimensions pertaining to the highest molecular weight sample, $\langle R^2\rangle_0$ is the unperturbed end-to-end distance, $\langle R^2\rangle_{0,\mathrm{f}}$ is the unperturbed end-to-end distance of a freely rotating chain, n is the number of main-chain bonds, and l is the bond length. The values for σ and C_∞ were calculated to be 6.71 and 91.9, respectively, for cellulose (M_w = 700 000) in 9% LiCl/DMAc. These values indicate that cellulose in this solvent system has greatly extended unperturbed chain dimensions. Table VI illustrates the effect of solvent on the unperturbed chain dimensions when cellulose–LiCl/DMAc is compared to cellulose–cadoxen[37,46] and cellulose–FeTNa.[47] Rather large differences in the unperturbed chain dimensions are observed in different solvents for cellulose. The σ and C_∞ obtained here for cellulose–LiCl/DMAc are the maximum of these three systems of cellulose. Therefore, the complexing nature of the LiCl/DMAc solvent system greatly enhances the stiffness of the cellulose backbone.

Persistence Length. The persistence length, q, the axial ratio, x, and the critical volume fraction for a stable anisotropic phase, v_2^*, were estimated by using eq 16,[48–50] 17, and 18[51]

$$2q = (\langle R^2\rangle_0/L) \quad (16)$$

$$v_2^* = 8/x(1 - 2/x) \quad (17)$$

$$x = q/d \quad (18)$$

where L is the contour length and d is the diameter of the chain (assumed to be (8 × 10^{-8}) cm).[7] The persistence length was estimated to be (252 × 10^{-8}) cm. This corresponds to an axial ratio of 31.5 and a critical volume fraction of approximately 24%. It should be noted that this calculation does not consider the LiCl/DMAc complex as part of the macromolecular structure. A theoretical model for interactive solvents has not been developed; therefore, the calculated value for v_2^* is only an estimate.

Table VII
Persistence Length q of Cellulose and Other Rigid and Semirigid Polymer/Solvent Systems

polymer (DS)[a]	solvent[b]	$q \times 10^8$, cm	ref
cellulose	cadoxen	42	52, 46
	FeTNa	123	47
	9% LiCl/DMAc	252	this work
cellulose acetate (2.46)	DMAc	130	44
cellulose nitrate (2.91)	acetone	206	52, 53
cellulose carbanilate (3)	dioxane	140	54
(hydroxyethyl)cellulose	water	82	52, 55
(hydroxypropyl)cellulose	ethanol	85	56, 57
ethyl(hydroxyethyl)cellulose	water	92	52, 58
poly(1,4-benzamide)	H_2SO_4	400	59
poly(n-hexyl isocyanate)	THF	425	60
poly(γ-benzyl L-glutamate)	DMF	900	61

[a] DS = degree of substitution. [b] Cadoxen: cadmium ethylenediamine hydroxide; FeTNa: iron sodium tartrate; THF: tetrahydrofuran; DMF: N,N-dimethylformamide.

Table VII compares the q values of related polymer/solvent systems. The q values of cellulose, cellulose derivatives, poly(benzamide), and poly(n-hexyl isocyanate), all semirigid polymer/solvent systems, are larger than those for typical vinyl-type polymers (on the order of 7–8 × 10^{-8} cm) but markedly smaller than those for a stiff-chain polymer such as poly(γ-benzyl L-glutamate).

Liquid Crystalline Behavior. Concentrations of up to 15% (w/w) cellulose (M_w = 182 000) have been obtained thus far in our work. Above 15%, undissolved swollen particles are suspended in the viscous solution. According to theory, the concentration needed to form a stable anisotropic phase (~24%) appears to exceed the solubility limit. A pure anisotropic phase has not been observed; however, a biphasic region was observed after the application of a small shearing action to a thin layer of the sample between a microscope slide and cover slip (Figure 10). Under cross-polarizers, large birifrengent areas, a pattern of bright and dark occlusions, exhibited typical threaded nematic texture. The textures observed are similar to those reported by Chanzy and Peguy[8] in the water/N-methylmorpholine N-oxide system. The "mesophase" is stable with time and can be directionally oriented. This behavior is similar to that observed by Ciferri and Valenti,[62,63] who speculated for the polyterephthalamide of p-aminobenzhydrazide (X-500) in LiCl/Me_2SO solutions a flow-induced transition from the isotropic to the anisotropic phase. The shear stress apparently resulted in a reduction of the critical polymer concentration required for mesophase formation.

The viscosity vs. concentration behavior at low shear of cellulose (M_w = 182 000) in 9% LiCl/DMAc is shown in

Figure 10. Photomicrograph of 15% (wt) cellulose in 9% LiCl/DMAc showing a large birefringent region under cross-polarizers at 320× (reduced to 60% of the original).

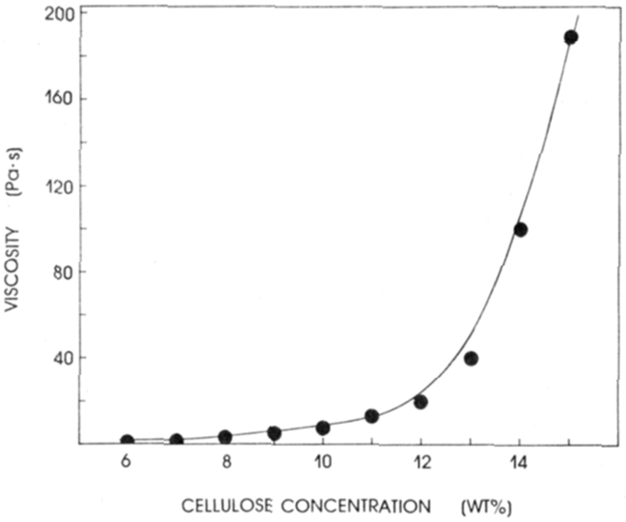


Figure 11. Relative viscosity vs. concentration (wt) at low shear for cellulose in 9% LiCl/DMAc.

Figure 11. A rapid increase in viscosity of 1 Pa·s at a concentration of 6% (w/w cellulose) to a value of 189 Pa·s at 15% was observed. The expected decrease in viscosity at some critical concentration of cellulose has not been observed, probably due to the limits of solubility or the difficulties of adequate mixing at these high viscosities. To date we have not been able to induce a transition to the anisotropic phase by shearing in a simple rotating cylinder viscometer.

Subsequent to our previous report[6] and initial submission of this manuscript, Ciferri[64] published optical rotary dispersion data and the phase diagram of cellulose in LiCl/DMAc. His results were consistent with our previous observation of anisotropic behavior. Ciferri also concluded that a metastable cholesteric mesophase occurred above the solubility limit (>17%). Therefore, we believe that the concentration at the solubility limit is in the pretransitional area, where the solution is mostly isotropic with anisotropic occlusions, and that shearing induces the appearance of the anisotropic phase.

Highly birefringent films and fibers with textures consistent with a highly developed cholesteric phase have been prepared by spinning LiCl/DMAc cellulose solutions into coagulation baths of water or methanol. Tensile strengths are comparable to those reported by Franks and Varga[65] for cellulose spun from cholesteric dopes in *N*-methylmorpholine *N*-oxide. In those cases, the cholesteric texture was preserved in the fibers after spinning. Presently, it is not clear to what extent, if any, the mesophase is responsible for the optical anisotropy of the oriented solution spun fibers.

Conclusions

It has been shown that the LiCl/DMAc solvent system is a highly specific, nondegrading solvent capable of dissolving 15% cellulose. The mechanism of dissolution appears to involve hydrogen bonding of the hydroxyl protons of cellulose with the chloride ion, which is in turn associated with the Li$^+$(DMAc) macrocation complex. Dilute solutions can be characterized easily via viscometry, low-angle laser light scattering, and quasi-elastic light scattering. Estimations of the Mark–Houwink–Sakurada equation and the unperturbed chain dimensions reveal that the LiCl/DMAc solvent system greatly enhances the stiffness of the cellulose backbone. Concentrated solutions demonstrate lyotropic liquid crystalline behavior, as evidenced by birefringence observed by polarizing microscopy. The appearance of a nematic phase from an isotropic solution is induced by shearing.

Studies are under way to further elucidate the effect of the molecular weight of cellulose in the development of lyotropic mesophases. In addition to the obvious interest in properties of films and fibers, studies continue on the utility of the LiCl/DMAc solvent for the characterization of unmodified cellulose and for the preparation of a wide range of cellulose derivatives from homogeneous solutions.

Registry No. FeTNa, 16070-48-7; NMP, 872-50-4; THF, 109-99-9; DMF, 68-12-2; DMAc, 127-19-5; LiCl, 7447-41-8; H_2SO_4, 7664-93-9; H_2O, 7732-18-5; cellulose, 9004-34-6; cellulose acetate, 9004-35-7; cellulose nitrate, 9004-70-0; cellulose carbanilate, 37251-21-1; (hydroxyethyl)cellulose, 9004-62-0; (hydroxypropyl)cellulose, 9004-64-2; ethyl(hydroxyethyl)cellulose, 9004-58-4; poly(1,4-benzamide), 24991-08-0; poly(*n*-hexyl isocyanate), 26746-07-6; poly(γ-benzyl L-glutamate), 25038-53-3; cadoxen, 14874-24-9; acetone, 67-64-1; dioxane, 123-91-1; ethanol, 64-17-5; 4-aminobenzoic acid homopolymer, 25136-77-0; γ-benzyl L-glutamate, 25014-27-1.

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