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(27) Madorsky[13] has shown that from isothermal measurements, an accurate value of E_d can be obtained if the residues have the same average MW and MWD (as the original sample). These conditions strictly hold only at 0% weight loss.
(28) Most of this chemical analysis was kindly provided by the Army Materials and Mechanics Research Center.
(29) Although the molecular weight–weight loss data were obtained from thermolysis at 350 ± 2 °C under vacuum, weight loss–time (isothermal degradation) data were obtained by degradation under vacuum at 355 °C. Still, the molecular weight–time results plotted in Figure 6 provide a good first approximation.

Mesophase Formation and Chain Rigidity in Cellulose and Derivatives. 1. (Hydroxypropyl)cellulose in Dimethylacetamide

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ABSTRACT: The phase diagrams of (hydroxypropyl)cellulose (HPC) in water at 20 °C and in dimethylacetamide (DMAc) between 20 and 130 °C were determined up to concentrations of $\sim$80% polymer. Phase equilibria were determined via optical microscopy, viscosity, ultracentrifugation, and analytical techniques. The molecular weight of the HPC samples investigated varied between 132 000 and 479 000. Fractions of these samples were used to determine the persistence length of HPC in DMAc from intrinsic viscosity measurements at 25 and 70 °C. The critical polymer volume fraction v_2* at which a cholesteric mesophase appears is $\sim$0.35 at room temperature and increases, in DMAc, with temperature. v_2* is not greatly affected by molecular weight. The ratio of the critical compositions in the biphasic region is considerably smaller than observed for other polydisperse systems. The persistence length of HPC in DMAc was found to be 65 Å (±15 Å) at 25 °C and 45 Å at 70 °C. An approximate correction for excluded volume effects would lower the above figure by $\sim$15 Å. The results are discussed in terms of recent theories of liquid crystalline solutions. Provided the axial ratio of the solute is calculated on the basis of the Kuhn statistical segment, the body of the results is satisfactorily described by the Matheson–Flory theory of semirigid mesogens and by the lattice theory of hard rods with anisotropic dispersion forces.

Several reports have appeared in recent years concerning the liquid crystalline behavior of concentrated solutions of cellulose and its derivatives. Flory[1] was probably the first to comment on the possibility of mesophase formation for cellulosic polymers. The patent literature[2] describes the use of anisotropic solutions of cellulose derivatives for the production of fibers endowed of superior mechanical properties. More recent patents[3] describe a process whereby cellulose dissolved in aqueous solutions of a cyclic amine oxide is spun to yield high-tenacity fibers. The latter technology appears to hold the greatest promise since it represents a new direct route for the obtainment of regenerated cellulose fibers. The use of nematic solutions of synthetic polymers such as poly(*p*-benzamide) (PBA) for the preparation of ultrahigh-modulus and -strength fibers is now well established[4,5] and prompted interest in the development of similar technologies for the cellulosic polymers.

More fundamental investigations have also been reported. In pioneering work, Werbowyj and Gray[6,7] reported the phase diagram of (hydroxypropyl)cellulose (HPC) in water. They observed the formation of iridescent colors, typical of cholesteric mesophases, above a polymer volume fraction $v_2* = 0.37$. This critical concentration was unaffected by the degree of polymerization of HPC in the molecular weight range 60×10^4 to 1×10^6. Onogi et al.[8] and Asada[9] have recently reported structural and rheooptical measurements of liquid crystalline solutions of HPC. Spherulitic structures were observed in these solutions, and shearing appeared to greatly improve the order of the cholesteric texture.

The phase diagram of cellulose acetate (CA) in trifluoroacetic acid was investigated by Navard et al.,[10] and that of cellulose in *N*-methylmorpholine *N*-oxide (MMNO) was considered by Chanzy and Peguy.[11] These studies indicated that, at variance with the HPC/H_2O system mentioned above, the critical concentration was dependent upon the degree of polymerization (DP). For cellulose, the critical concentration decreased from 45% to 20% (w/w)

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when the DP increased from 35 to 200. The critical concentrations for HPC, CA, and cellulose acetate butyrate in a range of solvents were analyzed by Bheda et al.[12] The effect of the nature of the solvent on v_2^* of CA was also reported by Aharoni.[13] A number of new solvents in which cellulose may form mesophases have also been reported (e.g., trifluoroacetic acid + chlorinated alkanes[14] and liquid ammonia + NH_4SCN[15]).

Some of the investigations have left open a number of problems concerning the interpretation of the results in terms of current theories for the formation of polymeric mesophases. In particular, the lack of dependence of v_2^* upon DP for HPC and the dependence observed instead for cellulose and CA could suggest that the former polymer possesses a semirigid chain and the latter polymers a rigid one.[16] In fact, according to the well-known Flory theory[17] for monodisperse rodlike particles, the critical concentration in athermal solvents decreases with the axial ratio x according to the approximate relationship

$$v_2^* \sim (8/x)(1 - 2/x) \qquad (1)$$

More recent treatments[18] valid for polymers having rigidity intermediate between the rigid rod and the random coil indicate that eq 1 still controls mesophase formation, provided the axial ratio refers to the length of the statistical rigid "segment", i.e., the persistence length, and not to the length of the whole molecule. However, when literature data for the persistence length of these polymers are analyzed (cf. seq.), it is not evident how to correlate rigidity with the v_2^*–DP dependence. It also appears that the reported persistence length data for HPC do not justify[7] the appearance of a mesophase at $v_2^* = 0.37$. Besides its theoretical significance, the v_2^*–DP dependence is of the utmost relevance in connection with high-strength fibers since the critical concentration must be kept relatively low to avoid problems[19] (deaeration, filtration, pumping, and stress dissipation) associated with the spinning of solutions more concentrated than ~20%. Among other features that have not been adequately investigated are the occurrence and properties of a biphasic region in the phase diagrams, the extent of thermotropicity, and a consideration of the role of polydispersity. For rigid rods, v_2^* in eq 1 is expected to be lower, and the biphasic region enlarged, when polydispersion occurs. A reinvestigation of these problems appears, therefore, in order.

Due to the occurrence of solvent effects on the rigidity of cellulosic polymers,[20,21] it is essential that phase diagrams and persistence lengths be determined in the same solvent. In this paper we reanalyze the behavior of HPC with respect to both the phase diagram and the persistence length. We extend the measurement reported by Werbowyj and Gray in aqueous solutions and also investigate the behavior in dimethylacetamide. The study of cellulose and cellulose acetate will be undertaken in future work.

Experimental Section

Materials. Three unfractionated (hydroxypropyl)cellulose samples (LF, GF, and EF) were kindly supplied by Hercules Inc. Reported in Table I are their intrinsic viscosities at 25 °C in ethanol, the corresponding degree of polymerization, and molecular weight, calculated with the relationships of Wirick and Waldman[22]

$$[\eta] = 7.2 \times 10^{-3}\mathrm{DP_w}^{0.900}$$
$$[\eta] = 2.6 \times 10^{-5}M_\mathrm{w}^{0.915} \qquad (2)$$

The flow time of the solutions in ethanol did not change when measurements were repeated after 2 days from the first determination. According to the producer, the molar substitution MS (average number of moles of propylene oxide per mole of anhydroglucose unit) is about 3. Wirick and Waldman,[22] however, characterized Hercules samples having MS between 4 and 5, decreasing with molecular weight. The latter number is greater than 3, which is the maximum degree of substitution of cellulose, due to the formation of poly(1,2-alkyleneoxy) side chains. The first form of eq 2 accounts for the small variation of MS with molecular weight. The molecular weight of the anhydroglucose unit corresponding to MS = 4.5 is ≃ 425. The samples were used as such for the determination of the phase diagram in H_2O and in dimethylacetamide (DMAc). For the determination of the persistence length of HPC in DMAc, fractions were obtained from the LF, GF, and EF samples by using a stepwise extraction from the flake polymer with anhydrous ethanol and *n*-heptane at 30 °C, as described by Wirick and Waldman.[22] The characterization of these fractions is included in Table I along with the weight fraction of each. Solutions used for the determination of the phase diagram were prepared by adding a weighed amount of solvent (H_2O or DMAc) to a weighed amount of dried polymer and stirring for at least 3 weeks. Polymer concentration, C_p, is given as grams of polymer per 100 g of solution. The polymer volume fraction, v_2, was calculated from the corresponding C_p by using the partial specific volume of HPC ($\bar{v}_2$) and the specific volumes of the solvents and assuming additivity. $\bar{v}_2$ was measured pycnometrically at 25 °C and found to be 0.821 mL/g in DMAc and 0.833 mL/g in H_2O.

Table I
Characteristics of Samples Investigated

sample	w[a]	$[\eta]$,[b] dL/g	$[\eta]$,[c] dL/g	$\overline{\mathrm{DP}}_\mathrm{v}$	$\overline{M}_\mathrm{v}$
LF unfractionated		1.42		355	150 400
LF_1 fraction	0.10	0.284	0.284	59	25 900
LF_2 fraction	0.280	0.585	0.494	132	57 000
LF_3 fraction	0.447	0.93	0.86	222	94 700
LF_4 fraction	0.537	1.18	1.075	289	122 900
LF_5 fraction	0.622	1.43	1.42	358	151 600
LF_6 fraction	0.705	1.90		490	206 800
LF_7 fraction	0.809	2.25	2.08	592	248 800
GF unfractionated		4.1		1152	479 000
GF_1 fraction	0.03	0.67	0.62	154	66 200
GF_2 fraction	0.19	2.40	2.12	636	267 000
EF unfractionated		1.26		311	132 000
EF_1 fraction	0.03	0.191	0.196	38	16 800
EF_2 fraction	0.15	0.41	0.415	89	38 700
EF_3 fraction	0.31	0.665	0.600	153	65 700

[a] Cumulative weight fraction. [b] In EtOH at 25 °C. [c] In DMAc at 25 °C.

Phase Diagrams. The critical concentration C_p^* for the appearance of the anisotropic phase at room temperature (ca. 20 °C) for samples LF and GF in H_2O or DMAc was determined by observing with a polarizing microscope (Reichert Zetopan) a small amount of solution placed between a slide and a cover slide. C_p was varied between 5% and 80%. The variation of C_p^* with temperature for samples LF and GF in DMAc was also monitored with the polarizing microscope using a Mettler FP/52 hot stage and determining the temperature at which the birefringence disappeared completely. Heating rate was 1 °C/min until about 30 °C below the transition temperature and 0.2 °C/min afterward. The determination was performed between C_p = 40% and C_p = 70%. Above the latter value the transition temperature is too high and bubbles developed within the sample. The temperature variation of the composition of the conjugated anisotropic phase was determined from the minimum in the viscosity–temperature plot. The measurement was performed[23] with a Weissenberg rheogoniometer (Model R-18) equipped with a cone and plate and operated at a shear rate ($\dot{\gamma}$) of 11×10^{-3} s^{-1}. These determinations were obtained for sample GF at temperatures between 40 and 90 °C and C_p between 50% and 60%.

The determination of the temperature of precipitation of HPC in H_2O was performed by observing under the microscope the temperature at which turbidity developed. Heating rate was 0.2 °C/min. The process was a reversible one, with turbidity dis-

Table II
Effect of Molecular Weight on Critical Parameters

sample	MW	$(C_p^*)_{20\,^\circ\mathrm{C}}{}^{\mathrm{H_2O}}$, %	$(C_p^*)_{20\,^\circ\mathrm{C}}{}^{\mathrm{DMAc}}$, %
LF (fraction)	30 000	41.5	
EF	132 000	39.0	
LF	150 400	38.5	40.0
GF	479 000	36.0	37.0

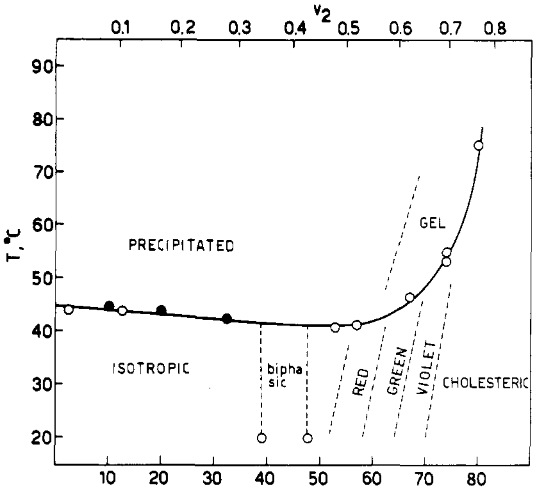

Figure 1. Phase diagram for HPC in H_2O: (○) sample LF; (●) sample GF.

appearing upon lowering of the temperature even a few tenths of a degree below the cloud point.

The variation of color with temperature (samples LF and GF in H_2O or sample LF in DMAc in the C_p interval between ~50% and 80%) was determined visually by placing the solutions in test tubes immersed in a thermostat. Heating rate was 3 °C/h.

The width and composition within the biphasic region were analyzed in more detail at 20 °C for sample LF in H_2O or in DMAc. Solutions were allowed to equilibrate at room temperature for at least 3 months. Centrifugation was then performed in polyallomer tubes at 44 000 rpm. A total of ~300 h of centrifugation was achieved by alternating 24-h centrifugation periods with 24-h rest periods. Under these conditions a good separation of isotropic and anisotropic phases was obtained. The volume of each phase was determined by calibration of the centrifuge tube, and the volume fraction of isotropic phase was thus calculated. The HPC concentration in the conjugated phases was obtained by determining the dry weight of a known amount of solution evaporated under vacuum at 50 °C.

The evolution of the morphology of the cholesteric phase was followed under the polarizing microscope by placing solutions of the LF or EF samples in DMAc (C_p = 66% and 71%) in a quartz cell having a thickness of 0.01 mm and sealed with Teflon film. These samples were also analyzed with a Jasco ORD-UV/5 spectropolarimeter, determining the variation of the optical rotation with wavelength λ between 700 and 400 nm at room temperature.

Persistence Length. Intrinsic viscosities in DMAc were determined as described elsewhere[24] for the fractions listed in Table I. Suspended-level Ubbelhode viscometers were used, with flow time for the solvent greater than 100 s. Measurements were performed at 25 and 70 °C (±0.05 °C). No difference in flow time was detected when a few hours elapsed from the first determination.

Results

Phase Diagrams. Figure 1 illustrates the phase diagram of HPC in H_2O. Data for the LF and GF samples are included. The general features of the diagram are similar to those reported by Werbowyj and Gray, although they did not determine the biphasic gap. At 20 °C, the isotropic phase is stable up to C_p ~ 38%, and the biphasic region occurs between C_p = 39% and C_p = 47%. The former value was determined microscopically and showed (cf. Table II) only a small variation for samples LF and GF. The latter value was determined from the extrapolation of the C_p-ϕ data to be presented below (Figure 2a). In any event, a solution with C_p = 49% was 100% anisotropic according to ultracentrifugation results since no isotropic phase could be separated upon very extensive centrifugation. At 20 °C, cholesteric colors appear in the pure anisotropic phase between C_p = 51% and C_p = 70%, the colors changing from red to violet as C_p increases. The occurrence of precipitation above 40 °C prevents an accurate determination of a temperature effect on the composition of conjugated phases. The manifestation of cholesteric colors, however, appeared to shift to higher C_p as T increased. The solubility decreased with temperature in the isotropic range but increased with temperature when the anisotropic solution is stable. Correspondingly, the appearance of the precipitate changed from a white suspension of particles to a semitransparent gel.

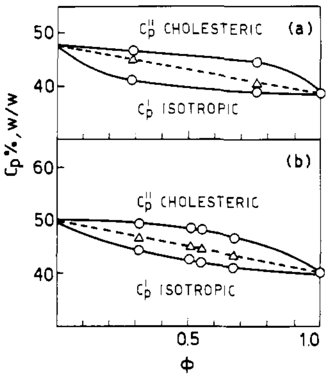

Figure 2. Variation of HPC concentration of isotropic and anisotropic phases isolated from biphasic mixtures at 20 °C. The trend of the overall C_p is indicated by the triangles. (a) Solvent, H_2O; sample, LF. (b) Solvent, DMAc; sample, LF.

Figure 2a illustrates the variation of the concentration of the coexisting isotropic (C_p') and anisotropic (C_p'') phases with the volume fraction of isotropic phase, ϕ. Data refer to the HPC (sample LF)/H_2O system. The compositions C_p' and C_p'' depend upon the overall concentration C_p within the biphasic gap. The latter determines ϕ.

Figure 3 illustrates the phase diagram of HPC in DMAc. The biphasic region occurs, at 20 °C, between C_p = 40% and C_p = 50%. A solution with C_p = 52% was 100% anisotropic according to ultracentrifugation data. The compositions of the conjugated phases at room temperature are those corresponding to the limiting values of the conjugated phases separated by ultracentrifugation. Again, C_p* was determined microscopically and showed only a small variation for LF and GF (cf. Table II). The C_p' and C_p'' are given in Figure 2b and show the same trend exhibited by the HPC/H_2O system (Figure 2a). The width of the biphasic region at temperatures above 20 °C was determined by hot-stage microscopy for C_p' and by viscosity for C_p''.

Viscosity–temperature curves are illustrated in Figure 4. The minimum is regarded as evidence of the incipient formation of the isotropic phase and the maximum as the temperature of complete isotropization. The position of

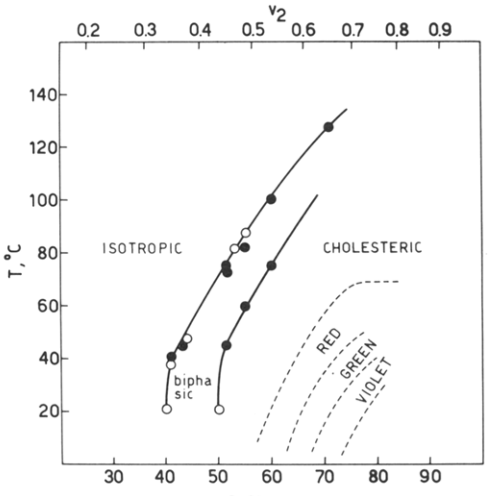

Figure 3. Phase diagram for HPC in DMAc. Open points, sample LF; black points, sample GF. Color boundaries appeared with sample LF only.

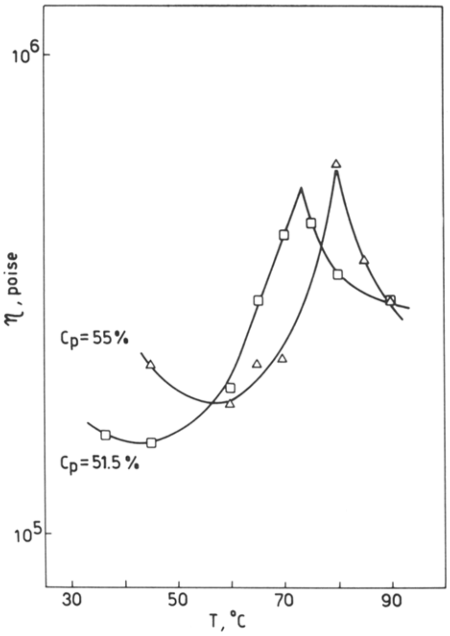

Figure 4. Typical viscosity–temperature behavior for concentrated HPC (sample GF) in DMAc at $\dot{\gamma} = 11 \times 10^{-3}$ s^{-1}.

the maximum coincides with the microscopic determination of C_p*-T pairs. For reasons discussed elsewhere,[25] the coincidence may be a fortuitous one.

The comparison of the diagrams of Figure 1 and 3 indicates the following.

(a) The biphasic region occurs at about the same v_2 interval in H_2O and DMAc. However, the manifestation of colors appears at larger v_2 in DMAc than in H_2O, suggesting a different role of the two solvents on helical pitch.

(b) There is only a minor effect of molecular weight on the biphasic equilibria in both DMAc and H_2O (for details cf. Table II). However, at variance with H_2O, no colors are manifested in DMAc by the higher molecular weight sample (GF). Above 70 °C all colors disappear for sample LF in DMAc.

(c) The absence of precipitation in the case of DMAc, Figure 3, allows the detection of a large thermotropic effect on the biphasic equilibria.

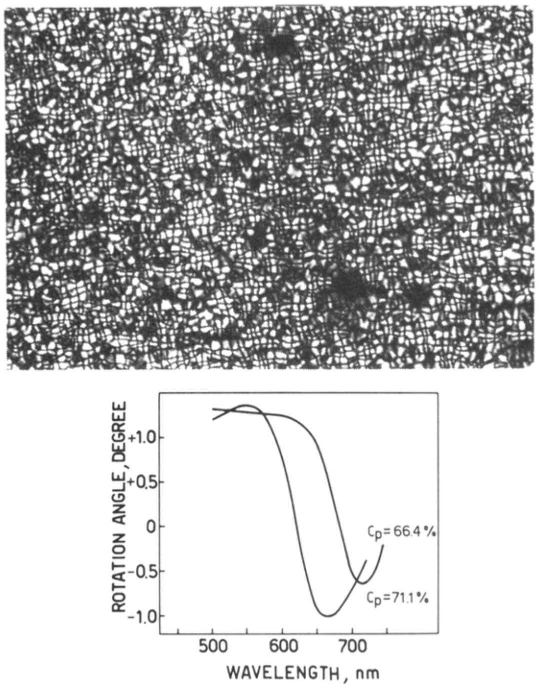

Figure 5. Top: Micrograph taken under the polarization microscope at room temperature of a DMAc solution of sample EF, C_p = 69%. Bottom: Optical rotation vs. wavelength for sample LF in DMAc at the indicated values of C_p. 0.01-mm-thick quartz cell.

Figure 5 illustrates a micrograph of sample EF in DMAc. The texture developed at the periphery of the sample left undisturbed in a thin quartz cell for at least 1 week (as deposited on the slide, the samples appeared colored but without a texture). The mosaic of small distorted crosses (focal conic texture) is similar to that reported by Werbowyj and Gray[6] for HPC in H_2O and reflects the occurrence of defects due to boundary effects. Also in the center part of the slide, regions of defects were sometimes observed. Development of stable homeotropic textures probably requires still thinner cells and complete control of moisture. Typical ORD curves are included in Figure 5. The wavelength at which the optical rotation changes sign decreased with C_p and with time, reaching a plateau in about a week (a further decrease was observed at still longer times). The values of λ_0 indicated, 620 and 680 nm, respectively, for C_p = 71.1% and 66.4% (determination made 1 week following slide preparation), are larger than those observed[6] in H_2O.

Persistence Length. The problem of determining the persistence length from viscosity data has been discussed in detail elsewhere.[24] Here we consider the theoretical intrinsic viscosity–molecular weight dependence for an unperturbed wormlike cylinder given by Yamakawa and Fujii[26]

$$[\eta] = \Phi L'^{3/2}/\lambda^3 M \tag{3}$$

where $L' = \lambda M/M_L$ is a reduced contour length, M_L being the mass per unit length of the chain, $\lambda = 1/2q$, q being the persistence length (λ^{-1} is the Kuhn segment), and Φ is a function of L' and of the reduced cylinder diameter d' tabulated by Yamakawa and Fujii. Theoretical $[\eta]$–M curves have been calculated according to eq 3 for different values of M_L, d', and q. M_L was taken equal to 77.7, 72.0, and 61.4 daltons/Å, corresponding, respectively, to a MS of 5, 4, and 3 (a value of 5.47 Å was taken for the residue vector[27]). The unreduced diameter d was allowed to change between 10 and 14 Å, 12.8 Å being the X-ray value for HPC reported by Werbowyj and Gray.[7] (We point out that the use of tabulated Φ values gave results consistent with the previously performed[24] calculations, based on eq 37–42 given by Yamakawa and Fujii.)

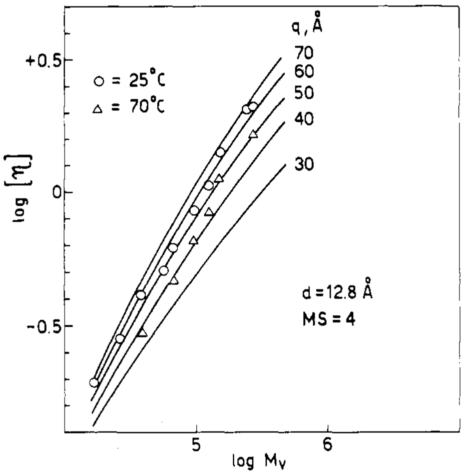

Figure 6. Full lines represent the theoretical intrinsic viscosity–molecular weight dependence for wormlike chains having the indicated values of q, M_L, and d. Open points: experimental values of $[\eta]$ for HPC fractions in DMAc at 25 and 70 °C.

Some theoretical $[\eta]$–M curves are given in Figure 6 (full lines). These have been calculated for arbitrary values of MS and d. The points represent the intrinsic viscosity experimentally measured in DMAc for the fractions characterized in Table I. The data are compatible with a persistence length of ~65 Å at 25 °C, a somewhat smaller value, ~45 Å, being indicated at 70 °C. These values are not corrected for excluded volume effects.[24]

The effect of variation of d and MS produced the following results. A decrease of ~25% on d produces an increase of about 3 Å on q. A decrease of about 25% of MS produces a decrease of about 15 Å on q. Wirick and Waldman[22] have considered the problem of a nonuniform distribution in unfractionated HPC samples. They concluded that the substitution is quite uniform, although there is a tendency for MS to be larger for shorter chains. The maximum variations measured did not exceed 25%. Therefore, in a polydisperse HPC sample there is the possibility of variations of MS affecting M_L and causing, on this account alone, an indetermination on q. However, the fractions used for the determination of q cover a rather narrow (and low) molecular weight range. The maximum variation of MS expected in this range (cf. Tables I–IV of Wirick and Waldman[22]) is about 0.5 and could have not greatly affected the reported q. We assess the total indetermination on q to be ±15 Å.

Discussion

We begin with the consideration of the persistence length data. A q value of 65 Å at 25 °C in DMAc corresponds to a persistence axial ratio of ~6. This is far too small to explain the observed formation of the mesophase in DMAc (and in H_2O) at $v_2^* \simeq 0.35$ on the basis of eq 1 and assuming validity of the treatment[18] for semirigid chains (cf. introductory section). An axial ratio of ~20 would be expected from eq 1. Even if the Kuhn statistical link λ^{-1} ($=2q$) is regarded as a more appropriate measure of the rigid segment,[7,18] eq 1 still fails to give a satisfactory prediction. Before proceeding further, we consider possible sources of errors on q. Werbowyj and Gray estimated q from the unperturbed mean-square end-to-end distance, $\langle r_0^2 \rangle$, using the light scattering data obtained by Wirick and Waldman for HPC in EtOH at 25 °C. Using Gaussian statistics ($\lambda^{-1} = \langle r_0^2 \rangle / L$), they calculated λ^{-1} values increasing from 130 to 210 Å when DP decreased from 4600 to 575. Placing more significance on the high molecular weight data (when Gaussian statistics should more likely apply),[29] we find q (corrected for excluded volume effects) to be of the order 65 Å. We have also analyzed Wirick and Waldman's raw data (their Table VII) according to the equation[30,31]

$$\langle s^2 \rangle = q^2 \left[\frac{1}{3} \frac{L}{q} - 1 + \frac{2q}{L} - \frac{2q^2}{L^2} \left(1 - \frac{1}{\exp(L/q)} \right) \right] \qquad (4)$$

where L is the contour length and $\langle s^2 \rangle$ is the mean-square radius. This equation, which is valid for wormlike chains, yields a q value of ~70 Å (corrected for excluded volume effects), which would not significantly improve the agreement with eq 1.

The correction for excluded volume effects is complicated by the lack of reliable theories of such an effect for wormlike chains (for a discussion cf. ref 24). The correction is ignored by most investigators, and it is a fortunate circumstance that the dimensions of cellulosic chains are not affected by considerable expansion due to excluded volume effects.[32,33] According to Norisuye and Fujita,[29] excluded volume effects become relevant only when the chain length is larger than ~100q. In view of these favorable circumstances, we have calculated an approximate correction for HPC by considering the expansion coefficients α reported by Wirick and Waldman[22] for the same polymer in EtOH at 25 °C. α is defined by the ratio $([\eta]/[\eta]_\Theta)^{1/3}$, where $[\eta]_\Theta$ is the viscosity measured in the absence of excluded volume. From their tabulated values, the constant C_M in the equations[31]

$$\alpha^5 - \alpha^3 = 2C_M M^{1/2} \psi_1 (1 - \Theta/T)$$

$$C_M = (27/2^{5/2}\pi^{3/2})(\bar{v}^2/NV_1)(\langle r_0^2 \rangle / M)^{-3/2} \qquad (5)$$

was evaluated. Here, ψ_1 is an entropy parameter, Θ is the Flory theta temperature, $\bar{v}$ is the partial specific volume of the solvent, and N is Avogadro's number. Using the highest value of C_M, we calculated α for the fractions used here (α decreased from 1.141 to 1.048 when molecular weight decreased from 267 000 to 16 800). $[\eta]_\Theta$ was then calculated and compared with the theoretical curves in Figure 6. The corrected q value, ~50 Å, is ~15 Å smaller than the uncorrected one.

Another possible source of error on q would be the occurrence of aggregation occurring in dilute solutions of DMAc. Werbowyj and Gray[7] noticed time effects during light scattering measurements, which suggested aggregation of HPC in H_2O. Our measurements show no evidence of aggregation in DMAc, in which the solubility is much greater than in H_2O (Figures 1 and 3). The dilute solution behavior of HPC in DMAc appears similar to that observed in EtOH (Table I), where molecular dispersion prevailed as revealed by light scattering analysis.[22] Another possible source of error on q would be the incorrect assignment of d, MS, and M_L (eq 3). However, the data presented under Results indicate that even relatively large errors on the absolute values of d and MS do not produce changes of q that could significantly improve the performance of eq 1.

A more subtle effect could be the occurrence of a "polydispersity of persistence lengths" arising from the small nonuniformity of substitution[22] already discussed. One could speculate that the higher molecular weight species could exhibit somewhat larger q values due to the reduced substitution observed for these species (cellulose, which has no substitution, behaves as a rodlike polymer[11]). To check the validity of this hypothesis we have considered the value of q obtained by using only the high molecular weight fractions ($[\eta] > 1.4$) listed in Table I. These data appear to fall on a theoretical log $[\eta]$–log M_v line having $q = 60$ Å with the assignment MS = 3 and $d = 12.0$ Å.

Although the occurrence of a polydispersity of q is a possibility, the effect is still within the errors affecting the determination of q.

We conclude that the axial ratio alone, as determined from dilute solution data, is unable to explain in terms of eq 1 the observed v_2^*. Some other factor must be considered.

Before entering into the discussion of these factors, we consider other features of the experimental phase diagrams, most of which appear not inconsistent with the theory. The results in Table II suggest that there is a small effect of DP on C_p^*. The effect is, however, a very small one, far smaller than that observed for cellulose[11] and CA[10] (cf. introductory section) or that predicted on the basis of eq 1 for rigid rods having an axial ratio proportional to DP. This result tends to support the conclusion[7,18] that, from the point of view of the C_p^* vs. DP dependence, HPC behaves as a semirigid chain. The small difference of C_p^* observed for samples LF and GF could be due to minor differences in the two samples[22] or to the low molecular weight tail of their distribution, which includes short, rigid species expected to conform with eq 1.

Considering now the biphasic gaps appearing in the phase diagrams in H_2O and in DMAc, we note that the ratio of the limiting concentrations of anisotropic and isotropic phases, about 1.2, is very close to the value expected for a monodisperse systems of rods.[17] The above ratio is considerably smaller than that, 1.5–1.9, we determined for polydisperse rods, PBA in DMAc[25] or poly(n-hexyl isocyanate) in dichloromethane.[34] The former polymer exhibits a most probable distribution. For HPC, the extensive fractionation data of Wirick and Waldman[22] indicate a considerably wider distribution. They report $\bar{M}_w/\bar{M}_n \sim 5$ for their sample B and $\bar{M}_w/\bar{M}_n \sim 11$ for their sample D (the latter exhibited a binodal distribution). Thus, in spite of the fact that HPC has a wider distribution than the two rigid polymers indicated above, the breadth of its biphasic gap closely conforms to that expected for a monodisperse system. Again, this conclusion is not in disagreement with the model of semirigid chain[18] in which a persistent segment controls mesophase formation, the actual molecular weight and its dispersion being largely inconsequential to both the location (v_2^*) and the width of the biphasic region.

Rather surprising is, however, the observation (Figure 2) that C_p' and C_p'' are not independent of ϕ, an expectation valid for a monodisperse system of rods[17] but not for a polydisperse one.[25,28] We have determined the molecular weight (from intrinsic viscosity) of the polymer occurring in the conjugated phases. The results indicate that high and low molecular weight species migrate in the anisotropic and isotropic phase, respectively. While the result is in line the expectation valid for a polydisperse system of rods,[25,28] the actual fractionation effect appeared considerably larger than observed for rodlike polymers. In fact, at $\phi = 0.5$, the ratio of the molecular weight in the two phases was $\sim$1.8 for the present system, both in H_2O and in DMAc (actual values were $\bar{M}_v = 180\,000$ and $\bar{M}_v = 109\,000$ in the anisotropic and isotropic phases, respectively). For PBA in DMAc/LiCl,[25] the corresponding ratio was $\sim$1.4. While the effect of a small polydispersity of q could greatly magnify the enrichment of high molecular species in the anisotropic phase, we believe that the above results are primarily affected by large nonequilibrium effects. During the ultracentrifuge runs the heavier anisotropic phase is at bottom of the polyallomer tube, where the larger molecular weights (and possibly some aggregates) can sediment. The diffusion of the latter species back into the isotropic phase may be an extremely slow process, in spite of our efforts (cf. Experimental Section) to facilitate it. One should appreciate the difficulties in working with these extremely concentrated and viscous solutions. The above complication would not vitiate, however, the determination of the width of the biphasic gap, which is essentially based on pure phases.

We now consider the large thermotropic effect exhibited by the phase diagram in DMAc. From Figure 3, v_2^* changes from $\sim$0.35 to $\sim$0.44 when T increases from 25 to 70 °C. In terms of eq 1 this change could be explained by a corresponding 20% decrease of x. In the corresponding temperature range (Figure 6), the persistence length exhibits a decrease of $\sim$30% before correction for excluded volume effects. We can approximately account for the latter effect by recalling that, at 25 °C, the corrected q is $\sim$50 Å. From literature data[32,33] the temperature coefficient of unperturbed dimensions ($\mathrm{d}\ln\langle r_0^2\rangle/\mathrm{d}T$) for cellulosic chains is on the order of -5.7×10^{-3} deg^{-1}. By applying such a correction, the corrected q value could be expected to decrease by $\sim$24% in the 25–70 °C temperature range. Thus, it appears that the temperature effect on the persistence length can grossly account for the thermotropicity observed in DMAc.

The foregoing discussion indicates that the feature of the results that is mostly at variance with theory is the inability of eq 1 to predict the correct value of v_2^* on the basis of q. Factors that may be considered to explain this discrepancy are (i) an increase of q with concentration, (ii) aggregation, (iii) anisotropic dispersion forces, and (iv) deficiency of the lattice theory[17] to predict the critical concentration for a given asymmetry. When one considers that, for conventional polymers, parameters such as $\mathrm{d}\ln\langle r_0^2\rangle/\mathrm{d}T$ are the same in dilute solutions and in the bulk,[35] one sees little ground for possibility (i), particularly in a one-component solvent.[36] Intermolecular forces leading to soluble aggregates of two or more HPC chains could occur in concentrated solution, particularly in H_2O, where evidence of HPC aggregation exists even in dilute solution. The conformation of the aggregated species should still be a semirigid one, albeit with a greater q value, to justify the observed invariance of v_2^* with DP (the possibility that all aggregated species might attain the same axial ratio, irrespective of DP, is less appealing). We have no evidence that aggregates of this type may form for HPC. Multiple helices have been reported for other polysaccharides.[37] HPC appears to be too much an irregular molecule to facilitate formation of these structures.

Flory and Ronca[38] and Warner and Flory[39] have recently extended the hard-rod theory leading to eq 1 to the case in which anisotropic dispersion forces are operative, both in the absence and in the presence of a diluent. These soft, asymmetric attractions are of the same type as those originally considered by Maier and Saupe[40] to describe the thermotropic behavior of low molecular weight liquid crystals. Warner and Flory[39] calculated phase diagrams for rods having axial ratios of 20 and 7. The intensity of soft interactions is determined by a characteristic temperature T^* and, therefore, their phase diagrams are plotted as xT^*/T vs. v_2. In the case $x = 7$, the athermal value of v_2^* ($\sim$0.93, reached when $T \rightarrow \infty$ or $T^* = 0$[38,39]) could be lowered to $\sim$0.63 in the presence of soft interactions, while still in the narrow biphasic region (breadth of the gap $\sim$1.2). For $x = 20$, the athermal limit of v_2^* ($\sim$0.36) could be lowered to $\sim$0.22 by soft interactions.

By assuming that all possible errors would act in the direction of increasing x ($q = 80$ Å, $d = 10$ Å) and by definitively regarding the Kuhn segment, rather than q,

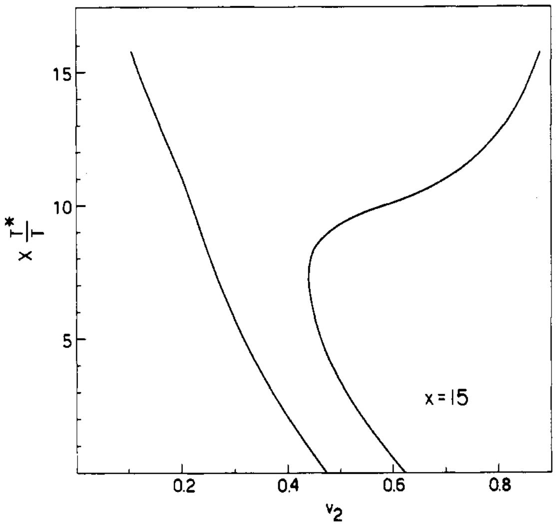

Figure 7. Phase diagram for rods with axial ratio $x = 15$ exhibiting soft interactions. Calculated from Warner and Flory's theory.

as the appropriate quantity to calculate x, the latter could reach an upper limit of ~16, according to our present data. We have therefore calculated the phase diagram for $x = 15$, according to Warner and Flory. The diagram, reported in Figure 7, shows that the athermal limit of v_2^* (0.46) can be lowered to ~0.35 when xT^*/T is ~3.8, still remaining in the narrow gap. At room temperature, this finding implies a value of T^* on the order of 75 K (assuming $T^* = 100$ K, $xT^*/T \sim 5$, and $v_2 \sim 0.32$). Thus, a reasonable[38] value for T^* could offer a justification for the v_2^* value experimentally observed for HPC, retaining the validity of the persistence length analysis and of the semirigid chain[18] treatment. From Figure 7 one can evaluate the expected variation of v_2^* in the temperature range 25–70 °C. Assuming $T^* = 75$ K, the latter variation is on order of 3%, much smaller than the thermotropic effect shown by the data in Figure 3. Thus, as discussed above, the thermotropicity observed for HPC is essentially controlled by the effect of temperature on unperturbed dimensions.

With the assumptions indicated above, the lattice theory could adequately describe the experimental behavior. The assumption that attractive interactions are operative is not less appealing than the assumption that athermal conditions prevail. In fact, the recognition that both hard and soft interactions are operative in liquid crystal solutions is the prevailing trend of recent treatments.[41] More open to criticism is the assumption that the Kuhn segment should be used for the evaluation of the axial ratio. This assumption, which is coherent with the treatment of Gaussian chains composed of rods (having length λ^{-1}) connected by flexible joints,[18] is a questionable one for a wormlike chain. Other data[42,43] analyzed in terms of eq 1 would also be consistent with an axial ratio about twice that calculated with the persistence length. Additional careful investigation of the relationship between v_2^c and q for other systems appears to be necessary for a final settlement of this important issue. One should also consider the possibility that the lattice theory does not accurately predict the value of v_2^c. In fact, the athermal v_2^c values predicted by the Isihara[44] and Onsager[45] theories are about half that predicted by eq 1. Use of the latter theory, with or without the inclusion of soft interactions, would offer a poorer agreement with experimental data than that obtained using eq 1.

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Registry No. (Hydroxypropyl)cellulose, 9004-64-2; dimethylacetamide, 127-19-5; water, 7732-18-5.

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