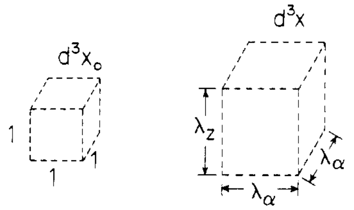
(d^3x_0) when the surfaces are displaced, are defined as shown in the following sketch:



Registry No. Dextran, 9004-54-0.

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Phase Diagram of Aqueous Solutions of (Hydroxypropyl)cellulose

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ABSTRACT: The phase diagram of aqueous solutions of (hydroxypropyl)cellulose has been determined for carefully fractionated samples having a degree of substitution between 2.8 and 3.0, a molar substitution between 5.8 and 6.3, and a molecular weight between 28 and 140 kg·mol^{-1}. The diagram is composed of three regions. Isotropic solutions are stable below 42 °C at polymer weight fractions lower than about 50%. Cholesteric liquid crystals are formed at concentration higher than 55% and phase separate at a lower temperature than isotropic solutions. The difference may be as large as 28 deg for the lowest molecular weight sample. At high temperature, only concentrated mesophases are homogeneous. All other compositions consist of a cholesteric phase and an infinitely dilute solution. A single biphasic region, whose width depends on temperature, extends over the whole water normal liquid range. Phase separation is responsible for unusual optical properties of some anisotropic solutions, including a negative temperature dependence of the cholesteric pitch.

Introduction

(Hydroxypropyl)cellulose (HPC) is a water-soluble cellulose derivative. It is usually synthesized by the reaction of propylene oxide on cellulose under alkaline conditions, giving lateral chains containing a variable number of hydroxypropoxy groups. Commercial samples having[1] a degree of substitution DS (i.e., the average number of oxygen of the original cellulose repeat unit bearing a substituent) above 2.8 and a molar substitution, MS (i.e., the average number of hydroxypropyl substituent per anhydroglucose residue), larger than 4 have been widely studied. Numerous properties of the polymer in dilute aqueous solutions have been examined, including phase separation,[1,2] configurational parameters,[3,4] conformation,[5] surface tension,[6] or adsorption behavior.[7] Concentrated solutions of HPC in a variety of aqueous and organic solvents form liquid crystals. The occurrence of an ordered phase is observed for most soluble cellulosic polymers[8,9] and is presumably related to the lack of flexibility of the cellulose backbone. The chirality of the anhydroglucose repeat unit promotes the formation of cholesteric mesophases; i.e., the order in the liquid crystal is characterized by a helicoidal supramolecular arrangement. The latter confers striking optical properties to the solution, for instance the reflection of circularly polarized light at a wavelength related to the pitch of the helicoidal arrangement.[10] Investigations have been devoted to the cholesteric phases of aqueous HPC, with emphasis on their optical properties,[11-14] their textures,[13,15-17] the comparison with theoretical predictions,[3,11] or the preparation of

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Table I
Molecular Weight and Chemical Structure of HPC Fractions

fractn	M_w,[a] kg·mol^{-1}	M_w/M_n[a]	DS[b]	MS[b]	MS/DS[c]
I	28	2.0	3.0	6.3	2.2
II	64	1.7	*d*	*d*	2.1
III	89	1.7	*d*	*d*	2.0
IV	140	1.8	2.8	5.8	2.0

[a] Estimated by size-exclusion chromatography of tetrahydrofuran solutions at 25 °C, using a column calibrated with polystyrene standards (Waters Model 590 liquid chromatograph, equipped with a differential refractometer). [b] Determined by ^{13}C NMR of solutions of the polymer in D_2O by procedures described in ref 24. The spectra were accumulated for 12–36 h with a Bruker WH-400 spectrometer operated at 100.6 MHz. [c] Average number of 2-hydroxypropoxy group per side chain, as measured from the relative number of internal to external methyl carbon atoms. The latter was taken from ^{13}C NMR spectra, recorded for 60 h on solutions in D_2O using a Varian XL-200 spectrometer operated at 50.3 MHz. [d] The data were not evaluated; the value of MS/DS listed in the last column is taken as an indication that both molecular weight and structure change smoothly from fraction I to fraction IV.

chiroptical filters.[18] In addition, dynamic rheological properties[19] and die swell[20] of HPC–water mixtures have been measured over the whole range of composition.

(Hydroxypropyl)cellulose exhibits a unique phase behavior in water[1-3,11,21-23] characterized by reversible transitions (i) at constant composition, upon heating above c.a. 40 °C, and (ii) at constant temperature, upon increasing the polymer concentration above ca. 40%. However, much discrepancy exists between the reported phase diagram of similar commercial unfractionated samples: while dilute solutions (polymer weight fraction <40%) are consistently reported to phase separate at 44 ± 2 °C, literature values of the transition temperature for a 60% (w/w) HPC solution vary between 36[22] and 65 °C.[23] Furthermore, the exact number of regions in the phase diagram, as well as the nature of the phases at equilibrium at high temperature, are still not known with certainty. The occurrence of a "gel" state is often mentioned[3,11,22,23] but neither a mechanism of gelation nor a description of the gel physical cross-links has been proposed. Also, the effect of the polymer molecular weight and structure have yet to be elucidated. In an attempt to clarify the HPC–water phase diagram, the phase-separation temperatures for solutions of carefully fractionated and characterized polymer samples have been determined by turbidimetry over the whole composition range. In addition, two questions have been specifically addressed, namely, (i) the nature of the white concentrated phase which separates upon heating a dilute isotropic solution and (ii) the effect of phase separation on the pitch of the cholesteric mesophase.

Experimental Section

Materials. (Hydroxypropyl)cellulose samples were prepared from a commercial polymer (Aldrich Co., nominal molecular weight 100 kg·mol^{-1}) by fractional precipitation at 25 °C in ethanol–heptane mixtures. In order to ensure equilibrium between supernatant and precipitate after each addition of nonsolvent, the mixture was heated at 60 °C until complete redissolution of the polymer-rich phase and cooled again to 25 °C. Nine fractions were precipitated in solvent mixtures containing between 35 and 45% of heptane, in agreement with results of a fractional dissolution in the same solvent system.[4] The polymer samples were recovered by evaporation of the ethanol–heptane solvent, redissolution in a small quantity of water, and freeze-drying. Their molecular structure was determined by NMR spectroscopy, using the method and the peak assignments given in the literature.[24] A detailed description of the preparation of the fractions and their characterization is given elsewhere.[25] Structural data are summarized in Table I where samples I–IV actually correspond to the ninth, eighth, seventh, and fifth fractions. The molar substitution is around 6, much higher than previously reported,[12] for commercial samples prepared in the late 70s. The high MS is in agreement with technical data for Klucel polymers recently produced by the current manufacturer (Aqualon Co., Wilmington, DE). As shown in Table I, slightly different parameters characterizing the substitution pattern of HPC are obtained depending on the instrument resolution. However, the same trend is observed: MS increases when the molecular weight decreases. Polymer samples were dried for at least a week under dynamic vacuum before use. Aqueous solutions were prepared with deionized water (resistivity > 16 MΩ·cm), obtained immediately before use with an ion-exchange purification system (Sybron-Barnstead Nanopure II).

Optical Properties. The optical properties of HPC aqueous solutions have been studied by UV–visible spectrophotometry (Hewlett-Packard 8450A diode array spectrophotometer). The solutions were prepared in sealed parallel-sided glass tubes (Vitro Dynamics, 0.4 × 4 mm i.d.). A piece of polymer sample, cut from an ethanol-cast film (prepared at a thickness close to 400 microns), was first introduced in the glass tube, previously sealed at one end. The appropriate amount of water was then added with a Hamilton microsyringe. The top end of the glass tube was finally sealed in a flame, while the part of the tube containing polymer and water was kept at dry ice temperature, in order to avoid degradation and/or solvent evaporation. Measurements were performed as a function of temperature in specially built temperature-controlled ovens: For temperatures higher than 30 °C, a heated copper block equipped with proportional controller (YSI Model 72) was used. Subambient studies were conducted in an oven cooled thermoelectrically with Peltier components.

The turbidity of solutions prepared in the whole composition range was determined from the absorbance at 700 nm as a function of temperature. Since the measured changes in turbidity are related to a phase separation where kinetic factors may play a significant role, the following procedure was applied. The solution was placed at the lowest temperature in the desired range. Spectra were recorded isothermally at constant time interval for at least 25 min. The oven was then heated to the next temperature. The *equilibrium* absorbance was extrapolated from a plot of absorbance versus reciprocal time. A linear dependence was generally observed, although the slope was often observed to vary. The above method is unlikely to eliminate all kinetic factors but is satisfactory for a cloud point determination: it generally reproduced the trend observed on the nonextrapolated values while reducing considerably the data scatter. Also, measurements performed on a given solution were quite reproducible, except for a shift of the values along the absorbance scale. Cloud points were estimated from the turbidity–temperature curves. When a well-defined temperature could not be determined because the transition lacked sufficient sharpness, an interval was estimated from the highest temperature at which the solution was homogeneous and the lowest temperature where the system was undoubtedly biphasic.

The wavelengths of reflection of liquid-crystalline solutions were taken as the maximum of the peak in their UV–visible spectra. Equilibrium wavelengths are reported; i.e., the solutions were kept at the observation temperature until they reached their equilibrium pitch. Cholesteric solutions in the 0.4-mm-thick tubes gave fairly symmetrical reflection peaks, with typical values of absorbance at maximum and half-height bandwidth on the order of 0.07–0.1 and 30–40 nm, respectively. The solutions were therefore considered to have a texture sufficiently close to planar to ensure a reliable estimation of the cholesteric pitch from UV–visible spectrophotometry.

A study of the optical properties of HPC solutions at high temperature by standard techniques is difficult because of the large persistent turbidity of the system. Circular reflectivity measurements, however, can still be performed at a transmittance lower than a few percent, because a circular dichroism instrument directly records a relative transmittance, namely, the difference between the intensity transmitted by the sample when illuminated with right and left-handed circularly polarized light. Circular reflectivity measurements were performed as a function of temperature with a Jasco J500C spectropolarimeter and a Mettler

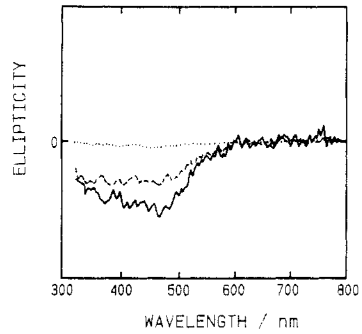

Figure 1. Circular reflectivity spectra of HPC fraction I in water (30% w/w) at different temperatures: 42 °C (dotted line); 44 °C (dashed line); 46 °C (full line). The ellipticity of a solution is a measure of its relative transmittance toward left- and right-handed circularly polarized light.

FP52 hot stage. The solutions were prepared by using the same procedure as for UV–visible spectrophotometry. Temperature-dependent experiments were conducted at a constant heating rate, slow enough to ensure equilibrium (0.2 deg·min^{-1}). Caution should be exercized in the conclusions drawn from spectra recorded on highly turbid biphasic systems, since the incident light could have its state of polarization altered by travel through a suspension of unhomogeneous refractive index. The results of Figure 1 are reliable, however, since no artefact could actually create optical activity. In Figure 6, the reflection wavelengths obtained by circular reflectivity are only used to confirm the trend observed by UV–visible spectrophotometry.

Results and Discussion

Nature of the Phase Precipitating from Dilute Solution. Aqueous solutions of HPC at polymer weight fraction lower than 40% are isotropic at room temperature but become extremely cloudy upon heating. After a sufficiently long time at high temperature, in the order of days, a white concentrated phase can be physically separated from a clear, very fluid solution. The precipitated phase is very viscous but exhibits definite fluidity since it does not retain its shape under its own weight. The lack of rheological properties characterized by a yield–stress, that would emphasize the presence of a network of reversible cross-links,[26] indicates that this phase does not qualify as a gel. The solution which precipitates from dilute solution at high temperature contains polymer at a concentration well above the critical concentration for the formation of a liquid crystal at room temperature,[18] which raises the question whether the precipitating phase is anisotropic. Circular reflectivity spectra of an isotropic solution containing 30% (w/w) of HPC sample I were recorded as a function of temperature. As shown in Figure 1, phase separation around 43 °C is accompanied with the onset of optical activity. The turbid solution transmits different amounts of left- and right-handed circularly polarized light, the maximum difference being recorded at a wavelength around 470 nm at 46 °C. Very similar spectra are observed at low temperature for the nonturbid cholesteric liquid crystals of HPC, in which the right-handed helicoidal arrangement of the molecules promotes the reflection of right-handed circularly polarized light.[12] Figure 1 strongly suggests that the concentrated phase formed upon heating possesses cholesteric order, the low wavelength tail in the spectra then originating from a random orientation of the cholesteric domains in the precipitating droplets. The persistence of the white coloration of this phase, even after prolonged standing at temperature as high as 80 °C, is an indication that biphasic HPC system form highly stable emulsions, where the dispersed droplets have the proper size to scatter visible light. This is consistent with the unusually large decrease of surface tension exhibited upon mixing HPC and water.[6] A phenomenon which is likely to have the same origin is observed upon stirring together two dilute solutions of HPC, one in water and the other in chloroform. Although the solvents are immiscible, a white viscous suspension is obtained, which does not physically separate into two layers over a period of days.

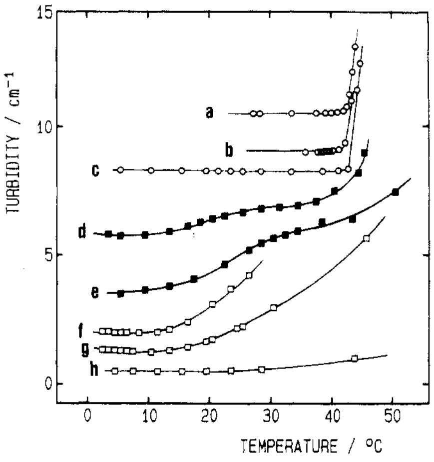

Figure 2. Turbidity of aqueous solutions of HPC fraction I as a function of temperature, as measured from the absorbance at 700 nm. The curves have been arbitrarily shifted along the turbidity scale. The polymer weight fraction in the solutions is (a) 7%, (b) 20%, (c) 30%, (d) 51%, (e) 55%, (f) 60%, (g) 65%, and (h) 75%. The increase in turbidity is taken as an indication of phase separation. Three different behaviors are observed, depending on whether the solution is isotropic (open circles), cholesteric (open squares), or biphasic (filled squares) at the lowest temperature of measurement.

Phase Diagram of Aqueous HPC. The large amount of scattering upon phase separation, associated with the absence of decantation on a short time scale, makes turbidimetry ideally suited to measure the transition temperatures in HPC–water systems. Figure 2 gives the turbidity of aqueous solutions of HPC (fraction I) as a function of temperature. Three different behaviors are observed, depending on the polymer concentration. Isotropic solutions (open circles, curves a–c) give almost identical curves, characterized by an abrupt increase of turbidity at a well-defined temperature between 40 and 45 °C. In contrast, cholesteric liquid crystals (open squares, curves f and g) show a variation of turbidity with temperature that depends on the polymer weight fraction. The more dilute anisotropic solutions (e.g., curve f) exhibit a relatively rapid increase of absorbance at an unexpectedly low temperature, less than 15 °C for a 60% solution. At higher polymer concentration, phase separation occurs at higher temperature and is accompanied with a smaller change in turbidity (curves g and h). Systems that are already biphasic at the lowest temperature (filled squares) reveal even more complex behavior, as the solutions, which already exhibited a fair amount of turbidity at low temperature, seemingly experience *two* phase separations upon heating. A similar increase of the turbidity in two steps was observed[11] for a 41% solution of unfractionated HPC. Solutions prepared from a polymer fraction of higher molecular weight and slightly lower MS, sample IV, exhibit very similar behavior, although the difference between isotropic and cholesteric solutions is less pronounced. The phase separation temperatures estimated from turbidity measurements are plotted as a function of the polymer concentration in Figure 3 for solutions of fractions I (lozenges) and IV (squares). The dependence of the transition temperature on the solution composition is at the origin of the shape of the turbidity curves of Figure 2. The latter simply reflects the change of concentration

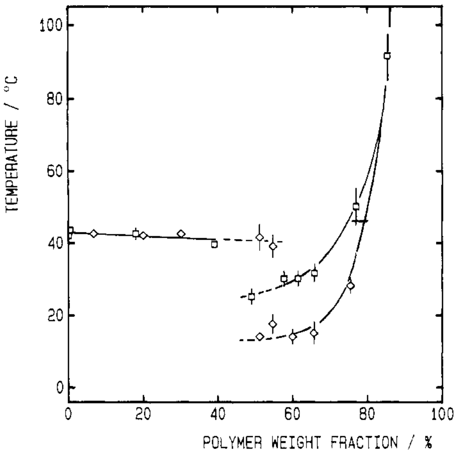

Figure 3. Cloud points of aqueous solutions of fractions I (lozenges) and IV (squares). The horizontal bar represents the composition of the liquid-crystalline phase precipitating at 46 °C from a 30% solution of fraction I. For convenience, the line joining the cloud points of dilute solutions intercepts the temperature axis, although the actual phase boundary is rather vertical and located at an infinitely small but nonzero polymer concentration.

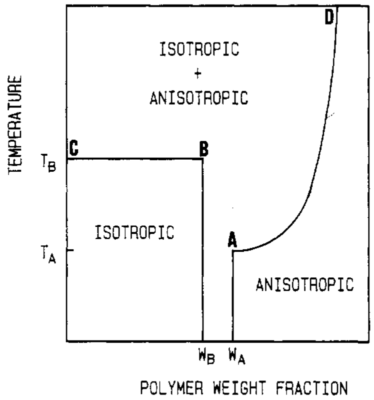

Figure 4. Schematic phase diagram of aqueous HPC solutions in the water normal liquid range. At any temperature, there exists a composition for which the solution is biphasic. However, three temperature ranges, delimited by T_A and T_B, can be distinguished, according to the width of this biphasic range.

per unit temperature experienced by the solution upon phase separation. For instance, isotropic solutions (curves a–c) give rise to a very sharp increase in turbidity, in agreement with the observation, from Figure 3, that the concentration of the phases in equilibrium above the cloud point is drastically different from the overall composition of the system. The change in concentration imparted to an anisotropic solution upon phase separation varies from large below 60% polymer by weight in negligible above 80%. In the latter case, the equilibrium concentration of polymer in the concentrated phase, for instance at 100 °C, is hardly a few percent higher than the overall composition, so that only a small amount of dilute phase has separated and the system exhibits a low turbidity.

The high fluidity of the isotropic phase in equilibrium with the white concentrated solution at high temperature is indicative of a very low polymer concentration. On the other hand, the equilibrium composition of the liquid-crystalline phase which precipitates at 46 °C from a 30% solution of fraction I (estimated as described later from the data of Figures 1 and 6) is indicated by the horizontal bar in Figure 3. It is located on the line joining the transition temperatures of anisotropic solutions of the same polymer sample (lozenges). These observations are consistent with the existence of a single biphasic domain at high temperature, as represented schematically in Figure 4: above a temperature T_B, corresponding to the transition temperature of isotropic solutions, only highly concentrated mesophases are stable. All other compositions phase-separate into a liquid crystal of polymer weight fraction given by the line AD and an infinitely dilute isotropic solution. At low temperature, a biphasic domain exist on a small concentration range,[3,11] delimited by w_A and w_B. No temperature dependence of w_A and w_B could be detected: regardless of their concentration, biphasic solutions at low temperature were not observed to become purely isotropic or anisotropic upon heating. Consequently, vertical boundaries at w_A and w_B are assumed. Curves d and e of Figure 2 are consistent with the sketch of Figure 4: solutions having a polymer weight fraction between w_A and w_B are biphasic in the whole water normal liquid range. They undergo two turbidimetry transitions upon heating which do not reflect any variation in the number or nature of the phases, but rather a change of their equilibrium composition. When the temperature reaches T_A, the cholesteric phase experiences a drastic transformation, as its composition has to change along the AD line. The rapid increase in polymer concentration is accomplished through the formation of drops of isotropic solution of composition w_B, which promotes an increase of turbidity. Upon further heating, a monotonous increase of the polymer concentration in the anisotropic phase is accompanied by an overall increase of the volume of isotropic solution. At the temperature T_B, the only stable isotropic solution is infinitely dilute. The isotropic phase in turn suffers a dramatic change in composition (from B to C in Figure 4), responsible for the second turbidity transition. The values of w_A and w_B define the location and width of the biphasic region at low temperature. Solutions of sample I having concentration of 51 and 55% belong to that range. The limits given in the literature[3,13] for unfractionated commercial HPC (nominal molecular weight above 60 kg·mol^{-1}) are 39–40 and 47%. The discrepancy probably originates from the lower molecular weight of fraction I, although the difference in molar substitution (4–4.5 in the literature, as compared to 6 in the present work) may also contribute to the difference.

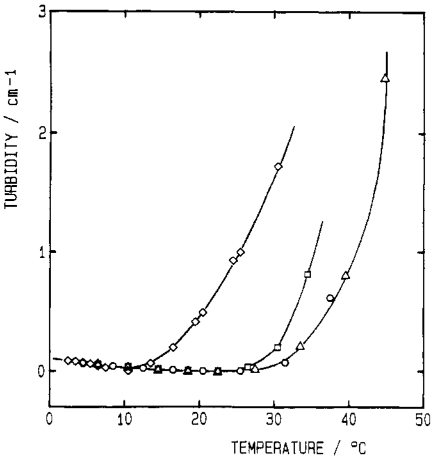

Figure 5. Turbidity as a function of temperature for aqueous mesophases of HPC fractions I (lozenges), II (squares), III (circles) and IV (triangles), having nearly the same weight fraction (65.7 ± 0.2%). The curves have been shifted along the absorbance axis in order to superpose the low-temperature portion of the curves.

The effect of molecular weight and/or molecular structure of the polymer on the phase diagram of its mixtures with water depends on the nature of the solution at low temperature. As shown in Figure 3, isotropic solutions of fractions I and IV phase separate at very similar temperatures, the difference, if any, being lower transition temperatures for sample IV. In contrast, the phase behavior of cholesteric solutions is extremely sensitive to the nature of the polymer sample: a difference of up to 18 °C is observed in Figure 3 between the cloud points of anisotropic solutions of fractions I and IV. Another illustration of this extreme dependence is presented in Figure 5, which gives the variation of turbidity as a function of temperature for aqueous mesophase of fractions I–IV, having nearly identical weight fractions. The phase behavior appears to closely reflect the molecular weight and structure of the polymer, as the decrease in the transition temperature accompanies the decrease in molecular weight and the small increase in the average number of hydroxypropyl substituents per glucopyranose unit, MS (Table I). The transition temperatures plotted in Figure 3 are in disagreement with the few quantitative phase diagrams given in the literature.[3,21,22] The reported data were collected on unfractionated commercial samples which are probably composed of a high variety of molecular weight and structure. In view of the sensitivity highlighted in Figure 3, this dispersion is likely to broaden the transitions and blunt the attributes of the diagram.

The main features of the HPC–water phase diagram—namely, (i) cholesteric mesophases are less stable upon heating than isotropic solutions and (ii) the difference in *transition temperature depends drastically on the structure* and/or molecular weight of the polymer—cannot be interpreted without an understanding of the origin of phase separation in aqueous HPC. The latter is strongly reminiscent of phenomena observed upon heating aqueous solutions of small molecules, e.g., diethyl ether[1] or isomeric glycol ethers,[1,27] and polymers, e.g., poly(ethylene glycol).[28] These molecules, including HPC, possess the ability to form hydrogen bonds with water while inducing considerable structural changes in the solvent through their apolar regions.[29] These changes can be pictured as an enhancement of the water structure around methyl and methylene groups of the solute, which minimize unfavorable contacts. The main factor in the thermodynamics of solution come from this *water structuring*, which brings about large negative contributions to both the enthalpy, ΔH_M, and the entropy of mixing, ΔS_M. In comparison, the contribution of the formation of hydrogen bonds between the water protons and the oxygen molecules of HPC is probably negligible, since the effect on the enthalpy consists of the small energy difference between a water–water and a HPC–water hydrogen bond, while the contribution to the entropy only involves the difference between the degree of order of a water molecule incorporated in one or the other hydrogen-bonded structure. Negative enthalpy and entropy result in a drastic temperature dependence of the free energy of mixing: at a sufficiently high temperature, the entropic term $-T\Delta S_M$, unfavorable to mixing, is predicted to overcome the negative heat of solution, resulting in a positive free energy and bringing about phase separation. Qualitatively, demixing, i.e., the substitution of most polymer–water contacts by polymer–polymer (in the concentrated phase) and water–water contacts (in the dilute phase), is related to the *melting* of the water edifice built around hydrophobic regions and, therefore, depends heavily on the molecular structure of the solute. In effect, the phase separation temperature of 2% isotropic aqueous solutions of HPC was found[1] to vary from 65 °C to about 40 °C when MS increases from 2 to 5. This is consistent with a reduced solubility in water when the polymer hydrophobicity increases, as measured for instance from the molar ratio of carbon to oxygen. The sensitivity of the transition temperature to the nature of the solute is again exemplified by the effect of a small change in the chemical nature of HPC:[2] the cloud point of a 1% solution is 2 deg lower for a polymer labeled with a low quantity of pyrene (one molecule every 438 glucopyranose units) than for pure HPC. The nearly constant phase separation temperature observed for isotropic solutions of fractions I and IV (Figure 3) show that T_B is insensitive to changes in molecular weight in the range defined by the fractions. The slight decrease in MS is not expected to improve significantly the solubility in dilute solution. The above description of HPC aqueous solutions explains the existence of two temperature ranges. Above T_B, the maximum number of water molecules that a HPC unit in an originally isotropic solution can accommodate depends only on temperature and is given by compositions located on the line AD of the phase diagram of Figure 4. The occurrence of demixing of cholesteric solutions at temperatures lower than T_B is unaccounted for. It is obviously related to the ordered nature of the solution but the expected contribution of the formation of a cholesteric liquid crystal to the thermodynamics of mixing cannot explain the observed difference. Predictions based on the lattice theory for solutions of semiflexible macromolecules[30] indicate that liquid-crystalline ordering is basically entropy driven. A liquid crystal forms spontaneously when the solution concentration is high enough so that the gain in combinatorial entropy upon mixing semirigid molecules in an ordered phase, as compared to mixing in an isotropic medium, exceeds the loss of orientational entropy upon ordering the solution. No enthalpy of transition is predicted nor required. Consequently, the entropy of mixing HPC and water to form an anisotropic solution, e.g., at a temperature lower than T_A and a concentration higher than w_B, should be higher (less negative) than the entropy to form an isotropic solution at the same temperature and concentration. In the absence of any enthalpic contribution, phase separation should then occur at a higher temperature for the liquid-crystalline solution. The reverse phenomenon is observed, stressing the existence of additional contributions to the enthalpy and/or entropy. In qualitative terms, the system behaves as if the molecular structure of the polymer were different in the isotropic and cholesteric phases. This could happen if HPC does not display the same surface to the solvent in the two phases, e.g., because of a different conformation of the polymer chain. Circumstantial evidence for a helical conformation in dilute solution of another cellulosic polymer, methylcellulose, has been recently produced,[31] based on induced circular dichroism measurements. Whether a conformational changes accompanies the isotropic to anisotropic transition remains a conjecture. However, the nearly parallel arrangement of the chains in the cholesteric phase confers some linearity to the polymer chains which could favor the formation of intramolecular hydrogen bonds, thereby increasing the ratio of carbon to available oxygen and altering the polymer affinity to water. It is also interesting to mention that a weight fraction of HPC (MS = 6) equal to 55%, i.e., approximately the lowest concentration at which a pure anisotropic phase forms at low temperature, corresponds to hardly two H_2O molecules per oxygen of the polymer. Therefore, the model of a significant number of water molecules experiencing an enhancement of structure around hydrophobic regions needs serious revision at high concentration. The properties of an isolated solvent molecule in a cholesteric matrix should rather be considered.

In the context of the above description, the difference between the fractions is difficult to understand on the basis

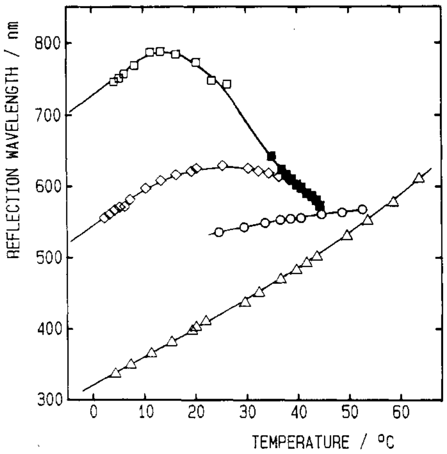

Figure 6. Wavelength of maximum reflection as a function of temperature for aqueous solutions of HPC fraction I. The polymer weight fraction is 60.0% (squares), 65.7% (lozenges), 69.7% (circles), and 75.5% (triangles). Some determinations for the 60% solution were performed by using circular reflectivity (filled squares).

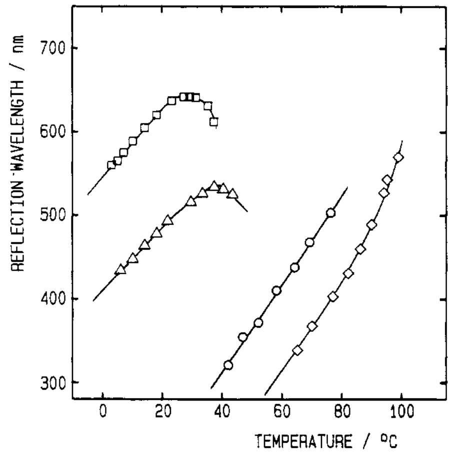

Figure 7. Wavelength of maximum reflection as a function of temperature for aqueous solutions of HPC fraction IV. The polymer weight fraction is 61.5% (squares), 65.9% (triangles), 77.0% (circles), and 85.8% (lozenges).

of molecular weight or molecular structure alone. The possibility remains that more subtle variations in the substitution pattern at constant DS and MS may exist between the fractions. Further work is needed to clarify the above effects. The cholesteric–isotropic phase transition temperatures are currently determined in other solvents, e.g., methanol, for the same fractions in order to assess the effect of molecular weight. Also, measurements of enthalpies of transition in the HPC–water system are being performed using adiabatic calorimetry, (i) upon heating at constant concentration and (ii) upon mixing a cholesteric phase with a sufficient amount of water to form an isotropic phase at constant temperature.

Effect of Phase Separation on the Optical Properties of HPC Liquid Crystals. Cholesteric liquid crystals of aqueous HPC selectively reflect circularly polarized light at a wavelength proportional to the pitch of their helicoidal supramolecular arrangement. At an appropriate concentration, the reflection may give rise to a peak in the UV–visible spectrum. Figures 6 and 7 give the wavelength of maximum reflection as a function of temperature for aqueous solutions of fractions I and IV, respectively. The figures reveal a complex dependence of the cholesteric pitch on temperature and composition.

Optical Properties in the Homogeneous Anisotropic Phase. At low temperature (below ca. 15 °C for fraction I), the pitch decreases when the polymer weight fraction increases, as shown, for instance, in Figure 8 from the concentration dependence of the reflection wavelength extrapolated to 0 °C. The difference between solutions of fractions I and IV is quite large: a variation of reflection wavelength of 50% is observed at a polymer weight fraction of 0.70. At a given concentration, the pitch increases with temperature in a roughly linear fashion. The data of Figure 6 were used to calculate the composition of the phase exhibiting the optical properties shown in Figure 1. The low-temperature part of the curves was extrapolated to 46 °C. From a plot of the reflection wavelength as a function of composition at this temperature, the weight fraction was estimated to be between 75 and 80%.

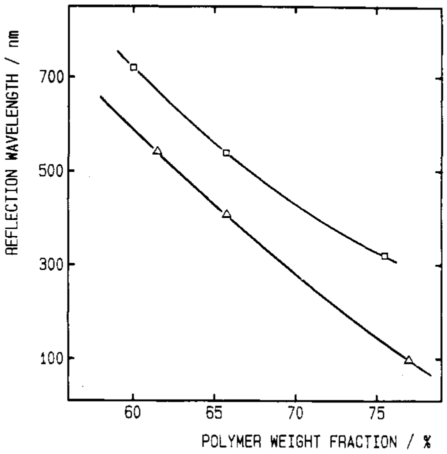

Figure 8. Wavelength of maximum reflection at 0 °C as a function of the polymer weight fraction for HPC fraction I (squares) and IV (triangles). The points have been calculated by a linear extrapolation of the low-temperature part of the curves of Figures 6 and 7.

Optical Properties in the Vicinity of and above the Phase Separation Temperature. At temperatures higher than the turbidity transition, the less concentrated cholesteric solutions exhibit a decrease in pitch upon heating. Although this unusual dependence is observed for all samples at weight fractions below 70%, it is especially manifest for solutions of fraction I, as in the top curve of Figure 6. Conventional spectrophotometry (open squares) could not be pursued above 27 °C because of the increasing turbidity of the sample. The effect was definitely established, however, using circular reflectivity measurements (filled squares). As the polymer concentration increases, the negative dependence is observed in an increasingly smaller temperature interval. At a weight fraction higher than about 0.75, the reflection wavelength shows no discontinuity as a function of temperature, although the turbidity curves still indicate that phase separation has occurred. Figure 6 suggests that all compositions below 75% assume, at high temperature, cholesteric arrangements of the same pitch. The curvature of the line separating the two regions of the phase diagram (AD in Figure 4) was earlier shown to determine how drastic a change in concentration a liquid crystal experiences upon phase separation. It is also responsible for the change in optical properties. Above T_A and at moderate concentration, a unique cholesteric phase exists, whose composition and pitch depend only on temperature. Its optical properties are the result of two competing effects: the decrease in pitch due to the increase in equilibrium polymer concentration and the increase of pitch upon heating. The less concentrated mesophases undergo a large change in concentration in a small temperature range, promoting a significant decrease in the reflection wavelength upon phase separation. At the same time, the variation of turbidity would be typically given by curve f in Figure 2. In contrast, the more concentrated liquid crystals (corresponding for instance to curve h, Figure 2) hardly experience any change in concentration, even upon heating in a large temperature interval, and therefore, their reflection wavelength shows a monotonous increase with temperature.

Conclusion

The phase diagram of aqueous solutions of (hydroxypropyl)cellulose is characterized by a single biphasic region, whose width depends on temperature, but which extends over the whole water normal liquid range. The reduced aqueous solubility of HPC at high temperature originates from the melting of the enhanced water structure built around hydrophobic regions of the polymer molecule. Cholesteric liquid crystals phase separate at lower temperatures than isotropic solutions. The difference may be as large as 28 deg for the lowest molecular weight sample. This behavior suggests that HPC chains display a more hydrophobic surface to the solvent in cholesteric phases than in isotropic solutions, possibly because of a different conformation. The less concentrated liquid crystals show unusual optical properties upon heating, indicative of an apparent negative temperature dependence of the cholesteric pitch. In contrast, more concentrated mesophases seem unaffected by phase separation. This is understood in terms of the competing effects of changes in temperature and equilibrium concentration of the anisotropic phase. The curvature of the phase boundary determines the predominant effect.

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