Influence of Dextran on the Phase Behavior of Suspensions of Cellulose Nanocrystals

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ABSTRACT: Acid hydrolysis of cellulose fibers produces suspensions of colloidal cellulose nanocrystals. At low concentrations these suspensions are isotropic, while at high concentrations the cellulose rods spontaneously organize into a chiral nematic liquid crystal phase. We have studied the effect of adding high molecular weight dextran to various concentrations of these cellulose suspensions. Adding dextran to an isotropic suspension caused no demixing of the two components. When dextran was added to a biphasic sample, it preferentially partitioned into the isotropic phase. Adding dextran to a completely anisotropic phase caused a phase separation into a dextran-rich isotropic phase and a dextran-poor anisotropic phase. The incorporation of dextran in the chiral nematic phase caused a marked increase in defects in the liquid crystalline texture.

Introduction

Cellulose, derived from both softwood kraft pulp and cotton filter paper, can be hydrolyzed with sulfuric acid to produce a suspension of colloidal cellulose nanocrystals.[1] Because of the rodlike shape of the nanocrystals, these suspensions display liquid crystalline behavior above a critical concentration, in agreement with Onsager's theory for rigid rodlike particles.[2] At low cellulose concentrations the suspensions are isotropic, with a random arrangement of rods, while at high concentrations the suspensions are anisotropic, with the cellulose rods packed in a chiral nematic arrangement. Just beyond the critical concentration for anisotropic phase formation is a biphasic region in which the isotropic and anisotropic phases coexist.[3]

This paper will examine the influence of dextran on the phase behavior of cellulose nanocrystals. Cellulose is a β-1,4 linked polymer of glucose, with a relatively rigid structure.[4] In this work, the cellulose is in the form of rodlike nanocrystals, with dimensions on the order of 100 nm by 10 nm, in which the cellulose chains are in a cellulose I crystalline array. Dextran is also a glucose polymer, but the molecular chain is more flexible, forming a branched coil-like conformation that consists of α-1,6 linkages with some α-1,3 branching.[5] This combination provides an interesting system to study, since the chemical constituents are very similar, with the major difference between the two components being their shape. It has been shown previously that if a physical property, such as shape or flexibility, of two components is different enough, a bulk demixing can occur.[6] In general, a random coil polymer or spherical particle will be excluded from an anisotropic phase made up of rodlike particles. This phenomenon has been shown to occur for several experimental systems.[6−13] The partitioning of the two different species has been explained by steric interactions between rods and coils[14,15] that cause a depletion attraction.[16]

In some experimental systems this drive to maximize entropy caused a complete exclusion of random coils from the ordered phase,[7] while in other systems detectable amounts of coiled polymers were found in the anisotropic phase.[8] In some cases, a more uniform distribution between the two phases was observed, the extent of which varied depending on the particular macromolecule added.[9] The various results reported in the literature indicate that this phase separation is sensitive to several factors such as the chemical nature, the relative size, and the concentration of the two components.

Essentially, the anisotropic phase tends to reject the presence of spherical molecules in order to maintain its orientationally ordered structure. In cases where the spherical particles can be incorporated into the ordered structure, their exclusion in the anisotropic phase does not occur, as exhibited in the lamellar phase of bacteriophage fd virus and polystyrene.[12] Investigations into systems of rods and coils have led to the discovery of several novel phases.[6,8,12] This paper is a preliminary investigation into the effect of blue dextran on the phase behavior of suspensions of cellulose nanocrystals. Blue dextran was chosen because the glucose chain units are very similar to those of the cellulose nanocrystals, and small amounts of a blue chromophore are covalently bonded to the chain, rendering the concentration of dextran readily quantifiable.

Experimental Section

Materials and Stock Solutions. A colloidal suspension of cellulose nanocrystals was prepared by hydrolyzing cotton filter paper (Whatman, 1) with 64 wt % sulfuric acid at 45 °C for 45 min. Prior to hydrolysis, the filter paper was cut into small squares and fed through a Wiley mill (Thomas Scientific) to pass a 1 mm mesh. Typically, 40 g of the ground paper was treated with 700 mL of acid. Immediately following hydrolysis, the suspension was diluted 10-fold with water to stop the reaction. The suspension was then concentrated by centrifugation and washed twice by diluting with water, mixing, and centrifuging. Next, the sample was dialyzed against water for several days. The final step to achieve a colloidal suspension was repeated sonification (Branson Sonifier, Model 350) for 7 min intervals for a total of 35 min, cooling in an ice bath between steps. The suspension was then allowed to stand over a mixed bed resin (Sigma) for 48 h and then filtered through hardened ashless filter paper (Whatman, 541). The final aqueous suspension was 2.4% concentration by weight. Previous experimental measurements on similarly prepared cellulose nanocrystals indicate that the surface charge density is about 0.15e/nm^2.[17]

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Table 1. Composition of Biphasic Samples with Fixed Total Dextran Concentration and Increasing Concentration of Cellulose Nanocrystals

sample	A	B	C	D	E
total cellulose concentration (wt %)	6.5	8.8	9.4	11.0	13.3
cellulose in isotropic phase (wt %)	6.5	7.2	8.1	10.5	10.8
cellulose in anisotropic phase (wt %)		9.6	10.5	12.0	14.0
volume of isotropic phase (mL)	3.00	2.24	1.67	1.14	0.64
volume of anisotropic phase (mL)		0.76	1.33	1.86	2.36
anisotropic phase volume fraction		0.25	0.44	0.62	0.79
conc of dextran in isotropic phase, μmol/L	0.307	0.382	0.442	0.607	0.892
conc of dextran in anisotropic phase, μmol/L		0.247	0.217	0.247	0.277
partition coefficient for dextran between phases		1.55	2.04	2.46	3.22

A 3 mg/mL solution of blue dextran (MW 2×10^6, Pharmacia Fine Chemicals) was prepared using purified water. The radius of gyration, R_g, for dextran of MW 2×10^6 is 34 nm.[18] The blue color of the dextran is due to 0.1 mmol of Reactive Blue 2 dye per gram of dextran that is bonded randomly to hydroxyl groups along the chain.[19] Each dye substituent contains three sulfonate groups, corresponding to about 600 charges per dextran coil.

Preparation of Cellulose−Dextran Suspensions. Samples of increasing cellulose concentration were prepared by allowing aliquots of the original suspension to evaporate for several days in large Petri dishes, forming both biphasic and anisotropic samples. Vials A−E each contained 3 mL of cellulose suspension, increasing in concentration from vial A to vial E, and 70 μL of blue dextran solution. Vials 1−5 were each filled with 2 mL of the same concentration of cellulose suspension, and an increasing amount of blue dextran was added to each of these vials. The blue dextran was added in solid form rather than in solution in order to maintain the same concentration of cellulose suspension in each vial. Evidence of phase separation was already visible after 1 h, but the vials were left to stand overnight. Samples were taken from the isotropic and anisotropic phases and diluted 3-fold prior to analysis. In a third set of samples, vials I−IV, blue dextran was added, in increasing amounts, to completely anisotropic samples and the resulting phase separation was followed over a period of one month.

Sample Analysis. UV−visible absorption spectra were measured using a Perkin-Elmer Lambda 14 UV/vis spectrometer, with the wavelength of maximum absorbance for blue dextran measured at 610 nm, using dextran-free suspensions of cellulose as the reference. The concentration of cellulose in the samples was determined gravimetrically, weighing the samples before and after the evaporation of water. For the samples containing blue dextran, the weight of the dextran was calculated from the absorbance spectra and subtracted accordingly. The volume fraction of the two phases was determined by measuring the heights of the anisotropic and isotropic phases in each vial. The size of the cellulose nanocrystals was determined by AFM, and the mean values (L = 110 nm and d = 10 nm) were used for calculations. To convert cellulose concentrations in weight percent to number density of nanocrystals, a cylindrical shape and a density of 1.6 g/mL were assumed for the nanocrystals. Photomicrographs were taken using a polarized light microscope (Nikon Microphot-FXA).

Results and Discussion

The effects of blue dextran addition were observed on suspensions of cellulose nanocrystals at concentrations where isotropic, biphasic, and anisotropic phases were initially present.

Isotropic Samples. Blue dextran was added to an isotropic suspension of cellulose rods, mixed by repeatedly inverting the vial, and allowed to stand. When no bulk demixing was observed, the concentration of blue dextran added was increased, up to the solubility limit of about 40 mg/mL. Still, no separation was evident after a period of several days. The depletion potential in systems of colloidal rods and spheres can be determined using the following equation[13,20]

$$W(h) = -\frac{2}{3}k_B T \varphi_r \frac{L}{D}\frac{R}{D}\left(1 - \frac{h}{L}\right)^3 \qquad (1)$$

where k_BT is the thermal energy, φ_r is the volume fraction of rods, L is the rod length, D is the rod diameter, R is the radius of the spheres, and h is the distance between the surfaces of the spheres. This equation is valid in the limit of $R \gg L$. Our system, with R:L approximately 1:3 (where R is taken as R_g for the coil), clearly does not meet this criterion, but we may use it to get a rough idea of the volume fraction of rods at which demixing may be expected. Using $3k_BT$ as the minimum attraction energy required,[13,21] we calculated the demixing transition to occur for a volume fraction of rods of about 12%. This volume fraction is above the volume fraction at which the isotropic−chiral nematic phase transition is expected to occur in our system, and so no demixing is expected for an isotropic suspension of cellulose rods, in accordance with our observations. Depletion-induced phase separation has been observed at rod concentrations below the isotropic−nematic transition, but for mixing of rods having a much higher aspect ratio with large colloidal spheres.[13]

Biphasic Samples. The cellulose suspension was concentrated by evaporation to produce several biphasic samples, increasing in anisotropic volume fraction from vial A to vial E (Table 1). When the blue dextran solution was added, the suspensions were mixed by repeatedly inverting the vials to obtain homogeneous suspensions. Immediately after mixing, the five vials looked identical; after a short period of time, the blue color began migrating upward in the biphasic samples. Upon standing overnight, the phase separation was complete, leaving a transparent blue upper phase and a cloudy lower ordered phase, as shown in Figure 1. The intensity of the blue color in the isotropic phase clearly increased from vial A to vial E.

The partitioning of blue dextran between the isotropic and anisotropic phases was quantified with an UV−visible spectrometer. The absorbance of blue dextran in the isotropic phase increased with increasing cellulose concentration. The absorbance in the anisotropic phase showed no distinct trend with cellulose concentration and was taken to be the same within experimental error for the four vials. Although the absorbance in the anisotropic phase was significantly less than the absorbance in the isotropic regions, the absorbance was not zero, indicating that the blue dextran was not completely excluded from the ordered phase.

The relative amount of blue dextran in each phase was quantified by calculating a partition coefficient,[22] K, the concentration of blue dextran in the isotropic phase, d_i, divided by the concentration of blue dextran

Table 2. Compositions of Biphasic Samples with Increasing Total Dextran Concentration and Fixed Concentration of Cellulose Nanocrystals

sample	1	2	3	4	5
total cellulose concentration (wt %)	10.3	10.3	10.3	10.3	10.3
cellulose in isotropic phase (wt %)	9.94	9.76	9.65	9.40	9.03
cellulose in anisotropic phase (wt %)	10.9	10.8	11.3	11.3	11.7
volume of isotropic phase (mL)	0.80	0.80	0.80	0.80	0.80
volume of anisotropic phase (mL)	1.2	1.2	1.2	1.2	1.2
anisotropic phase volume fraction	0.6	0.6	0.6	0.6	0.6
conc of dextran in isotropic phase, μmol/L		0.142	0.367	0.637	0.922
conc of dextran in anisotropic phase, μmol/L		0.052	0.127	0.217	0.277
partition coefficient for dextran between phases		2.72	2.88	2.93	3.33

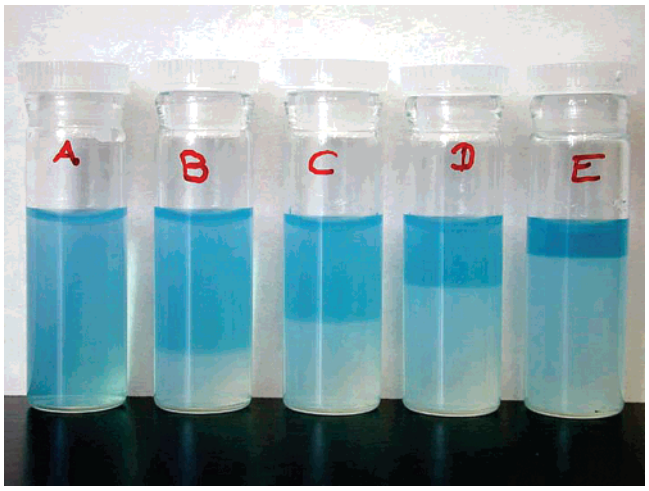

Figure 1. Digital photograph of samples with the same blue dextran concentration in each vial and increasing cellulose concentration from vial A to vial E (see Table 1), showing the preferential partitioning of blue dextran into the upper isotropic phase.

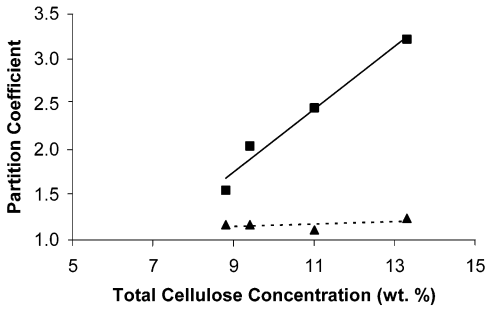

Figure 2. Partition coefficients for dextran between isotropic and anisotropic phases versus cellulose concentration for samples B−E. The upper trend line (squares) shows experimental values, and the lower trend line (triangles) shows theoretical values, calculated using eq 3.

in the anisotropic phase, d_a:

$$K = \frac{d_i}{d_a} \tag{2}$$

The partition coefficient increased as the total cellulose concentration increased, as shown in Figure 2. However, increasing the overall cellulose concentration changes important system variables such as the relative volume fraction and the cellulose concentration of each phase. As the total cellulose concentration increases, the cellulose concentrations both in the isotropic phase, c_i, and in the anisotropic phase, c_a, increase, and also diverge slightly, as has been observed previously for this system of polyelectrolyte rods.[3] This is contrary to the predictions for hard core monodisperse rods, where the concentrations in the isotropic and anisotropic phases are predicted to remain constant across the biphasic region. As the concentration difference between the isotropic and anisotropic phases increases, more blue dextran partitions into the isotropic phase. This experimental observation has been predicted by the following equation[23]

$$K = \exp(B_{rc}(c_r^n - c_r^i)) \tag{3}$$

where B_{rc} is the second virial coefficient of the rod−coil interactions, which depends on the relative sizes of rods and coils, and c_r^n and c_r^i are the number densities of rods in the nematic and isotropic phases, respectively. The order of magnitude of the rod−coil second virial coefficient is given by $B_{rc} \sim LD^{1/3}R_G^{5/3}$. Our experimental partition coefficient is larger and increases more with nanocrystal concentration than is predicted by this theory (Figure 2). Since our observed concentrations in each phase are not constant across the biphasic region, and the theory gives an order of magnitude only, the discrepancy is not unexpected.

To try and minimize the effect of varying phase compositions across the biphasic region, another set of vials was prepared with the same concentration of cellulose suspension in each vial and a constant anisotropic volume fraction of 0.6. Vial 1 was left blank, and increasing amounts of blue dextran were added to each subsequent vial. The compositions of the samples are given in Table 2. After phase separation it was readily visible that the blue dextran was enriched in the isotropic phase. As the concentration of blue dextran increased, the partition coefficient increased slightly. The experimental and theoretical partition coefficients are in closer agreement for the second set of vials. The experimental values for the partition coefficient were around 3.0 (Table 2), and values calculated from eq 3 were from 1.07 to 1.19, with both experimental and theoretical values increasing slightly as the dextran concentration increased.

All the vials were initially at the same cellulose concentration; however, after the dextran was added, the relative proportions of cellulose in each phase changed. This divergence in the isotropic and anisotropic cellulose concentrations on the addition of dextran is illustrated by a partial phase diagram (Figure 3). The number densities of cellulose rods and dextran coils were multiplied by R_g^3 to make the values dimensionless, following Sear's theory.[23] The squares represent experimental values; the solid lines, which are best fit to the data, mark the phase boundaries, and the dotted lines are the tie lines. The left-hand portion of the diagram is the isotropic region, I, the lower right-hand corner is the chiral nematic region, N, and the middle represents the biphasic region. The downward slope of the tie lines shows that the density of dextran coils in

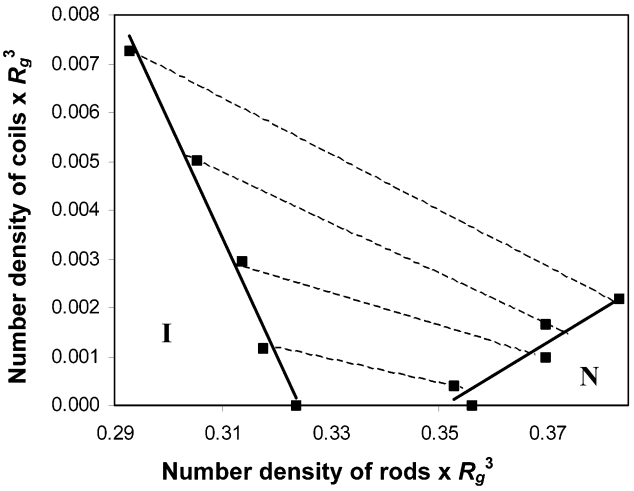

Figure 3. Partial phase diagram of a cellulose suspension with blue dextran added, using data from samples 1−5 (Table 2). The number densities of the rods and coils are multiplied by R_g^3, where R_g is the radius of gyration of the dextran coil, to make the values dimensionless. The isotropic region, I, is on the left-hand side, and the chiral nematic region, N, is in the lower right-hand corner. The downward sloping tie lines in the biphasic region indicate that the isotropic phase is rich in coils and the anisotropic phase is rich in rods.

the chiral nematic region is much less than that in the isotropic region. The addition of dextran causes a widening of the biphasic region. This occurs for two reasons: the negative slope of the isotropic boundary line indicates that rod density decreases in the isotropic phase, and the positive slope of the chiral nematic phase boundary indicates that rod density increases in the chiral nematic phase. There is a mutual exclusion between the cellulose rods and the dextran coils. As more dextran moves into the isotropic phase, the osmotic pressure increases. To balance the osmotic pressure, cellulose rods migrate from the isotropic phase to the chiral nematic phase, causing the observed widening of the biphasic region. The mutual exclusion of rods and coils was predicted theoretically by Flory, who stated that the addition of coils replaces the rods in the isotropic phase and the rod concentration in the nematic phase consequently increases.[14] In our work, the chiral nematic region has a significant tolerance for dextran coils, indicating that the coils are somehow incorporated into the ordered structure. Thus, we next examined the effect of adding blue dextran to a completely ordered phase of cellulose rods.

Anisotropic Samples. Blue dextran was added in increasing amounts, from approximately 1 to 7 μmol/L, to the completely anisotropic samples in vials I−IV. The blue dextran initially spread evenly throughout the cellulose suspensions, but after a few days a phase separation occurred into a dark blue upper phase and a lighter blue lower phase. The volume fraction of the upper phase increased during the first week and slowly leveled off over the period of a month (Figure 4). The more blue dextran that was added to the vial, the larger the final volume of the upper phase. Thus, over time the addition of dextran forced the suspension into a two-phase system. (This behavior contrasts with that of the more dilute biphasic samples, where the concentrations listed in Tables 1 and 2 remained constant for several months.)

The phase separation occurring in the anisotropic samples involves the upward migration of dextran and

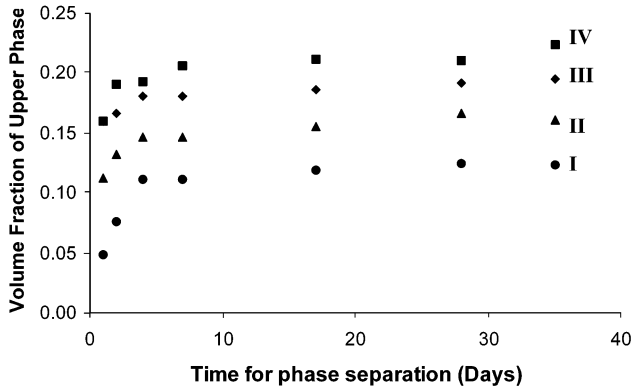

Figure 4. Volume fraction of the upper isotropic phase versus time for phase separation of an initially anisotropic sample (13 wt % nanocrystals) induced by adding increasing amounts of blue dextran to vials I−IV.

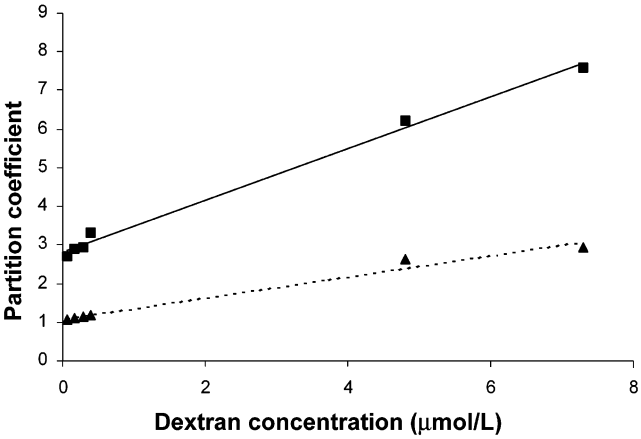

Figure 5. Partition coefficient versus dextran concentration for biphasic samples 2−5 and anisotropic samples III and IV. The upper trend line (squares) shows experimental values, and the lower trend line (triangles) shows theoretical values, calculated using eq 3.

the downward migration of cellulose rods, similar to the mutual exclusion between these two particles in the biphasic samples. The initial concentration of the anisotropic phase was 13% cellulose by weight. After the induced phase separation, the upper phase was 5.3% and 6.6% and the lower phase was 13.2% and 15.5% in vials III and IV, respectively. The blue dextran migrated preferentially into the phase with the lower density of cellulose rods, with partition coefficients of 6.2 and 7.6 for vials III and IV, respectively. (The volume of the upper phase in vials I and II was too small to separate for accurate measurements.)

Although there are still differences between experimental and theoretical partition coefficients, the results for the anisotropic samples correlate with those from the biphasic samples (Figure 5). The difference in rod concentration between the upper and lower phases plays a major role in the partitioning of dextran. With the biphasic samples, the initial concentration difference is augmented upon the addition of dextran, while for the anisotropic samples the addition of dextran instigates phase separation, creating a difference in rod concentration. There is a larger rod concentration difference for the initially anisotropic samples and therefore larger partition coefficients.

When the phases generated by adding dextran to an initially anisotropic sample were viewed between crossed

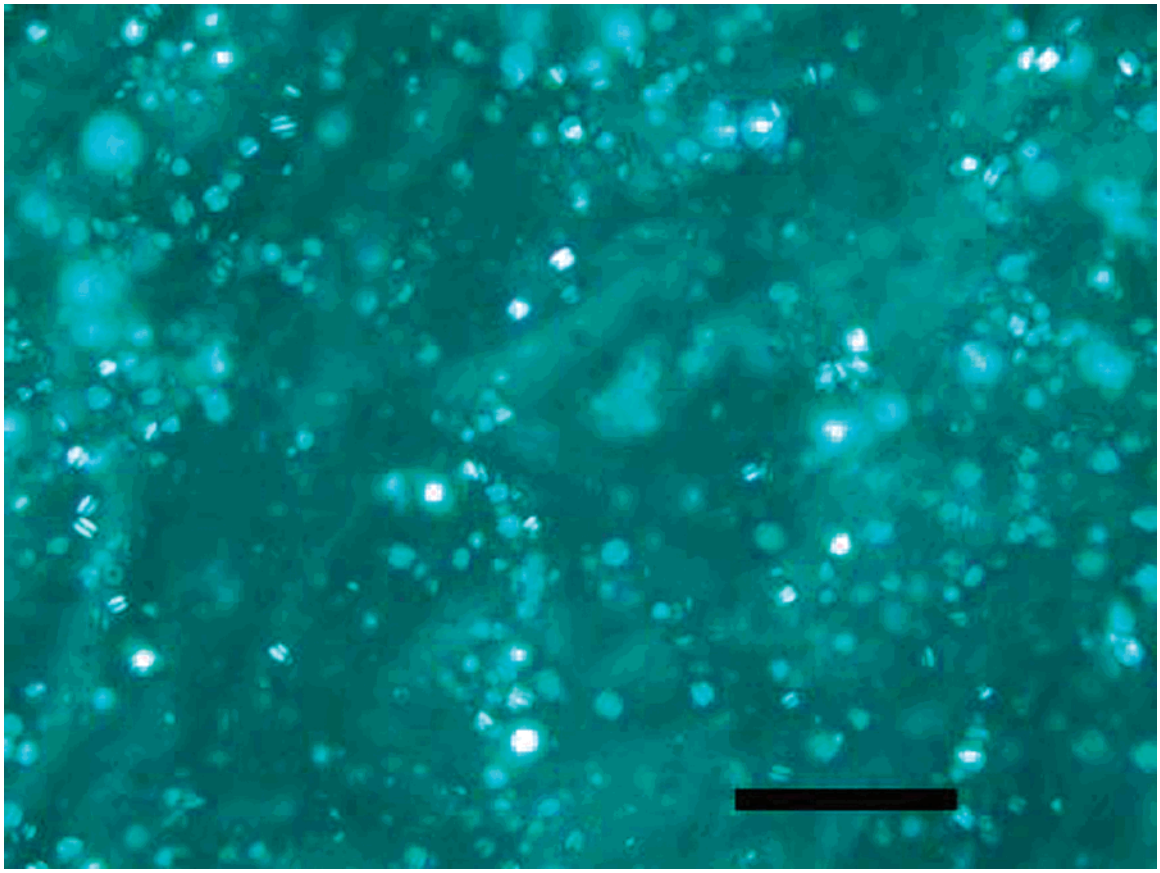

Figure 6. Photomicrograph between crossed polarizers of the upper dextran-rich phase (scale bar 100 μm).

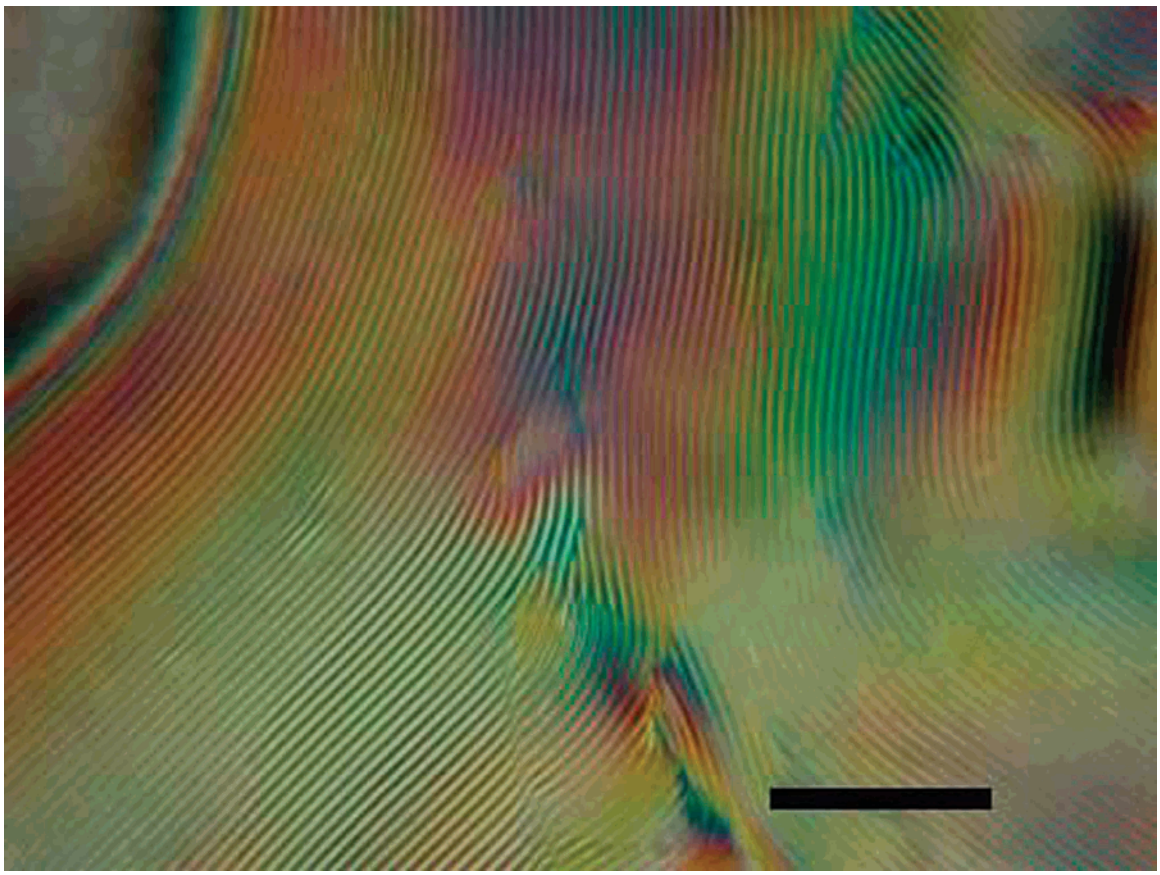

Figure 7. Photomicrograph between crossed polarizers of a completely anisotropic sample before the addition of blue dextran, showing the characteristic fingerprint texture and only a few disclinations (scale bar 100 μm).

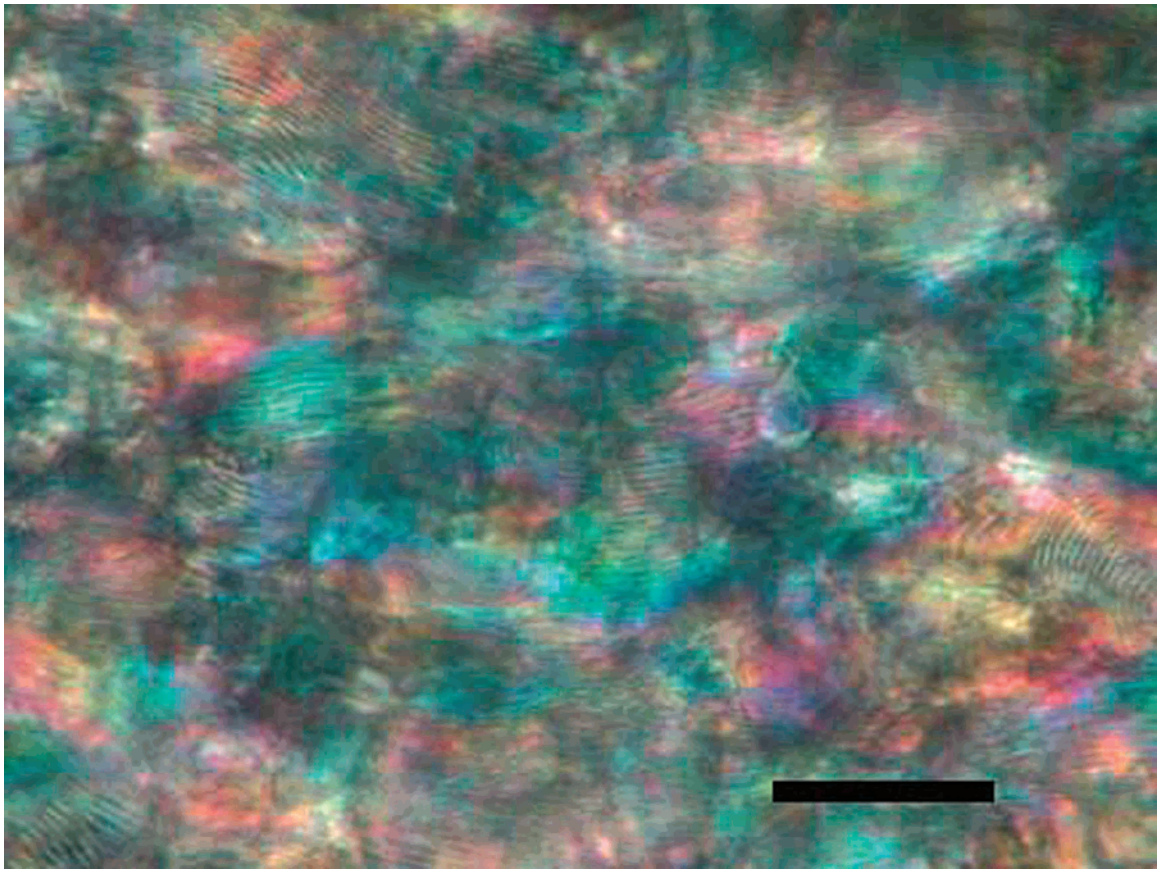

Figure 8. Photomicrograph between crossed polarizers of a lower dextran-poor phase, showing the distorted fingerprint texture and numerous disclinations (scale bar 100 μm).

polarizers, it was evident that the dextran-rich upper phase had become almost completely isotropic. The background was dark with a few bright tactoids, small volumes of suspension displaying short parallel white lines, indicating the initial stage of ordering of a chiral nematic liquid crystal (Figure 6). Before the addition of dextran, the anisotropic phase exhibited long continuous fingerprint lines with very few disclinations, characteristic of a well-ordered chiral nematic liquid crystalline phase (Figure 7). Adding dextran not only caused an isotropic phase to separate but also caused changes in the texture of the anisotropic phase. The fingerprint lines decreased in pitch and followed a more tortuous path with many disclinations (Figure 8). The fingerprint texture indicates that the structure is initially uniform and free from distortions and defects over macroscopic distances, in the absence of dextran molecules. Because of their size and shape, dextran coils cannot readily fit into the chiral nematic structure assumed by the suspension of rods. They are, however, compatible with dilute isotropic suspension of rods and apparently even with the more concentrated isotropic suspensions of rods in the two-phase region. However, the exclusion from the anisotropic phase is not complete. The question is, how do the coils fit into the ordered phase at relatively high coil and rod concentrations? Comparison of Figures 7 and 8 suggests that the dextran-rich phases are also defect-rich. The creation of distortions and defects in a liquid crystalline phase costs energy, thus destabilizing the ordered phase with respect to the isotropic phase and contributing to the appearance of the isotropic phase. Furthermore, by definition, defects are regions where the liquid crystalline director is undefined.[24] The dimensions of such regions must be at least of the order of the length of the rods, and it seems possible that the dextran coils can "hide" in these defects. Thus, we postulate that, in addition to the effects of size and shape, the defect texture of liquid crystalline phases may contribute to the partitioning of coils between the ordered and disordered phases in situations where the rod−coil interactions are athermal and concentrations are high.

Conclusion

The partitioning of dextran between isotropic and anisotropic phases of cellulose suspensions is influenced by, and has an influence on, the relative rod concentrations in each phase. In purely isotropic suspensions, the two components coexist, since the entropy of mixing dominates the interaction at low cellulose concentrations. In biphasic samples, the blue dextran is preferentially partitioned into the isotropic phase, the phase with the lower cellulose rod concentration. The addition of blue dextran to these samples causes a widening of the biphasic region due to a mutual exclusion between the cellulose rods and the dextran coils. In completely anisotropic samples, the addition of dextran induces a phase separation into a coil-rich, rod-poor isotropic phase and a coil-poor, rod-rich anisotropic phase. The presence of dextran in the anisotropic phase results in a distorted liquid crystalline texture.

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