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Uniaxial-biaxial phase transition in lyotropic nematic solutions: Local biaxiality in the uniaxial phase

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It has been recently shown that the system potassium laurate–decanol–water presents three nematic phases, two uniaxial and one biaxial. We are currently investigating the structure of these phases by scattering methods. The study reported here describes the first experiment, neutron scattering with contrast variation, which demonstrates that the aggregates in one uniaxial phase in the vicinity of the transition to the biaxial phase are statistically biaxial. This observation provides a new insight into the uniaxial-biaxial phase transition.

INTRODUCTION

Lyotropic nematics are solutions of aggregates of amphiphilic molecules in water with long-range orientational order. Two uniaxial phases were observed first. They were distinguished by the sign of their anisotropy of magnetic susceptibility.[1,2] Then structural studies by x-ray scattering suggested them to be formed of oblate or prolate aggregates of amphiphilic molecules whose average orientation of the axes defines the director of the phase.[3] More recently, they were shown to have birefringences of opposite signs.[4,5] It was the development of these latter studies which led to the discovery of a third nematic phase with biaxial symmetry.[4] The relative locations of the three phases in the phase diagram of the system considered here, potassium laurate–decanol–water,[6] are shown in Fig. 1. The biaxial phase lies in between the two uniaxial phases.

As said above for the structural studies of the uniaxial phases the analysis of the first x-ray[3] and neutron[7] diagrams led us to propose a first picture of either oblate or prolate aggregates. The uniaxial phase at high temperature turned out to be formed of prolate aggregates while the uniaxial phase at lower temperature turned out to be formed of oblate aggregates. These aggregates appear to have some polydispersity and are therefore statistically oblate or prolate; they have a low aspect ratio, in the range 2–3, and they are rather densely packed in the solution, as the amphiphile concentration is about 30% in weight. Because of the very nature of direct scattering experiments we could not discriminate between uniaxial phases made of uniaxial aggregates with their axis parallel to the director and uniaxial phases made of biaxial aggregates with one axis parallel to the director and the other orientationally disordered around the director. In this work we move to a second stage of the description where, after having designed an adequate experiment, we answer this important structural point in the case of the uniaxial phase considered as made of prolate aggregates up to now. We show that the aggregates are indeed biaxial statistically, with a noncircular section in a plane normal to the director. The uniaxiality of the phase is therefore due to the orientational disorder of these normal sections. We shall propose in the discussion that the transition to the biaxial phase corresponds to an orientational ordering of these sections.

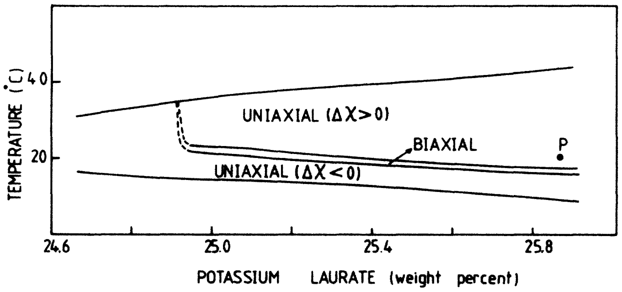

FIG. 1. Section of the phase diagram of the potassium laurate–decanol–D_2O mixture with protonated soap and protonated alcohol for a decanol content of 6.24%. Concentrations are expressed in weight percent. The limits of the phases are somewhat uncertain around 24.9%, hence the dotted lines, see Ref. 6. P is the representative point of the phase studied here.

METHOD

We model the most general aggregate as an ellipsoid with three axes,[7] long (l), short (s), and intermediate (i), as shown in Fig. 2. We are interested in the uniaxial phase where the director is defined by the alignment of the long axes (l), i.e., the "prolate phase." We want to study the (i,s) section and determine if it is isotropic ($i=s$) or anisotropic ($i>s$). This information cannot be provided directly by simple scattering experiments with scattering vectors perpendicular to the director ($q_\perp$). This is because of the uniaxiality of the phase which corresponds to an orientational disorder around the director and gives the scattered intensity an isotropic distribution. This type of experiment cannot but provide information which has the symmetry of the phase, not that of the aggregate. In order to obtain more precise information about the latter we shall take advantage of another geometrical feature of the aggregates. Indeed, it appears from Fig. 2 that the two possibilities differ not only by the radial distributions within their normal sections but also by the curvatures of these sections. If the normal section is isotropic ($i=s$) it is circular and its curvature is

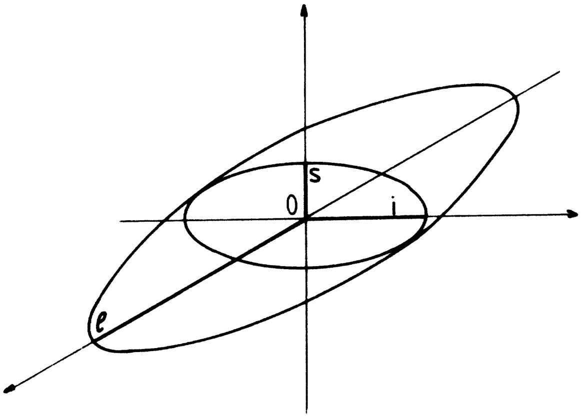

FIG. 2. Schematic representation of the most general aggregate with the (i,s) section studied here.

homogeneous; if it is anisotropic $(i > s)$ the section exhibits flat and curved regions and its curvature is no longer homogeneous. Therefore an alternative approach to the anisotropy of the normal section consists in searching for different curvatures in it. For this we must be able to label different interfacial curvatures selectively in order to make them accessible to scattering experiments.

Indeed, recent structural studies of two ternary soap–fatty alcohol–water systems with aggregates displaying heterogeneous interfacial curvatures show that such a labeling of the interfacial curvature is spontaneously realized as the relative concentration of soap and alcohol is modulated along the interface by its curvature.[8,9] The two molecules have similar configurations relative to the interface[10] but the local concentration of alcohol is lower in the curved regions than in the flat ones and that of soap higher in curved regions than in flat ones. The search for an eventual biaxiality of the aggregate therefore goes through the detection of concentration fluctuations within its section. We shall now show that this is possible applying the contrast-variation method in neutron scattering experiments.

The coherent scattering of neutrons by deuterons is much stronger than by protons and this provides a way to study the distribution of one type of organic molecules among others when, for instance, the first ones are deuterated.[11] Thus if we deuterate soap but leave decanol protonated we may expect the scattered intensity to be sensitive to the way the molecules are distributed in the aggregate. If the distribution is homogeneous, i.e., if the soap is uniformly present everywhere in the aggregate, the radiation is scattered by the whole aggregate. If, on the other hand, the soap is more concentrated in certain parts of the aggregate, only this part will scatter the neutrons. Moreover, we can control another parameter, the contrast of the aggregate with respect to the surrounding solvent, and this may help to discriminate between the two situations. This contrast depends on the average scattering length density of the solvent which can be continuously varied by mixing light and heavy water. Thus if the distribution of deuterated and protonated amphiphiles is homogeneous the aggregate has a uniform scattering-length density and when that of the solvent is varied the scattered intensity curves must remain similar. However, if the distribution is not homogeneous the scattering-length density of the aggregate is not uniform and when that of the solvent is varied different parts of the aggregates may be masked in their turn so that the scattered intensity curves will no longer simply scale the solvent variation. This is an apparent change of the form factor of the aggregate. We propose here to look for an eventual inhomogeneous distribution of the amphiphiles by comparing spectra obtained with aggregates where both amphiphiles are protonated, a reference case where the scattered-length density of the aggregate cannot be but homogeneous (an experimental fact showing that the contribution of the heterogenecity due to the polar heads is negligible will be given under "Results"), with spectra obtained with aggregates where one type of amphiphile is deuterated, which contain the information relative to the distribution.

EXPERIMENTAL

We have prepared two series of samples, one with protonated potassium laurate and decanol, the other with perdeuterated laurate and protonated decanol, in various mixtures of heavy and light water. The concentrations of the two series are slightly different in order to correct the change of transition temperatures and the slight change of aggregate size induced by the use of a deuterated amphiphile. By observations under a polarizing microscope, conoscopy and x-ray scattering we controlled all our samples to correspond to the same point of the uniaxial phase of prolate aggregates indicated in Fig. 1. The molar concentrations are 3.07% potassium laurate, 1.11% decanol, and 95.82% water for the series with protonated aggregates, and 3.19% potassium laurate, 1.22% decanol, and 95.59% water for the series with partly deuterated aggregates. The compositions of the solvents are given in the captions of Figs. 3 and 4.

The neutron scattering experiments were performed at Institut Laue-Langevin.[12] The spectrometer D17 was used. The range of scattering vectors covered was 0.03–0.26 Å^{-1}, the wavelength spread $\Delta\lambda/\lambda$ was 10% and the divergence of the incident beam was set at 6×10^{-3} rad. The samples were contained in quartz cells of 1 mm thickness mounted in a thermostated sample holder at 24 °C. The director of the phase was oriented by a magnetic field of 12 kG generated by an electromagnet set up on the spectrometer.

RESULTS

We consider only the scattered intensity curves obtained for scattering vectors $q_\perp$ perpendicular to the director which provide the structural information concerning the normal section (i,s) of the aggregates. These curves are shown in Fig. 3 for the aggregates made of protonated decanol and laurate, and in Fig. 4 for the aggregates made of protonated decanol and deuterated laurate. The curves measured for different scattering-length density of the solvent are similar in Fig. 3. They can be nearly deduced from each other by a translation along the vertical axis with logarithmic scale. This is no longer the case for the curves presented in Fig. 4. The similarity observed in Fig. 3 implies that the protonated aggregates behave like homogeneous particles and, more specifically, we are sure that the heterogeneity associated with the polar heads is a negligible contribution here. On the other hand, the nonsimilarity observed in Fig. 4 implies that the partly deuterated aggregates behave as inhomogene-

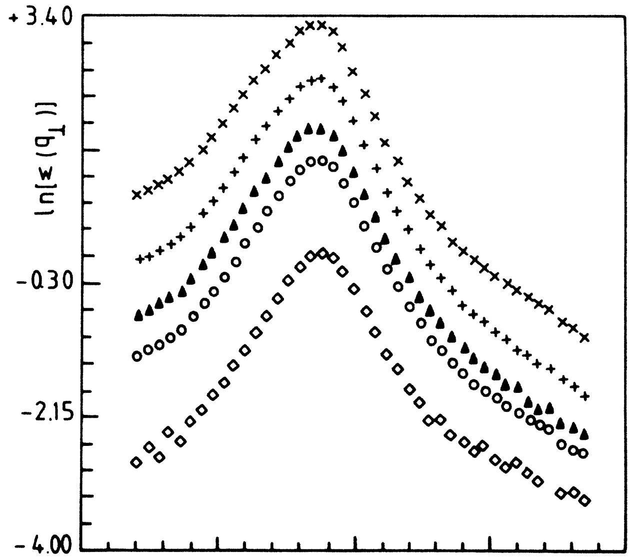

FIG. 3. Log of the scattered intensities on an absolute scale [$\Sigma(q)$ in cm^{-1}] measured in the plane normal to the director ($q_\perp$) for aggregates with protonated decanol and laurate in solvents of different compositions (molar ratio [H_2O]/[D_2O]: 0 = ×, 0.44 = +, 1 = ▲, 1.50 = ○, and 3.53 = ◇).

ous particles and the molecules of laurate and decanol are therefore not uniformly distributed along the interface of the normal section. Following our previous presentation of the method, this proves that the interfacial curvature along the normal section is not homogeneous; therefore this section is not circular, and the aggregates in this uniaxial phase are statistically biaxial. We recall that the statistics considered here are associated with the polydispersity.

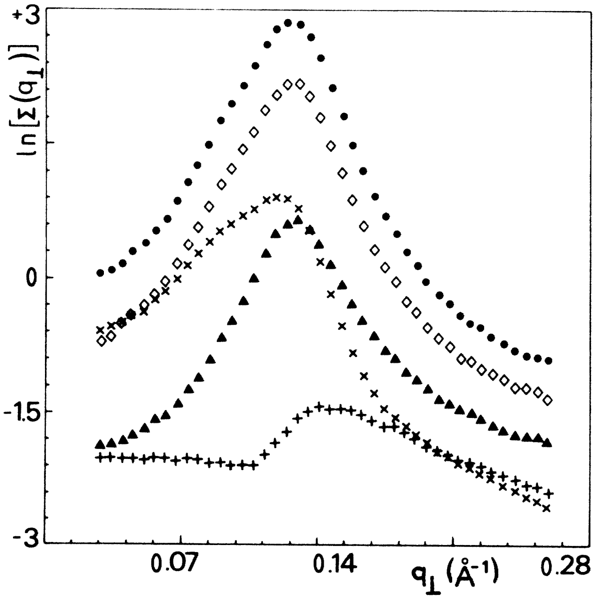

FIG. 4. Log of the scattered intensities on an absolute scale [$\Sigma(q)$ in cm^{-1}] measured in the plane normal to the director ($q_\perp$) for aggregates with protonated decanol and deuterated laurate in solvents of different compositions (molar ratio [H_2O]/[D_2O]: ∞ = ●, 3.54 = ◇, 0 = ×, 1 = ▲, and 0.44 = +).

DISCUSSION

In this study we have taken advantage of the microsegregation of soap and decanol molecules in the aggregates of a lyotropic nematic phase to get information about the shape of these aggregates.

We shall say a few words about the phenomenon of microsegregation first. It permits important variations of the interfacial curvature. It is therefore a factor which favors the existence of finite aggregates with anisotropic shapes at rather important concentrations.[13] The simultaneous realization of these three conditions has been presented as a necessity for the occurrence of nematic phases.[14]

The important point of this study now concerns the relation between the shapes of the aggregates and the symmetries of the phases. The fact that the aggregates are statistically biaxial in a uniaxial phase imposes that the (i,s) sections are orientationally disordered around the director defined by the long axes (l). The transition to the nearly biaxial phase might therefore be described as an orientational ordering of the (i,s) sections in a plane normal to the director so that the long axes (l) and the short ones (s) define two directors. Going further on, the transition to the second uniaxial phase, on the other side of the biaxial one, might be envisaged as the disappearance of the orientational order of the long axes (l) around the director defined by the short ones (s). This is the type of sequence which was predicted several years ago in a lattice model where the phase transitions were induced either by density or size changes.[15] A similar point of view was also proposed to analyze two recent studies of the same system. One is an x-ray study showing short-range translational orders of the same type in the three phases, which is not compatible with a local hexagonal packing of cylinders with circular section in the phase we have studied.[16] The second is a light-scattering study which shows important biaxial fluctuations in a uniaxial phase[17] and gives an estimate of a coherence length.[18] As suggested in Ref. 17, x-ray observations, which are made on characteristic lengths smaller than the coherence one, show a local biaxial order which should be averaged by orientational fluctuations to result in the macroscopic uniaxial or biaxial order of the phase.

Finally, the terminologies proposed by us and others to characterize the phases structurally (cylindrical, calamitic or prolate and lamellar, and discotic or oblate), are inadequate in the case studied here as they imply definite shapes for the aggregates. Awaiting more structural data, a less misleading terminology should be limited to the mention of the aggregate axes whose average orientations define the directors.

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