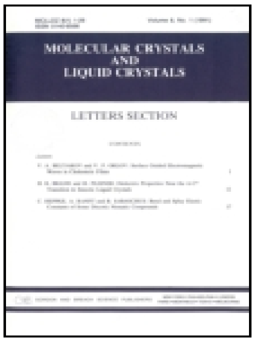

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# Uniaxial and Biaxial Nematic Phases in Sodium Dodecyl Sulphate - Decanol - $D_2O$ Mixtures. An Optical Conoscopy Study

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*The system SDS/decanol/water is investigated by polarized optical microscopy. A reported biaxial island is here confirmed by conoscopy, in the temperature interval 20°C to 26°C. Coexistence regions of the two uniaxial nematic phases (discotic $N_D$ + cylindrical $N_C$) are also confirmed, in different temperature intervals. While the biaxial phase is stable for at least 10 hours, in a reproducible way, along the same time the coexistence region evolves with time, and drops of the discotic phase grow immersed in a $N_C$ matrix. Results are explained in terms of recent theories dealing with stabilization of mixtures of cylinders and discs.*

**Keywords** uniaxial lyotropic nematic; biaxial lyotropic nematic; conoscopy; mixtures

## Introduction

Phase diagrams of lyotropic liquid crystals made of amphiphile and water were defined several decades ago [1, 2], and usually display hexagonal and lamellar phases. Their structures differ essentially from that of thermotropic liquid crystals because the building blocks are not the individual molecules, but micellar aggregates which change size and symmetry as a function of concentration, under influence of the hydrophobic effect and the interactions with water. Lyotropic nematic phases often occur with addition of additives (co-surfactant and /or salts) and appear usually in small ranges of the very complex ternary or quaternary phase diagrams, and the director may orient parallel or perpendicular to magnetic fields [3].

The discovery of a biaxial nematic phase $N_B$ inserted between the two uniaxial nematic phases (cylindrical $N_C$ and discotic $N_D$) on a specific lyotropic system made of potassium laurate (KL), decanol and heavy water [4] lead to long lasting interest by physicists, due to the puzzle of the second order phase transitions as a function of temperature, inexistent

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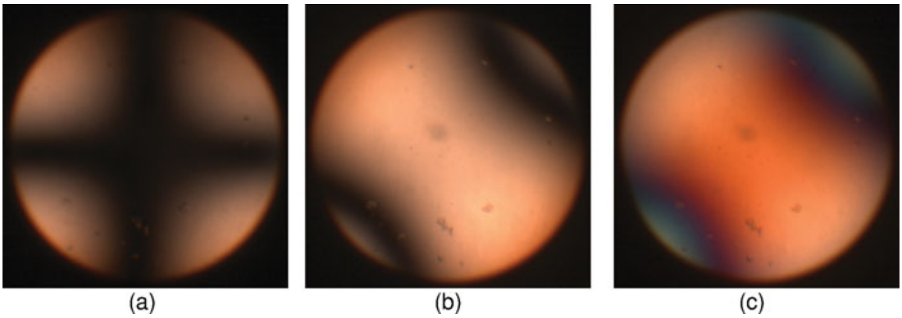

**Figure 1.** Conoscopic images of the $N_B$ phase: (a) microscope stage at 0° position, (b) stage at 45° position and (c) positive optical sign.

among thermotropic liquid crystals. A review on the micelles forming biaxial lyotropic nematic phases was published by one of us [5].

Systems with sodium dodecyl (lauryl) sulphate (SDS) are among the most studied micellar systems, also due to its interest in the detergent industry. The nematic domain in the system SDS/decanol/water was discovered by a group in São Paulo, Brazil [6], and the dependence of the phase diagram on the molar ratios [decanol]/[SDS] $= M_d$ and [water]/[SDS] $= M_w$ was stressed [7]. For $M_w = 45$ there is a sharp first order $N_C - N_D$ transition at $M_d \sim 0.38$ [8]. Later on, biaxial islands immersed in a coexistence region $N_C + N_D$, signature of a first order transition, have been discovered in studies with NMR in Lund, Sweden [9] in other molar regions of the SDS phase diagram.

Transformation of micelles with decanol addition (from spherocylinders to tablets) were explained by elastic theory using the concept of surfactant parameter [10]. Change in micelle symmetry from spherical to cylindrical and to planar by decanol addition, in the isotropic phase of SDS, was experimentally observed using small angle X-ray scattering [11]. Changes of the micellar configuration at the phase transitions and also in the domain of the uniaxial and biaxial nematic phases of KL have been proposed from analysis of the optical birefringence obtained from refractive index measurements [12].

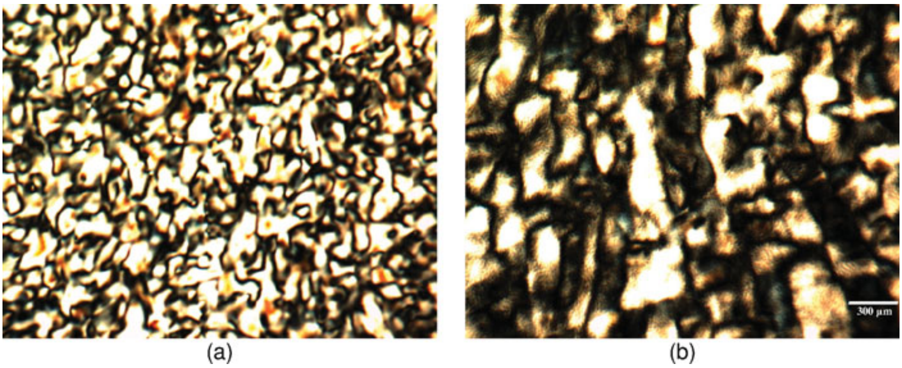

**Figure 2.** Lyotropic nematic textures: (a) $N_B$ phase and (b) $(N_D + N_C)$ mixture.

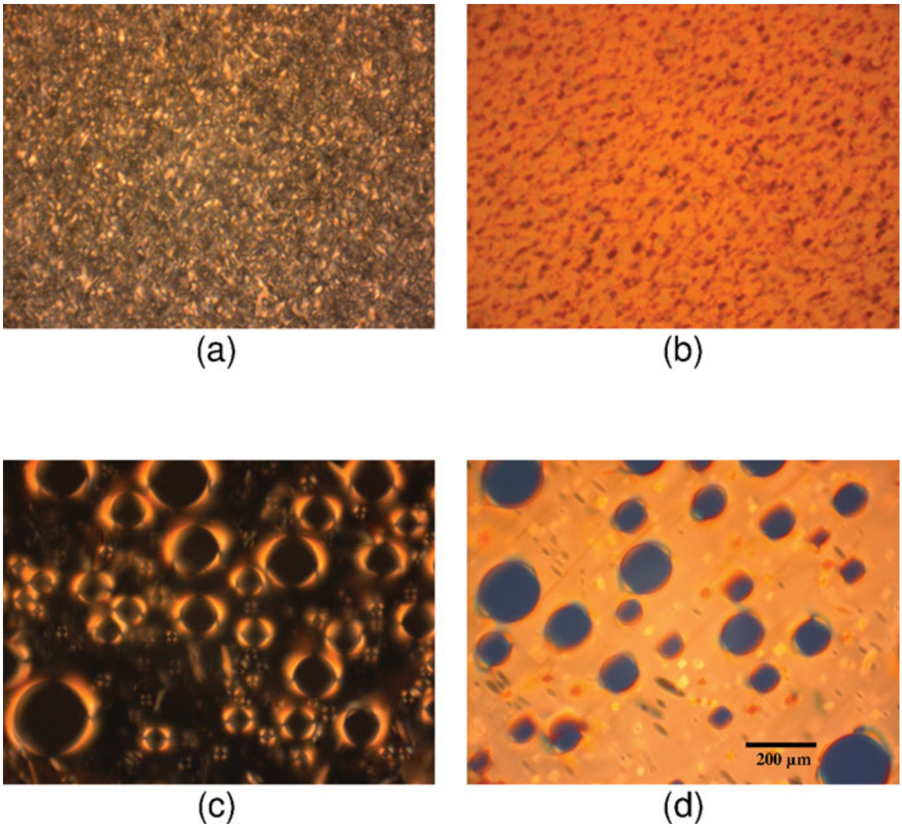

**Figure 3.** Temporal evolution of the ($N_D + N_C$) mixture: at 0 hours (a) stage at 0° position and (b) stage at 45° position. After 10 hours (c) stage at 0° position and (d) stage at 45° position.

Mixtures of cylinders and discs in the biaxial phase of KL was worked with statistical mechanics [13], and phase separation is prevented with the hypothesis of different relaxation times for form transformation and for micelle diffusion. It was theoretically shown later, in the context of quenched and annealed degrees of freedom, that in two temperature formalism and assuming a separation of relaxation times, a slight departure from complete thermalization is enough to stabilize a biaxial nematic phase [14]. In sequence, it was shown that, using a two temperature formalism to mimic the presence of two distinct relaxation times, a partial degree of annealing is already sufficient to stabilize a biaxial nematic structure [15].

The SDS system was recently investigated by measurements of the refractive indexes in the coexistence region [16] and in the biaxial island [17], and results show the differences in phase transitions between the SDS and KL systems.

In this work, polarized optical microscopy (POM) is used to obtain texture and conoscopy results to characterize the uniaxial phases and also their coexistence region as well as the biaxial phase in the SDS system, with the same methods used to study the KL system [18, 19].

The focus of this work is investigation of a biaxial island and of the uniaxial coexistence regions in the SDS system, following the published phase diagram by Quist in figure 3-a from ref. [9], varying the molar fraction [$D_2O$]/[SDS] around the molar ratio [dec]/[SDS] $\sim 0.324$. Results are discussed in terms of changes in micellar form.

## Materials and Methods

Commercially available compounds SDS (sodium dodecyl sulfate), decanol (DeOH) and $D_2O$, were obtained from Merck and Aldrich laboratories, with purity $> 99\%$. The concentration in weight percent are 29.41 of SDS, 5.23 of DeOH and 65.36 of $D_2O$, for $M_w \sim 32$; 27.19 of SDS, 4.83 of DeOH and 67.98 of $D_2O$, for $M_w \sim 36$ and 25.28 of SDS, 4.49 of DeOH and 70.23 of $D_2O$, for $M_w \sim 40$, all with $M_d \sim 0.324$. The samples were prepared in sealed flat rectangular glass cells, from Hellma GmbH & Co (length 44 mm, width 12.5 mm and 1.0 mm of light path), at a room temperature of 23°C, above the Krafft crystallization temperature. Thus prepared the samples remain in good conditions for at least a month, but samples investigated were at maximum 1 week old. The sample temperature was controlled by a water-flow regulator (Brookfield TC-502), yielding a temperature stability of $\pm$ 0.01°C.

These samples are characterized [20] using a commercial polarized optical microscope (POM) Leica DMLP, connected to a CCD camera to register the images. An Amici-Bertrand lens is inserted for conoscopy, when the interference figure (Maltese cross) is observed in the focal plane near the top of the objective. The isogyres open when the biaxial nematic sample in thermal equilibrium is rotated from the 0° position. This opening reaches a maximum value when the stage is rotated to the 45° position. A gypsum plate is inserted into the optical path to obtain the sign of the axiality, through the colors (yellow / blue) of the quadrants [18, 19]. It is well known that the uniaxial lyotropic nematic phase $N_C$ presents negative optical birefringence and positive anisotropy of diamagnetic susceptibility, while $N_D$ is optically positive and magnetically negative.

## Results

The published phase diagram by Quist in figure 3-a from ref. [9], for $M_d = [\mathrm{DeOH}] / [\mathrm{SDS}] \sim 0.324$ gives different phase sequences with temperature increase:

For $M_w = 32$, the sequence is $N_D$ – coexistence ($N_D + N_C$) – $N_C$ – coexistence ($N_C$ + lamellar) – isotropic I.
For $M_w = 36$, the biaxial island $N_B$ emerges from the crystalline state, with a phase transition sequence:
$N_B$ – coexistence ($N_D + N_C$) – $N_C$ – coexistence ($N_C$ + lamellar) – isotropic I phase.
For $M_w = 43$ the sequence is $N_C$ – coexistence ($N_C$ + Lamellar) – isotropic I

All published phase diagrams by Quist [9] start at 20°C, because below there occurs crystallization.

If the sample is cooled into the crystalline state, the nematic phase is not easily recovered on heating. For that reason results by POM, in both orthoscopic and conoscopic geometries, with analysis of textures and interference conoscopy here reported were also investigated above 20°C.

The temperature interval between $N_D$ and the coexistence region, for $M_w = 32$, is being further investigated in detail, and will not be discussed here.

(1) Biaxial phase in Quist's biaxial island

For $M_w = 36$ the biaxial phase was confirmed by optical conoscopy, in the temperature interval 20°C – 26°C, as shown in figure 1. The conoscopy images remained stable for 10 hours at a constant temperature. Reproduction of the biaxial phase was checked in more than 15 runs, with several samples.

In order to achieve good orientation, the sample rested for 7 days and was then submitted to a magnetic field of 1 tesla in the direction of the longer axis of the rectangular sample cell, for initially 10 hours. In this way a combination of surface orientation with magnetic orientation leads to an oriented sample, and the interference image typical of conoscopy is formed. The SDS samples are more difficult to orient than KL samples, because of the crystallization below $\sim 20°C$.

Rotation of the sample (and magnetic field) from 0° to 45° allows characterization of the sample biaxiality, with separation of the isogyres of the Maltese cross, as shown in figure 1. The optical signal was obtained with insertion of the gypsum plate, and it is positive. It should be remarked that the symbols $N_B^+$ and $N_B^-$, used by Quist, are usual in biaxial crystals and correspond to the relative values of the 3 different refractive indices. Two signals in the biaxial range of the KL system has been recently observed [18, 19].

(2) Coexistence of uniaxial nematic phases ($N_D + N_C$)

The coexistence of the two uniaxial phases was observed with $M_w = 36$ in the temperature interval 26° - 28°C and also with $M_w = 32$ in the temperature interval 32.5°C to 39°C, in agreement with Quist's phase diagram.

Results are similar for both values of $M_w$, only the temperature interval of coexistence is different. Figure 2 shows a texture of schlieren type, seen with magnification 50 x, at the transition from the biaxial phase to the coexistence region for $M_w = 36$. As the transition is approached the interference image by conoscopy loses intensity, and disappears.

Figure 3 shows initial results, at time 0 hours, and results after 10 hours, with formation of defined drops of uniaxial phases, which size grows with time. Drops of $N_D$ phase (sizes in the range 50, 85 to 200 $\mu$m) are immersed in a matrix of $N_C$ phase.

(3) $N_C$ phase

Above the coexistence region, with both $M_w = 36$ and 32, the $N_C$ phase occurs with increase in the temperature. For $M_w = 43$ the sequence of Quist's phase diagram was also confirmed, with a $N_C$ phase. A typical result is seen in figure 4. The optical signal is negative, as expected. The isotropic phase is obtained with further increase in temperature, with passage through other coexistence regions, in agreement with Quist's phase diagrams.

## Discussion

The sequence of phases of sample with $M_w = 36$, $N_B$ – coexistence ($N_D + N_C$) is quite unusual. Landau theories [21] predict the possibility of a direct transition $N_D$ – $N_D$, or a sequence of second order transitions $N_D$ – $N_B$ – $N_C$.

The direct transition is expected to occur with spinodal decomposition into the two uniaxial phases, without an intermediate biaxial phase. All attempts in several published papers to produce a biaxial thermotropic phase with mixtures of the two uniaxial phases, with two different thermotropic compounds, have failed.

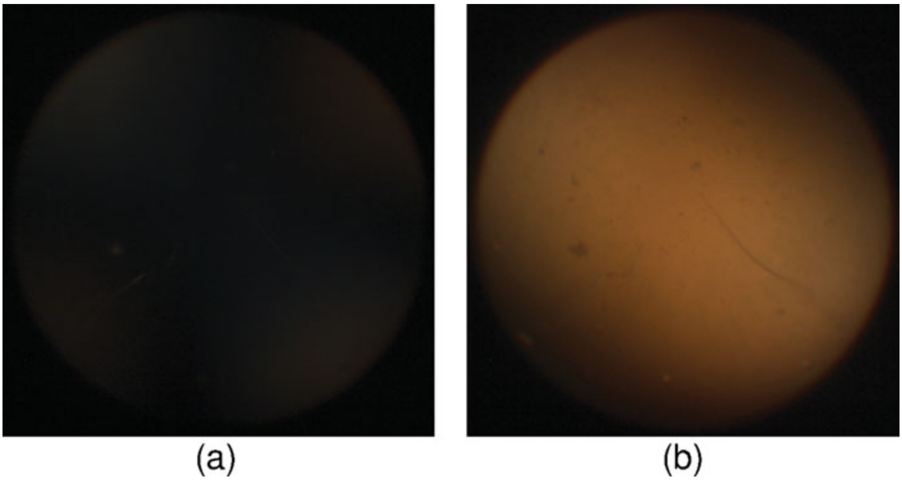
(a) (b)

**Figure 4.** Conoscopic images of $N_C$ phase: (a) fuzzy isogyre cross (stage at 0° position) and (b) rotated by a small angle.

The SDS system shows both a stable biaxial phase and a coexistence region, as revealed by different techniques: NMR [9], measurements of the refractive indices [16, 17] and now with POM.

We explain this unique behavior on basis of a theoretical model worked out for mixtures of cylinders and discs, in which explicit relations between the quadrupoles and the anisometries of the two shapes have been obtained [13]. Demixing of the two forms is prevented under the hypothesis that form transformation of micelles dominates over micelle diffusion, thus yielding a homogeneous mixture [13]. It was later shown that a two temperature formalism to mimic the presence of two distinct relaxation times gives theoretical basis for a stable biaxial phase in the mixture [14, 15].

The key point is that in lyotropic systems the two uniaxial forms are transforming in one another, as proposed in the model worked out for a single micelle on basis of the elastic bending energy connected with molecular shapes of surfactant and co-surfactant [10]. The change in shape and symmetry as a function of concentration and decanol addition is clearly understood, in face of the phase diagrams of lyotropic systems.

The tricky point is the change with temperature, possible to be understood taking into account the basic question of changes in molecular chain length and volume with temperature [5]. Hydrocarbon chains are characterized by a chain length contraction with increasing temperature, expressed by a negative temperature coefficient, which holds only in the chain direction, while the paraffin volume as a whole has a small positive temperature coefficient [22]. While the direction of the chain is contracting with increasing temperature, its other dimensions are expanding, thus cylinders and discs become more anisotropic with increasing temperature. In a cylinder two dimensions are contracting with temperature, while in discs only one dimension contracts, so that cylinders grow more quickly with increasing temperature. The population of forms and the corresponding average quadrupoles therefore suffer distortions as a function of temperature, inducing the change from $N_D$ to $N_C$ with increase in temperature.

The results with the SDS system indicate that the biaxial islands correspond to compositions with specific fractions of cylinders and discs, in a mixture which equilibrates the transformation of the two forms in one another, as occurs in chemical reactions in equilibrium, resulting a stable biaxial phase, over a temperature interval of more than 5°C.

The change in asymmetry and quadrupoles of the two forms with increasing temperatures breaks the equilibrium conditions, and the system enters in the region where the two forms tend to separate, with a time dependent spinodal decomposition.

## Conclusion

It was clearly shown by POM that in the system SDS / decanol / heavy water, for $M_w = 36$, a stable biaxial nematic phase exists in the temperature interval 20°C – 26°C, over a time period of at least 10 hours. Above this temperature the system enters in a coexistence region of the two uniaxial phases, and suffers spinodal decomposition in the same period of 10 hours. Longer time periods have not been explored yet. A similar coexistence region exists also for $M_w = 32$, but in a more extended temperature interval. These results show the possibility of design of mixtures able to display biaxial phases, under controlled conditions.

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