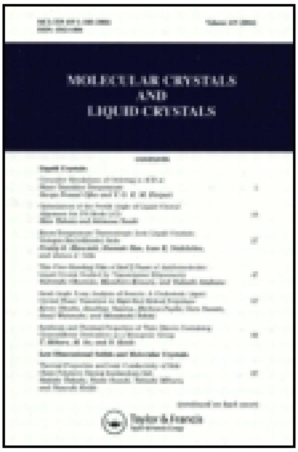

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Discotic Nematic - Calamitic Nematic Phase Transition in Sodium Dodecyl (lauryl) Sulphate - Decanol - D_2O

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Discotic Nematic – Calamitic Nematic Phase Transition in Sodium Dodecyl (lauryl) Sulphate – Decanol – D_2O

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The optical characterization of uniaxial nematic liquid crystals gives basic information on its birefringence and on the shape anisotropy of micelles in nematic lyotropic phases. In this work, these optical parameters were determined as a function of temperature along the sequence discotic nematic (N_D) – coexistence ($N_D + N_C$) – calamitic nematic (N_C) – isotropic (I) in a lyotropic mixture of the sodium dodecyl (lauryl) sulphate (SDS) – decanol (D_eOH) and D_2O for a specific concentration. Results for the uniaxial phases agree with previous assignments. Results in the coexistence region indicate an inhomogeneous mixture of the two uniaxial phases.

Keywords Lyotropic uniaxial nematic phases; phase coexistence; refractive index

1. Introduction

Nematic mesophases formed by lyotropic systems are of difficult theoretical treatment since theories constructed for thermotropic nematics do not easily apply to such complex systems. The building blocks are not defined objects, but micelles, which are transient assemblies of amphiphile molecules, usually charged, with hydrophobic characteristics in presence of water. Furthermore, usually additives as co-surfactants and salts are necessary to induce the nematic phases, which occur in small ranges of composition and temperature of very complex phase diagrams. Such nematic domains are surrounded usually by lamellar and hexagonal phases, and the topology of lyotropic phase diagrams is quite different from thermotropics. Interest of the community of thermotropic liquid crystals in such complex lyotropic nematics was however aroused when a lieder scientist of this community, A. Saupe, discovered a biaxial phase in a particular system, made of KL (potassium laurate),

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1-decanol and heavy water [1]. This biaxial lyotropic phase occurs in very small ranges of concentration and temperature, inserted between nematic calamitic (cylindrical) and nematic discotic phases, with second order transitions.

Thermotropic liquid crystal systems do not show transitions between uniaxial phases of different symmetry, and it was clear that the lyotropic biaxial phase depended on changes in the form (and eventually size and aggregation number) of the micelles with both concentration and temperature. Several properties of the bulk biaxial phase in the KL system have been afterwards studied, with various experimental techniques and theoretical approaches, but a complete understanding of this system has not yet been really achieved. Also, in a related system, based on sodium decyl sulfate (SdS), Saupe found that an intermediate biaxial phase is also formed for a certain concentration range while the observations in other range indicate a direct first-order transition between the two uniaxial phases [1].

A further complication to the problem of biaxial lyotropic phases was introduced when 15 years later two biaxial islands where discovered [2] in the system sodium dodecyl (lauryl) sulfate (symbol SLS or SDS)/decanol/heavy water, with a complex phase diagram with a topology different than that of the KL system. The two uniaxial nematic phases in the SDS system were discovered in the system with light water [3,4], where a biaxial phase was not found and a first order transition between the two uniaxial nematic phases was reported [5]. Even in the system with heavy water, the biaxial islands are surrounded by regions of phase coexistence, with first order phase transitions, and two biaxial regions N_B^+ and N_B^- were detected by NMR [2]. A review on the problem of the micelles forming biaxial nematic phases has been recently published by one of us [6].

This paper reports results on the system SDS/decanol/heavy water, using a technique for measurements of refractive indices already used in the system KL/decanol/heavy water [7,8]. The focus will be on measurements performed in the SDS system along the phase transitions sequence with change in temperature uniaxial discotic N_D – coexistence ($N_D + N_C$) – uniaxial cylindrical N_C, while the sequence in the KL system is N_D – N_B (biaxial) – N_C. Both sequences occur for specific values of the decanol/amphiphile and water/amphiphile molar ratios. Existing theories are also discussed in the conclusions of the paper.

2. Experimental

The lyotropic system investigated in this work [2] is a mixture of SDS (sodium dodecylsulphate), decanol (DeOH) and D_2O. These compounds are commercially available and were obtained from Merk and Aldrich laboratories. The molar ratios of this sample are: $M_w = D_2O/SDS \sim 32$ and $M_d = D_eOH/SDS \sim 0.324$, respectively. The lyotropic samples were prepared in sealed planar glass (refractive index, $n_g = 1.523$) cells (length 44 mm, width 12.5 mm and 1.0 mm of light path) from Hellma GmbH & Co. The 1-2 plane of the sample is defined with 1(2) axis parallel to the length (width) of the cells and 3 is the axis normal to the biggest surface of the sample holder. Homeotropic alignment of the discotic nematic sample was performed by a magnetic field of 10 kG parallel to the 1–2 axis of the laboratory frame combined with rotations of the sample around of the 3 axis. A sketch of the experimental setup is shown in Figure 1. When an homeotropic alignment is achieved with the director of the N_D phase oriented along the 3-axis, the nematic sample is removed from the electromagnetic field and placed in the Abbe refractometer

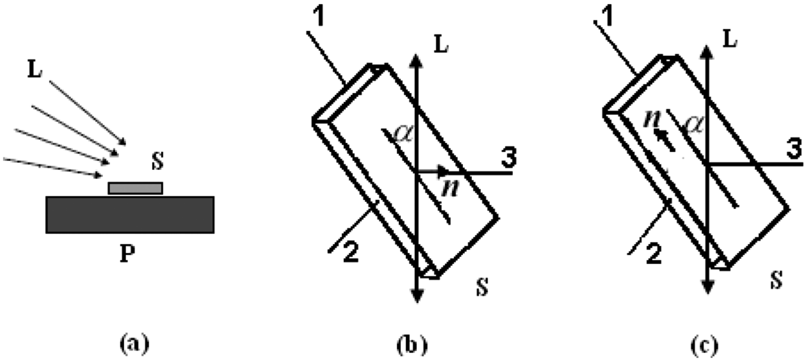

Figure 1. (a) sketch of the experimental setup. Incident light (L), Sample (S), Prism (P); (b) homeotropic configuration. For $\alpha = 0°$ (90°) → L perpendicular (parallel) to the director **n**; and (c) planar configuration. For $\alpha = 0°$ (90°) → L parallel (perpendicular) to the **n**.

(ATAGO model NAT-3T, sodium D line, $\lambda = 589.3\,\text{nm}$). The oriented sample was considered as a solid medium and for optical coupling we have used Canada balsam (refractive index $n_b = 1.530$) [9]. In this experiment, $n_{sample} < n_g < n_b$.

The refractive index measurements using this refractometer, with an accuracy of 2×10^{-4}, are based on the internal reflection of light at the interface between the nematic sample and the surface of an optical glass prism. The sample temperature, controlled by a Heto (CBN-18) circulating temperature bath, was stable to 0.01 K. In the N_C phase the planar alignment was obtained by the same magnitude of the magnetic field parallel to the 1-axis. An optical polarizer was coupled to the Abbe refractometer in order to get the ordinary (n_o) and extraordinary (n_e) refractive indices in N_D and N_C nematic phases.

3. Results and Discussion

By using optical microscopy [10] and refractive index measurements the phase sequence is determined as following: N_D – ($N_D + N_C$) – N_C – (N_C + lamellar) – I, in general agreement with the phase diagram from Quist on the same system [2]. Figure 2 shows the refractive index data as a function of temperature. Extraordinary (n_e) and ordinary (n_o) refractive indices in the domain of the N_D phase decrease when the temperature increases until the vicinity of the N_D – ($N_D + N_C$) transition. From these refractive indices one obtains the optical birefringence, $\Delta n_{32} = n_e - n_o = n_3 - n_2$ which is positive in the N_D phase. These results confirm the existence of the discotic nematic phase in accordance with the phase diagram proposed by P.O. Quist [2]. On the other hand, near the N_C– I phase transition, as the temperature increases n_e (n_o) increases (decreases), and in this way both indices, after the range of phase coexistence, tend to one index at the isotropic phase. The optical birefringence, $\Delta n_{12} = n_e - n_o = n_1 - n_2$, determined in this context is negative, being characteristic of the N_C phase, also in agreement with [2].

It is important to mention that the signal positive (negative) of optical birefringence has been connected to the shape anisotropy of micelles which takes place in discotic (calamitic) nematic lyotropic phases [11–13]. We stress that from the point of view of optical liquid crystal properties the N_D (N_C) phase is uniaxial positive

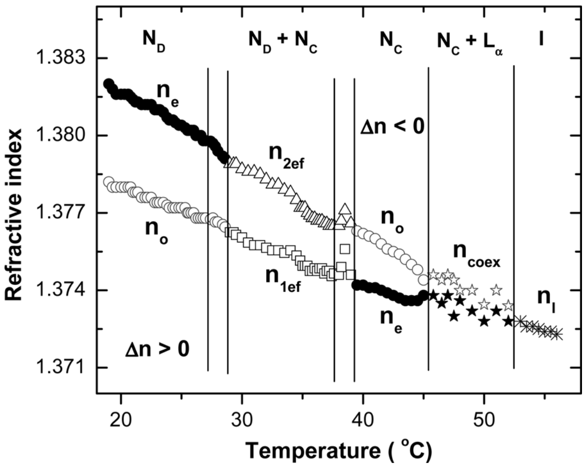

Figure 2. Refractive index versus temperature of SDS system. N_D, N_C, L_α and I are the discotic nematic, calamitic nematic, lamellar and isotropic phases.

(negative) material, where the optical axis is parallel to homeotropic (planar) orientational configuration of the director. The change of sign of optical birefringence, determined in these uniaxial nematic phases, is related to the fact that the hydrocarbon chains of the amphiphile molecules in the N_D phase are placed parallel to director, but in the N_C phase the hydrocarbon chains of the amphiphile molecules are placed perpendicular to director.

Let us now start to discuss the region between the uniaxial phases N_D and N_C, attributed to a coexistence region ($N_D + N_C$) in [2]. Figure 2 show the two effective indexes measured in this region, in a heating process starting from the N_D uniaxial phase, a higher value n_{2f} and a smaller value n_{1f}. The transition $N_D-(N_D+N_C)$ starts at 27°C, and corresponds to a small discontinuous decrease in the index n_{2f} (0.07%), while changes in behavior occur in the index n_{1f}, which changes from a decrease to an increase with temperature. This is compatible with a discontinuous transition in which the main homeotropic orientation changes very little, since it starts from a uniaxial N_D phase with homeotropic orientation. Both n_{2f} and n_{1f} are not linear in the coexistence interval 27–36.7°C, where the transition to N_C starts. The transition from the coexistence ($N_D + N_C$) to the uniaxial phase N_C has been followed by both heating and cooling cycles. The region 36.7–40.8°C is particularly unstable by heating, with oscillatory results. Values also fluctuate by cooling, and the average effective values for heating and cooling differ by 0.4%. The transition from the coexistence to the NC phase indicates existence of granulation, as might be expected from inhomogeneous mixtures or polycrystals.

The behavior of the coexistence region in SDS is different from what has been observed previously with the same technique in the biaxial phase of the KL system [7,8], which is inserted between the two uniaxial phases via second order transitions. At 45°C starts the transition from the uniaxial phase NC towards another coexistence region (with a lamellar phase from Quist's phase diagram [2]), and only at about 52°C the transition to the isotropic phase with a single refractive index (n_I). The behavior of the refractive indices indicates coexistence regions which do not correspond optically to a simple uniaxial or biaxial homogeneous oriented system.

Therefore the hypothesis of an oriented sample, considered as a solid medium, as done in the case of the KL system [7,8], was used here only in the uniaxial phases, but it does not hold for the coexistence regions, neither for the transitions around it. In the case of an oriented biaxial phase between the two uniaxial phases, the three indices related to the directions of Figure 1 can be obtained [7,8]. In the coexistence regions only two effective values are obtained. However an effective birefringence may be defined in the (N_D+N_C) region as $\Delta n_{eff}=n_{2f}-n_{1f}>0$. The coexistence region (N_D+N_C) in the SDS system by heating behaves as having an effective positive birefringence, indicating dominance of surface orientation of the N_D type, when heating from a N_D phase. In such conditions, the strongest change regarding molecules attached to the interface will occur at the entrance in the N_C region, and the observed fluctuation at the $(N_D+N_C)-N_C$ transition is a direct evidence of the changes which occur in the polar-apolar interface when micelles change curvature from flat bilayers in N_D to strongly curved micelles in the N_C phase. Such direct correlation between surface orientation and curvature of the micelles was first remarked by Radley & Saupe [14] and gives a clear indication of micellar form directly from surface orientation.

4. Conclusions

We conclude for an interpretation of the coexistence region in terms of an inhomogeneous mixture of the two uniaxial phases, in distinct coexisting domains. This favours the existence of a first order transition between the two uniaxial phases in the SDS system, as proposed by Quist using NMR in the same system, with heavy water [2] and already reported in the SDS system with light water [5]. From a theoretical point of view, Landau theory predicts phase diagrams of different topologies [15], in which two uniaxial phases may coexist or be separated by an intermediary biaxial phase. The question of stability of a biaxial phase of mixtures of cylinders and discs against demixing has been theoretically analyzed [16,17], and it depends on the specific interactions between cylinders and discs. Our results with SDS correspond to the predicted case of coexistence of the two uniaxial phases.

A detailed statistical model on a mixture of changing uniaxial micellar forms in lyotropic nematics has been worked out, with one of us as co-author [18], as discussed also in [6]. A good fit to Saupe's phase diagram with the biaxial phase in KL is obtained in the case of a smooth form transformation, while phase coexistence, as here reported for SDS, is predicted in case of a sharp form transformation, as seen in Figure 5 of [18]. In order to prevent demixing of the two forms it is considered that form transformation of micelles takes place over much shorter times than micelle diffusion, thus yielding a homogeneous mixture. Indeed it was recently shown [19] that with the assumption of a separation of relaxation times, using a two-temperature formalism, a partial degree of annealing is already sufficient to stabilize a biaxial nematic structure. The experimental results now presented for SDS give evidence that the behavior of these complex lyotropic nematic systems depend on the specific amphiphile and its hydration properties in presence of additives. But the transformation of cylinders into discs has not yet been fully modeled in the literature.

The transformation of one single micelle was been worked out (with one of us as first author) in terms of the bending energy of the polar-apolar interface and preferential partitioning of the amphiphile and the co-surfactant (alcohol in most cases) in respectively curved and flat regions of the micellar aggregate [20], as discussed also in [6]. The model developed in [20] consistently explains the main experimental results obtained in the shape transformation of micelles in the nematic phases of KL, SdS and SDS as well as in isotropic solution of SDS. This model has not been yet extended to treat the statistical mechanics of transitions in nematic phases, due to the theoretical difficulty in working with an internal degree of freedom to take into account the micellar shape transformation. Therefore the first truly statistical microscopic approach able to model experimentally observed lyotropic biaxial nematic phases, presented in [18] and discussed in [6], used instead a conventional lattice model, with a polydisperse mixture of cylinders and discs and a distribution of Maier–Saupe interaction constants. The possibility of continuous change of form passing through a biaxial shape also remains open, but such a continuous change in form could possibly in fact be statistically equivalent to a mixture of changing composition.

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