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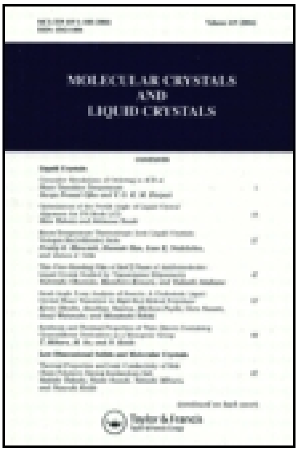

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Study of the Lyotropic System Sodium Dodecyl Sulfate (SDS) / Decanol / Heavy Water

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Study of the Lyotropic System Sodium Dodecyl Sulfate (SDS) / Decanol / Heavy Water

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Measurements of optical refractive indices (ordinary and extraordinary), as a function of temperature, are reported for the heavy water / SDS molar ratio $M_w = 36$, with a decanol / SDS molar ratio $M_d = 0.324$. The nematic biaxial phase emerges from the crystal phase (which occurs below 18°C) into a coexistence region with two uniaxial nematic phases (discotic N_D *and cylindrical* N_C), *before entrance in the* N_C *phase. The transitions are discontinuous, and the biaxial phase differs from the coexistence region* $N_D + N_C$. *Results indicate changes of the micellar object with temperature, and at the phase transitions.*

Keywords Biaxial nematic phase; refractive index; phase transitions

1. Introduction

Lyotropic nematic phases were discovered in 1967 [1] due to their interest as useful matrices for the NMR spectroscopic study of dissolved molecules. The original paper mentioned phases easily made from readily available chemicals, and were prepared from C_8 and C_{10} alkyl sulfates and alcohol. It was mentioned that the C_{12} analog produces a crystalline phase at room temperature. Academic interest on lyonematics increased with the discovery of the two types of uniaxial lyonematic phases, based on C_{10}, and existence of transitions between them as a function of concentration and temperature [2]. An intermediate biaxial lyonematic phase was later discovered in a system with potassium laurate (KL) [3], which resulted in long lasting interest, mainly by physicists, in view of both theoretical predictions and potential applications of biaxial phases, but the focus turned to the search for thermotropic biaxials [4].

The system sodium dodecyl sulfate (SDS) / water / additives, much used in detergent industry, was largely studied in initial works on micellar and lyotropic systems [5]. But its nematic phases, with decanol addition, were discovered only with the previous work of one of us [6,7]. The system SDS/water/decanol exhibited the two nematic uniaxial phases, but with a direct transition between them [7,8]. Later on, biaxial islands were discovered in specific regions on the phase diagram [9], but with characteristics different than obtained with the KL system.

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The micellar structures of such lyonematic phases remained an open problem [10], since there is not a perfect analogy between lyotropic and thermotropic liquid crystals at the molecular level, even if some properties at the macroscopic level are similar. 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 [11]. A theoretical model with mixture of polydisperse disc and cylindrical micelles is able to explain the KL biaxial phase, with the assumption that phase separation is prevented by different relaxation times for shape transformation by decanol addition and for micellar diffusion [12].

Recently we decided to return to the exploration of the system SDS/water/decanol, using optical methods. In a previous paper [13] the phase transition discotic nematic (N_D) – calamitic cylindrical nematic (N_C) was focused, with measurements of refractive indices (ordinary and extraordinary), as a function of temperature and analysis of the birefringence. The complete phase sequence investigated with increasing temperature was $N_D - (N_D + N_C) - N_C$ – isotropic I. Results indicated [13] inhomogeneous mixture of the two uniaxial phases N_D and N_C, in the coexistence region, without an intermediate biaxial phase, and also discontinuous transitions to N_C and I, corroborating the assignment made by Quist [9] of first order phase transitions.

In this work, we continue the exploration of the SDS phase diagram varying the heavy water / SDS molar ratio (M_w) for a decanol / SDS molar ratio $M_d = 0.324$, in order to access the phase transitions involving nematic phases. In the previous paper the sample studied had $M_w = 32$, where the coexistence occurs [13]. We report here optical measurements with temperature variation at $M_w = 36$, in the middle of the unusual “biaxial island” (N_B) reported in 1995 [9]. The biaxial phase N_B emerges from the crystalline state (which occurs below 18°C), with a phase transition sequence N_B – coexistence ($N_D + N_C$) – N_C – coexistence (N_C + lamellar) – isotropic I phase. The biaxial island could not be studied with the same methods developed by some of us in the study of the biaxial phase of KL [11,14], since the pre-condition of complete alignment as occurs in biaxial monocrystals was precluded by the adjacent solid gel phase.

2. Experimental

The lyotropic system investigated in this work is a mixture of commercially available compounds SDS (sodium dodecyl sulfate), decanol (DeOH) and D_2O, obtained from Merk and Aldrich laboratories. The molar ratio of this sample is: $M_w = D_2O$ / SDS = 36, with $M_d = D_eOH$ / SDS ~ 0.324. 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. A sketch of the experimental setup was previously shown [11]. The oriented nematic sample is analyzed in the Abbe refractometer (ATAGO model NAT-3T, sodium D line, $\lambda = 589.3$ nm). When the oriented sample is taken as a solid medium, optical coupling is considered using Canada balsam (refractive index $n_b = 1.530$) [15]. 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 a magnetic field of 10 kG parallel to the 1

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axis of the laboratory frame. An optical polarizer was coupled to the Abbe refractometer in order to get the ordinary (n_o) and extraordinary (n_e) refractive indices in the N_C nematic phases. In the biaxial phase N_B the magnetic field in the direction of the 1 axis was used to force orientation in the 1 direction, with the same method used to measure the biaxial phase of KL [11,14], but with SDS it is not possible to assure perfect orientation, as occurs in a biaxial crystal. In the coexistence region $N_D + N_C$ only residual magnetic orientation and surface orientation are present. Therefore in the biaxial phase N_B and also in the coexistence region $(N_D + N_C)$ the refractive indices correspond to "effective values," labeled as n_{1ef} and n_{2ef} in the coexistence region of SDS [13], and here labeled as n_{1ef} and n_{ef} in the biaxial phase of SDS, since the orientation is not perfectly defined.

3. Results and Discussion

The SDS sample with $M_d = 0.324$ is given in the phase diagram from Quist (figure 3a of [9]) at $M_w = 36$, in the middle of his biaxial island, with the phase sequence as a function of temperature $N_B – (N_D + N_C) – N_C – (N_C +$ lamellar $L_\alpha) –$ I. By using optical microscopy and refractive index measurements the phase sequence in our sample is in general agreement with the previously published results.

Figure 1 shows our refractive index data as a function of temperature. The transitions are in general not smooth and continuous, and the regions of transition are marked with vertical lines. The transition from the region $(N_C + N_D)$ to the phase N_C presents the largest discontinuities. Let us analyze in more detail the behavior of each of the refractive indices along the phase transitions between the nematic phases, admitting that the average micellar form changes with temperature.

- n_{1ef} in the N_B phase shows a small increase at the transition to the $(N_C + N_D)$ region, corresponding to the increase of micellar objects of the N_C type, and a marked increase after the middle of the $(N_D + N_C)$ region, when the N_C micellar object starts to dominate.

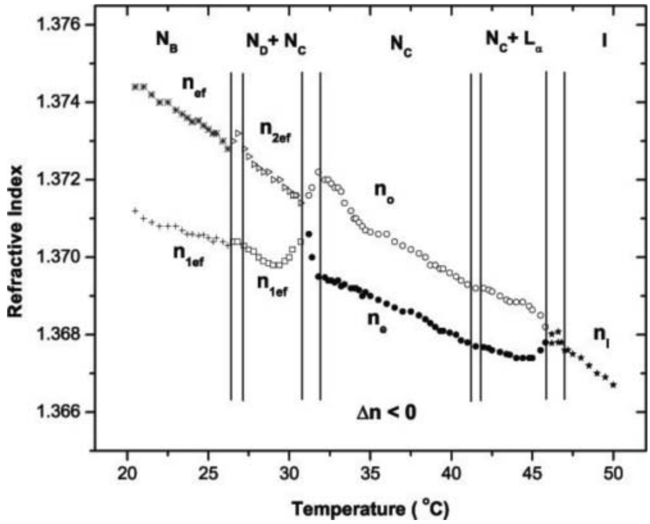

Figure 1. Optical refractive indices measured as a function of temperature along the various phases and phase transitions.

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- n_{ef} in the N_B phase decreases with temperature, in a way similar to the decrease of n_{2ef} in the coexistence region ($N_C + N_D$), but shows a defined discontinuity at the transition, which gives evidence that the phase N_B is in fact different than the coexistence region ($N_C + N_D$). But the origin of such difference is yet unclear.
- In the N_c phase the two indices are well characterized as n_o (ordinary) $= n_2 =$ n perpendicular and n_e (extraordinary) $= n_1 =$ n parallel, with defined orientation in relation to the magnetic field. The birefringence is $\delta n = n_e - n_o < 0$.
- There is indication that at the $(N_c + N_d) - N_c$ transition the birefringence may be changing sign, but this cannot be completely assured by these data, and the observed textures also do not allow a clear assignment.

Our results do not indicate existence of second order transitions, and results for the biaxial island are not equal to those for the coexistence region $N_D + N_C$ [13]. It should be remarked that different biaxial phases are theoretically possible [16].

The behavior of SDS differs from KL, as a consequence of chemical differences in the polar heads and in the hydration properties. The change of micelle form from spherocylinder to square tablet was modeled in terms of the elastic bending energy of the micelle in function of decanol addition, which is preferentially partitioned in the more flat regions of the micelle [17], and the model agrees with experimental results. Furthermore the change in micelle form as a function of temperature can be understood from the basic question of changes in chain length and volume with temperature and concentration. While the direction of the chain is contracting with increasing temperature, its other dimensions are expanding, conserving the whole paraffin volume of the molecule at a practically constant level over the temperature range of interest, and the population of micellar forms suffers distortions as a function of temperature [10,12].

In conclusion, the biaxial islands in the SDS system, first reported through NMR studies [9] are worth further investigation, since they are present in a suitable temperature interval, from 20°C to 27–28°C, depending on the relative concentration of its components.

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References

[1] Lawson, K. D., & Flaut, T. J. (1967). *J. Amer. Chem. Soc.*, *89*, 5489.
[2] Radley, K., Reeves, L. W., & Tracey, A. S. (1976). *J. Phys. Chem.*, *80*, 174.
[3] Yu, L. J., & Saupe, A. (1980). *Phys. Rev. Lett.*, *45*, 1000.
[4] Madsen, L. A., Dingemans, T. J., Nakata, M., & Samulski, E. T. (2004). *Phys. Rev. Lett.*, *92*, 5505.
[5] Ekwall, P. (1975). *Advances in Liquid Crystals, 1*. Academic Press: New York.
[6] Amaral, L. Q., Helene, M. E. M., Bittencourt, D., & Itri, R. (1987). *J. Phys. Chem.*, *91*, 5949.
[7] Amaral, L. Q., & Helene, M. E. M. (1988). *J. Phys. Chem.*, *92*, 6094.
[8] Amaral, L. Q. (1990). *Liq. Cryst.*, *7*, 877.
[9] Quist, P. O. (1995). *Liq. Cryst.*, *18*, 623.
[10] Amaral, L. Q. (2010). *Liq. Cryst.*, *37*, 627.
[11] Santoro, P. A., Sampaio, A. R., da Luz, H. L. F., & Palangana, A. J. (2006). *Phys. Lett. A.*, *353*, 512.
[12] Henriques, E. F., Passos, C. B., Henriques, V. B., & Amaral, L. Q. (2008). *Liq. Cryst.*, *35*, 555.

[13] Oliveira, D. A., Palangana, A. J., & Amaral, L. Q. (2011). *Mol. Cryst. Liq. Cryst., 247*, 1885.

[14] Souza, G. P., Oliveira, D. A., Luders, D. D., Kimura, N. M., Simões, M., & Palangana, A. J. (2010). *J. Mol. Liq.*, *156*, 184.

[15] Pinto, A. V. A., & Barbosa, A. A. (1998). *Mol. Cryst. Liq. Cryst.*, *309*, 45.

[16] Mukherjee, P. K., & Sen, K. (2009). *J. Chem. Phys.*, *130*, 141101.

[17] Amaral, L. Q., Santin Filho, O., Taddei, G., & Vila-Romeu, N. (1997). *Langmuir.*, *13*, 5016.

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