

Orientalional transitions in lyotropic nematic mesophases: Optical conosopic studies

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Dynamics of orientational and structural transformations between the optical uniaxial and biaxial lyotropic nematic mesophases has been investigated. These transformations have been studied using the polarizing optical microscopy technique and the conosopic images. Investigations have been carried out both under influence of the external magnetic field and without this field. Dynamics of transformations of the conosopic images at structural and thermotropic transitions are presented.

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1. Introduction

Lyotropic liquid crystalline systems exhibit large number of the physical isotropic phases and physical anisotropic mesophases. Lyotropic liquid crystalline mesophases are characterized by definite structural organisation, different packing of structural units and various spatial symmetries. Interesting and sufficiently important peculiarity of lyotropic liquid crystalline systems is availability of two optically uniaxial and one biaxial lyotropic nematic mesophases, i.e. the nematic-calamitic N_C , nematic-discotic N_D and biaxial nematic N_{bx} mesophases [1-7]. These mesophases are constructed by micelles with the long-range orientational order [8-11].

Unlike other lyotropic liquid crystalline mesophases (i.e. the hexagonal, rectangular, square, lamellar etc. mesophases), the lyotropic nematic mesophases have the structural units of definite sizes [2,12-17]. Besides, unlike the thermotropic nematic mesophases, in the lyotropic nematic mesophases the structural and physical properties are connected not only with state of structural units, i.e. lyotropic micelles, but also with shapes of micelles and displacement of the amphiphile molecules in these micelles. Such structural peculiarities of the lyotropic nematic mesophases provide their high sensitivity to different external effects (electric, magnetic and thermal fields, deformations, flows, surfaces, boundary conditions etc.). High sensitivity of the lyotropic nematic mesophases to external effects, large variety of the physical properties and availability of three types of the uniaxial and biaxial mesophases makes these mesophases very interesting objects of the physical investigations and perspective materials for technical and technological applications.

In this work, the orientational transition between the optical uniaxial and optical biaxial lyotropic nematic

mesophases, and processes of textural transformations have been studied. Character of the orientational transitions both under influence of the external magnetic field and without this field has been investigated using the crystallo-physics and crystallo-optics methods, and by studied of the conosopic images.

2. Experimental

In this work, the lyotropic nematic mesophases have been prepared as a mixture of sodium dodecylsulphate (SDDS), decanol (DeOH) and water (H_2O). Mixtures have been chose in accordance with phase diagrams, presented in [7]. Lyotropic systems as 25.50 wt% SDDS + 70.21 wt% H_2O + 4.29 wt% DeOH (sample 1) and 29.05 wt% SDDS + 66.66 wt% H_2O + 4.29 wt% DeOH (sample 2) have been used. SDDS was obtained from Merck and has a high purified grade (purity > 99.0%). H_2O , used as the general solvent, was distilled and deionized twice. DeOH, used as the cosolvent, was also from Merck and has also a high purified grade (purity > 99.0%). We would like to note that, essential differences in process of the orientational transition between the optical uniaxial and biaxial lyotropic nematic mesophases and processes of textural transformations for the samples 1 and 2 have not been observed.

Lyotropic systems were prepared in the standard way. SDDS, H_2O and DeOH have been weighed by precision balance with an accuracy of $\pm 10^{-4}$ g. SDDS+ H_2O mixtures were prepared and then DeOH in a definite concentration was added to the amphiphile+water mixture. The lyotropic systems were periodically mixed by the vortex shaker and magnetic mixer, and kept in thermostat at temperature 309.3 ± 0.1 K during ten days for homogenization.

The investigations have been carried out using samples as the sandwich-cells with fixed thickness. The thickness of lyotropic liquid crystalline layer in the sandwich-cells was $120.0 \pm 0.1 \mu\text{m}$. The sandwich-cells were hermetically closed at once after filling with liquid crystalline systems.

Investigations of the thermo-morphologic properties and dynamics of orientational transitions have been carried out using magneto-optical set-up and polarizing optical microscopy techniques. The set-up consisted of trinocular polarizing microscope with the conoscopic/orthoscopic observations, micro-photographic system, λ plates ($\lambda = 137 \mu\text{m}$ and $\lambda = 530 \mu\text{m}$, test-object, optical filters, quartz wedge and Berek compensator from Olympus Optical Co., heater-thermostat with digital temperature control system, differential Cu-Co thermocouples, power supply and multimeters. Crystallo-physics and crystallo-optics methods have been used in this work. The experiments for the orientational and structural transformations and for obtaining of aligned textures were made by permanent magnet. Field of 6.3 kG was available.

3. Results and discussion

In this work, the orientational and structural transformations between N_C and N_{bx} mesophases have been studied. Structural units of the N_C mesophase are the rod-like micelles, which have the symmetry of the ellipsoids of rotation [2,3,7,18]. In such micelle the ellipsoid axis of rotation is the long axis of the rod-like micelle. Therefore the director \vec{n} ($\vec{n} = -\vec{n}$) of the N_C mesophase is directed parallel to the long axis of the micelle. Structural units of the N_{bx} mesophase have the symmetry of the parallelepiped with the point group as D_2 [19,20]. As it is noted in [19,21-23], the orientational configuration of this mesophase is characterized by the three mutually orthogonal directors as the \vec{m} , \vec{l} and \vec{n} , which are fixed in the micelle. The director \vec{m} determines the average direction of larger length of micelle, the director \vec{l} determines the average direction of intermediate length of this micelle and the director \vec{n} determines the average direction of shorter length of the micelle. The directors \vec{m} and \vec{l} may be considered as optical axis. These three directors are not independent and are connected by $\vec{l} = \vec{m} \times \vec{n}$ [3,19,21]. Therefore it is enough to fix two of these directors and the third one can be easily determined. Take into consideration that the direction of the director \vec{l} is the direction of the principal diamagnetic susceptibility (χ_l), in accordance with results, which was obtained in [1], $\chi_l > \chi_m > \chi_n$ takes place.

Investigations showed that in the SDDS + H₂O + DeOH lyotropic system three lyotropic nematic mesophases, i.e. N_D , N_C and N_{bx} mesophases, take place in

strongly definite concentration and temperature intervals [7,24-26]. N_D and N_C mesophases in this lyotropic system occur in large temperature and concentration intervals, but N_{bx} mesophase occur in sufficiently narrow temperature and concentration intervals. Investigations showed that in this lyotropic system the $N_C - N_{bx}$ thermotropic phase transition takes place at 301.3 K. This result is in agreement with phase diagrams, presented in [7]. We would like to note that existence of the N_{bx} mesophase in sufficiently narrow temperature and concentration intervals has been also observed by various scientists in different lyotropic liquid crystalline systems, e.g. in the sodium decylsulphate + H₂O + DeOH, potassium laurate + H₂O + DeOH and tetradecyltrimethylammonium bromide + DeOH + H₂O lyotropic systems [1,8,23,24,27-32].

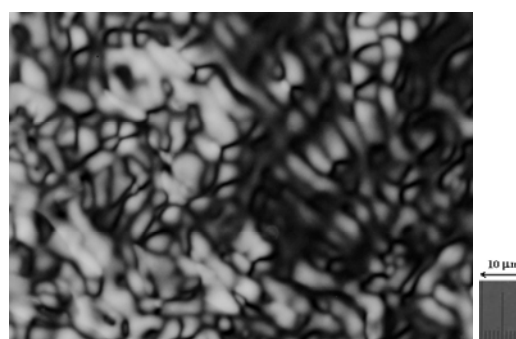


Fig. 1. Typical textures of the N_C mesophase in the SDDS+H₂O+DeOH lyotropic system. Temperature 303.3 K; Crossed polarizers; Magnification x100.

After filling the sandwich-cell with lyotropic system at 304.7 K, the schlieren texture has been observed for the N_C mesophase (Fig.1). As seen in this figure, this texture consists of the linear disclinations as the inversion walls and the singular points. Optical studies showed that in this texture the singular points with the optical positive and negative signs and with the disclination of the strength as $S = \pm 1/2$ and $S = \pm 1$ take place. Similar textures for the N_C mesophase have been also observed in [33-36]. Texture, presented in Fig.1, was mobile and perpetual transformations of the schlieren formations have been observed. After ~ 2 hours the alignment texture has been arisen. This texture is characterized by the conoscopic image (Fig.2a). This image indicates on the homeotropic alignment of the optically uniaxial mesophase. The conoscopic image of the N_C mesophase consists of two isogyres with equal length. The isogyre lines are parallel to oscillations of light, which is transmitted into the polarizer and analyzer. These isogyres are not connected with the difference in phase of oscillation, but are connected with the direction of oscillations. The isogyre lines are parallel to oscillations of light, which is transmitted into the polarizer and analyzer. These isogyres in Fig.2a are invariant relatively the center of the conoscopic image. As is known, the intersection the isogyres, i.e. the center of the conoscopic image, determines position of the optical axis of the uniaxial

crystal [37-39]. By rotation of the sandwich-cell between crossed polarizers, position of the center of the conoscopic image was stable. This indicates that the optical axis of the mesophase is strongly perpendicular to the reference surfaces of the sandwich-cell. We would like to note that absence of the isochromates in the conoscopic image is connected with low birefringence of the lyotropic nematic mesophases as compared with the thermotropic nematic mesophase [2,36,40-43].

By a decrease of temperature, the transformations of the conoscopic image have been observed. Investigations showed that the isogyres open near the $N_C - N_{bx}$ thermotropic phase transition. The conoscopic images near this phase transition are shown in Fig.2b,c,d. In the N_{bx} mesophase the conoscopic image consists of two isogyres as the hyperbolic lines. I.e. in the N_{bx} mesophase isogyres are opened. In this case distance between the melatopes of the hyperbolic isogyres becomes maximal (Fig.2e). Texture, which was observed for this situation, is presented in Fig.3. Optical investigations showed that such type of the microscopic texture corresponds to the biaxial crystalline state.

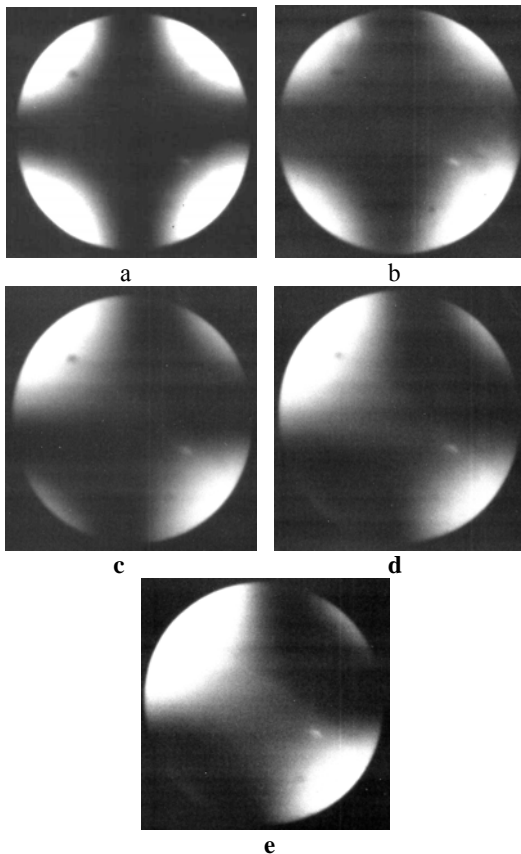


Fig. 2. Conoscopic images of the $N_C \rightarrow N_{bx}$ thermotropic phase transition. a- conoscopic image of the N_C mesophase; b, c, d - transitional conoscopic images; e- conoscopic image of the N_{bx} mesophase.

In this work we are interested on the sign of the optical anisotropy of the N_C and N_{bx} mesophases. The

displacement of the director \vec{n} and amphiphile molecules in the rod-like micelles of the N_C mesophase is different. Namely, the director \vec{n} of the N_C mesophase is in direction of the long axis of the rod-like micelle and perpendicularly to the amphiphile molecules (Fig.4). Such disposition of the director \vec{n} and amphiphile molecules in micelles of the N_C mesophase is cause of the negative optical birefringence ($\Delta n = n_{||} - n_{\perp} = n_e - n_o < 0$), i.e. the negative optical anisotropy of this mesophase. Besides, character of the conoscopic image, i.e. sufficiently spacious and diffuse cross, also indicates on the optically negative sign of the N_C mesophase under investigation. Similar conoscopic image has been also observed in [44] for the N_C mesophase with the optically negative sign in potassium laurate + DeOH + D₂O lyotropic system.

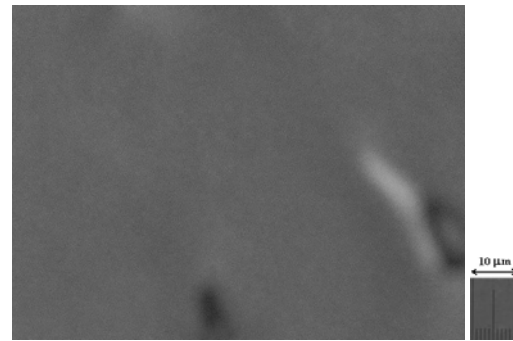


Fig. 3. Texture of the aligned N_{bx} mesophase. Temperature 298.9 K; Crossed polarizers, Magnification $\times 100$.

The optical sign of the N_{bx} mesophase has been determined by application of the gypsum plate. For this determination, the sandwich-cell was placed in the diagonal position. Investigations showed that yellow color on the concave side and blue color on the convex side of the isogyres take place for the conoscopic image of the N_{bx} mesophase. This fact indicates on the optically negative sign of the N_{bx} mesophase [37,45,46].

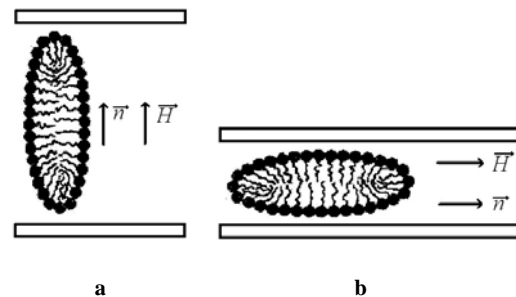


Fig. 4. Schematic representation of position of the director and magnetic field for the N_C mesophase under investigation. Homeotropic alignment (a) and planar alignment (b).

Investigations of the orientational behavior of the N_C mesophase in the external magnetic field have been carried out in this work. By application of the magnetic field perpendicularly to the reference surfaces of the sandwich-cell, fluent transformations of the schlieren texture, which is presented in Fig.1, have been observed. As the result of these transformations, the homeotropic texture of the N_C mesophase, which is characterized by the conoscopic image as the Maltese cross, has been obtained. On the other hand, by application of the magnetic field parallel to the reference surfaces of the sandwich-cell fluent transformations of the schlieren texture also have been observed. But in this case as the result of these transformations the planar texture of the N_C mesophase, which is characterized by the optical birefringence as $\Delta n = 3.1 \cdot 10^{-3}$, has been obtained. Schematic representation of the homeotropic and planar alignments of the N_C mesophase in the lyotropic system under investigation, and position of the director and magnetic field are presented in Fig.4. Such behavior of the rod-like micelles of the N_C mesophase in the SDDS + H_2O + DeOH lyotropic system under influence of the external magnetic field indicate that this mesophase has the positive diamagnetic anisotropy ($\Delta\chi > 0$). We would like to note that the positive diamagnetic anisotropy in N_C mesophase (and the negative diamagnetic anisotropy in N_D mesophase) in the SDDS + H_2O + DeOH lyotropic system has been also observed in [7,22]. Therefore, is clear that the N_C mesophase in the SDDS + H_2O + DeOH lyotropic system is characterized by the positive diamagnetic anisotropy and the negative optical anisotropy. On the other hand, the N_C mesophase with the positive diamagnetic anisotropy is known [1,47-53]. We would like to emphasize that the sign of the optical anisotropy in lyotropic nematic mesophases is determined by mutual displacement of the director \vec{n} and amphiphile molecules. But the sign of the optical anisotropy in these mesophases is not connected with the sign of the diamagnetic anisotropy. Obviously, the sign of the diamagnetic anisotropy of the rod-like micelles (and also the sign of this anisotropy in the disc-like micelles) can be connected with both the diamagnetic anisotropy of shapes of the anisometric micelles and also with diamagnetic anisotropy of the amphiphile molecules [2,54,55].

4. Summary

In the SDDS + H_2O + DeOH lyotropic system the N_C , N_D and N_{bx} nematic mesophases take place. Between the optically uniaxial N_C and optically biaxial N_{bx} mesophases the thermotropic phase transition has been observed. This transition was accompanied by orientation transformations. In lyotropic system under investigation, orientational transformations between the N_C and N_{bx} mesophases have been studied using optical conoscopic technique. A transformation of the conoscopic images for process of the $N_C \rightarrow N_{bx}$ thermotropic transition has been observed.

Investigations and analysis of the conoscopic images showed that the N_C and N_{bx} mesophases in the SDDS + H_2O + DeOH lyotropic system have optically negative sign. Besides, the magneto-optical studies of the N_C mesophase showed that this mesophase in the lyotropic system under investigations has positive diamagnetic anisotropy.

Registration Nos.: Sodium dodecylsulphate – SDDS (Merck, cat. No. 112012); Decanol – DeOH (Merck, cat. No.803463).

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