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LIQUID CRYSTALS

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Orientation of Lamellar Phases of Lyotropic Multicomponent Mixtures, Based on Cetyltrimethylammonium Bromide Cationic Detergent, in Magnetic Field

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Abstract—The orientation of the lamellar phases in lyotropic systems based on cetyltrimethylammonium bromide (CTAB) detergent has been studied by polarization optical microscopy and ^{2}H-NMR methods. The lamellar lyotropics studied are shown to align under a strong magnetic field of 11.7 T. According to ^{2}H-NMR data, structural transformations of the lamellar phases may occur during orientation when the sample temperature increases.

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INTRODUCTION

Many substances of biological origin may have a liquid crystal (LC) structure [1]. One example is cell membranes, which play an important role in the processes of energy conversion and cell-to-cell transport transfer of substances and information [2]. The lipids constituting the cell membranes can form lyotropic LCs. Synthetic lyotropic LCs are a model material for characterizing the structure and many properties of such biological systems [3–5].

Like thermotropic LCs, lyotropic nematics and smectics exhibit orientational properties, which manifest themselves in a change in the initial director orientation of lyotropic micelles in electric or magnetic fields (MFs), which cause splay, bend, and twist deformations, etc., in micelles.

In [6], the lyotropic LC phase was aligned for the first time in a weak MF. The phase was observed in a multicomponent mixture of sodium decylsulfate, *n*-decyl alcohol, Na_2SO_4, and D_2O. These lyotropic LC phases were found later to be lyonematics. Due to the anisotropy of magnetic susceptibility, the free energy of an ensemble of the molecules (micelles) of the lyotropic nematics in the external magnetic field H has a minimum at a quite certain orientation of the micelle director $\boldsymbol{n}$ with respect to the field. For the positive anisotropy of diamagnetic susceptibility, the director $\boldsymbol{n}$ tends to align along the field H; for the negative one, n tends to align perpendicular to the field. This property allows one to obtain, using an MF, well aligned homogeneous layers of lyomesophases for optical studies [7] and identify them [8].

In the multicomponent mixture under study, based on cetyltrimethylammonium bromide (CTAB) detergent (**CTAB**–*n*-decyl alcohol–NaBr–D_2O), not only nematic lyomesophases with discotic and cylindrical micelles but also hexagonal and lamellar phases were found and identified [4, 7, 8]. Most mixtures were obtained based on detergent with a hydrocarbon chain 12 carbon atoms long. The orientation of amphiphilic lyonematics was most often studied by the ^{2}H-NMR method. The ^{13}C-NMR spectral studies showed that hexagonal phases with high viscosity exhibit a rather high mobility of carbon atoms in the hydrocarbon chain of the **CTAB** detergent. This mobility exceeds that of the carbon atoms of the detergent chain in lamellar phases [8]. The alignment of lamellar LC phases was considered impossible because of their high viscosity. A sufficiently strong MF of 11.7 T was used to study the lamellar-phase alignment.

The alignment of the lamellar phase in a two-component system based on the **CTAB** detergent in D_2O was studied. The alignment was detected by the ^{2}H-NMR method, which is most convenient for this purpose [9]. Presently, hexagonal phases of two-component mixtures have been found, which are aligned in a MF [10, 11]. In [12], the lyotropic LC mixture cetylpyridinium chloride–*n*-hexyl alcohol–NaBr–D_2O was used as an aligning medium for NMR spectroscopy. It was also shown that the hexagonal phase formed in the phospholipid mixture is aligned in an MF of 7.05 T. An NMR study of the structure of cytochrome *C* in a lyotropic LC medium (which can partially align protein molecules) was performed in [13].

The polarization optical technique for determining the optical sign, birefringence, and optical indicatrix was applied to identify nematic phases of the lyotropic LC system **CTAB**–*n*-decanol–NaBr–D_2O in [7]. The aligned lamellar phase L_α shows an optical-indicatrix orientation similarly to the N_D^- phase. The studies of textures by the polarization optical method allow the easy identification of nematic, hexagonal, and lamellar phases. In this paper we report the results of studying the alignment of lamellar phases under MF of 11.7 T in a lyotropic system based on **CTAB** detergent.

EXPERIMENTAL

Lyotropic LC mixtures were synthesized using **CTAB** detergent (Serva), both as an individual compound $C_{16}TAB$ and, in some samples, as a mixture of $C_{12}TAB$, $C_{14}TAB$, and $C_{16}TAB$ (like in [4, 8]). The detergent homogeneity was verified by the ^{13}C-NMR method [4]. Homogeneous mixtures exhibiting particular mesophases were prepared by mixing individual components in a certain weight ratio, with further centrifugation in sealed glass ampoules having 9 mm in diameter and narrowed to 1–2 mm in the center. Each ampoule was a ready sample for ^2H-NMR study. ^2H-NMR spectra were recorded on a pulsed AM-500 Bruker spectrometer at a frequency of 76.8 MHz (with a polarizing magnetic field of 11.7 T) at 30 ± 0.5°C. The MF was applied parallel to the long axis of the ampoule. For rapidly aligned mixtures, the sign of the diamagnetic anisotropy of lyomesophase studied was determined by comparing the ^2H-NMR spectrum of a rotating sample with the ^2H-NMR spectrum recorded without sample rotation. If the diamagnetic anisotropy of the mesophase is positive, these spectra are different for an MF applied perpendicularly to the sample; rotation always destroys the sample alignment. If the diamagnetic anisotropy is negative, the ^2H-NMR spectra of the rotating sample do not differ from those recorded without rotation, provided that MF H_0 is applied perpendicularly to the sample.

All samples, for which the diamagnetic anisotropy sign was determined as described above, were then studied by the polarization optical method. The textures of lyomesophases were studied using POLAM L-311 and MIN-8 microscopes with a Berek compensator [4, 7] before and after exposure to dc MF.

RESULTS AND DISCUSSION

The composition of the lyotropic amphiphilic mixtures based on **CTAB** detergent in D_2O, the phases observed in these lyomixtures and identified by ^2H-NMR spectroscopy and polarization optical microscopy, and the characteristic quadrupole splitting of the ^2H-NMR signal of water are listed in the table.

Samples 5 and 6 (see table), which contain no NaBr salt, also exhibit lamellar phases. The composition of these samples is close to that of the lyotropic mixtures based on the cetyldimethylethylammonium bromide, as in [14]. The texture of the hexagonal phase is fibrillar; all lamellar phases had a texture with oily streaks [2]. In [10, 11], the LC-domain orientation in hexagonal lyomesophases in an MF was considered proven.

The formation of a texture with oriented focal conics, reported in [4], was observed at lyomesophase orientation in the capillary (thickness 0.5 mm, MF parallel to the capillary long axis). Figure 1 shows the textures of the lamellar phase L_α in samples 2–4. Figure 1a presents the texture of the nonoriented lamellar phase (sample 2, see table). It is a typical pseudoisotropic texture with oily streaks, which are the most widespread structural defects in lamellar phase textures. They are manifested as long stripes with a complex internal structure separating homogeneous regions of lamellar phase layers [2].

Composition of synthesized lyotropic mixtures, characteristic quadrupole splittings of the ^2H-NMR signal from water, and identified lamellar phases and their textures, according to the ^2H-NMR and polarization optical microscopy data

Sample no.	Mixture composition, wt %					$\Delta\nu_D$, Hz[c]	Phase
	Serva detergent[a]	Merck detergent[b]	NaBr	1-decanol	D_2O		
1		34.99			65.01	26.0	H_1
2		32.90	9.25	5.54	52.31	68.0	L_α
3	32.84		4.95	6.38	55.83	43.2	L_α
4	32.58		5.21	5.39	56.82	60.0	L_α
5		32.13		8.75	59.12	112.0	L_α
6		33.00		8.76	58.24	104.0	L_α

[a] Mixture of dodecyl- (25 mol %), tetradecyl- (65 mol %), and hexadecyl- (10 mol %) trimethylammonium bromides.

[b] Hexadecyltrimethylammonium bromide. Serva detergent was used in samples 5 and 6.

[c] Splitting of the deuterium water signal in a magnetic field of 11.7 T at 30°C (samples 1–4) and 55°C (samples 5 and 6).

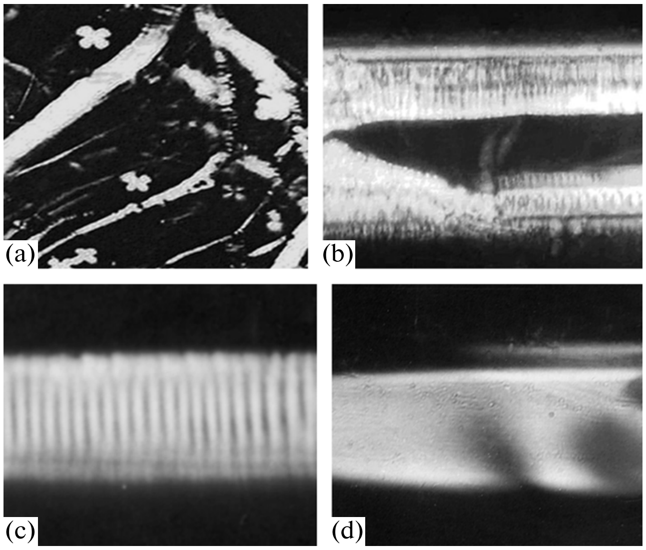

Fig. 1. Textures of the lamellar phases: (a) typical texture with oily streaks of the nonoriented lamellar phase of sample 2, (b) oriented lamellar phase of sample 3 at $H \approx 11.7$ T, (c) oriented focal conic texture of sample 3 in the capillary, and (d) planar texture of the lamellar phase of sample 4. Samples 3 and 4 were kept at $H \approx 11.7$ T for 1 h.

Figures 1b and 1c show the textures of the oriented lamellar phase after exposure to an MF $H_0 = 11.7$ T. Small focal conics of the lamellar phase (sample 3) oriented perpendicular to the capillary long axis can be seen in Fig. 1b; Fig. 1c presents the texture of the focal conics that are uniformly oriented perpendicular to the long axis of the planar capillary after exposure to an MF of 11.7 T applied along the capillary long axis for about 1 h. Figure 1d shows the texture of a colored homogeneous region of the lamellar phase (sample 4) formed after long exposure to an MF of 11.7 T. This texture is similar to the planar texture of nematic discotic lyomesophases with negative diamagnetic anisotropy after their exposure to an MF of 11.7 T. Such textures are characteristic of the lamellar phases observed upon aligning NaBr-containing samples in MF.

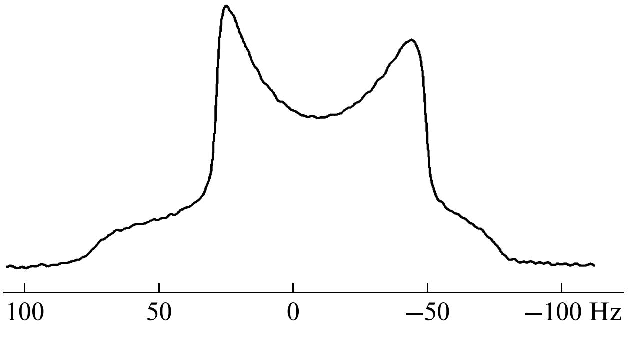

Fig. 2. ^{2}H-NMR spectrum of the nonoriented lamellar phase of sample 6.

In the samples without NaBr salt (samples 5 and 6), lamellar phases are aligned slowly. The doublet in the initial ^{2}H-NMR spectrum of the nonoriented lamellar phase has the powder-pattern shape (Fig. 2), a circumstance important for determining the orientation type of the phases under study. When the ^{2}H-NMR spectrum components grow out from the outer peaks of the powder pattern spectrum, the lamellae of a phase under study are aligned parallel to the applied MF H_0 (type 1); in the case of perpendicular orientation (type 2), the ^{2}H-NMR spectrum components grow out of the inner peaks of the powder pattern. The lamellar phases in the samples without NaBr belong to type 1 (Fig. 2, sample 5), while the lamellar phases in the samples with NaBr belong to type 2 [4, 7]. In the lamellar phases in NaBr-containing lyomixtures, the lamella director is aligned perpendicular to the MF H_0.

Figure 3 shows the temperature dependence of the ^{2}H-NMR spectrum of the lamellar phase in sample 6 (without NaBr). The spectra of the lamellar phase were recorded in an MF of 11.7 T, with the temperature in the NMR sensing element varying from room temperature (293 K) to about ~90°C (361 K) and vice

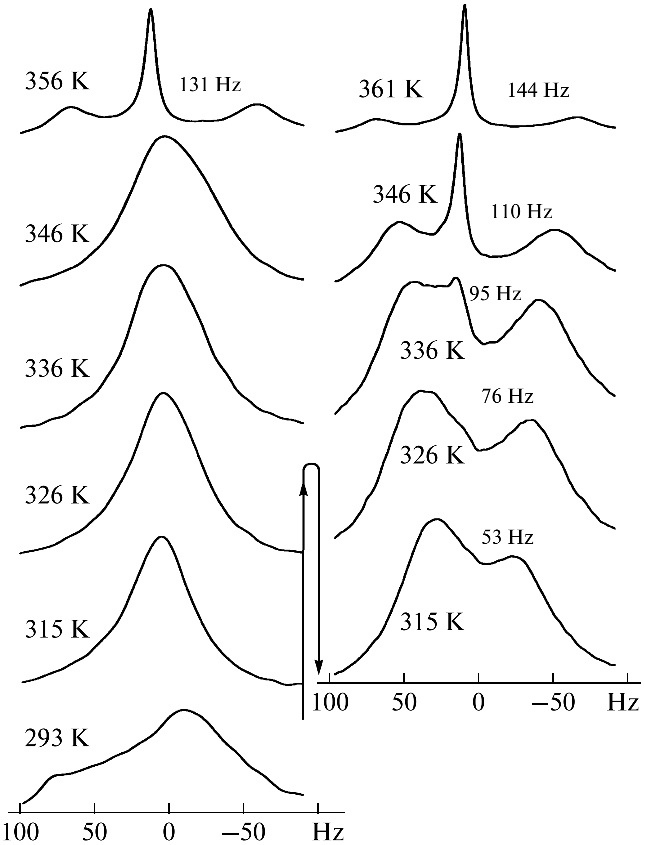

Fig. 3. Change in the ^{2}H-NMR spectra of the lamellar phase of sample 6 upon heating and cooling for 2 h in the probe head of the spectrometer. The individual spectra were recorded for 1 min with an interval of 15 min.

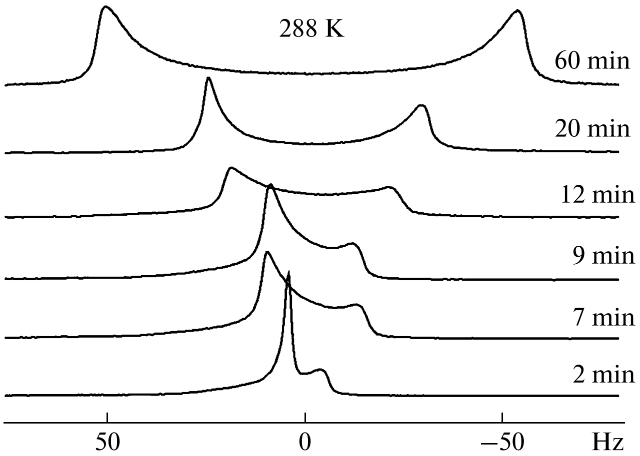

Fig. 4. Time dependence of the orientation of the lamellar phase of sample 5 obtained from the ^{2}H-NMR signal of deuterated water in a magnetic field of 11. 7 T at 288 K.

versa for approximately 2 h. Under these conditions, the temperature behavior of the sample orientation exhibits hysteresis. It can be seen that the splitting of the lamellar-phase signal depends strongly on temperature. An increase in temperature leads to a pronounced doublet component split up to 144 Hz (at 361 K). The measurement results indicate that the lamellar phases under study are aligned; the recorded NMR spectra of deuterium at different temperatures show possible structural transformations of these phases [4] under imposed conditions. This is also witnessed by the existence of a temperature hysteresis in the lamellar-phase NMR spectra recorded in the heating–cooling mode. In addition, the observed temperature behavior indicates that alignment is rather slow, even in a strong magnetic field of 11.7 T. This fact is illustrated by Fig. 4, which shows that about 1 h is required for the lamellar phase to be aligned in a magnetic field of 11.7 T at 25°C.

CONCLUSIONS

Using polarization optical microscopy and NMR methods, we showed that the lamellar lyomesophases observed in lyotropic systems synthesized based on CTAB detergent are aligned in a strong magnetic field of 11.7 T. The alignment occurs rather slowly even in a strong MF.

All the phases studied are an example of the so-called soft materials, i.e., materials whose properties depend strongly on external factors: magnetic and electric fields, temperature, etc. These properties of lyotropic LC materials are important for explaining bioactive functions, as well as the self-organization and segregation processes; they find applications in modern nano- and biotechnologies [15].

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