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Identification of Nematic Lyomesophases with Discotic and Cylindrical Micelles in Lyotropic Amphiphilic Systems

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Abstract—Nematic lyomesophases with discotic (N_D) and cylindrical (N_C) micelles in complex multicomponent lyotropic systems based on alkyltrimethylammonium bromide detergents have been identified by the ^{1}H-, ^{2}H-, and ^{13}C-NMR methods and polarization optical microscopy. The difference in the structures of the N_D and N_C nematic phases is especially pronounced in the ^{13}C-NMR spectra. Addition of chiral dopants to the lyomixture facilitates formation of the Ch_D and Ch_C cholesteric phases. According to the ^{13}C-NMR spectra, the micellar mobility in the cholesteric lyomesophases decreases in comparison with the nematic ones. The alignment of lyocholesterics under the action of an external magnetic field is found.

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INTRODUCTION

In 1967, Lawson and Flautt managed to align for the first time the lyotropic phase in a dc magnetic field [1]. The oriented lyotropic phase was formed in a multicomponent mixture composed of sodium decylsulfate, *n*-decyl alcohol, Na_2SO_4, and D_2O. The lyotropic liquid crystal (LC) phases capable of originating in a magnetic field were referred to as lyonematics. Most of such mixtures were synthesized on the basis of alkyl sulfates with the hydrocarbon chain length C_{12} (12 carbon atoms). Lyonematics with disklike (N_D and N_L) and cylindrical (N_C and N_H) micelles [2–6] and biaxial lyonematics (N_b) [7] are known. Most often, the orientation of amphiphilic lyonematics was studied experimentally by the ^{2}H nuclear magnetic resonance (NMR) method [2, 8, 9]. The signal from deuterium nuclei in anisotropic phases is split into a doublet. The value of splitting is proportional to the degree of order $S = \langle P_2(\cos\theta)\rangle$, where θ is the angle between the director of lyotropic LC and the axis of an individual conglomerate (micelle), and the orientational parameter $P_2(\cos\varphi)$. The angle φ characterizes the dependence of the orientation of the LC director on the direction of external magnetic field H_0 [8]. Study of lyotropic nematic phases in various amphiphilic systems is promising for the development of a perfect model of biomembranes and bilayers and the investigation of interphase transitions in biosystems. It is known, for example, that a partial macroscopic orientation in magnetic and electric fields is characteristic of the membrane of the ε *coli* bacteria [10]. Thus, analysis of the formation of lyonematic phases with various types of micelles in multicomponent amphiphilic systems and their alignment under the action of external magnetic, electric, and other fields is now an urgent problem. The application of the ^{13}C-NMR method to the investigation of lyosystems based on a nonionogenic detergent was reported in [11].

EXPERIMENTAL

We synthesized multicomponent lyosystems: cetyltrimethylammonium bromide (CTAB I)–*n*-decyl alcohol–NaBr–D_2O. The detergent used (Serva) was a mixture of dodecyl- (25 mol % $C_{12}Me_3A$Br), tetradecyl- (65 mol % $C_{14}Me_3A$Br), and hexadecyl- (10 mol % $C_{16}Me_3A$Br) trimethylammonium bromide. The composition of CTAB I was analyzed by the ^{13}C-NMR method on an AMX-500 Bruker spectrometer. In the multicomponent lyotropic mixtures synthesized on the basis of this multidetergent [5], we found the N_D and N_C nematic phases. For comparison, a lyomixture based on the detergent CTAB II (Serva), consisting of only hexadecyltrimethylammonium bromide ($C_{16}Me_3A$Br), was prepared. In the ternary lyotropic mixtures, the N_D and N_C nematic phases similar to those observed in [12] (where the lyomixtures were prepared on the basis of cetyldimethylethylammonium bromide) were formed. In our case, the nematic phases formed in the lyomixtures with the detergent CTAB II were inhomogeneous:

Composition of synthesized mixtures; identified mesophases; types of textures determined by polarization-optical microscopy; and the data on the characteristic quadrupole splitting of the ^{2}H-NMR signal of water. Samples 5 and 6 contained cetyldimethylethylammonium bromide detergent [12]

Sample no.	Phase	Texture	Temperature, K	$\Delta\nu_D$, Hz	Reference	Mixture composition, wt %					Chiral dopant
						CTAB I	CTAB II	1-decanol	NaBr	D_2O	
1	*Mi*		297			32.36		3.88	3.06	60.70	
2	N_C	marble	286	14.4		32.36		3.88	3.06	60.70	
3	N_D	schlieren	297	20.0		27.99		6.84	4.08	61.09	
4	N_D	schlieren	297	20.0		27.95		4.08	6.80	61.17	
5	*Mi*		297		[12]		22.95	2.05		75.00	
6	Ch_C	homogeneous planar	297		[12]		22.95	2.05		75.00	1.56 wt % cholesterol
7	Ch_D	schlieren	297			26.45		3.53	3.71	61.89	4.42 wt % *L*-arginine
8	L_α	confocal	297	117.0			32.13	8.75		59.12	
9	homogeneous phase was not formed						32.36	3.88	3.06	60.70	

the presence of the two phases was always observed in anisotropic systems at a fixed temperature corresponding to the presence of nematic lyomesophases.

The detergents CTAB I and CTAB II (Serva), n-decyl alcohol (reagent grade), and NaBr (reagent grade), cholesterol (Reakhim, Russia), and *L*-arginine (Reanal, Hungary) were used without additional purification. Deuterated water contained more than 99.8% D_2O. The presence of the detergent CTAB I in the lyosystem synthesized by mixing individual components in a certain weight ratio (see table) and further centrifugation of the mixture in sealed glass ampoules (8–9 mm in diameter and narrowed to 1–2 mm in the center) facilitated easy formation of nematic lyomesophases. Lyonematics in the mixtures with the detergent CTAB II were much harder to form. The mixtures were always heated to the isotropic-phase temperature 60–70°C, stirred for 60–100 min, cooled to room temperature, and centrifugated to obtain a homogeneous sample. Details of the investigation technique were reported in [4–6, 13]. The ^{2}H- and ^{13}C-NMR spectra were recorded on a pulsed Bruker spectrometer at a frequency of 76.8 MHz (with a polarizing magnetic field of 11.7 T) at 30 ± 0.5°C. The magnetic field was applied parallel to the long axis of the ampoule. The nematic N_D and N_C phases were identified by analyzing the ^{2}H- and ^{13}C-NMR spectra and the polarization optical microscopy data. Nematic mesophases with discotic micelles N_D exhibit a schlieren texture in thin layers (thinner than 100 μm) and capillaries. In thick capillaries (>100–120 μm), this texture becomes homeotropic. The nematic N_C phases in capillaries exhibit either marble or planar texture.

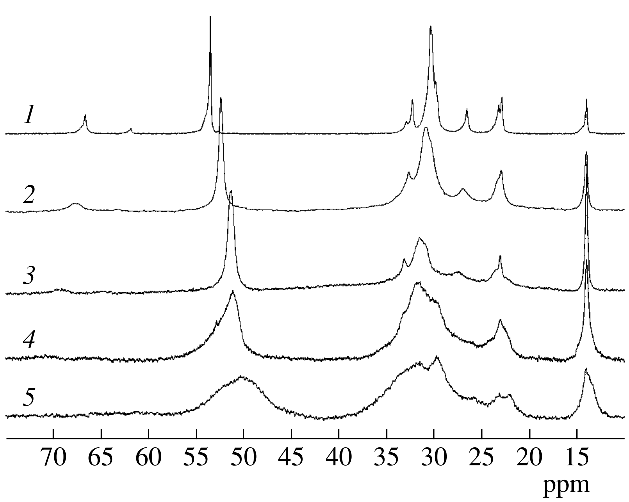

Fig. 1. ^{13}C-NMR spectra of samples 1, 2, and 3: (*1*) micellar phase, (*2*) N_C phase, (*3*) N_D phase, (*4*) $L_{\alpha 1}$ lamellar phase, and (*5*) L_α phase formed in the 32.12 wt % CTAB II–8.75 wt % *n*-decanol–59.12 wt % D_2O lyomixture in the absence of NaBr salt.

RESULTS

The composition of the amphiphilic mixtures prepared on the basis of the detergents CTAB I and CTAB II, the phases observed in these lyomixtures and identified by the ^{2}H- and ^{13}C-NMR methods and polarization optical microscopy, and the textures characteristic of these phases are listed in table.

It was shown previously [4, 5, 13] that the splitting $\Delta\nu_D$ in the ^{2}H-NMR spectra of anisotropic lyonematic N_C phases with cylindrical micelles is less than the splitting for the N_D phases with discotic micelles. This distinction can also be seen from the data in table. The difference in the structure of the N_D and N_C nematic lyomesophases is pronounced in the ^{2}H- and ^{13}C-NMR spectra. As an example, Fig. 1 shows the ^{13}C-NMR spectra of the CTAB I multicomponent mixture, *n*-decyl alcohol–NaBr–D_2O (table, sample 1). The highest mobility of the carbon atoms of the *N*-methyl groups of the detergent molecule is inherent in the nematic N_C phase (Fig. 1, curve *2*). The ^{13}C-NMR spectra of the N_C phase are similar to those of the micellar *Mi* phases at an identical composition of the mixture components (Fig. 1, spectra *1*, *2*; table, sample 1). It can be seen that the mobility of the carbon atoms of the terminal group $CN(CH_3)_3$ of the detergent molecule is most hindered in the N_D phase, although the N_D phases are less viscous than the N_C phases. In addition, Fig. 1 shows the ^{13}C-NMR spectra of the $L_{\alpha 1}$ lamellar phase (curve *4*) observed in the synthesized lyomixture with the composition 32 wt % CTAB I–9.25 wt % NaBr–5.54 wt % *n*-decanol–52.31 wt % D_2O (the value of splitting $\Delta\nu_D$ = 68 Hz at 297 K) [13] and the L_α phase formed in the 32.12 wt % CTAB II–8.75 wt % *n*-decanol–59.12 wt % D_2O mixture in the absence of NaBr ($\Delta\nu_D$ = 117 Hz).

A comparison of the ^{13}C-NMR data with the composition of the samples under study showed that the highest mobility of the carbon atoms of the long molecular chain of the detergent in LC phases is observed in the presence of the NaBr salt in the lyomixture. In the absence of NaBr, all mixtures form lyophases, which, according to the spectra, are characterized by a lower mobility of the carbon atoms in the methyl chain of the detergent molecules. The ^{13}C-NMR spectra of lamellar phases (Fig. 1, curves *4, 5*) illustrate the influence of the NaBr salt on the formation of polymorphic lamellar phases [13]. This influence manifests itself in the different mobilities of the carbon atoms in the alkyl chain of the detergent molecules. Analysis of the ^{1}H- (Fig. 2) and ^{13}C-NMR spectra and the polarization-optical microscopy data allowed us to identify the N_D and N_C nematic lyomesophases formed in the synthesized multicomponent mixtures based on the detergent CTAB I (see table).

The ^{1}H-NMR spectra of the N_C phase (Fig. 2, curve *2*; table, sample 2) and the N_D phase (sample 3, spectra *3*, *3a*; the latter is enlarged by a factor of ×32) show only the peaks of free-water protons. The ^{1}H-NMR spectrum of the micellar phase (spectrum *1*; table, sample 1) contains peaks from both free-water protons and protons of the alkyl chain of the detergent.

Addition of 4.42 wt % *L*-arginine to sample 4 (N_D phase) led to the formation of a cholesteric (*Ch*) lyomesophase with discotic micelles (Ch_D) in the lyomixture. The ^{13}C-NMR spectrum of the Ch_D phase (Fig. 3, spectrum *1*; sample 7) indicates that the motion of the carbon atoms of the alkyl chain of the detergent molecules is more hindered in this phase in comparison with the cholesteric phase with cylindrical micelles Ch_C (Fig. 3, spectrum *2*), which was observed as a result of addition of 1.56 wt % cholesterol to the lyomixture of sample 5 (table). The N_C and Ch_C phases are more viscous than the N_D and Ch_D phases. However, as can be seen from the NMR spectra, the motion of the carbon atoms of the alkyl chain of the detergent molecules is most hindered in the N_D and Ch_D phases. An analysis of the ^{13}C NMR spectra of the N_D and N_C nematic phases and the Ch_D and Ch_C cholesteric phases showed that the micellar mobility in the cholesteric lyophases is lower than in the nematic ones. Polarization optical measurements revealed a typical disordered cholesteric texture of the Ch_D phase (fingerprint texture; Fig. 4a, the bottom part of the capillary), which can be aligned by a magnetic

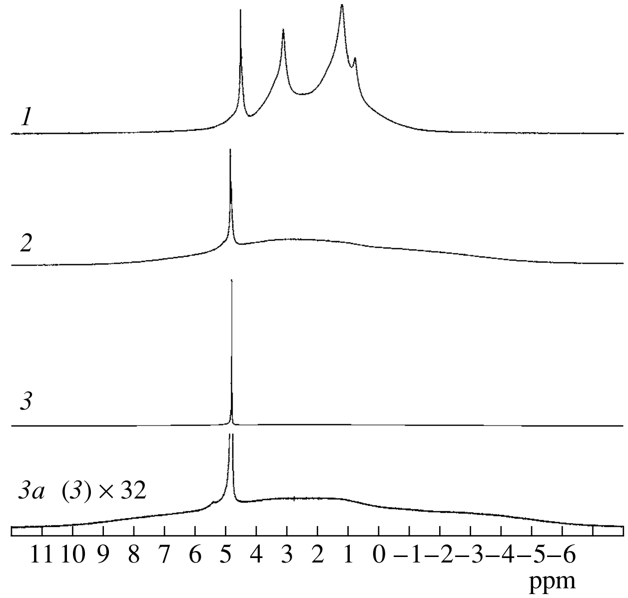

Fig. 2. ^{1}H-NMR spectra: (*1*) micellar phase of sample 1, (*2*) N_C phase of sample 2, and (*3*, *3a*) N_D phase of sample 3 (spectrum *3a* is spectrum *3* enlarged by a factor of 32).

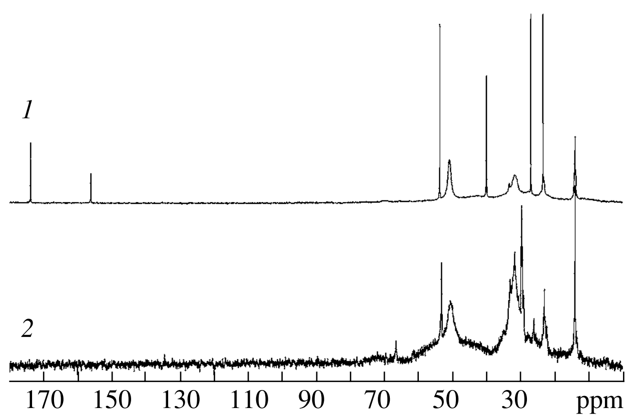

Fig. 3. ^{13}C-NMR spectra of cholesteric phases: (*1*) Ch_D phase, T = 297 K, sample 7; (*2*) Ch_C phase, T = 297 K, sample 6.

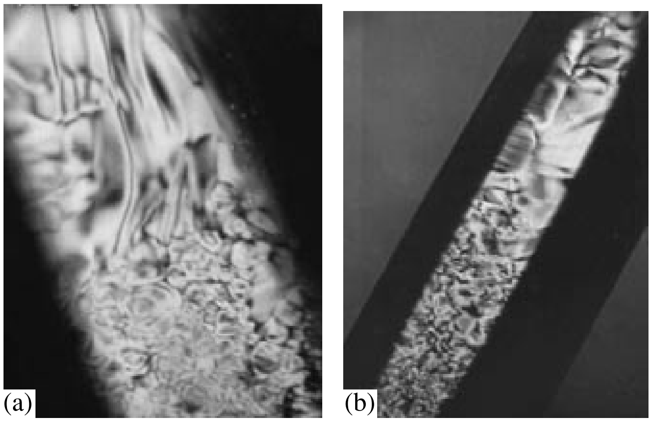

Fig. 4. Textures of cholesteric lyomesophases: (a) Ch_D phase of sample 7 and (b) Ch_C phase of sample 6. The bottom part shows the unaligned texture regions. In the top part, the texture regions are aligned by the external magnetic field $H = 11.7$ T applied parallel to the long axis of the capillary. The capillary thickness is $d = 100$ μm; the magnification is (a) ×250 and (b) ×100.

field ($H = 11.7$ T) applied parallel to the sample's long axis (Fig. 4a, the top part of the capillary). The Ch_C cholesteric phase forms a defect planar structure (Fig. 4b, the bottom part of the capillary) which likewise is aligned under the action of a magnetic field (Fig. 4b, the top part of the capillary). The λ^+ and τ^+ disclinations, which are typical of cholesterics, can be seen in the oriented texture of the Ch_C phase.

CONCLUSIONS

Thus, the analysis of the ^{1}H-, ^{2}H-, and ^{13}C-NMR spectra and the polarization-optical microscopy data obtained for the mesophases formed in the multicomponent mixtures synthesized on the basis of the CTAB detergent allowed us to identify nematic lyophases with discotic (N_D) and cylindrical (N_C) micelles. Addition of a small amount of chiral dopants (*L*-arginine and cholesterol) to these lyophases leads to the formation of the Ch_D and Ch_C phases. It was found from the ^{13}C-NMR spectra that the micellar mobility in cholesteric phases decreases in comparison with the nematic lyomesophases. The ^{13}C NMR method allows one to obtain information about the dynamics of the carbon atom motion in the alkyl chain of the detergent molecules in the lyomesophases with various structures.

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