Crystallography Reports, Vol. 47, No. 5, 2002, pp. 849–855. From Kristallografiya, Vol. 47, No. 5, 2002, pp. 914–921.
Original English Text Copyright © 2002 by Kiirend, Chumakova, Pehk.

LIQUID CRYSTAL

Lamellar Polymorphism in Multicomponent Lyotropic Amphiphilic Systems Based on Alkyltrimethylammonium Bromide Detergents[1]

E. O. Kiirend*, S. P. Chumakova, and T. J. Pehk***
** National Institute of Chemical Physics and Biophysics, Akadeemia 23, Tallinn, 2b Estonia*
*** Shubnikov Institute of Crystallography, Russian Academy of Sciences,*
Leninskiĭ pr. 59, Moscow, 117333 Russia

Received August 10, 2001

Abstract—Lamellar polymorphism in multicomponent lyotropic systems based on alkyltrimethylammonium bromide detergents has been studied by polarization microscopy and ^{1}H-, ^{2}H-, and ^{13}C-NMR spectroscopy. The $L_{\alpha 1}$, $L_{\alpha 1\text{-}h}$, and $L_{\alpha h}$ lamellar phases are revealed, identified, and characterized. The alignment of the $L_{\alpha 1\text{-}h}$ lamellar phase in high magnetic fields is established. *© 2002 MAIK "Nauka/Interperiodica".*

INTRODUCTION

As is well known, molecules of detergents in aqueous solutions are prone to association. The formation of different structures and aggregates results in lyotropic polymorphism. This rich polymorphism is often associated with changes in temperature, component concentration, and the application of external electric and magnetic fields [1, 2]. There exist nematic disklike (N_D) [3–7], cylindrical (N_C) [4–8], hexagonal (H) [9], and several types of lamellar (L) phases [10–12]. A structural unit in lamellar phases is a bilayer associate of detergent molecules surrounded by water. The structural basis of cell membranes is a lipid bilayer, and, therefore, the lamellar phases are simple universal models of cell membranes [13–15]. On heating, the cubic C and lamellar L_α phases are destabilized and, as a result, the reversed hexagonal phase H_{II} is formed in the model lipids systems [15]. The interest in studies of the lamellar phase is associated with the intermediate L_α/H_{II} phase transformation. This type of transformation may play an important role in the functioning of biomembranes [16].

In the two-component didodecyldimethylammonium bromide–water system, the lamellar phase observed consists of two phases: $L_{\alpha 1}$ and $L_{\alpha 2}$. The $L_{\alpha 1}$ phase (Helfrich phase) is characterized by a pseudoisotropic texture and the accompanying Maltese crosses. The $L_{\alpha 2}$ lamellar phase with a mosaic texture is more structurized than the $L_{\alpha 1}$ phase [11, 17].

The $L_{\alpha 1}$, $L_{\alpha 1\text{-}h}$, and $L_{\alpha h}$ lamellar phases are established in the mixtures of C_{12} and C_{14} alkylpolyglycosides [18, 19]. In this case, only the $L_{\alpha h}$ phase is characterized by a pseudoisotropic texture with the homeotropically oriented micelles [19]. The $L_{\alpha 1\text{-}h}$ phase is characterized by a woven texture-like thermotropic S_C phases [20] or a schlieren texture characteristic of the nematic N_C lyomesophases with cylindrical micelles [19].

The changes in the bilayer structure result in the formation of the vesicular, planar smectic L_α, or sponge L_3 phases [21]. Moreover, in the lamellar phases, the bilayers can be rearranged and form various supramolecular structures [10, 22–25].

At present, the focal conic domains of the first type (FCD-I) with a negative Gaussian curvature (texture with oily streaks) are considered as the main structural elements in the classical L_α ($L_{\alpha h}$) lamellar phases. The focal conic domains of the second type (FCD-II) with a positive Gaussian curvature are characteristic of the $L_{\alpha 1}$ (L_α) phases [23, 25]. The textures of lamellar the $L_{\alpha 1}$ (onion) phase show the characteristic Maltese crosses [22, 26]. For the first time, spherical domains were observed in the Gomati lamellar phases [24]. Sometimes, the lamellar phases are subdivided into classical L_α and swollen L_α^{H} phases [12, 26–28].

The study of lamellar phases in multicomponent lyotropic molecular systems broadens our knowledge of the variety of the phases and their transformations in lyotropic liquid crystals (LC). The mixture of C_{12}, C_{14}, C_{16}-alkyltrimethylammonium bromides, NaBr, *n*-decyl alcohol, and D_2O is known to form lamellar, nematic and other phases forming different textures, including schlieren [6, 7] and marble textures. The identification and study of the textures in this system is hindered because of the possible phase transformation of the classical $L_{\alpha h}$ lamellar phase under the effect of the steady shear flow with the formation of the multilamellar vesicular $L_{\alpha 1}$ phase [29]. The lamellar phases with

---

[1] This article was presented by the authors in English.

bilayer structural elements can display different flow-induced orientational effects [30]. The orientation of the bilayer can give rise to the formation of the multilamellar onion phase. Thus, the identification of the lamellar phases in synthetic lyotropic systems is an important step in the studies of LC systems. We analyzed these phases using NMR spectroscopy and optical polarizing microscopy.

EXPERIMENTAL

Multicomponent cetyltrimethylammonium bromide (CTAB)–*n*-decanol–NaBr–D_2O mixtures were prepared within the concentration ranges corresponding to nematic phases [4]. ^{13}C NMR analysis showed that CTAB from Serva was really a mixture of dodecyl- (25 mol %), tetradecyl- (65 mol %), and hexadecyltrimethylammonium (10 mol %) bromides. This mixture is also of interest from the theoretical standpoint, because it was established that different lengths of the alkyl chain in the detergent molecules influence the formation, structure, and properties of the phases formed [31]. The reference detergent was cetyltrimethylammonium bromide (CTAB) (100 mol %) from Merck, because NaBr and *n*-decanol (chemically pure, Reakhim, USSR) could be used without any additional purification. Water contained more than 99.8% of D_2O (Izotop, USSR). The ingredients were mixed in several cycles of centrifugation in sealed glass ampoules 9 mm in diameter with a narrow 2–3 mm neck until the formation of a homogeneous mixture. The samples with a low *n*-decanol concentration were heated up to 60–70°C. The use of the mixed alkyltrimethylammonium bromide-based detergent (Serva) resulted in the faster formation of homogeneous mixtures. Samples with the ampoules were placed into standard 10-mm-long NMR sample tubes. The ^1H, ^2H, and ^{13}C NMR spectra were measured on a Bruker AMX-500 instrument at frequencies of 500.1, 76.8, and 125.8 MHz in a polarizing magnetic field of 11.7 T without sample rotation. The temperature was controlled by a B-VT-1000 unit (Bruker). The ^1H, ^2H, and ^{13}C NMR measurements were made using a lock resonance circuit and without change of the measuring head, which provided fast switching of the NMR spectrometer to all three nuclei under observation. The quadrupole splitting of the water signal in the ^2H NMR spectrum indicated the formation of lyomesophase in the mixture. The temperature dependence of this spectrum gave information about the phase transformations in the samples. The simultaneous presence of two phases in the sample was indicated by the formation of doublets with different $\Delta\nu_D$ values in the ^2H NMR spectra. The ^{13}C NMR spectra were useful for establishing long-range interactions and atom mobility in the detergent molecules of the lyomesophases. The prepared mesophases were characterized with the aid of polarization microscopy on POLAM L-311 and MIN-8 instruments.

RESULTS

Studying aggregation in lyotropic amphiphilic systems, we took into account the possible formation of isotropic solutions, micelles, and various LC and solid phases. These aggregational effects are reflected in the NMR spectra. Figure 1 shows the NMR spectra of different phases of a multicomponent CTAB–*n*-decanol–NaBr–D_2O system obtained at temperatures close to room temperature. The NMR spectrum of the deuterochloroform solution of CTAB–*n*-decanol mixture (a) is compared with the NMR spectra of the micellar solution (b), N_C phase with the marble texture (c), and the solid phase (d). The NMR spectra of the latter three states were obtained from sample 1 of the composition given in the table. The real solution provided the formation of sharp signals. The existence of two types of organic molecules in the ^1H spectrum can be determined only from the analysis of the integrated intensities of different absorption bands (Fig. 1, Ia). At the same time, the ^{13}C NMR spectrum provided the resolution of the signals from almost all the atoms of CTAB

Identification of the lyomesophases and types of their textures using the data of optical-polarizing microscopy and the compositions of the mixtures and the characteristic split of the NMR signal from ^2H nuclei of water in the samples studied

Sample	Phase	Texture type (Fig. 2)	T, K	$\Delta\nu$, Hz	Mixture composition, wt %				
					detergent CTAB (Serva)	detergent CTAB (Merck)	NaBr	*n*-decanol	D_2O
1	Micellar		297		32.36		3.06	3.88	60.70
1	N_C	c	286	14	32.36		3.06	3.88	60.70
2	$L_{\alpha h}$ (FCD-I)	a	297	43	32.84		4.95	6.38	55.83
3	$L_{\alpha 1}$ (FCD-II)	b	297	68		32.90	9.25	5.54	52.31
4	$L_{\alpha 1\text{-}h}$	d, e	297	42	26.85		7.04	5.08	61.03
5	H_I	b	297	26		34.99			65.01
6	Micellar		297		35.00				65.00

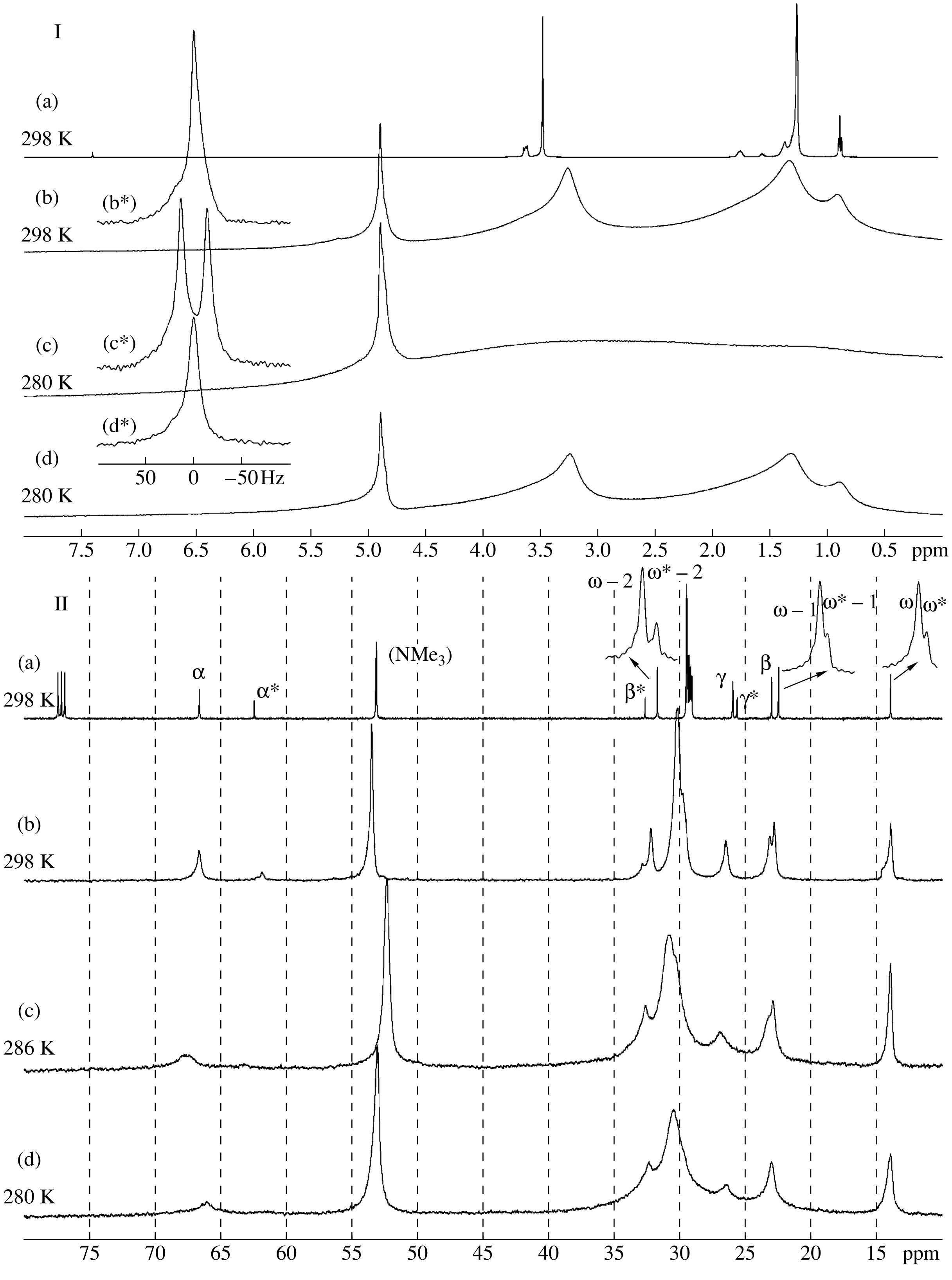

Fig. 1. (I) The ^{1}H and ^{2}H and (II) ^{13}C NMR spectra of different aggregate states of the CTAB–*n*-decanol–NaBr–D_2O system (sample 1). (a) Isotropic solution in $CDCl_3$; (b) micellar phase; (c) LC N_C phase with the marble texture; (d) solid-state phase. Here, α, β, and γ are the signals of the ^{13}C NMR spectrum of the atoms in the α- , β-, and γ-positions of the functional group (–OH, –NMe_3) and ω, ω – 1, and ω – 2 are the signals in the α- , β-, and γ-positions of the end atoms of the alkyl chains of the molecules.

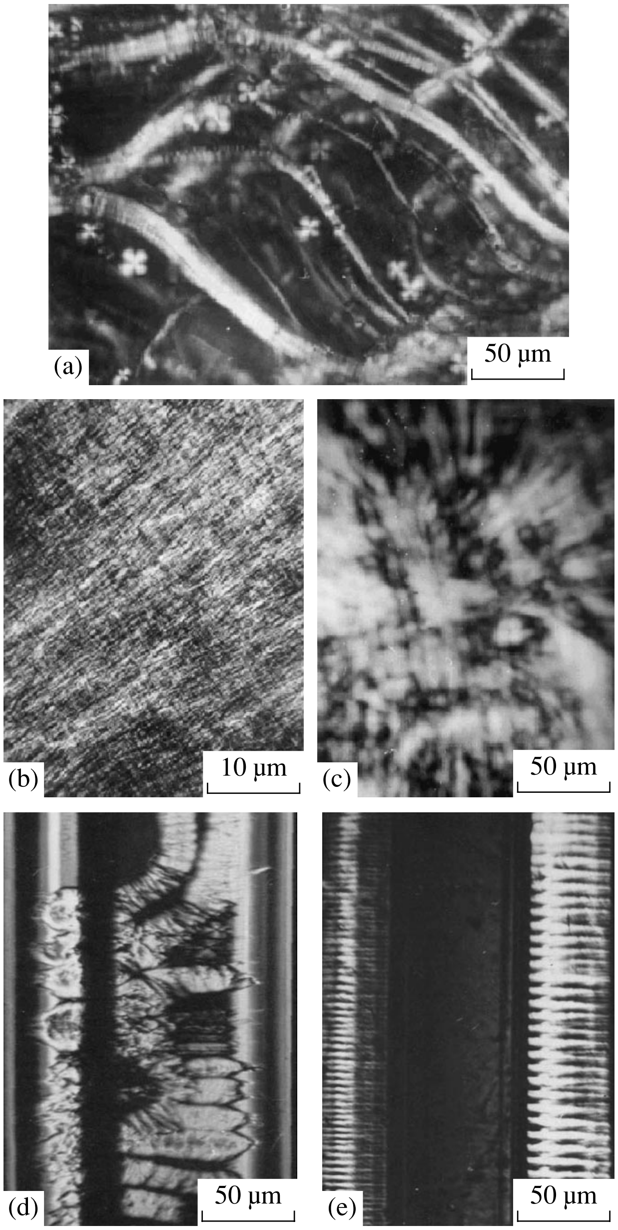

Fig. 2. Lyomesophase textures in the CTAB–*n*-decanol–NaBr–D_2O system: (a) homeotropic texture with oily streaks of the $L_{\alpha h}$ phase (sample 2), ×45; (b) texture of the $L_{\alpha 1}$ phase (sample 3); (c) marble texture (sample 1), ×45; (d) smectic-like texture with focal conics of the lamellar $L_{\alpha h\text{-}1}$ phase (sample 4), ×60; (e) oriented confocals of the $L_{\alpha h\text{-}1}$ phase in a capillary (sample 4), ×60.

and *n*-decanol (Fig. 1, IIa; signals from *n*-decanol are marked with asterisks). The lines due to all the central atoms from the alkyl chains were difficult to identify because of their overlap. However, different chemical shifts of the end atoms of the alkyl chain ($\Delta\delta_{\omega}$ = 0.01 ppm, $\Delta\delta_{\omega-1}$ = 0.01 ppm, and $\Delta\delta_{\omega-2}$ = 0.02 ppm) show the sensitivity of the ^{13}C NMR shielding to the long-range effects (Fig. 1, IIa).

The ^1H NMR spectrum of the micellar phase (Fig. 1, Ib) results in the strong broadening of the signals and, therefore, only three broad bands are seen—those of α protons from the hydrophilic end groups, end protons of methyl group, and other protons of the alkyl groups of molecules (Fig. 1, Ib). A relatively narrow signal at 4.8 ppm is attributed to water. The ^2H NMR spectrum of micellar solution showed no quadrupolar splitting. The ^{13}C NMR spectrum of the micellar phase has also broadened signals, but the presence of two types of organic molecules is still clearly seen (Fig. 1, Ib*). The most pronounced broadening is observed for α carbons of heteroatoms. The formation of micelles induces important selective effects in chemical shifts of carbon atoms ^{13}C. We observed the shifts of N-methyl and alkyl chains and the middle carbon atoms of the alkyl chains toward lower fields, which is characteristic of micelle formation (this was established by the NMR studies of various micellar solutions) (our unpublished data). This seems to be explained by the presence of *trans* alkyl conformers in the middle carbon atoms of alkyl chains.

The formation of a LC phase is clearly seen from the NMR spectra of both hydrogen isotopes: in the ^1H spectrum, in addition to a relatively narrow water signal, there is also an unstructured broad absorption band. In the ^2H spectrum, quadrupole splitting with strong temperature dependence is observed (Fig. 1, Ic, Ic*). The changes observed in the ^{13}C NMR spectrum are less dramatic and are associated with a further broadening of the signals and further shifts of the middle carbon atoms of alkyl chains toward low fields and the shift of the signals of carbon atoms of N-methyl toward high fields. At lower temperatures, the solid phase is formed, the quadrupole splitting of the D_2O ^2H NMR signal is no longer observed, and the ^1H spectrum resembles that of the micellar phase (Fig. 1, Ic*). The ^{13}C NMR spectrum still has broadened signals that are especially well pronounced for the α-carbon atoms. Signals from the central atoms of the alkyl chains and the carbons of N-methyl groups are shifted in the opposite directions, which is characteristic of the micellar phase (Fig. 1, IIc).

The compositions of the mixtures (see table) were selected in such a way that they would include the nematic region of the known phase diagram [4, 7]. The nematic lyomesophases in this system were studied in [4, 6, 7]. The composition of the lyotropic systems forming the lamellar phases (27–33 wt % of detergent, 4–6 wt % of *n*-decanol, 4–9 wt % of NaBr, and 55–65 wt % of D_2O) is close to those of the nematic phases. At the same time, the lamellar phases also exist at lower temperatures than the nematic ones and are characterized by higher viscosity. The characteristic feature of these phases are high values of quadrupole splitting of $\Delta\nu_D$ in the ^2H NMR spectra [6, 7].

Fig. 3. The ^{13}C NMR spectra from the (a) $L_{\alpha h}$, (b, c) $L_{\alpha 1}$, and (d) $L_{\alpha h\text{-}1}$ phases. The spectrum of the $L_{\alpha 1}$ phase indicates the formation of two phases on cooling from the temperature of the isotropic state (360 K) to initial room temperature (295 K).

The identification of the LC phases was made by polarization microscopy. The textures of different lamellar phases prepared from the multicomponent lyotropic mixtures are shown in Fig. 2. The texture of the classical lamellar phase $L_{\alpha h}$ (table, sample 2) is shown in Fig. 2a and is a typical pseudoisotropic texture with oily streaks and focal conic domains of the first type and negative Gaussian curvature (FCD-I). In the ^{13}C NMR spectra of the lamellar $L_{\alpha h}$ phase (Fig. 3a), the lines are broadened much more than those observed in the LC N_C phase from sample 1 (Fig. 1, IIc). The signals from α carbon atoms of the $L_{\alpha h}$ phase are so broadened that they cannot be identified against the background noise of the zero line. The quadrupolar splitting

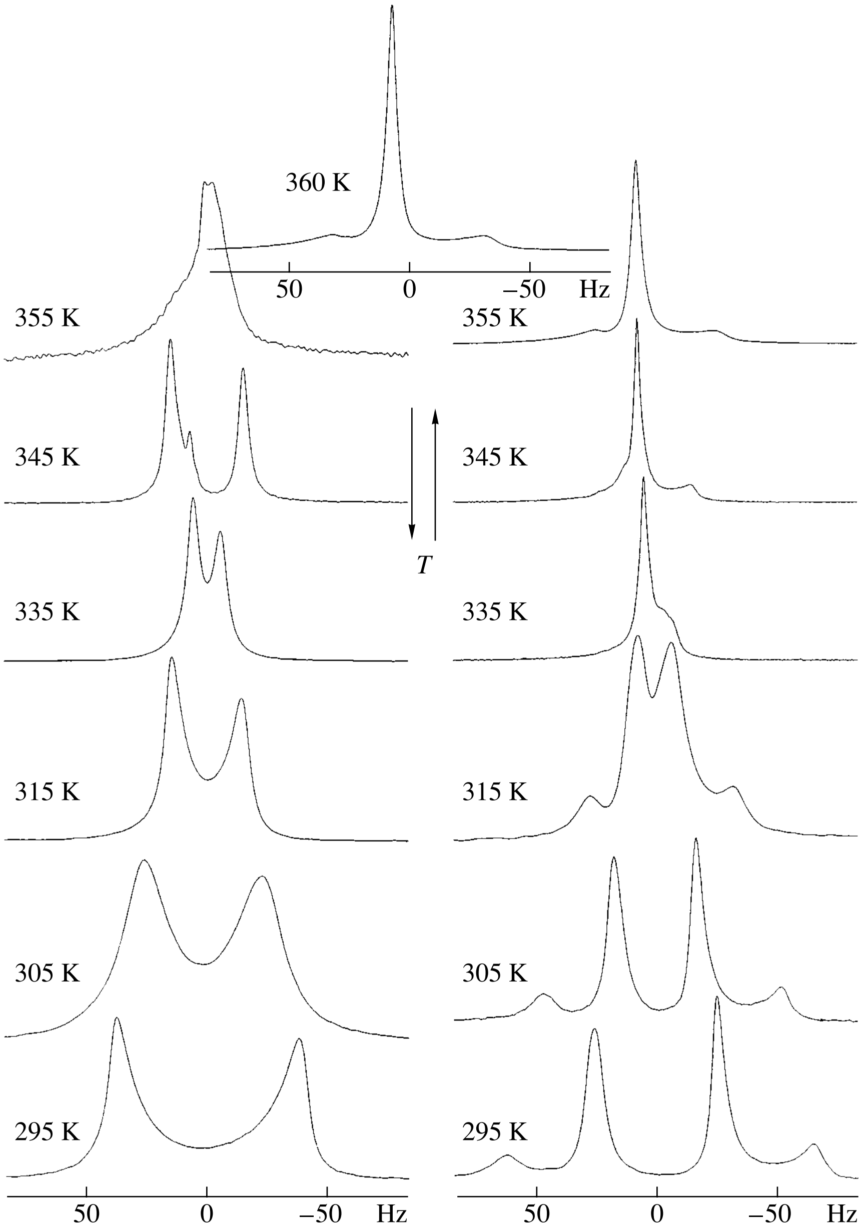

Fig. 4. Temperature dependence of the ^{2}H NMR spectrum of the lamellar $L_{\alpha 1}$ phase (sample 3) in the 11.7 T magnetic field in the heating and cooling cycles.

of the line of the $L_{\alpha h}$ phase in the ^{2}H spectrum (~43 Hz) is more pronounced than that for nematic lyomesophases (~18–20 Hz) [4, 7, 32].

At lower c/s (cosurfactant/surfactant) ratios in the lyotropic systems, one observes the formation of the lamellar $L_{\alpha 1}$ phase with an FCD-II-type texture and positive Gaussian curvature [23, 25]. The woven texture of the lamellar phase from sample 3 is shown in Fig. 2b. The temperature dependence of the ^{2}H NMR spectrum of this phase was studied on heated and cooled samples in a spectrometer (Fig. 4). The sample at room temperature was heated up to the temperature of the transition to the isotropic phase, T_c, and then was cooled back to room temperature (^{2}H NMR spectra in Fig. 3). In this case, the memory effect by the LC phase was observed. The quadrupole splitting $\Delta\nu_D$ at the given temperature depended (Fig. 4) on the history of the sample; cooling the sample in a magnetic field of the NMR spectrometer resulted in the formation of some additional phases. This behavior is also reflected in the ^{13}C NMR spectra: cooling the sample in a magnetic field provides the formation of two absorption bands from the main peak of alkyl chains and their

($\omega - 1$) atoms (cf. Figs. 3b, 3c). Thus, the $L_{\alpha 1}$ phase is transformed from the isotropic state in a strong magnetic field back into the mixture of two LC phases. The memory effect observed is of a complicated nature. The ratio of the two phases formed depends on the cooling conditions of the sample. The details of this process need additional studies.

In $L_{\alpha 1\text{-}h}$ phase (sample 4), the transformation of the smectic phase with the focal conics into the texture (Fig. 2d) with highly oriented confocals (Fig. 2e) was observed. This may be associated with the orientation of the lamellar phases at temperatures lower than $<T_c$. Recently, the orientation of the lamellar phases in strong magnetic fields was observed [33, 34]. The ^{13}C NMR spectrum of the $L_{\alpha 1\text{-}h}$ phase show a slight broadening of the lines in comparison with the lines of the $L_{\alpha h}$ phase (Figs. 3a, 3d).

The viscosity of the samples prepared from the detergent produced by Merck was higher than that of the samples based on the detergent produced by Serva, while the compositions of all the other components were the same. The samples prepared from CTAB gave the lamellar $L_{\alpha 1}$ phase (sample 3) and the hexagonal H_{I} phase (sample 5). Both phases have similar woven textures (Fig. 2b). The most viscous hexagonal H_{I} phase is very stiff; however, the ^{13}C NMR spectra indicate that the mobility of alkyl chains in the hexagonal phase is higher than in the lamellar phases. Thus, the micromobility determined from the NMR spectra is inconsistent with the macromobility determined from the viscosity measurements. The ^{13}C NMR spectrum from sample 6 practically coincides with that of the N_C phases (Fig. 1, Ic). This signifies that the mobilities of alkyl chains in the micellar and nematic N_C phases have close values.

CONCLUSION

The data reported here show the complex nature of the aggregational processes occurring in the lyotropic amphiphilic systems based on alkyltrimethylammonium bromide detergents. Different aggregational states and their mutual transformations can be studied with the aid of multinuclear NMR spectroscopy and optical polarization microscopy. In the present study, several lamellar phases, $L_{\alpha 1}$, $L_{\alpha 1\text{-}h}$, and $L_{\alpha h}$, have been identified and characterized. The alignment of the lamellar phases in strong magnetic fields has also been established.

REFERENCES

1. W. H. Gelbert, A. Ben-Shaul, and D. Roux, *Micelles, Membranes, Microemulsions and Monolayers* (Springer-Verlag, New York, 1994).
2. D. Attwood and A. T. Florence, *Surfactant Systems, Their Chemistry, Pharmacy and Biology* (Chapman and Hall, London, 1983).
3. K. D. Lawson and T. J. Flautt, J. Am. Chem. Soc. **89**, 5489 (1967).
4. B. J. Forrest and L. W. Reeves, Chem. Rev. **1**, 1 (1981).
5. L. Q. Amaral, O. Santin Filho, G. Taddei, *et al.*, Langmuir **13** (19), 5016 (1997).
6. É. O. Kiĭrend, S. P. Chumakova, and T. I. Pekhk, Kristallografiya **31** (4), 732 (1986) [Sov. Phys. Crystallogr. **31**, 432 (1986)].
7. É. O. Kiĭrend, S. P. Chumakova, and N. R. Ivanov, Kristallografiya **38** (6), 201 (1993) [Crystallogr. Rep. **38**, 817 (1993)].
8. L. Q. Amaral, C. A. Pimentel, M. R. Tavares, *et al.*, J. Chem. Phys. **71**, 2940 (1979).
9. C. V. Teixeira, R. Itri, and L. Q. Amaral, Langmuir **15** (4), 936 (1999).
10. K. M. McGrath, Langmuir **13** (7), 1987 (1997).
11. M. Monduzzi, F. Caboi, F. Larche, *et al.*, Langmuir **13** (8), 2184 (1997).
12. J. Gustafsson, G. Oradd, G. Lindblom, *et al.*, Langmuir **13** (4), 852 (1997).
13. I. G. Chistyakov, *Liquid Crystals* (Nauka, Moscow, 1966).
14. G. H. Brown and J. J. Wolken, *Liquid Crystals and Biological Structures* (Academic, New York, 1979; Mir, Moscow, 1982).
15. J. Borne, T. Nylander, and A. Khan, Langmuir **16** (26), 10044 (2000).
16. C. J. Chu and F. C. J. Szoka, J. Liposome Res. **4** (1), 361 (1994).
17. F. Caboi and M. Monduzzi, Langmuir **12** (15), 3548 (1996).
18. G. Platz, C. Thunig, and H. Hoffmann, Ber. Bunsenges. Phys. Chem. **96** (5), 667 (1992).
19. G. Platz, J. Polike, C. Thunig, *et al.*, Langmuir **11** (11), 4250 (1995).
20. G. Platz and C. Thunig, Langmuir **12** (7), 1906 (1996).
21. W. Helfrich, Z. Naturforsch. C **28**, 693 (1973).
22. H. Hoffmann, C. Thunig, P. Schmiedel, *et al.*, Langmuir **10**, 3972 (1994).
23. Ph. Boltenhagen, O. D. Lavrentovich, and M. Kleman, Phys. Rev. A **46** (4), 1743 (1992).
24. R. Gomati, J. Appell, P. Bassereau, *et al.*, J. Phys. Chem. **91**, 6203 (1987).
25. O. Regev and F. Guillement, Langmuir **15** (13), 4357 (1999).
26. J. Oberdisse, C. Couve, J. Appell, *et al.*, Langmuir **12** (5), 1212 (1996).
27. M. C. Holmes, M. S. Leaver, and A. M. Smith, Langmuir **11** (1), 356 (1995).
28. S. S. Funari, M. C. Holmes, and G. J. T. Tiddy, J. Phys. Chem. **98**, 3015 (1994).
29. P. Panizza, D. Roux, V. Vuillaume, *et al.*, Langmuir **12** (2), 248 (1996).
30. J. I. Escalante, M. Gradzielski, H. Hoffmann, *et al.*, Langmuir **16** (23), 8653 (2000).
31. C. C. Ruiz and J. Aguiar, Langmuir **16** (21), 7946 (2000).
32. B. E. Weiss-Lopez, C. Gamboa, and A. S. Tracey, Langmuir **11** (12), 4844 (1995).
33. G. Briganti, A. L. Segre, D. Capitani, *et al.*, J. Phys. Chem. B **103** (5), 825 (1999).
34. M. A. Firestone, D. M. Tiede, and S. Seifert, J. Phys. Chem. B **104** (11), 2433 (2000).