

Isooriented Lyotropic Lamellar Phase in the C₁₂E₆/D₂O SystemGiuseppe Briganti[†]

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Aqueous solutions of a nonionic surfactant, *n*-dodecylhexaoxyethylene glycol [C₁₂H₂₅ (OCH₂CH₂)₆ OH], termed C₁₂E₆, have been studied in the mole ratio range $W_0 = 5.6\text{--}14.9$, where $W_0 = [\text{D}_2\text{O}]/[\text{C}_{12}\text{E}_6]$. There, below a given temperature, a smectic lamellar phase exists. As shown by ¹H and ²H NMR spectra, cooling induces the isotropic phase to become an almost completely isooriented lamellar phase when the magnetic field strength is high (14.1 T). In presence of high magnetic fields, the phase diagram is slightly different with respect to the originally reported one, and the coexistence of an isotropic phase and of the isooriented lamellar one can be observed. In a wide temperature range, only the isooriented lamellar phase is present; it is stable out of the magnetic field for several months. A careful study of the ²H splitting as a function of temperature and concentration indicates the onset of fluctuating cylinder inside the lamellar phase and defines their onset and region of existence. Optical polarizing microscopy experiments confirm the above observation, showing the occurrence of fine grained, mosaic optical textures.

Introduction

The NMR spectrum of heavy water is dominated by the interaction of the deuteron quadrupole moment with the molecular electric field gradient active on the nucleus. The resulting spectrum contains information on the distribution of the relative orientation of the nuclear quadrupole moment with respect to the electric field gradient (efg) and is dependent on the orientation of the efg with respect to the external magnetic field.

When D₂O is present in anisotropic media, translational and rotational anisotropy effects are reflected in the ²H NMR spectrum.¹ For instance, in axial symmetry conditions for the domains (oriented cylinders), the nuclear quadrupolar components are preferentially oriented parallel with respect to the external magnetic field, whereas in planar symmetry conditions (oriented lamellae) the perpendicular components predominate.² This means that the hydrocarbon chains orient perpendicular to the magnetic field; thus cylinders and lamellae align parallel and normal with respect to the field, respectively.

In lyotropic phases at least two dynamic processes can be detected by NMR: a slow one, due to the overall motion of the hydrophobic layers, and a fast one, associated with the

tumbling of water molecules at the interface.³ The width of the observed quadrupole splitting mostly depends on tumbling dynamics, whereas the overall spectral shape depends on the degree of orientation of the domains with respect to the magnetic field vector and on the symmetry properties of the phase itself.⁴ When the system is isotropic, static effects are missing and a single peak is observed.

In liquid crystalline phases and in absence of preferential orientation with respect to the magnetic field director, Pake doublet is observed. For polyphasic systems the overall ²H spectrum is the result of the overlapping of spectra due to the different phases, provided that the water exchange between them is slow.⁵ In that case deuteron magnetic resonance experiments are suitable to analyze some physicochemical properties of liquid crystalline phases through the quadrupolar ²H spectra of heavy water molecules.⁶

In this paper we report on an NMR study of the lamellar phase observed in the binary system heavy water–dodecylhexaoxyethylene glycol, [D₂O]/[C₁₂E₆], under the influence of strongly orienting magnetic fields. The system has been widely investigated in the past.^{7,8}

We show here that use of high magnetic fields and proper thermal cycles allow us to get an almost complete orientation of the lamellar domains with respect to the magnetic field director. Such effect is retained for long times, even in samples kept outside the magnet for weeks.

The observed spectral shape show significant orientation with respect to the magnetic field director. This fact allows, among

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other things, a better definition of deuterium spectral profiles and indicates a significant alignment of the lyotropic domains. In the present paper we discuss such effects, taking into account previous spectroscopic and structural observations reported on the above systems.^{9,10}

Materials and Methods

$C_{12}E_6$ was purchased from Tokyo Kasei, Japan. D_2O , isotopic purity 99.8%, was purchased from Carlo Erba S.p.A., Italy.

Samples were prepared according to a previously described procedure.⁷ To ensure a good quality to the textures and macroscopic appearance of the lamellar phase, samples were heated slightly above the transition temperature, allowed to equilibrate for some minutes, and then slowly cooled to 300 K into a thermostatic bath, or inside the probe head. Typical cooling rates were 0.5 K per minute.

NMR measurements were performed on a Bruker AMX 600 spectrometer, operating at 600.13 on proton and 96.12 MHz on deuterium nuclei, respectively, and on a Bruker AC 200 spectrometer, operating at 30.70 MHz on deuterium. All instruments were equipped with Bruker variable temperature controller units.

To ensure an undistorted shape of the 2H spectral profiles, the measuring windows were kept fully open (120 kHz), and the initial delay between the transmitter pulse and the opening of the receiver system, D_0 , was as short as possible (6 μs). This ensures no cutoff effects in the FT transformation of 2H NMR spectra. Relaxation delays always longer than 5 s. No lock system was used. At least 16 transients were collected.

Samples to be investigated in optical polarizing microscopy were prepared as follows. Small amounts of the original solutions were placed in quartz capillaries for X-ray scattering (inner diameter, ϕ , 1 mm) by a syringe and sealed. Thereafter they were located into 5 mm ϕ NMR tubes, which were flame sealed. Samples were heated to 350 K and allowed to cool in the 14.1 T magnet at a controlled rate (0.1 K/min). To ensure an almost complete alignment, samples were periodically checked by deuterium NMR.

Optical polarizing microscopy was performed at ≈ 300 K by a CETI optical microscope (Antwerp, Belgium) equipped with crossed polaroids, filters, and a photographic camera. As a rule, 10–40 magnifications were used. A complete description of the microscope properties and setup has been reported elsewhere.¹¹

In most instances the optical textures reported in Figures 1 and 2 were observed for samples subjected to alignment in 14.1 T magnetic field. In other cases batonnets or fanlike textures have also been observed. The recognition of optical anisotropic textures was made according to the classification system of Rosevear.¹²

Results and Discussion

Above a certain temperature, whose value depends on concentration, all solutions are isotropic: below it they form a lyotropic lamellar phase. The above phase is characterized by parallel layers of hydrocarbon chains, 34 Å thick and nearly constant with concentration (ideal swelling conditions). The layers are separated by water molecules and surfactant hydrophilic groups. The thickness of the polar region (containing water and hydrated polyoxyethylene groups) decreases from ≈ 43 to 39.8 Å in the concentration range we have investigated.^{8,10}

2H and 1H NMR measurements were performed at 14.1 T on the system $[D_2O]/[C_{12}E_6]$, for mole ratios W_0 between 14.9 and

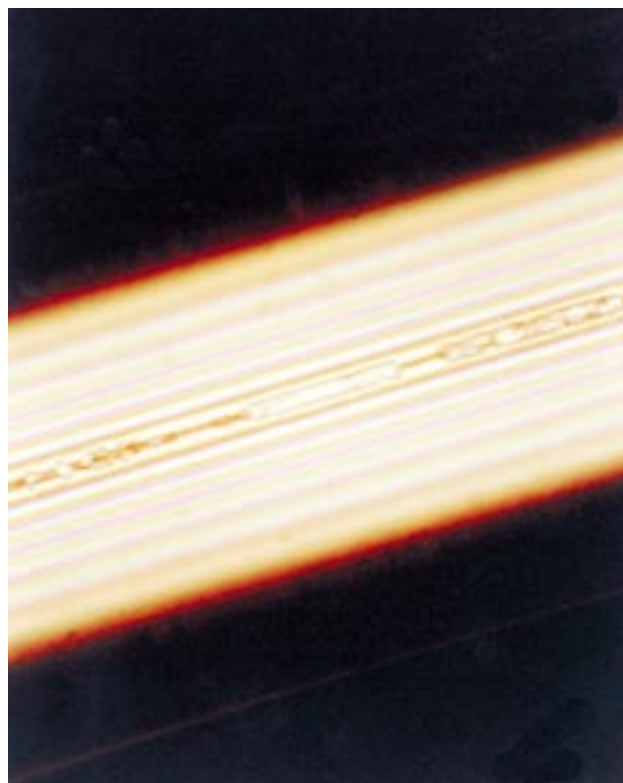


Figure 1. Optical polarizing micrograph of a sample with $W_0 = 9.6$, at ≈ 300 K previously oriented in the 14.1 T magnet. The photo was taken in polarized light with magnification 10 \times .



Figure 2. Optical micrograph of a sample with $W_0 = 9.6$, at ≈ 300 K previously oriented in the 14.1 T magnet viewed in white light and magnification 10 \times .

5.6, i.e., in the range where the occurrence of a lamellar phase has been previously described.⁷ In the following we report the most relevant aspects of the present system, inferred by 2H and 1H NMR as well as by optical polarizing microscopy experiments.

2H NMR. An example of the unusual features observed as a result of cooling/heating cycles is given in Figure 3a where the

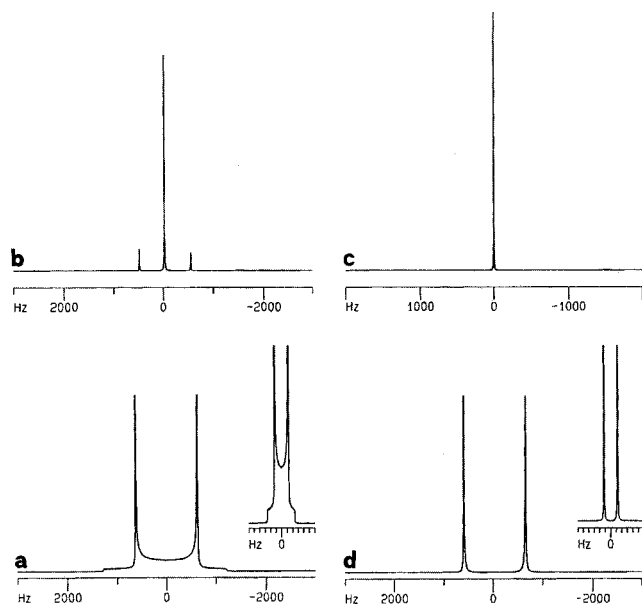


Figure 3. ^2H NMR spectra at 92.12 MHz of a sample of molar ratio $W_0 = 9.6$: (a) the lamellar phase was grown in a thermostat and measured at 300 K, in the inset the spectrum is shown with the vertical axis expanded by a factor four, the parallel components of the Pake doublet are clearly resolved; (b) at 323 K a strong central peak due to the isotropic phase is observed, while only the parallel components of the Pake doublet are present; (c) at 335 K; and (d) at 300 K, after cooling from the isotropic phase within the magnetic field, in the inset the vertical expanded spectrum is also shown. No parallel components of the Pake doublet are observed and no appreciable difference is found by keeping the sample reported above at 300 K for months and then running the NMR spectrum again.

^2H spectrum for a mixture of mole ratio $W_0 = 9.6$ is shown. According to the original phase diagram, the lamellar phase exists up to ≈ 343 K. The sample was heated above that temperature and slowly cooled to 300 K within a thermostatic bath. The related spectral shape is a Pake doublet with a quadrupolar splitting, $\Delta(^2\text{H})$, of 1247 Hz. In the spectrum the orientation distribution function with respect to the magnetic field is typical of a polycrystalline powder (powder pattern spectrum).

By slowly raising the temperature within the spectrometer, from 300 K, i.e., well below the phase boundary, a mixture of lamellar and isotropic spectral components is observed, Figure 3b (for instance, at 323 K the measured quadrupole splitting, ≈ 1177 Hz, coexists with an isotropic singlet). The spectrum indicates that a mixture of the two phases is present. Since only the parallel components of the Pake doublet are observed, then the lamellar phase is fully isooriented. Thus, as a consequence of warming the sample inside the magnet, the onset of the isotropic phase is accompanied by a full orientation of the lamellar phase in equilibrium with it.

The rate of water exchange between the two phases is slow on an NMR time scale, as required to observe both lines in the ^2H NMR spectrum. By raising the temperature above the phase boundary within the spectrometer, only a sharp peak is present, see Figure 3c, reflecting an isotropic orientation distribution of aggregates.

Cooling the sample back down to 300 K inside the magnetic field, the spectrum shown in Figure 3d is obtained. It does not match the general shape of a Pake doublet and only the perpendicular edges are observed, $\Delta(^2\text{H}) = 1256$ Hz. Frequencies due to any other orientation are missing and the quadrupolar ^2H spectrum indicates the occurrence of iso-oriented domains.⁵

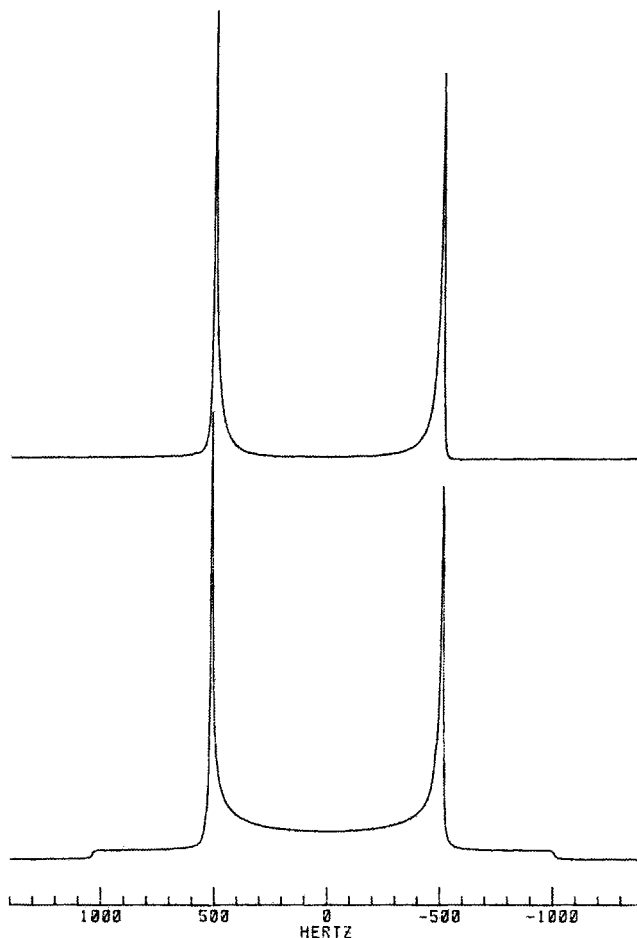


Figure 4. ^2H NMR spectra at 30.70 MHz (4.7 T magnetic field) for a sample of molar ratio $W_0 = 9.6$ and 300 K. In the bottom the sample was previously cooled from the isotropic phase inside a thermostatic bath, (note the occurrence of parallel components); in the top the sample was previously cooled within the 14.1 T magnetic field. The effect of the highly orienting magnetic field is still retained at lower magnetic field, and only the perpendicular components are observed.

Thus, heating the sample in the presence of strong magnetic fields, up to completion of the phase transition process, and slowly cooling it back to room temperature gives an almost completely isooriented lamellar phase. The effect is observed in the whole range of existence of the phase, and is accompanied by a slight change in the phase transition temperature. For instance, at a mole ratio of 7.5, the smectic phase formation in the magnet occurs at 2 K below the value measured outside it.⁸

The reported alignment depends on the strength of the applied magnetic field.¹³ No effect of the field can be seen in the ^2H NMR spectra of the same sample, when performed on a 1.9 T magnetic field. The spectrum of a sample previously cooled in a thermostatic bath, matches the one of the same sample grown in the 1.9 T magnetic field, data not shown.

In Figure 4, 30.70 MHz ^2H NMR spectra (magnetic field strength 4.7 T) for samples at $W_0 = 9.6$ are shown. In the bottom of figure the spectrum is obtained by slowly cooling the sample in an external thermostatic bath, while in the top of figure the spectrum is due to the sample cooled in the 14.1 T magnetic field at least 1 month before measuring it again at 4.7 T. The orienting effect due to the high magnetic field is retained.

Cooling the same sample inside the 4.7 T field does not give rise to an isooriented lamellar phase. This observation agrees with the literature;¹³ in fact, the orienting effect depends on the field strength square.

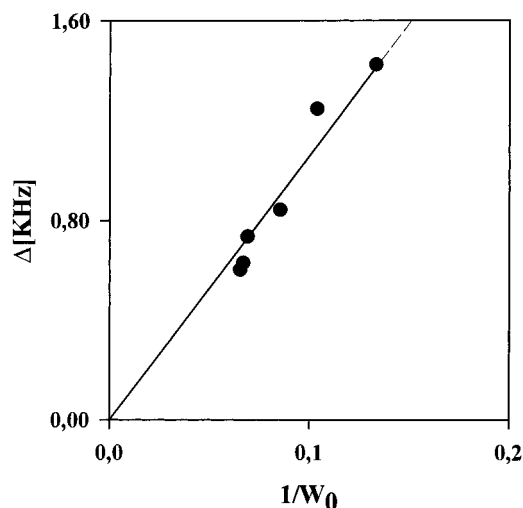


Figure 5. Dependence of deuterium quadrupolar splittings in the lamellar phase as a function of $1/W_0$ at 310 K. An average hydration number, $n = 7.4 \pm 0.4$, is obtained. The line through experimental points represents the linear best fit according to the equation $\Delta = n\Delta_b \cdot (1/W_0)$ where Δ is the distance between the perpendicular components in the Pake doublet and Δ_b its maximal value.

In current models for lyotropic lamellar phases, the long axes of the surfactant molecules are preferentially oriented perpendicular to the magnetic field.¹⁴ Thus the lamellae are, on the average, preferentially oriented parallel to the magnetic field director (i.e., their symmetry axes are perpendicular to the

magnetic field). Accordingly, only the normal components of the spectrum can be observed. This observation is in agreement with studies on lamellar mesophases containing phospholipids¹⁴ but was never observed on binary systems such as the $C_{12}E_6$ /water system. (We will not discuss the very special case of lyotropic nematic phases.¹⁵)

In the isooriented situation, at temperature and mole ratios fixed, the splitting for samples subjected to the above thermal cycles is slightly larger than the one measured when the samples are cooled outside the magnet. Evidence comes from the analysis of the spectral profiles (work in progress). Thus, high magnetic fields not only influence the alignment of the lamellar phase but also modify the time average associated with the tumbling of water molecules. Accordingly, a broadening of the doublet separation is observed.

The relative amounts of the coexisting isotropic and lamellar phases can be inferred from the integrals of the spectral profiles. This is helpful, since the amount of isotropic phase is markedly different when measured on heating or cooling cycles. The effect depends on concentration, on the temperature difference with respect to the original phase boundary value, and is consistent with an overcooling effect. For instance, at a $W_0 = 7.5$ the onset of the smectic phase occurs at 2 K below the original value. (An extended analysis of the magnetic field effect on the phase diagram is in progress.)

The Pake doublet splitting increases on increasing the surfactant content, see Figure 5. The corresponding data have been analyzed assuming the validity of a two-site approximation

TABLE 1: Splitting between the Perpendicular Components of 2H NMR Spectra, in hertz, at 14.1 T^a

<i>T</i> (K)	$W_0 = 5.6$		$W_0 = 7.5$		$W_0 = 9.6$		$W_0 = 12.3$		$W_0 = 14.9$	
	$\Delta H_{\uparrow\uparrow}$	$\Delta H_{\uparrow\downarrow}$	$\Delta H_{\uparrow\uparrow}$	$\Delta H_{\uparrow\downarrow}$	$\Delta H_{\uparrow\uparrow}$	$\Delta H_{\uparrow\downarrow}$	$\Delta H_{\uparrow\uparrow}$	$\Delta H_{\uparrow\downarrow}$	$\Delta H_{\uparrow\uparrow}$	$\Delta H_{\uparrow\downarrow}$
300	1533.7	1535.3	1570.1	1576.2	1246.6	1255.8				
301										
302							843.8	828.6		
303	1499.9	1483.2								
304	1481.6	1469.4					828.6	830.1		
305	1458.7	1458.7	1506.0	1515.2			825.5	836.2		
306							830.1	838.5		619.5
307	1437.4	1440.4					834.7	840.8		624.1
308										628.7
309	1425.2	1426.7								630.2
310	1413.0		1426.7	1438.9	1246.6	1258.9	846.9	850.0	624.1	633.2
311			1411.4	1423.6						
312	1397.7								631.7	637.8
313			1371.8	1379.4						
314	1394.7		1364.1	1368.7					634.8	643.9
315							865.2	868.2		
316			1336.7	1345.8					639.3	650.0
317			1327.5							
318			1315.3						645.5	656.1
320							869.8	886.5	647.0	663.8
322									654.6	671.4
323					1176.5	1194.8				
324									662.2	680.5
325					1161.2	1176.5				
326									671.4	688.2
327					1142.9	1159.7				
328					1135.3	1147.5			683.6	698.9
329					1126.1	1141.4				
330					1115.4	1129.2	878.9	894.2	715.6	711.1
331					1103.2	1118.5	880.4	892.9		
332					1092.5		874.3	888.1	735.5	727.8
333					1078.8	1091.0	868.2	885.0	752.3	737.0
334							863.7	882.0	761.4	749.2
335					1036.1	1055.9	859.1	877.4		
336							853.0	871.3		
337							846.9	865.2		
338							849.9	856.0		

^a Arrows indicate that the temperature is increasing or decreasing. Boldface values indicate the coexistence of a lamellar and an isotropic phase.

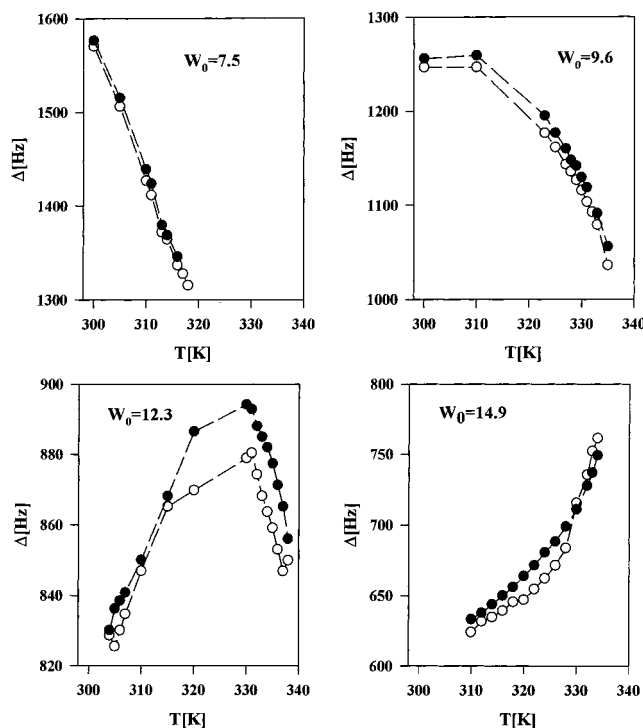


Figure 6. ^2H NMR at 92.12 MHz (14.1 T), as a function of temperature for samples in the lamellar phase at different W_0 . Empty symbols refer to samples prepared in a thermostatic bath and measured on increasing the temperature, full symbols to samples cooled from the isotropic phase inside the 14.1 T field. W_0 values are reported in the top of the Figures. Dashed lines are an eye guide.

for the state of water molecules, which can be bound at the interface or free. If the quadrupole coupling constant of deuterium is independent of its state and if the bond order parameter of free water is null, the quadrupole splitting can be related to the number of water molecules bound at the interface.^{10–16} In fact, the splittings increase more or less linearly with the surfactant mole fraction in the mixture and the slope is grossly proportional to the hydration number per surfactant. Proper data fitting gives an average hydration number of 7.4 ± 0.4 per headgroup termination, in agreement with neutron scattering data, performed on the corresponding dilute solutions.¹⁷ Thus, even if the two-site model for water binding is oversimplified,¹⁸ it seems rather correct.

The quadrupole splitting depends on concentration, temperature and on the history of the sample (i.e., cooled inside or outside the magnet), see Table 1. At low water content, a plot of $\Delta(^2\text{H})$ versus temperature gives a straight line with negative slope, Figure 6a. However, the linear behavior is missing on increasing the water content, Figure 6b. At still higher water-to-surfactant ratios two straight lines are observed, Figure 6c and d. Since $\Delta(^2\text{H})$ is proportional to the bond-order parameter, which, in turn, describes the time averaged orientation of water molecules in a given mesophase, then the temperature dependence of $\Delta(^2\text{H})$ values can be related to (1) a modification of the properties of bound water molecules,¹⁹ (2) changes of the EO conformation, (3) changes in the interfacial curvature, and (4) modifications of the bound-free exchange rate.²⁰

In other words, since $\Delta(^2\text{H})$ is proportional to the order parameter which, in turn, describes the time averaged orientation of the water molecules in the mesophase, its temperature-dependent behavior can be related either to a modification of the properties of the embedded water molecules¹⁹ and/or to changes of the lamellar phase. This interpretation agrees with findings of Rançon and Charvolin.^{21,22} Their X-rays diffraction

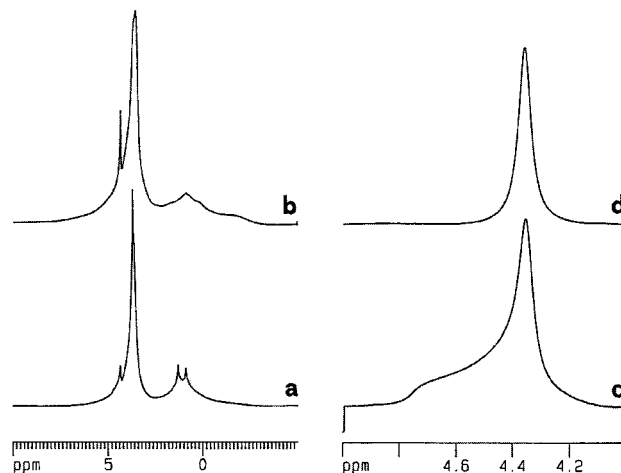


Figure 7. ^1H NMR spectra at 600.13 MHz of a sample at $W_0 = 9.6$ and $T = 300$ K. On the left (a and b), the full spectral range is reported, while on the right (c and d), only the spectral region relative to the water resonance is shown. Spectra in a and c are due to a sample grown outside the magnet while spectra in b and d refer to the same sample slowly cooled in the 14.1 T magnet.

and synchrotron light investigations on the lamellar phase, at concentration larger than $W_0 = 9.6$, indicates the presence of a fragmentation of the amphiphilic bilayers into cylinders arranged on a local hexagonal lattice.

The presence of these cylinders in fast exchange with the lamellar domains causes a decrease of the deuterium splitting exactly as the one found. In this way a transition point is observed, as function of temperature and concentration. The transition point defines the onset of a fluctuating hexagonal phase within the lamellar phase.

Thus the different thermal evolution of $\Delta(^2\text{H})$ at different concentration can be interpreted as due to the presence and amount of the fluctuating hexagonal phase. For symmetry reasons¹⁶ the hexagonal phase has a splitting between perpendicular components exactly half than the one for the corresponding lamellar phase and its presence should result in a decreased splitting.

Note also that the dependence of $\Delta(^2\text{H})$ on temperature at different mole fractions depends on the degree of entangling of the polar moieties, due to the reduction of the interlayer spacings, and on the observed decrease of the area per polar headgroup.⁸

^1H NMR. ^1H spectra performed at 600.13 MHz confirm ^2H data and show well resolved parallel and perpendicular components of the resonance due to residual HOD. In fact the ^1H resonance of water (i.e., the HOD signal) shows clearly a chemical shift anisotropy, where the asymmetric components, parallel (\parallel) and perpendicular (\perp), respectively, can be assigned. In Figure 7a and b the ^1H NMR spectra are reported for the sample at $W_0 = 9.6$ and 300 K. Figure 7a and c refer to the sample cooled in an external thermostatic bath; there the asymmetric components of the water signal, at 4.71 and 4.35 ppm, respectively, are well resolved. Slowly cooling the sample into the high magnetic field induces the occurrence of only one component in the water spectral region at 4.35 ppm, Figure 7b and d.

Taking into account information from the corresponding ^2H spectra, it can be safely assumed that the resonance at 4.35 ppm is due to the perpendicular component. Thus ^1H spectra in Figure 7 agree with the spectral shape observed in other oriented systems for nuclei with a much greater chemical shift anisotropy, such as phosphorus and fluorine.^{14,16}

Optical Microscopy. Optical polarizing microscopy investigations were performed on samples previously subjected to thermal treatment in high magnetic fields. The observed alignment is presumably due to a combination of magnetic field and capillary effects. It must be pointed out that the alignment of lyotropic domains is observed in samples located in 5 and 1 mm \varnothing tubes.

Anisotropic optical textures have been found: as an example, micrographs for one selected mixture are reported. The occurrence of fine grain mosaic textures, of nearly uniform extinction, was observed in polarized and white light, Figures 1 and 2. Significant exceptions to the above behavior are observed in close proximity of the capillary edge (occurrence of fanlike textures) and close to the air–liquid crystal interface (batonnets).

We made also a comparison with the optical textures observed in structurally related systems which orient in magnetic fields, for instance those observed by Radley and Saupe.¹⁵ Unfortunately, the relatively high sample thickness, with consequent problems on the optical resolution and focusing, does not allow us to quantify the above effects. Studies on thin oriented samples in planar geometry are in progress.

In uniaxial mesophases two parameters are relevant to rationalize the system ordering, the optic axis and the related anisotropy (i.e., the difference between measurements taken parallel or perpendicular to a given optic axis). In the geometry we have used (small capillaries) there is not possibility to quantify the above effect, as can be done, conversely, in planar geometry. This is the reason we always observe a region of nearly constant alignment with respect to the capillary axis director.

The average size of the domains must be small, to account for the occurrence of fine (sandy) anisotropic mosaic textures. The observed orientation is presumably due to a combination of magnetic fields and capillary (wall) effects. That is why significant variations with respect to the observed textures are observed only in close proximity of curved surfaces (i.e., close to the air–lamellar interface and close to the capillary edge).

Conclusion

The above observations indicate that the free energy contributions responsible for surfactant–surfactant and surfactant–water interactions, governing the overall phase behavior, are modulated

by the orientation of surfactant molecules with respect to the external magnetic field. High magnetic fields are required to observe the reported behavior. Similar effects were previously observed on phosphatidylcholine membranes¹² but never in the $[D_2O]/[C_{12}E_6]$ system. It must be pointed out that the isooriented structure is stable and can be maintained outside of the field at least for several months: this is quite unusual.

So that $C_{12}E_6$ is to our knowledge, the first stable smectic phase isooriented by a magnetic fields.

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