

Phase Diagram of the C<sub>12</sub>E<sub>6</sub>/D<sub>2</sub>O System Revisited: Effect of Strong Magnetic Fields<sup>†</sup>Donatella Capitani,<sup>\*,‡</sup> Cinzia Casieri,<sup>§</sup> Giuseppe Briganti,<sup>⊥</sup> Camillo La Mesa,<sup>¶</sup> and Anna L. Segre<sup>‡</sup>

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Lytotropic mixtures composed by heavy water and C<sub>12</sub>E<sub>6</sub> (*n*-dodecylhexaoxyethylene glycol [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>(OCH<sub>2</sub>-CH<sub>2</sub>)<sub>6</sub>OH], with different mole ratios, *W*<sub>0</sub>, have been studied in the presence of high magnetic fields. Depending on both thermal history and magnetic conditioning, a significant orientation of the samples is obtained and the phase boundaries are slightly modified with respect to the originally reported ones. The resulting <sup>2</sup>H spectra show the presence of two components, one iso-oriented and another one partially oriented. To quantify the amount of oriented spectral components a full simulation was performed, based on 0th, 2nd, and 4th rank Legendre polynomials. Experimental investigation is focused on the hexagonal mesophase, but information is also given on the lamellar phase. The iso-orientation of samples is kept for several months. The presence of a large amount of iso-oriented phases is confirmed by optical polarizing microscopy experiments.

## Introduction

Deuterium magnetic resonance, <sup>2</sup>H NMR, studies on surfactant–D<sub>2</sub>O systems give information on the state of water molecules interacting with the amphiphile. Such spectroscopic investigations can be related to the polymorphic behavior of these mixtures and are helpful to clarify the occurrence and nature of lyotropic phases.<sup>1</sup>

The NMR spectrum of heavy water is dominated by the interactions of the deuteron quadrupole moment with the electric field gradient active on the nucleus. In isotropic phases, where all directions of the field gradient have the same probability, the molecular motions average the quadrupole interactions to zero and a sharp peak is observed in the spectrum. In anisotropic liquid crystalline phases, conversely, the orientation of the nucleus quadrupole moment is not averaged to zero by molecular motions and a residual contribution is retained. Thus, in the NMR spectrum, a Pake doublet is observed in absence of preferential orientation with respect to the magnetic field director.<sup>2</sup>

The splitting between the perpendicular components, i.e., the doublet separation, depends on the fraction of deuterons in a given anisotropic site, on the quadrupolar coupling constant, and on the order parameter of heavy water molecules in that site. In the case of rapid exchange between free and bound states, the splitting reflects the bound fraction, hence it is modulated by intensive variables and composition.<sup>3</sup>

Provided the exchange rate between different sites is slow, the observed <sup>2</sup>H spectrum is the result of an overlapping of more signals.<sup>4,5</sup> Accordingly, the coexistence of different phases and

the transitions between them can be studied. In fast exchange conditions, conversely, average <sup>2</sup>H splitting, Δ(<sup>2</sup>H), are observed. In the latter case, a careful analysis of Δ(<sup>2</sup>H) values allows to define the occurrence of phase transitions, for instance the nucleation of an hexagonal phase within a lamellar one,<sup>6,7</sup> etc.

Previous studies on the lamellar phase of C<sub>12</sub>E<sub>6</sub>/D<sub>2</sub>O system indicate that high magnetic fields modify the phase behavior and orient the lyotropic domains.<sup>6</sup> In fact, the shape of deuterium spectral profiles and the optical textures of samples conditioned by magnetic fields showed the occurrence of significant orientation.

The present contribution deals with the effect of strong magnetic fields on the orientation of an hexagonal mesophase in the C<sub>12</sub>E<sub>6</sub>/D<sub>2</sub>O system. Evidence is supported by proton and deuterium spectral profiles, computer simulation of the spectral profiles, and optical polarizing microscopy.

For completeness, we report NMR data and computer simulations on the lamellar phase, which was investigated between 300 and 340 K.

## Experimental Section

**Materials.** *N*-Dodecylhexaoxyethylene glycol [CH<sub>3</sub>(CH<sub>2</sub>)<sub>11</sub>-(OCH<sub>2</sub>CH<sub>2</sub>)<sub>6</sub>OH], C<sub>12</sub>E<sub>6</sub>, was purchased from Tokyo Kasei, Japan. D<sub>2</sub>O, 99.8% isotopic purity, was from Carlo Erba S.p.A., Italy. Replacement of water with deuterium oxide was made on a mole fraction basis.

Samples were prepared according to a previously described procedure.<sup>6</sup> They were heated at temperatures higher than the transition one, allowed to equilibrate for some minutes, and slowly cooled to 300 K inside a thermostatic bath, or in the probe head.

Typical cooling rates are 0.5 K min<sup>-1</sup>. The above procedures ensure a good quality to the microscopic textures and to the macroscopic appearance of liquid crystalline samples in polarized light.

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**Methods. NMR.** All NMR spectra were run in 5 mm o.d. tubes. <sup>1</sup>H NMR spectra were measured on a Bruker AMX600 spectrometer operating at 600.13 MHz. <sup>2</sup>H spectra were recorded at 92.12 MHz (on AMX600), at 30.70 MHz (on a Bruker AC200), at 61.4 MHz (on a Bruker AM400) and at 12.44 MHz (on a Stelar Spinmaster spectrometer). All instruments were equipped with variable temperature control units.

The measuring window was fully open (120 kHz), and the delay between the closure of the transmitter and the opening of the receiver system,  $D_0$ , was kept as short as possible. In the AMX600 spectrometer as well as in the Spinmaster,  $D_0$  is 8  $\mu$ s, while on AC and AM instruments it is  $\approx 15 \mu$ s. This ensures no cutoff effects in the FT of deuterium spectra at 92.12 MHz and distortions rather small on spectra obtained at lower frequencies. Relaxation delays were longer than 5 s. No lock system was used. At least 16 transients were collected. The above procedures ensure a negligible distortion of spectral profiles.

**Optical Microscopy.** Optical polarizing microscopy was performed on samples located into 2 mm o.d. quartz tubes for X-ray scattering, which were sealed after preparation. When prepared inside a magnetic field they were located into 5 mm o.d. NMR tubes; their NMR spectrum is very similar to the corresponding one obtained with a 5 mm o.d., but obviously more noisy. The samples were heated to 350 K and allowed to cool in the probe head at controlled speed (0.1 K min<sup>-1</sup>). To ensure an almost complete alignment, the anisotropic phases were periodically checked by <sup>2</sup>H NMR and by visual inspection between crossed Polaroids.

The microscope was a Ceti polarizing unit, Antwerp, Belgium, equipped with polarizers, filters, and a photographic camera: as a rule 10 $\times$  magnifications were used. Unless otherwise stated, measurements were performed at 300 K. When required samples were heated by a hot stage operating between 293 and 343 K with a resolution of 0.1 K. A description of the microscope setup is given elsewhere.<sup>8</sup>

The recognition of optical anisotropic textures was made on samples located between glass slides, according to Rosevear's classification.<sup>9</sup>

**Data Analysis and Spectral Simulation.** According to the superposition principle for NMR spectra of coexisting phases in the slow exchange regime,<sup>10,11</sup> partially oriented samples show complex spectral profiles, obtained by summing simpler ones.

Under the effect of strong magnetic fields, molecular order has been observed. The complex profiles of partially ordered spectra can be quantified by <sup>2</sup>H spectral simulation.

We simulated spectra corresponding to the following conditions: (1) small crystallites with their main axes randomly distributed in an ideal powder pattern spectrum; (2) samples with partially ordered domains;<sup>12,13</sup> and (3) single crystals with main axis oriented at  $\theta$  degrees with respect to the applied magnetic field (0° for the hexagonal and 90° for the lamellar crystals, respectively).

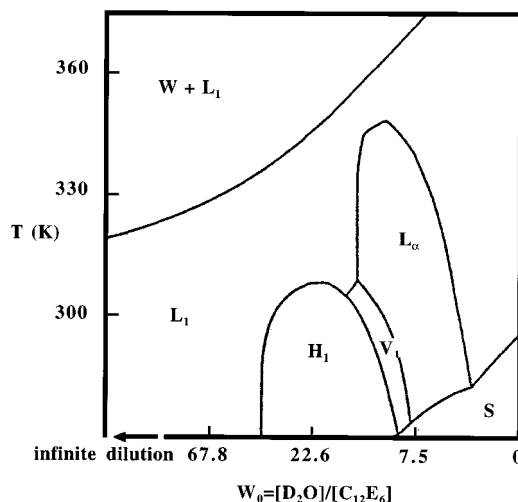
NMR spectra can be simulated by combining the above-mentioned contributions, weighted with proper coefficients.

Random or ordered spectra were simulated by the theoretical equation

$$f(\omega) = 8\pi^2 \sum_{l=0,2,4} a_l f_l(\omega) \quad (1)$$

where

$$\omega = \frac{\Delta}{2} (3 \cos^2 \vartheta - 1) \quad (1')$$



**Figure 1.** Phase diagram of the D<sub>2</sub>O/C<sub>12</sub>E<sub>6</sub> system, plotted as a function of the heavy water to surfactant mole ratio,  $W_0$ . The phase boundaries are taken from ref 14.

is the normalized frequency setting the central resonance at  $\omega = 0$ . The term  $\Delta$  in eq 1' indicates the quadrupolar splitting.

$f_l(\omega)$  in eq 1 is a weighted superposition of different spectral components and  $f_l(\omega)$  are given by

$$f_l(\omega) = \frac{1}{\Delta\sqrt{3}} \frac{1}{\left[1 + \frac{2\omega}{\Delta}\right]^{1/2}} P_l \left[1 + \frac{2\omega}{\Delta}\right]^{1/2} \quad (2)$$

where  $P_l$  are Legendre polynomials.<sup>12,13</sup> The 0th order polynomial term gives the Pake pattern (a random powder spectrum), whereas higher rank terms account for partial ordering.

For simulating the spectra relative to iso-oriented domains (single-crystal mode), the product of a Pake pattern with a Lorentzian function centered at a frequency corresponding to the required angle was used.

The above contributions do not account for lifetime broadening. On this purpose, each  $f(\omega)$  was transformed into a time-domain mode by an FFT algorithm (courtesy of the CERN library), multiplied by an exponential function with proper time constant,  $T_2$ , then back-Fourier transformed into the frequency domain.

By summing properly the weighted orientational distributions, the fitting functions were generated. When required, partially ordered spectral profiles were also introduced.

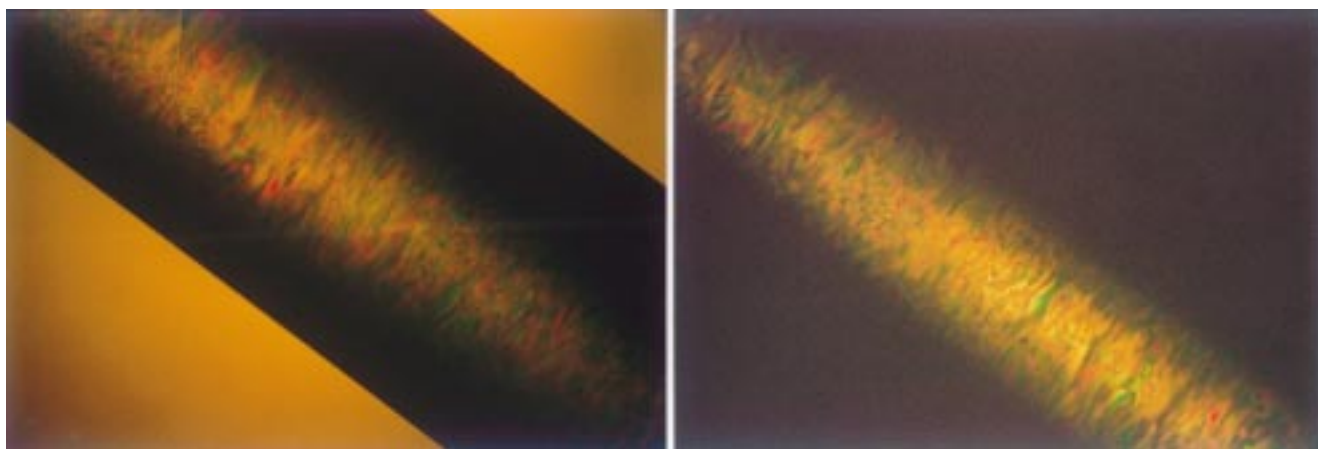
To evaluate the relative amount of iso-oriented contributions, the overall spectral areas were calculated and normalized. All parameters were evaluated by fitting the weighted sums of square deviations up to convergence. We used the MINUIT program (CERN library) to find the minimum of the  $\chi^2$  function with respect to each parameter.

A convenient measure of the fit quality was the reduced chi-square function,  $\chi^2_n$  where  $n = N - m$ , is the number of degrees of freedom left after fitting  $N$  points into  $m$  parameters. The iteration procedure continued up to a convergence limit of  $10^{-13}$  for  $\chi^2$  function.

## Results and Discussion

A schematic phase diagram of the system C<sub>12</sub>E<sub>6</sub>/D<sub>2</sub>O, partly redrawn from the literature,<sup>14</sup> is given in Figure 1.

Mixtures of water and surfactant with mole ratios  $W_0 = [\text{D}_2\text{O}]/[\text{C}_{12}\text{E}_6] > 38$  at 300 K give an isotropic micellar solutions.<sup>15,16</sup> On increasing the surfactant concentration the following phase sequence is observed: (1) a hexagonal me-



**Figure 2.** Optical polarizing micrographs of a sample with  $W_0 = 30.5$ , at  $\sim 300$  K previously oriented in the 14.1 T magnet. The photos were taken in polarized (left) and white (right) light with magnification  $10\times$ .

sophae ( $14 \leq W_0 \leq 38$ ); (2) an intermediate isotropic phase ( $11 \leq W_0 \leq 14$ ); (3) a lamellar phase ( $4 \leq W_0 \leq 11$ ); and (4) a reverse solution phase.

The region of existence of the intermediate isotropic phase is narrow in the composition–temperature plane. As to its structural assignment, conflicting evidence is given in the literature.<sup>17,18</sup>

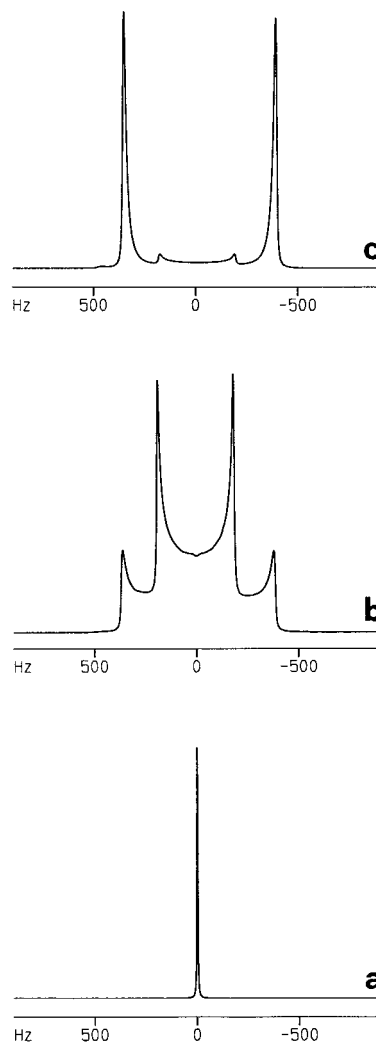
In presence of high magnetic fields (14.1 T), the phase boundaries are slightly different with respect to the originally reported ones. In addition, the shape of the spectral profiles turns out to be different from the canonical powder pattern ones.

The physicochemical behavior and the spectral properties of the different phases shall be discussed in the following sections.

**Hexagonal Phase.** *Optical Polarizing Microscopy.* To ascertain the occurrence of orientational effects due to applied magnetic fields, some samples were investigated by optical polarizing microscopy. To avoid errors due to sample handling, small capillaries were used. In this way the optical resolution on the anisotropic textures is poor, but orientational effects can be easily detected.

In Figure 2 we report, as an example, the appearance of a sample previously oriented in a high magnetic field. The orientation of domains is evident, in the form of concentric cylinders with their symmetry axes (in common to the capillary axis.) The orientational effect decreases on increasing the distance from the glass. Accordingly, the domains are with their symmetry axes parallel to the magnetic field director; i.e., the surfactant molecules are oriented perpendicular to the magnetic field, which is parallel to the symmetry axis of the capillary. Such an (orientational) effect disappears upon heating/cooling cycles, in absence of applied high magnetic fields.

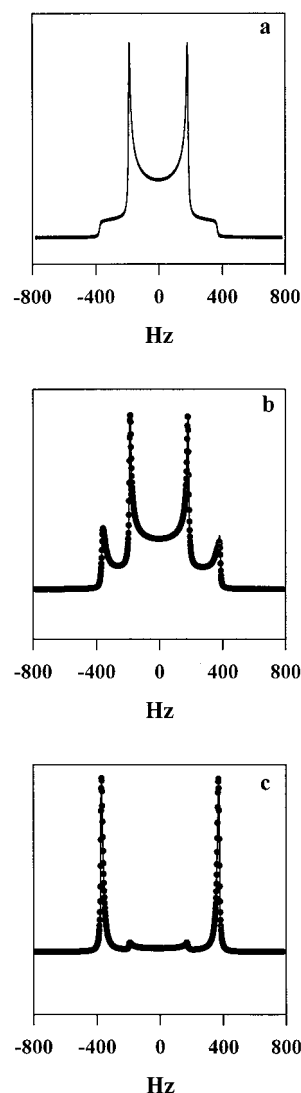
<sup>2</sup>H NMR. In Figure 3 spectra are reported for a selected sample,  $W_0=30.5$ , giving information on its thermal-magnetic history. Here, and almost everywhere in the following, we refer to samples thermostated outside the magnetic field, mode i, heated in the probe head up to the formation of a solution phase, mode ii, and cooled back to 300 K, mode iii. On increasing the temperature, the hexagonal phase becomes fully isotropic (Figure 3a) above a certain  $T$  value and the process obeys a first-order phase transition. In fact, at a given temperature, an abrupt change from the hexagonal to isotropic phase is observed, while the coexistence of isotropic and anisotropic spectral components has never been detected. Note that the experimental uncertainty in setting the temperature is 0.1 °C. Moreover, heating–cooling cycles around the transition temperature are immaterial in setting the phase transition.



**Figure 3.** (a) <sup>2</sup>H NMR spectrum at 92.12 MHz of a sample of  $C_{12}E_6/D_2O$  with  $W_0 = 30.5$ . Temperature 313 K; the sample is in the isotropic phase. (b) The same sample at 300 K in the hexagonal mesophase; this sample was cooled from 313 to 300 K in a thermostat. (c) The same sample slowly cooled inside the high magnetic field. In both spectra b and c  $\Delta(^2H) = 371$  Hz.

Slowly cooling the melt gives rise to an anisotropic spectrum where the occurrence of large parallel components can be seen.

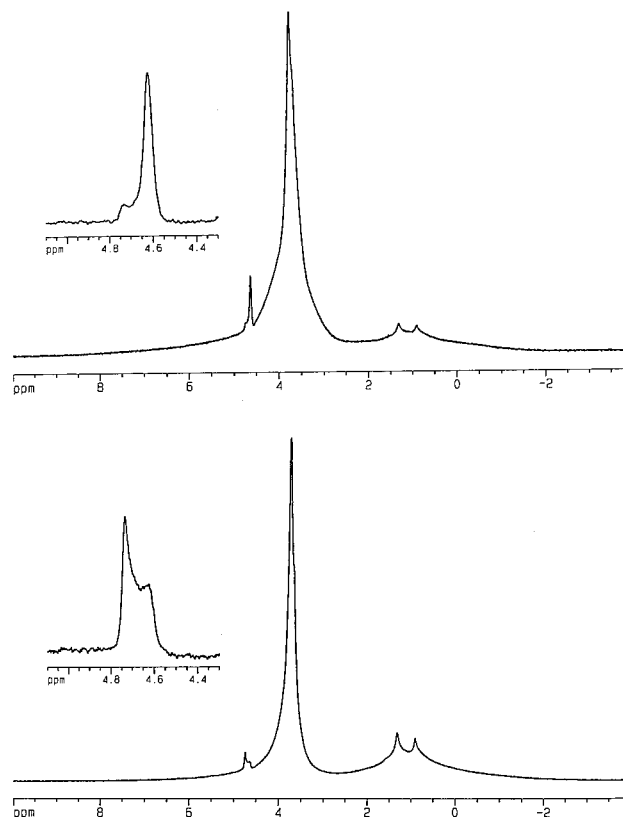
It must be noted that a noticeable amount of parallel wings is already evident in the sample prepared in mode i (Figure



**Figure 4.** (a) Theoretical Pake doublet without any preferential orientation;  $\Delta(^2\text{H}) = 369$  Hz. (b) (●) Same experimental spectrum as in Figure 3b, the full line, (—) refers to a data best fit with a partially oriented Pake doublet plus two lines corresponding to the parallel components. The coefficients of the Legendre polynomials used in this simulation are:  $a_0 = 1$ ,  $a_2 = 0.4$ , and the quadrupolar splitting results  $\Delta(^2\text{H}) = 369$  Hz. The broadening for the powder is  $T_2 = 27$  ms while, for the iso-oriented component, with  $0^\circ$  orientation at  $f(^2\text{H}) = 375$  Hz, the broadening is  $T_2 = 46$  ms. The amount of pure parallel component is  $\approx 14\%$ . (c) (●) Same experimental spectrum as in Figure 3c; (—) best fit of data has the following parameters:  $a_0 = 1$ ,  $a_2 = 0$ ,  $\Delta(^2\text{H}) = 370$  Hz,  $T_2 = 32$  ms for the powder;  $f(^2\text{H}) = 374$  Hz and  $T_2 = 31$  ms for the iso-oriented component. The amount of pure parallel component is  $\approx 83\%$ .

3b). In spectra relative to anisotropic phases obtained in mode iii (Figure 3c), deviations from a standard Pake pattern are extremely strong and partial orientation can be inferred from the shape of quadrupolar wings. Thus, upon cooling inside the magnet, the parallel components grow and originate an iso-oriented spectrum superimposed to a partially oriented one. The preferential orientation is parallel with respect to the magnetic field; i.e., the surfactant molecules are perpendicular to the magnetic field;<sup>6</sup> see also the optical microscopy section.

Such effect is not unusual; for instance,  $^2\text{H}$  spectra of phospholipid lamellar dispersions show resonance patterns with distorted line shapes. Their axially symmetric powder patterns were ascribed to the preferential parallel orientation of lipid molecules in the bilayer with respect to the magnetic field.<sup>10,18</sup>



**Figure 5.**  $^1\text{H}$  NMR spectrum at 600.13 MHz and  $T = 300$  K of the sample with  $W_0 = 30.5$ . (Bottom) Sample cooled from the fuse in an external thermostat. (Top) The same sample cooled inside the high magnetic field. In the inserts, the resonance of the water peak is shown in an expanded scale.

In lyotropic C<sub>12</sub>E<sub>6</sub>/D<sub>2</sub>O mixtures the magnetic field is exerting a significant orienting effect (torque) on the domains. In samples stored outside the magnet, mode i, the orienting effect is still present, partial order can be observed, and two extra lines, corresponding to iso-oriented domains, appear. The area underlying such lines is only 14% of the total area, but evident. To quantify the above effects, spectra of Figure 3, b and c, were compared with a simulated Pake doublet, having the same splitting between its perpendicular components (see Figure 4a). As can be seen, in the simulated Pake doublet the amplitude of parallel components is much lower than in real spectra, where preferential orientation occurs.

The spectra in Figure 4, b and c, were simulated by combining a partially oriented spectrum with an iso-oriented one, whose position is coincident with that of the parallel components. The full spectral profile was calculated by using 0th and 2nd rank Legendre polynomials; in this way partial orientation is explicitly accounted for. It must be pointed out that most simulations reported until now use polynomials up to the eighth rank.<sup>12,13</sup> The present experimental spectra have high signal-to-noise ratios and higher rank Legendre polynomials are not necessary in the simulation procedures.

**$^1\text{H}$  NMR.**  $^1\text{H}$  NMR spectra for a sample cooled in mode i (bottom), and in mode iii (top), respectively, are reported in Figure 5. The spectral region of the water resonance is also reported on an expanded scale. Spectra relative to the hexagonal phase, with relatively high water content, show splitting anisotropy smaller than in the lamellar phase of the same system.<sup>6</sup> Proton resonances other than water ones are broad and poorly defined;<sup>2</sup> for the above reasons they shall not be discussed here.



**TABLE 1: Splitting between the Perpendicular Components,  $\Delta H_{\perp}$ , of  $^2\text{H}$  NMR Spectra (in Hz) at 14.1 T for Samples in the Hexagonal Phase with Different  $W_0$** 

$T$ (K)	$W_0 = 30.5$	$W_0 = 25.0$	$W_0 = 20.4$	$W_0 = 18.5$
300	370.8	457.8	528.0	563.1
301	366.2	456.2	523.4	555.4
302	363.2	450.1	515.7	546.3
303	358.6	445.6	511.2	537.1
304	355.5	441.0	505.1	523.4
305	352.5	436.4	495.9	508.1
306	346.4	428.8	486.8	
307	343.3	424.2	473.0	
308	337.2	415.0	456.2	
309		401.3		
310				

The observed spectral shape of residual HOD (Figure 5) is similar to that of  $^{31}\text{P}$  spectra in oriented phospholipid membranes,<sup>10,18</sup> and to  $^{19}\text{F}$  spectra in the octylammonium fluoride–water system.<sup>19</sup>

A chemical shift anisotropy in the  $^1\text{H}$  spectrum of water can be observed. The orienting effect of the field is concomitant with a growth of the high-field component and corresponds to the increase of the parallel component contributions observed in deuterium spectra. Hence, the asymmetric components originated by the chemical shift anisotropy can be unambiguously assigned. The chemical shift anisotropy observed in the water peaks is probably dominated by the anisotropy in the sample bulk susceptibility. This same effect is also evident in the deuterium NMR spectra where there is a shift between the centres of the parallel and perpendicular peaks.

**Effect of Composition.** To clarify the dependence of orienting effects on composition, as well as on thermal and magnetic history, samples of different composition were investigated. For this purpose, the following experimental protocol was used: (1) samples were cooled from the isotropic melt in a thermostatic bath, outside the magnet, down to 300 K; (2) NMR experiments were run, at 300 K and 14.1 T; (3) a slow, controlled, increase of temperature was imposed to samples in the magnet; at each temperature, up to completion of the phase transition,  $^1\text{H}$  and  $^2\text{H}$  spectra were collected; (4) the resulting solutions were allowed to equilibrate for 20 min above the transition temper-

ature; and (5) they were slowly cooled inside the spectrometer, and  $^1\text{H}$  and  $^2\text{H}$  spectra were collected at each temperature down to 300 K.

Data relative to the above procedures for four different concentrations are summarized in Table 1, while characteristic spectra are shown in Figure 6. As can be seen, the quadrupolar splitting decreases on increasing the temperature (Table 1). The resulting reduced order parameter, inferred from  $^2\text{H}$  spectra performed at different temperatures, can be related to an increasing system mobility.

Peculiar to the hexagonal phase is the occurrence of low orienting effects on heating followed by cooling the sample in a magnetic field, presumably ascribed to the high viscosity of such phase. The orienting effect due to the magnetic field is more relevant close to the phase borders; see Figure 6.

Moreover, within the experimental error, cooling or heating the sample within the field, the observed splitting appears to be the same.

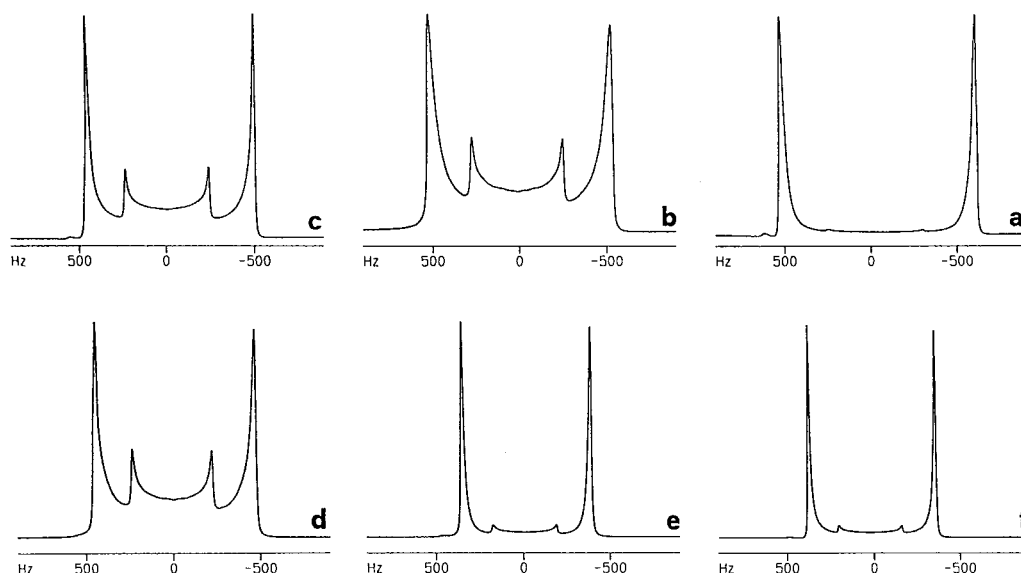
**Water Binding.** The quadrupolar splitting of heavy water is linearly dependent on the  $\text{C}_{12}\text{E}_6/\text{D}_2\text{O}$  mole ratio, Figure 7. This is useful in the determination of surfactant hydration. In a two-sites approximation, in fact, water molecules are assumed to be bound or free.<sup>20</sup> The exchange rate between bound and free states is fast on an NMR time scale and the resulting quadrupolar splitting is the time-averaged result of two terms, according to

$$\Delta(^2\text{H}) = p_f \Delta_f + p_b \Delta_b \quad (3)$$

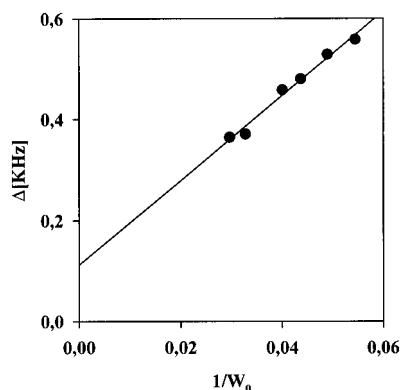
where  $p_f$  and  $p_b$  are the fraction of water molecules in free and bound state, respectively.  $\Delta_b$  is proportional to the bond order parameter,  $S_b$ , times the quadrupolar coupling constant. Thus, if the mole fraction of the components is known, the coupling constant is independent of site and if  $\langle n \rangle$  is the average hydration number per polar headgroup, it results

$$\Delta(^2\text{H}) = \Delta_f + \langle n \rangle (X_A/X_W) \Delta_b \quad (3')$$

where  $X_A$  and  $X_B$  are the mole number of surfactant and heavy water, respectively, (while  $p_f = 1 - p_b$  disappears in the final expression).



**Figure 6.**  $^2\text{H}$  NMR spectra at 92.12 MHz and  $T = 300$  K of samples in the hexagonal phase at different concentration: (a)  $W_0 = 18.4$ ; (b)  $W_0 = 20.4$ ; (c)  $W_0 = 22.9$ ; (d)  $W_0 = 25.0$ ; (e)  $W_0 = 30.5$ ; (f)  $W_0 = 33.7$ . All samples have been cooled from the isotropic phase to the hexagonal phase within the high magnetic field.



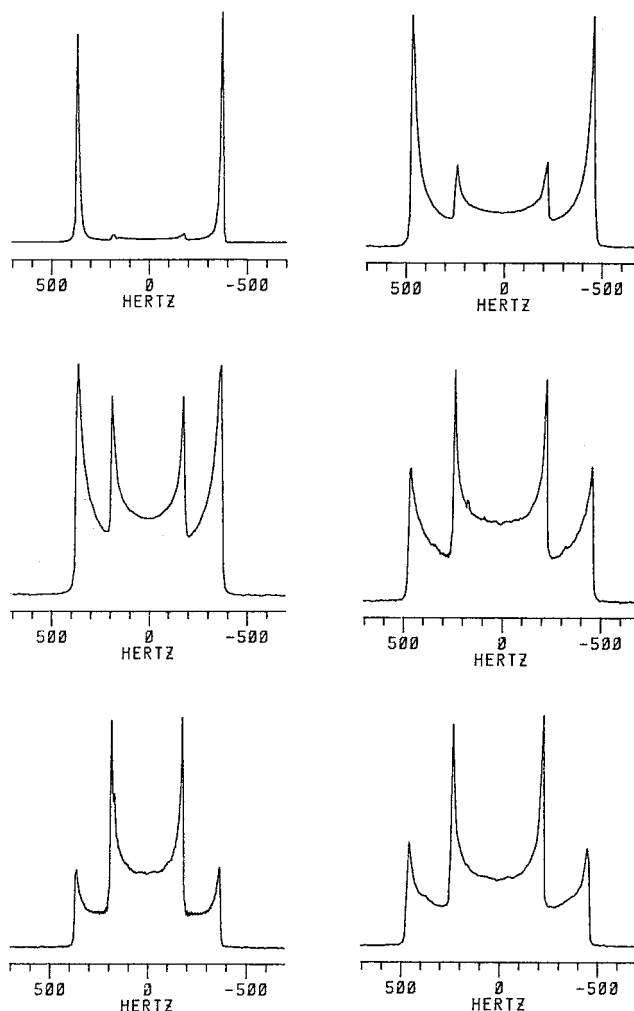
**Figure 7.** Hexagonal phase <sup>2</sup>H NMR spectra at 92.12 MHz, Δ(<sup>2</sup>H) as a function of 1/W<sub>0</sub>.

If the two-site approximation holds and the bond order parameter of free water is null, a plot of Δ(<sup>2</sup>H) versus the mole ratio gives a straight line which slope is proportional to the average hydration number. In the plot of Figure 7 the angular coefficient gives an average hydration number of 19; however, the intercept is not zero. This implies that p<sub>b</sub>, ⟨n⟩, or S<sub>b</sub> is an implicit function of composition: otherwise, the two-site approach should not be true.

**Spectral Profiles and Field Strength Effects.** Let us compare now the splitting as a function of temperature for samples subjected to the heating-cooling cycles reported above. For instance, in the sample at W<sub>0</sub> = 30.5 the alignment is significant; as inferred from the spectral simulation, at least 83% of domains are oriented. It must be pointed out, however, that far from the phase border the splitting is not very sensitive to thermal treatments and the observed alignment quite moderate. Near the phase border(s) the effect is more significant, but lower than in the lamellar phase.

Additional NMR experiments were run at different field strengths (4.7 and 9.4 T). Large deviations from a theoretical Pake doublet shape are observed on cooling inside the magnet, with a significant increase of the external parallel components. According to the literature, the magnetically induced order is proportional to the square of the applied field strength.<sup>21</sup> In the same sample at W<sub>0</sub> = 22.9, a very small difference in the ordering parameter of the D<sub>2</sub>O is evident, as observed on the perpendicular components respectively 460 Hz at 9.4 T and 477 Hz at 14.1 T. The effect of the field is much stronger in determining the amount of fully ordered sample; for instance it is larger by a factor 1.5 at 14.1 T than at 9.4 T, (data not shown). Thus, the line-shape distortion with respect to a theoretical Pake doublet is lower at lower fields. <sup>2</sup>H NMR spectra at 30.7 MHz (4.7 T) for samples at W<sub>0</sub> = 30.5 and 25.0, respectively, are reported in Figure 8. Some orientation can still be observed, but the amplitude of the effect is much less. Rough estimates on alignment dependence from the field strength indicate that an almost complete orientation would occur at 18 T. Accordingly, the relative amount of ordered domains is a function of the field strength at which the samples have been conditioned. It must be pointed out, at this point, that the alignment of samples in the hexagonal phase is much less significant compared to the lamellar one.

As mentioned above, we used a combination of single crystal and partially oriented contributions in the simulation procedures. Since polynomials up to the 2nd rank have been used, it comes out that the orientational order of the liquid crystalline domains does not only depend on the square of applied field strength and other contributions affect the amount and the distribution function of orientational order.

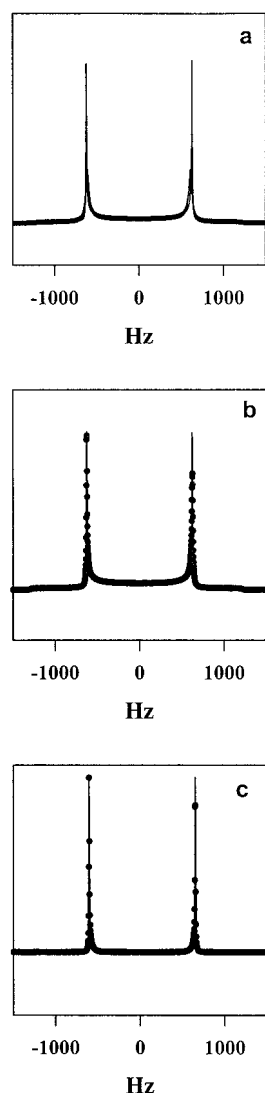


**Figure 8.** <sup>2</sup>H NMR spectra measured 30.7 MHz (4.7 T), T = 300 K; left side spectra refer to a sample with W<sub>0</sub> = 30.5, right side spectra refer to a sample with W<sub>0</sub> = 25.0. (bottom) Grown in an external thermostat, i.e., zero field; (middle) grown at 4.7 T; (top) grown at 14.1 T, i.e., into a high field. The strong orienting effect of the high field is clearly observable.

Note that in our experimental conditions, i.e., quite large diameters, no surface effects (glass) have been observed.

**Lamellar Phase.** We have previously demonstrated that cooling isotropic samples in proper experimental conditions give rise to fully oriented lamellar phases.<sup>6</sup> The effect has been observed in the whole region of existence of the phase and the iso-oriented samples are stable out of the magnet for months. The system orientation is normal with respect to the magnetic field director and, consequently, the long axes of the surfactant molecules are perpendicular to the magnetic field.

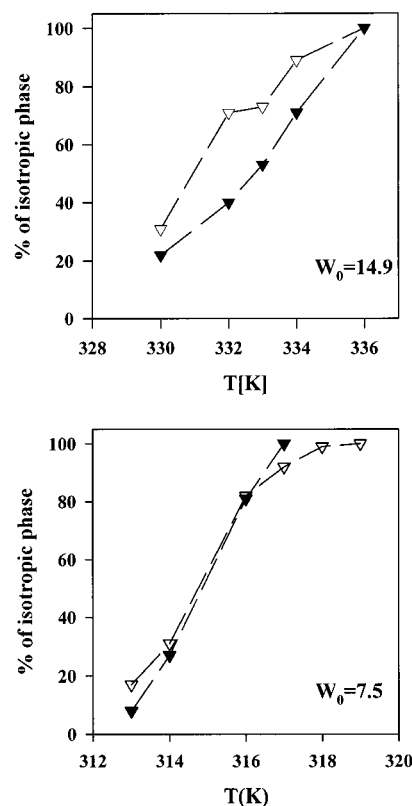
Spectra before and after cooling samples within the magnetic field are respectively reported in the middle and in the bottom of Figure 9. In the lamellar phase, strong differences with respect to the Pake doublet are observed. In the experimental spectrum in Figure 9 (dots), for instance, upon cooling the sample in the presence of the magnetic field, a significant loss of intensity of the parallel edges can be observed; see the spectra differences easily observable in Figure 9, b and c. The calculated spectrum (solid line) is reported, for comparison, in the same figure. The splitting between perpendicular edges measured on cooling the sample from the isotropic to the lamellar phase, mode iii is always slightly greater than the one measured on rising the temperature. In addition, at certain temperatures lamellar and isotropic phases coexist.



**Figure 9.**  $^2\text{H}$  NMR spectra of a lamellar phase with  $W_0 = 9.6$  at  $T = 300$  K. (a) Full simulation of a Pake doublet without any preferential orientation;  $\Delta(^2\text{H}) = 1245$  Hz. (b) (●) Experimental spectrum obtained from a sample grown in an external thermostat, (—) data best fit with a partially oriented Pake doublet plus two lines corresponding to the perpendicular components. For the powder the coefficients of the Legendre polynomials used in this simulation are:  $a_0 = 1$ ,  $a_2 = 1$ ,  $a_4 = -1$ , and the quadrupolar splitting results  $\Delta(^2\text{H}) = 1244$  Hz and the broadening is  $T_2 = 18$  ms. For the iso-oriented component with  $90^\circ$  orientation,  $f(^2\text{H}) = 624$  Hz and  $T_2 = 29$  ms. The amount of pure perpendicular component is  $\approx 51\%$ . (c) (●) Experimental spectrum of a sample grown from the melt inside the 14.1 T field, (—) best fit of data gives an iso-oriented component with the following parameters:  $f(^2\text{H}) = 627$  Hz,  $T_2 = 29$  ms. The amount of pure perpendicular component is  $\approx 100\%$ .

To quantify the relative amounts of the two phases we assume the validity of slow exchange regime between them. Accordingly, we compare spectra recorded in mode i and mode iii, at the same temperature. As shown in Figure 10, the relative amount of isotropic phase is markedly different in the two sets of data. Moreover, the Pake doublet splitting recorded on heating is always slightly larger than that obtained cooling the temperature.

This effect may be due to thermal hysteresis, of which however we have no experimental evidence. Alternatively, a very slow equilibrium between partially oriented, iso-oriented, and isotropic phases, respectively, can be invoked.<sup>22</sup>



**Figure 10.** Percentage of isotropic phase as function of temperature in samples with  $W_0 = 14.9$  and  $7.5$ . Empty symbols refer to sample grown in a thermostatic bath and measured at increasing temperature; filled symbols refer to sample progressively cooled inside the magnet. The estimated error in the integral figures is about 2%.

The effect of a very low magnetic field strength on the lamellar samples was also investigated. No field effect was observed in the  $^2\text{H}$  NMR spectra of a  $W_0 = 9.4$  sample, at 12.44 MHz (1.9T) (data not shown).

## Conclusions

The purpose of the present contribution was to shed light on orientational effects due to high-strength magnetic fields. For this purpose, the hexagonal and the lamellar phases occurring in the  $\text{C}_{12}\text{E}_6\text{-D}_2\text{O}$  system have been investigated in some detail. The results can be summarized as follows:

1. Both anisotropic phases partially orient in the presence of high magnetic fields. The effect is observed on either cooling and heating mode, with significant differences only for the lamellar phase.
2. As a rule, the orientational effect played by the magnetic field is more relevant in the lamellar than in the hexagonal phase, presumably because of significant differences in viscosity.
3. Optical microscopy investigation on samples subjected to high-strength magnetic fields supports the assumptions inferred from  $^1\text{H}$  and  $^2\text{H}$  NMR spectra.
4. Simulation procedures have been used to quantify the relative amount of orientation with respect to the canonical expected one. For this purpose, use of Legendre polynomials only up to the 4th rank was required.

Information on low-frequency motions is probably essential in understanding the viscous isotropic region between the lamellar and the hexagonal phase. Such studies require, perhaps, more spectroscopic information from field cycling NMR and self-diffusion experiments. Work is in progress on this line.

Investigation on the effect of the size of the polar head is in progress.

## References and Notes

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- (22) The presence of three phases in equilibrium is possible only for the critical point, but probably, the phase with slower transforming kinetic is a metastable state, as undercooled water.