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# Investigations into the Phase Behavior of Nonionic Ethoxylated Surfactants Using $^2\text{H}$ NMR Spectroscopy

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Deuterium NMR spectroscopy was applied to study the phase behavior of three nonionic surfactants containing the same alkyl chain length ( $\text{C}_{13}/\text{C}_{15}$ ) and increasing numbers of ethoxylate (EO) units (7, 11, and 20). These surfactants were dissolved in  $\text{D}_2\text{O}$ , and the quadrupole interaction of the spin of the deuterium nucleus with the protonated surfactant structural units was investigated. The results showed singlets for the liquid normal micelles, for cubic and inverse micellar phases. In contrast, liquid crystalline structures of the hexagonal and lamellar phases showed a powder pattern with a quadrupole splitting. The hexagonal phase showed a smaller splitting than the lamellar phase. By following the quadrupole splittings as a function of surfactant concentration at constant temperature, the phases produced could be clearly identified. In addition, the results showed a gradual transition from hexagonal to lamellar phases, and in some concentration regions, a mixture of the two phases could be inferred from the results. The influence of temperature (at constant surfactant concentration) was also investigated for some surfactant solutions. The results showed a gradual decrease followed by a sharp reduction in the quadrupole splittings (reaching zero) at the temperature at which melting of the liquid crystalline structure occurred.

## Introduction

Investigation of the liquid crystalline phases produced in surfactant solutions at high concentrations<sup>1–3</sup> is important from both a fundamental and an applied point of view. The liquid crystalline structures produced by nonionic surfactants have been investigated by several authors.<sup>5,6</sup> Most of the studies have applied methods such as plane-polarizing light microscopy, light scattering, and low angle X-ray and neutron scattering, and these methods produced a detailed picture of the structure of the liquid crystals produced.

Recently, we have combined plane-polarizing light microscopy investigations with differential scanning calorimetry (DSC) and rheology to study the phase diagrams of a series of nonionic surfactants of the alcohol ethoxylate type.<sup>7</sup> The results obtained showed a significant change in phase behavior of these systems as the ethoxylate (EO) chain length was increased (from 7 to 20 units) at a constant alkyl chain length ( $\text{C}_{13}/\text{C}_{15}$  mixture). These surfactants are commercial materials (produced by ICI) with the trade name Synperonic A series (i.e., Synperonic A7, A9, A11, and A20). When the EO chain length was 7 or 9 units, hexagonal and lamellar structures were produced above a certain surfactant concentration (on the order of ~30% for A7 and ~33% for A9). However, when the EO chain length was increased to 11 units, a cubic phase appeared between the hexagonal and lamellar phases. At much higher EO chain length (A20), the lamellar phase was not produced and a large cubic phase region appeared before the hexagonal phase.

These results could be accounted for in terms of the critical packing parameter concept of Israelachvili et al.,<sup>8</sup> i.e.

$$P = v/al \quad (1)$$

where  $v$  is the volume of the alkyl chain of length  $l$  and  $a$  is the cross-sectional area of the hydrophilic head group. With A7 and A9 (where  $P > 1/3$ ) both hexagonal and lamellar structures are possible, whereas with A20 (very high  $a$  value) the lamellar structure is not possible.

In an attempt to obtain more information about the structure of the liquid crystalline phases, we have recently applied a  $^2\text{H}$  NMR technique, and this is the subject of the present paper.  $^2\text{H}$  NMR spectroscopy provides valuable information about the phase behavior of lyotropic liquid crystalline systems. Deuterium NMR spectra can easily be used to identify both single phase and multiphase samples. A single anisotropic liquid crystalline phase exhibits a characteristic NMR line shape which depends on the anisotropy, geometry, and domain size of the liquid crystalline aggregates and on the motion of the  $\text{D}_2\text{O}$  molecules. For multiphase samples, the spectrum is composed of the sum of the individual phase spectra for each phase. A detailed theoretical treatment of deuterium quadrupole band shapes for lyotropic liquid crystalline phases has been reported by several authors.<sup>9–12</sup> The quadrupole interaction of the spin of the deuterium nucleus ( $I = 1$ ) and an axially symmetrical electric field gradient at the nucleus gives rise to two absorption bands which are separated by a quadrupole splitting  $\Delta(\theta)$  (where  $\theta$  is the angle between the symmetry axis of the aggregate and the direction of the static magnetic field). For isotropic systems  $\Delta(\theta)$  is averaged to zero and hence single NMR peaks are obtained. Spectra with  $\Delta(\theta) \neq 0$  are in general obtained for anisotropic systems. For uniaxial mesophases

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the aggregates possess axes of rotation with at least 3-fold symmetry (asymmetry parameter of the electric field gradient  $\eta = 0$ ). In this case, all values of  $\theta$  are present and characteristic Pake<sup>13</sup> or powder pattern spectra are produced. The value of the quadrupole splitting can be used to differentiate between such liquid crystalline phases. As an example, the observed quadrupole splitting in a hexagonal phase is theoretically predicted to be half that observed in a lamellar phase under certain general conditions.<sup>14</sup>

## Experimental Section

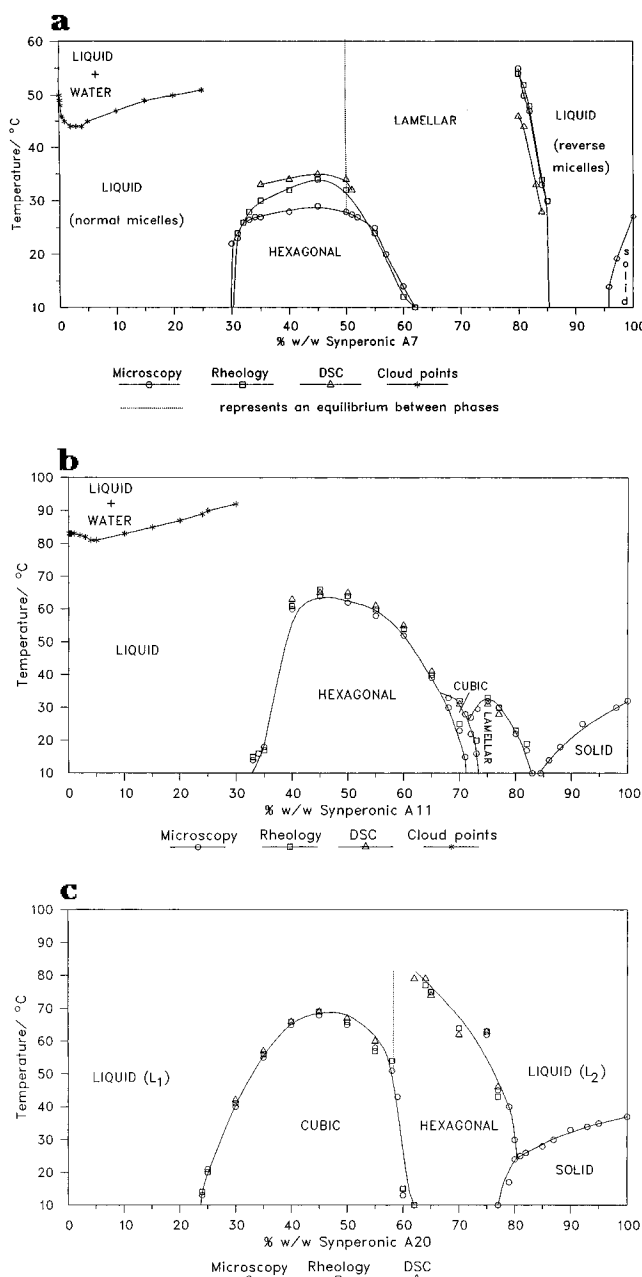
**Materials.** Synperonic A surfactants were supplied by ICI Surfactants (Wilton, U.K.) and used as received. They were made by the ethoxylation of Synperol alcohol which consists of 66% C<sub>13</sub> and 34% C<sub>15</sub> alkyl chains. The ethoxylation process gives rise to a wide distribution of ethoxylate chains and hence the numbers 7, 11, and 20 represent an average of these ethoxylate chains. The heavy water (D<sub>2</sub>O) was obtained from Aldrich Chemicals, U.K. (purity 99.9%), and was used without further purification.

**Sample Preparation.** Samples were prepared by weight by adding heavy water to the surfactant and then heating and stirring the mixture to give a homogeneous solution.

**<sup>2</sup>H NMR Spectroscopy.** Deuterium NMR spectra were recorded on a JEOL GX400 spectrophotometer operating at a deuterium frequency of 61.37 MHz. The system used a 10 mm tunable probe-head with a 90° pulse of 33  $\mu$ s. The sample temperature was maintained by the spectrophotometer variable temperature controller which had been calibrated by direct insertion of a thermocouple into a standard sample. Each spectrum was recorded after the sample had equilibrated at the preset temperature and the magnetic field for about an hour. All data were obtained using a single pulse sequence, without sample spinning or field frequency lock. Before Fourier transformation, 256 transients at a repetition rate of 0.5 s were averaged. Experiments on a typical sample showed that the <sup>2</sup>H  $T_2$  relaxation rate was sufficiently slow to make the use of a quadrupolar echo pulse sequence unnecessary and that spectra run with single pulse excitation followed by a single sampling interval delay to remove "pulse breakthrough" or "ring-down" were indistinguishable from those run using a quadrupolar echo sequence.

## Results and Discussion

Figure 1 shows the phase diagrams of the surfactants used in this study, namely A7, A11, and A20. As mentioned in the Introduction, these phase diagrams were obtained using the three techniques of plane-polarizing light microscopy, DSC, and rheology. The various phases found are clearly indicated in the phase diagrams. As an illustration, Figure 2 shows the deuterium NMR spectra of Synperonic A7 samples at various surfactant concentrations and at a constant temperature (23 °C). As is clear from this figure, there is a distinct difference in the NMR spectra with increase in surfactant concentration. For example, up to about 30% A7 (in the normal micellar solution, see Figure 2a,b) a singlet appears. In the concentration range 35–45% A7 the spectra show clearly developed powder patterns (Figure 2c–e). In other words, the spectra show that at 23 °C the state of the samples is a pure uniaxial liquid crystalline phase. This regime corresponds to the hexagonal phase in the phase diagram of Synperonic A7 (Figure 1a). At higher surfactant concentrations, i.e., 50% and 55% A7, a mixture of two coexisting phases (Figure 2f,g) appears which is characterized by different quadrupole splittings. These splittings correspond to the hexagonal and lamellar phases. These results support our rheological data which indicated that the transition from hexagonal to lamellar phases is gradual and that a mixture of the two phases can coexist. This

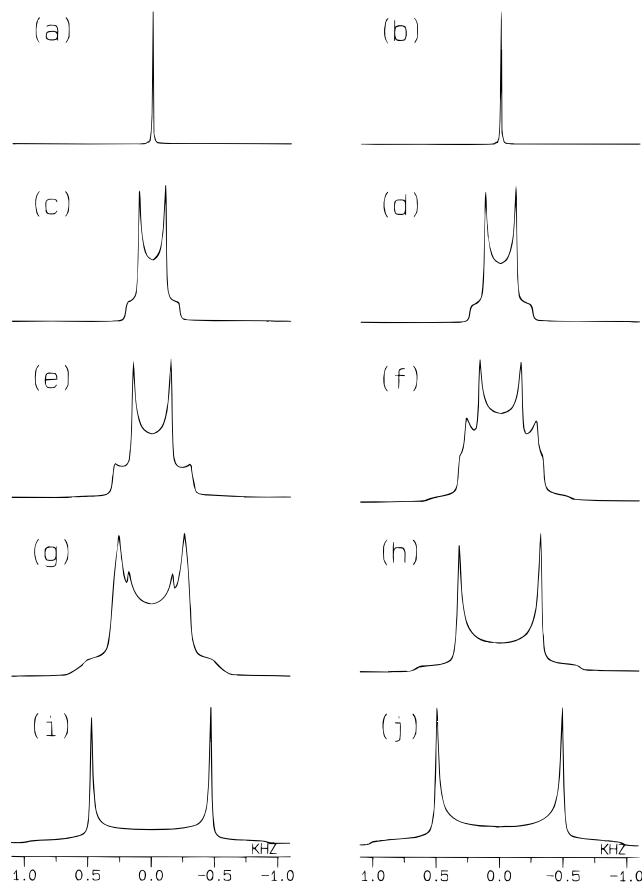


**Figure 1.** Phase diagrams of Synperonic A/water systems: (a) A7, (b) A11, and (c) A20.

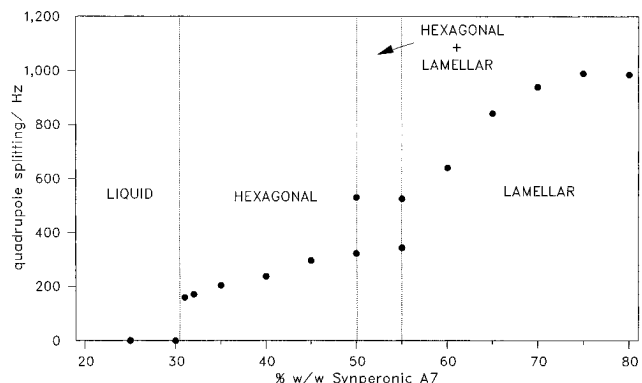
behavior is predicted by the phase rule, and it is interesting to note such a coexistence region (which can be very narrow) with the present commercial surfactants that consist of several components. In the regime of high surfactant concentration from 60% to 80% A7 (Figure 2h–j) powder patterns are again observed indicating a pure uniaxial phase which is identified as the lamellar phase. Figure 3 shows a plot of the quadrupolar spectra as a function of percent (w/w) Synperonic A7. In the liquid region (up to about 30%) only singlets are obtained (zero splitting). The quadrupole splittings start to appear in the hexagonal region (i.e., above 30%) and they gradually increase in magnitude with further increase in surfactant concentration until 45%. This concentration denotes the limit of the pure hexagonal phase. Above this concentration, the lamellar phase begins to form and in the region 50–55% two phases coexist in a mixture, which explains the two splittings obtained in this concentration range. Above 55% A7, the phases produced are predominantly lamellar and this results in an increase in quadrupolar splittings with increasing surfactant concentration, reach-

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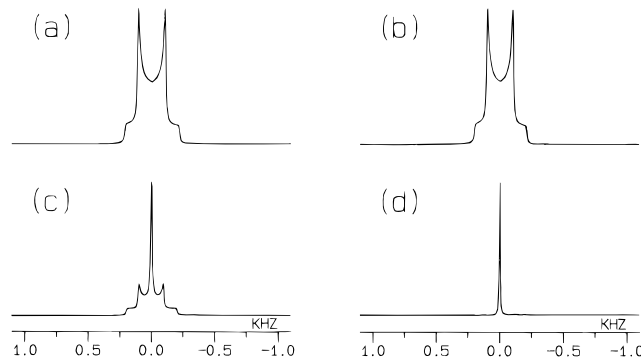
**Figure 2.** Deuterium NMR spectra of various Synperonic A7 samples at 23 °C: (a) 25%, (b) 30%, (c) 35%, (d) 40%, (e) 45%, (f) 50%, (g) 55%, (h) 60%, (i) 70%, and (j) 80%.



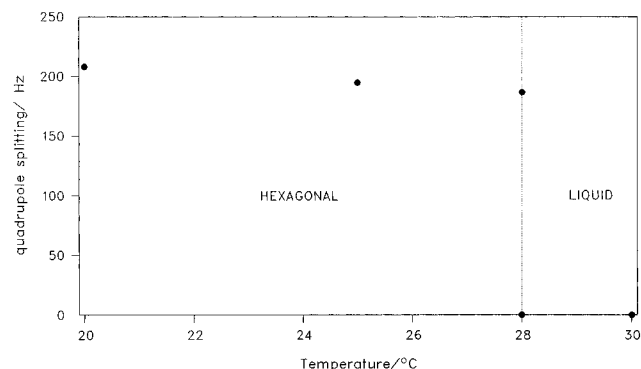
**Figure 3.** Deuterium quadrupole splittings versus concentration of Synperonic A7 in D<sub>2</sub>O at 23 °C.

ing a maximum at 75% A7. Above this concentration, inverse micelles begin to form and this results in a reduction in the quadrupole splittings with further increase in surfactant concentration.

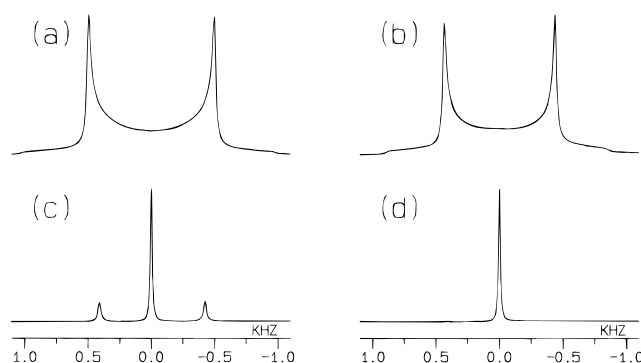
A typical set of spectra showing the effect of temperature on the quadrupole splittings of 35% A7 (hexagonal phase) is shown in Figure 4. This sample gives the characteristic powder pattern for a pure uniaxial phase at 20 °C (Figure 4a). The hexagonal phase structure is retained on heating to 25 °C (Figure 4b). However, increasing the temperature to 28 °C (Figure 4c) causes melting of most of the liquid crystalline structure which is manifested in a two-phase system consisting of a doublet (hexagonal phase) and a central singlet (liquid phase). The deuterium NMR spectrum at 30 °C (Figure 4d) contains a singlet which indicates the presence of only the liquid phase, i.e., the hexagonal phase has disappeared completely. Figure 5



**Figure 4.** Deuterium NMR spectra of 35% Synperonic A7 as a function of temperature: (a) 20 °C, (b) 25 °C, (c) 28 °C, and (d) 30 °C.



**Figure 5.** Variation of deuterium quadrupole splittings of 35% Synperonic A7 with temperature.

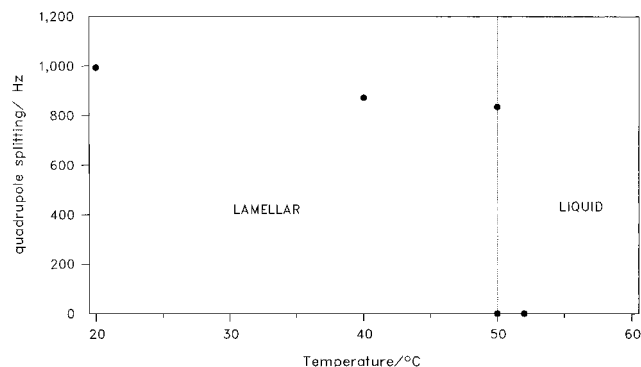


**Figure 6.** Deuterium NMR spectra of 80% Synperonic A7 as a function of temperature: (a) 23 °C, (b) 40 °C, (c) 50 °C, and (d) 52 °C.

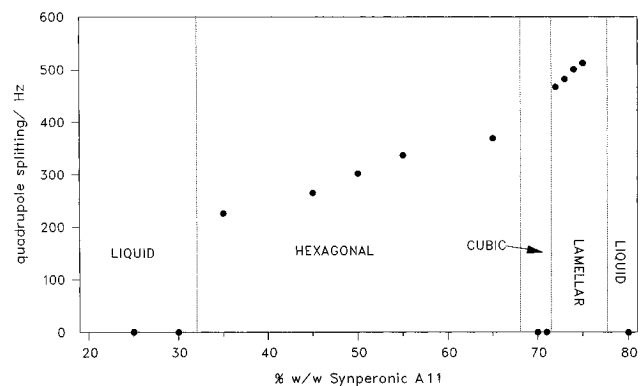
shows a plot of the quadrupole splittings of 35% A7 as a function of temperature. It can be seen that the quadrupole splittings decrease with temperature until a two-phase region is obtained consisting of the hexagonal phase and the isotropic liquid phase (zero splitting). The melting of 80% A7 (lamellar phase) shown in Figures 6 and 7 follows a similar trend. At 20 °C (Figure 6a) a powder pattern indicating a uniaxial phase is produced. A smaller quadrupole splitting is observed at 40 °C (Figure 6b). The temperature dependence of the quadrupole splittings for both lamellar and hexagonal phases can be explained in terms of the gradual move to a lower hydrophilic/hydrophobic interface curvature which is driven by the decreasing area of the hydrophilic head group due to a dehydration of the ethoxylate chains.<sup>15,16</sup> Within a distinct mesophase region these changes are microscopic but they

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**Figure 7.** Plot of deuterium quadrupole splittings of 80% A7 versus temperature.

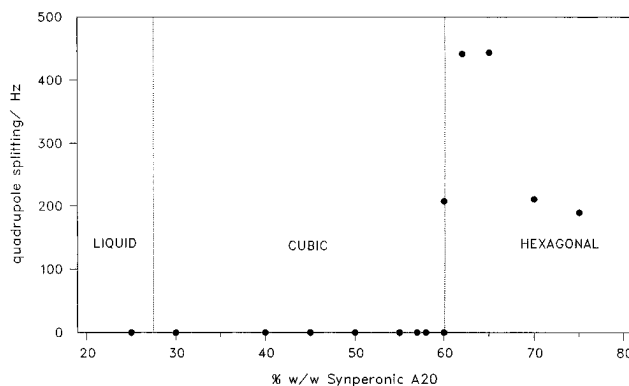


**Figure 8.** Variation of deuterium quadrupole splittings with concentration of Synperonic A11 at 25 °C.

become apparent at the phase boundaries as they lead to perturbations of the macroscopic phase structure. Hence a decrease in the quadrupole splitting is observed before the transformation to the liquid phase. Increasing the temperature to 50 °C results in melting of most of the liquid crystalline phase and hence a two-phase system consisting of a doublet (lamellar phase) and a singlet (liquid phase) as observed in Figure 6c. At 52 °C the only present phase is the liquid phase (see Figure 6d).

With Synperonic A11 the area of the hydrophilic head group is much larger than that of Synperonic A7 and hence the formation of structures with a higher interfacial curvature is facilitated. This is reflected in the previously established phase diagram of Synperonic A11 (Figure 1b) which shows a substantial hexagonal phase region persisting to very high temperatures followed by a very small cubic phase region. As expected, the lamellar phase occurs over a small concentration range and persists to lower temperatures than with Synperonic A7. Figure 8 shows the variation of the quadrupole splittings of Synperonic A11 samples at various concentrations at 25 °C. For surfactant concentrations of 25% and 30% a single line (zero splitting) is obtained which is indicative of an isotropic phase. This phase is identifiable as the liquid phase by comparison with the previously established phase diagram. From 35% to 65% A11 doublets are obtained which correspond to the hexagonal phase in Figure 1b. The cubic phase extends up to 71% A11. This is then followed by another concentration regime which extends up to 75% A11 and is identified as the lamellar phase by comparison with the phase diagram. Again as with A7 the lamellar phase is characterized by a larger quadrupole splitting than the hexagonal phase. Finally 80% A11 gives a singlet with zero splitting which is in fact the liquid phase.

The Synperonic A20 system (Figure 1c) shows a markedly different phase behavior when compared to the



**Figure 9.** Deuterium quadrupole splittings versus concentration of Synperonic A20 at 23 °C.

other two surfactants. It forms a substantial cubic phase region which is followed by a hexagonal phase. No lamellar phase is detected with Synperonic A20. This phase behavior is consistent with the very large hydrophilic part relative to the hydrophobic part which in turn opposes the formation of structures with a low interfacial curvature. Figure 9 shows a plot of quadrupole splittings as a function of surfactant concentration for various Synperonic A20 samples at constant temperature (23 °C). Samples in the concentration range 25–75% A20 have been investigated. Three concentration regimes are evident from Figure 9. The liquid phase (25%) gives a singlet with zero splitting. This is followed by a cubic phase region (30–58%) which again does not produce a quadrupole splitting. The isotropic systems in these two concentration regimes can only be distinguished by comparison with the other techniques (see Figure 1c). For 60% A20 the deuterium spectrum shows a two-phase system consisting of a hexagonal phase characterized by a doublet and a singlet (zero splitting) for the cubic phase (see Figure 1c). The hexagonal phase samples in the high-concentration regime (62–75%) produce powder patterns characteristic of a pure uniaxial system.

## Conclusions

Deuterium NMR spectroscopy offers a powerful tool for identification of the phase changes that occur in surfactant systems as a function of increasing concentration. Using this technique, we showed that the change from a liquid normal micellar solution to hexagonal and lamellar phases is accompanied by a significant change in the NMR spectra. By plotting the quadrupole splittings as a function of surfactant concentration at constant temperature various phases could be identified. In addition, the results confirmed our previous findings using rheological techniques that the transition from hexagonal to lamellar phases is gradual and at some concentrations a mixture of the two phases can coexist. Our results also showed the effect of increasing the head group area (at a constant alkyl chain length) on the phase behavior. With increasing this area (by increasing the number of ethoxylate units in the chain), the lamellar phase region became smaller and eventually it disappeared completely when the EO chain length reached 20 units. Deuterium NMR could also be used to study the effect of temperature on the phases produced.

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