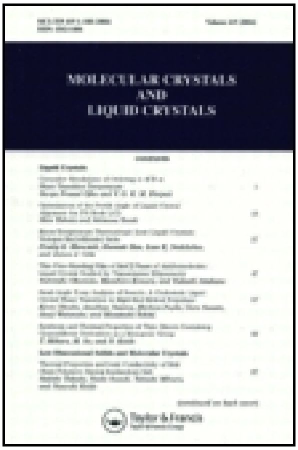

Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

A Defective Lamellar Phase in a Nonionic Surfactant Water System Studied by NMR Methods

Luigi Coppola [a], Raffaella Gianferri [a], Isabella Nicotera [a] & Cesare Oliviero [a]

[a] Department of Chemistry, University of Calabria, Rende (CS), 87036

To cite this article: Luigi Coppola, Raffaella Gianferri, Isabella Nicotera & Cesare Oliviero (2003): A Defective Lamellar Phase in a Nonionic Surfactant Water System Studied by NMR Methods, Molecular Crystals and Liquid Crystals, 398:1, 157-167

To link to this article: http://dx.doi.org/10.1080/15421400390221619

Mol. Cryst. Liq. Cryst., Vol. 398, pp. 157–167, 2003
Copyright © Taylor & Francis Inc.
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421400390221619

A DEFECTIVE LAMELLAR PHASE IN A NONIONIC SURFACTANT WATER SYSTEM STUDIED BY NMR METHODS

Luigi Coppola, Raffaella Gianferri, Isabella Nicotera,
and Cesare Oliviero
Department of Chemistry – University of Calabria –
87036, Rende (CS)

Lamellar phases of some surfactant water system are not infinite, continuous lamellar planes but several experimental findings showed that they contain water-filled defects with highly curved edges. Here, the polydomain lamellar phase of the pentaethylene glycol dodecyl ether($C_{12}E_5$)/decane/water system has been studied by ^{1}H-NMR pulsed field gradient experiments (PGSE) and ^{2}H-NMR line shapes of D_2O, at a constant surfactant (S) to oil (O) weight ratio of 51.8/48.2. Within the lamellar phase of this system, which was observed at S+O weight fraction from 5 to 82 wt%, three types of bilayer organisation have been found. At low surfactant+oil concentrations, <45 wt% S+O, the lamellar phase consists of a stack of flat parallel bilayers while within a intermediate-concentration regime water-filled bilayers exist, as demonstrated by the presence of three-dimensional water diffusion. At concentration higher than 68 wt% S+O this defected lamellar phase oriented in the magnetic field, giving a mono-domain structure.

Keywords: pulsed filed gradient spin-echo (PGSE)NMR method; ^{2}H-NMR line shapes; poly(oxyethylene) surfactants; lyotropic lamellar phases

INTRODUCTION

Mesomorphic phases appear in a variety of aqueous surfactant systems. With increasing surfactant concentration most systems exhibit the hexagonal-cubic-lamellar phase progression, sometimes with additional phases occurring in the narrow concentration interval separating the three classical phases.

The n-alkyl polyethylene glycol ethers, more commonly known as poly(oxyethylene) surfactants, were widely used as emulsifying agents and detergents. They have the general formula $CH_3(CH_2)_{n-1}(OCH_2CH_2)_mOH$, shortened to C_nE_m. Poly(oxyethylene) surfactants formed many of classical lyotropic liquid crystalline phases upon dissolution in water [1–3] as well as many new and interesting intermediate phases [4–6]. The addition of a hydrophobic third component to the binary surfactant-water mixture promoted the formation of microemulsions [7–10]. There is a wide range of phase diagrams available for this class of surfactants and their physicochemical properties are described in many reference books [11–13].

In this paper we investigated the lamellar phase present in the system pentaethylene glycol dodecyl ether ($C_{12}E_5$)/water/decane at a constant surfactant (S) to oil (O) weight ratio of 51.8/48.2. The phase equilibria of this system were already investigated by some of us [14]. It has been demonstrated that a lamellar phase (L_α) lies within an accessible experimental temperature range (30–40°C) and covers a wide range of concentrations (5 wt% $<$ (S+O) $<$ 82 wt%), making this system suitable for temperature and concentration scan experiments.

In non-ionic systems, the lamellar phase swells under the influence of the so-called undulation force. After dilution of the lamellar phase the amplitude of the undulation forces increases as the periodicity increases, accounting the observed decrease in the quadrupolar splitting [10]. Lamellar phases are particularly interesting because of their importance in biological science and in a number of scientific and technological applications. In the classical image it consists of infinity large planar bilayers of amphiphilic molecules alternating with solvent layers at negligible repeat distance, organised in a polydomain structure. On the contrary, during the last decade this image was revised and, today, the existence of both strongly undulating bilayers and bilayers with solvent filled defects are generally accepted. In the recent years especially the defective or perforated lamellar structure has attracted the researchers interest [5,15–20].

In this study the water spin-echo attenuation is measured by the Pulsed Field Gradient Spin Echo (PGSE) ^{1}H-NMR experiments and is compared to ^{2}H-NMR line shape from deuterons (of D_2O-enriched water) in some samples of the different regions of this water-based lamellar phase. The structure of the lamellar phase formed in this non-ionic ternary system was studied by following the concentration dependence of the water echo-attenuation by a set of PGSE experiments performed at 35°C. As in our previous studies, a comparison was made between aggregate structures observed at high dilution and the overall phase lamellar behaviour.

MATERIALS

$C_{12}E_5$, was obtained from Nikko Limited, (Tokyo, Japan), with a quoted purity in excess of 99% as measured by gas chromatography. Decane and heavy water (D_2O) was purchased from Sigma Chemicals (Steinheim, Germany). These materials have purity better than 99.8% and were used without any further purification. Double distilled and deionised water was used for the liquid crystalline mixtures.

The samples for the experiments were prepared from a stock solution of $C_{12}E_5$ and decade (with a weight ratio of S/O = 51.8/48.2) and a stock solution of water and heavy water (with a weight ratio of $H_2O/^2H_2O$ is 98/2). The samples were prepared by weighing the desired amount of S+O mixture and water directly in NMR tubes. They were flame-sealed immediately, mixed by a Vortex 708 (ASAL, Italy) and homogenised in a single phase. The examined samples were at S+O weight fraction from 5 to 80 wt%. The samples were then homogenised in the lamellar phase and left there for two days before performing any experiments.

METHODS

^{2}H-NMR

^2H_2O-NMR spectra were performed by a FT-NMR Bruker WM 300 spectrometer operating at 46 MHz on a wide-band probe (10 mm). An airflow regulator, yielding the temperature stability of ± 0.3°C, controlled the temperature at 35°C in the measuring probe. The quadrupolar echo technique was used for data acquisition, without sample spinning or field frequency lock. Typical experimental conditions were: 15 μs for the pulse width and a pulse separation of 60 μs. Before Fourier transformation 256 transients, at a repetition rate of 0.5 s, were averaged.

It is well established that for a lamellar arrangement of surfactants (i.e. lamellar phases) the ^{2}H-NMR spectrum of a C-^{2}H group consists of a superposition of doublets separated by:

$$\Delta\nu_Q = \frac{3}{2}\chi\left[\frac{3\cos^2\theta - 1}{2}\right]|S_{CD}| \tag{1}$$

where χ is the quadrupole coupling constant and θ is the angle between the director of lamellae and the main magnetic field. Eq. (1) states that surfactants experience an effectively cylindrical symmetry around their long axis and that spectrum is described by a single order parameter $S_{DC} = 1/2\,\langle 3\cos^2\beta - 1\rangle$, where β is the angle between the C-^{2}H bond and the phase director. For a sample consisting of a random distribution of liquid crystalline microdomains (random oriented lamellar liquid crystals) all angle θ are represented and a characteristic ^{2}H-NMR spectrum with "peaks" ($\theta = 90°$) and "shoulders" ($\theta = 0°$) is observed. A quadrupolar splitting, Δ, is usually referred to $\theta = 90°$.

Equation (1) is valid for water deuterons as well. Applying the "two-site" model [21] where we have two different sites for the water, one on the surface of the aggregates (bound water) and the other being free bulk water, and assuming a fast exchange between the surface and the bulk water and a zero splitting of bulk water, we can simplify Eq. (1) as:

$$\Delta = \Delta \upsilon_Q(\theta = 90^\circ) = \frac{3}{4}\chi_w P|S_w| \tag{2}$$

where P is the fraction of water molecules at surfactant/water interface and χ_w and S_w are the quadrupolar constant and the order parameter of the bound water, respectively. χ_w is independent of the site and thus constant (220 kHz). In the case of macroscopically oriented samples, a simple doublet will be observed; the quadrupolar splitting will depend on the orientation of the phase director with respect to the main magnetic field.

PGSE-NMR

In a PGSE NMR experiment [22,23] the mean square displacement of the diffusing entity in a given direction, during the observed time Δ, is measured by the attenuation of the spin-echo intensity and is given by the relation:

$$d = (2D\Delta)^{1/2} \tag{3}$$

where D is the self-diffusion coefficient. In neat water at room temperature, D is close to $3 \cdot 10^{-9}\,\mathrm{m^2/s}$ and is consistent with a mean square displacement of ca. 20 μm.

For molecules undergoing an unrestricted motion (i.e. with a free three-dimensional displacement, 3d) the spin-echo attenuation on a PGSE experiment is given by [24]:

$$\mathrm{R_{3d}} = \exp\left[-(\gamma\delta \mathrm{g})^2\,\mathrm{D}\left(\Delta - \frac{\delta}{3}\right)\right] = \exp[-\mathrm{K\,D}] \tag{4}$$

where $\mathrm{K} = (\gamma\delta\mathrm{g})^2\ (\Delta - \delta/3)$, γ is the proton gyromagnetic ratio, g is the magnetic field gradient strength, δ is the width of the gradient pulses and Δ is the time occurring from the start of one pulse to the start of the next gradient pulse.

Lyotropic mesophases are constituted by a numerous and randomly oriented domain and the simple condition of Eq. (4) are clearly not met. For a case of water molecules restricted in a randomly (large) oriented bilayers, which the water molecule are not able to penetrate, and if the bilayers are not separated more then 10^3 A°, the water molecules are free to diffuse in only two dimensions, 2d. Therefore the Eq. (4) was modified as [25,26]:

$$R_{2d} = \frac{\sqrt{\pi}}{2}\exp(-KD)\frac{\operatorname{erf}\left[i(KD)^{1/2}\right]}{\left[i(KD)^{1/2}\right]} \tag{5}$$

where erf is the ***error*** function and ***i*** the imaginary unity. An analogous relation was also derived for a one-dimensional diffusion [26].

Equations (4) and (5) can be plotted in a diagram ***ln***R ***versus*** KD (Fig. 1) which provides a signature to the actual diffusion conditions. In such a diagram Eq. (4) gives a dashed straight line (3d in Fig. 1), Eq. (4) gives a sharper curved line (2d in Fig. 1).

As a consequence, the existence of an "ideal" lamellar mesophase can be recognised provided that the observed spin-echo attenuation shape for entrapped water follows Eq. (5). It has been reported that deviations from the theoretical 3d trends for an ideal lamellar phase have been interpreted as a consequence of defects in the structure. A transition from 2d to 3d

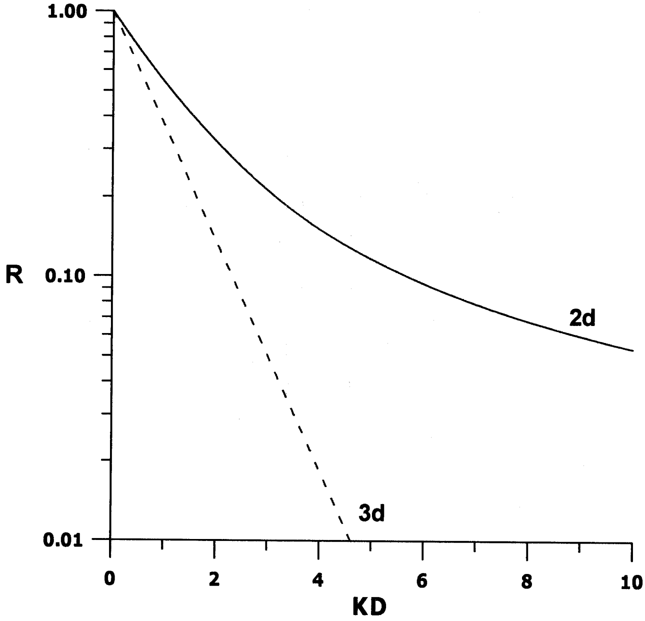

FIGURE 1 Echo attenuation trend as a function of K for an unrestricted water diffusion (3d), a two-dimensional diffusion typically in L_α (2d).

behaviour was analysed in terms of bilayer sheets with water-filled defects [27].

In this study, ^{1}H-NMR PGSE experiments were made on a Bruker 300 Mz spectrometer. The spin-echo attenuations of water were measured at 35°C as a function of the lamellar composition (wt% S+O) by the Fourier Transform PGSE technique described by Stilbs [22]. We used the following experimental condition: δ was varied from 1 to 70 ms while Δ and g were held constant at 140 ms and 0.50 T/m, respectively.

RESULTS AND DISCUSSION

Some selected ^{2}H-NMR spectra of ^2H_2O are shown in Figure 2. The spectrum of 5 wt% S+O sample (Fig. 2a) appears as a single broad isotropic line showing a width of several tenths of herz.

This quadrupolar line shape is typical of very diluted lamellar mixtures where the contribution of bulk water is dominant. In this case the collapse of deuterium quadrupolar splitting appears dramatic.

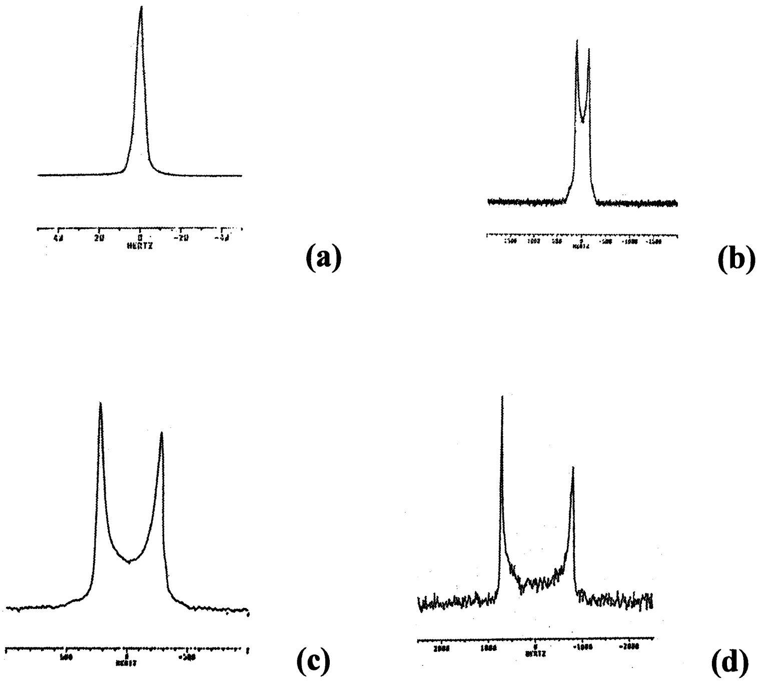

FIGURE 2 ^{2}H-NMR spectra obtained for the samples at: a) 5 wt% S+O; 45 wt% S+O; c) 65 wt% S+O and d) 81 wt% S+O at 35°C.

The ^{2}H-NMR spectra of the samples at 45 and 65 wt% (Fig. 2b and 2c) assume the typical line shape of spherical powder patterns and indicate the presence, in this composition interval, of a single-phase lamellar region. ^{2}H-NMR line shapes in mixtures at a concentration higher than 68 wt% S+O show the characteristics of a lamellar phase aligned in the magnetic field. An example is the spectrum from the lamellar phase of the 81 wt% mixture showing an evident doublet.

The Figures 3 and 4 show the results of spin echo attenuation data from PGSE experiments performed at 35°C with the diffusive observation time, Δ, fixed at 140 ms. The water echo attenuation decays as a function of K are reported for different lamellar compositions. The continuous line represents the fitting of the Eq. (5) to the experimental data. On the contrary the dashed line represents the fitting using Eq. (4).

As it is possible to notice at the lower concentration used here, from 5 to 45 wt% S+O, spin-echo attenuation plots exhibit a marked curvature. The data reflect very well a two-dimensional diffusion of water (Figs. 3a–c). Above this interval of composition the echo attenuation curves deviate from the 2d diffusion trends. As an example is reported the 65 wt% S+O mixture (Fig. 4a) which shows an echo attenuation decay that reflects a 3d diffusion of water.

While a non-restricted 3d diffusion of water was recorded in mixtures within the composition range from 48 to 65 wt%, at higher concentration the echo attenuation plots have an intermediate position between the 2d and 3d diffusion.

The analysis of these PGSE-NMR experiments is in good agreement with quadrupolar NMR line shapes of ^2H_2O reported before. The Eq. (5), derived in the conditions randomly oriented arrays of lamellar elements, each with axis of planar symmetry, is applicable only in the concentration range 5–65 wt% S+O where the sample is formed by a randomly oriented lamellar domains. Since it is obvious from the ^{2}H-NMR data that, at higher concentrations, the lamellar domains were partially oriented, the Eq. (5) is not applicable anymore.

Therefore the PGSE data confirm the existence of an ideal lamellar phase in the concentration range 5–45 wt% where the echo attenuation data follows perfectly the powder distribution curve for 2d water diffusion. In this composition regime the self-diffusion coefficients obtained have a remarkable low value of ca. $6 \cdot 10^{-10}$ m^2/s, which is similar to that obtained on the ideal lamellar phase of the AOT/water system for a comparable water lamellar regime [28].

The echo attenuation plots recorded in the concentration range 48–65 wt% showed a sharp transition to an apparently 3d behaviour. The spin echo attenuation is now Gaussian in the observed time function K, indicating that water molecules are no longer confined to single director

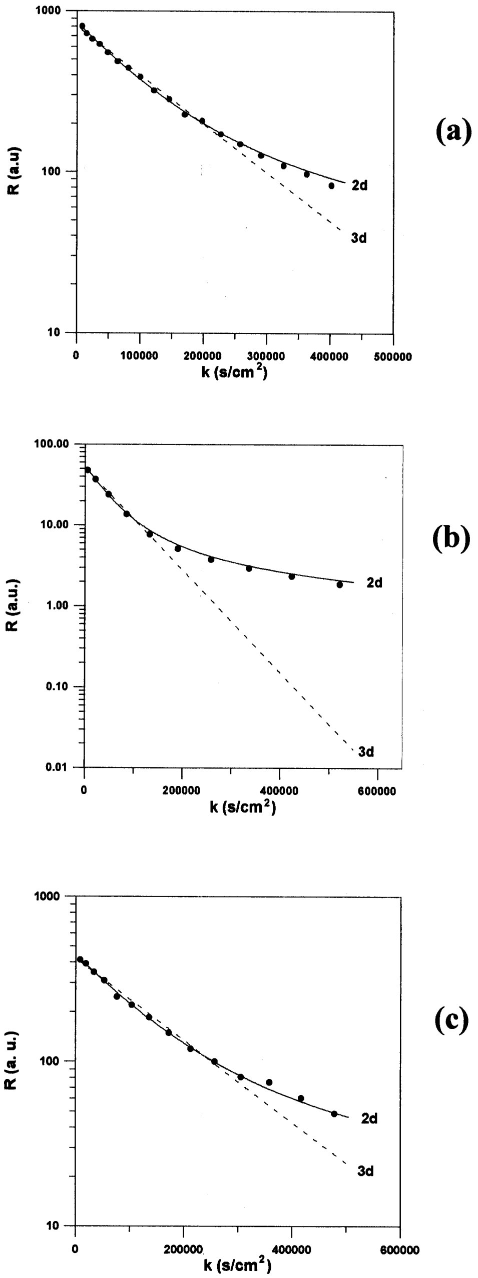

FIGURE 3 Echo attenuation plots of lamellar phase samples: a) 5 wt% S+O; b) 35 wt% S+O and c) 45 wt% S+O. The calculated lines 3d and 2d are best fits to data using Eqs.(4) and (5), respectively.

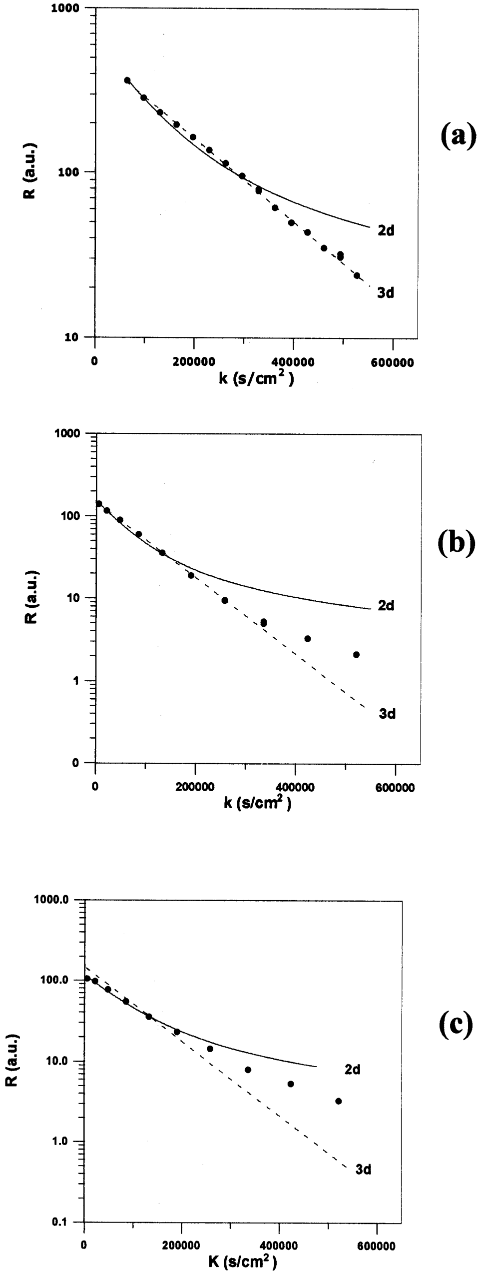

FIGURE 4 Echo attenuation plots of lamellar phase samples: c) 65 wt% S+O; d) 71 wt% S+O and e) 81 wt% S+O. The calculated lines 3d and 2d are best fits to data using Eqs. (4) and (5), respectively.

orientations. The most probable cause of this evident behaviour may be attributed to defects present in the structure, and precisely to water- filled holes. In fact the presence of holes on the bilayers allow the water molecules to move out of the two restricted two directions of ideal lamellar bilayers. Additionally, the more the lamellae are perforated the more the deviation of the echo attenuation gets marked up to assuming the 3d signature. For the sample at 65 wt% S+O (Fig. 4a) the bilayers are tremendously perforated as long as the echo attenuation follows the 3d diffusion.

The echo attenuation trends obtained in lamellar mixtures with a composition higher of 68 wt% (Figs. 4b and 4c) are attributable to the orientation of domains and are the consequence of a partial reduction of the volume fraction of the water-filled defects in the hydrophobic layer.

CONCLUSION

This study has demonstrated that PGSE and quadrupolar line shapes represent a useful combination of NMR techniques to investigate the structure of lyomesophases in a wide composition interval. The morphology of the lamellar phases on the nonionic surfactant system $C_{12}E_5$/decade/water has been studied at 35°C and in lyotropic mixtures from 5 to 82 wt% S+O. Echo attenuation plots showed clearly the presence of structural defects as water-filled holes in the bilayers, while ^{2}H-NMR spectra of ^2H_2O revealed an orientations of the lyotropic domains.

Considering the PGSE and ^{2}H NMR data, three different lamellar structures were observed and they are schematically represented in Figure 5.

The first one consists of classical lamellar bilayers, L_α, flat and randomly oriented, that extend up to a surfactant+oil composition of 45 wt%. The

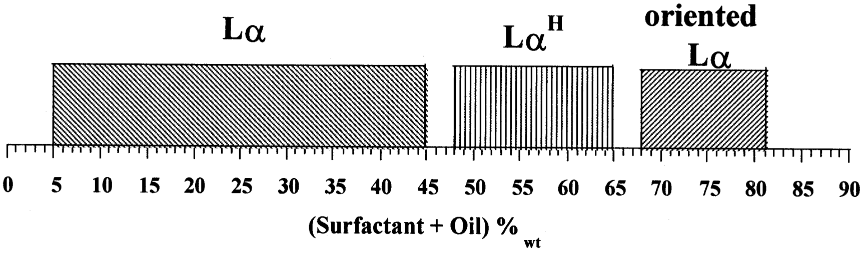

FIGURE 5 Lamellar microstructures as obtained by NMR data at 35°C and reported as a function of the surfactant + oil composition for the system $C_{12}E_5$/decane/water.

second lamellar structure lies in the concentration range 48–65 wt% S+O and is made of nonoriented bilayer sheets containing water-filled defects, L_α^H. Finally, above the composition of 68 wt% S+O an oriented lamellar phase was observed, whose volume fraction of water-filled defects is reduced being decreased the overall water composition.

REFERENCES

[1] Mitchell, D. J., Tiddy, G. T. J., Waring, T., Bostock, T., & McDonald, M. P. (1983). *J. Chem. Soc. Faraday Trans. 1*, *79*, 975.
[2] Tiddy, G. T. J. (1980). *Phys. Rep.*, *57*, 1.
[3] Olsson, U. & Wennestr̈om, H. (1994). *Adv. Colloid Interface Sci.*, *49*, 113.
[4] Le, T. D., Olsson, U., Wennestr̈om, H., & Schurtenberger, P. (1999). *Physical Review*, *60*, 4300.
[5] Funari, S. S., Holmes, M. C., & Tiddy, G. T. J. (1994). *J. Phys. Chem.*, *98*, 3015.
[6] Burgoyne, J., Holmes, M. C., & Tiddy, G. T. J. (1995). *J. Phys. Chem.*, *99*, 6054.
[7] Kunieda, H. & Shinoda, K. (1982). *J. Dispersion Sci. Technol.*, *3*, 233.
[8] Kahlweit, M. & Strey, R. (1985). *Angew. Chem. Int. Ed. Engl.*, *24*, 654.
[9] Olsson, U., Shinoda, K., & Lindman, B. (1986). *J. Phys. Chem.*, *90*, 4083.
[10] Olsson, U., Nagai, K., & Wennestr̈om, H. (1988). *J. Phys. Chem.*, *92*, 6675.
[11] Schick, M. J. (1987). *Non ionic surfactants: Chemical Analysis*, Marcel Dekker Inc.: New York, Vol. 23.
[12] Von Os, N. M., Haak, J. R., & Rupert, L. A. M. (1993). *Physico-Chemical Properties of Selected Anion, Cationic, & Nonionic Surfactants*, Elsevier Science Pub. B. V.: Amsterdam.
[13] Cross, J. (1987). *Nonionic Surfactants: Chemical Analysis*, Marcel Dekker Inc.: New York, Vol. 19.
[14] Bagger-Jorgensen, H., Coppola, L., Thuresson, K., Olsson, U., & Mortensen, K. (1997). *Langmuir*, *13*, 4204.
[15] Kekicheff, P. & Cabane, B. (1984). *J. Phys. Lett.*, *45*, 813.
[16] Rancon, Y. & Charvolin, J. (1988). *J. Phys. Chem.*, *92*, 6339.
[17] Leaver, M. S. & Holmes, M. C. (1993). *J. Phys. II France*, *3*, 105.
[18] Hoffmann, H., Munkert, U., Thunig, C., & Valiente, M. (1994). *J. Colloid Interface Sci.*, *163*, 217.
[19] Holmes, M. C., Leaver, S. L., & Smith, A. M. (1995). *Langmuir*, *11*, 356.
[20] Quist, P. Q., Fontell, K., & Halle, B. (1994). *Liq. Cryst.*, *16*, 235.
[21] Rendall, K. & Tiddy, G. J. T. (1984). *J. Chem. Soc. Farday Trans. 1*, *80*, 3339.
[22] Stilbs, P. (1987). *Prog. NMR Spetrosc.*, *18*, 1.
[23] Stejskal, E. O. & Tanner, J. E. (1965). *J. Chem. Phys.*, *42*, 288.
[24] Stejskal, E. O. (1965). *J. Chem. Phys.*, *43*, 3597.
[25] Callaghan, P. T. (1984). *Aust. J. Phys.*, *37*, 359.
[26] Celebre, G., Coppola, L., Ranieri, G. A., & Terenzi, M. (1994). *Mol. Cryst. Liq. Cryst.*, *238*, 117.
[27] Chidichimo, G., Coppola, L., La Mesa, C., Ranieri, G. A., & Saupe, A. (1988). *Chem Phys. Lett.*, *145*, 85.
[28] Coppola, L., Muzzalupo, R., Ranieri, G. A., & Terenzi, M. (1995). *Langmuir*, *11*, 1116.