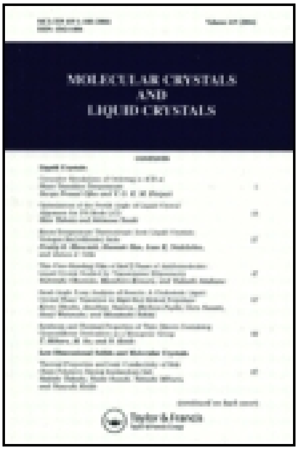

Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl17

NMR Investigation of the Lamellar Mesophase Occurring in the System Aerosol OT-Water

G. Chidichimo [a], C. La Mesa [a], G. A. Ranieri [a] & M. Terenzi [a]

[a] Chemistry Department, University of Calabria, 87030, Arcavacata di Rende, Cosenza, Italy

To cite this article: G. Chidichimo, C. La Mesa, G. A. Ranieri & M. Terenzi (1987): NMR Investigation of the Lamellar Mesophase Occurring in the System Aerosol OT-Water, Molecular Crystals and Liquid Crystals Incorporating Nonlinear Optics, 150:1, 221-236

To link to this article: http://dx.doi.org/10.1080/00268948708074798

Mol. Cryst. Liq. Cryst., 1987, Vol. 150b, pp. 221–236
Photocopying permitted by license only

Printed in the United States of America

NMR Investigation of the Lamellar Mesophase Occurring in the System Aerosol OT-Water

G. CHIDICHIMO, C. LA MESA, G. A. RANIERI and M. TERENZI

Chemistry Department—University of Calabria, 87030 Arcavacata di Rende, Cosenza, Italy

The lamellar mesophase occurring in the system water aerosol OT (AOT) has been studied by combining nuclear magnetic resonance methods, such as deuterium quadrupole measurement (D-NMR) and pulsed field gradient (PFG-NMR), with optical microscopy.

At low AOT content the mesophase shows a biaxial character and consists of defective structures, which have been interpreted as rippled lamellae. In the range between 20 and 28 AOT wt% the mesophase is a mixture of regular and rippled lamellae; for larger AOT content the system can be considered a normal lamellar mesophase.

The system is strongly influenced by mechanical effects, which force the lamellae to assume defective configurations. Quadrupole splittings have been analyzed in terms of a "ripple model" and the angle of ripple deformation has been obtained.

INTRODUCTION

The properties of lyotropic liquid crystals have been widely described in the last decade. Particular attention has been focused on the modifications induced by temperature or by the addition of further components.[1–3] In some cases the lyotropic mesophases can be deformed by the occurrence of defects[4,5]: for instance the reciprocal arrangement of lamellar domains can be reversibly deformed, as inferred from studies on mesophases subjected to Couvette shearing[6] and from NMR experiments.[7,8]

A lyotropic system intensively studied in the past is the binary system water–aerosol, OT (sodium-bis-2-ethylhexyl sulfosuccinate). The first investigation on such system was performed by Luzzati and coworkers[9] while the complete phase diagram, shown in Figure 1, is due to Winsor et al.[10,11] The latter authors observed a modification of the optic sign for the birefringence of the lamellar mesophase in the range between 30–40 AOT wt%.

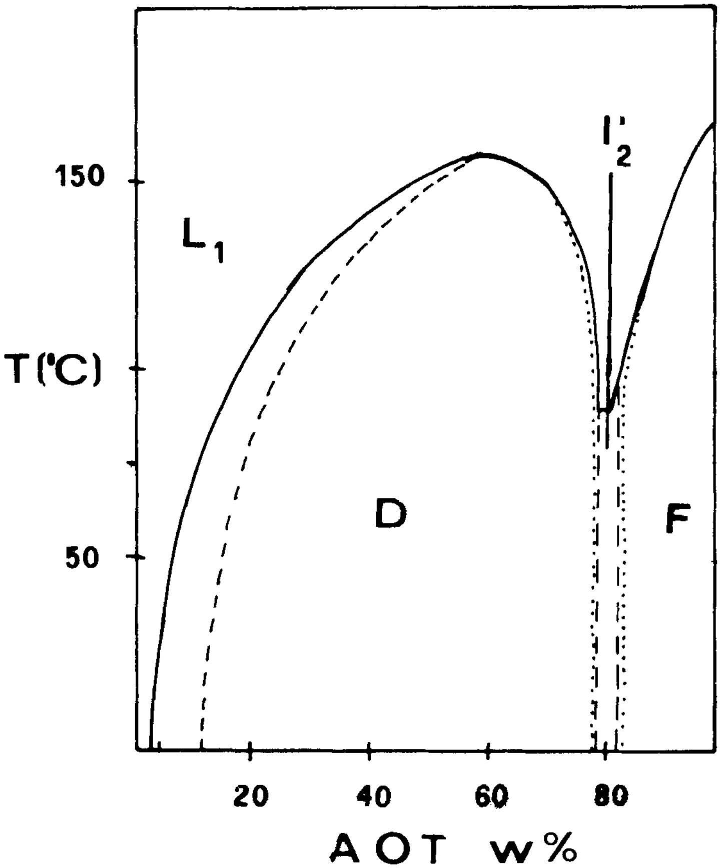

FIGURE 1 AOT/water phase diagram redrawn from Ref. 11. The denomination is according to Ekwall[1]: D, lamellar; I'_2, viscous isotropic; *F*, reverse hexagonal; L_1, micellar.

According to X-ray diffraction[12] the lamellar mesophase occurring in the above system can be divided in three concentration ranges. Two of them show ideal swelling behaviour and are separated by a nonswelling one. The data have been interpreted assuming some modification of the lamellar domains.

Recently Callaghan and Sodermam examined water diffusion in the lamellar mesophase of the system AOT-water.[13] They explained the data, as well as the above mentioned X-ray findings, suggesting that:

a. at low AOT content, since the diffusion of water is unusually small, the interlayer spacings should contain curved barriers which hinder water motion;

b. the intermediate range should be characterized by a certain amount of interlamellar bilayer disks.

Other physical properties of the system, as electrical conductivity,[14] optical birefringence[15] and Raman scattering[16] have been extensively studied, but an explanation of the results is still incomplete.

We report studies on the lamellar mesophase of the system AOT-water obtained by combining D-NMR, PFG-NMR and optical microscopy. While performing preliminary experiments, we observed that the D-NMR spectra were strongly affected by mechanical treatments, as hand shaking and centrifuging. For these reasons the lyotropic mixtures have been investigated under different experimental conditions, such as:

a. whit samples kept at rest, at 323 K, for at least one month, after mixing and homogenizing;
b. immediately after back and forth shaking and centrifuging;
c. 50 hours after the above mechanical treatment.

EXPERIMENTAL

Materials

The surfactant (sodium di-2-ethylhexyl sulfosuccinate), from Carlo Erba, was dissolved in hot methanol. The resulting solution was filtered, cooled and vacuum dried. The product was dissolved in hexane, filtered and vacuum dried. The whole procedure was twice repeated. The final product was an anhydrous white waxy paste, birefringent under polarizing microscope (fanlike Texture 222.5).[17] The surfactant was stored in a dry-box until use. Water was bidistilled, deionized and degassed; heavy water, 99.7% isotopically enriched, was from Merck. Methanol and hexane were high purity products (Merck).

The samples were prepared by weighing proper amounts of the components in glass tube, which were centrifuged, sealed off and heated at 323 K until equilibrium was obtained. Samples for optical microscopy were prepared by pressing small amounts of the lyotropic mixtures between glass slides treated with a silane polymeric solution.

The samples' thickness was fixed to 50 μm by a mylor frame interposed between the slides.

Methods

Deuterium quadrupole splittings were measured by a FT-NMR Brucker WM 300 spectrometer, working at about 46 MHz. Typical experimental set-up was: number of transients 400–1000, pulse width 30 μsec, repetition time 1 sec. The working temperature was 290 K.

Water translational diffusion was measured by a pulsed NMR spectrometer, working at 35 MHz on ^{1}H. The temperature control of the measuring vessel was ensured by an oven which allowed the constancy of temperature within 0.1°C. Further details on the set-up of the apparatus have been reported elsewhere.[18] The diffusion coefficients have been calculated according to standard literature procedures.[19] Polarizing microscopy and conoscopy studies were performed on a Leitz polarizing microscope.

RESULTS AND DISCUSSION

The system has been investigated over a wide concentration range; samples concentrations being reported in Table I.

The spectral vibrations induced by mechanical stresses have been studied by recording NMR spectra:

i. after leaving the samples at rest for about one month;
ii. soon after back and forth shaking and centrifuging;
iii. in intermediate conditions among i and ii (e.g. 50 hours after shaking and centrifuging).

We shall use the terms relaxed, unrelaxed or partially relaxed to define the samples in conditions 1, 2, and 3, respectively.

TABLE I

Composition of the analyzed samples.

Sample	AOT wt%
1	15.60
2	20.01
3	23.59
4	26.20
5	28.00
6	29.00
7	34.00
8	35.24
9	39.00
10	40.08
11	43.80
12	46.97
13	49.36
14	52.50
15	53.28
16	57.13

D-NMR SPECTRAL PROFILES

Let us consider the powder patterns obtained in relaxed conditions (Figures 2 and 3). Below 20 AOT wt%, the spectra consist of a single broad line, whose width increases on increasing the AOT content.

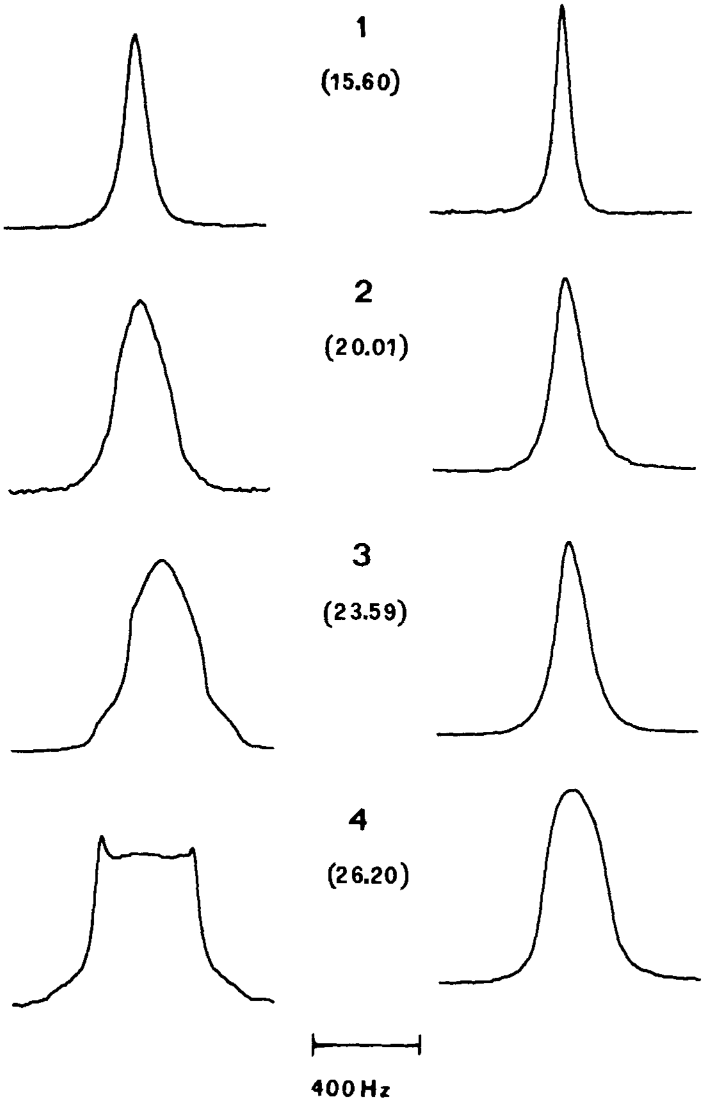

FIGURE 2 Deuterium NMR spectra of samples 1, 2, 3, 4 of Table I. Left hand side: spectra obtained in relaxed condition. Right hand side: spectra recorded after shaking.

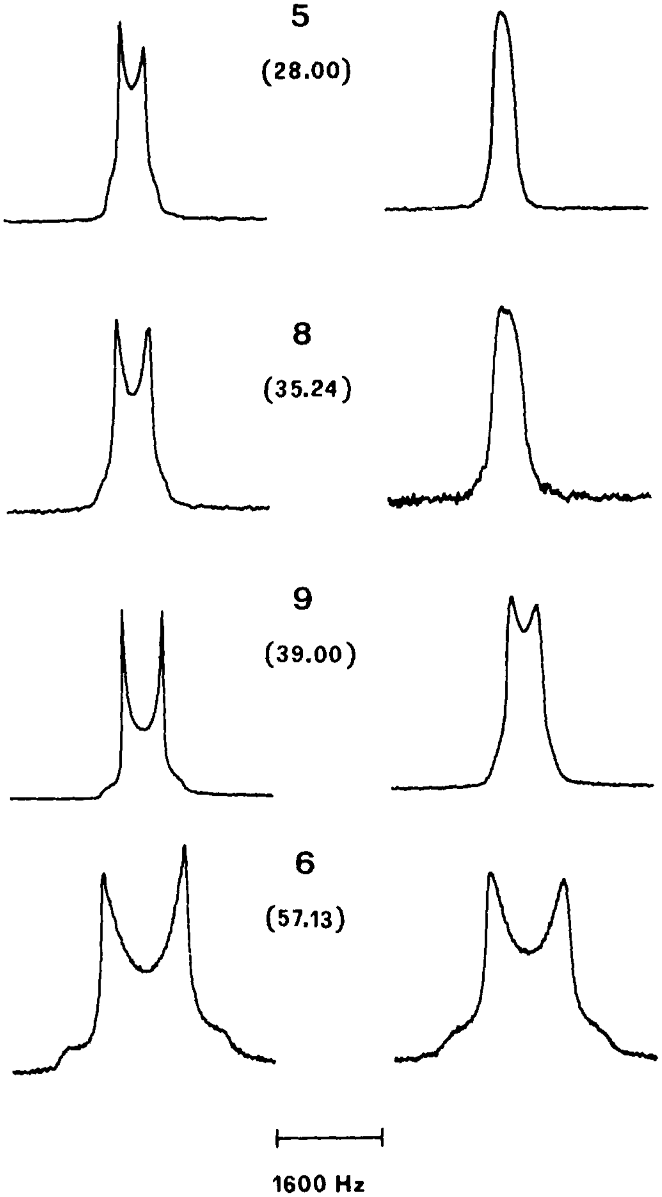

FIGURE 3 Deuterium NMR spectra of samples 5, 8, 9, 16 of Table I. Left hand side: spectra obtained in relaxed condition. Right hand side: spectra recorded after shaking.

Since the phase is optically anisotropic the lack of quadrupole splitting in the spectra can be explained in terms of very high biaxial powder patterns.

In the range 20–28 AOT wt%, NMR spectra result from the overlapping of two subspectra, one similar to those previously described and the other being a spherical uniaxial powder pattern. The uniaxial component increases on increasing the AOT content. For concentrations above 28 AOT wt% the relaxed samples give uniaxial spherical powder patterns. No significant variations can be observed between spectra obtained below 20 AOT wt%, in relaxed and unrelaxed conditions; while spectra from shaken samples at about 20 AOT wt% are only slightly sharper than those obtained in relaxed sample.

In the range between 20 and 28 AOT wt% spectra recorded from unrelaxed systems (3 and 4 in Figure 3) do not show uniaxial components but only a broad single line. Such a line becomes broader on increasing the AOT content and can be interpreted as a highly biaxial powder pattern.

Spectra obtained from shaken samples above 28 AOT wt% have a more complex shape: they could be interpreted in terms of the overlapping of several powder patterns having different order and asymmetry parameters (spectra 5–8 in Figure 3).

When comparing data recorded in relaxed and unrelaxed conditions, in the range 39–60 AOT wt%, it can be seen that the mechanically induced deformations introduce a slight biaxiality and a more efficient broadening in the spectral profiles (6–9 in Figure 3).

The quadrupole splitting, ΔQ, measured both in relaxed and unrelaxed conditions, and the symmetry parameter, η, measured in unrelaxed systems, are reported in Figure 4. For spectra resulting from the overlapping of several powder components the quadrupole splitting, was estimated from the broader external singularities. The errors can be as high as 20%. For some samples it was not possible to make a reasonable evaluation of the asymmetry parameter.

Spectra obtained in relaxed samples suggest that the phase diagram can be divided in three sub-regions:

a. above 35 AOT wt% the spectra consist of uniaxial, spherical powder patterns and the system can be considered a defectless lamellar mesophase;

b. in the concentration range from 20 to 30 AOT wt% normal lamellae coexist with defective aggregates which give asymmetric spectral profiles;

c. below 20 AOT wt% only defective structures exist.

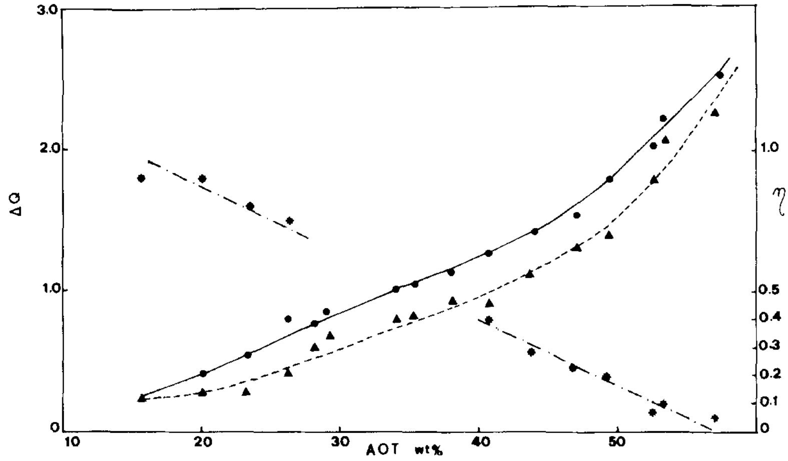

FIGURE 4 The deuterium quadrupole splittings (KHz), as a function of AOT wt% in relaxed (●) and unrelaxed (▲) conditions. On the right hand side of the figure is reported the biaxiality, η, of the samples (*).

Spectra obtained in unrelaxed conditions, for compositions around 30 AOT wt% are similar to those observed in more diluted relaxed samples. This indicates that mechanical stresses promote the formation of defective lamellae. Only after a long time, some months, the systems relax back to their equilibrium conditions.

The most relevant observation is that, in the full composition range, some degree of asymmetry and reduced quadrupolar splittings are induced in the spectra by shaking. Water molecules move around amphiphilic aggregates and cover distances of thousands of Å during measurement time; so the asymmetric character of powder patterns indicates the presence of phase biaxiality.

On the basis of the above observations, we suggest that the "lamellar" mesophase of the AOT-water system is always a mixture of lamellae and biaxial aggregates. Mechanical stresses increase the amount of defective structures. Spectral profiles obtained in partially relaxed conditions show intermediate features between those observed in relaxed and unrelaxed conditions.

MICROSCOPY EXAMINATION

Conoscopic observations have been performed on a 20 AOT wt% sample to verify the occurrence of biaxiality.

Conoscopic isogyres consist of two arms, having different widths, which form a cross and evolve in two hyperbolic brushes upon rotation of the stage. The maximum separation between the brushes was observed after a 45° rotation from the position where the isogyres form a cross. Such a behaviour confirms the presence of optical biaxiality.

WATER DIFFUSION

Water translational diffusion coefficient, *D*, was measured by PFG-NMR. Results are shown in Figure 5.

The upper and lower trends in Figure 5 report data in relaxed and unrelaxed conditions, respectively. A comparison between the two sets of data shows that diffusion can be largely reduced upon shaking, because of the onset of defects in the lamellar domains. Such a behaviour, in agreement with D-NMR data, suggest that the defective structures are of the same kind in the whole composition range of AOT-water system.

Around 30 AOT wt% the diffusion is reduced up to a factor of 2, indicating that the motion of water molecules between defective la-

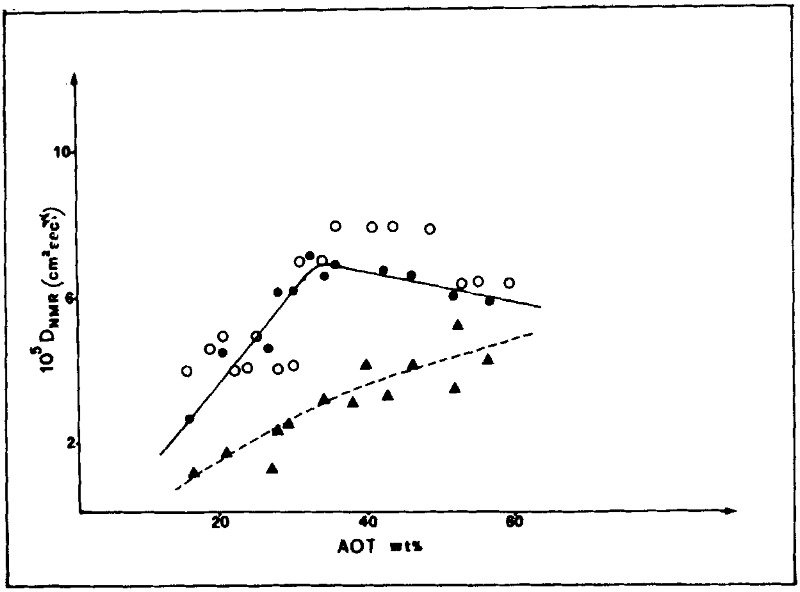

FIGURE 5 Water translational diffusion coefficients D (cm^2/sec) in unrelaxed (▲) and relaxed (●) conditions as a function of AOT wt%. By comparison are reported data from Callaghan and Soderman,[13] (○).

mellae is statistically allowed in only one direction, and not in two, as expected in regular lamellar systems.

In relaxed conditions *D* increases on increasing the AOT content, according to the progressive onset of defectless lamellae. Maximum diffusion occurs at about 30 AOT wt%; thereafter the decrease in diffusive trend can be explained in terms of gradual reduction of free water undergoing fast diffusion.[18] The positive slope of diffusion for unrelaxed samples can be explained assuming that, on increasing the surfactant content, the defective aggregates progressively become less distorted, in agreement with the gradual decrease of the asymmetry parameter.

NATURE OF THE DEFECTIVE AGGREGATES

The defective structures induced by shaking, or naturally occurring in diluted samples, are responsible for the:

1. relatively low water diffusion with respect to that measured in typical lamellar systems[18];
2. biaxial character of the averaged electric field gradient tensor acting on deuterium nuclei;
3. reduced degree of order of water molecules;
4. optical biaxiality of the mesophase.

We attempted to account for the above properties following Callaghan and Soderman.[13] Accordingly water layers can be partly hindered by barriers, formed by amphiphilic molecules included in regions of negative curvature, with their polar heads facing inward (Figure 6a). The aqueous regions should have the form of inverted ribbons, and diffusing molecules should give rise to biaxial patterns of reduced width,[20] furthermore water diffusion should be severely reduced. The above hypothesis presents the following drawbacks. To justify the high biaxiality of D-NMR spectra the inverted ribbons should be considered as slightly squeezed cylinders.[20] Consequently the domains should be similar to a sort of hive having ribbon-sized cells. Such a model could be valid at high AOT content, at the border with the inverted hexagonal mesophase, but seems unrealistic at low AOT content. On the other hand, mixtures in the concentration range between 20 and 30 wt% appear quite fluid, while inverted ribbon mesophases are expected to be very viscous.

An alternative hypothesis which accounts for the observed properties of the mixtures is that the defective aggregates consist of rippled lamellae, similar to those reported for some phospholipid bilayer

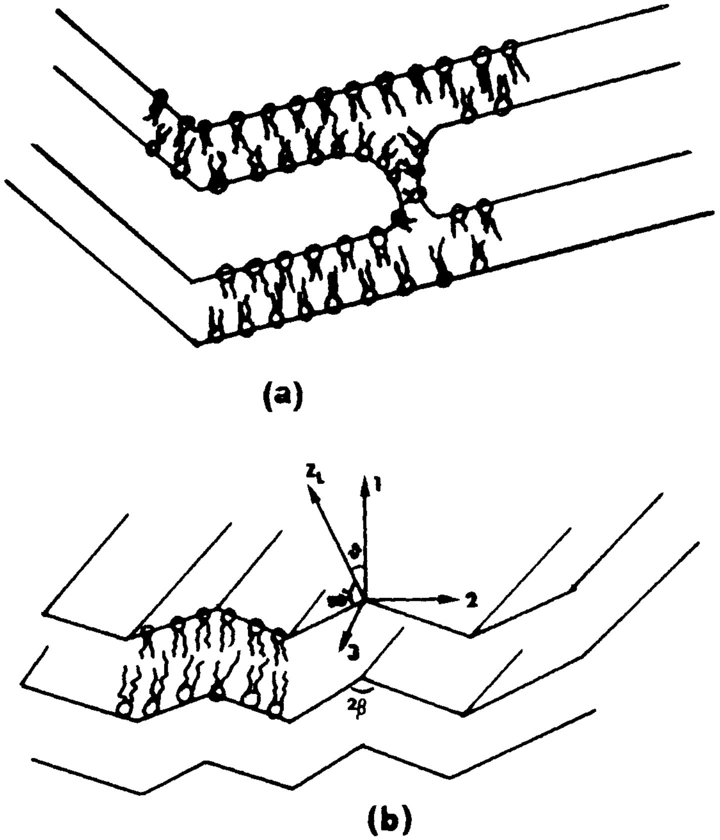

FIGURE 6 a) Model of defective phase according to Callaghan and Soderman.[13] b) Schematic view of the ripple phase and principal axis frame of the averaged electrical field gradient tensor.

membranes.[21] A schematic picture of rippled lamellae is reported in Figure 6b.

According to this model, water molecules travelling among interlayer spacings, should collide with lipid walls more frequently than in the case of flat lamellae. If the ripple repetition distances were shorter than the average distances water molecules can travel during time of measurement, the system would be similar to an ensemble of randomly oriented capillars. This could be the situation in unrelaxed samples, where the diffusion coefficient is reduced by a factor of two, as a consequence of mechanical stresses.

RIPPLE MODEL THEORY

D-NMR data have been interpreted according to Doane et al.[22] The quadrupole splitting Q and the asymmetry parameter, η,[23] are defined as:

$$\Delta Q = \frac{3e^2Q}{2\hbar}V_{zpzp}; \quad \eta = \frac{V_{xpxp} - V_{ypyp}}{V_{zpzp}} \tag{1}$$

where V_{xpxp}, V_{ypyp}, and V_{zpzp} are the components of the electrical field gradient tensors (EFGT) acting on the observed nuclei, averaged over the molecular motion, and measured along their principal axis frame (i.e. along the director frame of the mesophase); Q, e and $\hbar$ are the quadrupole moment, the electron charge and the Planck constant respectively.

In an ideal lamellar mesophase $\eta = 0$ and the only measured quantity is $\Delta Q_L = 3e^2Q/2\hbar\ V_{zLzL}$, being zL the axis normal to the lamellar surface (see Figure 6b).

If the aggregate is rippled the EFGT components become further averaged since diffusing water molecules change their mean orientation as they travel among every quarter of period in the ripple (Figure 6b). The main axis will coincide with the axis 1, 2, or 3 in Figure 6b. If V_{zLzL} is known the ripple averaged EFGT components can be obtained from[24]:

$$V_{11} = V_{zLzL}(3\cos^2\theta - 1)/2 \tag{2a}$$

$$V_{22} = V_{zLzL}(3\sin^2\theta\sin^2\phi - 1)/2 \tag{2b}$$

$$V_{33} = V_{zLzL}(3\sin^2\theta\cos^2\phi - 1)/2 \tag{2c}$$

where θ and ϕ are the polar angles defining the direction of zL in the frame 1, 2, 3. ϕ can be assumed to be 90° or 270° without loss of generality; while $\theta = 90° - \beta$, where β is the ripple angle.

As a result Equation 2 can be rewritten as:

$$V_{11} = V_{zLzL}(3\sin^2\beta - 1)/2 \tag{3a}$$

$$V_{22} = V_{zLzL}(3\cos^2\beta - 1)/2 \tag{3b}$$

$$V_{33} = V_{zLzL}/2 \tag{3c}$$

The following cases can be considered:

a. If 54.73° $\leq \beta < 90°$, the principal axes are $zp = 1$; $yp = 3$; $xp = 2$ and:

$$\frac{\Delta Q_R}{\Delta Q_L} = (3\sin^2\beta - 1)/2 \tag{4a}$$

$$\eta_R = \frac{(1 - \sin^2\beta)}{(\sin^2\beta - 1/3)} \tag{4b}$$

which can be interrelated according to:

$$\frac{\Delta Q_R}{\Delta Q_L} = 1/(1 + \eta_R) \tag{4c}$$

b. If 45° $\leq \beta \leq$ 54.73° the principal axes are $zp = 3$; $yp = 1$; $xp = 2$; consequently:

$$\frac{\Delta Q_R}{\Delta Q_L} = -1/2 \tag{5a}$$

$$\eta_R = 3(2\sin^2\beta - 1) \tag{5b}$$

c. If 35.27° $\leq \beta \leq$ 45° we have $zp = 3$; $yp = 2$; $xp = 1$ and:

$$\frac{\Delta Q_R}{\Delta Q_L} = -1/2 \tag{6a}$$

$$\eta_R = 3(1 - \sin^2\beta) \tag{6b}$$

d. For 0° $\leq \beta \leq$ 35.27°; $zp = 2$; $yp = 3$; $xp = 1$ and:

$$\frac{\Delta Q_R}{\Delta Q_L} = \left(1 - \frac{3}{2}\sin^2\beta\right) \tag{7a}$$

$$\eta_R = \frac{3\sin^2\beta}{2 - 3\sin^2\beta} \tag{7b}$$

which when combined with each other give:

$$\frac{\Delta Q_R}{\Delta Q_L} = 1/(1 + \eta_R) \qquad (7c)$$

The experimental results are compared with theory in Figure 7; they satisfactorily fit the predicted trend for a ripple angle in the range between 50° and 65°, or between 25° and 40°. In fact it is not possible to discriminate among complementary values of the ripple angle, which give the same values of the reduced order and of the asymmetry parameter (Equations 4 and 7). Since structures with ripple angles between 25° and 40° are unfavored because regions of very high curvature should coexist with flat regions, we suggest that the lamellar mesophase of the AOT-water system can assume a rippled configuration with ripple angles ranging between 50 and 65 degrees.

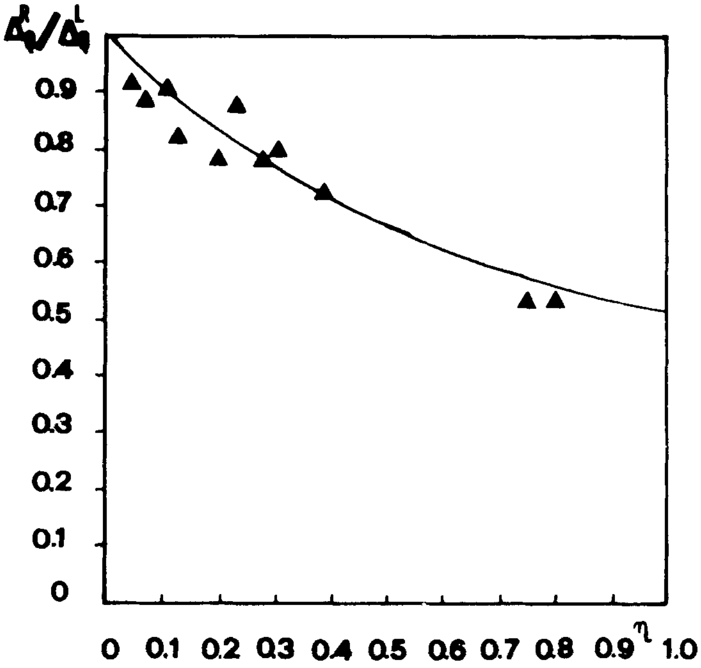

FIGURE 7 Comparison of theoretical behaviour of $\Delta Q_R/\Delta Q_L$ against η (continuous line) and experimental data (▲).

CONCLUSIONS

At low concentration, below 20 AOT wt%, the system is a rippled phase and no relevant structural modifications are induced by shaking or centrifuging the samples, but only small modification of the ripple angle, which could explain the decreasing of water diffusion. In the range between 20 and 28 AOT wt%, relaxed samples are mixtures of lamellae and rippled aggregates; mechanical shaking promotes a fully rippled configuration. The defectless lamellar mesophase, occurring in relaxed conditions at high AOT content can be also deformed in rippled aggregates.

This study suggests that when analyzing experimental data concerning the AOT-water lyotropic system, mechanically induced deformations must be taken into account. In our opinion this effect could be the reason of the anomalous X-ray behaviour, describing by Fontell.[12]

Acknowledgment

The financial support was from CNR and MPI grants.

References

1. P. Ekwall, in "Advances in Liquid Crystal," Vol. 1, p. 1, ed. by G. H. Brown, Academic Press (1975).
2. G. J. Tiddy, *Phys. Rev.*, **57**(1), 1 (1980).
3. K. Fontell, *Mol. Cryst. Liquid Cryst.*, **63**, 59 (1980).
4. H. Helfrich, in "Physics on Defects," p. 715, ed. by R. Balian, North Holland, (1981).
5. L. S. Yu and A. Saupe, *J. Am. Chem. Soc.*, **102**, 4879 (1980).
6. L. Bohlin and K. Fontell, *J. Colloid Interface Sci.*, **67**, 229, (1978).
7. W. G. Miller, F. D. Blum, H. T. Davis, E. I. Franses, E. W. Caler, P. K. Kilpatrick, K. I. Nietering, J. I. Puig and L. E. Scriven, in "Surfactans in Solution," ed. by K. L. Mittal and B. Lindman, Vol. 1, p. 175, Plenum—New York (1984).
8. A. Khan, B. Jonsson and H. Wennerstrom, *J. Phys. Chem.*, **89**, 5180 (1985).
9. a) V. Luzzati, H. Mustacchi, A. Skoulios and F. Husson, *Acta Cryst.*, **13**, 660 (1960); b) F. Husson, H. Mustacchi and V. Luzzati, *ibidem*, **13**, 668 (1960).
10. P. A. Winsor, *Chem. Rev.*, **68**, 1, (1968).
11. D. Park, J. Rogers, R. W. Toft and P. A. Winsor, *J. Colloid Interface Sci.*, **32**, 81 (1970).
12. K. Fontell, *J. Colloid Interface Sci.*, **44**, 318 (1973).
13. P. T. Callaghan and O. Soderman, *J. Phys. Chem.*, **87**, 1737, (1983).
14. I. Lundstrom and K. Fontell, *Chem. Phys. Lipids*, **15**, 1 (1975).
15. J. Rogers and P. A. Winsor, *J. Colloid Interface Sci.*, **30**, 247 (1969).
16. R. Friman, I. Lundstrom and K. Fontell, *Chem. Phys. Lipids*, **18**, 73 (1977).
17. F. B. Rosevear, *J. Am. Oil Chem. Soc.*, **31**, 628 (1954).

18. G. Chidichimo, D. De Fazio, G. A. Ranieri and M. Terenzi, *Chem. Phys. Lett.*, **117**, 514 (1985).
19. a) E. O. Stejskal and J. E. Tanner, *J. Chem. Phys.*, **42**, 288 (1965); b) E. O. Stejskal, *J. Chem. Phys.*, **43**, 3597 (1965).
20. G. Chidichimo, A. Golemme and J. W. Doane, *J. Chem. Phys.*, **82**, 4369 (1985).
21. E. Sockmann, D. Ruppel and G. Gebhardt, in "Liquid Crystals of One and Two Dimensional Order," p. 309, ed. by H. Helfrich and G. Heppke, Springer-Verlag, Berlin (1980).
22. L. H. Strenk, P. W. Westermaun, N. Vaz and J. W. Doane, *Biophys. J.*, **48**, 355 (1985).
23. J. W. Doane, in "Magnetic Resonance Studies of Phase Transitions," p. 171, ed. by F. J. Owens, C. P. Poole and H. A. Farach, Academic Press, New York (1979).
24. A. Abragam, in "The Principles of Nuclear Magnetism," p. 475, Oxford University Press, London (1961).