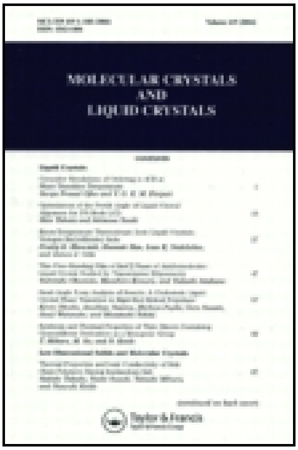

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^{2}H-NMR Investigation of Aerosol OT/Water/n-Hexane Liquid Crystalline Mixture

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^{2}H-NMR Investigation of Aerosol OT/Water/*n*-Hexane Liquid Crystalline Mixture

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Lyotropic lamellar mesophases formed by mixtures of Aerosol OT (AOT), *n*-hexane and water have been investigated by ^{2}H-NMR. The spectral profiles obtained from perdeuterated *n*-hexane depend upon the mechanical treatment of the samples. Spectra recorded immediately after centrifugation of the specimens have been compared to the ones obtained after an interval of about 15 days. Analysis of spectral profiles indicates that mechanical stress induces two effects: a reduction of the quadrupolar splitting and an asymmetry of the electric field gradient tensor acting on the deuterium nuclei. The magnitude of these effects is constant along the hexane chain, indicating a modification of the lyotropic aggregates. Data are interpreted in terms of a model in which ripples are induced on the lamellar bilayers by the mechanical treatment. Results are in agreement with the behaviour observed in the lamellar mesophase of the two component system AOT/Water.

Keywords: lyotropics, aerosol OT, NMR

I. INTRODUCTION

The study of the structure of lyotropic mesophases has recently drawn an increasing attention.[1–3] Within this field, the occurrence of defects and deformations in the "ideal" structures has attracted the interest of several researchers.[4–6] In fact, such structural features not only can be important for their influence on the properties of the mesophase, but also, in some cases, they can be associated with the onset of a different phase. One system that proved to be suitable for investigating structural deformations is the one formed by sodium-bis-2-hetylhexyl sulfosuccinate, also known as Aerosol OT (AOT), and water. Several studies of this system exist,[7,8] including the ones regarding its phase diagram,[9] x-ray diffraction experiments[10] and water diffusion measurements[11] but nevertheless, some features of the system are not yet understood. In particular, the peculiar viscosity change observed after stirring or other mechanical manipulations of the system, has only recently become a subject of investigation.[12]

In this case, a ^{2}H-NMR investigation[12] of the AOT/D_2O system, combined with water diffusion data, suggested that lamellar aggregates can become rippled under the mechanical action introduced by centrifugation, or simply by shaking. Such a conclusion was mainly drawn on the basis of the time evolution of the shape and the width of ^{2}H-NMR spectra of deuterated water after centrifugation. Water molecules, however, can diffuse, during the NMR measurement time, for distances which are much larger than the dimensions of simple amphiphilic aggregates. As a consequence, their average orientation will not only be influenced by the specific features of a single aggregate but also by the presence of aggregates which may be different in size, shape or in the extension of geometrical defects. For these reasons the ^{2}H-NMR spectral profiles obtained from D_2O in lyotropic systems do not generally allow to distinguish between the simultaneous presence of different types of aggregates and the presence of a single kind of aggregate with several regions of different curvature. We can discriminate between these two cases if we follow the orientational properties of molecules which do not exchange among different aggregates during measurements.

With this purpose, and in order to have a clearer view of the structural features of the mesophases formed by AOT, we decided to study the three component lamellar mesophase formed by mixing AOT, water and *n*-hexane. We recorded ^{2}H-NMR spectral profiles from perdeuterated hexane molecules, which are expected to dissolve in the hydrophobic core of the lyotropic aggregates and to exchange among aggregates with a typical time which is much longer than the NMR measurement. The addition of a small amount of *n*-hexane does not substantially affect the macroscopic properties under mechanical stress and the phase diagram. Viscosity, for example, increases enormously when a sample kept at rest for a long time (days) is shaken or centrifuged, both with and without *n*-hexane. The phase diagram of the AOT/water/hexane system is also essentially the same as in the AOT/water system,[13] at least for *n*-hexane concentrations below 10%.

II. EXPERIMENTAL

The surfactant AOT was purchased from Carlo Erba and it was used after a two stage purification. The salt was first dissolved in hot methanol and the resulting solution was cooled, filtered and vacuum dried. The same process was repeated using hexane instead of methanol. This procedure was repeated twice. The final product was an anhydrous, waxy paste. Hexane and deuterium depleted water were purchased from Merck. Deuterated hexane was prepared by isotopic exchange from the protonic species, which was kept for a full week under a D_2 pressure of 5 atm. at 80°C. The deuterium enrichment was verified to be 80% by comparing the ^{1}H-NMR spectra of the deuterated and the protonic species.

Samples for NMR measurements were prepared by weighing the appropriate amounts of products in 10 mm glass tubes. Tubes were sealed in order to avoid composition variations during the subsequent homogenization procedure, which was accomplished by alternatively heating and centrifuging the samples. Before recording spectra, samples were kept at rest for one month, in such a way that the structural modifications induced by the mechanical manipulations could completely relax. Spectra were first recorded from relaxed samples, which were then centrifuged at 50 Hz for 1 minute before the NMR experiment was repeated. ^{2}H-NMR spectra were recorded on a Bruker WM 300 spectrometer, operating on deuterium at 46.05 MHz. The quadrupolar echo technique[14] was used for data acquisition and a number of scans ranging between 3000 and 5000 was necessary to achieve a good signal to noise ratio.

III. RESULTS AND DISCUSSION

Spectra of the perdeuterated hexane in ternary mixtures containing a fixed amount of 5.5 wt % of hexane-d_{14} are shown in Figure 1. This figure illustrates the spectra obtained from samples having different compositions (the AOT percentage is indicated). On the same line, the spectrum obtained from a relaxed sample is compared with the one recorded from the same sample after centrifugation. Before entering into the detailed discussion of the ^{2}H-NMR powder patterns, we notice that a very small, sharp central peak is always present in the spectra. We ignore the origin of this spectral component. Perhaps it is due to hexane vapors in equilibrium with the lyotropic mixture.

Let us discuss, first of all, spectra 1–5 (left column in Figure 1) recorded from the relaxed samples. Spectra 2–5 clearly consist of a superposition of three different powder pattern components.[15] Each component can be connected with one of the three inequivalent deuteriums of *n*-hexane: the methyl ones and the ones on methylenes 2 and 3. The difference in the width of each powder is due to the different conformational motions of the various segments of the carbon chain. Figure 2 shows the quadrupole splittings of the three different deuteriums species as a function of the AOT concentration. The quadrupolar splitting, for a deuterium powder spectrum, is the difference in frequency between the two outer shoulders. It is trivial to attribute the central isolated spherical powder pattern to the methyl deuterons since such chain terminals must undergo a more efficient conformational motional averaging (rotation around the C–CD$_3$ bond) with respect to the methylene deuterons. Following the same line we can conclude that the larger splitting should be attributed to the central methylene deuterons.[16] It is important to notice from Figure 2 that the relative magnitude of the different splittings is constant over the whole concentration range. This is an evidence that the conformational motions of *n*-hexane do not change at different AOT concentrations and depend only on the phase features. It should be also mentioned that the splittings show two jumps around 30% and 40% AOT, confirming the observation[10] that at room temperature it is possible to identify three concentration ranges in the lamellar mesophase.

We have computer simulated spectra 3 and 5 in Figure 1 taking into account that the spectral frequencies associated with the ith deuterium group are given by[17]

$$\nu_i^{\pm} = \nu_i^0 \pm \frac{3}{4}\nu_{Q(i)}\left(\frac{3\cos^2\theta - 1}{2} + \frac{\eta_i}{2}\sin^2\theta\cos 2\phi\right) \qquad (1)$$

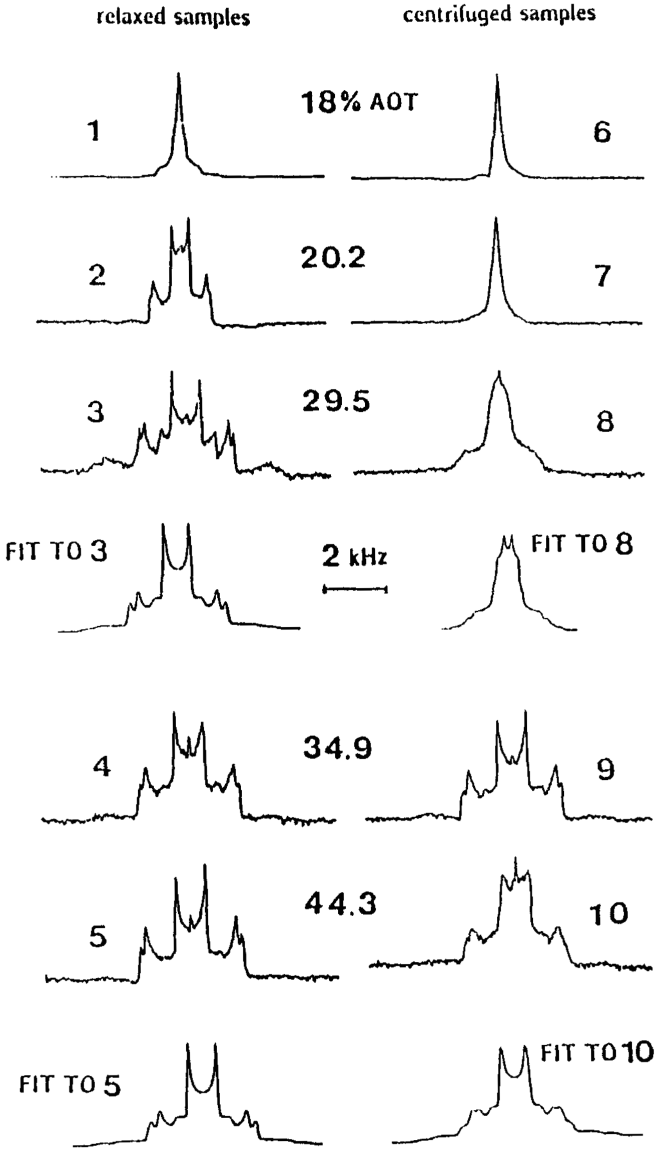

FIGURE 1 ^{2}H-NMR spectra of *n*-hexane d_{14} in AOT/Water/Hexane lyotropic mixtures. The AOT weight concentration is reported and the *n*-hexane content is 5.5 wt% for all samples.

where ν_i^0 represents the Larmor frequency of the nucleus and θ and ϕ are the polar angles which define the orientation of the static magnetic field in the principal axes system of the averaged electric field gradient tensor on the nucleus. $\nu_{Q(i)}$ and η_i are the averaged quadrupole coupling constant and the motionally induced asymmetry parameter, respectively. In the case of spectra 3 and 5 a good fitting has been achieved by assuming $\eta = 0$ for all the observed nuclei. This confirms that the corresponding mesophases are uniaxial, as expected for regular lamellar sys-

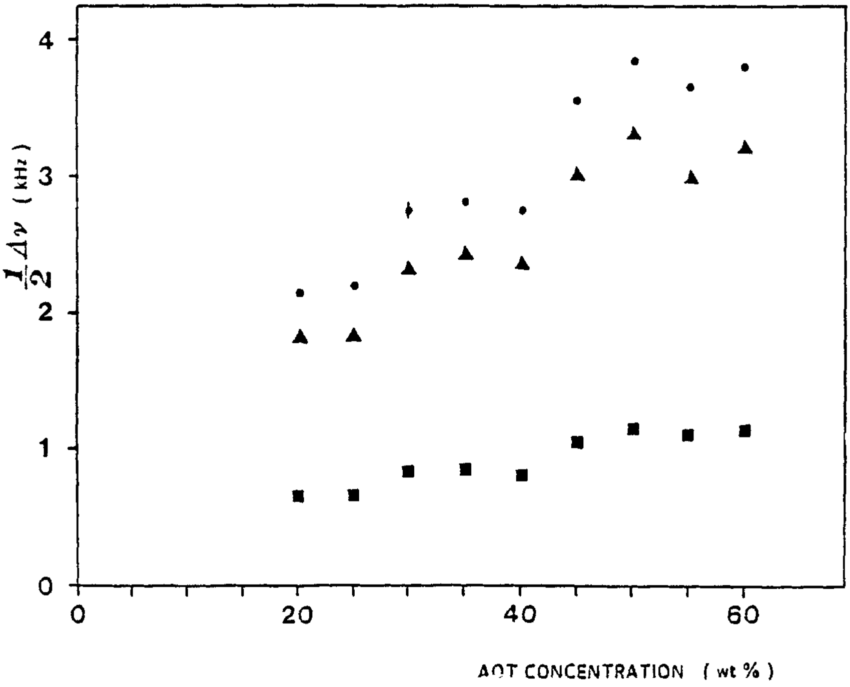

FIGURE 2 The three different quadrupolar splittings measured from perdeuterated *n*-hexane in AOT/Water/Hexane mixtures as a function of the AOT content.

tems. Such a feature can be observed in the relaxed systems for AOT concentrations above 20% but it is lost for lower AOT content. For example, the shape of the spectrum obtained with 18% AOT is very far from a uniaxial spherical powder pattern. This particular spectral profile is instead more similar to the ones recorded from centrifuged samples at low AOT content. In general, as shown in Figure 1, the uniaxial powder patterns observed for relaxed systems evolve into asymmetrical, narrower spectral profiles as a consequence of mechanical stress. This behaviour was also observed in the D_2O spectra in the AOT/Water binary system,[12] and it was linked to a ripple mechanically induced deformation of the aggregates. We can then think that the same kind of deformations are spontaneously occurring in the relaxed samples at low AOT concenetration or that, in this concentration range, they relax in a much longer time. This fact is also indicated by the observation that the viscosity of the samples with AOT concentration below 20% is always rather high even if they are relaxed.

The choice of a model to explain the features of our relaxed system is linked to several considerations. First of all it has been shown[12] that water diffusion is higher in the relaxed system, which is a lamellar phase. This rules out the possibility of any breaking of the lamellae as a consequence of shaking. Then we have to consider that the biaxiality, already observed in the water spectra, is also present in the hexane spectra. Since the diffusion of these molecules is restricted to a single aggregate, at least during the ^{2}H-NMR measurement time, biaxiality must be a consequence of the shape of the single aggregate. Another experimental evidence to consider is the large increase in the viscosity of the samples after shaking. A model that considers rippled bilayers, i.e., bilayers which are continuous but not flat, as shown in Figure 3, is in agreement with all these experimental observations. In fact, in rippled bilayers water diffusion is lower than in plane bilayers, the ^{2}H-NMR spectrum from a molecule diffusing inside the rippled bilayer is biaxial[18] and the increase of the viscosity can be explained with the fact that a rippled bilayer cannot slide over the other one.

We have reproduced the spectral profiles 8 and 10 in Figure 1 by assuming the same asymmetry parameter for the three different types of deuterium nuclei in *n*-hexane. We also assumed that the quadrupole coupling constant in the centrifuged samples, $\nu^C_{Q(i)}$, could be obtained by scaling the corresponding coupling constants measured in the relaxed samples, $\nu^R_{Q(i)}$:

$$\nu^C_{Q(i)} = f\nu^R_{Q(i)}, \tag{2}$$

f being the scaling factor. A good agreement could be obtained between experimental and calculated powder patterns for the values of η and f reported in Table I. In the same table the value of $1/(1 + \eta)$ is listed. It has been shown[12] that, if the induced modification is of the type described in Figure 3, the reduction of the spectral width due to the molecular diffusion across the rippled structure must be linked to the asymmetry parameter of the averaged electric field gradient tensor by:

$$f = \frac{1}{1 + \eta}. \tag{3}$$

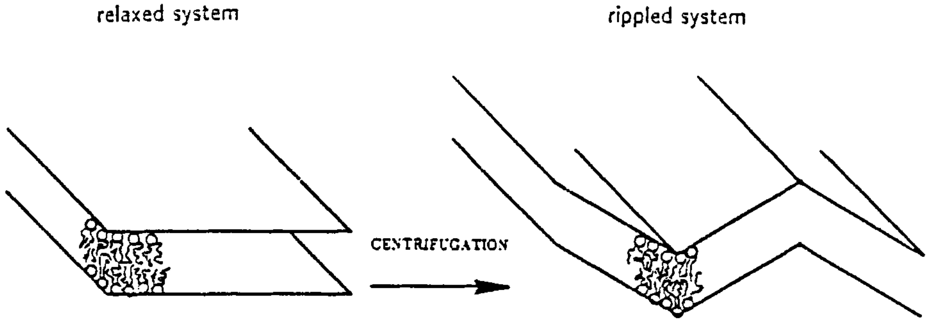

FIGURE 3 Schematic illustration of the ripple deformation induced on the lamellar bilayers by centrifugation.

TABLE I

Values of η and $f = \nu^C_Q/f^R_Q$ used to reproduce spectral profiles 8 and 10 obtained from centrifuged samples

Sample	η	f	$1/(1 + \eta)$
8	0.5	0.56	0.67
10	0.12	0.97	0.89

Considering the oversimplifications of the model, the agreement is quite good, being the difference between f and $1/(1 + \eta)$ only ~10%, of the same order than for the water data.[12]

It should be pointed out that the same scaling factor f has been used for the fitting of the three different signals whose sum results in the observed spectra. This is a further indication of the absence of any influence of centrifugation on the conformational motions of *n*-hexane. In addition, since with a single value of η and f it is possible to reproduce quite well spectra obtained from centrifuged samples, a wide distribution in the size or in the shape of lyotropic aggregates can be excluded. In fact, in this last case the fit of the spectra would have also required a distribution in η and f. Previous data[12] obtained by ^{2}H-NMR of D_2O in the same system, could not give a definite answer to this issue, as a consequence of the different diffusion properties of water and *n*-hexane.

IV. CONCLUSIONS

This study confirms that the variations of the physical properties introduced by centrifugation of the AOT/Water lamellar system are due to modifications of the layers. Data are in good agreement with a model which considers rippling of the bilayers. A dispersion in the shapes or in the sizes of the aggregates can be excluded by the evidence that spectral profiles of deuterated *n*-hexane in the mechanically stressed samples can be reproduced starting from those of the relaxed systems and introducing a single scaling factor f and a single asymmetry parameter η.

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