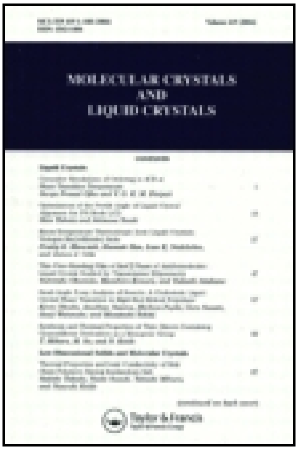

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The Structure of a Lyotropic Liquid Crystalline Phase that Orients in a Magnetic Field

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The Structure of a Lyotropic Liquid Crystalline Phase that Orients in a Magnetic Field

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The structure of a lyotropic liquid crystalline phase with positive diamagnetic anisotropy (type I), that spontaneously orients in a magnetic field has been studied by means of water NMR quadrupole splittings, NMR diffusion and polarized absorption spectroscopy. It is concluded that this phase is built up of long rodlike aggregates. A preliminary study of a sample with negative diamagnetic anisotropy (type II) shows that this phase probably consists of lamellar aggregates. It is suggested that these phases are suitable as orientation matrices for studies of chromophores with polarized light spectroscopy.

INTRODUCTION

About ten years ago Lawson and Flautt[1,2] discovered that some lyotropic liquid crystalline phases are able to orient spontaneously in a magnetic field when an electrolyte is added. Since then several studies of this type of systems have been reported.[3–6] The most important application of such phases is to use them as order matrices for solute molecules for nuclear magnetic resonance (NMR) studies.[3–5] These phases have the great advantage compared with, e.g. thermotropic liquid crystalline systems, that both lipid and water soluble substances can be conveniently dissolved in the system. Usually thermotropics have high solubility for hydrophobic compounds only. Although these lyotropic systems have been utilized and studied extensively, their phase structure has not yet been fully established.

In this communication we have attempted to determine the structure for one of these lyotropic mesophases that orient in a magnetic field. The samples studied have positive diamagnetic anisotropy (type I).[6] We have utilized several spectroscopic techniques such as deuteron NMR, pulsed NMR for diffusion studies and polarized absorption spectroscopy.

EXPERIMENTAL

The samples studied contained sodium decylsulfate, sodium sulfate and heavy water. Their compositions were taken from Ref. 6 and the method of preparation was the same. The samples were macroscopically aligned in two ways; (i) by placing the sample tube in a magnetic field, (ii) by pressing the sample between glass plates.[7] It should be noted that in the first alternative the samples kept the orientation for several hours after being removed from the magnetic field.

^{2}H NMR spectra were recorded at 15.351 MHz on a Varian XL 100 NMR spectrometer operating in the FT mode. To obtain a typical spectrum usually about 500 transients were accumulated.

The amphiphile diffusion studies were performed with a technique based on a standard NMR method[8] for measurements of diffusion coefficients in systems, where high resolution NMR spectra are observed. Normally such spectra are not obtained for an anisotropic liquid crystalline system. However, by a macroscopical alignment of the mesophase, high resolution spectra can be observed by orienting the sample so that the director (the symmetry axis) and the magnetic field direction make an angle of 54.7° (the "magic angle"). With such an oriented sample the conventional pulsed NMR technique with pulsed magnetic field gradients may be used to determine the diffusion coefficients.[9,10] The experimental equipment was a Bruker 322s pulsed NMR spectrometer supplemented with a homebuilt pulsed magnetic field gradient unit. The diffusion coefficient is obtained from the attenuation, E_g/E_0, of a spin echo by varying the strength of the magnetic field gradients (δ or g) or the distance, Δ, between them according to the relation derived by Stejskal and Tanner[6]

$$\ln \frac{E_g}{E_0} = (\gamma g \delta)^2 D \left(\Delta - \frac{\delta}{3} \right)$$

where δ is the width and g the height of the magnetic field gradients, γ is the gyromagnetic ratio and D is the diffusion coefficient. Typical settings in an experiment are $\Delta = 15$ ms, $\delta = 2$ ms, while g varies between 0 and 2.5 T m^{-1}. All measurements were performed relative to a glycerol reference with a known diffusion coefficient.[11] The probe temperature was 28°C throughout. Polarized absorption spectra were obtained from samples that had been kept in a magnetic field for at least 12 h. These mesophases contained a small amount of dissolved retinal. The spectrometer used was a Varian, Cary 219. The absorption spectra were recorded with the linear polarizers parallel ($A_{\parallel}$ mode) and perpendicular ($A_{\perp}$ mode) to the magnetic field, **B**. Polarized absorption was also recorded for retinal in some lamellar liquid crystals aligned between glass plates.

RESULTS AND DISCUSSION

Water ^{2}H NMR studies

The orientation in a magnetic field of a sample with the composition 39.8% sodium decylsulphate, 4.5% Na_2SO_4 and 55.7% ^2H_2O (weight percentage) was monitored by observing the change of the deuteron quadrupole splitting with time. For a fully oriented sample the deuteron NMR spectrum consists of two equally intense peaks with the separation $\Delta(\theta)$, the quadrupole splitting, given by[12, 13]

$$\Delta(\theta) = |\Sigma p_i \nu_Q^i S_i (3\cos^2\theta_{LD} - 1)| \tag{1}$$

where p_i, is the fraction of deuterons in site **i**, $\nu_Q^i = \frac{3}{4}\chi$ (χ is the quadrupole coupling constant), S_i is an order parameter describing the average orientation of the water molecules in the site **i** with respect to the director and θ_{LD} is the angle between the z-axes of the laboratory and the director coordinate systems.

For a nonoriented (powder) spectrum the quadrupole splitting becomes:

$$\Delta = |\Sigma p_i \nu_Q^i S_i| \tag{2}$$

Figure 1 illustrates how the ^{2}H NMR spectrum changes with time. From this figure it can be seen that the initial spectrum has a shape typical of a powder sample. The spectrum gradually changes with time to a shape typical of an oriented sample having two sharp peaks. If the oriented sample is rotated 90° around the NMR tube axis the spectrum in Figure 2 is obtained. In this spectrum the quadrupole splitting is reduced to one half of its original value before the sample was rotated. Equation 1 then shows that the director of the *oriented* sample lies parallel with the applied magnetic field, **B**.

Samples were also macroscopically aligned between glass plates. Some typical NMR spectra obtained at different discrete angles between the normal to the glass plate and the magnetic field are shown in Figure 3. It can be inferred from this figure that the NMR spectra have characteristic shapes at different angles. Similar spectra have recently been obtained for a hexagonal phase aligned between glass plates.[14, 15] From a simulation of these spectra it

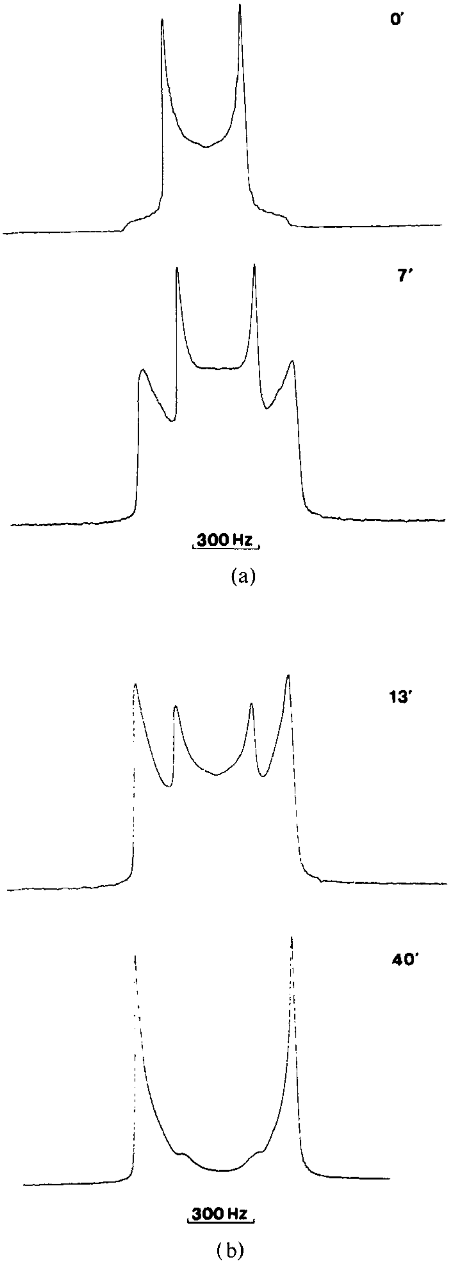
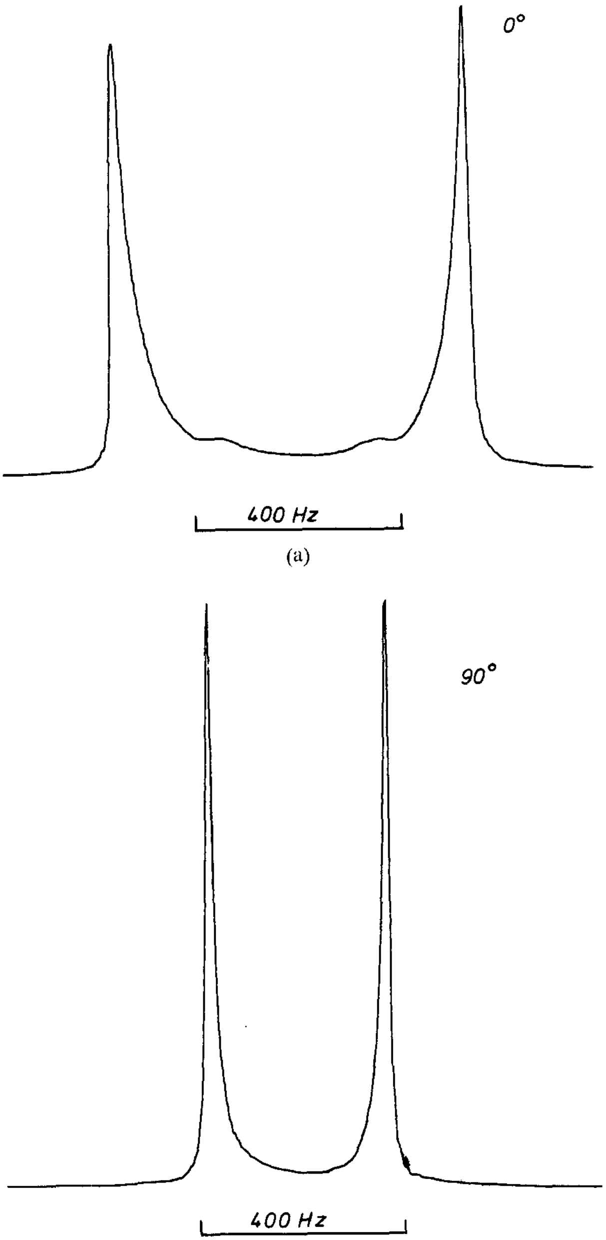


FIGURE 1 ^{2}H NMR spectra of ^2H_2O at different time intervals, going from a typical powder pattern at 0' and ending with an oriented sample after 40' in the magnet. All spectra are for a type I sample.



(a)

(b)

FIGURE 2 ^2H NMR quadrupole splittings of ^2H_2O for a type I sample, oriented with the director parallel (a) and perpendicular (b) to the magnetic field after a rotation of the oriented sample by 90°. The difference in the splittings obtained is equal to 2.

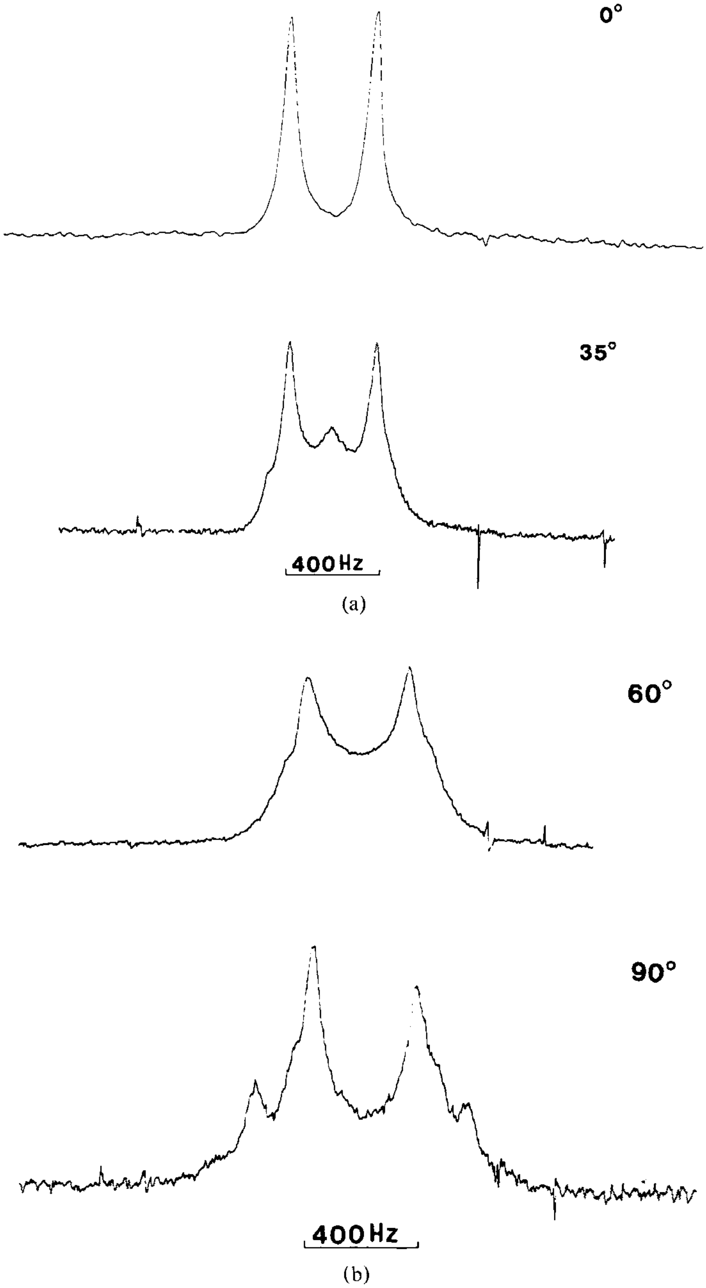


FIGURE 3 ^{2}H NMR quadrupole splittings for a type I sample macroscopically aligned between glass plates and oriented at different approximate angles in the magnetic field.

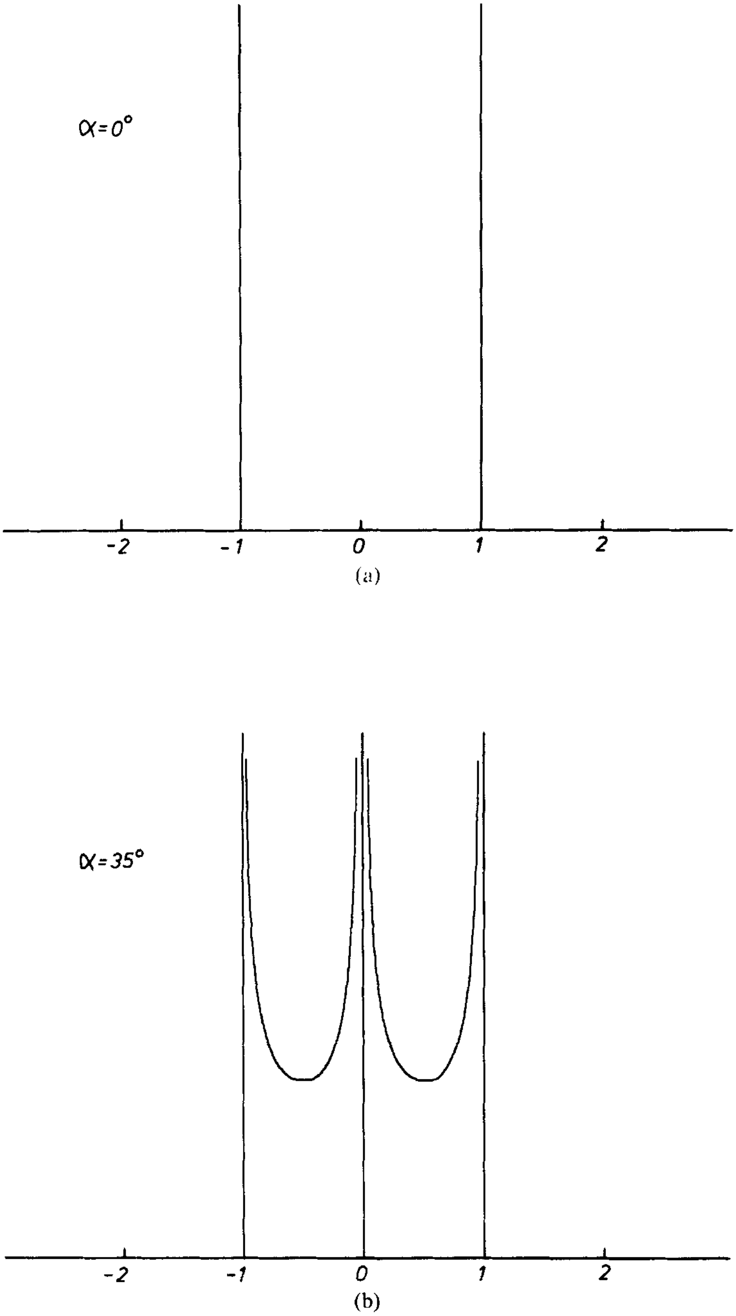
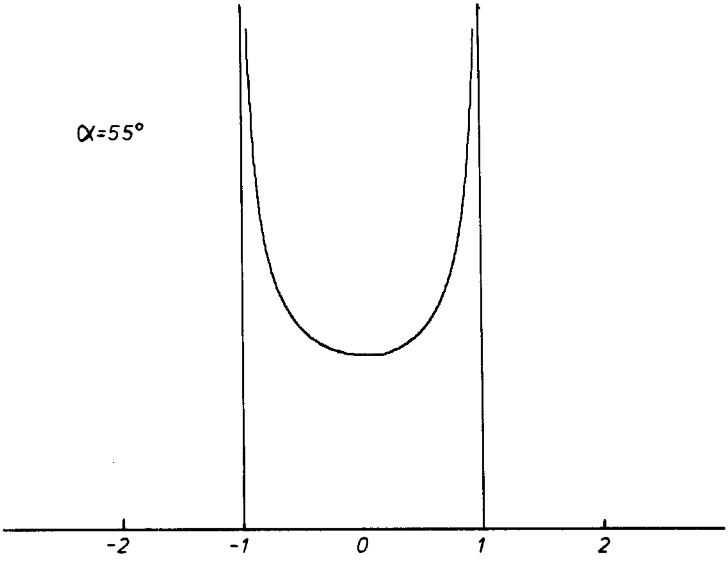
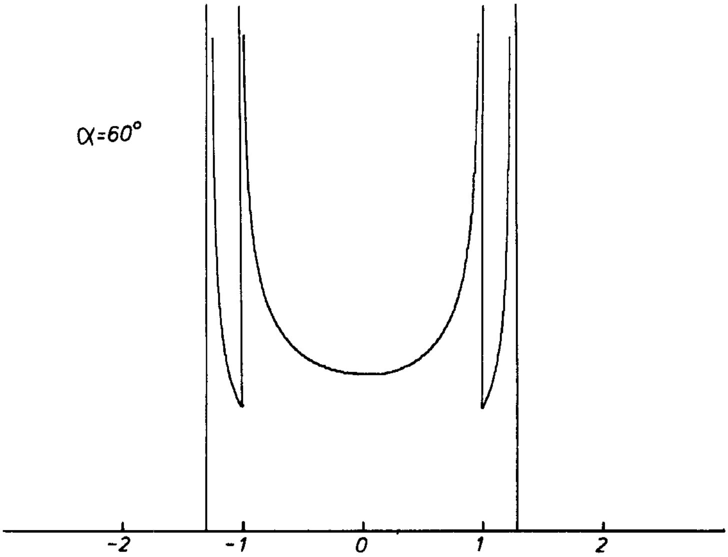


FIGURE 4 *continued*

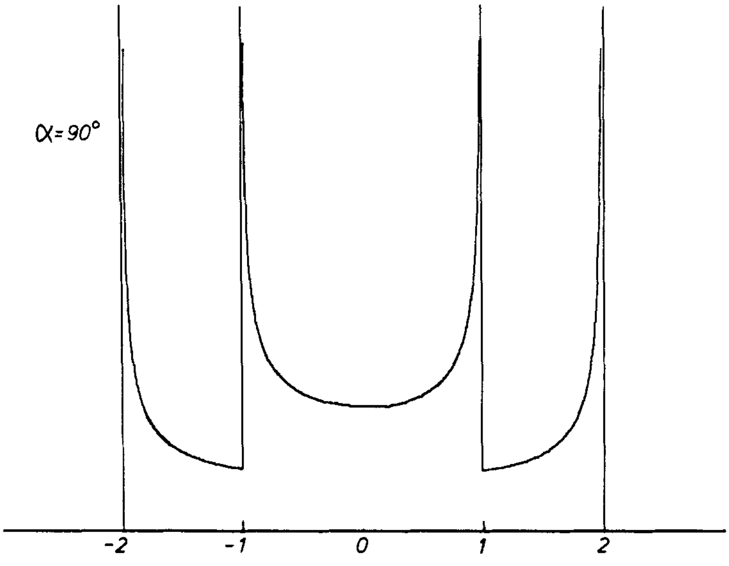


(c)



(d)

FIGURE 4 *continued*



(e)

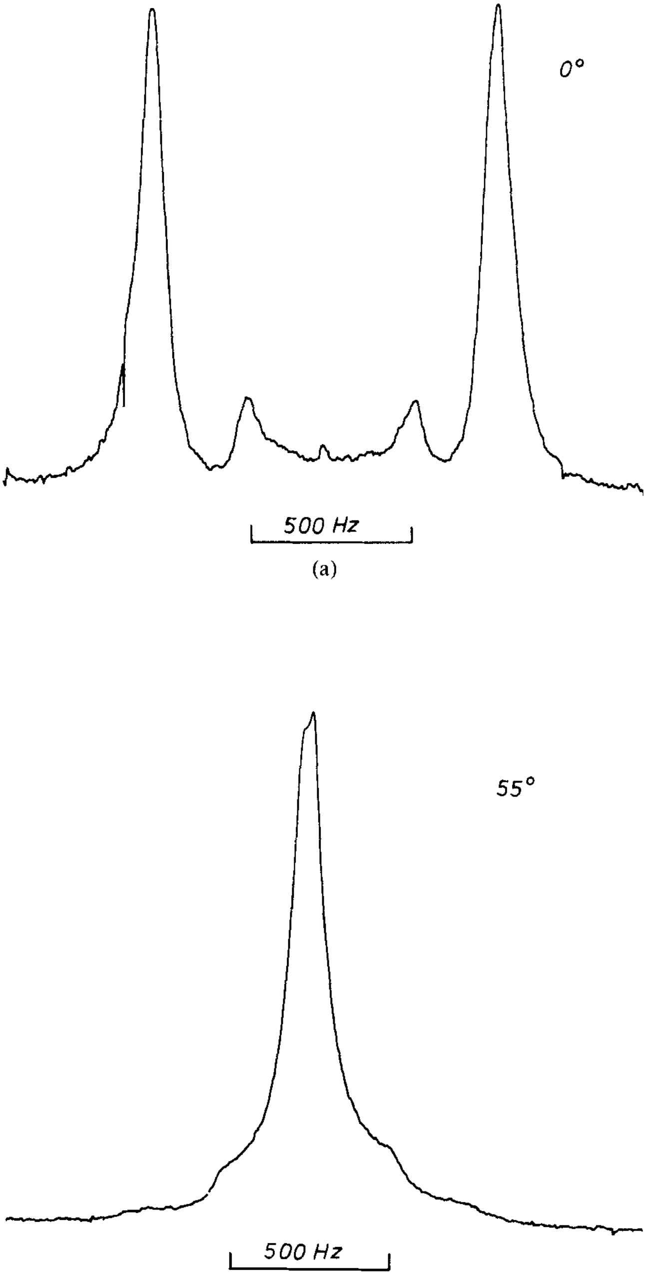
FIGURE 4 Simulated spectra for a sample having its directors randomly oriented in the plane of the glass plates. The glass plates are oriented at different angles α in the magnetic field as in Figure 3 (see text for details). The frequency scale is in units of $4\nu/3\chi \cdot S$.

was concluded that the director is randomly oriented in the plane of the glass plates. We have simulated spectra with the director randomly oriented in a plane, using the equations for the line shape $g(\nu)$ as derived by Wennerström.[16]

$$\begin{aligned}
g_+(x) &= \left(\frac{1+x}{3}\right)^{-1/2}\left(\sin^2\alpha - \frac{1+x}{3}\right)^{-1/2}; \; -1 \le x \le 3\sin^2\alpha - 1 \\
g_-(x) &= \left(\frac{1-x}{3}\right)^{-1/2}\left(\sin^2\alpha - \frac{1-x}{3}\right)^{1/2}; \; 1 - 3\sin^2\alpha \le x \le 1 \qquad (3) \\
g(x) &= g_+(x) + g_-(x)
\end{aligned}$$

where $x = 4\nu/3\chi S$ and α is the angle of rotation of the plates in the magnetic field. Figure 4 shows spectra calculated from the above equations for some discrete α-values.

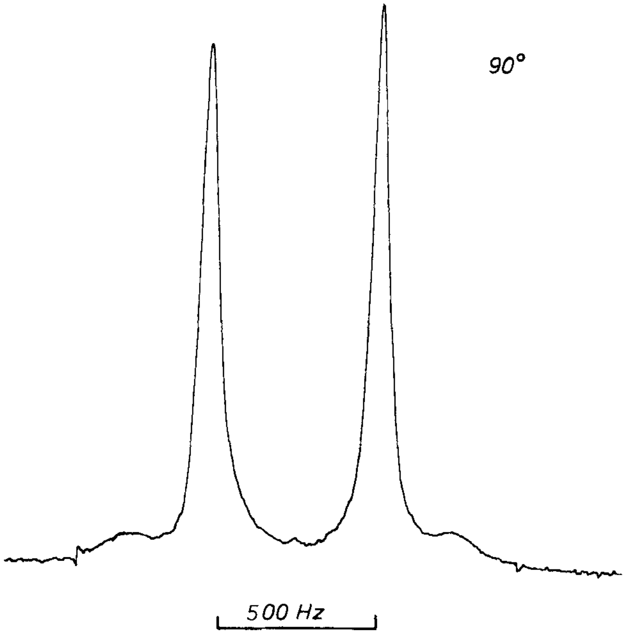
Thus Figures 3 and 4 strongly indicate that the director is randomly oriented in the plane of the glass plates. A similar preliminary study of samples with negative diamagnetic anisotropy (type II) (sodium decylsulfate, sodiumsulfate, decanol, heavy water) suggests that in this case the director is perpendicular to the glass plates (Figure 5).



(a)

(b)

FIGURE 5 *continued*



(c)

FIGURE 5 ^{2}H NMR splittings of ^2H_2O for a type II sample macroscopically aligned between glass plates. These spectra are in agreement with a lamellar phase aligned parallel to the glass plates.

Polarized absorption studies

In order to gain further information on the structure of the amphiphilic aggregates building up the type I phase we have also performed polarized absorption studies of the orientation of a solubilized hydrophobic chromophore, retinal. The results obtained for the type I phase were then compared with orientation studies of retinal in some lamellar liquid crystalline phases. These latter samples were macroscopically aligned between glass plates and the aligned lamellae were then studied in the light spectrometer at an inclined incidence of linear polarized light as illustrated in Figure 6 (*cf.* also Ref. 17 and 18). The dichroic ratio, D_ω, for a lamellar sample, having the angle ω between the direction of the propagation of light and the normal to the lamellae is given by the equation

$$D_\omega = \frac{A_\omega}{A_\perp} = 1 + 3S(1 - S)^{-1}n^{-2}\sin^2\omega \qquad (4)$$

where S is the order parameter and n is the refractive index of the lamellar phase. A_ω and $A_\perp$ are the measured absorbances with the electric field

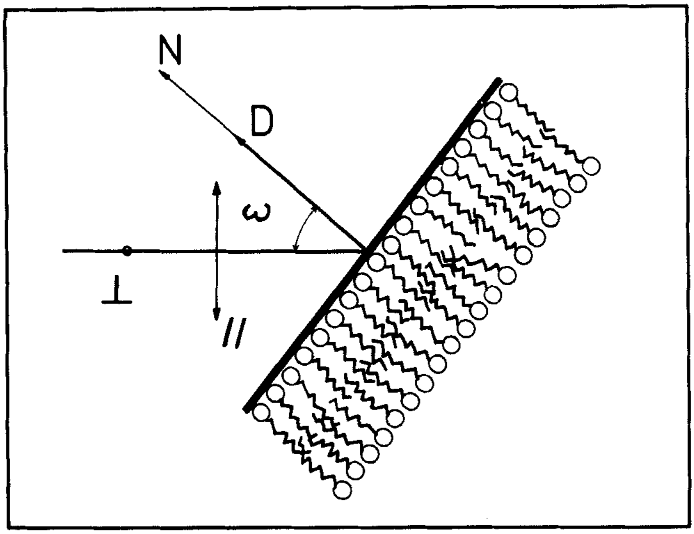


FIGURE 6 Schematic picture showing the polarizations and the direction of propagation of the incident light with respect to the normal N of the plates. The normal coincides with the director, D, of the lamellae.

vector of light forming the angles ω and $\pi/2$ relative to the director, respectively. For a lamellar sample composed of 16.94% w/w sodium octanoate, 35.77% w/w decanol, 47.29% w/w water and spurious amounts of retinal we obtained $S = 0.41 \pm 0.02$ ($n = 1.43$). Samples containing sodiumoctyl sulphate, decanol and water gave order parameters of similar values. The dependence of S on the composition was found to be small at these high water contents (Johansson, L. B.-Å., Soderman, O., Fontell, K. and Lindblom, G., to be published.) Thus the retinal molecule is highly oriented in these lamellar phases, probably due to its aldehyde group which is more or less "anchored" at the polar-nonpolar interface of the lamellae.

Figure 7 summarizes the data obtained from polarized absorption studies on retinal solubilized in small amounts in a type I sample oriented in a magnetic field, **B**. Two different field strengths have been used, namely 2.3 T and 6 T. For the latter field strength a superconducting magnet was used, where the sample tube axis is along the magnetic field instead of perpendicular to it as for 2.3 T, and therefore the orientation of the director of the sample is perpendicular to each other in the two cases. The order parameter is related to the measured absorbances, $A_\parallel$ (parallel to the director) and $A_\perp$ (perpendicular to the director) through the dichroic ratio, ψ (i.e. $\omega = 90°$ in Eq. 4)

$$D = \frac{A_\parallel}{A_\perp} = \frac{1 + 2S}{1 - S} \tag{5}$$

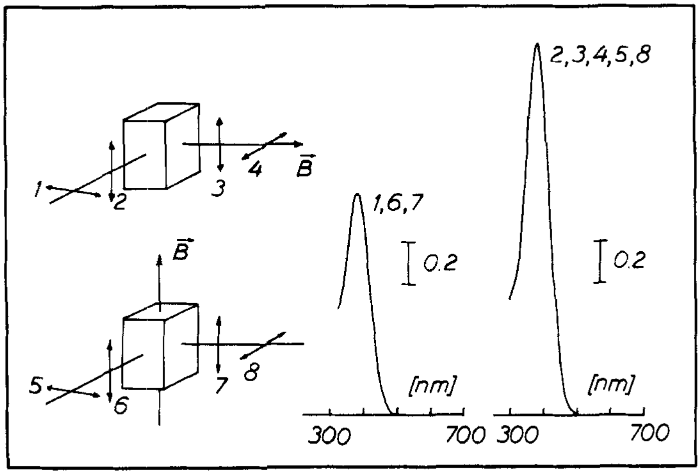


FIGURE 7 Absorbance of retinal solubilized in a type I sample measured with different directions of the linear polarization relative to the magnetic field vector, **B**. Two different magnetic field strengths have been utilized namely 2.3 T and 6 T, represented by the upper left and the lower left drawings, respectively.

The order parameter obtained in the experiments at both magnetic fields was found to be equal to -0.17 (± 0.02). It should also be noted, as can be seen in Figure 7, that the absorbance, when the incident light is along the magnetic field, i.e. along the director, is independent of the polarization direction.

Spectroscopic,[12,19] NMR diffusion[10] and thermodynamic[20] observations strongly indicate that the local environment for an amphiphilic molecule is the same in a rodlike and a lamellar aggregate. Assuming that this is true also for retinal, the order parameters for the sample with rodlike aggregates is $-\frac{1}{2}$ of that for the lamellar liquid crystalline sample. We obtain -0.17 for the type I phase as compared to 0.41 for a lamellar sample. This, together with our NMR data, strongly indicate that the type I phase structure consists of rodlike aggregates.

NMR diffusion studies

We have also investigated whether the rodlike aggregates of the type I phase extend only over a small distance or if they have lengths of macroscopical distances. In previous works,[9,10,15] we have shown that such problems are best tackled by studying the amphiphile translational diffusion using pulsed NMR with pulsed magnetic field gradients. The diffusion coefficient along the rodlike aggregates was determined for a macroscopically aligned sample in a magnetic field. The aligned sample was oriented in the magnet so that the angle between the director and the magnetic field was equal to the "magic angle", 54.7°. By applying magnetic field gradients over the sample the diffusion coefficient was obtained from the spin echo as described in the experimental section. The amphiphile diffusion coefficient along the rods was determined with this method and was found to be $D_L = 8.7 \cdot 10^{-11}$ m^2/s. This value compares well with the lateral diffusion coefficient previously determined for octylsulphate in a lamellar mesophase.[9] Since no restricted diffusion is observed it can be concluded that the rods must be quite long and by using, $\langle x^2 \rangle = 2Dt$, the length of the rods can be estimated to be longer than 2000 nm.

CONCLUDING REMARKS

Taken together, all our findings strongly indicate that the type I phase consists of long rodlike aggregates (in agreement with the location in the phase diagram). These rods orient themselves along the magnetic field direction (or, when glass plates are used, randomly in the plane of the glass plates). It is hard to conceive of any other structure that will explain all our experimental results. Our preliminary results suggests that the type II structure consists of lamellar aggregates.

Finally, it should be noted that magnetically orientable lyotropic mesophases are very suitable to use as matrices for studies of oriented polar molecules not only with NMR but also with polarized light spectroscopy methods.

Acknowledgements

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