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Investigation of the Ribbon Structure of a Lyotropic Liquid Crystal by Deuterium Nuclear Magnetic Resonance

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This paper reports observation, in a mixture of potassium palmitate-d_3, potassium laurate, and water, of a lamellar phase above 41°C, a phase of elongated cylindrical aggregates below 36°C, and, in the intermediate temperature region, a phase in which the ^{2}H-NMR spectral patterns can be calculated from a model of elongated ribbon-shaped aggregates. The size of the ribbons can be determined from the spectra and is found to vary with temperature. The results are consistent with ^{2}H-NMR spectra of ^2H_2O in the same and other ternary mixtures.

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Lyotropic phases intermediate in concentration or temperature between the lamellar and hexagonal phases (elongated cylindrical aggregates) have been of current interest.[1-3] Some of these studies have been stimulated by the recent discovery of a biaxial lyotropic nematic found to exist in a short temperature interval between nematic phases of type I (elongated aggregates) and of type II (lamellar aggregates).[4] One such study is that of Hendrikx and Charvolin,[2] who have examined the phase diagram of the ternary system sodium decyl sulfate/1-decanol/water over a concentration range around that which forms lyotropic nematics. In an x-ray study they found a range of concentrations which revealed a centered rectangular lattice. From their measured values for the lattice parameters and from known concentrations of amphiphile and water they inferred a structure of elongated ribbonlike aggregates. By altering the relative concentration of decanol and sodium decyl sulphate they could then obtain the lamellar or hexagonal structure of elongated cylindrical aggregates.

In this study we use a different ternary mixture, namely 63 wt.% potassium palmitate-d_3, 7 wt.% potassium laurate, and 30 wt.% water from which we also observe a structure of elongated ribbonlike aggregates. In this system, however, we find polymorphic behavior directly as a function of temperature which allows us to more conveniently study the aggregates with deuterium NMR and compare the spectral patterns they exhibit with those of the lamellar phase and the hexagonal phase.

Experimental ^{2}H-NMR spectral patterns from the deuterated methyl site of potassium palmitate-d_3 are shown in Figs. 1(a)–1(d) for three different phases. We have also recorded the ^2H_2O deuterium spectral patterns from identical samples [Figs. 1(g) and 1(h)].

Above 41 °C uniaxial patterns (i.e., with asymmetry parameter $\eta = 0$) such as that shown in Fig. 1(a) are characteristic of that observed for the deuterated methyl group of potassium palmitate-water mixtures in the lamellar phase.[5,6] X-ray measurements have confirmed the lamellar structure.[7] The ^2H_2O signal at these temperatures, shown in Fig. 1(g), is also characteristic of a lamellar phase.

At temperatures below 36 °C spectral patterns such as that shown in Fig. 1(d) with a value of $|\nu_Q|$ approximately one-half that of the lamellar phase are characteristic of those observed for elongated cylindrical aggregates observed in oth-

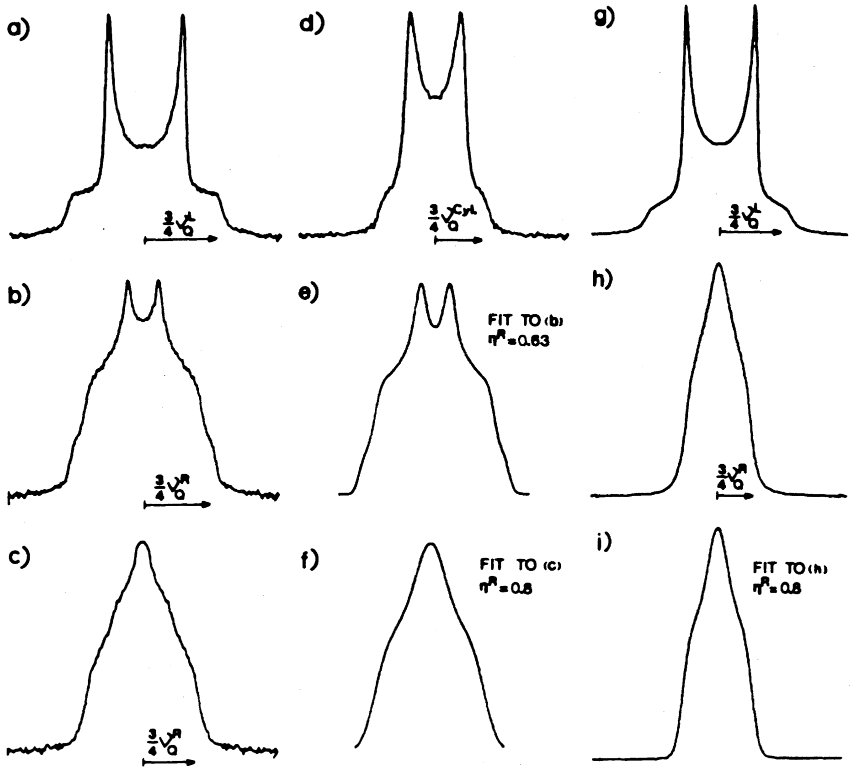

FIG. 1. Recorded and fitted deuterium NMR spectral patterns from potassium palmitate-d_3 in a mixture with 7 wt.% potassium laurate and 30 wt.% water recorded within different phases: (a) the lamellar phase; (b), (c) the intermediate phase; (d) the cylindrical aggregates phase. (e), (f) Theoretical fitted spectra corresponding to traces (b) and (c), respectively. (g), (h) Recorded spectral patterns from ^2H_2O in the lamellar-phase and the intermediate-phase region, respectively. (i) A theoretical fitted curve corresponding to trace (h). The full spectral width of the experimental traces is 10 kHz for traces (a)–(d) and 5 kHz for traces (g) and (h).

er systems such as, for example, potassium palmitate/60 wt.% water.[6-8]

In the intermediate temperature range from 41 to 36 °C we observe biaxial patterns ($\eta \neq 0$) for potassium palmitate-d_3 as shown in Figs. 1(b) and 1(c), as well as for ^2H_2O as shown in Fig. 1(h). Care had to be taken to allow sufficient time (~ 1 h) in order that the sample would reach thermal equilibrium before the data were recorded at each temperature setting. Such biaxial spectra were computer fitted by theoretical line shapes[9] following standard procedures[9] and the best fits to Figs. 1(b), 1(c), and 1(h) are shown in Figs. 1(e), 1(f), and 1(i), respectively.

In calculating the fits we consider a model for the ribbon aggregate like that illustrated in Fig. 2. The central region of the aggregate (region L) is lamellarlike whereas the sides of the ribbon (region C) are formed by a bisected cylinder. When a molecule is in the lamellar region the principal axis, z_l, of the electric field gradient associated with the deuterium quadrupole interaction is normal to the bilayer whereas when the molecule is in region C the principal axis z_C is along the axis of the cylinder.

We now recognize that the dimensions of the cross section of the ribbon are small compared to the distance through which a molecule will diffuse during the time scale of the NMR measurement. A diffusing molecule will therefore sample both regions of the ribbon many times to yield a time-averaged quadrupole interaction with a principal-axis frame x,y,z, as illustrated in Fig. 2. Following the usual convention $|V_{xx}| \leq |V_{yy}| \leq |V_{zz}|$, where the V_{ii} are the components of the time-averaged electric field gradient, two cases can arise: case A, where the time-averaged principal z axis is parallel to z_L, and case B, where it is parallel to z_C.

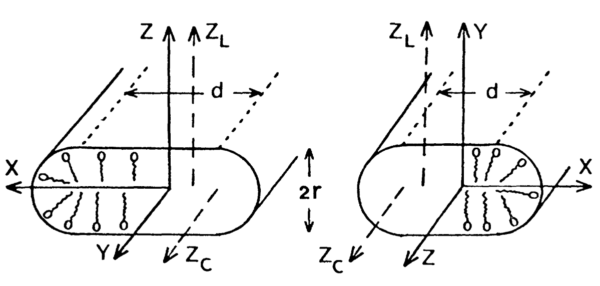

FIG. 2. Schematic view of the ribbon aggregates in two different situations accordingly to the orientation of the time-averaged principal-axis frame x,y,z of the electric-field gradient with respect to the orientation of the ribbon.

In case A, taking only the positive half of the spectral frequency, ν, and defining θ_0 and φ_0 as the polar and azimuthal angles which express the orientation of the magnetic field, $\vec{H}$, in the x,y,z frame, we obtain $\nu_L^A = \frac{3}{4}\nu_Q^L P_2(\cos\theta_0)$ and

$$\nu_C^A = -\tfrac{3}{8}\nu_Q^C[P_2(\cos\theta_0) + \tfrac{3}{2}\sin^2\theta_0 \cos 2\varphi_0]$$

in regions L and C, respectively, where ν_Q^L and ν_Q^C are the quadrupole coupling constants and $\nu_Q^L = -2\nu_Q^C$.

In case B, the frequencies ν^B for regions L and C take on the forms

$$\nu_L^B = -\tfrac{3}{8}\nu_Q^L[P_2(\cos\theta_0) + \tfrac{3}{2}\sin^2\theta_0 \cos 2\varphi_0]$$

and $\nu_C^B = \frac{3}{4}\nu_Q^C P_2(\cos\theta_0)$, respectively.

In calculating the time average which results from molecular diffusion during the time of the experiment we introduce a probability, W, that a molecule resides in region L and a corresponding probability, $1-W$, that it resides in region C. As the molecules diffuse back and forth between region L and region C there is a switching of the frequency ν to take on eventually the average value $\bar{\nu}$ which we identify as ν_R for the ribbon phase and calculate according to[10] $\bar{\nu} = W\nu_L + (1-W)\nu_C \equiv \nu_R$. The result is a time-averaged quadrupole coupling constant, ν_Q^R, and the motionally induced asymmetry parameter, η^R, for the ribbon structure which have the form (Fig. 3, solid lines)

$$\nu_Q^R = -\frac{3W+1}{2}\nu_Q^C, \quad \eta^R = \frac{3-3W}{1+3W} \tag{1}$$

for $\frac{1}{3} \leq W \leq 1$, that is for case A, and

$$\nu_Q^R = \nu_Q^C, \quad \eta^R = 3W \tag{2}$$

for $0 \leq W \leq \frac{1}{3}$ (case B).

It is seen from Eq. (1) that, for $\frac{1}{3} \leq W \leq 1$, we have $|\nu_Q^R / 2\nu_Q^C| = 1/(1+\eta^R)$ (solid line in inset in Fig. 3). In fact, this is one test of the model in that a measured value of ν_Q^R should predict the measured value of η^R or vice versa.

It is observed that both experimental values of ν_Q^R and η^R for the lipid molecules are noticeably temperature dependent. It is therefore natural to expect that, for the lipid molecules, the time-averaged orientation of the principal-axis frame x, y, z satisfies case A since only then both ν_Q^R and η^R may vary simultaneously (Fig. 3). Further evidence for this choice can be obtained by plotting $|\nu_Q^R / 2\nu_Q^C|$ vs η^R as shown in the inset in Fig. 3 (crosses) to observe a reasonable agreement with the theoretical curve described by Eq.

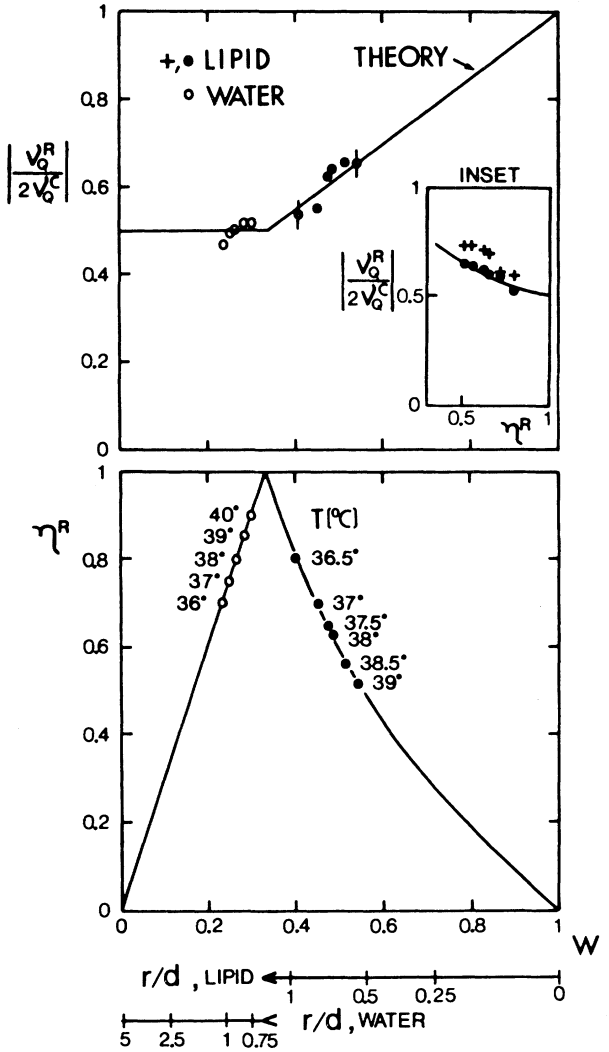

FIG. 3. Plot of the reduced value, $|\nu_Q^R/2\nu_Q^C|$, of the quadrupole splitting, ν_Q^R, and the motionally induced asymmetry parameter, η^R, vs W, the probability for a molecule to reside in region L (Fig. 2): The lower horizontal axes give the values of the ratio r/d characteristic of the cross section of the ribbons (Fig. 2) for the lipid and water molecules.

(1) (Fig. 3, solid line in inset). In this plot we took for ν_Q^C the experimental value $\nu_Q^{\text{cylind}} = -1.85$ kHz [Fig. 1(d)]. A better agreement can be obtained by letting ν_Q^C be a fitting parameter (actually the only one). With $\nu_Q^C = -2.0 \pm 0.1$ kHz we obtain a good agreement as illustrated in Fig. 3 (dots) and its inset (dots). The error bars express primarily the uncertainty in determining ν_Q^C.

The situation for the water molecule is entirely different. Although ν_Q^R does show a weak temperature dependence, any attempt to assign the orientation of the principal-axis frame of the water molecule to that of case A yields contradictions. However, considering case B, we obtain a reasonably good agreement between data and theory (Fig. 3, circles). Namely, from Eq. (2) $|\nu_Q^C| = |\nu_Q^R| = 1.28$ kHz and this value agrees well with the experimental value $\frac{1}{2}|\nu_Q^L| = 1.23$ kHz [Fig. 1(g)].

The fact that we are led to consider case A for the lipids and case B for the water molecules is not an inconsistency, as can be shown by relating the values of W to the shape and size of the cross section of the ribbon (see Fig. 2). In the case of the deuterated lipid we can relate $W \equiv W_l$ to the ratios of the cross-sectional areas of region L and region C to obtain $W_l = (1 + \pi r/2d)^{-1}$. From the calculated values for W_l this equation yields values for r/d ranging from 0.534 to 0.928 as the temperature is decreased (Fig. 3, middle horizontal axis). These values indicate that the shape of the ribbon is more nearly cylindrical than lamellar and that it is becoming more cylindrical in shape as the temperature approaches the transition to the phase of cylindrical aggregates ($T_c = 35.5\,^\circ\text{C}$) and are in agreement with preliminary x-ray studies.[7] Furthermore, if we assume that the parameter d/r is scaled as an order parameter according to $(T - T_c)^\beta$ we find that $\beta = 4.0 \pm 0.1$.

It is more difficult to model an expression for $W \equiv W_w$ since the water molecule not only diffuses over the surface of the ribbon aggregate but also between aggregates, and the structure of the water between aggregates is not known, although this may be a way to determine its structure. It is, however, useful to examine a simplified model whereby we consider only the averaging due to the water molecules' diffusing over the surface of the ribbon aggregate. In this case $W_w = 2d/(2d + 2\pi r) = (1 + \pi r/d)^{-1}$. When compared to W_l it is seen that $W_l < W_w$ for all values of r/d, which is consistent with our observed results. Furthermore, it is interesting to note that the values of r/d determined from the above expression for W_w range from 0.743 to 1.047 as the temperature decreases (Fig. 3, lower horizontal trace), in fair agreement with the values for r/d determined from W_l, particularly in view of the crudeness of the model.

Finally, we report that we have also observed similar features with ^{2}H-NMR on ^2H_2O in the ribbon structure in the mixture sodium decyl sulfate, 52.5 wt.%; decanol, 5.2 wt.%; and ^2H_2O, 47.6 wt.%, which is the material in which Hendrikx and Charvolin[2] discovered the ribbon structure with x rays.

In both ternary mixtures studied we always saw the presence of another phase in addition to the ribbon phase. In the potassium palmitate mixture, at temperatures below the lamellar phase, we observed that a small portion of the bulk sample always appeared to exhibit a very broad underlying spectrum characteristic of a rigid, highly ordered lipid, possibly indicating a phase equilibrium with the gel phase.

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