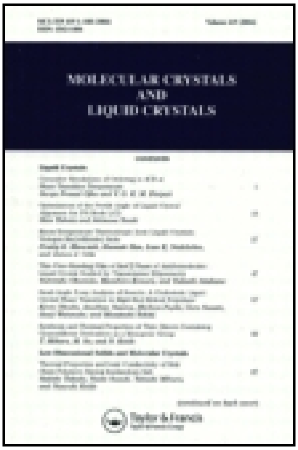

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Electron Paramagnetic Resonance Investigations of a Lyotropic Liquid Crystal

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Electron Paramagnetic Resonance Investigations of a Lyotropic Liquid Crystal

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The hexagonal M_1 phase of the potassium caprylate/water system has been examined by EPR spectroscopy over the temperature range 22°C–110°C, using the spin label 5-doxyl stearic acid. The spectra show motional narrowing behaviour. Analysis in terms of an assumed isotropic motion has been carried out and the results are found to be consistent if an "effective" hydrodynamic radius is assumed. Symmetry changes in the mesophase are also revealed.

Keywords: lyotropic liquid crystals, hexagonal m_1 phase, EPR spectroscopy, hydrodynamic radius

1. INTRODUCTION

Lyotropic mesophases with micellar aggregates are produced by dissolving amphiphilic substances in polar solvents.[1-3] The mixtures can be made from two or more components and water is commonly used as the solvent or one of the solvents because of its high polarity. The

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physical properties of lyotropic liquid crystal phase result mainly from the interactions of the amphiphilic molecules with the polar solvent, but the temperature and concentration of the components have important effects. The latter parameter is sometimes crucial, and a small variation in percentage of the components can sometimes produce a drastic change of the mesophase structure.[4]

The EPR spectroscopy of labelled samples has been demonstrated to be a very powerful technique for the investigation of such systems.[4–10] In this work, we have employed EPR to study molecular and micellar dynamics of a lyotropic system which forms a simple hexagonal M_1 mesophase. Our aim was to obtain information about micellar dimensions by a suitable analysis based on a reasonable hypothesis of isotropic motion.

2. EXPERIMENTAL

The system examined was a binary compound of potassium caprylate (PC) and water which forms three different phases, as shown in Figure 1. I is the region in which single molecules or spherical micelles are dispersed in water. There is no orientational or translational order, that is, I is the region of the isotropic phase. M_1 is the ordered mesophase in which the liquid crystal is formed. The micelles acquire a cylindrical shape and lie in a hexagonal array. Finally, G is the gel (lamellar) phase. Between these regions there are extended two-phase regions.

Three different compositions of the mixture, namely 55%, 60% and 63% by weight of amphiphile were selected to give samples near the ends and in the middle of the M_1 mesophase range. The purity of the amphiphile used was demonstrated to be 99.5% by chromatography. The precision of the balance employed was of $\pm 10^{-4}$ gr. The mixtures were sealed and repeatedly heated to 80°C, to ensure complete homogenization.

The spin probe 5-doxyl stearic acid, also known as I(12,3)[4] produced by SYVA (Palo Alto, California, USA) was used in solution 3.25×10^{-2} M in ethyl alcohol. Detectable signals were obtained by adding 1 μl of the solution to ~ 1 cc of PC + water mixture. This composition corresponds to about 1 part of spin probe per 2×10^5 parts of amphiphile. About 3 cm of each labelled solution was injected into pyrex tubes of 1 mm internal diameter (i.d.). All capillaries were sealed and placed in the spectrometer cavity, inside a quartz tube of 3 mm i.d. containing silicon oil as thermal bath. The temperature

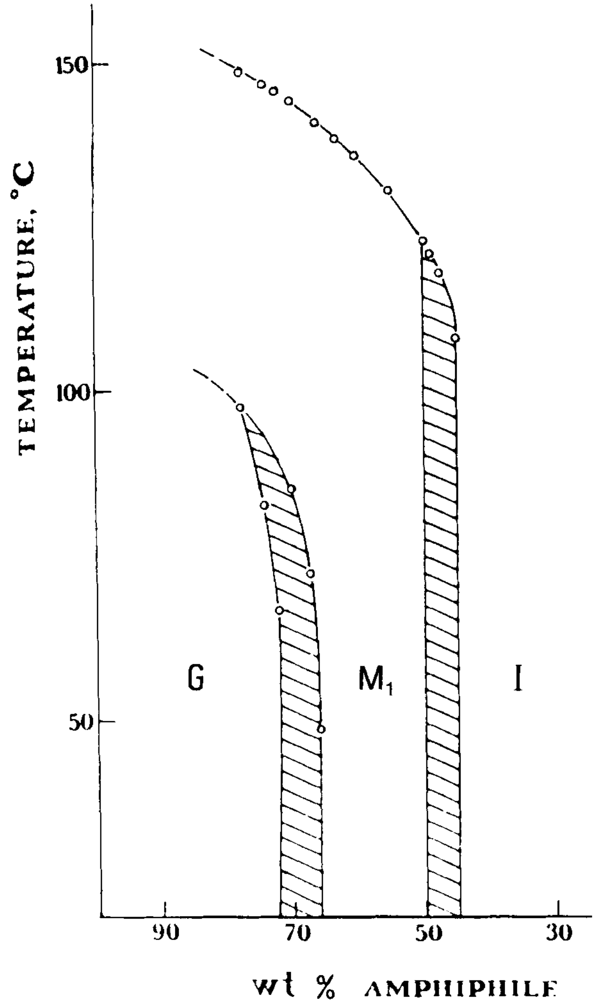

FIGURE 1 Phase diagram of the binary mixture potassium caprylate + water.

was regulated by a Varian E-257 temperature controller and measured by a copper-constantan thermocouple connected to a Fluke 2176A digital thermometer accurate to within + 0.2°C.

First derivative EPR spectra were recorded using an X-band Varian spectrometer (model E-112) operated in the absorption mode. The magnetic field was fixed at 3258 G. The microwave power was adjusted to 2 mW without saturation effects. It was found that modulation amplitudes of up to 1 G did not cause any appreciable effects on the width and amplitude of the spectral lines. However, the modulation amplitude was set at a value of 0.8 G since this setting gave the best signal-to-noise ratio and the error in the amplitude measurements was minimized. The receiver gain was fixed between 1.6 and 6.3 × 10^4, in order to record the maximum signal amplitudes. The scan range for the magnetic field was fixed at 50 G. This value was found to give the whole spectrum. Amplitudes and splittings were obtained from the recorded spectra, the latter were taken as the crossing points with the base line.

3. RESULTS AND DISCUSSION

Figure 2 shows a series of spectra recorded for one of our samples. Other samples gave similar features. The mesophase of our system is composed of cylindrical micelles arranged in a hexagonal array and the shape of the spectra characterizing such a phase[4-6] is attested. The behaviour of the spectral lines is typical of the motional narrowing region. The peaks are not resolved in the outermost and innermost regions. Therefore, we are not able to extract separate components of the parallel and perpendicular hyperfine splitting and, in consequence, we cannot obtain the S_{33} parameter from the spectra.

A simulation procedure for obtaining well-determined correlation times for *anisotropic* motion requires a value for the S_{33} parameter (see Reference 11). But as we were unable to obtain such a value, we adopted an alternative approach in which different correlation times characterizing anisotropic motions are not calculated. The first step was to confirm that the line broadening is really produced by the micellar dynamics. In order to determine this, we recorded spectra of a solution of the spin probe in water alone, without PC. We set the experimental conditions identical to those for the PC samples. Only the amplifier gain was adjusted each time in order to reproduce the central line amplitudes of the PC spectra at the nearest temperature. We obtained line widths less than 1 G for the right line, against values from about 2 to 9 G for the PC samples. The much reduced value of the water sample with respect to PC samples clearly show that spin probe molecular motions are much more rapid in water than in the liquid crystal phase. These results reveal that spin probe molecules are very closely linked to the micellar aggregates.

In Table I we compare the hyperfine splittings measured in all our samples and observe similar mean values. It is likely that molecular tumbling and micellar rotations are both rapid enough to average the

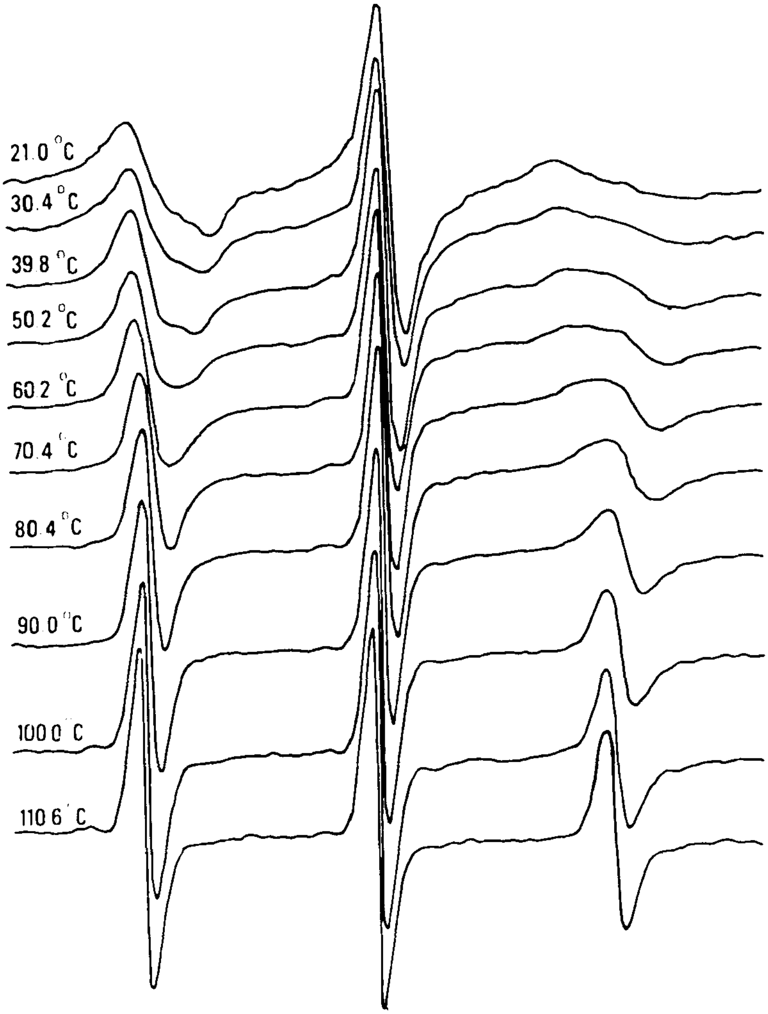

FIGURE 2 EPR spectra of the sample consisting of PC 55% + water 45%.

spectral parameters to nearly isotropic values. From this, we can attempt a data analysis based on an approximation of isotropic motion. The width δ of hyperfine lines which represent the interaction of the unpaired electron with the nitrogen nucleus, can be fitted by the equation[10,12]:

$$\delta\,(m) = A + Bm + Cm^2 \qquad (1)$$

TABLE I

Mean values of the hyperfine splittings (in gauss) for H_2O and liquid crystal samples. The percentages indicate the amphiphile concentration in the latter. For each of the samples, the variations of such splittings as a function of temperature were within 0.2 gauss.

H_2O	55%	60%	63%
15.8	15.6	15.5	15.2

where m is the nuclear spin quantum number equal to -1, 0, and 1 for the right, central and left line respectively, and coefficients, A, B and C depend on molecular parameters. In the approximation of isotropic motion, the correlation time τ is related to the coefficients B or C by the following relations[11]:

$$B = 2.58 \times 10^{-2}\,\omega[(2A_{zz} - A_{xx} - A_{yy})(2g_{zz} - g_{xx} - g_{yy}) + 3(A_{xx} - A_{yy})(g_{xx} - g_{yy}))]\cdot\tau \tag{2a}$$

$$C = 2.83 \times 10^{5}\,[(2A_{zz} - A_{xx} - A_{yy}) + 3(A_{xx} - A_{yy})] \tag{2b}$$

$\omega = 5.75 \times 10^{10}$ rad/sec is the electron Larmor frequency, $g_{xx} = 2.0093$, $g_{yy} = 2.0055$, $g_{zz} = 2.0027$, and $A_{xx} = 5$, $A_{yy} = 7$, $A_{zz} = 32\ G$, are the principal-axis values of the **g** and **A** tensors are given in the legend of Figure 4, Reference 12. In a situation of complete isotropy and without line distortion, the values for τ obtained by B and C should coincide, but this is not the case. We have:

$$\tau_B = -1.32 \times 10^{-9}\,B \tag{3a}$$

$$\tau_C = 1.30 \times 10^{-9}\,C \tag{3b}$$

Coefficients A, B and C are easily derived from the recorded line widths and by using (1). For Lorentzian lines[10]:

$$\delta(i)/\delta(k) = [I(k)/I(i)]^{1/2} \tag{4}$$

$I(k)$ and $I(i)$ being peak-to-peak amplitudes and $i,k = 1,0,1$. We assume this approximation since it allows us to reduce the experimental errors. In consequence, the equations for A, B and C become:

$$A = \delta(0) \tag{5a}$$

$$B = (1/2)\ \delta(0)\{[I(0)/I(1)]^{1/2} - [I(0)/I(-1)]^{1/2}\} \tag{5b}$$

$$C = (1/2)\ \delta(0)\{[I(0)/I(1)]^{1/2} + [I(0)/I(-1)]^{1/2} - 2\} \tag{5c}$$

These last equations are the most convenient for deriving correlation times. In Figure 3, we report our results.

To estimate the effects of **A** and **g** anisotropies, we observe that $A_{zz} - A_{xx} = 73$ MHz and $\beta H_0 h^{-1}(g_{xx} - g_{zz}) = 22$ MHz and compare such frequencies with $1/\tau_C$. We find effects between 0.9% and 9.4% due to **g** and between 3% and 32% due to **A**. The highest values are, as may be expected, at the lowest temperatures.

Order is also indicated[11,13-15] as responsible for the discrepancies observed between τ_B and τ_C. The behaviour of $\tau_C - \tau_B$ vs. T suggests a possible connection between this quantity and the degree of order, but a quantitative relation is not known even for systems having only orientational order.[15] In our system, both orientational and translational features have to be taken into account and, to our knowledge, the problem cannot be solved with EPR data alone.

The log τ plots all have different behaviour at low and high temperatures, the latter appearing almost linear. The changes do not appear as discontinuities, and they could be a consequence of the gradual transition from a state of high strong anisotropy to one of isotropy, reflecting the gradual decrease of order and increase of thermal motion with increasing temperature.

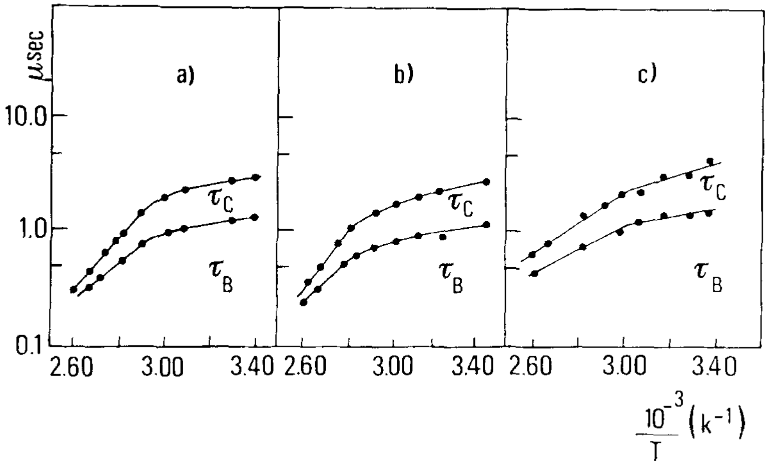

FIGURE 3 Arrhenius plots of the correlation times for the three samples. a, b, and c refer to the samples with amphiphile percentages of 55%, 60% and 63%, respectively. See the text for details.

The microviscosity coefficient can be estimated by means of the Debye diffusion model, according to the Equation:

$$\eta = 3KT\tau/4\pi R^3 \tag{6}$$

where R is the hydrodynamic radius. If we assume 3.6 Å as the value for R, the hydrocarbon chain radius of sodium caprylate,[4] a value close to ours, we obtain unreasonably high values for η. It would need to reach about 100°C in order to give the measured value of ~0.05 poise determined by Seelig at ~20°C.

A plausible reason for this discrepancy is our use of an uncorrected R term. In fact, because of the co-existence of molecular tumbling and micellar rotation, it is not reasonable to take R as a *molecular* radius. A more plausible meaning is of "effective" hydrodynamic radius, that is, the radius of a spherical particle which tumbles with the same correlation times. We can obtain a rough estimate of this effective radius by assuming 0.05 poise as the viscosity of our samples at our lowest experimental temperatures. The values we obtain for R are 6.6 Å and 8.8 Å corresponding to $\tau_B = 0.5 \times 10^{-9}$ sec and $\tau_C = 3.5 \times 10^{-9}$ sec, respectively, and $T = 22°\mathrm{C}$. Let us assume:

$$R = [R_1 R_2]^{1/2} \tag{7}$$

R_1 being the molecular radius and R_2 the radius of the cylindrical rod. With $R = 8.8$ Å and $R_1 = 3.6$ Å we obtain $R_2 \simeq 22$ Å, a value not too different from the 26 Å given in Reference 4. This seems to confirm the greater reliability of τ_C over τ_B as an indication of the isotropic correlation time, as already suggested[14,16] for different reasons.

In conclusion, isotropic analysis seems able to account for micellar dimensions when the assumption of an "effective" hydrodynamics radius and τ_C as isotropic correlation time is made. Furthermore, behaviour of the measured correlation times with temperature are consistent with the expected changes of structure in the mesophase.

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