Conductance measurement in the micellar nematic and lamellar smectic phases of the cesium perfluoro octanoate-H_2O system at high magnetic fields

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We report conductance measurements in the cesium perfluoro octanoate (CsPFO)–H_2O system at high magnetic fields, up to 10 T. The conductance was measured as a function of temperature in the isotropic phase, and parallel to the director in the nematic and lamellar smectic phases. The conductance was also measured as a function of the aligning magnetic field. The conductance shows little variation at the nematic-to-lamellar transition, confirming previous measurements. An interpretation of the conductance in terms of micellar dimensions is given.

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INTRODUCTION

Over a decade ago, Saupe and co-workers [1] reported conductance measurements on aligned micellar nematic liquid-crystalline phases. The most significant result of these studies was that at the transition from the discotic-nematic (N_D) to the lamellar smectic (L) phase, the principal values of the conductivity tensor (k_1 parallel to the director, and k_2 perpendicular to the director) did not show any marked changes; in fact, k_1 showed little change between the N_D and L phases. The implications of this result were significant in that they contradicted the notion of a lamellar smectic phase consisting of infinite bilayers.

This surprising result was verified in other micellar systems [2,3], and two approaches developed in modeling the L phase. The first [4–7] assumes that the smectic planes in the lamellar phase are extended bilayers which include significant amounts (up to 30%) of water in their structure (possibly through screw dislocations) thus providing continuity of the aqueous phase through the smectic planes. The second approach [8,9] assumes an analogy to the smectic-A (Sm-A) phase of thermotropic liquid crystals, where in the nematic-smectic transition the structural units rearrange from a random translational configuration to stacked two-dimensional liquid planes. The structural unit in this approach remains the disk-shaped micelle. Both pictures involve significant amounts of water in the smectic planes, but they differ in the continuity of the hydrophobic part. In the Sm-A analog, where the structural unit is the micelle, the maximum dimension of the hydrophobic part is on the order of 100 Å. In the incomplete bilayer this dimension is much larger.

Subsequent experimental evidence lends support to both the incomplete bilayer and the Sm-A analog. The diffusion of oil-soluble dyes [10], in the decylammonium chloride–NH_4Cl–H_2O system measured parallel and perpendicular to the director differ significantly between the N_D and lamellar phase. Also, the diffusion of the perfluorinated tails in the lamellar phase of the cesium perfluoro octanoate (CsPFO) system [11] is one order of magnitude higher perpendicular than parallel to the director. On the other hand, neutron- [12,13] and x-ray-diffraction measurements [8,9] in the nematic and lamellar phase reveal that the two phases have features normal to the director which are of comparable magnitude.

Extensive numerical calculations for the conductance anisotropy,

$$\alpha=3(k_1-k_2)/(k_1+2k_2)\ , \tag{1}$$

were presented for systems corresponding to each of the two proposed pictures [3,14]. The numerical calculations assumed that the hydrophobic regions are not penetrable to the charge carriers, and thus conduction occurs uniformly in the water surrounding the hydrophobic regions. The results of the numerical calculations did not reveal any significant differences between the two pictures, for amphiphile-to-water ratios commonly seen in micellar mesophases. In fact, using acceptable dimensions, the measured anisotropies for various systems could be interpreted equally well using either model[15].

As the lamellar phase cannot be aligned by ordinary magnetic fields, the study of lamellar phases presents a difficulty from the experimental point of view. The CsPFO-H_2O system, introduced by Boden, Corne, and Jolley [16], played a significant role in the study of micellar phases. This two-component system shows many interesting features in its phase diagram. For our purposes, it is noted that at intermediate concentrations, the CsPFO system has an N_D phase with positive diamagnetic anisotropy. The significance of the latter is that the nematic director aligns parallel to an externally applied magnetic field. The N_D to lamellar transition appears continuous for CsPFO concentrations less than about 48% by weight. Thus cooling from the N_D to the lamellar phase in the presence of a magnetic field results in an aligned lamellar phase.

Conductance measurements of k_1 in aligned samples of the CsPFO system [15] show field-dependent results in the N_D phase as the transition to the lamellar phase is approached. This dependence results from the walls of the conductance cell, which align the director perpendicular

to the direction of the applied field. Thus near the cell walls, the conductance of the sample is essentially k_2. As $k_2 > k_1$ for the N_D and the lamellar phase, the sample may appear less anisotropic. In addition, as the temperature is lowered into the lamellar phase, the thickness of the wall-aligned part increases, reducing the measured anisotropy even further. With cylindrical cells of 2-mm inside diameter in a 1-T field, the wall-imposed alignment became dominant below the N_D-lamellar transition, resulting in increase of the conductance with time [17]. It was also observed [3] that k_1 in the lamellar phase decreases by about 1–2 % over a period of 24 h in the presence of a magnetic field. This decrease is attributed to healing of defects in the lamellar structure.

From the above it is clear that incomplete alignment and persisting defects may result in higher k_1 values. To address this problem, we measured k_1 in the CsPFO system using high magnetic fields.

EXPERIMENTAL PROCEDURE

CsPFO was prepared by neutralizing CsOH (Alfa) with perfluoro-octanoic acid (PCR, Inc.). The salt was recrystallized 3 times from cold ethanol. The sample was prepared by mixing 47.9% CsPFO, by weight, with 52.1% distilled, deionized water. The sample was thoroughly mixed by a magnetic stirrer for a week, filtered once through a Millex-HV (Millipore Corp) 0.45-μm membrane, resealed, and mixed for another week. Observation of the bulk sample under crossed polarizers showed an N_D-to-isotropic transition at 41 °C and an N_D-to-lamellar transition at 34 °C. The sample composition is so that the N_D-to-lamellar phase transition occurs several degrees above the temperature of the magnet bore, while retaining the continuous nature of the transition.

The conductance cell consisted of a vertical cylindrical glass tube (3.5-mm inside diameter). The platinum electrodes were fixed on cylindrical pieces of Teflon. One electrode was sealed to the lower end of the cell with epoxy (Epo-Tek 377). The sample was introduced into the cell, and the cell was sealed with the Teflon stopper holding the top electrode. The stopper was coated with a thin film of vacuum grease. The distance between electrodes was 2.5 cm. The cell was placed in a thermally insulated cylindrical aluminum thermostat that allowed ±0.2 °C temperature stability, as measured by a thermistor (Fenwall UUA32J4) in contact with the cell. The cell was connected in series to a 400-Ω standard resistor, and a 0.4-V, 1-kHz voltage was applied to the combination. The conductivity of the sample was determined by measuring the voltage drops across the cell and the standard resistor, using two digital multimeters (3455A, Hewlett Packard), and the calibration constant of the cell. The thermostat was lowered into the bore of a Bitter magnet. The sample temperature was then raised to 47 °C, which is in the isotropic phase. A 5-min waiting period was allowed for equilibrium at 47 °C, and for all subsequent temperature settings. The magnetic field was set to 5 T, and the measurements were started.

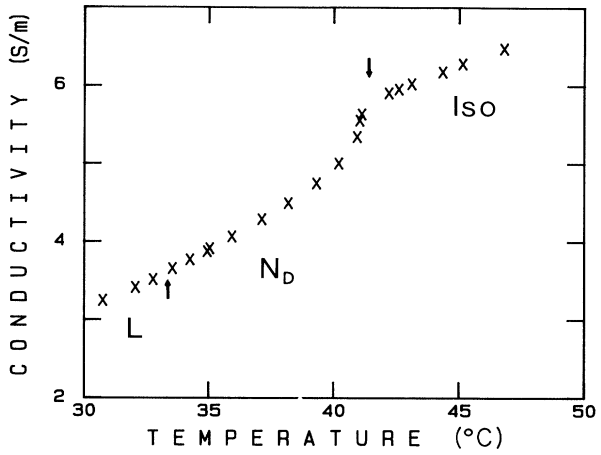

FIG. 1. Conductance parallel to the director versus temperature for a 47.9% (by weight) mixture of CsPFO in H_2O, in the presence of a 5-T aligning magnetic field. The measurements were taken on cooling from the isotropic phase, with a 5-min equilibration time at each point. The arrows mark the boundaries between the isotropic (Iso), the nematic (N_D) and the lamellar phase (L).

RESULTS

Figure 1 shows values of k_1 for various temperatures on cooling from the isotropic phase. In agreement with previous measurements, the conductance in the isotropic phase varies linearly with temperature, and the conductance along the director decreases as the sample is cooled into the N_D phase. The decrease is a result of the oblate shape of the micelles. The k_1 values decrease monotonically below this transition. The N_D-to-lamellar transition occurs at 34 °C, with no distinctive features on the variation of k_1 with temperature. From previous measurements, where both k_1 and k_2 were available [2,3], we know that the average value $\langle k \rangle = (k_1 + 2k_2)/3$ at any temperature was in excellent agreement with the extrapolation of the conductance line from the isotropic phase. We can use this observation to estimate the conductance anisotropy. Thus, we determined the best linear fit to the data in the isotropic phase, with temperatures above 43 °C, and extrapolated this line to the N_D and lamellar range. At 30.75 °C (approximately 3 °C below the N_D-to-lamellar transition), $\langle k \rangle = 4.5$, $k_2 = 5.13$, and the anisotropy $\alpha = -0.42$. This estimate is in very good agreement with the values of Ref. [15], obtained with 1.35-T aligning field. The estimated values of α are about 25–35 % higher than the values reported by Boden *et al.* [2,9], which were taken with weaker aligning fields.

After completion of the first experiment, the temperature was increased, and two points in the N_D and isotropic phase were verified. The sample was subsequently cooled to 34.2 °C, and the field was increased to 10 T. Upon equilibration, the power to the heating coils of the thermostat was disconnected, and the sample was allowed to cool freely. Conductance measurements were taken at 3-min intervals. The results are plotted in Fig. 2. As the measuring thermistor is in contact with the outer surface of the glass cell, the temperature on this plot is

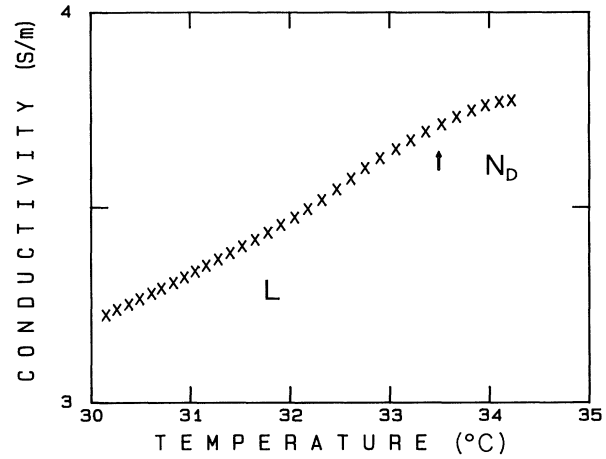

FIG. 2. Conductance parallel to the director versus temperature for 47.9% CsPFO on H_2O, in the presence of a 10-T aligning magnetic field. The measurements were taken in 3-min intervals as the sample was free cooling from the nematic phase. The arrow marks the boundary between the nematic (N_D) and the lamellar phase (L).

somewhat lower than the temperature at the interior of the cell. Due to the thermal nonuniformity of the sample, the slope changes observed in previous work with slower temperature scans are absent in this measurement. In addition, comparing to Fig. 1, we note that the conductance values are not affected by doubling the aligning field value.

As a final experiment we investigated the field effects at constant temperature. The percentage increase in the conductance as the magnetic field was increased from 5 to 10 T are listed below for four temperature settings:

32.05 °C	(lamellar)	0.02%
35.03 °C	(nematic)	0.2%
41.37 °C	(isotropic)	0.3%
51.35 °C	(isotropic)	0.03%

For the two temperatures in the isotropic phase, the field was stepped up from zero (the values listed above correspond to the change between 5 and 10 T). We did so in order to determine possible induced alignment, which appears to be the case for the 41.37 °C measurement (just above the nematic-isotropic transition). From measurements of magnetic-field-induced birefringence, we expect that the induced alignment at 51.35 °C be about one order of magnitude less than the induced alignment at 41.37 °C. The 0.03% decrease at 51.35 °C represents the resolution of the present conductance measurements. It is interesting to note that the induced anisotropy in the isotropic phase can be determined using conductance measurements, as illustrated by the measurement at 41.37 °C.

To our knowledge a measurement of induced anisotropy using conductance has not been previously published, and may prove a viable method for micellar systems. For such systems [18], the birefringence is rather small ($n_0 - n_e \approx 10^{-4}$) and the required resolution for induced birefringence measurements at 10 T is in the order of $\Delta n \approx 10^{-8}$. [19] From Fig. 1 we note that $k_2 - k_{k_1}$ is in the order of 2 S/m and k in the isotropic phase about 6 S/m. The resistance of the cell is about 400 Ω, and an equivalent resolution would be in the order of 0.1 Ω, which is quite feasible.

DISCUSSION AND CONCLUSIONS

The measurements presented here show that the conductance parallel to the director in the lamellar phase of the CsPFO system is comparable in value to that of the adjacent nematic phase. The fields used in the present experiments are one order of magnitude higher and the corresponding aligning torque (proportional to the square of the applied field) is two orders of magnitude higher than the fields used in previously reported experiments. The k_1 values and the estimated values for the conductance anisotropy are in good agreement with those of Ref. [15]. Thus we conclude that for the cell design used in the present experiments, and those of Ref. 15, the effects of the misaligned layer at the surface of the conductance cell are already insignificant for fields above 1 T.

As the aligning torque is two orders of magnitude higher than in previously reported experiments, the healing of defects interrupting the continuity of the smectic planes in the lamellar phase should be proportionally accelerated. The data in Fig. 2 span a time interval of about 1 h, yet no significant reduction of k_1 is observed. We therefore conclude that if the high k_1 values in the lamellar phase are indeed due to defects (e.g., screw dislocations) fields up to 10 T have no apparent effect in healing such defects. Higher fields may be required.

Boden *et al.* [9] presented x-ray-diffraction and conductance data for a CsPFO mixture with the amphiphile occupying $\phi = 0.35$ of the volume. They interpreted the data assuming that the structural unit in both the N_D and the lamellar phase is a micelle of oblate spheroidal shape. In view of the higher conductance anisotropy values measured with the stronger aligning field, it is appropriate to examine the agreement between the conductance and x-ray data. We will follow the analysis of Boden *et al.* which is based on the model developed by Fricke [20] for oblate spheroids of axial ratio a/b, where a is the minor axis and b the major axis. The ratio k_2/k_1, as measured by Boden *et al.* is 1.32. The present measurements give $k_2/k_1 = 1.55$. From Fricke's model, the ratio of the principal values of the conductivity is given as

$$\frac{k_2}{k_1} = \frac{M+\phi(1-M)}{2-\phi(1-M)} \frac{2-M}{M} , \tag{2}$$

where M is given by the integral

$$M = ab^2 \int_0^\infty \frac{d\lambda}{(b^2+\lambda)^2(a^2+\lambda)^{1/2}} . \tag{3}$$

The aspect ratio a/b can be calculated from simultaneous solution of Eqs. (2) and (3) for given k_2/k_1. The values of Boden *et al.* yield $a/b = 0.44$. The present measurements $a/b = 0.31$, and using $a = 22$ Å as derived from x-ray data [9], we find that the major axis of the spheroid micelle would be 71 Å. This aspect ratio is in very good

agreement with the value predicted for disk-shaped micelles in Ref. [15], based on numerical solution of Laplace's equation. A complete comparison of the two models will be given elsewhere.

Finally, we note that optical-birefringence [18] studies of the critical behavior at the nematic-to-isotropic transition of the CsPFO system on the isotropic side of the transition support mean-field behavior. On the nematic side of the transition, the optical birefringence data [19] indicate crossover behavior as a function of concentration, while the conductance measurements [21] show universal behavior with $\beta=0.34$. There are no conductance data on the isotropic side of the transition. It was suggested by Boden *et al.* [21], that the discrepancy may reflect contributions from the reorientational motion of the surfactant molecules to the birefringence. As noted above, the magnetic-field-induced anisotropy in the isotropic phase can be resolved using conductance measurements, and it would be interesting to investigate the critical behavior of this system on the isotropic side of the transition with a simultaneous conductance and optical birefringence measurement.

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