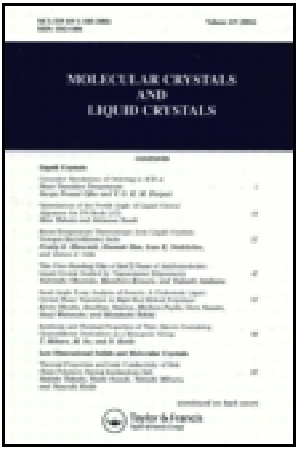

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ELECTRICAL CONDUCTIVITY MEASUREMENTS OF THE ORIENTATIONAL ORDER PARAMETER IN THE MICELLAR NEMATIC PHASE OF THE CAESIUM PENTADECAFLUOROCTANOATE/WATER SYSTEM

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Abstract Electrical conductivity measurements are presented for the micellar mesophases of the caesium pentadecafluoroctanoate/heavy water ($CsPFO/{}^2H_2O$) system The electrical conductivity monitors the diffusivity of the counterions around the micelles and transforms as a second rank tensor with a reference frame coincident with the principal axes of the inertial tensor. This means that the second rank orientational order parameter can be calculated from measurements of the angular dependence of the conductivity of a macroscopically aligned sample. Values of the order parameter in both the lamellar and nematic phases have been obtained in this way. The value obtained for the order parameter exponent $\beta = 0.31 \pm 0.03$ in the nematic phase of a sample with a weight fraction of CsPFO of 0.55 is substantially smaller than the corresponding value as obtained by earlier birefringence measurements

INTRODUCTION

The CsPFO/water system is of especial interest because it exhibits a micellar nematic phase of type N_D^+ [1] over an unprecedented range of concentration (0.225 to 0.632 weight fraction w of CsPFO) and temperature (285.29 to 351.23K).[2] This phase is intermediate to a micellar lamellar phase L_D

at lower temperatures and an isotropic micellar solution phase I at higher temperatures. The aggregates have been shown[3-5] to be discrete discoid micelles in all of the three phases. Significantly, the lamellar phase consists of planar arrays of discoid micelles, not the classical infinte bimolecular layers. The isotropic micellar solution to nematic to lamellar sequence of transitions is, therefore, quite analogous to the isotropic liquid to nematic to smectic A sequence observed for thermotropic mesogens with lath shaped molecules. Thus, it is of considerable interest to investigate the nature of these transitions and to compare them with what is known about their thermotropic counterparts.

Here we focus on the measurement of the orientational order parameter S. Of especial interest will be the form of the power law for the nematic order parameter

$$(S - S^*) = A(T^* - T)^\beta \tag{1}$$

where T^* is the superheating limit of the nematic phase. The nematic to isotropic transition is much weaker than that of thermotropics. In fact, for concentrations less than $w = 0.35$, the temperature interval $T_{IN} - T_{NI}$, between the upper and lower boundaries to the transition, varies linearly with w, that is, the transition would become second order at infinite dilution![2] Values for the nematic order parameter along the transition line have been estimated from NMR measurements[2] and found to decrease with decreasing concentration of CsPFO, a result inconsistent with the predictions of the Maier-Saupe mean field theory. The values obtained for the order parameter exponent β also appear to decrease on dilution [$w = 0.50$: $\beta = 0.57 \pm 0.06$; $w = 0.398$; $\beta = 0.34 \pm 0.06$].[6,7] To account for this variation of β with concentration, it has been suggested that there is a transition from classical mean field behaviour ($\beta = 0.50$) to tricritical behaviour ($\beta = 0.25$). However, it is necessary to be cautious because these order parameters were obtained directly from optical birefringence measurements. The variation of the birefringence with temperature is dependent upon both the size and shape of the micelles in addition to their orientational order parameter. In view of the substantial change in the diameter of the micelle with temperature across the nematic phase,[4] it is quite incorrect to relate the optical birefringence directly to nematic order parameter as was done in the above studies. It is vital to separate the contributions from micelle size and order parameter variation and also from any changes due to the reorientational motion of the amphiphilic molecules within the micelle. Below we show how this can be done using electrical conductivity measurements.

CALCULATION OF ORDER PARAMETER FROM CONDUCTIVITY MEASUREMENTS

The conductivity experiment[8] measures the partially averaged component $\tilde{\kappa}_{zz}(\emptyset)$ of the conductivity tensor $\underline{\kappa}$ along the direction of the applied electric field $\vec{E}$ which is taken to be along the z-axis of the laboratory frame L(x,y,z). This is given by

$$\tilde{\kappa}_{zz}(\emptyset) = \kappa_i + \frac{2}{3} P_2(\cos\emptyset)\,S(\kappa_\parallel - \kappa_\perp)_M \qquad (2)$$

where $\emptyset$ is the angle between the direction of $\vec{E}$ and the mesophase director and S is the orientational order parameter of the micelles. $\kappa_\parallel$ and $\kappa_\perp$ are the unaveraged components of the tensor in the micellar frame M(a,b,c) and $\kappa_i = (\kappa_\parallel/3 + 2\kappa_\perp/3)_M$.

From Eq. (2) we obtain

$$\frac{\Delta\tilde{\kappa}}{\kappa_i} = S\,\frac{(\kappa_{\parallel}-\kappa_{\perp})_M}{(\kappa_{\parallel}/3 + 2\kappa_{\perp}/3)_M} \tag{3}$$

where $\Delta\tilde{\kappa} = \tilde{\kappa}_{zz}(0°) - \tilde{\kappa}_{zz}(90°)$. Thus, to obtain values for S we need values for $\kappa_{\parallel}$ and $\kappa_{\perp}$ in the micellar frame. These have been calculated using the Fricke model,[9] for the conductivity of a suspension of non-conducting ellipsoidal particles. This gives

$$\kappa_{\alpha} = \kappa_{o}\,\frac{(1-\phi_M)(1-f)}{1+\phi_M/x_{\alpha}}, \qquad \alpha = a,b,c \tag{4}$$

where κ_o is the intrinsic conductivity of the counterions, f is the fraction of counterions bound to the micelle, ϕ_M is the volume fraction of micelles, and x_{α} is solely a function of the axial ratio of the micelle.

The values of $\tilde{\kappa}_{zz}(0°)$ and $\tilde{\kappa}_{zz}(90°)$ for a sample with $w = 0.55$ are plotted as a function of temperature in Figure 1. Values for the order parameter were calculated using the procedure outlined above and values for the axial ratio of the micelle obtained from X-ray diffraction measurements.[4] The results are summarised in Figure 2.

DISCUSSION

The temperature dependence of the order parameter across the nematic and lamellar phases is reminiscent of the behaviour of thermotropics. The values of S at T_{LN} (0.71) and T_{NI} (0.32) and the weak temperature dependence of S in the lamellar phase are quite similar. But, in the nematic phase S increases much faster on cooling than the molecular order parameter of thermotropic nematics. This behaviour has its origin in the variation with temperature of the diameter of

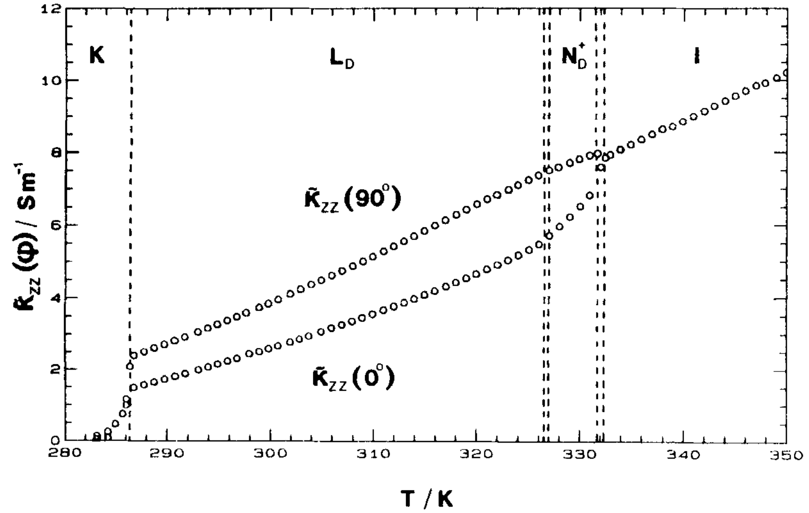

FIGURE 1. The electrical conductivity $\tilde{K}_{zz}(\emptyset)$ measured as a function of temperature at 10 kHz in a sample of CsPFO/D_2O where *w* = 0.555 ± 0.02.

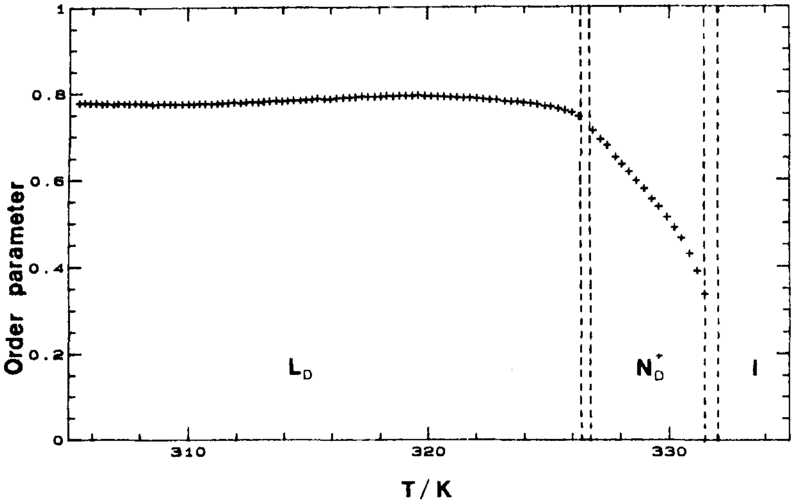

FIGURE 2. Orientational order parameter, *S*, of the micelles as a function of temperature.

the micelle the growth in the diameter of the micelle on cooling shifts the effective T_{NI} to higher temperatures.

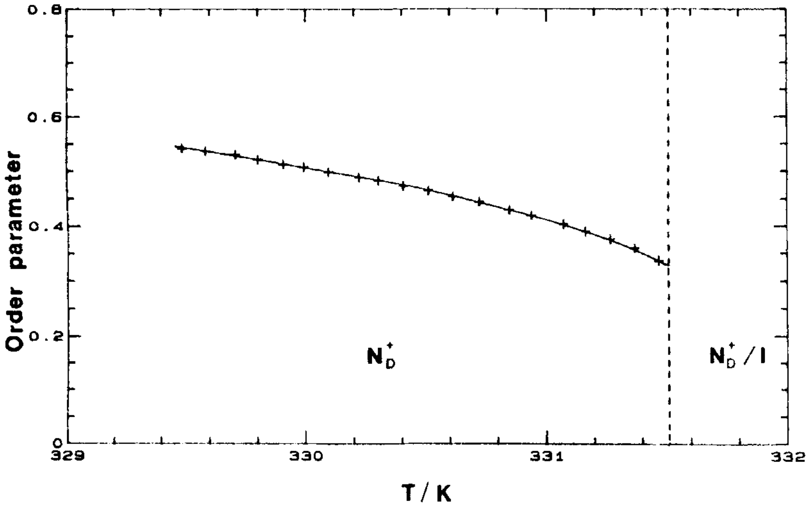

FIGURE 3. Fitting of equation (1) to the orientational order parameter within two degrees of T_{NI}. The fit gives $\beta = 0.31 \pm 0.03$.

A value for the order parameter exponent β has been obtained by a four parameter fit of Eq. (1) to the experimental S over a two degree interval. The best fit gave: $\beta = 0.31 \pm 0.03$, $T^* = 330.82 \pm 0.02$ (c.f. $T_{NI} = 330.663 \pm 0.010$), $S^* = 0.15 \pm 0.02$ and $S(T_{NI}) = 0.32 \pm 0.01$. This value for β is significantly smaller than the value of 0.57 ± 0.06 previously obtained[6] by birefringence measurement for a $w = 0.50$ sample. In fact, it is quite close to the value of 0.34 ± 0.06 similarly measured[7] for a $w = 0.398$ sample. Thus it could well be that the value of the exponent may not vary significantly along the transition line. But we must be cautious about such conclusions at this juncture in view of the uncertainty of the values for β obtained from optical birefringence measurements.

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