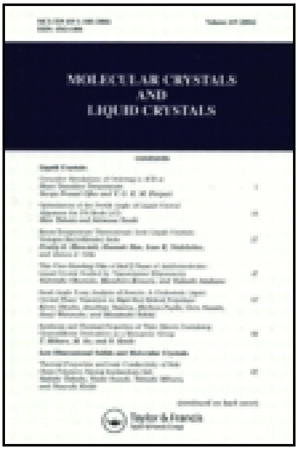

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NEMATIC ORDERING IN LYOTROPIC LIQUID CRYSTALS

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Abstract We report birefringence measurements of the nematic order parameter of the lyotropic liquid crystal formed by aqueous solution of cesium perfluoro-octanoate (CsPFO). For a mole fraction x = 0.035 of CsPFO the first order jump at the nematic-isotropic transition is about twice that in a sample with x = 0.025. The results are analyzed using a Landau-de Gennes model.

Lyotropic nematic liquid crystals occur at high enough concentration of some surfactant solutions that micelles interact strongly enough with each other to cause long range order. Several examples of these systems have been found and studied, and appear to behave in many respects like their thermotropic counterparts. On a microscopic scale, however, these two types of liquid crystals are quite different. In the thermotropic case, the interaction forces of consequence are for the most part between molecules, whereas in the lyotropic solutions, the interacting units can consist of hundreds of surfactant molecules each. The interactions are mediated by a solvent, often ionic, and the micelles are not likely rigid or of uniform size or shape.

The ideas of statistical mechanics postulate that collective behavior should be a function of the underlying symmetry, and not strongly dependent upon microscopic details. These lyotropic systems thus give us a very suitable environment in which to test these ideas, by comparing their behavior with thermotropic liquid crystals. To the extent they are the same as thermotropic nematics, they also permit control of new variables, such as concentration of surfactant or electrolyte, which affect the basic interactions and possibly the symmetry.

In this paper, the nematic (N) to isotropic (I) phase transition in a binary mixture of cesium perfluoro-octanoate (CsPFO), $C_8F_{17}COOCs$, and water has been studied via optical birefringence techniques. CsPFO in water forms disklike micelles which tend to line up with their symmetry axes along an applied magnetic field[1]. Liquid crystalline mesophases are formed over quite a wide concentration range, without the necessity of adding other ingredients. The phase immediately below the nematic phase in temperature is the lamellar, or neat soap (NS) phase, which is analogous to a thermotropic Smectic A phase. The CsPFO was prepared as described by Rosenblatt et al.[2] and mixed with water by molar concentration x of CsPFO. The surface effect of flat parallel glass plates with 0.1mm spacing was sufficient to induce reliably homeotropic alignment, in which the director is perpendicular to the plates, when the sample was annealed in the nematic or neat soap phase. The samples were heated slowly from the neat soap phase through the nematic and into the isotropic phase, where the optical birefringence went to zero. The scans were repeated to rule out error from possible drifting of the transition temperatures due to water loss from the sample.

The tendency of the lyotropic to align homeotropically along a flat glass surface enables one to measure both indices of refraction directly [3] using an Abbe Refractometer. Our results are given in Figure 1 . We see that the average index of refraction is very close to that of pure water, and that the total birefringence well below the order-disorder transition is less than 0.004, almost two orders of magnitude smaller than typical thermotropic optical birefringences.

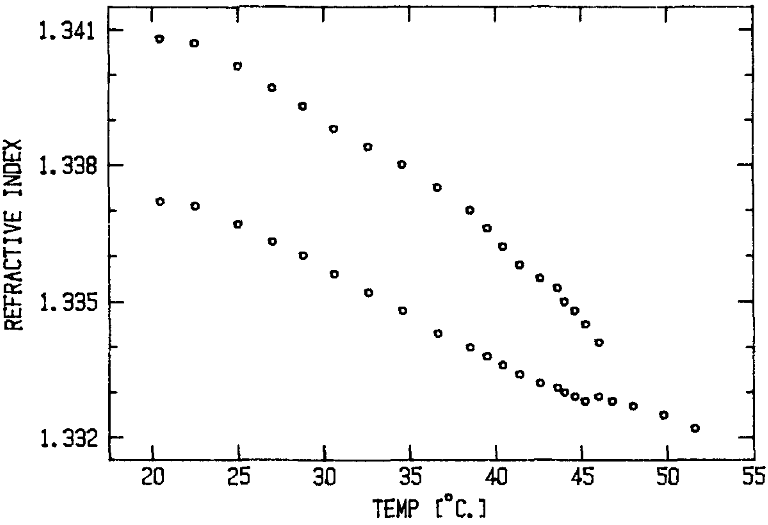

FIGURE 1. Refractive indices for an aqueous solution of CsPFO, x = 0.036, as measured on an Abbe Refractometer.

This relatively small birefringence in lyotropic liquid crystal mixtures allows us to make the convenient approximation that the birefringence is linear in the nematic order parameter S.

$$n_{\parallel} - n_{\perp} \sim S \qquad (1)$$

$$\text{where } S = 1/2 \langle 3\cos^2(\theta) - 1\rangle \qquad (2)$$

As is evident from this data, a more sensitive technique is required if one wants to do detailed studies of the critical behavior via the birefringence. This is accomplished by placing an aligned sample and a photoelastic modulator between crossed polaroids and using a phase sensitive detector to extract a passed laser signal at the modulator driving frequency. The amplitude of that frequency component is proportional to the sine of the phase shift. With homeotropic alignment, it was necessary to tilt the sample cell, so that both the ordinary and extraordinary axes were probed. For these measurements, the sample was loaded into a commercial spectrophotometer cell with 0.1mm path length and flat quartz windows, sealed to prevent water loss, and placed in a temperature controlled oven with resolution and stability of 1 mK. Since the maximum phase shift for these measurments was less than $\pi/2$ radians, a compensator was needed to normalize the output signal to ± 1 before taking the arc sine to convert it into an optical phase shift. This phase shift is linear with the birefringence and hence, with the order parameter S as well.
Our high resolution results of birefringence vs. temperature for two different mixtures are shown in Figure 2. The lower curve is from a sample having $x = 0.025$ and $T_k \approx 31.266°C$, with the upper one being more concentrated with $x = 0.035$ and $T_k \approx 44.925°C$. The birefringence is calculated from the measured phase shift, the sample tilt angle, thickness and average refractive index. The absolute value is quite sensitive to the tilt angle. At an external tilt angle of 45°, it changes by 13% per degree of tilt, thus, error in measuring this angle can easily account for any discrepancy between Figure 1 and Figure 2, as well as affect the relative amplitudes in Figure 2. Key features include what appears to

be power law behavior throughout most of the nematic phase, as well as a linear decrease at the N-I transition and a small bump (but no discontinuity) at the nematic to neat soap transition.

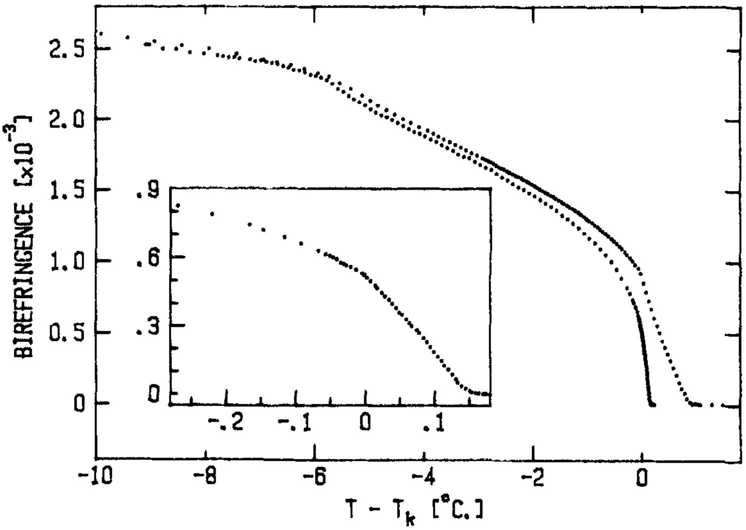

FIGURE 2. High resolution birefringence data for CsPFO. The molar concentrations and transition temperatures are $x = 0.035$, $T_k \approx 44.925$ for the upper curve, and $x = 0.025$, $T_k \approx 31.266$ for the lower curve. The inset shows an expanded view near T_k for the $x = 0.025$ sample.

The inset in Figure 2 shows an expanded view of the N-I transition for the $x = 0.025$ curve. Here we can see more clearly the features. The phase diagram of CsPFO has been mapped out by Boden et al.[1] using microscopy and deuterium NMR spectroscopy. The nematic-isotropic transition is found to be first order everywhere and displays a finite width coexistence region, much like an impurity induced coexistence region in thermotropic compounds. This can be understood as follows:

a well annealed nematic system of uniform concentration should, as it is heated, remain intact until it reaches that temperature T_k at which isotropic phase first appears. The isotropic phase which is in equilibrium with the nematic will contain a higher fraction of water; water thus leaves the nematic phase, raising the transition temperature for the remaining nematic to become isotropic. This process will continue if the temperature is raised slowly enough to allow mass transport, until finally a completely homogeneous isotropic phase forms. The parameter T_c^*, defined in Equation (3), is thus different by the coexistence range, as seen from the isotropic and the nematic phases. The relative differences, $T_c^*-T_k$ and $T_c^*-T^\dagger$, should be approximately equal, however. We note from the data that the coexistence range changes with concentration of CsPFO, being about 900 mK for $x = .035$, and 150 mK for $x = .025$. We take the noticeable kink in the birefringence curve to be the N-I transition temperature T_k. For the purposes of analyzing data in the nematic phase, we may ignore any data in the coexistence region beyond that.

To analyze the data, it is natural to try a Landau-de Gennes model[4]. Detailed discussions are available in the literature [5-6], so only the key points will be covered here. It is particularly reasonable, since mean field theory has been shown to work for the pretransitional behavior in the isotropic phase [2]. There are potential difficulties with the Landau expansion. Since the order parameter takes on a finite and increasing value, one might expect that higher order terms in a free energy expansion would be necessary to describe the behavior on the nematic side of the transition. Also, since the N-I transition is necessarily first order, there is a limit on how close to the extrapolated second order transition temperature one can probe.

We expand the free energy near the transition as a Landau-type power series in the order parameter S. The cubic term is required by symmetry, and at least one higher order term is required for stability.

$$\Phi(S) = \Phi_0 + \frac{3}{4} AS^2 + \frac{1}{4} BS^3 + \frac{9}{16} CS^4 + \frac{9}{40} DS^5 + \frac{9}{16} ES^6 \quad (3)$$

where $A = a(T-T_c^*)$, T_c^* being the virtual second order transition temperature for pretransitional fluctuations in the isotropic.

In the simplest case, we take up through the quartic term. The result of this approximation is to give us a nematic phase order parameter which is a constant plus a parabola

$$S - S^\dagger = (T^\dagger - T)^{.5} \quad (4)$$

Note that the presence of the cubic term gives us a background order parameter term, $S^\dagger$. $T^\dagger$, with its corresponding $S^\dagger$, is, in the context of mean field theory, the point beyond which the nematic phase cannot be superheated. The actual first order transition temperature is labeled T_k, and falls between T_c^* and $T^\dagger$.

If, however, one drops the 4th order term and uses the 6th order term, one finds a similar form with an exponent of .25 (when the coefficient of the cubic term is small). This is the standard tricritical point value of the exponent. In general, one might expect that the behavior could be approximated by a simple power law of the form:

$$S - S^\dagger = (T^\dagger - T)^\beta \quad (5)$$

Poggi et al.[7] report consistency with mean field theory and $\beta = 0.5$ for the thermotropic compounds MBBA and HBN, whereas Keyes[8] has shown the same data to be consistent with a power law of 0.25. The data are inconclusive, although other experiments on other compounds[9-10] tend to rule out the critical value $\beta = 0.5$ result for thermotropics in favor of the tricritical value.

The CsPFO system is a novel one in the sense that the N-I transition is even more nearly second order than in other liquid crystals, as determined from light scattering[11] and magnetic birefringence measurements[2] in the isotropic phase, as well as the data presented here. $(T_k - T_c^*)$ has been shown to be as low as 20mK for the pretransitional nematic fluctuations in the isotropic phase[2]. Since a large part of the inherent difficulty in measuring β is due to the inability to probe the region close to $T^\dagger$, this is a very important feature. Also, by changing the concentration, we are able to vary the free energy coefficients.

While we are unable to state an absolute value of the order parameter from our measurements, since our samples never reach S=1, we can make reasonable estimates. From lower temperature measurements on the x = 0.035 sample, the extrapolated birefringence appears to saturate in the vicinity of 0.0032 on the scale of the figure. The N-NS value is about 0.0023, giving $S_{N-NS} \approx 0.7$, which is in the same range as expected for many thermotropics. At the kink of the N-NI transition, there is a birefringence of about 0.00095, thus $S_k \leqslant 0.3$, which is slightly less than in most thermotropics.

For the other sample, x = 0.025, limits on cooling the sample prevent extrapolating to a saturation value. However, if we also take the value of $S_{N-NS} \approx 0.7$, we find that $S_k \approx 0.17$, which is even closer to a second order transition.

We analyze our data in the context of the above discussion by fitting them to a simple power law plus a background term. The method is a non-linear least-squares algorithm. We must decide what temperature range of data to fit. A wider range to be fit puts a more stringent test upon the model, provided the model is valid far from the transition. The highest temperature points of value are those just before the T_k kink. Poggi et al. [7] used a range of about 1 degree for their fits. Others have used ranges from about 1 degree up to most or all of the nematic range. In our case, we used a range less than 3 or 4 degrees, since coupling to the Smectic order becomes important near the N-NS transition, which for our samples is about 5 or 6 degrees below T_k. We have fit both sets of data to the power law form, over both the 1 and 3 degree ranges, and with the critical exponent β fixed at 0.5, 0.25 and allowed to vary. Note that these are 3 and 4 parameter fits to a modest curvature, so that we must carefully assess the meaningfulness of any such results, especially since unnormalized chi-square values are the basis of comparison.

In the $x = 0.035$ sample, the mean field β value of 0.5 was found to fit quite well over both the 1 and the 3 degree range fits. This is shown in Figure 3. The tricritical value of $\beta = 0.25$ fit almost as well for the 1 degree range, much the same as Keyes demonstrated [8] for the data of Poggi et al. [7]. This broad minimum in the chi-square can be attributed to the high number of parameters for such a smooth curve, as well as any randomness in the experimental data points. We found the value of $S^\dagger$ to be negative when $\beta = 0.25$, however, and we reject the fit, since negative $S^\dagger$ is non-physical. When a 3 degree range was fitted using $\beta = 0.25$, the fit program did not converge within a reasonable range of values, and $S^\dagger$ again tended to go negative. A best fit to the 3 degree range actually gave β = 0.57 ± .06, however upon examining the data and fitted curves by eye, no improvement was evident, suggesting that a properly normalized chi-square would be less than 1, and thus the mean field value of 0.5 would again be correct within the precision of our experiments.

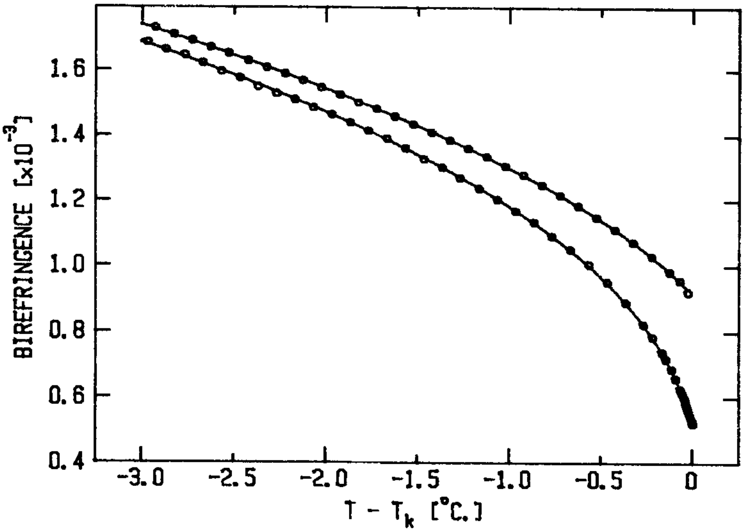

FIGURE 3. The nematic data for CsPFO. The upper curve, x = 0.035, is shown with a fit with β = 0.50. The lower curve, x = 0.025, is plotted with its best fit of β = 0.40.

For the x = .025 sample, the mean field value of β = 0.5 is not quite as good, showing a small but distinct systematic error. For both the 1 and 3 degree ranges, β = 0.25 gave a lower chi-square than β = 0.5, but again gave physically meaningless values of $S^{\dagger}$ (negative) which should be discounted. The best fits for both ranges gave intermediate values of β, with β = 0.40 (+.04, -.06), giving a chi-square one-tenth that for β = 0.5 in the 3 degree fit. This is shown in Figure 3. This is an indication that higher order terms in the free energy are important, but they do not fully dominate the quartic term.

A further check on the above results is to compare fitted values of $S^\dagger$ and $T^\dagger$ to the values expected from the simple Landau theories. These results are summarized by Gramsbergen et al. [6] to be, in the $\beta = 0.5$ mean field approximation:

$$S^\dagger = 3/4\ S_k \tag{6}$$

$$T^\dagger = T_k + (T_k - T_c^*)/8 \tag{7}$$

The $S^\dagger$ values for $\beta = 0.5$ all agree quite well with Equation (6) and the measured S_k. The temperature T_k is difficult to determine accurately, but within the experimental accuracy (7), predicts results consistent with magnetic birefringence measurements [2].

What statements can be made regarding the relative importance of the coefficients in Equation (3)? The cubic coefficient B is negative, since the nematic phase S is known to be positive [1]. One may deduce from the magnetic birefringence data of Rosenblatt et al. [2] that the fourth order constant C is positive and nonzero. For the $x = 0.035$ sample, there is no need to consider higher terms to explain the data. When $x = 0.025$, we see two effects. First, the first order discontinuity has decreased. This suggests that B decreased with respect to C and the higher order coefficients. The second observation is the reduction of the effective exponent β, suggesting an increased importance of higher order terms relative to the quartic.

In conclusion, we have measured the optical birefringence behavior in the lyotropic liquid crystal CsPFO and have related it to the nematic order parameter. The first order discontinuity can be altered somewhat by varying the water content. This allows us to obtain more significant estimates for the effective exponent β close to the N-I transition than has previously been possible in thermotropic materials, and also allows us to watch the approach to a possible tricritical point on the phase diagram. The values of β suggest agreement with a Landau (mean field) model, with higher order terms becoming more important as the transition becomes more second order.

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REFERENCES

1. N. Boden, P. H. Jackson, K. McMullen and M. C. Holmes, Chem. Phys. Lett. 65, 476 (1979).
2. Charles Rosenblatt, Satyendra Kumar and J. D. Litster, Phys. Rev. A 29, 1010 (1984).
3. Tom Haven, Keith Radley and Alfred Saupe, Mol. Cryst. Liq. Cryst. 75, 87 (1981).
4. P. G. De Gennes, Phys. Lett. 30A, 454 (1969).
5. T. W. Stinson, J. D. Litster and N. A. Clark, J. Phys. (Paris) 33, C1-69 (1972).
6. E. F. Gramsbergen, L. Longa and W. H. de Jeu, Phys. Rep. (to be published).
7. Y. Poggi, P. Atten and J. C. Filippini, Mol. Cryst. Liq. Cryst. 37, 1 (1976).
8. P. H. Keyes, Phys. Lett. 67A, 132 (1978).
9. H. Kneppe, V. Reiffenrath and F. Schneider, Chem. Phys. Lett. 87, 59 (1982).
10. J. Thoen and G. Menu, Mol. Cryst. Liq. Cryst. 97, 163 (1983).
11. Satyendra Kumar and J. D. Litster (to be published).