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Pressure Dependence of the Nematic-to-Isotropic Transition in the Lyotropic Liquid Crystal Cesium Perfluoro-Octanoate

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We report light-scattering measurements under pressures up to 1000 bars of nematic short-range order in the isotropic phase of the lyotropic liquid-crystal system cesium perfluoro-octanoate and water. The nematic-to-isotropic transition temperature is a nonlinear function of pressure which changes strongly with concentration and dT_{NI}/dp is from 10 to 100 times smaller than in typical thermotropic nematics. We also find the bare correlation length in the isotropic phase to be $12.5 \pm 2 \text{ \AA}$.

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Lyotropic nematic liquid-crystalline phases are formed by long-range orientational ordering of nonspherical micellar aggregates of amphiphilic molecules. These phases have been discovered only relatively recently, and are of interest not only to liquid-crystal physicists but also to those concerned with the statistical mechanics of surfactants, micelles, and microemulsions. Because they are multicomponent systems and involve the ordering of micelles, which may change size and shape with concentration and temperature, they are inherently more complex than most thermotropic liquid-crystal systems. Recent experiments¹ showed that the properties of lyotropic nematic phases formed from disklike micelles are qualitatively similar to those of thermotropic nematics. Thus, the properties are determined primarily by the symmetry of the nematic phase and the spatial dimensionality; the extra degrees of freedom provided by the complex nature of the ordering aggregates do not play a major role. However, there are quantitative differences in the behavior of lyotropic and thermotropic nematics; we explore some of those differences in this article.

The micelles that form nematic phases may be approximately disklike (DM) or cylindrical (CM) in shape. The uniaxial nematic liquid-crystal phases of these systems are further classified as type I or type II according to whether the diamagnetic susceptibility is greater along or transverse to the nematic symmetry axis. The micellar nematic-to-isotropic phase transition has been studied both by light scattering and by magnetic birefringence¹ in both type-I and type-II DM materials; these studies showed that the similarities between lyotropic and thermotropic nematics include the following. The nematic-to-isotropic (NI) transition is first order, as required by symmetry in the absence of strong fluctuations.² The pretransitional behavior in the isotropic phase exhibits the same classical mean-field critical exponents expected near a second-order transition at a temperature T_C^* preempted by a first-order transition at T_{NI} . A measure of the strength of the first-order transition is $T_{NI} - T_C^*$, which is proportional to the latent heat at the transition. In the system decylammonium chloride (DACl), am-

monium chloride, and water¹ this quantity is $\approx 0.6 \text{ K}$, not too different from known thermotropic nematics. However, magnetic birefringence measurements in the type-I DM system cesium perfluoro-octanoate (CsPFO) in water showed a strong concentration dependence of $T_{NI} - T_C^*$. It was observed¹ that $T_{NI} - T_C^* = 15 \text{ mK}$ for a CsPFO molar concentration $x = 0.020$, and increased to 600 mK for $x = 0.045$. The very small value of $T_{NI} - T_C^*$ is quantitatively different from known thermotropic nematics and is of fundamental interest because it allows a much closer approach to the spinodal temperature T_C^* and possibly greater insight into the effect of fluctuations on the NI transition, along with information about the collective behavior of strongly interacting micellar solutions.

In this article we present measurements of the pressure dependence of T_{NI} in a lyotropic nematic liquid crystal; the CsPFO system³ was chosen for the reasons outlined above. We studied four different mole fractions: $x = 0.0285$, 0.0250 , 0.0220 , and 0.0215 . We found that T_{NI} , in addition to being a strong function of x , is a nonlinear function of pressure; the pressure dependence of T_{NI} , however, is much smaller than one finds in thermotropic nematics. Similar behavior at the hexagonal-to-isotropic transition of nonionic surfactants has just been reported.⁴

Samples of CsPFO were synthesized according to the procedures of Ref. 1 and recrystallized from absolute ethanol. The high-pressure cell had three optical windows, one of which allowed light scattered at 90° from the incident direction to be measured. The cell was pressurized by a hydraulic pressure-generating system originally built by P. W. Bridgeman in 1926. Hexane was used as the pressure-transmitting fluid. The samples of approximately 0.5 cm^3 were contained in precision glass test tubes and separated from the transmitting fluid by a type-316 stainless steel piston with O-ring seals. The temperature was controlled to $\pm 0.02^\circ \text{C}$ by a circulating water bath. Reproducibility of T_{NI} at the end of a run was taken as evidence that no leak had occurred.

The mean intensity of light scattered at an angle of

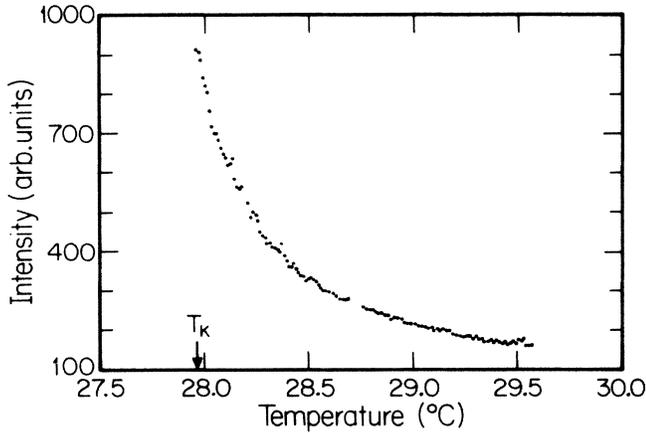


FIG. 1. Light-scattering intensity in the isotropic phase of a CsPFO sample with mole fraction $x = 0.022$ soap. The spinodal temperature T_K^* for this sample is 27.127°C . T_K marks the NI transition.

90° was measured as a function of temperature at each pressure. To correct for any drift in laser power, the incident and scattered light intensities were measured simultaneously. While the temperature could be reduced in steps, we obtained identical critical exponents and transition temperatures when the temperature was reduced continuously at a rate of 20 mK/min . All data were taken by this second technique. Figure 1 shows a typical curve of measured scattered intensity versus temperature thus obtained. T_{NI} was taken to be the temperature at which the curve of inverse intensity, I^{-1} , versus temperature first showed a break in slope indicative of the onset of a two-phase region. Our results are consistent with a first-order transition over the range of x we studied, in agreement with the data of Rosenblatt.¹

Our main results are the pressure and temperature dependence of $T_{\text{NI}}(x, p)$ shown in Figure 2. For all samples there is substantial curvature to the plot of T_{NI} as a function of the absolute pressure, p . Even for the $x = 0.0285$ sample, which looks closest to linear, the goodness of fit parameter χ^2 for data up to 1000 bars was 10 times smaller when a p^2 term was included. We fitted each set of data by variations of

$$T_{\text{NI}}(p, x) = T_0 + c_1 p + c_2 p^2 + c_3 p^3. \quad (1)$$

First, we determined c_1 by fitting data for $p \leq 300$ bars with c_2 and c_3 set equal to zero. While c_1 was small for

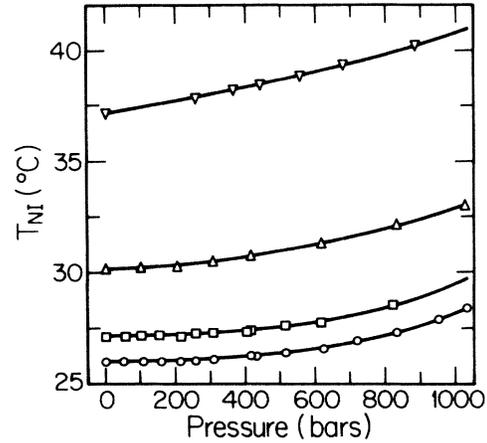


FIG. 2. Pressure dependence of T_{NI} for samples with CsPFO mole fraction $x = 0.0215$ (circles), 0.0220 (squares), 0.0250 (triangles), and 0.0285 (inverted triangles). The solid lines are fits by Eq. (2) with the parameters of Table I.

the $x = 0.0215$ and 0.0220 samples, it was not negative for any of the four. We next determined the parameters needed to fit all of the data. For the $x = 0.0285$ and $x = 0.0250$ samples, adding c_2 improved the fit substantially and yielded essentially the same value for c_1 as the linear fit to data for $p \leq 300$ bars. For these samples, including the c_3 coefficient did not improve χ^2 significantly and the fit gave a very small value for c_3 . We concluded that the first three terms of Eq. (1) were an adequate representation for the samples with $x = 0.0250$ and 0.0285 . For the other two samples the results were more complex. The first three coefficients gave a larger χ^2 than we expected and negative values of c_1 . Adding the c_3 coefficient gave much improved results, but with $c_2 = 0$ we found an equally good fit which also gave a value for c_1 in agreement with the data for $p \leq 300$ bars. Accordingly, the $x = 0.0220$ and 0.0215 samples were fitted by Eq. (1) with $c_2 = 0$. The results of our fits are given in Table II; the χ^2 values were normalized by the assumption of an error of $\pm 25\text{ mK}$ for T_{NI} at each pressure.

Motivated by the different ways that Eq. (1) fitted the different samples, we also tried fits with T_{NI} as a simple power law of pressure. We found the data could be well fitted by the following empirical expression:

$$T_{\text{NI}}(x, p) = T_0 + A p^y, \quad (2)$$

TABLE I. Parameters obtained from fits by Eq. (2).

x	T_0 ($^\circ\text{C}$)	A (K bar^{-y})	y	χ^2
0.0285	37.15 ± 0.03	$(6.1 \pm 0.2) \times 10^{-4}$	1.255 ± 0.01	1.5
0.0250	30.13 ± 0.04	$(1.51 \pm 0.03) \times 10^{-5}$	1.75 ± 0.01	1.1
0.0220	27.13 ± 0.04	$(6.6 \pm 0.6) \times 10^{-8}$	2.51 ± 0.03	2.9
0.0215	25.97 ± 0.03	$(3.4 \pm 0.2) \times 10^{-8}$	2.60 ± 0.01	1.7

TABLE II. Parameters obtained from fits by Eq. (1).

x	T_0 (°C)	c_1 (K bar ⁻¹)	c_2 (K bar ⁻²)	c_3 (K bar ⁻³)	χ^2
0.0285	37.14 ± 0.04	(2.3 ± 0.2) × 10 ⁻³	(1.3 ± 0.3) × 10 ⁻⁶	0	1.1
0.0250	30.12 ± 0.04	(5.4 ± 0.6) × 10 ⁻⁴	(2.2 ± 0.1) × 10 ⁻⁶	0	1.7
0.0220	27.10 ± 0.04	(2.9 ± 1.0) × 10 ⁻⁴	0	(2.2 ± 0.3) × 10 ⁻⁹	2.6
0.0215	25.95 ± 0.04	(2.8 ± 1.0) × 10 ⁻⁴	0	(2.1 ± 0.3) × 10 ⁻⁹	2.0

where $y(x)$ varies between 1.25 when $x=0.0285$ and 2.60 when $x=0.0215$, and $A(x)$ is a pressure-independent coefficient that varies with x . The fitted results by Eq. (2) are shown as solid lines in Fig. 2; the fits by Eq. (1) would be indistinguishable in the figure.

The scattered intensity for scattering vector q is proportional to $\chi_S[1+\xi^2q^2]^{-1}$, where χ_S is the generalized susceptibility for nematic order-parameter fluctuations, and ξ is a correlation length for nematic short-range order. In the mean-field case, $\chi_S=\chi_0(T/T_C^*-1)^{-1}$, and $\xi=\xi_0(T/T_C^*-1)^{-1/2}$. Therefore, when mean-field behavior obtains, one expects

$$I^{-1} \sim T - T_C^* - T_C^* \xi_0^2 q^2. \quad (3)$$

For the $x=0.0285$ sample, I^{-1} vs T was linear over the whole temperature range, thus confirming mean-field pretransitional behavior, and gave $T_{NI}-T_C^*=0.27 \pm 0.03$ °C. The magnetic birefringence results¹ at $q=0$ interpolate to $T_{NI}-T_C^*=0.060$ °C for $x=0.0285$. Our scattering vector was $q=0.0023$ Å⁻¹; from Eq. (3) we obtain a bare correlation length $\xi_0=12.5 \pm 2$ Å. This is an order of magnitude smaller than the value reported⁵ for the system potassium laurate, 1-decanol, and D₂O, and is only slightly larger than one finds in thermotropic nematics.

Plots of I^{-1} vs T for our other samples with $x \leq 0.025$ show some deviation from linearity; the scattering near T_{NI} is weaker than it should be. A similar subtle departure from the Landau-de Gennes model has also been noted by Larson⁶ for light scattered by 90°; he finds, however, that I^{-1} is a linear function of T for light scattered at a smaller angle for which $q \sim 4 \times 10^{-4}$ Å⁻¹. This may be related to subtle changes in the micelles near T_{NI} and will be discussed in a forthcoming paper.⁷

As the NI transition is first order, we may apply the Clausius-Clapyron equation

$$dT_{NI}/dp = T_{NI}\Delta V/L \quad (4)$$

to our data. We take the 1-bar values of dT_{NI}/dp from Table II. A detailed interpretation is difficult because CsPFO is a binary system and we have no information on the partial molar volumes of the constituents. However, we can make the following qualitative observations. First, in all samples dT_{NI}/dp is substantially smaller than the value 4.6×10^{-2} K bar⁻¹ for p -axoxyanisole,⁸ which is typical for thermotropic nematics. Second, $T_{NI}(p)$ in thermotropics does not show the strong non-

linearity we find for CsPFO. To some extent, the smaller dT_{NI}/dp in lyotropics is caused by the lower compressibility of water; it seems unlikely that this can account for more than a factor two. The Clausius-Clapeyron equation indicates that the ratio of the isotropic-nematic volume change ΔV to the latent heat L is a strong function of soap concentration and pressure. Since previous work¹ suggests that coefficients in the Landau-de Gennes free-energy expansion for CsPFO are similar to those for thermotropics, it must be that ΔV is at least 10 to 100 times smaller. Intuitively, the small ΔV is not too surprising since one might expect that the fluid water between the micelles, which is about half the sample volume, would permit micellar reorientations with very small overall density changes. We note that as x changes from 0.0285 to 0.0215, $T_{NI}-T_C^*$ changes by a factor 3 from ~ 60 to ~ 20 mK while $\Delta V/L$ changes by a factor ~ 10 . The nonlinear dependence of T_{NI} on p probably results from subtle changes in micelle aggregation number and shape with pressure;⁹ this is a complicated subject¹⁰ which deserves further study.

To summarize the salient results of our study of the CsPFO system, we recall that T_{NI} is a very nonlinear function of p even below 1 kbar, that dT_{NI}/dp is much smaller than in thermotropics, and that ΔV at the NI transition varies even more rapidly than the latent heat does with soap concentration. A successful model for the CsPFO micellar nematic will have to explain these observations.

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