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Pretransitional effects in the isotropic phase of a lyotropic nematic liquid crystal

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We report quantitative observations of the pretransitional fluctuations in short-range nematic order and the divergence of the magnetic birefringence in the isotropic phase of a lyotropic liquid crystal. The results are analyzed to obtain the anisotropy of the diamagnetic susceptibility and the coefficients in a Landau expansion of the free energy.

Lyotropic liquid crystals are formed by surfactant molecules in a suitable solvent, often an aqueous electrolyte. A recent popular discussion of these materials and the interest they hold for physicists has been given by Pershan.[1] Many lyotropic phases seem analogous to those of thermotropic liquid crystals, and their study should help to elucidate the role of symmetries and space dimensionality in statistical mechanics. Investigation of the properties of lyotropic phases should also reveal much about the properties of their constituent molecules.

Lyotropic nematic phases[2,3] are formed by the interaction of nonspherical micelles and have been designated[3] type I or II according to whether the diamagnetic susceptibility is greater along or transverse to the nematic symmetry axis. Either type I or II nematics may, in principle, be formed by the orientational ordering of disklike (DM) or rodlike (CM) micellar solutions. Previous studies[4,5] have shown that decylammonium chloride (DACl) micelles in a water-ammonium chloride solution have a type-II DM nematic phase which is closely similar to the nematic phase of thermotropic liquid crystals. Here we report the results of a quantitative study, carried out by light scattering and magnetic birefringence, of pretransitional effects in the isotropic phase of DACl as it prepares to form a nematic phase on cooling. We found behavior quite similar to that at the nematic-isotropic transition in thermotropic materials and can describe our data quantitatively using the Landau–de Gennes phenomenological model[6] proposed for thermotropic materials.

Decylammonium chloride (DACl) was prepared by neutralizing *n*-decylamine, purchased from the Aldrich Chemical Co., in cold diethyl ether with hydrochloric acid. The product was purified by recrystallization from a mixture of ethanol and petroleum ether (1:4) in an ice bath. Mixtures of DACl, NH_4Cl, and distilled deionized water were prepared in concentrations[7] that exhibit lamellar, nematic, and isotropic phases at convenient temperatures. For example, combining 100-g DACl with 9.87-g NH_4Cl in 113.4-g H_2O gave a nematic-isotropic phase change at $T_K = 63°C$ and a lamellar-nematic transition at $T_c = 43°C$. The samples were mixed by vigorous shaking and sonication.

Light scattering was used to measure the mean-squared fluctuations in nematic short-range order in the isotropic phase. The liquid-crystal mixture was placed in an optical cell with 1-cm path length that was housed in an oven whose temperature was controlled and measured with a precision of 1 mK. A linearly polarized argon-ion laser beam (~ 100 mW at 514.5 nm) illuminated the sample. Depolarized light scattered at 90° was passed through a pinhole aperture and imaged on the photocathode of an EMI 9863 photomultiplier. The laser power was carefully monitored and an absolute intensity calibration was obtained by using a 0.005% suspension of 91-nm diameter polystyrene latex spheres.

A 1-cm pathlength cuvette was used to hold the sample in the magnetic birefringence measurements. The apparatus used a He-Ne laser in combination with a Pockels cell modulated at 2.8 kHz and has been described in detail elsewhere.[8] Sensitivity in birefrince Δn was better than 10^{-8}, temperatures were controlled to 10 mK, and Δn was found to be linear in H^2 to fields $H > 10$ T.

To analyze our results, we review the predictions of the Landau–de Gennes model,[6] drawing upon the results of a previous analysis of Stinson, Litster, and Clark.[9] The nematic order parameter is a second-rank traceless tensor which can be phenomenologically defined by the anisotropy of the diamagnetic susceptibility tensor

$$\chi_{\alpha\beta} = \bar{\chi}\delta_{\alpha\beta} + \frac{2\Delta\chi}{3} Q_{\alpha\beta} \ . \tag{1}$$

In (1) $\Delta\chi$ would be the anisotropy for a perfectly ordered nematic which would have, say, $Q_{zz} = 1$ and $Q_{xx} = Q_{yy} = -\frac{1}{2}$. In the isotropic phase with no applied field all $\langle Q_{\alpha\beta}\rangle = 0$. The free-energy density in the isotropic phase can be expanded in a power series in $Q_{\alpha\beta}$ as

$$\Phi = \Phi_0 + \frac{A}{2} Q_{\alpha\beta}Q_{\beta\alpha} - \frac{B}{3} Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha} + \frac{C}{4}(Q_{\alpha\beta}Q_{\beta\alpha})^2 - \tfrac{1}{2}\chi_{\alpha\beta}H_\alpha H_\beta + \tfrac{1}{2}L_1 \partial_\alpha Q_{\beta\gamma}\partial_\alpha Q_{\beta\gamma} + \tfrac{1}{2}L_2 \partial_\alpha Q_{\alpha\gamma}\partial_\beta Q_{\beta\gamma} + \cdots \ , \tag{2}$$

where summation over repeated indices is implied and $\partial_\alpha = \partial/\partial x_\alpha$. In a Landau model $A = a_0(T - T_c^*)$ while the other coefficients are constant. The symmetry of the order parameter requires the cubic invariant and as a consequence the nematic-isotropic transition is first order; if B were zero a second-order transition would occur at $T = T_c^*$. By writing the optical dielectric constant as

$$\epsilon_{\alpha\beta} = \bar{\epsilon}\delta_{\alpha\beta} + \frac{2\Delta\epsilon}{3} Q_{\alpha\beta} \tag{3}$$

one can readily show[9] that a magnetic field applied to the isotropic phase will induce a birefringence

$$\Delta n = \frac{\Delta\epsilon \Delta\chi H^2}{9\bar{n}a_0(T - T_c^*)} , \tag{4}$$

where $\bar{n} = (\bar{\epsilon})^{1/2}$, when the lowest-order terms of (2) are considered. The correlation lengths for fluctuations in $Q_{\alpha\beta}$ are very small compared to the wavelength of light in thermotropic materials and the same appears to be true for DACl; under these conditions and our experimental geometry (only light scattered by off-diagonal fluctuations in $\epsilon_{\alpha\beta}$ is collected) the scattering cross section is given by[9]

$$\frac{1}{lP_0}\left(\frac{dP_s}{d\Omega}\right) = \left(\frac{\omega_0}{c}\right)^4 \left(\frac{\Delta\epsilon}{4\pi}\right)^2 \frac{2k_B T}{9a_0(T - T_c^*)} , \tag{5}$$

where P_0 is the incident laser power at frequency ω_0, l is the length along the beam of the volume from which light is scattered, and power dP_s is scattered into solid angle $d\Omega$. Equations (4) and (5) suffice to analyze our results.

The experimental results for the birefringence are shown in Fig. 1 for two samples with slightly different water content and transition temperatures that differ by about 2 K. The birefringence is actually negative as we have type-II micelles, and we show its magnitude. The behavior is in agreement with Eq. (4) and extrapolation of $H^2/\Delta n$ to zero gives T_c^*; the first-order nematic-isotropic transition occurred at $T_K = T_c^* + 0.8$ K. The slopes $H^2/\Delta n$ differ slightly. Light scattering was done on the sample labeled a which has a slope -6.2×10^{15} (G^2K^{-1}). From Ref. 7 we obtain $\bar{n} = 1.40$ and $\Delta\epsilon = 1.6\times10^{-2}$; thus $\Delta\chi/a_0 = -1.27\times10^{-13}$ K/G^2.

Turning to the light scattering experiments, we calculated[10] $(1/P_0 l)(dP_s/d\Omega) = 1.06\times10^{-2}$ cm^{-1} for 0.005% of 91-nm spheres in water scattering 514.5-nm light at 90°. Correcting for absorption by the polarizer and different collection solid angle caused by the solution's refractive index we obtained the absolute scattering cross section for the isotropic phase of DACl shown in Fig. 2. The figure also shows the fit of the data to Eq. (5) with $a_0 = 2.9\times10^4$ ergs K^{-1} cm^{-3}. As with the magnetic birefringence measurements, we found $T_K = T_c^* + 0.8$ K. From these results we deduce $\Delta\chi = (-3.7 \pm 1)\times10^{-9}$ ergs cm^{-3} G^{-2}; this agrees satisfactorily with recent magnetic measurements of Stefanov and Saupe[11] if we assume $Q_{zz} \simeq 0.4$ just below the nematic-isotropic transition. The value of a_0 is about 20 times smaller than one typically observes in thermotropics[9] which have $\sim 2.3\times10^{21}$ molecules cm^{-3}. Our solution had $\sim 1.4\times10^{21}$ molecules cm^{-3} of DACl. Thus at the nematic-isotropic transition the entropy change per molecule[9] is roughly $0.23k_B$ in thermotropics and $0.018k_B$ in DACl; when the latter is multiplied by any reasonable aggregation number (≥ 50) the entropy change per micelle is seen to be $> 0.9k_B$, several times that per molecule of thermotropics.

If terms higher than quartic are ignored in (2) and we assume $Q_{zz} = 0.4$ just below the transition, then it is possible to estimate[9] $B \simeq 2.1\times10^5$ ergs cm^{-3} and $C \simeq 3.8\times10^5$ ergs cm^{-3}. These estimates are somewhat unreliable since we have forced only three terms in the expansion to describe a large jump at T_K. A proper mean-field calculation, contrast-

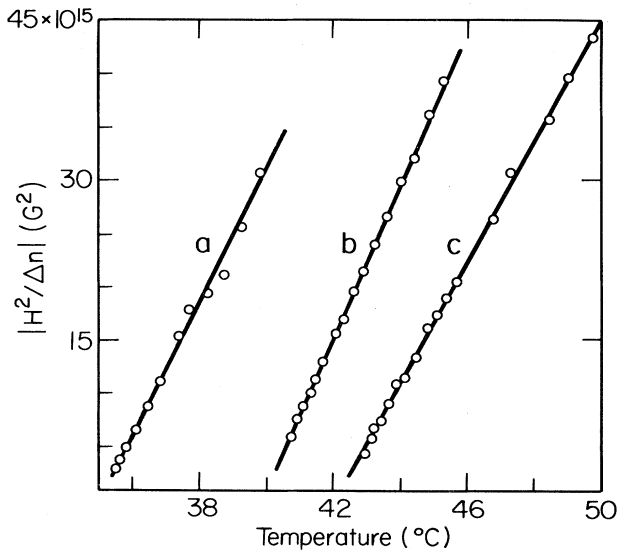

FIG. 1. The reciprocal of Cotton-Mouton coefficient ($H^2/\Delta n$) as a function of temperature on two mixtures with the same [DACl]/[NH_4Cl] ratio. a represents one sample and b and c the other sample; the difference in transition temperatures between b and c is due to slight evaporation of water. The solid lines are fitted to the mean-field result of Eq. (4).

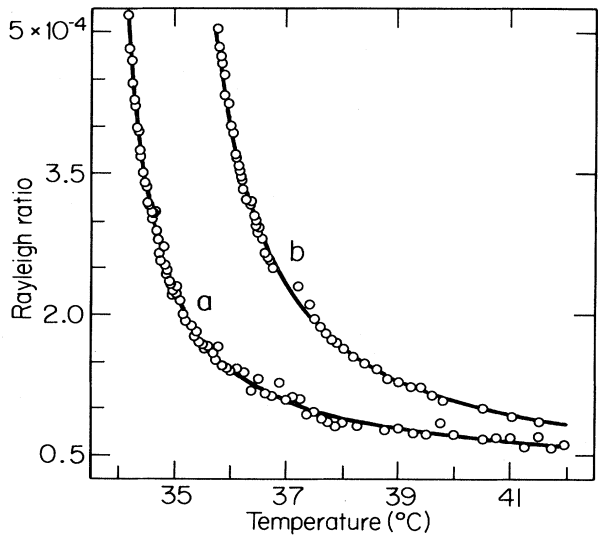

FIG. 2. Temperature dependence of Rayleigh ratio for DACl mixture of Fig. 1 line a. The two scans show different transition temperatures due to evaporation of water. The solid lines are fitted to Eq. (5).

ed with the Landau expansion of (2), has a single adjustable coupling constant and predicts[12] $T_K - T_c^* = 0.0918 T_K \simeq 30$ K. This is one of the most interesting puzzles about the nematic-isotropic transition in both thermotropic and lyotropic nematics. The pretransitional fluctuations diverge as $(T - T_c^*)^{-1}$, consistent with mean-field calculations, and the discontinuity in Q_{zz} is not far off the theoretical[12] value 0.43. Nevertheless, $T_K - T_c^*$ is some 30 times smaller than calculated. There is, as yet, no satisfactory theoretical explanation for this situation. It has been shown[13] that fluctuations cause the nematic-isotropic transition to be second order in $2+\epsilon$ dimensions in spite of the cubic invariant in the Landau expansion, thus it seems reasonable that a proper consideration of fluctuations in three dimensions might explain these observations.

The Ginzburg criterion[14] can be used to examine the validity of a mean-field model within the context of Eq. (2). The quadratic term alone predicts

$$\langle Q_{zz}^2 \rangle = (3k_B/4\pi a_0 \xi_0^3)(T/T_c^* - 1)^{1/2} , \quad (6)$$

where, taking $L_1 = L_2 = L$, the correlation length $\xi = \xi_0 (T/T_c^* - 1)^{-1/2} = (L/A)^{1/2}$. If we then replace $Q_{\alpha\beta}Q_{\beta\alpha}$ by $\frac{3}{2}\langle Q_{zz}^2 \rangle$ and $Q_{\alpha\beta}Q_{\beta\gamma}Q_{\gamma\alpha}$ by $\frac{5}{4}\langle Q_{zz}^2 \rangle^{3/2}$ in (2) we find the magnitude of the cubic term becomes equal to the quadratic term and fluctuations become important when

$$T/T_c^* - 1 = [25B^2 k_B/108\pi (T_c^*)^2 a_0^3 \xi_0^3]^{2/3} . \quad (7)$$

To evaluate this we need to estimate ξ_0. For thermotropics $\xi_0 \simeq 7$ Å (Ref. 15); since we expect L to be proportional to the Frank constant K_3, which is 4 times smaller in DACl (Ref. 4) than typical thermotropics, we estimate $\xi_0 \simeq 16$ Å in DACl. Evaluating (7) we might expect fluctuations to become important when $T - T_c^* \lesssim 0.4$ K. This admittedly crude calculation suggests that fluctuations could indeed affect the phase transition behavior. In any event, our experiments show that nematic ordering of small rodlike molecules and large disklike micelles are remarkably similar. The behavior is governed by the symmetry of the ordered phase and not by the details of the ordering units.

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[1] P. S. Pershan, Phys. Today 35, No. 5, 34 (1982).
[2] K. D. Lawson and T. J. Flautt, J. Am. Chem. Soc. 89, 5489 (1967).
[3] K. Radley, L. W. Rieves, and A. S. Tracey, J. Phys. Chem. 80, 174 (1976).
[4] T. Haven, D. Armitage, and A. Saupe, J. Chem. Phys. 75, 352 (1981).
[5] S. Kumar, L. J. Yu, and J. D. Litster, Phys. Rev. Lett. 50, 1672 (1983).
[6] P. G. de Gennes, Phys. Lett. 30A, 454 (1969); Mol. Cryst. Liq. Cryst. 12, 193 (1971).
[7] K. Radley and A. Saupe, Mol. Cryst. Liq. Cryst. 44, 227 (1978).
[8] C. Rosenblatt and J. T. Ho, Phys. Rev. A 26, 2293 (1982).
[9] T. W. Stinson, J. D. Litster, and N. A. Clark, J. Phys. (Paris) 33, C1-69 (1972).
[10] H. Denman, W. Pagonis, and H. Heller, *Angular Scattering Functions for Spheres* (Wayne State University Press, Detroit, 1966).
[11] M. Stefanov and A. Saupe, paper presented at the 9th International Liquid Crystal Conference, Bangalore, 1982 (unpublished).
[12] V. W. Maier and A. Saupe, Z. Naturforsch. 15a, 287 (1960).
[13] D. R. Nelson and J. Toner, Phys. Rev. B 24, 363 (1981).
[14] V. L. Ginzburg, Fiz. Tverd. Tela (Leningrad) 2, 2031 (1960) [Sov. Phys. Solid State 2, 1824 (1960)].
[15] T. W. Stinson and J. D. Litster, Phys. Rev. Lett. 30, 688 (1973).