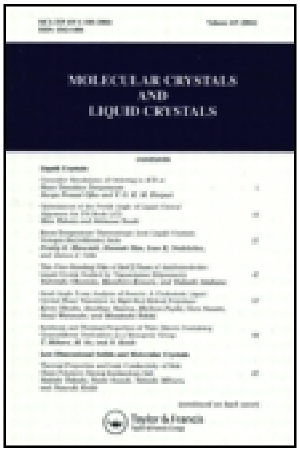

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Charles Resenbatt [a]
[a] Francis Bitter National Magnet Laboratory, massachusetts Insitute of Tecnhology, Cambridge, MA 02139, USA

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Temperature-Dependent Supercooling Limit in the Isotropic Phase of a Micellar Liquid Crystal

CHARLES ROSENBLATT

Francis Bitter National Magnet Laboratory, Massachusetts Institute of Technology, Cambridge, MA 02139 USA

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Magnetic birefringence measurements are reported for the binary mixture cesium perfluoro octanoate and water above the nematic–isotropic phase transition temperature T_c^*. Within 3 K of T_c^* the susceptibility exhibits behavior close to that predicted by mean field theory; beyond 3 K, however, deviations become more significant. It is argued that these deviations arise from a temperature-dependent supercooling limit, rather than entropy effects due to possible micelle size changes with temperature.

Keywords: micelles, liquid crystal phase transitions, nematic phase, supercooling

Micellar liquid crystals (MLCs) are composed of surfactant molecules, with perhaps a cosurfactant and/or an electrolyte, in an aqueous medium. Under proper conditions of temperature, concentration, and pressure the amphiphiles can aggregate into anisometric micelles, which in turn can form several classical liquid crystalline phases.[1] Unlike the situation in many single-component thermotropic liquid crystals, however, the individual units (micelles) which comprise micellar liquid crystals do not necessarily retain their integrity as the externally-controlled parameters are varied. A particularly extreme example of this phenomenon can be found[2] in the ternary system potassium laurate (KL), 1-decanol, and D_2O, where $\partial s/\partial T|_{\{W_i\}}$ changes sign deep into the nematic phase, becoming negative at low temperatures. Here s is the molecular aggregation number of the micelle,

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T the temperature, and W_i the concentration of component i. As the temperature is further decreased, the micellar aspect ratio shrinks sufficiently to induce a re-entrant low temperature isotropic phase. Although few other examples are as spectacular as this, virtually all MLCs exhibit some sort of structural change with concentration and temperature.

In recent years a considerable body of literature has appeared concerning the binary system cesium perfluoro octanoate (CsPFO) + water, first described in detail by Boden et al.[3] Unlike most other MLCs, the CsPFO system does not require a third component for the formation of a nematic phase and, again unlike hydrocarbon systems, forms micellar disks possessing a positive magnetic susceptibility anisotropy, i.e., $\Delta\chi > 0$. It is thus a convenient micellar system in which one can study the isotropic (I), oblate nematic (N), and smectic A phases and their respective transitions. At the NI transition, for example, it was shown[4,5] that the quantity $T_c^* - T^*$ can become extremely small as a function of weight fraction W of CsPFO, where T^* is the supercooling limit of the uniform isotropic phase and T_c^* is the first order phase transition temperature. Above this quasi-second order transition the susceptibility exponent γ was found[4] to be mean field with a value 1.01 ± 0.04 over a nearly 3 K temperature range. Moreover, within 300 mK of T^* the field-induced birefringence Δn was no longer found to be linear in H^2, where H is the applied field. The deviations from linearity diverge as $(T - T^*)^{-\Delta}$, where the characteristic "gap" exponent was $\Delta = 1.75 \pm 0.25$. As is usual, the analysis for the two exponents assumed structural integrity of the micelles as well as temperature-independent intermicellar interactions. Over a sufficiently small temperature region this is probably a good approximation, with one caveat. Gelbart et al. have predicted[6] significant structural changes at the NI phase transition arising from a coupling between the nematic order parameter and micelle concentration at a fixed composition. Using X-rays, however, Boden found[7] no evidence for this effect in CsPFO, and thus the authors of Ref. 4 were probably correct in not accounting for an explosive growth in micelle size right at the NI transition. Nevertheless, over somewhat larger temperature ranges the temperature dependences of micelle structure and interactions may indeed play a crucial role in various pretransitional measurements. The purpose of this paper then, is to report on susceptibility measurements for a mixture of CsPFO + H_2O over an 8 K range above T^*, where I found significant deviations from an effective mean field susceptibility exponent. This result is unlike that of several thermotropic materials, which exhibit an exponent $\gamma = 1$ over several tens of degrees far from the transition.[8,9] Since close to T^* the exponent in CsPFO was found to be mean field, these deviations cannot arise from critical behavior commensurate with either an $N = 5$ or $N = 1$, $d = 3$ N-vector model in the isotropic phase.[10-12] Rather, the data is examined in light of possible structural or intermicellar interaction variations with temperature.

CsPFO was synthesized according to the procedure in Ref. 4 and recrystallized from absolute ethanol. The sample consisted of weight fraction $W = 0.400 \pm 0.002$ of CsPFO, the rest being deionized H_2O, and was contained in a stoppered 1 cm pathlength glass cuvette. T_c^* was monitored over 22 days and was found to increase by less than 40 mK, corresponding to an increase in W due to evaporation of less than one part in one thousand. The cuvette was housed in a temperature-controlled brass oven, which in turn was situated in an 11.2 T Bitter magnet possessing a transverse optical bore. Details of the oven and birefringence apparatus are given elsewhere.[13]

The field H was swept from zero to 10 T in 30 s and the induced birefringence Δn was computer recorded. For this particular experiment temperature control was better than 3 mK over the duration of the sweep for the first temperature point, and better than 15 mK thereafter. The first data point was taken within 50 mK of T^* and exhibited the expected nonlinear behavior in Δn vs. H^2; the Cotton-Mouton coefficient $C(T) \equiv \partial \Delta n / \partial H^2 |_{H=0}$ was obtained from the linear coefficient of a fit quadratic in H^2. Subsequent data points were spaced approximately 400–700 mK apart and, as expected, Δn was found to be linear in H^2. Good agreement was thus found between birefringence fits linear in H^2 and the linear coefficient of fits quadratic in H^2. $C(T)$ vs. T was obtained over the range $T_c^* < T \lesssim T_c^* + 8$ K in relatively uniform temperature steps, unlike the fit for the exponent γ in Ref. 4, where the density of data points sharply increased with a decrease in reduced temperature.

In the context of a Landau model it can be shown that[14]

$$C(T) = \frac{\Delta\epsilon \Delta\chi}{9\bar{n}a_0(T - T^*)} \equiv \frac{\Phi}{(T - T^*)} \tag{1}$$

where $\Delta\epsilon$ and $\Delta\chi$ are the dielectric and magnetic susceptibility anisotropies for fully saturated order, $\bar{n}$ the average refractive index, and a_0 the coefficient of the term quadratic in the nematic order parameter $\tilde{Q}$ in the Landau free energy. In Figure 1, $1/C$ is plotted against temperature for a typical set of data. (The experiment was performed five times in order to quantify the experimental error.)

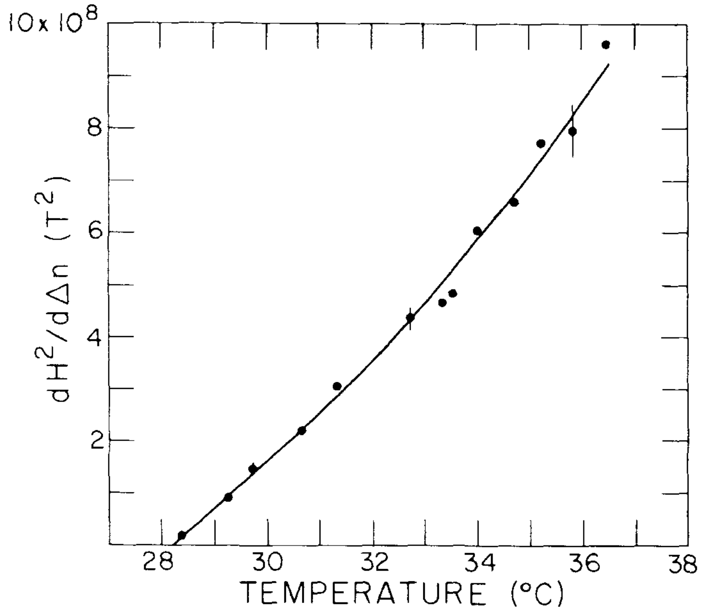

FIGURE 1 The inverse Cotton-Mouton coefficient $1/C$ [$\equiv dH^2/d\Delta n$] vs. T for a typical experimental run. The solid line is logarithmic least-squares fit for this particular run with parameters $\Phi = 1.25 \times 10^{-8}\ T^{-2}$ K, $b = 0.038$, and $T^* = 28.175$°C [cf. Eq. (2)], in good agreement with the average of all five experimental runs (see text). Typical error bars are shown.

Although Eq. (1) predicts a linear temperature relationship for C^{-1}, deviations from linearity are clearly observable, especially for $T \gtrsim T^* + 3$ K. To better quantify the results the Cotton-Mouton coefficient was rewritten in the *ad hoc* form

$$C(T) = \frac{\Phi}{(T - T^*)} e^{-b(T - T^*)}. \qquad (2)$$

This form was chosen for calculational convenience and becomes more transparent when inverted and expanded in powers of $(T - T^*)$:

$$1/C = (T - T^*)/\Phi + b(T - T^*)^2/\Phi + \ldots \qquad (3)$$

This expression should be compared with Eq. (1) and Figure 1. To obtain the parameters Φ, T^*, and b, the logarithmic form of Eq. (2), viz, $\log C = \log\Phi - \log(T - T^*) - b(T - T^*)$ was used for all five sets of data. For each fit the quality of the fit as determined by

$\sqrt{\chi^2}$ was approximately ±4%, as readily evident in Figure 1. Values of Φ reproduced well from one set of data to another, although b exhibited far more scatter since it represents a small correction to a large number. The average values were found to be $\Phi = (1.23 \pm 0.04) \times 10^{-8}\, T^{-2}$ K and $b = 0.041 \pm 0.010$ K^{-1}. This value of Φ can be compared with an earlier corrected measurement[5] of $(1.28 \pm 0.1) \times 10^{-8}\, T^{-2}$ K at the same concentration over a significantly smaller temperature region. It should be noted that owing to a recently discovered calibration error, all Φ values reported in Ref. 5 are 3% too high. The value quoted above has been corrected for this error. Thus, reasonable reproducibility from sample to sample has been obtained.

The main issue of this paper, however, is not the reproducibility of Φ, but rather the origin of the deviations from Eq. (1) as reflected by the parameter b. In earlier papers I've argued[5] that the quantity a_0 in Eq. (1) is related to the orientational entropy of hard cylinders, obtaining a_0 up to and including the first virial correction in terms of an Onsager calculation. Recently Photinos and Saupe derived[15] the Cotton-Mouton coefficient C for a general potential. Specializing their expression to the case of fixed amphiphile concentration N_A and variable micelle number density ρ (where the aggregation number s of the micelle is N_A/ρ), we can write

$$1/C \propto \frac{\rho}{N_A^2}\, T\left[1 - 5 \sum_{\kappa \geq 1} \kappa B_\kappa \rho^\kappa\right] \tag{4}$$

where the factor N_A^2 comes from the scaling form for $\Delta\epsilon\Delta\chi$ [Ref. 5] and

$$B_\kappa = \frac{1}{(4\pi)^{\kappa+1}}$$

$$\int P_2(\cos\theta_1)P_2(\cos\theta_2)\beta_\kappa(\Omega_1, \Omega_2, \ldots, \Omega_{\kappa+1})d\Omega_1 d\Omega_2 \ldots d\Omega_{\kappa+1}. \tag{5}$$

Note that $\rho/N_A^2 = 1/\rho s^2$ and, for micelles retaining their integrity (constant s), Eq. (4) is identical to the Photinos-Saupe form. In Eq. (5) β_κ represents the irreducible cluster integrals of the products formed by the function $f_{ij} = \exp(-u_{ij}/k_B T) - 1$, where u_{ij} is the pair potential and k_B is Boltzmann's constant. In the subsequent discussion I retain only the first correction term $\kappa = 1$. The cluster integral can be qualitatively treated by noting that for separations $\lesssim$ the largest of the micellar dimensions, $u_{ij} \gg k_B T$ and $f_{ij} \simeq -1$. The integral of f_{ij} over this distance contains two terms: an orientationally isotropic part arising from the integral over distances $\lesssim$ the *smaller* micelle dimension, and an anisotropic part arising from the remainder of the integral. This integral thus represents the negative of the effective excluded covolume β_1^{ex}. At larger separations where $u_{ij} \lesssim k_B T$, f_{ij} can be expanded in a series in $1/T$: $f_{ij} = -u_{ij}/k_B T + u_{ij}^2/2k_B^2 T^2 - \ldots$, resulting in an additional contribution to β_1 which goes as $-(1/T)\,\beta_1' + \mathcal{O}(1/T^2)$. Thus $\beta_1 = -\beta_1^{ex} - (1/T)\,\beta_1' + \mathcal{O}(1/T^2)$ and, from Eq. (5), we obtain an analogous form for B_1. Substituting these results into Eq. (4), we find

$$
\begin{aligned}
1/C &\propto \frac{\rho}{N_A^2}\, T\left[1 - 5\rho\left(-B_1^{ex} - \frac{1}{T}B_1' + \mathcal{O}\left(\frac{1}{T^2}\right)\right)\right] \\
&= \frac{\rho}{N_A^2}\left[T\left(1 + 5\rho B_1^{ex}\right) + 5\rho B_1' + \mathcal{O}\left(\frac{1}{T}\right)\right]. \qquad (6)
\end{aligned}
$$

Note that terms of $\mathcal{O}(1/T)$ and higher can be expanded around the supercooling temperature T^* and contribute a correction to both the T-coefficient and constant terms in Eq. (6). Owing to Coulombic screening these contributions tend to be small, however. More about this later. Keeping only the leading terms in Eq. (6) and in terms of Landau theory, $\rho(1 + 5\rho B_1^{ex})$ is proportional to a_0 and

$$
T^* = \frac{-5\rho B_1'}{1 + 5\rho B_1^{ex}}. \qquad (7)
$$

B_1^{ex} represents the $Tr\bar{Q}^2$ dependent part of the excluded volume term and is negative. Similarly, B_1' represents the $Tr\bar{Q}^2$ part of the longer-range interactions; in order that $T^* > 0$ this term must also be negative.

For particles retaining their integrity, such as thermotropic molecules, B_1 is independent of temperature and, from Eq. (6), we would expect to find the mean field behavior of Eq. (1). For micelles, however, both particle configuration and u_{ij} can be temperature dependent. From Eq. (6), therefore, it's clear that the observed deviations can arise from changes in micelle size, reflected primarily in ρ and B_1^{ex} and thus a_0, from changes in the potential at large separations, reflected in B_1' and thus T^*, or from both. An experiment of this sort alone cannot distinguish between the various effects, and complementary information is needed. Very recently Boden obtained results[7] from an X-ray experiment in which he found the micelle aggregation number to be a weakly varying function of temperature in the isotropic phase, decreasing by approximately (8 ± 5)% over the range $T_c^* \leq T \leq T_c^* + 8$ K. From his results certain conclusions can be drawn. Averaging my five sets of data, the slope of $1/C$ vs. T at $T \simeq T^* + 8$ K is about 85% higher than it is at $T = T^*$. To achieve such a change solely through a_0 [cf. Eq. (6)] would require an increase in micelle concentration ρ and a concomitant decrease in occupation number s with temperature. (Note that the term $5\rho B_1^{ex}$ is of order 1/3 and, to leading order in ρ, $B_1^{ex} \sim \rho^{-3/2}$ (Ref. 5), where the symbol "~" should be read "scales as.") To a good approximation then, $a_0 \sim \rho$ and thus a nearly 50% decrease in micelle size would be required in order to reflect the experimental change in $1/C$ over the 8 K range. Given Boden's X-ray results, however, this is clearly not the case, and thus a_0 remains relatively temperature independent.[16] Another possible source for the susceptibility results is a temperature dependence in the term B_1', which arises from weaker, long range interactions and is responsible for the supercooling temperature T^*. I now define T^* as the extrapolated temperature intercept of $1/C$ vs. T in the limit of $1/C \rightarrow 0$. If the micelle shape or size changes *slightly* with temperature, or if the intermicellar interactions are temperature dependent, we might also expect to find an effective supercooling limit $T_{\text{eff}}^*(T)$ which is a function of temperature. We can understand $T_{\text{eff}}^*(T)$ by noting that for a *nearly* temperature-independent micelle size, a_0, $\Delta\epsilon$, and $\Delta\chi$ are virtually constant, and thus Φ is nearly constant [cf. Eq. (1)]. Then $T_{\text{eff}}^*(T)$ is the effective temperature-dependent supercooling limit which must be substituted into Eq. (1) to fit the data with Φ held constant. Clearly $T_{\text{eff}}^*(T)$ must be a decreasing function of T in order that C^{-1} rise faster than linearly in temperature [cf. Figure 1]. Thus from Eqs. (1) and (2) we can write $T_{\text{eff}}^*(T)$ as

$$T_{\text{eff}}^*(T) = T - (T - T^*)e^{b(T - T^*)}, \tag{8}$$

independent of Φ. At $T = T^* + 2$ K, $T_{\text{eff}}^* = T^* - 0.17$ K, and at $T = T^* + 8$ K, $T_{\text{eff}}^* = T^* - 3.11$ K, a change of only 1% of the value of T^*.

The precise origin of a decrease in T_{eff}^* cannot, unfortunately, be isolated by this experiment. At first glance Eq. (7) would suggest that a *small* decrease in micelle concentration ρ (i.e., an increase in s) would result in a smaller T_{eff}^*. There are two problems with this argument: the results of Ref. 7 suggest that ρ would most likely increase with temperature and such an effect would not likely exhibit the strong pretransitional behavior suggested by Eq. (8). On the other hand, micellar solutions which *increase* slightly in ρ with temperature (i.e., decrease slightly in occupation number s with temperature), as suggested by Ref. 7, also exhibit a decrease in aspect ratio. Such an effect would tend to reduce the anisotropic interactions, as represented by B_1', perhaps sufficiently to offset the concomitantly increasing ρ in the numerator of Eq. (8). (Remember that $B_1' < 0$.) Nevertheless, the lack of any obvious pretransitional behavior remains disturbing. Another possible source of a decreasing T^*_{eff} with temperature is related to fluctuations near the transition. Fisch et al. deduced[17] a bare correlation length $\xi_0 \simeq 12$ Å for the NI transition in CsPFO. Over the temperature range of the experiment, then, ξ would vary from some 1000 Å to about 80 Å, in other words, from many micellar diameters down to one or two. These fluctuations could conceivably couple to the charge cloud around the micelle, to the intramicellar molecular order, or again perhaps to the average micellar occupation number s, thereby affecting B_1' to a small degree. Such an effect would likely exhibit pretransitional behavior and, as pointed out earlier, only a small change in B_1' is needed. Yet a third possible source for the effect is a coupling to smectic fluctuations. Based upon the continuity of electrical conductivity at the smectic A–nematic transition, Boden et al. have suggested[18] that CsPFO exhibits a smectic A phase consisting of discrete micelles, rather than continuous lamellae; such a result was earlier found in the ternary system decylammonium chloride, NH_4, and water.[19] At $T = T^* + 7\,\text{K}$ the reduced temperature relative to the nematic–smectic A phase transition is only twice that relative to the NI transition, and thus translational fluctuations might be expected to couple to the observed pretransitional behavior. Phenomena of this sort have been investigated by means of light scattering in thermotropic liquid crystals,[8,9] although unlike the micelle case the departures in those systems from expected mean field behavior were strongest close to the NI transition and exhibited a downward curvature. Upon heating the thermotropics several degrees above T_c^*, $1/C$ became linear in T over a temperature range of as much as 40 K, in marked contrast to the micellar system. It's likely then, that any coupling mechanism between nematic interactions and smectic order would be completely different for the two cases. In the micelle case, for example, smectic fluctuations may affect the counterion distribution around the micelle. One should bear in mind, however, that it is still difficult to reconcile a coupling to smectic order with the apparent pretransitional character of the observed deviations as NI transition temperature is approached.

As mentioned earlier, there is yet a fourth possible source for the behavior in Figure 1. In Eq. (6) terms of $\mathcal{O}(1/T)$ and higher were discarded. In fact, if the full expansion of f_{ij} were retained, and the resulting integrals expanded about the supercooling temperature, not only would T^* and a_0 be renormalized slightly, but quadratic and higher order terms in $(T - T^*)$ would appear [cf. Eq. (3)] in the Cotton-Mouton coefficient. These terms, however, tend to be very small due to the rapid fall-off of u_{ij} with distance, and it is highly improbable that these corrections could significantly contribute to the nonlinear behavior in Figure 1. Thus this possibility can be discounted.

The purpose of this investigation was to determine if and how NI pretransitional phenomena in micellar liquid crystals differ from those of thermotropics. Well above T_c^* it's clear that Eq. (1) is not obeyed unless Φ, T_{eff}^*, or both are functions of temperature. Based upon the results of Boden,[7] I have concluded that Φ is nearly constant over an 8 K temperature range in the isotropic phase. Rather, T_{eff}^* is a decreasing function of T, owing to changes in the longer range part of the intermicellar potential. The particular source of this change isn't clear at this time and most likely requires experimental work using complementary techniques such as NMR and neutron scattering.

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