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Physics Abstracts

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Electrolyte effects on a nearly second order nematic-isotropic phase transition in a micellar liquid crystal

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Résumé. — Le diagramme de phase et les résultats des mesures de susceptibilité magnétique de la phase isotrope observés pour le crystal liquide lyotrope de césium perfluoro octanoate + eau en présence de sel de CsCl, sont présentés dans ce manuscrit. Basé sur l'évolution du coefficient de Cotton-Mouton et dans le contexte d'un des modèles d'Onsager, nous spéculons sur la structure des micelles en fonction de la concentration d'électrolyte.

Abstract. — The phase diagram and results from magnetic susceptibility measurements in the isotropic phase are presented for the lyotropic liquid crystal cesium perfluoro octanoate + water in the presence of an added salt CsCl. Based upon the evolution of the Cotton-Mouton coefficient and in the context of an Onsager-type calculation we speculate on the micellar conformation as a function of electrolyte concentration.

During the past several years micellar liquid crystals have been receiving an ever increasing amount of attention. Composed of a surfactant and perhaps a cosurfactant and/or electrolyte in an aqueous medium, the anisometric micelles often exhibit a rich phase diagram whose critical behaviour at times mimicks [1, 2] and at times is at odds [3] with traditional thermotropic liquid crystals. One such system is the binary mixture cesium perfluoro octanoate (CsPFO) + water, which forms disk-like micelles with a positive net diamagnetic anisotropy [4]. Although the nematic-isotropic phase transition is everywhere first order, in the low concentration region of CsPFO it is only very weakly so, and $T_c^* - T^* < 30$ mK [5, 6]. Here T_c^* is the first order phase transition temperature on the isotropic side of the transition [7] and T^* is the extrapolated supercooling limit. Nevertheless, in this concentration regime both X-ray experiments in the smectic A phase [8] and magnetic susceptibility measurements in the isotropic phase [6] indicate that the disks are becoming *larger* (i.e., more eccentric) with decreasing surfactant concentration. If the nearly second order transition were indicative of a nearby Landau point [9], one would rather

expect a *smaller* effective eccentricity in this region, as seen experimentally in the ternary system potassium laurate-decanol-D₂O [10]. The behaviour of CsPFO thus remains an enigma awaiting a more detailed elucidation of the relationship between micellar structure and the critical behaviour at the NI transition.

In this Letter we report the results of magnetic susceptibility measurements in the isotropic phase as a function of concentration of an added electrolyte, CsCl, at a fixed weight ratio of water to CsPFO. Several features were observed upon increasing the weight fraction W_e of the electrolyte : 1) $T_c^* - T^*$ increased by an order of magnitude; 2) both T_c^* and T_{NA} , where T_{NA} is the nematic-smectic A transition temperature, increased, although the temperature extent of the nematic phase, $T_c^* - T_{NA}$, decreased; and 3) the quantity $(T - T^*) C \equiv \Phi$ decreased sharply, where C is the Cotton-Mouton coefficient. Based upon a Landau free energy and an Onsager formulation [11] for the entropy of ordered disks, the data suggest certain trends in the micellar configuration.

The CsPFO was synthesized according to the procedure in reference [5] and recrystallized from absolute ethanol. The samples contained a constant weight ratio of H₂O to CsPFO of 1.500 ± 0.007 and a weight fraction W_e of CsCl between 0 and 0.074; the absolute weight fractions of water and surfactant were varied accordingly. The density of the mixture was found to be 1.24 ± 0.02 g/cm³, independent of W_e . Samples were contained in a 0.2 cm pathlength stoppered cuvette housed in a temperature-controlled oven. The oven was in turn situated in a 10.7 T Bitter magnet possessing a transverse optical port. Details of the oven and birefringence apparatus are given elsewhere [12]. The field H was swept from zero to 10 T in 30 s and the induced birefringence Δn was computer recorded. Over the duration of the sweep, temperature control was better than 3 mK.

Well above T^* the birefringence was found to be linear in H^2 and the Cotton-Mouton coefficient $C(W, T) \equiv \partial \Delta n / \partial H^2 |_{H=0}$ was determined by a linear least-squares fit to the data. Closer to T^* ($T - T^* < 200$ mK) deviations from linearity were observed; here the initial slope $\partial \Delta n / \partial H^2 |_{H=0}$ was determined from a least-squares fit to a polynomial quadratic in H^2 . Data were taken over a temperature range $T_c^* < T < T_c^* + 2$ K and in all cases C^{-1} was found to be linear in temperature, indicating a mean field susceptibility exponent $\gamma = 1$. (The possibility that nonclassical values were observed for β in the nematic phase has been discussed elsewhere [3].) Given the apparent mean field behaviour in the isotropic phase, the Cotton-Mouton coefficient can be shown to be [13]

$$C(W_e, T) = \frac{\Delta \varepsilon \Delta \chi}{9 \bar{n} a_0 (T - T^*)} \equiv \frac{\Phi}{(T - T^*)} \quad (1)$$

where $\Delta \varepsilon$ and $\Delta \chi$ are the volume dielectric and magnetic susceptibility anisotropies for fully saturated order, $\bar{n} = (\bar{\varepsilon})^{1/2}$, and a_0 is the coefficient of the quadratic term in the Landau free energy expansion. The two fitted parameters $T^*(W_e)$ and $\Phi(W_e)$ were obtained from the $C(W_e, T)$ data using a logarithmic fitting procedure. Fitted values of T^* vs. W_e are shown in figure 1, and observed values of $T_c^* - T^*$ are shown in figure 2. Plotted in figure 3 are values of $T_c^* - T_{NA}$ vs. W_e . From these data it is clear that both ordered phases are stabilized by the addition of CsCl, with the smectic A phase particularly enhanced. In addition, the discontinuity in the first order transition, as measured by $T_c^* - T^*$, increases as a function of W_e . The quantity $\Phi \equiv \Delta \varepsilon \Delta \chi / (9 \bar{n} a_0)$ is plotted in figure 4 and, as readily apparent, is a strongly decreasing function of salt concentration.

In an ionic micellar system there are three primary components to the pair potential : 1) steric repulsions due to excluded volume effects, 2) screened Coulombic repulsions, and 3) weaker long ranged van der Waals attractions. Although the relative importance of the three interactions in a nematic micellar system is currently a topic of intense scrutiny, due to the high surfactant concentrations needed to form an ordered phase it is clear that both excluded volume and electro-

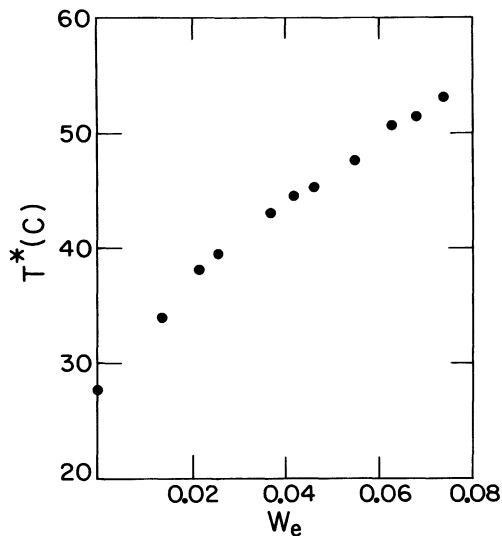


Fig. 1. — Supercooling limit T^* vs. weight fraction W_e of CsCl.

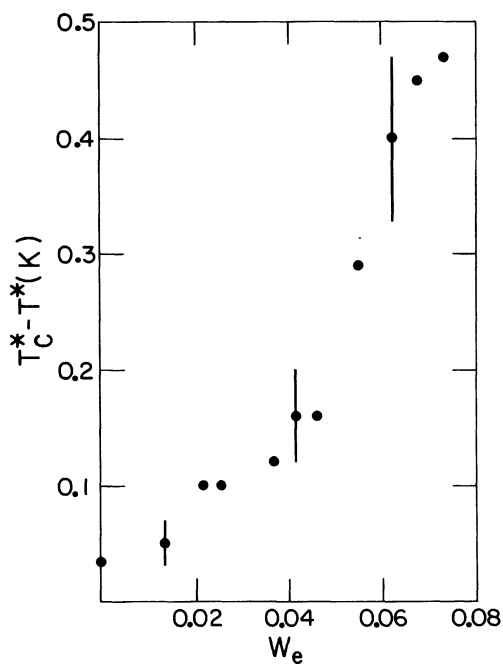


Fig. 2. — $T_c^* - T^*$ vs. W_e . Typical error bars are shown.

static repulsions play very significant roles. Addition of an electrolyte can modify both, however [14]. For example, by decreasing the effective ionic head group area, higher salt concentrations favour lamellar over rod-like structures, and both are favoured over spheres, obviously altering the steric interactions. But electrostatic screening is a double-edged sword : in addition to

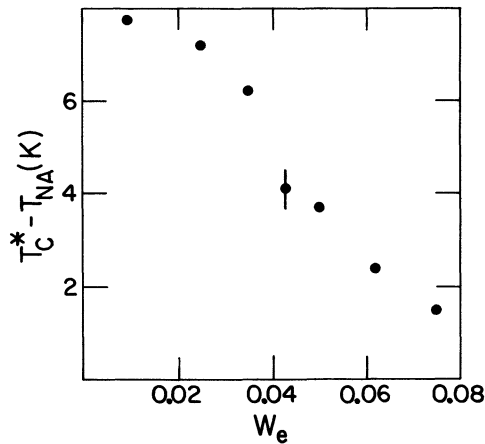


Fig. 3. — $T_c^* - T_{NA}$ vs. W_e . Typical error bar is shown.

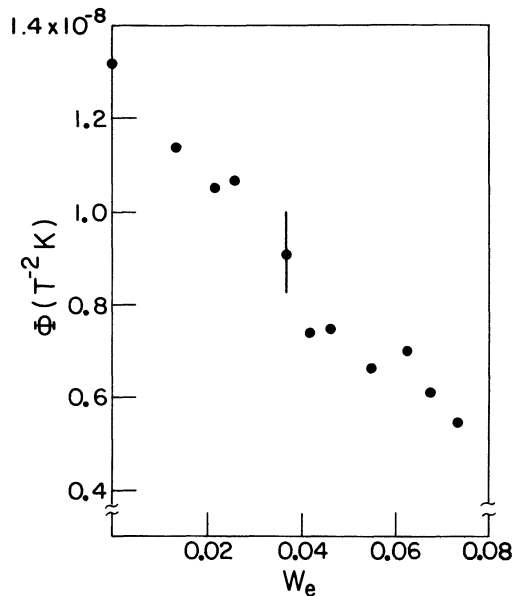


Fig. 4. — Φ vs. W_e (cf. Eq. (1)). Typical error bar is shown.

favouring more eccentric disk-shaped micelles, intermicellar Coulombic repulsions are also reduced [15]. For example, it has been shown with spherical micelles that sufficient added salt can effectively screen the Coulombic repulsions and result in a negative pair potential [16, 17].

Given the relatively high surfactant concentration of the sample, it is instructive to investigate the part of the free energy F due to orientational entropy. We first consider an assembly of rigid, disk-like nonionic micelles monodisperse in aggregation number s . The only interaction considered is hard core, which, as is well known, can result in a nematic phase [11]. Both $\Delta\varepsilon$ and $\Delta\chi$ (cf. Eq. (1)) are expected to scale as the amphiphile number density N_A times a shape factor f [$f < 1$]

[6]. Which is related to the fraction of amphiphiles located in the core (as opposed to the rim) of the micelle. For larger micelles, proportionally more molecules are located in the core [18] and f , which is a monotonically increasing function of s , is consequently larger. Moreover, in the context of a Landau model $-\text{Tr } a_0 \tilde{Q}^2$ represents to $\mathcal{O}(\text{Tr } \tilde{Q}^2)$ an orientational entropy changes S per unit volume between the $\tilde{Q} = 0$ and $\tilde{Q} \neq 0$ states, where \tilde{Q} is the nematic order parameter. As argued earlier [6] this entropy has a direct orientational component S_0 and a translationally-coupled orientational component S_T . Assuming Onsager's orientational distribution function $f(\theta) = (\alpha/4 \pi \sinh \alpha) \cosh(\alpha \cos \theta)$ [11], where $\alpha^4 \propto \text{Tr } \tilde{Q}^2$ for small α , to the level of the second virial coefficient we can obtain [6] the entropy S to $\mathcal{O}(\text{Tr } \tilde{Q}^2)$ and thus obtain $a_0 [= -S/\text{Tr } \tilde{Q}^2]$:

$$a_0 \sim \frac{N_A k_B}{90 s} - \frac{N_A^2 k_B}{1\,440 s^2} \left[\frac{1}{4} \pi^2 d^3 + \frac{1}{2} \pi(\pi + 3) ld^2 + \pi dl^2 \right] \tag{2}$$

where k_B is Boltzmann's constant, d is the micelle diameter and l its thickness. Note that the first term represents S_0 and the second term S_T . It should also be noted that although the entropy is expanded in powers of the order parameter to $\mathcal{O}(\text{Tr } \tilde{Q}^2)$, it is not our intention to predict an NI phase transition on entropic grounds; Onsager has shown [11] that higher order terms in the expansion would be needed. Rather, we wish to relate the $\text{Tr } \tilde{Q}^2$ -dependent part of the entropy to the experimental results in terms of Landau theory, that is, equation (1). Finally, note that \bar{n} deviates by no more than 2% from the pure water value $\bar{n} = 1.33$ over a wide concentration range. Gathering all these factors together we find from equation (1) that

$$\Phi \sim \frac{90 s f^2 N_A}{k_B \left[1 - \frac{N_A}{16 s} \left(\frac{1}{4} \pi^2 d^3 + \frac{1}{2} \pi(\pi + 3) ld^2 + \pi dl^2 \right) \right]}. \tag{3}$$

For this experiment $N_A \sim 5 \times 10^{20} \text{ cm}^{-3}$, $l \sim 21 \text{ \AA}$ (Ref. [8]), $d \sim 3 l$ (Ref. [8]), and from the density data the occupation number s is expected to be in the neighbourhood of 150. With these approximations we find that the contribution from S_T is already about one-third that of S_0 , and thus Φ given by equation (3) must be considered only a fair approximation at best. In fact, if either N_A or the micelle dimensions were to increase much more, the second virial approximation would completely break down. (At higher densities the y -expansion [19, 20] or scaled particle theories [21, 22] can be introduced, although the lack of precise information for the micellar dimensions may not warrant the calculational difficulties. The same holds true for lattice theories [23-25]).

We now consider ionic micelles with electrostatic interactions. We assume that the bare size is unaffected by the added electrolyte, and that one can make the approximation [11] that the Coulombic interactions tend mainly to increase the effective micellar dimensions in equation (3), so long as the Debye screening length κ^{-1} is sufficiently small. For very long, charged, cylindrical colloids Onsager has shown [11] that, from the standpoint of the entropic part of F , the effective micellar diameter increases by a term proportional to and of order κ^{-1} , where $\kappa^2 = 4 \pi \mu / \epsilon_w k_B T$. ϵ_w is the d.c. dielectric constant of the aqueous medium (~ 80), μ is the ionic strength $\sum_i n_i e^2$, and n_i is the concentration of the ionic species i , excluding the colloids themselves [26]. In the absence of an electrolyte we take the number density of Cs^+ counterions to be $\sim 0.6 N_A$ [27], and thus find $\kappa^{-1} \sim 6 \text{ \AA}$. Owing to the relatively high surfactant concentrations this figure is quite small, being approximately twice the diameter of the Cs^+ ion [28]. In such a high concentration region the quantitative validity of Debye-Hückel theory becomes doubtful, and again caution must be exercised in interpreting the data. Nevertheless, in light of these electrostatic interactions the *effective* diameter and width in equation (3) must be increased above the bare values [11] while

holding N_A/s nearly fixed. (One consequence of the renormalized micellar dimensions is an effective decrease in the aspect ratio d/l . More about this later). Upon the subsequent addition of an electrolyte the screening length κ^{-1} decreases and thus Φ is expected to decrease (cf. Eq. (3)) as well. For the experiment at hand a salt concentration $W_e = 0.075$ corresponds to an unrenormalized additional ion density of approximately $3.3 \times 10^{20} \text{ cm}^{-3}$, such that κ^{-1} is now approximately 3.5 \AA . Clearly, this figure should not be taken at face value but rather interpreted qualitatively as representing a decrease in the average intermicellar Coulombic interaction. Thus, by taking the effective micelle dimensions as the hard core size plus the Debye length for the softer Coulombic interactions, we expect from equation (3) a decrease in Φ of approximately 30 % in going from $W_e = 0$ to $W_e = 0.075$, which is to be compared with an experimental decrease of 55-60 % [cf. Fig. 4]. Given the approximations needed to arrive at the theoretical predictions, the agreement with experiment is actually quite gratifying.

The origin of the increases in both the nematic-isotropic and smectic A-nematic transition temperatures (Figs. 1 and 2) with W_e is quite complex. In addition to screening the micelle-micelle electrostatic interactions, an added salt tends to increase the occupation number of the core bilayer relative to the rim, effectively increasing the bare diameter [14]. An analogous effect in other systems exhibiting rod-like micelles has been nicely documented by means of neutron and light scattering [17, 29, 30]. In terms of equation (3) with N_A nearly constant, to leading order Φ would be expected to scale as the occupation number s . (It is interesting to note that the denominator remains nearly constant since d scales approximately as $s^{1/2}$ when the core-to-rim occupation ratio is sufficiently large). Given, however, that Φ is experimentally a *decreasing* function of W_e , we conclude that the occupation number s , and therefore diameter d , grows at most only very weakly with W_e , in contrast to some other systems [17, 29, 30]. The growth in the bare diameter must, in fact, be more than offset by the decrease in the effective diameter due to electrostatic screening.

Although the effective diameter apparently decreases with W_e , it was earlier observed that the aspect ratio d/l increases with added salt concentration. In a model of charged anisometric colloids Rosenfeld and Gelbart pointed out [15] that for sufficiently large κ^{-1} , a finite line charge will behave like a point charge; similarly, a long screening length tends to make a flat disk appear more isometric. Thus, from the standpoint of *anisotropic* Coulombic interactions over length scales $> \kappa^{-1}$, we might expect a stronger tendency for the system to form ordered phases as W_e and the aspect ratio increase and κ^{-1} decreases. This argument disregards, of course, the effects of attractive van der Waals interactions, which become more important at higher W_e [16, 17].

Much of the discussion presented in this paper is by necessity speculative, owing to the paucity of related experimental work. Factors such as the large radius of the Cs^+ ion have not been considered in detail and may, in fact, have a significant influence on the experimental results. Dowell has suggested, for example, that since the in-plane edge-to-edge micellar separation is of order 7 \AA , one or two large core Cs^+ ions may associate spontaneously with two micelles forming a sort of micelle-micelle complex [31]; this may not be the case with Li^+ or Na^+ ions which have fewer nonvalence electron shells and tend to hydrate. Nevertheless the main result of this work is that pretransitional behaviour at the nematic-isotropic transition in CsPFO is strongly influenced by the presence of an electrolyte. Scattered results in other micellar liquid crystals exist [32-35], but clearly much more work, particularly along the lines of neutron scattering, remains to be done.

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