



HAL
open science

Order-disorder transitions in solutions of discoid micelles

N. Boden, S.A. Corne, M.C. Holmes, P.H. Jackson, D. Parker, K.W. Jolley

► **To cite this version:**

N. Boden, S.A. Corne, M.C. Holmes, P.H. Jackson, D. Parker, et al.. Order-disorder transitions in solutions of discoid micelles. *Journal de Physique*, 1986, 47 (12), pp.2135-2144. 10.1051/jphys:0198600470120213500 . jpa-00210408

HAL Id: jpa-00210408

<https://hal.science/jpa-00210408>

Submitted on 4 Feb 2008

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers.

L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Classification

Physics Abstracts

61.25 — 61.30E — 64.70E

Order-disorder transitions in solutions of discoid micellesN. Boden, S. A. Corne, M. C. Holmes ⁽¹⁾, P. H. Jackson, D. Parker and K. W. Jolley ⁽²⁾

Department of Physical Chemistry, University of Leeds, Leeds LS2 9JT, U.K.

(Reçu le 19 novembre 1985, révisé le 8 août 1986, accepté le 21 août 1986)

Résumé. — On présente des mesures de diffusion des rayons X, de conductivité électrique et de RMN sur un échantillon de pentadécafluorooctanoate de césium (CsPFO) à 55 % en poids dans l'eau lourde ($^2\text{H}_2\text{O}$). Ce matériau présente une transition du premier ordre de lamellaire à nématique entre 325,13 et 325,50 K, et une transition de nématique à micellaire isotrope, également du premier ordre, entre 330,23 et 330,83 K. On montre que la particule mésogène de base est dans les trois phases une micelle discoïde discrète, donc que la phase lamellaire est formée de plans de micelles discoïdes. L'épaisseur de la micelle est de l'ordre de 2,2 nm. Dans la solution micellaire isotrope, le diamètre moyen de la micelle croît lentement lorsque la température est abaissée. A la transition isotrope-nématique, ce diamètre augmente de manière discontinue, passant de 5,26 nm ($N_A = 88$) pour la limite supérieure à 5,82 nm ($N_A = 113$) pour la limite inférieure ; par contre il n'y a pas de discontinuité de taille à la transition nématique-lamellaire où le diamètre est 6,38 nm ($N_A = 140$). La croissance de la micelle dans la phase nématique semble être tirée essentiellement par la variation en température du paramètre d'ordre, qui vaut 0,35 à la transition nématique-isotrope et 0,72 à la transition nématique-lamellaire. Ce comportement correspond aux prédictions des théories de Gelbart *et al.*, mais la transition vers la phase lamellaire n'est pas forcée par une croissance explosive des micelles en bicouches. Les figures de diffraction des rayons X sont remarquablement différentes de celles qui sont généralement observées dans les phases nématiques et smectiques A de matériaux analogues. Nous soutenons que ceci est dû à un empilement assez lâche des micelles (fraction volumique 0,35) ; en fait, dans les trois phases, les micelles pourraient bien subir des fluctuations orientationnelles de grande amplitude et non corrélées. Par conséquent les corrélations orientationnelles à courte distance sont absentes ou de portée très réduite. Ceci apparaît de façon manifeste dans les valeurs anormalement élevées du paramètre d'ordre orientationnel qu'on déduit des spectres de rayons X (0,92 à 0,71 dans la phase nématique). Nous suggérons que ces paramètres d'ordre sont déterminés principalement par les fluctuations collectives à longue portée du directeur. Ainsi, on aboutit pour la phase nématique à un modèle dans lequel les fluctuations orientationnelles individuelles des micelles sont essentiellement découplées des fluctuations collectives du directeur.

Abstract. — X-ray scattering, electrical conductivity and NMR measurements are presented for a sample of caesium pentadecafluorooctanoate (CsPFO) (55 per cent by weight)/water ($^2\text{H}_2\text{O}$). A first order lamellar to nematic phase transition occurs at 325.13 (1) to 325.50 (1) K and a first order nematic to isotropic micellar solution transition occurs at 330.23 (1) to 330.83 (1) K. The fundamental mesogenic particle is shown to be a discrete discoid micelle in all three phases, that is, the lamellar phase consists of planes of discoid micelles. The thickness of the micelle is of the order 2.2 nm. In the isotropic micellar solution, the average diameter of the micelle grows slowly on cooling. At the isotropic to nematic transition, it increases discontinuously from 5.26 nm ($N_A = 88$) at the upper boundary to 5.82 nm ($N_A = 113$) at the lower boundary, but there is no discontinuity in size at the nematic to lamellar transition where the diameter is 6.38 nm ($N_A = 140$). The growth of the micelle in the nematic phase appears to be driven mainly by the variation with temperature of the orientational order parameter (this is 0.35 at the nematic to isotropic transition and 0.72 at the nematic to lamellar transition). This behaviour is as predicted by the theories of Gelbart *et al.*, yet the transition to the lamellar phase is not driven by the predicted explosive growth of the micelles into bilayers. The X-ray scattering patterns are characteristically different from those generally observed in the analogous thermotropic nematic and smectic A phases. It is argued that this is because the micelles (volume fraction 0.35) are relatively loosely packed: in fact, in all of the three phases they may well undergo large amplitude uncorrelated

⁽¹⁾ School of Physics and Astronomy, Lancashire Polytechnic, Preston PR1 2TQ, U.K.

⁽²⁾ Department of Chemistry and Biochemistry, Massey University, Palmerston North, New Zealand.

reorientational fluctuations. Short range orientational correlations are consequently either absent or very limited in their extent. This is manifest in the unexpectedly large values (0.92 to 0.71 in the nematic phase) of the orientational order parameters obtained from the X-ray measurements ; it is suggested that these order parameters are mainly determined by the long-range collective director fluctuations. Thus, the model which emerges for the nematic phase is one in which the individual orientational fluctuations of the micelles are essentially decoupled from the collective director fluctuations.

1. Introduction.

The fundamental structural aspects of all liquid crystals is the existence of long range orientational order of the constituent particles, while long range positional order is either limited or completely absent [1]. The designation of the orientable unit is not, however, always unambiguous, particularly in the case of the lyotropic amphiphilic class of liquid crystal systems. The principal smectic phases obtained on dissolution of an amphiphilic compound (soaps, synthetic surfactants, biological surfactants) in water are the columnar (two-dimensional arrays of columnar aggregates interspersed with water) and the lamellar (alternating layers of biomolecular aggregates and water) [2, 3]. These aggregates were hitherto believed to be of indefinite size and the amphiphilic molecule was considered as the orientable unit [4]. But the discovery [5] of lyotropic amphiphilic nematic phases (currently envisaged as solutions of orientationally ordered discoid (N_D) or columnar shaped (N_C) micelles) points to the aggregate as the orientable particle. The resolution of this paradox is to be found in the detailed structures of the aggregates in these nematic phases, and the structural transformations they undergo at transitions into smectic phases.

The surprising feature of micellar nematic phases is that they occur in solutions of unexpectedly high concentrations (between 0.1 and 0.5 volume fraction of amphiphile). Their very existence is seemingly a contradiction to the fundamental postulate which is invoked in models to explain the concentration dependence of the structures of aqueous solutions of amphiphilic compounds [6-9]. This is that the dominant inter-aggregate interaction is repulsive (electrical double layer, excluded volume or hydration force) and the associated contribution to the free energy of the system is minimised by reorganization of the amphiphilic molecules into a smaller number of larger aggregates. Its effect would be to cause micelle growth and sphere-to-rod transitions in dilute solutions and transitions to infinite rods (columnar phase) and bilayers (lamellar phase) in concentrated solutions. For this reason it has been argued that nematic phases are intrinsically unstable [10] and it has been variously suggested that they are really defective lamellar or columnar phases [11]. Some support for these views seemingly comes from the fact that nematic phases have tended to be found over very restricted concentration intervals in complex mixtures of an ionic surfactant, water, a long chain alcohol and/or simple salt [12]. But, X-ray

diffraction measurements [13-16] are indicative of discrete micelles with axial ratio in the range 2 to 4 for N_C phases and 0.25 to 0.5 for N_D phases, although the X-ray orientational order parameters are inexplicably high (0.7 to 0.9). The implications are that nematic phases exist because, contrary to expectations, small anisotropic micelles are stable in concentrated solutions.

The most probable explanation as to why nematic phases have only been found in a few systems to date is that we do not at present understand the factors which govern the structure and ordering of amphiphilic aggregates in concentrated solutions and thus we do not know the kind of systems in which to search for them. Some clues, however, are beginning to emerge. The caesium pentadecafluorooctanoate (CsPFO)/water system has been shown to exhibit a nematic phase of discoid micelles (N_D) over an unprecedented range of concentration (0.10 to 0.43 volume fraction of CsPFO) and temperature (283 to 350 K) and which occurs intermediate to a lamellar phase and an isotropic micellar solution [17]. The occurrence of the N_D phase over such an extensive range of concentration is attributed to the hydrophobicity of the fluorocarbon chain which promotes the formation of bilayer aggregates as opposed to the cylindrical ones invariably encountered with linear chain hydrocarbon surfactants. Another seminal system is formed by the disc-like non-ionic amphiphilic mesogen TP6EO2M (2,3,6,7,10,11-hexa-(1,4,7-trioxaoctyl) triphenylene). This forms a nematic phase of columnar shaped micelles which is also stable over an extensive range of concentration (0.1 to 0.5 volume fraction of TP6EO2M) and which is intermediate to a columnar-hexagonal phase and an isotropic micellar solution [18]. The topology of this amphiphilic molecule precludes the formation of bilayer aggregates and hence the hexagonal to lamellar transition, usually encountered with increasing concentration with conventional amphiphilic molecules, is prohibited. The message is that nematic phases with extensive concentration and temperature ranges do occur in simple two component systems of the appropriate lyotropic amphiphilic mesogen. Moreover, their existence highlights the hitherto unrecognized fact that small anisometric micelles are stable over extensive concentration and temperature ranges.

The above conclusion has far reaching implications for the nature of the sequence of transitions: isotropic micellar solution \rightarrow nematic phase \rightarrow lamellar/columnar phase. The previous notion that these transition are driven by an explosive growth in the

structure of the aggregate may not be generally correct. The possibility of simple order-disorder transitions involving discrete micelles cannot be ruled out. Indeed, support for such a mechanism for the nematic to lamellar transition in the CsPFO/ $^2\text{H}_2\text{O}$ system is provided by electrical conductivity measurements [19].

To resolve the question of the nature of this transition and also to investigate the extent of any coupling between aggregate structure and mesophase order, we present here the principal findings of a combined NMR, X-ray diffraction and electrical conductivity study of a sample of CsPFO (55 per cent by weight)/water ($^2\text{H}_2\text{O}$). It is unequivocally shown that the fundamental particle is a discrete discoid micelle in all three phases. The diameter of the micelle is shown to be a function of temperature, mesophase structure and the orientational order parameter. A unique procedure is outlined for the calculation of the orientational order parameter of the micelles from a combination of X-ray and electrical conductivity data. The results suggest that in the nematic phase the micelles undergo essentially free, uncorrelated reorientation, in marked contrast to the behaviour of thermotropic nematics [20].

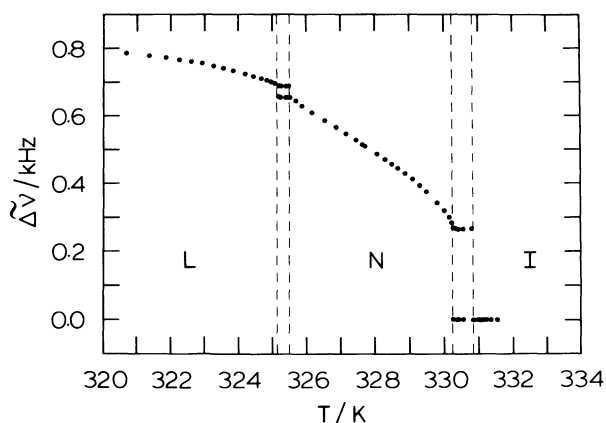


Fig. 1. — The variation of the partially averaged deuterium quadrupole splitting $\tilde{\Delta\nu}$ of $^2\text{H}_2\text{O}$ in a sample of CsPFO (55.04 ± 0.02 per cent by weight)/ $^2\text{H}_2\text{O}$ as observed on heating through the lamellar to nematic and nematic to isotropic transitions. Both transitions are first order in nature. The lower ($T_{LN} = 325.13$ (1) K) and upper ($T_{NL} = 325.50$ (1) K) boundaries for the lamellar to nematic transition were determined as the temperature of the discontinuity in the temperature dependence of the splitting as was the lower boundary ($T_{NI} = 330.23$ (1) K) of the nematic to isotropic transition. The upper boundary ($T_{IN} = 330.83$ (1) K) for this transition was obtained by monitoring the integrated intensity of the isotropic singlet peak with temperature. This parameter shows a linear dependence on temperature from zero at T_{NI} to a maximum constant value at T_{IN} and above.

2. Results and discussion.

2.1 NMR AND X-RAY. — Deuterium NMR spectroscopy (Fig. 1) shows that the sample undergoes a first order lamellar to nematic transition, a first order nematic to isotropic transition, and that the anisotropic diamagnetic susceptibility of the nematic phase is positive [17]. The X-ray scattering patterns (Fig. 2) of the nematic phase are indicative of discoid micelles with their symmetry axes aligned along the direction of the nematic director (z axis). The intense reflections in the *meridional* plane arise from the « face-to-face » separation d_{\parallel} of the micelles in the direction of the director, whilst the broad, weak, « moustache » comes from the « side-by-side » separation d_{\perp} of the micelles in the plane perpendicular to the director. We note that if the micelles were columnar shaped, the sharp reflections would have been in the *equatorial* plane as they would then arise from the « side-by-side » separation of the micelles. We can, therefore, assign the nematic phase as type N_D^+ [21].

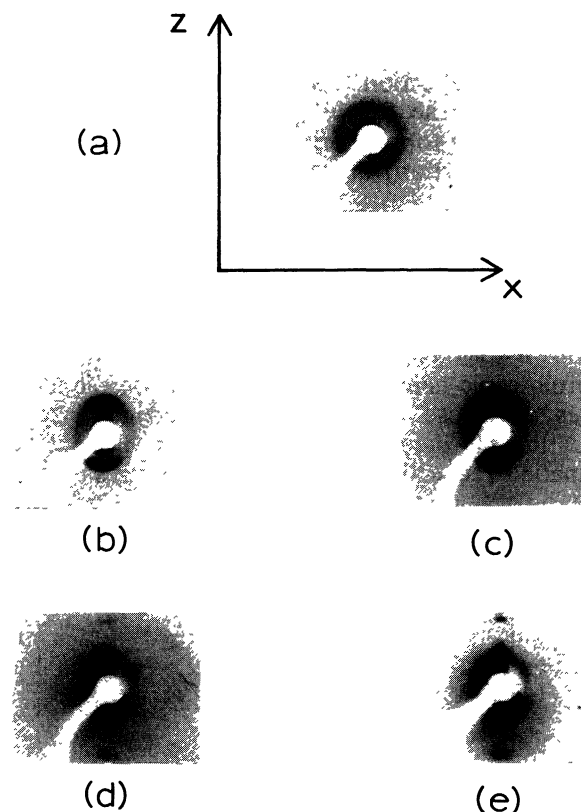


Fig. 2. — X-ray scattering patterns [(a) Isotropic micellar solution at 334 K ; (b), (c) and (d) nematic phase at respectively 329, 328 and 327 K ; (e) lamellar phase at 322 K] observed with a pinhole camera, monochromatic $\text{Cu K}\alpha$ radiation of wavelength 0.154 nm, point collimation, Lindemann sample tube (0.5 mm i.d.) to flat plate distance of 113.5 mm, and with the nematic director aligned (by a 0.4 T magnetic field) parallel to the z axis (*meridian*) and perpendicular to the x axis (*equator*) which is the direction of the long axis of the sample tube.

As the nematic phase is cooled figures 2b to 2d the *meridional* reflections sharpen and a weak second order reflection appears, whilst, in contrast, the intensity of the *equatorial* moustache weakens. At the nematic to lamellar phase transition (Fig. 2e), there is no discernible change in either the separations or shapes of the reflections. There is, therefore, no evidence for a large discontinuity in the structure of the aggregate at this transition. The discoid micelles appear simply to condense on to the planes of the lamellar phase rather than grow explosively into indefinitely extending bimolecular lamellae. Thus, the transition is quite analogous to the nematic to smectic A transition exhibited by thermotropic mesogens. But, in the latter case, there is a marked sharpening of the *meridional* reflection [22] on cooling through the transition. The explanation for this discrepancy in behaviour at the phase transition can be found in the different molecular structures of the two kinds of system. In thermotropic mesophases, the mesogenic particles (molecules) are closely packed, whilst in the amphiphilic mesophases these particles (micelles) are very loosely packed as they are separated by water. For example, in the system under investigation the volume fraction of micelles is only 0.35. Thus, the micelles have a considerable degree of both positional and orientational independence. The effect this has on the width of the meridional reflection (Fig. 3) can be understood by reference to the following expression for the line width ΔS [23] for scattering from a one-dimensional lattice (z -direction) of particles :

$$\Delta S \approx \left\{ \left(\pi^2 \delta^2 / 2 d_1^3 \right)^2 + \left(1 / N d_1 \right)^2 \right\}^{1/2}, \quad (1)$$

where $N d_1$ is the size of a single « domain » and δ is the half-width of an assumed Gaussian distribution in the nearest neighbour separation d_1 . In the case of thermotropic nematics δ is small, because the molecules are close packed, and the second term in equation (1) determines the linewidth. But, at the nematic to smectic A transition, N diverges and the

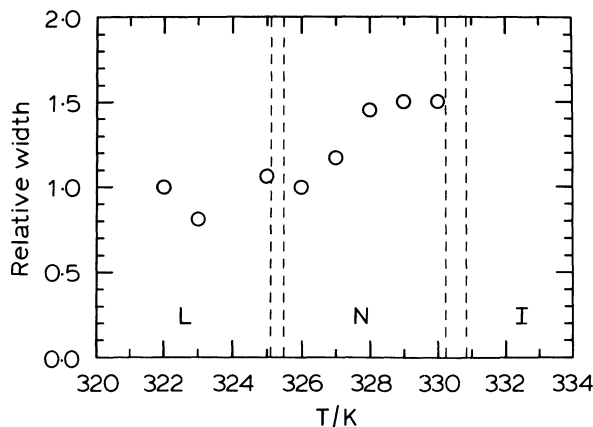


Fig. 3. — Relative widths at half-maximum height of the meridional reflection in the z direction versus temperature. The values have been normalized to the value $1.3 \times 10^{-4} \text{ nm}^{-1}$ at the lamellar to nematic transition.

first term takes over as the dominant contribution. In a micellar nematic δ is large and the linewidth seems to be dominated in both the nematic and lamellar phases by the first term in equation (1). Taking this to be the case, we find δ has the value 0.20 nm at T_{NL} ($\Delta S = 1.3 \times 10^{-2} \text{ nm}^{-1}$) and 0.68 at T_{NI} ($\Delta S = 4.5 \times 10^{-2} \text{ nm}^{-1}$). Since $d_1 \approx 4.0$ nm across the nematic range (Fig. 5a), we see that there is considerable positional disorder in the local packing of the micelles. A lower limit for the value of N in the nematic phase can be estimated by assuming the line width is governed by the second term in equation (1): this gives a value of 21 at T_{NL} and 6 at T_{NI} . Thus, the longer range positional correlations must be fairly extensive.

Values for the average volumes (expressed as aggregation numbers in Fig. 5b) have been calculated from the inter-micellar distances in figure 5a. They are seen to increase markedly on cooling. The « stepped » nature of the data is a consequence of the steps in d_{\perp} in figure 5a and which arise from the resolution (± 0.1 nm) of the densitometer used to read the X-ray films. For the interpretation of the electrical conductivity measurements, to be described in the next section, values for the axial ratio $R = a/b$, where a and b are the lengths of the minor and major axes of the micelle, are required. To obtain these it is necessary to assume an analytic shape for the micelle. Here we take the simplest and most plausible one, namely that of an oblate ellipsoid. Values for b were calculated assuming the micelles are arranged on close-packed planes, that is $b = 2 d_{\perp} / \sqrt{3}$. The corresponding values for a were

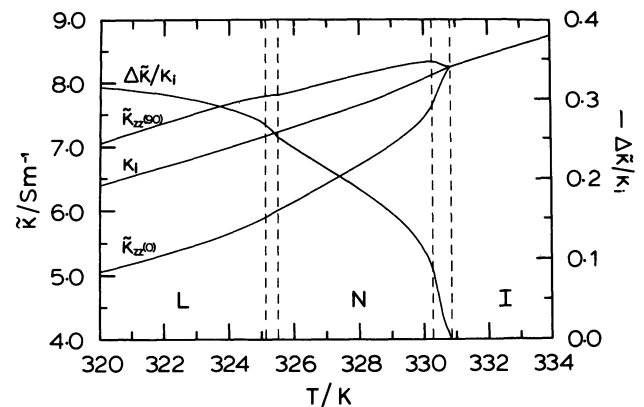


Fig. 4. — The electrical conductivity $\tilde{\kappa}_{zz}(\phi)$ as a function of temperature measured at 10 kHz in a sample of CsPFO (54.99 ± 0.02 per cent by weight)/ $^2\text{H}_2\text{O}$. $\tilde{\kappa}_{zz}(0^\circ)$ and $\tilde{\kappa}_{zz}(90^\circ)$ are the conductivities measured, respectively, parallel and perpendicular to the mesophase director, whilst κ_i corresponds to $\tilde{\kappa}_{zz}(54^\circ 44')$ in both the nematic and lamellar phases. The relative anisotropy of the electrical conductivity is $\Delta\tilde{\kappa}/\kappa_i \equiv (\tilde{\kappa}(0^\circ) - \tilde{\kappa}(90^\circ))/\kappa_i$. The observed conductivities in the mixed phase regions are weighted averages of the conductivities of the separate phases.

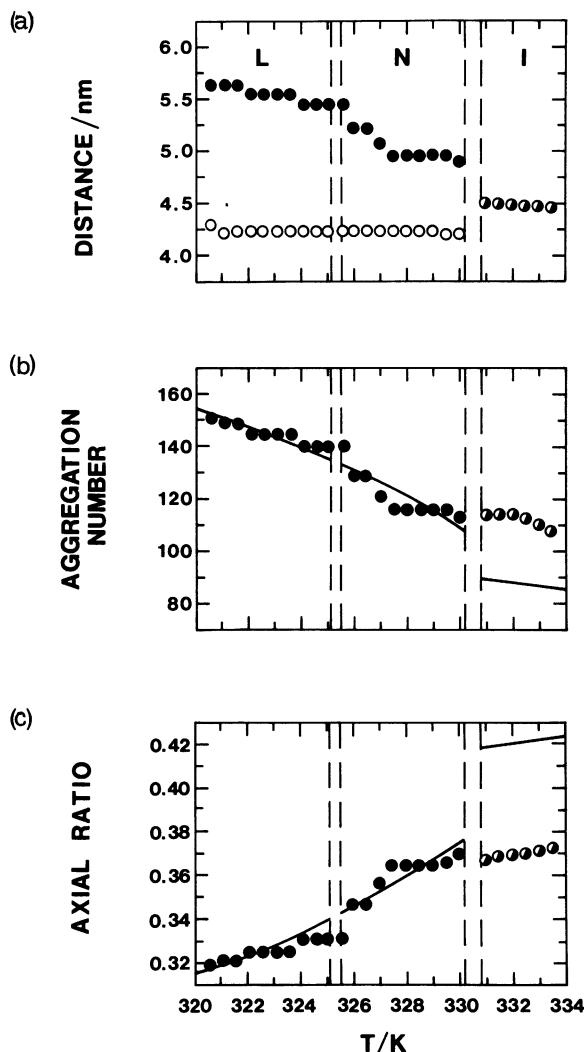


Fig. 5. — (a) Inter-micellar distances calculated from the maxima of the scattering curves using Bragg's Law: d_1 (○) is the « face-to-face » separation measured along the *meridional* direction and d_{\perp} (●) is the « side-to-side » separation measured along the *equatorial* direction in the lamellar and nematic phases, whilst d_0 (●) is the « centre-to-centre » separation calculated from the maxima of the intensity curves in the isotropic micellar solution.

(b) Average volume of the micelle V_M given as the aggregation number N_A obtained by dividing V_M by the volume of the amphiphile $V_A = 3.6 \times 10^{-28} \text{ m}^3$. V_M was calculated from the number density of micelles and the volume fraction of amphiphile ($\phi = 0.351$). In the nematic and lamellar phases volumes were calculated from $V_M = \frac{2}{\sqrt{3}} d_1 d_{\perp}^2 \phi_A$ which assumes the micelles are hexagonally packed on planes with separation d_1 and that the separation of the (11) planes is d_{\perp} . In the isotropic phase the volume was calculated from $V_M = \frac{3}{4} \sqrt{3} \phi_A d_0^3$ which assumes the X-rays are scattered from the (111) planes of a fcc lattice with separation d_0 . (This is a gross over simplification as the local structures of the nematic and isotropic phases are not expected to be significantly different. The *meridional* and *equatorial* reflections of the nematic phase are not resolved in the diffraction pattern from the isotropic micellar solution.) The continuous line represents values calculated from the conductivity measurements.

(c) Axial ratios R of the micelles which have been calculated from the micelle volume in (b) assuming the micelle is an oblate ellipsoid with minor axis length of 2.2 nm. The values calculated from the X-ray measurements are denoted by ● and ○ and those from the electrical conductivity measurements by the continuous line.

found to be roughly constant at 2.2 nm. This means that the increase in volume mainly arises from a growth in the diameter of the micelle. The choice of an ellipsoid micelle means that the value for a will be an upper limit. But it is quite a reasonable one when compared with the length l_m (1.24 nm) of an « ordered » pentadecafluorooctanoate anion. The axial ratios given in figure 5c were calculated using $a = 2.2$ nm. The values quoted in figure 5 for all of the quantities considered here will represent averages over the distribution in the size of the micelles.

2.2 ELECTRICAL CONDUCTIVITY. — The electrical conductivity monitors the diffusivity of the counterions around the micelles under the influence of an applied electrical field \mathbf{E} [19]. For a non-conducting, ellipsoidal micelle undergoing reorientational fluctuations with respect to the mesophase director it can be shown that the conductivity transforms as a second rank tensor with a principal axis system coincident with that of the moment of inertia tensor. The experiment measures the partially averaged component $\tilde{\kappa}_{zz}(\phi)$ of the conductivity tensor $\tilde{\kappa}$ along the direction of the electric field \mathbf{E} which is

taken to be along the z -axis of the laboratory frame $L(x, y, z)$. This is given by

$$\tilde{\kappa}_{zz}(\phi) = \kappa_i + \frac{2}{3} P_2(\cos \phi) S(\kappa_{\parallel} - \kappa_{\perp})_M, \quad (2)$$

where ϕ is the angle between the direction of \mathbf{E} and the mesophase director, S is the orientational order parameter of the micelles and κ_i is the value of the conductivity in the absence of long range order ($\overline{P_2} = 0$). $\kappa_i = (\kappa_{\parallel}/3 + 2\kappa_{\perp}/3)_M$, where the subscript M denotes the unaveraged components of the tensor in the micellar frame $M(a, b, c)$. In the liquid crystalline phases $\kappa_i = \tilde{\kappa}_{zz}$ ($54^{\circ}44'$) (i.e. $P_2(\cos \phi) = 0$).

Equation (2) describes the phenomenological relationship connecting the conductivity to the size, shape and reorientational motion of the micelles. It ought to be possible to extract information about the orientational order of the micelles in the nematic phase using our knowledge about their size and shape obtained from X-rays. To proceed we need a

model for the electrical conductivity. We have modified and tested a model first proposed in 1924 by Fricke [24]. For an isotropic solution of non-conducting ellipsoidal micelles this is

$$\kappa_i = \frac{\kappa_0 (1 - \phi_A) (1 - f)}{1 - \phi_A (1 + \beta_i)} \quad (3)$$

where κ_0 is the intrinsic conductivity which is assumed to arise solely from the counterions (this assertion is supported by the absence of any discontinuity in κ_i at the nematic to lamellar transition). $(1 - f)$ is the fraction of counterions which are free to conduct charge, that is, f is the fraction of counterions bound to the micelle. The factor $(1 + \beta_i)$ represents the obstruction effect of the micelles: $\beta_i \equiv (\beta_{\parallel}/3 + 2\beta_{\perp}/3)$ where β_{\parallel} and β_{\perp} are constants determined by the axial ratio of the micelle. To test the applicability of equation (3) values of β_{\parallel} and β_{\perp} were calculated from the X-ray data in figure 5c. This enables values of $\kappa_0 (1 - f)$ to be calculated using equation (3). The variation with temperature of this quantity is found to reproduce that of the molar conductivity of the Cs^+ ions at infinite dilution in heavy water, except that there is a discontinuity in absolute value at the nematic to isotropic transition. This we attribute to systematic errors arising from the interpretation of the X-ray measurements in the isotropic phase. Using the Debye-Hückel-Onsager equation to calculate the concentration dependence of the molar conductivity of Cs^+ ions gives a value of 0.75 for f . This is close to the value of 0.8 expected for anionic surfactants [25]. We have, therefore, concluded that equation (3) provides a consistent interpretation of the electrical conductivity measurements.

The details of the above analysis are to be published elsewhere. Here, we focus on the application of equation (3): first, to the calculation of what we consider to be a more precise representation of the variation with temperature of the axial ratio of the micelle, and then, in the next section, to the determination of the micellar orientational order parameter. The values obtained for the axial ratio are compared in figure 5c with those directly obtained from the X-ray data. The values are in good agreement in the lamellar and nematic phases, (they must be!), but they differ by roughly 12 per cent in the isotropic phase. This is simply another manifestation of the approximate nature of the interpretation given to the X-ray diffraction pattern in the isotropic phase. We believe that the discontinuity in the micelle size as depicted by the conductivity data is real. However, it is pertinent to consider here whether the discrepancy between the two sets of data for the isotropic phase could originate from a change from a spherical to a discoid micelle at the isotropic to nematic transition. The aggregation number for a classical spherical micelle ($N_A(\text{min}) = 4\pi l_m^3/3V_A$) is 22 and is substan-

tially smaller than the X-ray value. It is, of course, possible that within the isotropic phase the micelles undergo shape fluctuations [26] on a time scale which is short compared to the period of the conductivity measurement (2×10^{-3} s). The micelles would then appear to be spherical in the conductivity experiments. This hypothesis can be tested using equation (3). We find that this would require an increase in κ_i of 7 per cent as compared to the observed increase of 2 per cent at the nematic to isotropic transition. Thus, there are no reasons to believe that there is any major change in the structure of the micelle attendant upon this transition.

2.3 ORIENTATIONAL ORDERING OF MICELLES. — The measurement of the order parameter characterising the long range orientational order of the micelles in the nematic and lamellar phases presents a challenging problem to the experimentalist. There are two principal problems, the first is the need to allow for the effects of any change in micelle size on the property being measured, and the second is the need to correct for the internal motions of any probe molecule located within the micelle. The X-ray method [27] is not complicated by these two effects. We would expect that the micellar reorientational order parameter could in principle be obtained from the angular intensity distribution $I(\theta)$ of the *meridional* reflection where θ is the angle between the radius vector and the z -axis. The values obtained for the $\text{CsPFO}/^2\text{H}_2\text{O}$ system are plotted in figure 6; they vary from 0.92 at T_{NL} to 0.71 at T_{NI} and are typical of the values which have been previously obtained from X-ray measurements on other micellar nematic phases [14, 15, 28]. But these values are inexplicably large, especially when compared with those for thermotropic nematic phases. The latter have molecular order parameters which are typically 0.3-0.4 at T_{NI} [29].

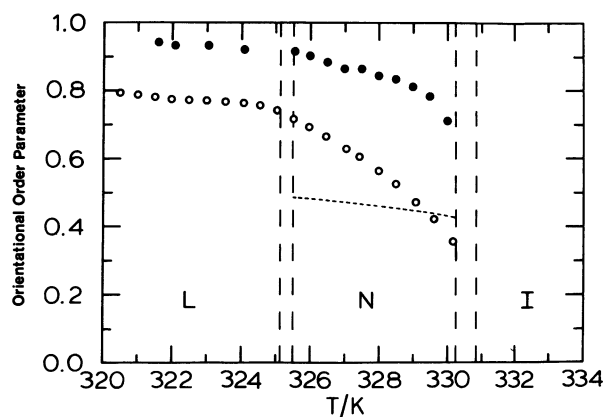


Fig. 6. — Orientational order parameters of the micelles in CsPFO (55 per cent by weight)/ $^2\text{H}_2\text{O}$ as obtained from the intensity distribution of the meridional X-ray reflection (●) and as calculated from the electrical conductivity measurements in figure 4 using equation (4) (○). The broken line represents the Maier-Saupe theory.

compared with those for thermotropic nematic phases. The latter have molecular order parameters which are typically 0.3-0.4 at T_{NI} [29].

The electrical conductivity measurements provide an alternative and complementary route to the micellar order parameter. Thus, from equation (2), we obtain

$$\frac{\widetilde{\Delta\kappa}}{\kappa_i} = S \frac{(\kappa_{\parallel} - \kappa_{\perp})_M}{(2\kappa_{\perp}/3 + \kappa_{\parallel}/3)_M}, \quad (4)$$

where $\widetilde{\Delta\kappa} \equiv \widetilde{\kappa}_{zz}(0^\circ) - \widetilde{\kappa}_{zz}(90^\circ)$. To obtain values for S we need values for κ_{\parallel} and κ_{\perp} in the micellar frame. These have been calculated using in equation (3) corresponding values for β_{\parallel} and β_{\perp} as calculated from the axial ratios in figure 5c. Substitution of the results into equation (4) with the corresponding $\widetilde{\Delta\kappa}/\kappa_i$ gave the values for S summarized in figure 6. S is seen to be 0.35 at T_{NI} and 0.72 of T_{NL} , values typical of the corresponding ones observed for thermotropic mesogens, as is also the weak temperature dependence in the lamellar (smectic A-like) phase. The variation of S with temperature in the nematic phase is, however, far stronger than the characteristic temperature dependence observed for thermotropic nematics [29]. An explanation for this behaviour is presented below. But, first, we shall focus on the cause of the discrepancy in the values of the order parameters obtained from the two sets of experiments.

It is pertinent to refer here to the optical birefringence studies of the nematic order in samples with volume fractions ϕ_A of 0.24 and 0.30, as recently reported by Larson and Litster [30]. The variation of the birefringence with temperature across the nematic phase is very similar in its behaviour to that of the relative anisotropy of the electrical conductivity $\widetilde{\Delta\kappa}/\kappa_i$ (Fig. 4). Both of these quantities are dependent upon the size and shape of the micelles in addition to their orientational order parameter. It is, therefore, quite incorrect to relate the optical birefringence directly to the nematic order parameter as these authors have done, because of the substantial change in the axial ratio of the micelle with temperature across the nematic phase. To obtain values of the order parameter and their variation with temperature from birefringence measurements it is vital to separate the contributions from the size and order parameter variations; this requires an approach analogous to the one presented above for conductivity measurements. The same criticism can be made about other optical birefringence studies of orientational order parameters in nematic micellar solutions [31, 32].

The order parameters obtained from the X-ray measurements seem anomalously high. Yet the X-ray method has given reasonable values for thermotropic nematic phases [27]. The discrepancy between the values of the order parameters as obtained by the two techniques must have its origin in the

different ways in which they sense the reorientational fluctuations of the micelles. The order parameters obtained from the electrical conductivity measurements represent the ensemble average of the orientational fluctuations of the micellar axes $M(a, b, c)$ with respect to the laboratory frame $L(x, y, z)$ over a time scale determined by the measurement period (2×10^{-3} s for the measurements in Fig. 4). This will include a contribution from fluctuations in the orientation of the micellar axes with respect to the local director and also a contribution from long range collective distortions in the orientation of the director. Assuming these two contributions are independent [33], the observed order parameter can be expressed

$$S = \langle \overline{P_2(\cos \beta)} \rangle \langle P_2(\cos \alpha) \rangle \quad (5)$$

$$= \overline{P_{2,M}} P_{2,\hat{n}}$$

where the bar and angular brackets denote averages over, respectively, the reorientational fluctuations of the micelles and the director fluctuations. β is the angle between the symmetry axis of the micelle and the instantaneous direction of the local director, that is $P_{2,m}$ is the order parameter modulus for the micelle. α is the angle between the direction of the local director and the symmetry axis of the bulk mesophase, that is $P_{2,\hat{n}}$ is the director or spatial order parameter. Thus, S as determined from electrical conductivity measurements is to be identified with the macroscopic reorientational order parameter. Now, in contrast, the angular intensity distribution $I(\theta)$ in the meridional reflection of the X-ray diffraction pattern represents the instantaneous ensemble average orientational distribution of the intermicellar vectors. The short range micellar reorientational fluctuations are not expected to make a significant contribution to this distribution because of the low volume fraction of the micelles. It seems reasonable, therefore, to assert that the intensity distribution has its origin mainly in the long range director fluctuations.

To test the above assertion we have examined the optical diffraction patterns obtained using a laser beam and « masks » of two-dimensional model structures [34]. The optical diffraction patterns for model lamellar phases with the micelles represented as ellipsoids randomly distributed on « planes » are found to be quite similar in form to the observed X-ray diffraction patterns irrespective of whether the ellipsoids have perfect orientational order or uncorrelated orientational disorder. Clearly, the X-ray diffraction patterns are solely determined by the correlations in the positions of the centres-of-mass of the micelles and are relatively insensitive to the orientations of the individual micelles. Similar conclusions derive from « experiments » with model nematic structures. In particular, it is seen that the meridional reflection is broadened into an arc only by a collective orientational distribution of the local intermicellar vectors and not by a distribution of the

orientations of the individual micelles. These « experiments » are therefore consistent with the above assertions about the way in which the orientational fluctuations of the micelles contribute to the observed X-ray diffraction pattern.

It is tempting to speculate and identify the X-ray order parameter solely with long range director fluctuations. This would necessitate the local reorientational fluctuations to be essentially of a single particle nature. This is not impossible in view of the low volume fraction (0.35) of micelles. Indeed, their dimensions are such that they could undergo independent isotropic reorientation without any steric interaction. We contrast this behaviour with the situation in thermotropic nematics where the molecules are closely packed making the local reorientation motion highly correlated [20]. If the X-ray order parameter were to be solely identified with $\bar{P}_{2,\hat{n}}$, we would obtain, from the electrical conductivity order parameters, values for $\bar{P}_{2,M}$ of 0.49 at T_{NI} , and 0.78 at T_{NL} . These will correspond to upper limits and as such are not unreasonable values. It is, however, most important to keep in mind that the above arguments are speculative and require further investigation.

Finally, we return to the question of the origin of the temperature dependence of the micellar order parameter in the nematic phase and from now onwards we shall mean by this the value S as obtained from the conductivity measurements. As we have seen, S increases, on cooling, much faster than the molecular order parameter of thermotropic nematics ; which is generally in accord with Maier-Sanpe molecular field theory [29]. The enhancement in the temperature dependence of the nematic order parameter has its origin in the variation with temperature of the diameter of the micelle. The effect of growth in the diameter of the micelle on cooling is to shift the nematic to isotropic transition to higher temperatures ; this is the cause of the observed rapid rise in the order parameter. In the isotropic phase, the micelle grows fairly slowly on cooling. A similar growth rate is also observed in the lamellar phase at temperatures lower than those considered in this paper. The most striking feature is undoubtedly the discontinuity in size at the isotropic to nematic transition : the diameter increases from 5.26 nm ($N_A = 88$) at T_{IN} to 5.82 nm ($N_A = 113$) at T_{NI} . (Note, that for a discoid micelle the diameter grows as the square root of N_A .) In the nematic phase, the rate of growth is greatest just below the phase transition and it gradually falls off on cooling across the nematic phase and into the lamellar phase (Fig. 5c). Clearly, there is a contribution to the growth of the micelle from some factor other than the intrinsic effect of temperature on the intra- and intermicellar interactions. An indication of the magnitude of this contribution is obtained by comparing the actual with the expected (by extrapolation from the isotropic phase) diameters at T_{NI} (5.82 c.f. 5.2 nm) at T_{NL} (6.38 c.f. 5.37 nm) and at 320 K in the lamellar phase (6.96 c.f. 5.50 nm). This additional

contribution can only arise from the coupling of the internal structure of the micelle to the properties of the mesophase. This can only be the long range orientational order as this is the only significant structural distinction between the nematic and isotropic phases. There is no marked discontinuity at the nematic to lamellar transition showing the absence of any growth due to coupling with long range positional order.

Gelbart *et al.* [9] have applied Onsager's theory [35] to the isotropic to nematic transition and the stability of the nematic phase in solutions of rod shaped micelles. The micelles are assumed to be coupled *via* an excluded volume type of interaction. The model qualitatively predicts some, but not all, of the features of the behaviour of the CsPFO/²H₂O system. In particular, it predicts the growth of micelles accompanying their long range orientational ordering. The growth at the isotropic to nematic transition is driven by the loss of orientational entropy upon alignment — this is minimized by reorganization of the system into a smaller number of larger micelles. In the model, this coupling between growth and alignment is stabilized, but only over very restricted concentration intervals, by the entropy of mixing and also by the rotational and transitional entropies of the micelles. It is also argued that alcohols are generally necessary to stabilize nematic phases because they inhibit the growth of micelles. But this is only a temporary respite and with increasing concentration the growth alignment coupling gives rise to an explosive growth of the micelles into either infinite rods or bilayers at the transition into, respectively, a hexagonal or lamellar phase. In the CsPFO/²H₂O system alcohol is not necessary to stabilize the nematic phase, nor do the discoid micelles grow into infinite bilayers at the nematic to lamellar transition. Nor do we believe that there is anything unique about this system. Nevertheless, the rapid rise of the order parameter with temperature is consistent with a size-alignment coupling as predicted by the model.

To compare the properties of the isotropic to nematic transition with Onsager's model we use the results of a recent Monte Carlo simulation of this transition in a fluid of thin hard discs [36]. The critical densities ($\rho^* = \rho \sigma^3$, where σ is the diameter of the discs) of the coexisting phases at the transition are $\rho_{IN}^* = 3.78$ and $\rho_{NI}^* = 4.07$. These predictions should be universal and independent of temperature or concentration. We can therefore compare them with the behaviour of the CsPFO/²H₂O system : $\rho_{IN}^* = 1.59$ and $\rho_{NI}^* = 1.74$. Thus, the transition occurs for smaller values of this product than predicted, yet their ratios are roughly in agreement. It could be argued that this is because in real systems the intermicellar interactions will be of longer range than excluded volume ones. This would increase the apparent size of the micelles and shift the transition to lower concentrations. However, we have seen that the micelles can reorientate essentially free

from steric interactions, which suggests that Onsager type are inappropriate.

The rapid rise in the nematic order parameter on cooling is a consequence of the growth of the micelle effected by the growth-alignment coupling. The nematic order parameter will be proportional to the strength of the anisotropic component of the intermicellar interaction [29]. This is expected to increase in proportion to the micelle diameter which varies as the square root of the aggregation number. Interestingly, Galerne *et al.* [32] have recently reported that the variations with temperature of the orientational order parameter in the N_D phase of the potassium laurate/1-decanol/ $^2\text{H}_2\text{O}$ system follow the variations of the shape anisotropy of the micelles. This behaviour would be quite consistent with that of the CsPFO/ $^2\text{H}_2\text{O}$ system, but the arguments presented for the former system are equivocal. The variation of the optical birefringence which is claimed to be directly proportional to the micellar order parameter could simply be a reflection of the variation in the size of the micelle. However, from the arguments presented here it follows that there must be a change in order parameter attendant upon any change in diameter of the micelle and we can conclude that the behaviour of the two systems is in good accord.

3. Conclusion.

We conclude by emphasising that it has been unambiguously demonstrated here, for the first time, that lamellar phases consisting of planar arrays of discoid micelles do exist. The basic mesogenic particle in both nematic and lamellar phases is undoubtedly the micelle. In the « classical » lamellar phase, the bilayer aggregate is envisaged to be of indefinite size, yet it is still correct to regard it as the mesogenic unit. It is very likely that a variety of lamellar phases will eventually be discovered, somewhat analogous to the thermotropic smectic phases. Indeed, there have recently been reports of the existence of microscopic, highly curved defects within the planes

of the bilayers of a number of different lamellar phases [15, 37, 38].

The result that the lamellar phase consists of planar arrays of discoid micelles, rather than the classical indefinitely extending bimolecular layers, has implications for our perception of the lamellar to nematic transition. Clearly, it is quite analogous to the thermotropic nematic to smectic A transition manifested by mesogens with elongated lath-shaped molecules. Perversely so, in view of the symmetries of the particles involved. There are, however, differences in behaviour which stem from the relatively low packing fraction (0.35) of the micelles; in particular, correlations in the orientations of neighbouring micelles appear to be rather weak. Conversely, the long range interactions seem to confer a high degree of correlation in the positions of neighbouring micelles in the nematic phase. Thus, the model which emerges for the nematic phase is reminiscent of the Landau picture [33] in which the individual micelles reorient essentially independently about the local nematic director whose orientation in turn fluctuates as a result of the long range director fluctuations.

During the refereeing of this paper, the authors learned about similar electrical conductivity measurements by Photinos and Saupe (Photinos, P. J., and Saupe, A., *J. Chem. Phys.* **84** (1986) 517) on the closely related ammonium heptadecafluorooctanoate/ H_2O system. Their results are very similar to those reported earlier by us [19] and also herein, but their analysis is quite different, being dependent upon numerical calculations of the conductivity for arrays of fixed discs. They also differ from us in their conclusions in that they argue that the lamellar aggregates are essentially defective bilayers along the lines proposed by Holmes and Charvolin [15].

Acknowledgements.

We thank the Science and Engineering Research Council for research studentships to S.A.C., P.H.J. and D.P.

References

- [1] DE GENNES, P. G., *The Physics of Liquid Crystals*, (Oxford Univ. Press) 1974.
- [2] LUZZATI, V., in *Biological Membranes*, Ed. Chapman, D., (Academic Press) 1986, p. 71.
- [3] EKWALL, P., *Adv. Liq. Cryst.* **1** (1975) 1.
- [4] CHARVOLIN, J., *J. Chim. Phys.* **80** (1983) 15.
- [5] LAWSON, K. D., FLAUTT, T. J., *J. Amer. Chem. Soc.* **89** (1967) 5489.
- [6] PARSEGAN, V. A., *Trans. Faraday Soc.* **62** (1966) 848.
- [7] FORSYTH, P. A., MARCELJA, S., MITCHELL, D. J., NINHAM, B. W., *Adv. Colloid Sci.* **9** (1978) 37.
- [8] MITCHELL, D. J., TIDDY, G. J. T., WARING, L., BOSTOCK, T., McDONALD, M. D., *J. Chem. Soc., Faraday Trans. 1* **79** (1985) 975.
- [9] GELBART, W. M., MCMULLEN, W. E., BEN-SHAUL, A., *J. Physique* **46** (1985) 1137 ; MCMULLEN, W. E., GELBART, W. M., BEN-SHAUL, A., *J. Chem. Phys.* **82** (1985) 5616.
- [10] TIDDY, G. J. T., *Phys. Rep.* **57** (1980) 7.
- [11] TIDDY, G. J. T., WALSH, M. F., in *Aggregation Processes in Solution*, Eds. Wyn-Jones, E. and Gormally, J. (Elsevier Pub. Co.) 1983, p. 151.
- [12] FORREST, B. J., REEVES, L. W., *Chem. Rev.* **81** (1981) 1.
- [13] CHARVOLIN, J., LEVELUT, A., SAMULSKI, E. T., *J. Physique Lett.* **40** (1979) L-587.
- [14] HENRIKX, Y., CHARVOLIN, J., RAWISO, M., LIEBERT, L., HOLMES, M. C., *J. Phys. Chem.* **87** (1983) 3991.

- [15] HOLMES, M. C., CHARVOLIN, J., *J. Phys. Chem.* **88** (1984) 810.
- [16] BODEN, N., HOLMES, M. C., *Chem. Phys. Lett.* **109** (1984) 76.
- [17] BODEN, N., JACKSON, P. H., McMULLEN, K., HOLMES, M. C., *Chem. Phys. Lett.* **65** (1979) 476.
- [18] BODEN, N., BUSHBY, R. J., HARDY, C., *J. Physique Lett.* **46** (1985) L-325 ;
BODEN, N., BUSHBY, R. J., HARDY, C., *Chem. Phys. Lett.* **123** (1986) 359.
- [19] BODEN, N., CORNE, S. A., JOLLEY, K. W., *Chem. Phys. Lett.* **105** (1984) 99.
- [20] FABER, T. E., in *Liquid Crystals : Their Physics, Chemistry and Applications*, Eds. C. Hilsim, and E. P. Raynes (R. Soc. London) 1983, p. 115.
- [21] BODEN, N., RADLEY, K., HOLMES, M. C., *Mol. Phys.* **42** (1981) 493.
- [22] LEADBETTER, A. J., in *The Molecular Physics of Liquid Crystals*, Eds. Luckhurst, G. R. and Gray, G. W. (Academic Press) 1979, p. 283.
- [23] GUINIER, A., *X-ray Diffraction*, (Freeman) 1963, p. 72 : $\Delta S = \Delta(2\theta) \cos \theta / \lambda$ where $\Delta(2\theta) = 1.11 \Delta'(2\theta)$, θ is the Bragg angle, and $\Delta'(2\theta)$ is the angular width at half height of the Bragg peak (p. 124 and 135).
- [24] FRICKE, H., *Phys. Rev.* **24** (1924) 575 ; *J. Phys. Chem.* **57** (1953) 934.
- [25] CUTLER, S., MEARES, P., HALL, D. G., *J. Chem. Soc. Trans. Faraday I* **74** (1978) 1758.
- [26] OWENSON, B., PRATT, L. R., *J. Phys. Chem.* **88** (1984) 2905.
- [27] CHRISTYAKOV, I. G., CHAIKOVSKII, V. M., *Mol. Cryst. Liq. Cryst.* **7** (1969) 269 ; and references therein.
- [28] FIGUEIREDO NETO, A. M., GALERNE, Y., LEVELUT, A. M., LIEBERT, L., *J. Physique Lett.* **46** (1985) L-499.
- [29] LUCKHURST, G. R., in *The Molecular Physics of Liquid Crystals*, Eds. Luckhurst, G. R. and Gray, G. W. (Academic Press) 1979, p. 85.
- [30] LARSON, B. D., LITSTER, J. D., *Mol. Cryst. Liq. Cryst.* **113** (1984) 13.
- [31] GALERNE, Y., MARCEROU, J. P., *Phys. Rev. Letters* **51** (1983) 2109.
- [32] GALERNE, Y., FIGUEIREDO NETO, A. M., LIEBERT, L. *Phys. Rev. A* **31** (1985) 4047.
- [33] WARNER, M., *Mol. Phys.* **52** (1984) 677.
- [34] CHRISTYAKOV, I., in *Advances in Liquid Crystals*, Vol. 1, ed. Brown, G. H., (Academic Press) 1975, p. 143.
- [35] ONSAGER, L., *Ann. N. Y. Acad. Sci.* **51** (1949) 627.
- [36] FRENKEL, D., EPPENGA, R., *Phys. Rev. Lett.* **49** (1982) 1089 ;
ibid, *Mol. Phys.* **52** (1984) 1303.
- [37] KEKICHEFF, P., CABANE, B., RAWISO, M., *J. Physique Lett.* **45** (1984) L-813.
- [38] PAZ, L., DI MEGLIO, J. M., DVOLAITZKY, M., OBER, R., TAUPIN, C., *J. Phys. Chem.* **88** (1984) 3415.
-