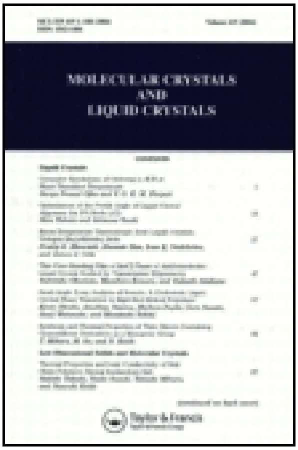

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On the Nature of Interaggregate Interactions in Lyotropic Liquid Crystalline Phases[†]

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The mesogenic unit of lyotropic nematic liquid crystals is either a columnar (N_c) or discoid (N_D) micelle. There is growing evidence that these micelles exist as discrete entities in both the isotropic phase and for disk shaped micelles, in the lamellar phase bounding the nematic. Here, the evolution of micelle size as measured by X-ray scattering from orientated samples of caesium perfluorooctanoate/water, has been followed as a function of concentration and temperature across all three phases. The micelle size is found to initially increase with increasing amphiphile concentration, but to decrease at higher concentrations. This behaviour is shown to be consistent with an attractive interaggregate interaction.

Keywords: lyotropic, lamellar, nematic, X-ray scattering, micelles, interactions

INTRODUCTION

Nematic micellar solutions occur between isotropic micellar solutions and 'smectic' phases (hexagonal or lamellar), in the concentration interval *ca.* 0.1 to 0.5 volume fraction of amphiphile, and below ca. 350 K.[1] They have been shown to be aqueous solutions of orienta-

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[†] Presented at the International Liquid Crystal Conference Berkeley 1986.

tionally ordered discoid N_D and columnar N_C micelles.[2,3] Arguably, the most striking evidence for their existence is that small anisometric micelles are stable at unexpectedly high concentrations. Indeed, it is to be noted that the current statistical mechanical models predict that discoid micelles are intrinsically unstable with respect to infinite bilayers.[4] This had led to the belief that N_D phases can only be obtained by the addition of a long chain alcohol.[5,6] The caesium pentadecafluorooctanoate (CsPFO)/water system has, however, been shown to exhibit a stable N_D phase over wide concentration and temperature ranges.[7] Clearly, it is of importance to investigate the factors which control the size and shape of the micelles in these concentrated solutions. To this end we report here a small angle X-ray scattering investigation of the concentration-temperature dependence of the size of the discoid micelles in CsPFO/^2H_2O system.

The CsPFO/^2H_2O system is currently the most attractive N_D mesophase available for experimental study. There are three reasons for this.[7] First, it is a simple two component system; there is no need to add either salt or a co-surfactant. Second, the nematic phase is stable over an unprecedented range of concentrations (0.10 to 0.43 volume fraction of CsPFO) and temperature (283 to 350 K). Third, it is diamagnetically positive N_D^+ which means that macroscopically aligned samples of nematic and lamellar phases can be obtained simply by cooling the isotropic/nematic phase in a magnetic field. Recently, it has been shown[8,9] that the fundamental mesogenic aggregates are discrete discoid micelles in all of the three phases. Significantly, the lamellar phase consists of planar arrays of discoid micelles, rather than the classical infinite bimolecular layers. The nematic to lamellar transition is, therefore, in a sense analogous to the thermotropic, nematic to smectic A transition and has been modelled by a molecular-field theory.[10] The rotational viscosity coefficient in the nematic phase has been shown to diverge on approaching this smectic A-like phase.[11] Studies of the pre-transitional behaviour at the isotropic to nematic transition have shown that the temperature interval $T_c^* - T^*$ (T_c^* is the temperature corresponding to the onset of phase separation, i.e. T_{IN}, and T^* is the supercooling limit of the isotropic phase) decreases with amphiphile concentration and becomes less than 20 mK.[12,13]

EXPERIMENTAL

Samples of caesium perfluorooctanoate in ^2H_2O were weighed into glass tubes containing a constriction and after sealing, the tubes were centrifuged back and forth until thoroughly mixed. Samples were then transferred into 0.5mm Lindemann capillaries and phase transition temperatures checked by optical polarising microscopy. X-ray experiments were conducted using a pin hole camera of length 114mm or using the small angle X-ray synchrotron source at Daresbury with a camera length of 890mm. In both cases the scattering patterns were recorded on film and the nematic and lamellar phases were aligned by cooling from the isotropic phase in a magnetic field.

RESULTS AND DISCUSSION

A sequence of X-ray scattering pictures recorded as a function of temperature using synchrotron X-rays is shown in Figure 1. The isotropic phase is characterised by a diffuse ring whose maximum corresponds to a distance d_0 and the nematic phase by an oval pattern (with reinforcement of the scattering parallel to the liquid crystal director) from which the intermicelle separation both parallel, $d_{\parallel}$ and perpendicular $d_{\perp}$ to the director may be extracted. The lamellar phase shows sharp Bragg peaks with higher orders corresponding to $d_{\parallel}$ and weak lateral bands parallel to the direction of the director corresponding to the intra-lamellar separation of the micelles $d_{\perp}$. (Since the lateral reflections are quite distinct in both nematic and lamellar phases the discoid micelles must have a narrow polydispersity which might be expected from the controlling influence of the highly curved disk edges.[14]) It should be noted that d_0 and $d_{\perp}$ are only approximate values for the micelle separation since these are strictly liquid like reflections. Using d_0, $d_{\parallel}$ and $d_{\perp}$ estimates may be made of the mean aggregation number, **n** of the micelles in all three phases. For isotropic phase:

$$\bar{\mathbf{n}} = \frac{3}{4}\sqrt{3}\,\phi_a d_0^3/v_a$$

and for the nematic and lamellar phases

$$\bar{\mathbf{n}} = \frac{\sqrt{3}}{2}\,\phi_a d_{\perp}^2\, d_{\parallel}/v_a$$

where ϕ_a is the volume fraction of amphiphile and v_a is the volume of a single amphiphile molecule. The numerical constants at the front of each expression arise from the simple packing geometries assumed (fcc for the isotropic and hexagonal close packing of discoids into

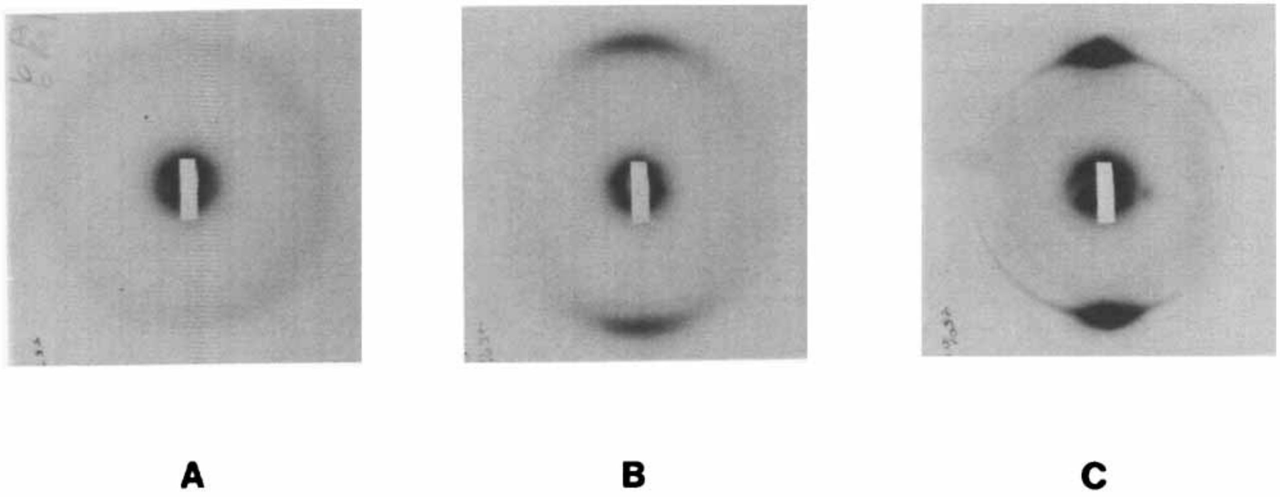

FIGURE 1 X-ray scattering using the small angle scattering facility at Daresbury, from a 55% by weight caesium perfluoro-octanoate/^2H_2O sample at three temperatures:
(A) 338.5K, isotropic micellar solution,
(B) 329.0K, nematic (N_D) phase,
(C) 308.5K, lamellar phase.

planes for nematic and lamellar phases). Figure 2 shows the variation of $\bar{n}$ with weight fraction of amphiphile at four temperatures whilst Figure 3 shows $\ln\bar{n}$ plotted versus $\ln X_a$ where X_a is the mole fraction of amphiphile.

At each temperature, $\bar{n}$ passes through a maximum at ~0.42 weight fraction. Figure 2 also shows the $I \rightarrow N_D$ and $N_D \rightarrow L$ transitions from which it is apparent that the variation of $\bar{n}$ with concentration is not related by the phase behaviour. (There is a small change in $\bar{n}$ at $I \rightarrow N_D$ but the present measurements are not sensitive to it because of the change in packing model.) For weight fraction <0.42, $\bar{n}$ increases with increasing amphiphile concentration; indeed $\bar{n}\ \alpha X_a^P$ where $p \lesssim 0.5$. Theories of dilute noninteracting micellar solutions[4] predict $p = 0.5$ for rod-shaped micelles. But the same theories predict that discoid micelles are unstable and should therefore spontaneously grow into infinite bilayers. The results presented here demonstrate the short-comings of the theories.

At high concentration, i.e. at weight fractions ≥ 0.42, $\bar{n}$ *decreases* with increasing amphiphile concentration. Such behaviour is contrary to the expectations[15] of micellar growth. The observed behaviour can

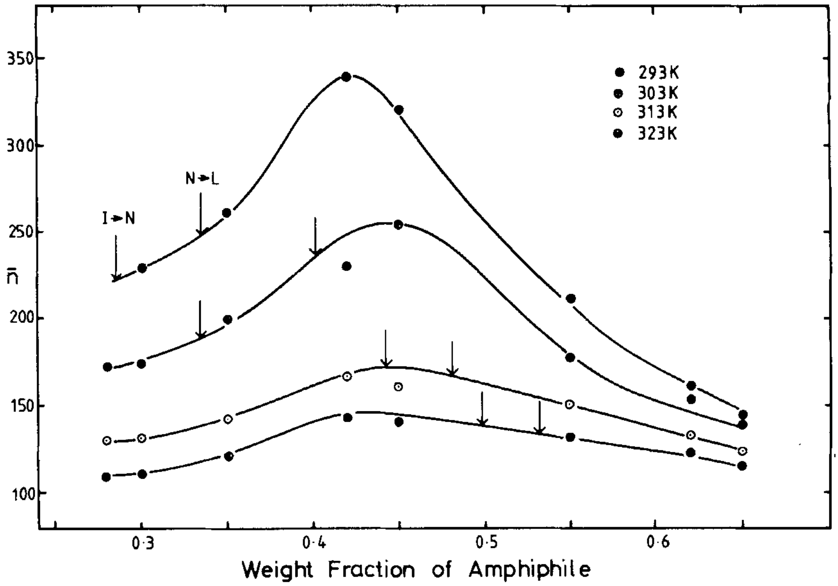

FIGURE 2 Mean micelle aggregation number versus weight fraction of amphiphile at four temperatures. The solid lines are aids to the eye only. The arrows indicate the location of IN_D and N_DL phase transitions at each temperature.

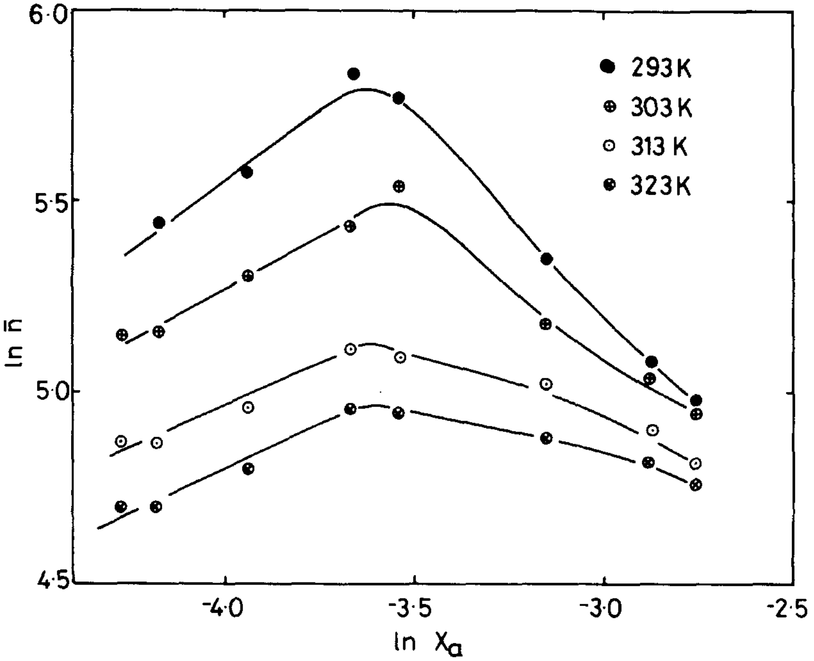

FIGURE 3 ln n̄ versus ln X_a at four temperatures. The solid lines are aids to the eye only.

be understood by considering the chemical potential for an amphiphile molecule of an **n** monomer discoidal micelle.[4,16]

$$\tilde{\mu}_n = \tilde{\mu}_n^o + \frac{1}{n}\ln\frac{X_n}{n} + \tilde{\mu}_n^\theta + \frac{1}{n}\sigma_n + \frac{1}{n}\chi_n \qquad (1)$$

where

$$\tilde{\mu}_n^o = \tilde{\mu}_\infty^o,\ \tilde{\mu}_{\infty,d}^o + \alpha' g(n).$$

Here, $\tilde{\mu}_{\alpha,d}^o$ is the chemical potential of a monomer in the flat portion of a disk and the term $\alpha' g(n)$ represents the difference in chemical potential between the flat faces and the curved rim. This latter term is a function of the micelle size, $g(n)$ and also the interfacial tension contained in the term α'. Since the latter term is large for a fluorocarbon system there is a very strong tendency to reduce surface curvature and for the micelles to grow larger.

The second term in Equation 1, $\frac{1}{\mathrm{n}} \ln \frac{X_n}{n}$ represents the entropy of mixing which encourages the formation of smaller micelles with increasing X_n and is the dominant term for dilute solution.

The third term $\tilde{\mu}_n^0$ takes account of the rotational and translational entropy contributions to the chemical potential. It has the same functional form as the entropy of mixing term and is therefore most significant at low concentrations. Gelbart *et al.*[16] have shown however, that its effect is to limit micelle growth, preventing 'explosive' growth rather than producing a reduction in size.

The term $\frac{1}{n} \sigma_n$ represents the entropy loss due to the establishment of long-range orientational order of the micelles. The results clearly show that this term is not significant in the context of the changes in $\bar{\mathrm{n}}$ seen here.

Finally, the term $\frac{1}{n} \chi_n$ represents the interaction between micelles. Gelbart *et al.*[15] have considered this interaction to be modelled by an Onsager hard core interaction which is a fair representation for any repulsive intermicellar interaction. They showed that it strongly enhanced micelle growth and would inevitably lead to 'explosive' growth into infinite cylindrical aggregates without the control exerted by the other terms in Equation 1.

The dominant terms in Equation 1 are therefore the first and last terms, although, since $p \leq 0.5$ at low concentration and $\bar{\mathrm{n}}$ decreases at high concentration, it implies that the interaction term is attractive rather than repulsive. The origin of this attractive interaction is unclear although recently Sogami and Ise[17] have shown the coulombic interaction in a macroionic system may become attractive at larger distances. The interaction is mediated by the free counter-ions and gives rise to a secondary minimum in the intermicellar potential energy curve. The position of the minimum is determined by the Debye length of the macroions which would be consistent with the observed intermicellar separation observed in this system.

CONCLUSIONS

The demonstration that small discoid micelles are quite stable in concentrated surfactant solutions is of enormous importance. First, it means that the simple statistical mechanical models[4] are incorrect. The attempt to modify these models by including terms to represent the role of added co-surfactants are inappropriate; this is manifest in the stability of the micelles in the caesium perfluorooctanoate/water system. Secondly, it has been shown for the first time that the intermicellar interaction for charged micelles can be attractive. This is very likely to be the explanation for the stability of these micellar solutions.

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References

1. N. Boden, R. J. Bushby, L. Ferris, C. Hardy and F. Sixl, *Liquid Crystals*, **1**, 109 (1986).
2. J. Charvolin, A. M. Levelut and E. T. Samulski, *J. Phys. Lett.* (Orsay), **40**, L587 (1979).
3. Y. Hendrix and J. Charvolin, *J. Phys.* (Orsay), **42**, 1427 (1981).
4. J. N. Israclachvili, D. J. Mitchell and B. W. Ninham, *J. Chem. Soc. Faraday II*, **72**, 1525 (1976).
5. Y. Hendrickx, J. Charvolin and M. Rawiso, *J. Coll. Interface Sci.*, **100**, 597 (1984).
6. W. M. Gelbart, W. E. McMullen, A. Masters and A. Ben-Shaul, Langmuir, **1**, 101 (1985).
7. N. Boden, P. Jackson, K. McMullen and M. C. Holmes, *Chem. Phys. Lett.*, **65**, 476 (1979).
8. N. Boden, S. A. Corne and K. W. Jolley, *Chem. Phys. Lett.*, **105**, 99 (1984).
9. N. Boden, S. A. Corne, M. C. Holmes, P. H. Jackson, D. Parker and K. W. Jolley, *J. Phys.* (*Orsay*) **47**, 2135 (1986).
10. M. C. Holmes and N. Boden, *Mol. Cryst. Liq. Cryst.*, **124**, 131 (1985).
11. N. Boden, K. McMullen and M. C. Holmes, *Magnetic Resonance in Colloid and Interface Science*, eds. J. P. Fraissand and H. A. Resing (Reidel, 1980) p. 667.
12. C. Rosenblatt, S. Kumar and J. D. Litster, *Phys. Rev.*, **A29**, 1010 (1984).
13. C. Rosenblatt, *Phys. Rev.*, **A32**, 1115 (1985).
14. W. E. McMullen, A. Ben-Shaul and W. M. Gelbart, *J. Coll. Inter. Sci.*, **98**, 523 (1984).
15. W. M. Gelbart, A. Ben-Shaul, W. E. McMullen and A. Masters, *J. Phys. Chem.*, **88**, 861 (1984).
16. W. M. Gelbart, W. E. McMullen and A. Ben-Shaul, *J. Phys.* (*Orsay*) **46**, 1137 (1985).
17. I. Sogami and N. Ise, *J. Chem. Phys.*, **81**, 6320 (1984).