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A small angle neutron scattering study of the caesium pentadecafluoro-octanoate/ $^2\text{H}_2\text{O}$ and two associated ternary systems

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Caesium pentadecafluoro-octanoate ($\text{CsPFO}/^2\text{H}_2\text{O}$) has been extensively studied in recent years. It exhibits a lamellar phase to low temperature and high surfactant concentration and an isotropic micellar phase (L_1) to high temperature and low surfactant concentration. Between these two phases there is a narrow nematic phase which is composed of disk shaped micelles. Previous work on the lamellar phase with x-ray scattering, nmr and ionic conductivity has shown that the lamellar phase consists of bilayers which are broken by water filled defects. We have recently presented extensive SANS measurements on the lamellar phase of the binary system and with added electrolyte (CsCl) and cosurfactant ($1\text{H}-1\text{H}$ -perfluoroheptan-1-ol). The results unequivocally show the lamellar phase to be surfactant continuous with elongated water filled holes which are differently affected by adding surfactant, cosurfactant or electrolyte. In this paper we summarize these results and further extend them because SANS also provides information from the scattering line shape about the positional order of the lamellar plane. This can be correlated with the inter-lamellar interaction and its modification by additives.

Introduction

The competing interactions of the polar headgroups and the alkyl chains of surfactant molecules results in a wide range of lyotropic liquid crystalline phases. Perhaps the best understood of these are the lamellar and hexagonal phases [1,2]. The structure of the lamellar phase can be thought of as alternate layers of surfactant and water, with the charged headgroups providing an interface between the alkyl chains and the aqueous layer. A number of small angle scattering studies over the last few years have demonstrated the existence of lamellar phases in lyotropic liquid crystals which contain water filled defects with highly curved edges, L_α^H [3-12]. The conclusions from these studies have been supported by other measurements such as ^2H nmr [13], ionic conductivity [14], water self diffusion [15] and nmr spectral density measurements [16]. These measurements have been made on both ionic [3-10] and nonionic systems [11,12]. The interpretation of the scattering patterns and the existence of the defected structure is established beyond doubt. A remaining important problem was that of the precise nature of the defects; whether the bilayers were water continuous, surfactant continuous or bicontinuous.

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One lyotropic system which has received considerable attention is the binary ionic system caesium pentadecafluorooctanoate (CsPFO)/water [7,9,10,13-15]. The phase diagram is well established [13] and exhibits isotropic micellar (L_1), defected lamellar (L_α^H) and nematic (N_D) phases. This system is unusual in that it forms the latter two phases without the addition of a cosurfactant or salt. The evidence from small angle x-ray (SAXS) and neutron scattering (SANS) of an intra-lamellar structure combined with the knowledge that the nematic phase consists of disk micelles led to the proposal that the basic unit in all three phases is the disk micelle [7,13]. The changes of phase could then be ascribed to disorder-order transitions [13,14]. Although there was some evidence to support this model, it was rather circumstantial and depended heavily upon the models adopted to interpret the experimental measurements.

Recently, we have shown, using SANS, [9,10] that a more satisfactory model is obtained with a surfactant continuous bilayer structure pierced by water filled defects with highly curved edges. Increasing the surfactant concentration in the binary system causes the defects to shorten in length towards circular pores although their number density remains constant. Adding both CsCl and 1H-1H-perfluoroheptan-1-ol causes the number density of defects to decrease although their shape remains constant. In both cases the bilayers are approaching classical bilayers. These different types of behaviour can be attributed to the differences in the modifications to the intra-aggregated interactions. It is interesting to compare the addition of 1H-1H-perfluoroheptan-1-ol and CsCl since the latter also affects the electrostatic interactions between bilayers leading to changes in the shape of the inter-lamella Bragg reflection. It is these changes that we consider here in this paper.

Results and Discussion

Samples were prepared as in refs [9,10] and the neutron scattering experiments were carried out on LOQ at the SERC neutron scattering facility, ISIS [9]. Samples were aligned to form single crystals by cooling from the isotropic phase through the nematic phase to a temperature of 40°C in the lamellar phase. An example of a typical neutron scattering pattern is shown in figure 1. The concentrations of added CsCl or 1H-1H-perfluoroheptan-1-ol were chosen to give the same value of inter-lamellar spacing and to show no evidence of intra-lamella defect structure. Figure 2 shows the scattering profiles from the 1H-1H-perfluoroheptan-1-ol and the CsCl containing samples both compared with the peak from the binary system which has been shifted in Q to make comparison possible.

As can be seen from figure 2 there is very little difference between the reflection profiles for the binary system and that with added 1H-1H-perfluoroheptan-1-ol, although in the latter system the water filled defects have disappeared and the bilayer is effectively a classical bilayer. (The small differences on the low Q side of the reflection are probably due to the effect of the intra-lamella reflection from material which is not fully aligned by the magnetic field.) In contrast the addition of CsCl has not only stimulated the loss of defects but also the reflection has acquired pronounced wings at the base although the width at half height remains unchanged. This effect arises from displacement disorder of the lamellae [17] i.e. the spacing between the lamellae is no longer sharply defined although the average remains the same. More particularly it is akin to the situation where the spacing, d between planes varies between $d(1 - \epsilon)$ and $d(1 + \epsilon)$ in a sinusoidal fashion with a wavelength Λ . Theoretically [17], the reflection would remain unchanged in width but would acquire satellite lines at $\pm 1/\Lambda$ whose intensity as a ratio of that of the main reflection is given by

$$\frac{I_{\text{sat}}}{I_0} = \frac{\Lambda^2 \epsilon^2}{4d^2}$$

Using this simple model and subtracting the scattering curve of the 1H-1H-perfluoroheptan-1-ol containing sample from that of the CsCl containing sample, two small satellite peaks of comparable width to the original main peak are generated. From their position and intensity relative to the main peak

Figure 1: A typical SANS pattern from a magnetically aligned 50% by weight CsPFO / $^2\text{H}_2\text{O}$ sample at 40°C in the L_α^H phase, from ref [9]. The principle peaks along the x axis are the inter-lamella reflections whilst the weak reflections along the y axis are from the intra-lamella water filled defects.

Figure 2: A comparison of the inter-lamella reflection profiles taken along the x axis. The open squares are the profile from the CsPFO / 1H-1H-perfluoroheptan-1-ol / $^2\text{H}_2\text{O}$ system, the closed squares from the CsPFO / CsCl / $^2\text{H}_2\text{O}$ system whilst the solid line is from the binary system with the same total surfactant / water ratio. The latter profile has been shifted in Q to make comparison possible and they have all been scaled to a maximum value of unity.

$\Lambda \cong 57\text{nm}$ and $\varepsilon = 0.08$. Thus although for both samples $d = 6.0\text{nm}$, in the case of the CsCl containing sample there is a variability of $\pm 0.4\text{nm}$ in this distance which extends over a distance of some ten bilayer spacings.

Conclusions

Adding a cosurfactant or an electrolyte to a CsPFO/water system affects the intra-aggregate interactions promoting the loss of interfacial curvature, the loss of water filled defects and the evolution towards classical bilayers. The difference between the two additives is that the electrolyte also modifies the inter-aggregate interactions, screening their electrostatic interaction. This results in a greater variability in the inter-aggregate distance or displacement disorder which experimentally is manifest as wings appearing on both sides of the inter-aggregate reflection peak, from which the variability in d was found to be 0.4nm .

References

- [1] Luzzati, V., Biological membranes, ed D. Chapman, Academic Press, London and New York, (1968), p71.
- [2] Ekwall, P., Advances in Liquid Crystals; Brown, G. H., Ed; Academic Press: New York, 1975, Vol. 1.
- [3] Holmes, M. C. and Charvolin, J., *J. Phys. Chem.*, **88**, (1984), 810.
- [4] Hendriks, Y., Charvolin, J., Kekicheff, P., Roth, M., *Liquid Cryst.*, **2**, (1987), 677.
- [5] Hendriks, Y., Charvolin, J., Rawiso, M., *Coll. Inter. Sci.*, **100** (1984) 99.
- [6] Kekicheff, P and Cabane, B., *Acta Cryst.*, **B44**, (1988), 395.
- [7] Holmes, M. C., Reynolds, D. J. and Boden, N., *J. Phys. Chem.*, **91**, (1987).
- [8] Holmes, M. C., Charvolin, J. and Reynolds, D. J., *Liquid Cryst.*, **3**, (1988), 1147.
- [9] Leaver, M. S. and Holmes, M. C., *J. de Phys. II*, **3**, (1993), 105.
- [10] Holmes, M. C., Smith, A. M. and Leaver, M. S., submitted.
- [11] Funari, S. S., Holmes, M. C. and Tiddy, G. J. T., *J. Phys. Chem.*, **96**, (1992), 11029.
- [12] Funari, S. S., Holmes, M. C. and Tiddy, G. J. T., submitted.
- [13] Boden, N., Corne, S. A., Holmes, M. C., Jackson, P. H. and Jolley, K. W., *J. de Phys.*, **47**, (1986), 2135.
- [14] Boden, N., Corne, S. A. and Jolley, K. W., *J. Phys. Chem*, **91**, (1987), 4092.
- [15] Holmes, M. C., Sotta, P. and Deloche, B., in preparation.
- [16] Quist, P. and Halle, B., paper in press
- [17] Guinier, A., X-ray Diffraction, Freeman & Co, San Francisco, (1963).