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A small angle neutron scattering study of the lamellar phase of caesium pentadecafluorooctanoate (CsPFO)/1H-1H-perfluoroheptan-1-ol/²H₂O

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Abstract. — The ionic surfactant system CsPFO/²H₂O has been extensively studied in recent years. It exhibits a defected lamellar phase (L_a^H) at low temperature or high surfactant concentration followed by nematic (N_D) and isotropic (L_1) phases as temperature increases or surfactant concentration decreases. Previous work on the lamellar phase, mainly by X-ray and neutron scattering techniques, has revealed an intra-lamella structure of water filled defects although the precise nature of these defects remains controversial. The addition of the cosurfactant 1H-1H-perfluoroheptan-1-ol to the binary system has been studied by optical microscopy and SANS. As the cosurfactant is added the phase transition temperatures increase and the nematic phase is replaced by a broad $L_1 + L_a^H$ two phase coexistence region. SANS shows that the reflection from the intra-lamella structure weakens and shifts to lower Q . The number density of defects decreases with increasing cosurfactant although their shape remains roughly constant being elongated holes. Using these results and those for the binary system a more precise picture of the defect structure, which is consistent with theoretical models of the defected lamellar phase, has been obtained.

1. Introduction.

The competing interactions of the polar headgroups and the alkyl chains of surfactant molecules result 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. Scattering studies have shown that there are structural defects within the bilayer in a number of binary and

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ternary systems. Their first observation was in the decylammonium chloride/water/ammonium chloride system [3, 4] where addition of electrolyte suppressed the hexagonal phase and promoted a nematic phase of discoidal micelles between the isotropic and lamellar phases. The lamellae in the latter phase contained water filled defects which were uncorrelated between layers [4].

The addition of a cosurfactant to a binary system promotes flatter interfaces, for example Parsegian and Mather [5, 6] showed that a hexagonal to lamellar transition can be promoted upon the addition of alcohol. The addition of a non-ionic alcohol to an ionic surfactant/water system results in a dilution of the surface charge since the alcohol molecules distribute themselves between the surfactant molecules and the chains of the alcohol molecules are assumed to pack in the same way as the alkyl chains of the surfactant in the micelle core. Gelbart *et al.* [7] have shown theoretically that the addition of a cosurfactant to a system composed of rod-shaped micelles leads to an increased micelle size. They concluded that to produce the most stable aggregate the cosurfactant molecules must reside in the flatter part of the micelle and hence the flat part of the aggregate grows at the expense of the curved edges. This will lead to an increase in aggregate size, promote phase stability and lead to an elevation of the phase transition temperatures.

Considerable experimental work on the sodium decyl sulphate (SdS)/decanol/water [8-11] and the potassium laurate (KL)/decanol/water [12, 13] systems have established the existence of defected lamellar structures. Using contrast variation neutron scattering it has been shown that there is a microsegregation of one type of molecule in the curved part of the aggregate. Although not explicitly shown, the knowledge that the addition of alcohol promotes a hexagonal to lamellar transition leads to the conclusion that the cosurfactant molecules partitioned to the flatter part of the aggregates. The experiments of Hendriks *et al.* [9] showed that when decanol is added to the SdS/water system, the scattering from the intra-lamella defects fades and the phase approaches a classical bilayer, although the precise geometry of the defects was equivocal. At lower decanol concentrations, as the lamellar phase approaches the hexagonal and ribbon phases the intra-lamellar defects become partially correlated between layers [11] with a structure of ribbon or rod shaped aggregates arranged in planes.

Defected lamellar phases have also been found in binary surfactant/water systems. In the sodium dodecyl sulphate (SDS)/water system neutron scattering studies [14-17] have shown that the lamellar phase contains partially correlated defects which act as precursors to a centred tetragonal phase, T_α which could be thought of as a lamellar phase in which the defects, or holes have very long range correlations indeed. Lamellar phases of nonionic surfactants may also contain correlated [18] and uncorrelated [19] defects. In the case of the $C_{22}EO_6$ /water system [19] the defected lamellar phase constitutes a separate phase from the classical lamellar phase and was given the label L_α^H .

In none of the systems, where the intra-lamella defects are uncorrelated between layers, has it been possible to unequivocally identify the geometry of the defects. The three possible topologies that the lamellae could adopt are water-, surfactant- or bi-continuous. That is the lamella could consist of individual disk micelles arranged onto planes or continuous lamellar planes of surfactant with water-filled holes or randomly arranged ribbon-like aggregates in planes with aqueous regions separating them. It is difficult to distinguish further between these possibilities from scattering studies because of Babinet's principle [3, 20].

Bagdassarian *et al.* [21] used two different theoretical models for the free energy of defects to examine in some detail curvature defects in lamellar phases. These models show that as the amphiphile volume fraction is increased there are transitions between lamellar phases with different defect geometries and with decreasing surface area per molecule. The defects lower the local free energy in a system constrained by interaggregate interactions to take up a

lamellar structure, whereas without this constraint the molecules would minimize their local free energy by taking a cylindrical geometry. At the lowest amphiphile concentration a ribbon phase is predicted followed by a random network of line defects and at the highest concentration circular pores.

A binary ionic system which exhibits a defected lamellar phase and which has been well studied in recent years is the caesium pentadecafluorooctanoate (CsPFO)/water system [22-28]. The phase diagram is well established [29] and exhibits isotropic micellar (L_1), nematic (N_D) and defected lamellar (L_α^H) 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 [22, 24, 29]. The changes of phase could then be ascribed to disorder-order transitions [22, 24, 26, 29]. For example, the L_1 - N_D transition would be associated with the disk micelles acquiring orientational order whilst for the N_D - L_α^H transition they become positionally ordered onto planes.

Although there was some experimental evidence to support the disk model, it is rather circumstantial and depends heavily upon the models adopted to interpret the experimental measurements. The scattering from the intra-lamella defects using an X-ray source is continuous with that from the nematic N_D phase [24, 30] suggesting that the structural unit remains the same across the phase transition. ^2H NMR of the lamellar phase indicates a high degree of curvature which the disk model could help to explain [22, 27]. The relatively high conductivity of the Cs^+ counter ion across the lamellae supports the proposition of a defected lamellar structure and has been interpreted as being consistent with disk micelles [26, 28].

There are several problems with the model of discrete disks. First, the observation that the disk micelle must decrease in size with increasing surfactant concentration [24]. This can only be accounted for by invoking attractive inter-micellar interactions which are difficult to explain physically. A second problem is how the system can sustain many small micelles, each having highly curved edges, in close proximity to each other and over such a wide range of surfactant concentration and temperature. We have recently shown, using SANS, [31] that the defects are retained in the lamellar phase to which surfactant is added but that the addition of an electrolyte, caesium chloride, to the binary system CsPFO/ $^2\text{H}_2\text{O}$ system causes the scattering, from the intra-lamella defects, to be lost. A much more satisfactory picture of the lamellar phase is obtained if it is assumed to consist of continuous layers of amphiphile pierced with water-filled defects.

In this paper we examine the effect of the addition of the cosurfactant 1H-1H-perfluoroheptan-1-ol to the binary CsPFO/ $^2\text{H}_2\text{O}$ system. Rosenblatt [25] was able to show using magnetic susceptibility measurements that the addition of this alcohol to the binary CsPFO/ $^2\text{H}_2\text{O}$ system increased the phase transition temperatures. By assuming that this was entirely due to the growth of disk aggregates, he predicted their size as the amount of cosurfactant was varied. Our measurements show that the effect of adding a cosurfactant is rather similar to that discussed above for other systems but here we have been able to distinguish between the structural models of uncorrelated defected lamellar phases.

2. Experimental.

2.1 SAMPLE PREPARATION. — The CsPFO was prepared as in reference [31] with a development of the method of Nakayama [32]. The cosurfactant 1H-1H-perfluoroheptan-1-ol (Fluorochem Ltd., purity > 99 %) was chosen because it was readily available and has a similar chain length to CsPFO. It is not possible to have a fully fluorinated alcohol since a CF_2

bond next to an -OH group will be readily hydrolysed, so this alcohol molecule has one CH_2 group with the alcohol functional group attached to it. It has been assumed that the presence of this CH_2 group will not affect the chain packing within the micelle.

The 1H-1H-perfluoroheptan-1-ol was added to the binary CsPFO/ $^2\text{H}_2\text{O}$ system so that the ratio of surfactant to water molecules remained constant at 1/27.3 and the number of fluorinated chains remained constant. To satisfy these conditions it was necessary that for every surfactant molecule removed, one alcohol molecule was added. Hence the addition of alcohol dilutes the surface charge of a micelle whilst the number of fluorinated chains remains the same. 1H-1H-perfluoroheptan-1-ol was added up to 0.35 M which corresponded to one alcohol for every five CsPFO molecules.

The desired amounts of the CsPFO, 1H-1H-perfluoroheptan-1-ol and $^2\text{H}_2\text{O}$ (Fluka Chemicals, purity > 99.8 %) were weighed into constricted glass tubes and flame sealed. The samples were mixed by centrifuging the sample back and forth through the constriction. This continued until a uniform optical texture was seen when the sample was viewed between cross polarizers. Samples were stored in the isotropic phase (where possible) for several days before use.

2.2 OPTICAL MICROSCOPY. — A qualitative survey of the CsPFO/1H-1H-perfluoroheptan-1-ol/ $^2\text{H}_2\text{O}$ liquid crystalline phases was obtained by optical microscopy using a Vickers M72 polarizing microscope. The samples were contained in flame sealed 0.2 mm path length flat capillaries. Attached to the microscope was a Linkham TH600 temperature control stage with an adjustable heating and cooling rate. The temperature readings were considered accurate to ± 0.1 C.

2.3 SMALL ANGLE NEUTRON SCATTERING (SANS). — The neutron scattering experiments were carried out at the Rutherford Appleton Laboratory. The low angle scattering experiment (LOQ) was used because of its sensitivity in the size range 2 to 100 nm. The samples were contained in 1 mm path length quartz glass Helma cells with an electrical heater to control the temperature of the samples to ± 0.1 °C. Samples were studied both as unaligned powder samples and also, where possible, aligned by cooling in a magnetic field of ~ 1 T from the isotropic phase through the nematic phase. The geometry of the aligned samples is shown in figure 1.

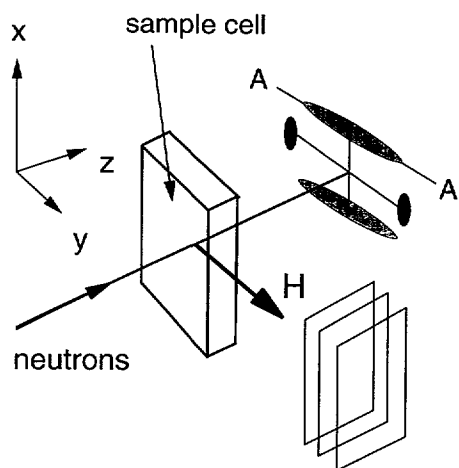


Fig. 1. — The geometry of the neutron scattering experiment with the sample aligned by the magnetic field H . Also shown to the right below is a representation of the orientation of the lamellar planes.

3. Results.

3.1 OPTICAL MICROSCOPY. — A phase diagram obtained by optical microscopy is shown in figure 2. The lamellar phase exhibits the typical « oily streak » texture whilst the nematic phase produces a characteristic schlieren texture. At low concentrations, < 0.15 M alcohol, the system has the same principal three phases seen in the binary system. A nematic phase N_D bordered to higher temperatures by an isotropic phase L_1 , and at lower temperatures a lamellar phase. As the alcohol concentration is increased the nematic phase is replaced by a wide isotropic and lamellar two phase coexistence region.

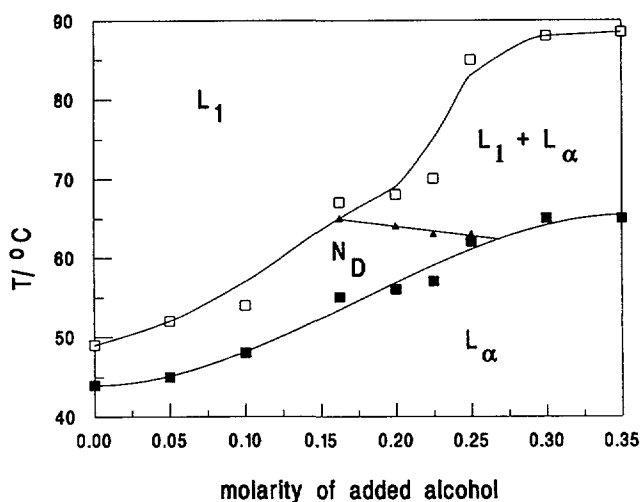


Fig. 2. — Phase diagram for CsPFO/1H-1H-perfluoroheptan-1-ol/ H_2O with the mole ratio of surfactant and cosurfactant to water maintained at 1/27.3. The diagram is obtained from optical microscopy. Open squares indicate the transition between L_1 and liquid crystalline phases, filled squares the transition to a single lamellar phase and the filled triangles the approximate boundary between the nematic, N_D and the biphasic, $L_1 + L_\alpha$. The solid lines are aids to the eye.

As the concentration of 1H-1H-perfluoroheptan-1-ol is increased there is an associated increase in the temperature of the N_D to L_1 transition. It is interesting that at cosurfactant concentrations of 0.25 M and above, the transition temperatures appear to stabilize at ~ 64 °C and ~ 87 °C respectively. Cosurfactant addition tends to increase micelle size but other factors such as the entropy of mixing will tend to decrease it [7]. It can be imagined that there is a limiting size for a given temperature beyond which the free energy favours lamellar phase formation [21]. It was not possible to explore beyond 0.35 M because the samples could no longer be mixed, presumably because the large two phase coexistence region lead to phase separation.

3.2 SANS RESULTS. — The scattering from the CsPFO/ H_2O was investigated as a function of added 1H-1H-perfluoroheptan-1-ol at a fixed temperature of 40 °C where only the lamellar phase occurs. Figure 3 shows the changes in the two dimensional scattering pattern, the two sharp « Bragg » peaks correspond to scattering from the inter-lamella spacing, $d_{||}$, whilst the less intense lateral band arises from scattering from the intra-lamellar spacing, d_{\perp} , i.e. the

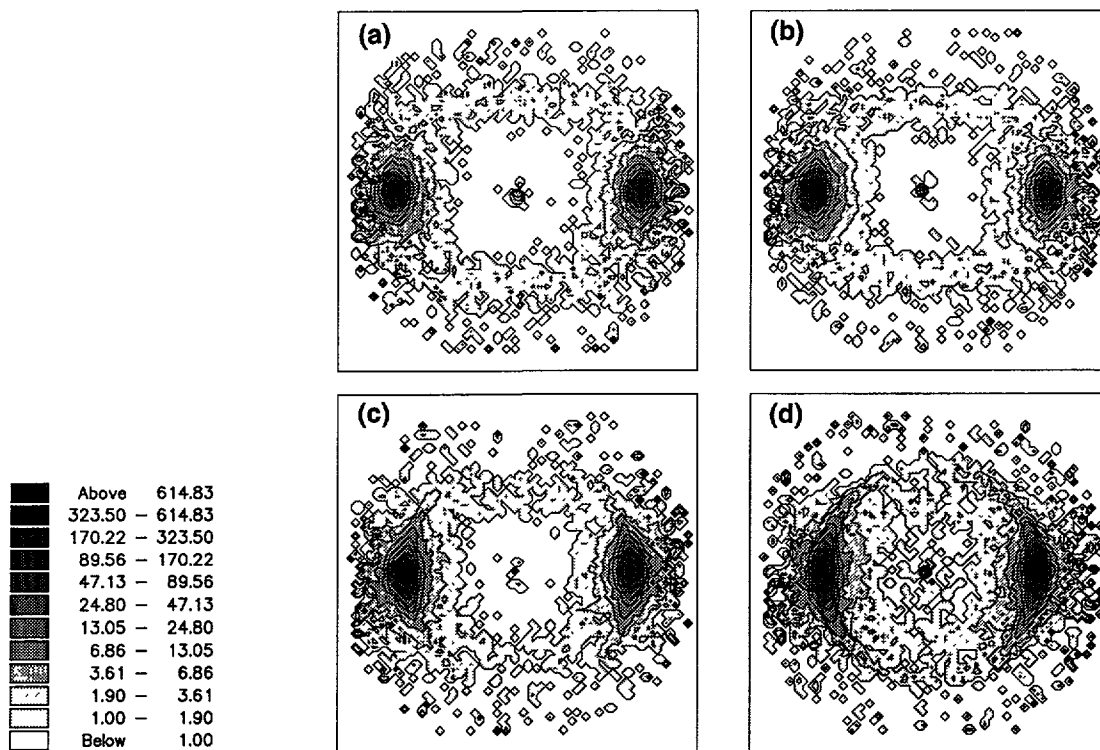


Fig. 3. — The neutron scattering from ordered lamellar phase samples at 40 °C : a) 0.0 M ; b) 0.05 M ; c) 0.1 M and d) 0.16 M 1H-1H-perfluoroheptan-1-ol. The horizontal direction corresponds to scattering parallel to the lamellae (y direction in Fig. 1) and the vertical direction perpendicular to lamellae (x direction in Fig. 1).

mean distance between the water-filled defects. Figure 4 shows the scattered intensity as a function of Q from the powder samples.

As the cosurfactant concentration increases, the weaker, broader lateral reflection to smaller Q , from the intra-lamellar structure shows a decrease in intensity and a shift in position corresponding to an increase in d_{\perp} , as shown in figure 5 and table I. These two processes indicate an increase in the separation of the defects in the lamellar phase and a decrease in their number density. The inter-lamella spacing d_{\parallel} , measured from the position of the Bragg reflection, also increases with cosurfactant concentration because water, previously located within the defects, moves into the inter-lamella region.

The increase in the inter-lamella reflection intensity is explained by the form factor of the bilayer. Taking the Fourier transform of the neutron scattering cross-section profile for the bilayer, should give the envelope prescribed by the variation of intensity of the Bragg peak with Q . Unfortunately, here the range of Q values is too small and there are too many uncertain parameters, to make fitting worthwhile. However, what can be seen of the profile does match the shape of that taken from the intra-lamella reflection parallel to the y axis, (along AA' in Fig. 1) which has the same origin [4].

The results of table I parallel those of electrolyte addition [31] although here they are very much clearer. In the case of the electrolyte experiments there was the additional effect of ions screening the interaggregate electrostatic interaction allowing a loss of correlation between the aggregates and resulting in a broadening of the intra-aggregate reflection leading to its

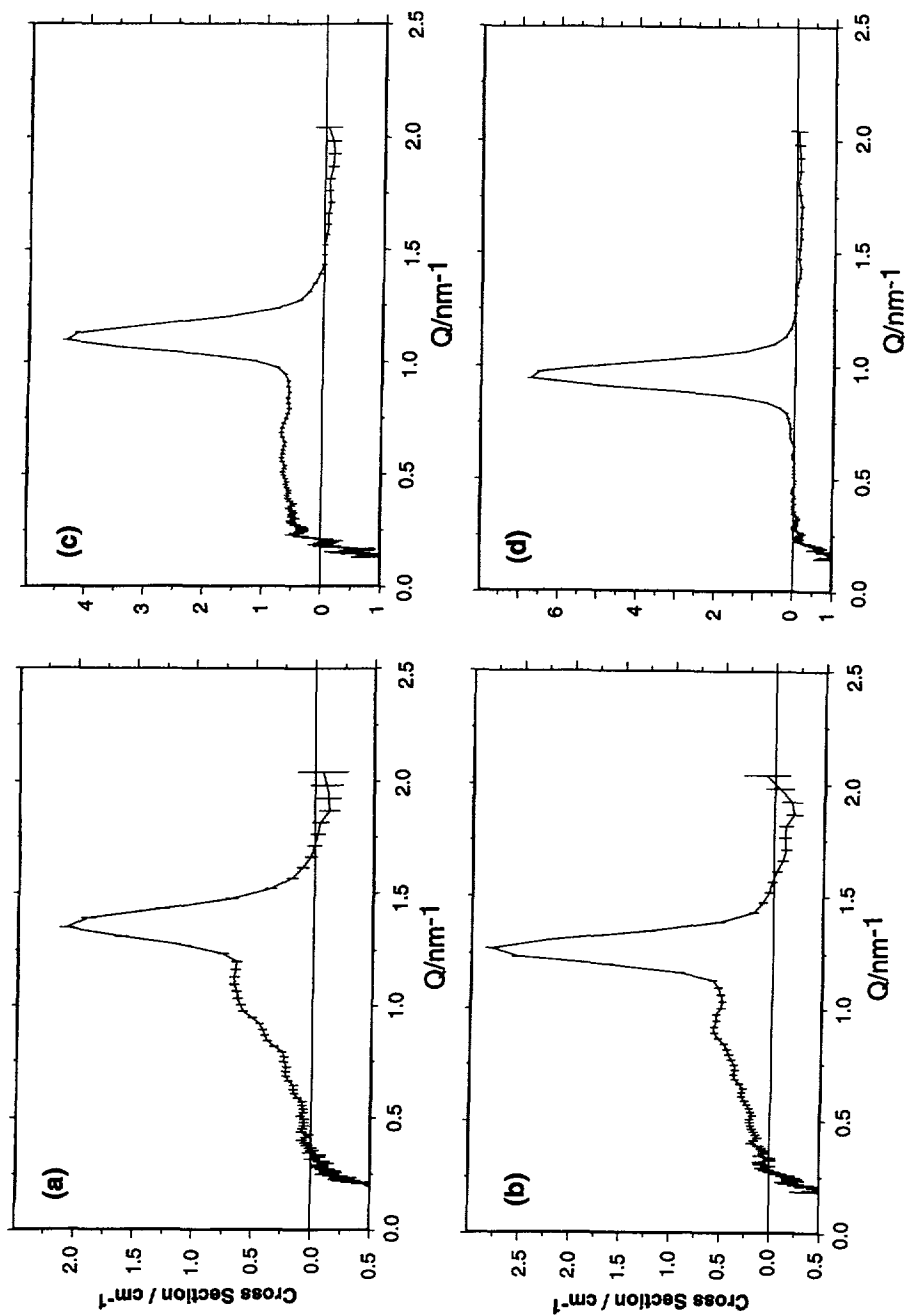


Fig. 4. — Scattering cross-section against Q from powder samples of the lamellar phase at 40 °C: a) 0.0 M; b) 0.1 M; c) 0.25 M and d) 0.35 M 1H-1H-perfluoroheptan-1-ol.

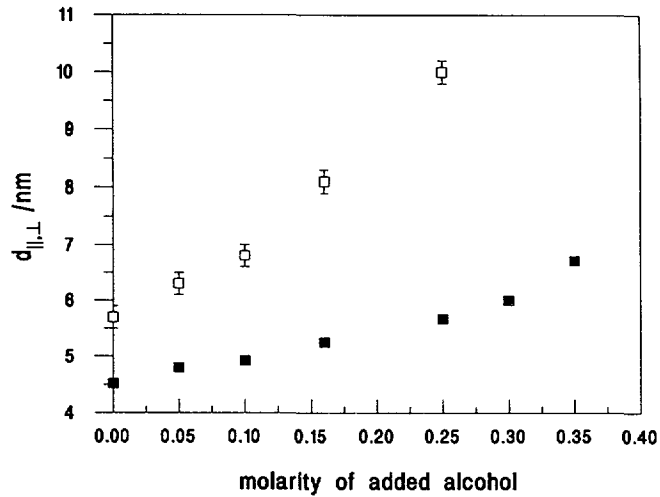


Fig. 5. — d_{\parallel} , filled squares and d_{\perp} , open squares plotted as a function of added 1H-1H-perfluoroheptan-1-ol.

Table I. — Inter- and intra-lamellar distances, d_{\parallel} and d_{\perp} respectively, from the SANS measurements, taken at 40 °C.

Molarity of alcohol/ Moles	$(d_{\parallel} \pm 0.05)$ /nm	$(d_{\perp} \pm 0.2)$ /nm
0	4.52	5.70
0.05	4.80	6.13
0.10	4.97	6.83
0.16	5.25	8.10
0.25	5.67	9.96
0.30	6.00	—
0.35	6.71	—

premature disappearance. There is no such problem here and the intra-lamella reflection remains visible although weakened to 0.25 M added cosurfactant.

In the lamellar phase at alcohol concentrations of 0.3 M or above there is no evidence of any structure within the lamellae. The bilayer thickness calculated assuming it to be a perfect classical bilayer is 2.0 ± 0.1 nm which agrees well with the previous result from electrolyte addition [31].

4. Analysis and discussion.

In our previous paper we were unable to unequivocally identify whether the lamella structure was water continuous (disk micelles on planes), surfactant continuous (planes pierced by holes) or bicontinuous (irregular ribbon structure) although the last was considered the most likely. The results presented here together with those from the binary system, table II, and the knowledge that the bilayer width lies in the rather narrow range from 1.9 to 2.45 nm (the length of two all-*trans* surfactant molecules) allows these models to be examined more critically.

Table II. — Experimental values of d_{\parallel} and d_{\perp} taken from reference [31] for the L_{α}^H phase (except for $X_a = 0.45$ which is in the N_D phase) of CsPFO/H₂O at 40 °C. X_a is the weight fraction of surfactant.

X_a	ϕ_a	$(d_{\parallel} \pm 0.05)/\text{nm}$	$(d_{\perp} \pm 0.2)/\text{nm}$
0.45	0.262	4.80	6.1
0.50	0.302	4.59	6.0
0.55	0.346	4.38	5.5
0.60	0.394	3.99	5.1
0.65	0.446	3.72	5.0
0.70	0.503	3.48	4.7
0.75	0.565	3.25	4.5

It was shown in reference [31] that the scaling behaviour of the aggregate volume could be written :

$$\tilde{v}_p = k \phi_a d_{\parallel} (d_{\perp})^p \quad (1)$$

where \tilde{v}_p is a generalized volume parameter, ϕ_a is the volume fraction of surfactant and k is a constant which depends upon the packing of the aggregates (e.g. for ribbons $k = 1$ but for hexagonally packed disks $k = 2/\sqrt{3}$). d_{\parallel} and d_{\perp} were defined above and $p = 2$ for water continuous structure (disks), $p = 1$ for bicontinuous structure (infinite ribbons) and $p = 0$ for infinite, unbroken lamellar. For a surfactant continuous structure (lamellae pierced by circular holes) the scaling behavior is similar to that of the water continuous structure :

$$\tilde{v}_w = d_{\perp}^2 (d_{fc} - k \phi_a d_{\parallel}) \quad (2)$$

where v_w is the volume of a water filled hole and d_{fc} is the fluorocarbon bilayer thickness. The distance d_{\perp} , in a ribbon lamellar structure, is the separation between two adjacent ribbons whilst in a disk micellar or lamella containing holes, the disks or holes are assumed to be hexagonally arranged and d_{\perp} , is the spacing of the (10) lines in the two dimensional hexagonal lattice. The hexagonal arrangement is similar to the expected liquid like arrangement.

Changing the packing arrangement, slightly changes the numerical constant, k in equation (1) but does not change the conclusions.

In the following analysis equations (1) and (2) are developed for specific models of the bilayer, namely a water continuous structure in which the surfactant is confined to discrete disk micelles, a surfactant continuous structure in which the bilayer is pierced by circular holes and a bicontinuous structure in which the surfactant forms infinite parallel ribbons. For disks and holes the edges are assumed to be hemi-toroidal whilst for the ribbons the edges are assumed to be hemi-circular cylinders. In order to test these models it is necessary to know the bilayer thickness, d_{fc} . Here it has been taken as 2.1 nm, lying between the limiting values of 2.0 and 2.4 nm, since, although there may be a continuous bilayer at 0.35 M cosurfactant, it is more probable that there still remain a few defects whilst 2.4 nm seems unlikely even for these rigid fluorocarbon chains. In practice the choice of d_{fc} , makes little difference to the conclusions drawn. Using the scattering results and d_{fc} , the dimensions of the aggregates for each model may be calculated. A criterion is necessary to distinguish between the models. A rather strong condition is that the separation of the surfactant aggregates both parallel and perpendicular to the lamella normal should be rather similar since they are determined by the same electrostatic forces. Thus the water layer dimensions parallel and perpendicular to the lamella normal, d_{\parallel}^w and d_{\perp}^w are calculated and compared. For all models d_{\parallel}^w is given by

$$d_{\parallel}^w = d_{\parallel} - d_{fc} . \quad (3)$$

4.1 RIBBONS. — Figure 6 defines the dimension parameters used. From the geometry of the ribbon

$$d_{\perp}^w = d_{\perp} - d_{fc} - 2a \quad (4)$$

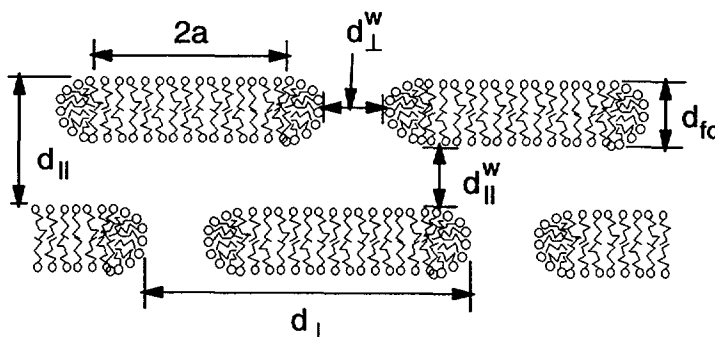


Fig. 6. — Definition of the geometrical parameters used in the models.

but from the volume per unit length of a ribbon aggregate

$$2ad_{fc} + \frac{\pi d_{fc}^2}{4} = \phi d_{\perp} d_{\parallel}$$

therefore

$$d_{\perp}^w = d_{\perp} \left(1 - \frac{\phi d_{\parallel}}{d_{fc}} \right) - \left(1 - \frac{\pi}{4} \right) d_{fc} .$$

Both d_{\parallel}^w and d_{\perp}^w can now be calculated ; the results for the binary system are shown in figure 7 and for the cosurfactant addition in figure 8.

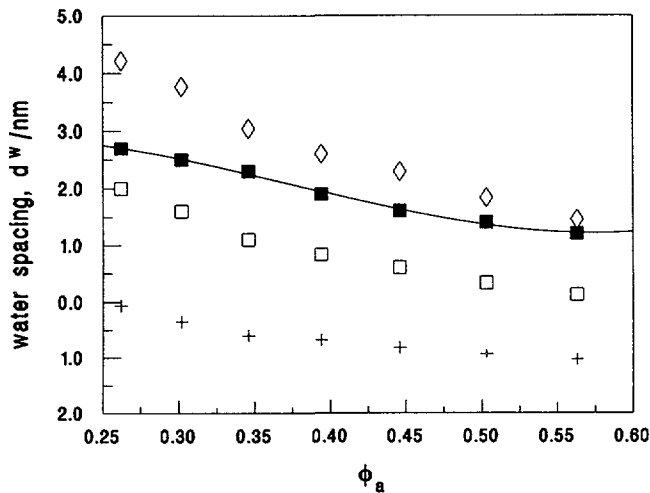


Fig. 7. — Water spacing plotted as a function of volume fraction, ϕ_a for the binary system. Closed squares, d_{\parallel}^w ; open diamonds, d_{\perp}^w (holes); open squares, d_{\perp}^w (ribbons); crosses, d_{\perp}^w (disks). The solid line is an aid to the eye.

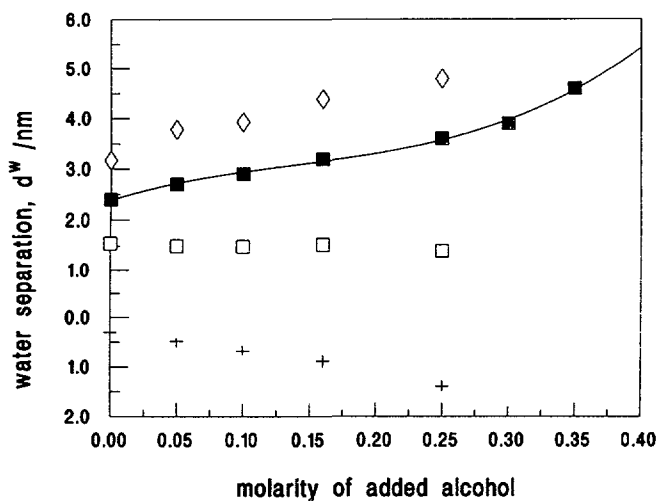


Fig. 8. — Water spacing plotted a function of added 1H-1H-perfluoroheptan-1-ol. Closed squares, d_{\parallel}^w ; open diamonds, d_{\perp}^w (holes); open squares, d_{\perp}^w (ribbons); crosses, d_{\perp}^w (disks). The solid line is an aid to the eye.

4.2 DISK MICELLES. — The disk micelles are assumed to be ordered onto planes and to have a hexagonal packing arrangement in the planes. Both equations (3) and (4) still hold although now a represents the radius of the flat part of the disk excluding the hemi-toroidal edge. Using the volume of the disk gives

$$\frac{16}{\pi \sqrt{3}} \frac{\phi d_{\perp}^2 d_{\parallel}}{d_{fc}^3} = 2 q^2 + \pi q + \frac{4}{3} \tag{5}$$

where $q = 2a/d_{fc}$. Equation (5) is solved to find q and thus d_{\perp}^w . The results for the binary system are shown in figure 7 and for the cosurfactant addition in figure 8.

4.3 BILAYERS PIERCED BY HOLES. — The holes in the continuous bilayer planes are assumed to have a hexagonal arrangement. Both equations (3) and (4) still hold although now a represents the radius of the inside of the hole taken to the start of the flat interface and including the hemi-toroidal edge. Using the volume of a hole gives

$$\frac{16}{\pi \sqrt{3}} \frac{d_{\perp}^2}{d_{fc}^3} (d_{fc} - \phi d_{\parallel}) = 2q^2 - \pi q + \frac{4}{3} \quad (6)$$

where $q = 2a/d_{fc}$. Equation (6) is solved to find q and hence d_{\perp}^w . The results for the binary system are shown in figure 7 and for the cosurfactant addition in figure 8.

For the water continuous model (disk micelles) both experiments show (Figs. 7 and 8) that d_{\perp}^w (disk) is not only very much less than d_{\parallel}^w but is negative which is unphysical. Increasing d_{fc} to 2.4 nm does not give a significant improvement. The disks must be either severely distorted in shape or there must be considerable movement of the disk micelles out of the bilayer plane by displacement or rotation. Distortion seems unlikely since it would necessitate regions of high surface curvature and the close approach of the edges of neighbouring micelles both of which would be energetically unfavourable. Displacement of the micelles out of the plane is also not a feasible explanation because it would result in displacement disorder [20] and a broadening of the Bragg reflection in the SANS along the x -axis which is not observed, figure 4. Finally, large rotations of the micelles out of the lamellar plane are also problematic since the electrostatic interactions between lamellae are sufficiently strong to give well defined Bragg reflections and would not allow the necessary large orientational fluctuations. The disk model can be dismissed as untenable in agreement with the conclusions reached by Quist *et al.* [33] in the SDS system and with our own measurements of water self diffusion in this system [34].

Figures 7 and 8 show that

$$d_{\perp}^w (\text{ribbon}) < d_{\parallel}^w < d_{\perp}^w (\text{hole}).$$

For the binary system d_{\perp}^w (ribbon) is closer to d_{\parallel}^w at low surfactant volume fraction, ($\phi_a = 0.262$), i.e. close to the boundary with the nematic phase but is closer to d_{\perp}^w (hole) at high volume fraction, ($\phi_a = 0.565$). It may be imagined that just below the transition from the nematic phase into the lamellar phase the lamellae are pierced by rather long rectangular holes which shrink in length as the surfactant concentration is increased until they become almost circular holes at the highest volume fraction. Using the values of d_{\parallel}^w , d_{\perp}^w (ribbon) and d_{\perp}^w (hole) from figure 7, an estimate can be made of how much ribbon lamellar and how much hole lamellar would be necessary to give the measured d_{\parallel}^w . The length of ribbon associated with each hole can then be calculated. Although a rough calculation it gives a length of about 13 nm. The evolution of the bilayer from defected bilayer to classical continuous bilayer proceeds by the reduction of hole size and concomitant removal of intra-lamella water to the inter-lamella space.

In the ternary system the behaviour is rather different. d_{\parallel}^w lies almost exactly between d_{\perp}^w (hole) and d_{\perp}^w (ribbon) indicating once again that the holes are probably rather elongated with curved ends. Now, however, d_{\perp}^w is increasing rapidly with increasing cosurfactant addition, d_{\perp}^w remains static for the ribbon model and changes only slowly for the circular pore model. This indicates that here the pores piercing the bilayer are unaffected in shape or size by

the cosurfactant addition but rather the cosurfactant promotes the growth of flatter interface and thereby reduces the number density of defects.

5. Conclusions.

The defected lamellar phase, L_{α}^H has a surfactant continuous structure in both the binary and ternary systems. The defects in the bilayer structure are elongated pores. In the binary system they have an aspect ratio ~ 6 close to the transition to the nematic phase but this decreases to nearly unity at the highest concentrations considered. The progression to classical lamellar phase is *via* a process of decrease in defect area by the shortening of rectangular holes rather than a change in the number density of the defects. It was noted in reference [31] that the intensity of the intra lamellar reflection actually increased slightly relative to the Bragg peak with increasing surfactant concentration supporting this conclusion. It is further supported by water self diffusion measurements [34]. Presumably further increases in surfactant concentration would lead to a change in number density although this would be difficult to see experimentally in this system. This picture is entirely consistent with the predictions of reference [21]. Going from high to low surfactant concentration we see circular holes or pores elongate to form a random network of defects. The transition from ribbon to random defects was predicted to be first order whilst that from random line to pore was weaker [21]. Experimentally no transition between different types of lamellar phase was seen. It may be that the whole L_{α}^H phase is of a « random defect » type ; the nematic phase intervening before the « ribbon » phase is seen. Thus, the model of reference [21] is experimentally confirmed here. An increase in surfactant concentration reduces the length of the random line defects whilst their density remains constant.

In the ternary system, the defects retain their shape, the addition of the cosurfactant causing a reduction in their number density. The associated decrease in curved interface is reflected by a gradual monotonic increase in the ^2H NMR quadrupolar splitting of the solvent $^2\text{H}_2\text{O}$ [35].

It is interesting to speculate whether changing the system parameters would allow the ribbon phase to be seen, together with its transition to the random defect phase. Also, since both systems show unequivocally that the lamellar phase has a surfactant continuous structure whilst it is well established that the higher temperature nematic phase is composed of individual aggregates, it is interesting to ask at what point the system forms a surfactant continuous structure.

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