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Water self diffusion in caesium pentadecafluorooctanoate (CsPFO)/H₂O and CsPFO/CsCl/H₂O and its relationship to structure

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Abstract. — The lamellar phases of some surfactant water systems are not infinite, continuous lamellar planes but scattering experiments show that they contain intra-planar structure. This is believed to be water filled defects with highly curved edges. Here, oriented samples of the defected lamellar phase, L_{α}^H of the caesium pentadecafluorooctanoate (CsPFO)/H₂O and CsPFO/CsCl/H₂O systems have been studied using ¹H-NMR pulse field gradient measurements of the water self diffusion. The water coordination number per surfactant in the lamellar phase is found to be 4.8 ± 0.2 and obstruction factors for water diffusion parallel and perpendicular to the lamella normal are obtained. The latter confirm the defected nature of the lamellar phase. Using structural data from neutron scattering, theoretical obstruction factors have been calculated with no adjustable parameters and agree well with experiment. Both water diffusion and neutron scattering are sensitive to the same defect structure. Although tending to confirm a model of surfactant continuous lamellae broken by elongated water filled defects, the diffusion measurements cannot unequivocally distinguish between different structural models for the defects. The measurements do show that addition of surfactant or of electrolyte leads to the « healing » of the defects and an approach to a classical lamellar phase structure.

1. Introduction.

The structure of the lyotropic liquid crystalline lamellar phase formed in concentrated surfactant water mixtures is well established and consists of infinite, continuous bilayers formed by the surfactant molecules separated by water layers. It is located at the mid-point of the phase diagram of a normal surfactant water system, having zero surface curvature, between the positive surface curvatures of the micellar and hexagonal phases to lower concentration and the negative curvatures associated with the so-called reversed phases at high surfactant concentration. A number of lamellar phases, L_{α}^H have been reported [1-17] in which it has been

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suggested that the bilayers are pierced by water filled defects or holes. These defects appear to be irregular and without correlation between adjacent layers or with only correlation between a few layers. There are, however, « intermediate » phases which have been reported [18, 19] where the bilayer structure is retained and where the holes are regularly spaced and show long range correlation between layers on a centred tetragonal, T_a lattice. All of these phases are thermodynamically stable and distinct from the classical L_a phase. This is exemplified by the first order phase transition reported in the nonionic surfactant hexaethylene glycol-*cis*-13-docosenyl ether ($C_{22}EO_6$) with water (2H_2O) between the L_a and the L_a^H phases [7].

One lyotropic system which has received considerable attention is the binary ionic system caesium pentadecafluorooctanoate (CsPFO)/water [9, 11-17, 20-24]. The phase diagram is well established [9, 11, 15, 16] and exhibits isotropic micellar (L_1), defected lamellar (L_a^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 [12, 13]. The changes of phase could then be ascribed to disorder-order transitions. 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, it has been shown, using SANS, [15-17] 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 salt (CsCl) and alcohol (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. The addition of CsCl also screens the electrostatic interactions between bilayers leading to a weakening of the inter-lamellar interactions, displacement disorder of the lamellae and to shape changes in the Bragg reflections [17]. It is difficult to obtain further information about the shape of the intra-lamellar defects from the scattering experiments alone because of Babinet's Principle, i.e. scattering from a bilayer of discrete disk micelles will be the same as that from a surfactant continuous lamellar containing water filled holes of the same size [25].

Although the interpretation of the scattering patterns and the existence of water filled defects in these lamellar systems appears certain, it would be reassuring if the structure determined by small angle scattering could be directly correlated with a transport process such as water self diffusion. In this paper water self diffusion is measured by the 1H -NMR pulse field gradient technique. The measurements are used to directly confirm that the neutron scattering is seeing water filled defects in the lamellar phase by obtaining a correlation between results from the two techniques. The utility of water self diffusion measurements in distinguishing between the structural models that have been proposed for the defect structure is also tested.

The pulsed field gradient NMR measurement of self diffusion coefficients [26, 27] of both solvent water and the surfactant molecule itself have been successfully employed for a number of years in helping to elucidate the structure of the lamellar, L_a [28-34] and more recently the bicontinuous cubic and L_3 or « sponge » phase [35, 36]. The cell model of self diffusion in these systems is well established [35]. Here we apply the technique to the L_a^H phase in the CsPFO/ 2H_2O and CsPFO/CsCl/ 2H_2O systems [9, 10, 12, 14-17]. They provide excellent model systems on which to make self diffusion measurements of the solvent water because the lamellar phase is bounded over much of its concentration range, by a lyonematic phase,

N_D [9]. This enables monodomain samples containing a single director orientation to be produced by cooling the sample in a magnetic field through the nematic phase [10-12]. Since the lamellar phase of a perfluoro-alkyl surfactant system has a positive diamagnetic susceptibility anisotropy, the director aligns along the magnetic field direction. The orientation of the director is retained in the lamellar phase even when the sample is rotated through 90°.

2. Experimental.

Samples of caesium pentadecafluorooctanoate (CsPFO)/²H₂O and CsPFO/CsCl/²H₂O were made as in reference [15]. Their phase transition temperatures were measured on an optical polarizing microscope and checked against the phase diagrams for the binary and ternary systems which have already been published [9, 15, 16]. All the ternary samples studied had the mole ratio H₂O/CsPFO fixed at 27.3 : 1 making these measurements comparable to the scattering results reported in reference [15]. One difference should be noted. All the measurements reported in this reference were made on samples containing ²H₂O rather than ¹H₂O used here. The effect of using ¹H₂O rather than ²H₂O is that at a given mole ratio the phase transition temperatures for L₁ to N_D and N_D to L_a^H are depressed by 4.4 °C. Measurements at fixed temperature were therefore made at 35 °C rather than the 40 °C used in reference [15] to make the experiments directly comparable. The volume fraction of surfactant is calculated from the equation

$$\phi_a = \frac{1}{1 + \frac{\rho_a}{m_a} \left(\frac{m_w}{\rho_w} + \frac{m_e}{\rho_e} \right)}$$

where ρ_i and m_i refer to the density and mass of the i -th component and a, w and e refer to amphiphile, water and electrolyte respectively.

¹H-NMR pulse field gradient water self diffusion measurements were made on a Bruker Minispec PC120 20 MHz spectrometer fitted with a 200 G/cm field gradient device and a Haake temperature controller. Details of the standard method developed by Stejskal and Tanner [26, 27] and its basic theory have been extensively covered in the literature [28]. A matched pair of field gradient pulses of duration δ are inserted into a 90°- τ -180° or Carr-Purcell pulse sequence for the determination of T_2 . The spin echo which occurs a time τ after the second 180° pulse is, as a result of diffusion, attenuated by an amount R given by

$$R = \exp \left(- \gamma^2 \delta^2 g^2 D \left(\Delta - \frac{\delta}{3} \right) \right)$$

where γ is the gyromagnetic ratio for the nucleus being observed, g is the applied field gradient, δ is the duration of the gradient pulse, Δ is the time period from the start of the first gradient pulse to the start of the second and D is the diffusion coefficient. Plots of $\ln R$ against $\delta^2 \left(\Delta - \frac{\delta}{3} \right)$ will yield a straight line graph of gradient $-\gamma^2 g^2 D$, provided there are no restrictions to diffusion on a length scale of $d \leq \sqrt{2 D \tau}$, which here corresponds to a distance of between 1 and 10 μm . δ and Δ were varied between 0.3 and 2 ms and 12 and 17 ms, respectively. Experimentally, under all conditions reported here the plots were linear over 2 decades and therefore it was concluded that there were no mesoscopic defects on this range scale. All gradients were measured relative to a calibration standard of undoped, triple distilled water at 25 °C which has a self diffusion coefficient of $2.30 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$ [37] and values of D were considered to be accurate to $\pm 5 \%$.

3. Results.

3.1 TEMPERATURE DEPENDENCE. — The temperature dependence of D was measured for two samples both having a fixed mole ratio of $\text{H}_2\text{O}/\text{CsPFO} = 27.3$, one with no added CsCl , the other with 4 % by weight added CsCl . The results are shown in figures 1a and b and the temperature dependence of pure water, D_w is shown for comparison. In the isotropic phase only \bar{D} , the diffusion coefficient averaged over all directions, can be measured. The measured

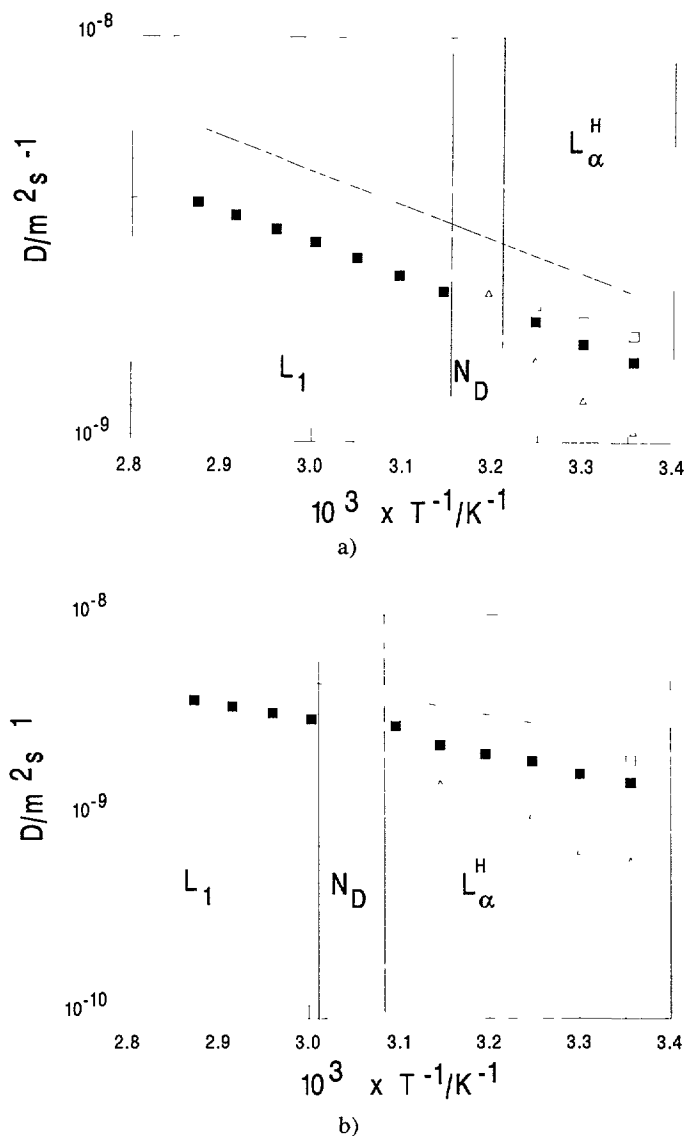


Fig. 1. — The temperature dependence of the diffusion coefficient, D measured for two samples having a fixed mole ratio of $\text{H}_2\text{O}/\text{CsPFO} = 27.3$, (a) no added CsCl and (b) with 4 % by weight added CsCl . Filled squares, \bar{D} averaged over all directions ; open triangles, D_{\parallel} parallel to the director ; open squares, D_{\perp} perpendicular to the director and the solid line is the coefficient for water, D_w .

values of \bar{D} are 67 and 63 % of D_w and the activation energies are rather similar, 0.164 eV/molecule and 0.151 eV/molecule respectively for the two samples whilst for D_w it is 0.173 eV/molecule. This shows that the same processes as found in water are controlling the diffusion in the two isotropic phases.

In the narrow nematic region only D_{\parallel} , the diffusion along the director direction, can be measured since the director rapidly reorients in the magnetic field. In the lamellar phase

\bar{D} , D_{\parallel} and D_{\perp} , could all be measured. \bar{D} measured and calculated from $\bar{D} = \frac{D_{\parallel}}{3} + \frac{2 D_{\perp}}{3}$ agreed within the limits of experimental accuracy. Once again the activation energies for

\bar{D} in the two samples and in water were almost identical (0.194 eV/molecule for 0 % CsCl, 0.181 eV/molecule for 4 % CsCl and 0.173 eV/molecule for pure water). In both cases the activation energy in the L_{α}^H phase was some 15 % larger than in the L_1 phase and were slightly larger than that for D_w whereas in the L_1 phase they had been slightly less.

In the magnetically aligned samples, both D_{\parallel} and D_{\perp} could be measured and showed similar behaviour. D_{\perp} was larger than \bar{D} and decreased less rapidly with temperature (0.138 eV/molecule for 0 % CsCl and 0.147 eV/molecule for 4 % CsCl) whilst D_{\parallel} was smaller and decreased more rapidly (~ 0.4 eV/molecule for 0 % CsCl and 0.41 eV/molecule for 4 % CsCl).

3.2 SURFACTANT CONCENTRATION DEPENDENCE. — Figure 2 shows the dependence of \bar{D} , D_{\parallel} and D_{\perp} measured at 35 °C upon surfactant volume fraction, ϕ_a , with no added CsCl. Volume fraction has been used rather than concentration because the diffusion coefficient is controlled by the volume of the obstructing particles. \bar{D} varies linearly with ϕ_a and has virtually the same gradient on either side of the nematic phase although there is a small but real step change in the intercept of these lines going from L_1 to L_{α}^H . Unfortunately D_{\parallel} and D_{\perp} can only be measured for three concentrations because of the increasing difficulty of

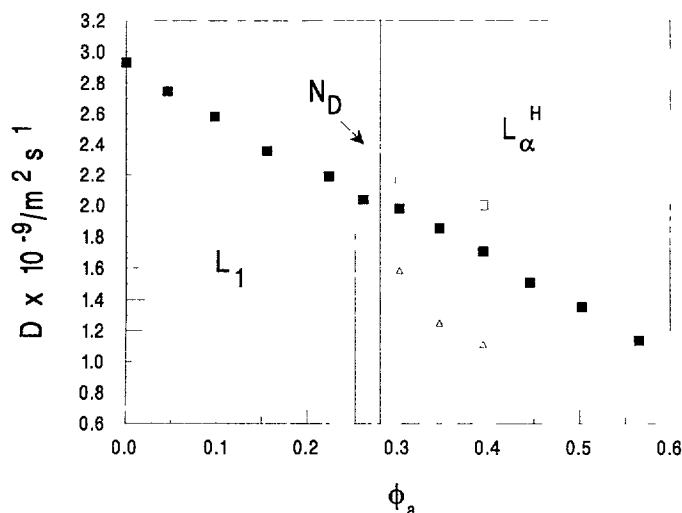


Fig. 2. — \bar{D} , filled squares, D_{\parallel} , open triangles and D_{\perp} , open squares measured at 35 °C as a function of surfactant volume fraction, ϕ_a .

aligning the sample at higher surfactant concentrations. This is because of the much higher liquid crystal phase transition temperatures, the replacement of the nematic phase by an isotropic/lamellar two phase region [9] and the increasing viscosity of the samples.

3.3 ELECTROLYTE (CsCl) CONCENTRATION DEPENDENCE. — The effect of added CsCl on \bar{D} , D_{\parallel} and D_{\perp} measured at 35 °C is shown in figure 3, again D_w is shown for comparison. (Note that the addition of up to 8 % by weight of CsCl had little effect on D_w .) \bar{D} and D_{\parallel} decrease with increasing CsCl concentration whilst D_{\perp} remains constant within the limits of experimental error. At 8 % added CsCl only \bar{D} could be obtained for the same reasons reported above for the binary system.

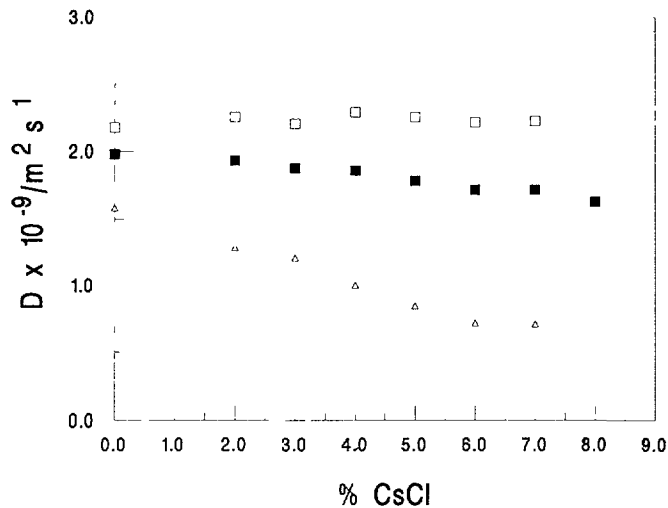


Fig. 3. — \bar{D} , filled squares, D_{\parallel} , open triangles and D_{\perp} , open squares measured at 35 °C as a function of added CsCl and again D_w , the dashed line, is shown for comparison.

4. Analysis and discussion.

The observed self diffusion coefficient D_{obs} is given by

$$D_{\text{obs}} = \beta_t(1 - p) D_t + \beta_b p D_b \quad (1)$$

where D_t and D_b are, respectively, the diffusion coefficients for « free » water in the bulk and water « bound » to the interfacial region, p is the fraction of total water which is bound and β_t and β_b are obstruction factors for free and bound water. For most surfactant water systems D_b is two orders of magnitude slower than that for free water and D_t can be replaced by D_w to a very close approximation so that equation (1) can be rewritten as

$$D_{\text{obs}} = \beta_t(1 - p) D_w. \quad (2)$$

For example in an ideal, disordered lamellar system of infinite continuous bilayers

$$D_{\parallel} = \beta_{\parallel}(1 - p) D_w = 0, \quad \text{since } \beta_{\parallel} = 0$$

and
$$D_{\perp} = \beta_{\perp}(1 - p) D_w = (1 - p) D_w, \quad \text{since } \beta_{\perp} = 1.$$

Thus $\bar{D} = 2(1 - p)D_w/3$ and therefore $\beta_t = 2/3$. This value of β_t has been verified experimentally for a number of classical lamellar phases [28, 29].

It is the obstruction factor which allows the measurements of self diffusion coefficient to be linked to mesophase structure. However, equation (2) presents a problem since it contains both β_t which we are trying to find and p , the fraction of bound water, which is unknown. This problem was considered by Chidichimo *et al.* [30]. Within a single phase and at a fixed temperature, β_t can be found by measuring the diffusion coefficient as a function of surfactant concentration, provided that the structure and hence β_t and n , the number of interfacially bound water molecules per surfactant molecule, does not change. β_t is then given by

$$\beta_t = \frac{D_1 - K_{11} D_2}{(1 - K_{11}) D_w} \quad (3)$$

where D_1 and D_2 are diffusion coefficients measured at water weight fractions W_1 and W_2 and K_{11} is given by

$$K_{11} = \frac{W_2(1 - W_1)}{W_1(1 - W_2)} \quad (4)$$

Equations (3) and (4) were applied to the measurements of D_{\perp} as a function of surfactant concentration shown in figure 2 ($D_{\perp} = 2.23, 2.16$ and $2.00 \times 10^{-9} \text{ m}^2 \text{ s}^{-2}$ for 0.50, 0.55 and 0.60 weight fractions of surfactant respectively). Since D_{\perp} measures the diffusion of water parallel to the lamellae, it is unlikely to be significantly affected by changes to the structure within the lamellae, thus β_{\perp} and n also are unlikely to change significantly with concentration. (Note that the same cannot be said of β_{\parallel} .) Using this method, a mean value of β_{\perp} was calculated to be 0.92 ± 0.05 . The corresponding value of p for the 0.50 weight fraction sample is 0.174, giving the number of « bound » water molecules per surfactant molecule, n to be 4.8 ± 0.2 . The value of β_{\perp} is close to the expected value of unity for a planar structure and the value of n is also physically reasonable. Taking a more pessimistic view, the measurements of D_{\perp} and equation (2) simply allow limits to be put on β_{\perp} and n . β_{\perp} has a maximum, but unlikely, possible value of 1 which leads to $n = 6.6$, and n has a minimum, but equally unlikely, possible value of zero, which leads to $\beta_{\perp} = 0.76$. This gives the limits $6.6 > n > 0$ and $1.0 > \beta_{\perp} > 0.76$.

In the analysis that follows it will be assumed that n remains constant at 4.8, enabling p and $\bar{\beta}_t$ to be calculated. Figure 4 shows $\bar{\beta}_t$ as a function of ϕ_a for the binary system and figure 5 is a plot of $\bar{\beta}_t$ against the percentage of added CsCl. In both cases $\bar{\beta}_t$ is greater than the theoretical value of 2/3, indicating that the lamellae contain water filled defects. Addition of surfactant or CsCl causes $\bar{\beta}_t$ to decrease and approach 2/3 at the high concentration limit indicating that the defects are reducing in size or number density and that the structure approaches that of an infinite continuous lamellar phase : a conclusion arrived at independently from the scattering experiments [15, 16].

In addition to using $\bar{\beta}_t$, the behaviour of β_{\parallel} , the obstruction factor parallel to the lamella normal, which should be correlated with the intra-lamellar structure measured by SANS can also be found. β_{\parallel} has been calculated from the experimental values of $\bar{\beta}_t$ by using

$$\bar{\beta}_t = \frac{1}{3} \beta_{\parallel} + \frac{2}{3} \beta_{\perp} \quad (5)$$

where β_{\perp} is set equal to the value of 0.92 found above.

SANS experiments give d_{\parallel} , the bilayer repeat in the lamella normal direction and

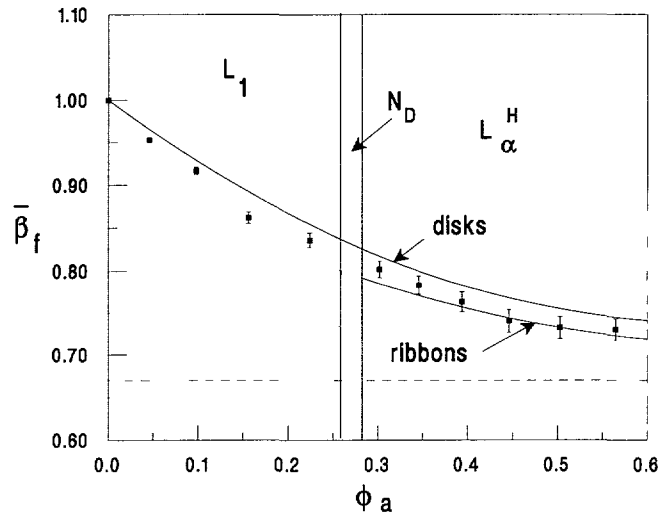


Fig. 4. — $\bar{\beta}_f$ as a function of ϕ_a for the binary system. The two continuous lines represent values of $\bar{\beta}_f$ calculated from the dimensions tabulated in table I and using a disk and a ribbon model. The dashed line represents the limiting value for a lamellar phase of 2/3.

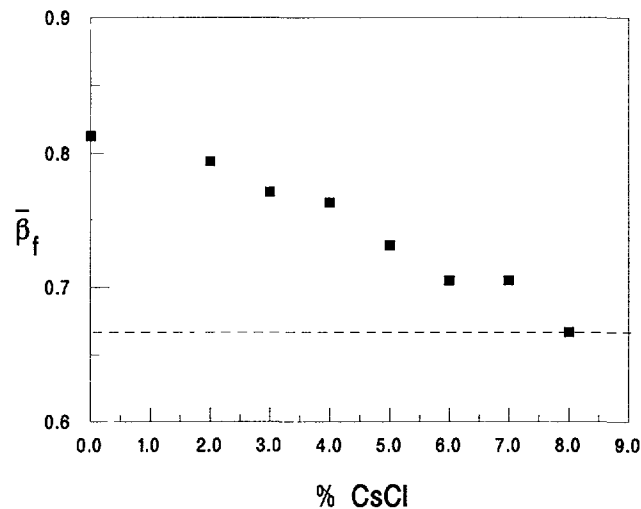


Fig. 5. — $\bar{\beta}_f$ as a function of the weight percent of added CsCl. The dashed line represents the limiting value for a lamellar phase of 2/3.

d_\perp the mean separation of the intra-lamella structure. These distances are summarized as functions of volume fraction for the binary system in table I. Similar results, for d_\parallel only, in the system with added CsCl are to be found in reference [15]. These are used to estimate the fractional area of lamellae composed of water filled defects, f_w [12], which is given by

$$d_{fc} = \frac{\phi_a d_\parallel}{(1 - f_w)} \quad (6)$$

Table I. — *Experimental values of d_0 , $d_{||}$ and d_{\perp} from SAXS [12] and SANS [15] for CsPFO/H₂O at 40 °C. In the L_1 phase only a single isotropic peak from the average micelle separation, d_0 is seen and quoted.*

Weight fraction of CsPFO	ϕ_a	$(d_{ } \pm 0.05)/\text{nm}$	$(d_{\perp} \pm 0.2)/\text{nm}$	Phase
0.25	0.126	$d_0 = 6.6$		L_1
0.30	0.153	$d_0 = 6.4$		L_1
0.40	0.224	$d_0 = 5.9$		L_1
0.45	0.262	4.80	6.1	N_D
0.50	0.302	4.59	6.0	L_{α}^H
0.55	0.346	4.38	5.5	L_{α}^H
0.60	0.394	3.99	5.1	L_{α}^H
0.65	0.446	3.72	5.0	L_{α}^H
0.70	0.503	3.48	4.7	L_{α}^H
0.75	0.565	3.25	4.5	L_{α}^H

where d_{fc} is the bilayer thickness. Scattering experiments at high concentrations of CsCl [15] or added cosurfactant [16] show that for the classical bilayer in this system $d_{fc} \approx 2.1$ nm. Using this value and rearranging equation (6) allows f_w to be calculated at each volume fraction or CsCl concentration.

$\beta_{||}$ depends upon the fractional area of water filled holes in the lamellae, f_w . It also depends upon the layer separation as well which itself depends on f_w via equation (6). (Note that here the layer separation is changing much less rapidly.) Thus a correlation is expected between $\beta_{||}$ and f_w which is tested in figure 6 for both the binary and the ternary systems. The excellent, almost linear, correlation in both binary and ternary systems indicates further that the neutrons are « seeing » intra-lamella water filled defects through which the water molecules can diffuse rather than any larger scale defects between lamellar domains.

Given this strong correlation, a theoretical obstruction factor for each value of ϕ_a has been calculated from the SANS determined structural parameters, table I. To do this it is necessary to make an assumption about the form of the defects in the lamellae. Although it has been shown [16] that the most likely structure is that of surfactant continuous lamellae with elongated holes or defects, we shall consider two structural models for the defects of the L_{α}^H phase ; disk micelles and an irregular ribbon structure. The latter is closest to the structure proposed in reference [16].

Jönsson *et al.* [35] have published a model for the self diffusion of small molecules in colloidal systems based on the solution of Laplace's Equation. Taking the values of

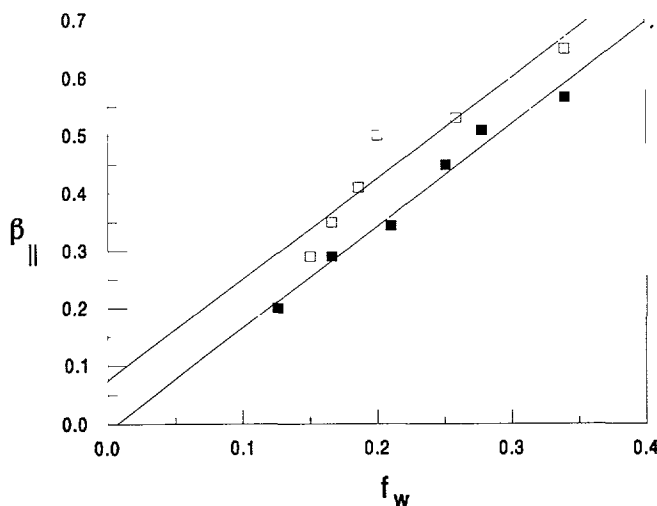


Fig. 6. — $\beta_{||}$ as a function of f_w , the binary system, filled squares and the ternary system, open squares.

d_0 , $d_{||}$ and d_{\perp} from table I and using the equations in reference [12] for the volume of a disk shaped micelle, V_m in the isotropic phase :

$$V_m = \frac{3\sqrt{3}}{4} \phi_a d_0^3 \quad (7)$$

and in the lamellar phase :

$$V_m = \frac{2}{\sqrt{3}} \phi_a d_{||} d_{\perp}^2 . \quad (8)$$

The thickness of the micelle, d_{lc} is assumed to be that of a classical bilayer when the addition of CsCl or 1H-1H-perfluoroheptan-1-ol has removed all evidence of defects, i.e. 2.1 nm [15, 16]. The eccentricity, e is then given by :

$$e = \left(\frac{4 V_m}{\pi d_{lc}^3} \right)^{1/2} \quad (9)$$

For each volume fraction, e may be calculated (typically e varies between 2.5 and 2.8) and, using the theory of Jönsson *et al.* [35], $\bar{\beta}_l$ can be calculated, figure 4. In the isotropic phase calculated and experimental values are quite close but as the lamellar phase boundary is approached and within it, the experimental results tend to be lower than the theoretical predictions. The calculated values of $\bar{\beta}_l$ are rather insensitive to changes in the eccentricity and using e as an adjustable parameter, a fit to the experimental results requires an eccentricity of ~ 4.5 which is well outside the experimental errors in the scattering results. However a small decrease in the water coordination number of 6 % would shift the « experimental » values of $\bar{\beta}_l$ upwards to give reasonable agreement with the calculated values.

A surfactant continuous lamella with elongated water filled defects is modelled by considering infinite ribbons forming structures of the type shown in figures 7a and b. The dimensions shown in figures 7a and b are obtained from the neutron scattering measurements

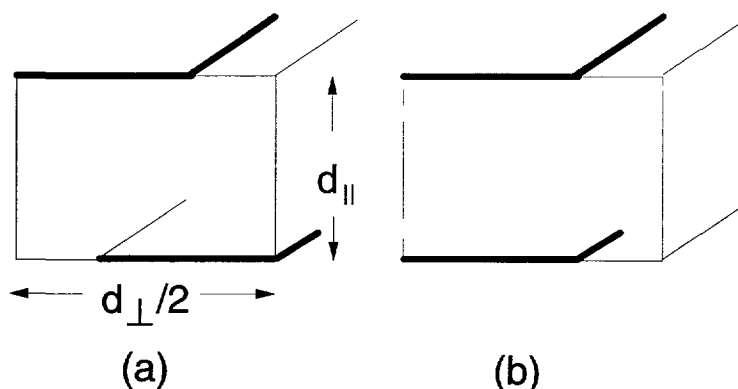


Fig. 7. — The model structures used to calculate β for the ribbon model. a) Infinite, parallel, anticorrelated ribbons and b) infinite, continuous, correlated ribbons.

[15, 16] and the thickness of the water filled channels can be calculated from these measurements by assuming a bilayer thickness of 2.1 nm [16]. The Gauss-Seidel numerical method has been used to solve Laplace's equation in two dimensions for both situations and a simple average taken. This model may seem rather artificial. Indeed, if the real defected lamellar phase has a ribbon structure, it is clear from neutron scattering studies that it is irregular and with no correlations between the layers. Furthermore, from one lamella to the next, the ribbons are not necessarily parallel to each other but probably intersect. Values of $\bar{\beta}_f$ obtained numerically, which are plotted in figure 4, are consistently lower than those of the disk model and lie within the experimental error of the experimental results.

5. Conclusions.

These water self diffusion measurements show that over a substantial range of temperature and concentration the lamellar phase is not a classical lamellar phase but contains water filled defects, enabling water diffusion to take place parallel to the lamella normal so that the average obstruction factor, $\bar{\beta}_f$ is greater than the theoretical value of 2/3 already observed in some lamellar phases. Addition of both surfactant and electrolyte (CsCl) cause $\bar{\beta}_f$ to decrease towards its theoretical value of 2/3, confirming that in both cases the defects are « healing » to give classical bilayers. These measurements also allow very reasonable values of β_\perp and the water coordination number for this system ($n = 4.8$) to be found. Since the neutron determined fraction of lamella area occupied by water filled defects is directly correlated with the obstruction factor measured parallel to the lamella normal, β_\parallel it is concluded that both techniques are sensitive to the same defect structure. This is further confirmed by our ability to calculate β_\parallel from the structural parameters without any adjustable parameters. In distinguishing between the models of the defect structure, the diffusion measurements are less sensitive and more equivocal. However the water diffusion results are consistent with the model of the lamellar phase suggested by the neutron scattering results, that is surfactant continuous lamellae broken by elongated water filled holes.

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