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# Lamellar Liquid Crystal and Other Phases in the System Sodium Dodecyl Sulfate, Hexylamine, Water, and Heptane

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Phase equilibria have been studied for the system composed of sodium dodecyl sulfate, hexylamine, heptane, and water. Greatest emphasis has been placed on the lamellar liquid crystal region and X-ray diffraction measurements. Equations are developed or modified to allow determination of the degree of penetration of water into the amphiphilic double layer as a function of water or amphiphile concentration. It is found that the interfacial area occupied by the polar or ionic head groups of amphiphiles increases with increasing water content. © 1987 Academic Press, Inc.

## INTRODUCTION

As mentioned in two previous reports (1, 2), the present system composed of sodium dodecyl sulfate (SDS), hexylamine (Ha), water, and heptane (Hp), exhibits some novel properties, such as very high water solubilization into the microemulsion at a very low surfactant content. Emphasis in the earlier work was put on the association structures of the reverse micellar or microemulsion regions. Important structural parameters, such as the molecular ratio between SDS and Ha in the interfacial film of microemulsion droplets and the size of these droplets, were estimated via conductivity measurements on these microemulsion systems. In the present work, special attention has been paid to the liquid crystal region. Experimental results obtained from low-angle X-ray diffraction and phase equilibrium studies are reported.

Although general features of lyotropic lamellar liquid crystal structures are well known (3–5), information about the details of the structure, such as conformation of the carbon chains of amphiphilic molecules, interaction among these molecules, solubilized hydrocar-

bon, and solvent, usually water, is not easy to obtain. Solubilized hydrocarbon may have a great deal of influence on the structure of liquid crystals. For example, in Friberg's pioneering work (6) about the effect of solubilized hydrocarbons on the structure of lamellar liquid crystals, he and his co-workers pointed out that addition of certain hydrocarbons to a particular liquid crystal may lead to a change in the angle between the normal to the bilayer interface plane and the molecular axis of the amphiphiles. In the present system, effects of solubilized hydrocarbon on the lamellar structure and the interaction between amphiphilic and water molecules have been studied. Particularly, water penetration into the amphiphilic bilayer is considered. A modified equation relating the interlayer spacing to water and amphiphile concentrations is derived. Thus it becomes possible to estimate the extent of water penetration at constant ratio of SDS to hexylamine plus heptane. If the measurements of the interlayer spacing are made at constant ratio of SDS to water, an approximate equation, which is also developed in this work, may be used to evaluate the limiting values of the thickness of the bilayer composed of pure SDS or of pure hexylamine.

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## MATERIALS AND METHODS

*Materials*

Hexylamine was purchased from Eastman Kodak (Cat. No. 117 7559, 99%) and used as received. Heptane was from Fisher (Cat. No. 03008) and used without further purification. Sodium dodecyl sulfate (SDS) was purchased from BDH and recrystallized twice with absolute ethanol. Water was triple distilled.

*Methods*

Unlike the determination of reverse micellar or microemulsion regions, where the titration method was useful (1), determination of liquid crystal areas was more difficult and tedious mainly due to the high viscosities encountered. A quick search for the possible liquid crystal region could be done by titration and centrifugation, followed by microscopic examination between crossed polarizers. Then series of samples were prepared along lines radiating from each corner of the ternary or pseudo-ternary phase diagram in the approximate boundary area of the liquid crystal region, followed by centrifugation, long time storage, and careful microscopic examination. Lamellar and hexagonal liquid crystals can readily be distinguished from each other by their different microscopic patterns (3).

The normal micelle or  $L_1$  region was determined in a way similar to that of the microemulsion or  $L_2$  area, but centrifugation was required because of foam formation in this region. In order to locate the extremely narrow, isolated, isotropic liquid phase (see Fig. 1), samples were prepared with very small SDS concentration increments, down to 0.05%. Long time storage was also necessary.

X-ray diffraction patterns were determined using a Kiessig low-angle camera from Richard Seifert (7). Ni-filtered  $\text{CuK}\alpha$  radiation was used and the reflection was measured by a Tennelec position-sensitive detection system (Model PSD-100). A small amount of the liquid crystal sample was sucked into a thin-wall glass capillary. The capillary with the two ends sealed was mounted on the sample holder for deter-

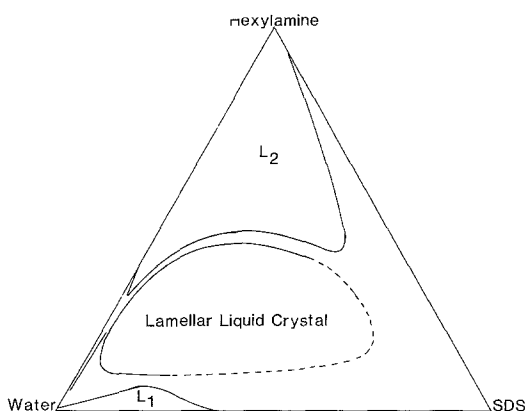


FIG. 1. Phase diagram for the system water-SDS-hexylamine showing the  $L_1$  and  $L_2$  phases, a lamellar liquid crystalline phase, and a very small isotropic liquid phase.

mination of the diffraction pattern. Bragg's law was used to calculate the interlayer spacing:

$$\lambda = 2d \sin \theta, \quad [1]$$

where  $\lambda = 1.542 \text{ \AA}$  and  $\theta$  is the diffraction angle. For the camera used in this experiment,  $\theta$  is calculated using the equation

$$\tan(2\theta) = \frac{Z_c D_c}{2(PL + x)}, \quad [2]$$

where  $D_c$  (cm) is the measured distance between the two symmetric diffraction maxima,  $PL$  (mm) is the path length from the sample to the detector,  $x$  (mm) is the correction factor for the path length, and  $z_c$  is the conversion factor from the detector to the recorder.  $Z_c$  can be calibrated by measuring the powder diffraction pattern of a sample with a known  $d$ -spacing.

Some comments about the preparation of liquid crystal samples for X-ray diffraction is in order. The liquid crystal samples were prepared by weighing the desired amounts of SDS, hexylamine (or the mixture of hexylamine and heptane), and water into a test tube with a screw cap. The sample was then mixed on a vibromixer, followed by centrifuging with a microcentrifuge so that any solid SDS powder or liquid droplets sticking on the wall of the test tube collected on the bottom. This procedure was repeated several times until the

sample appeared homogeneous. A final centrifugation step was done with a high-speed centrifuge so that all bubbles were driven out of the liquid crystal sample. Then the sample was thermostated for several hours in a water bath at 25°C to reach equilibrium. If the sample was too thick to be mixed well on the vibromixer, a specially constructed glass tube was used. The tube with one end previously sealed had a constriction in the middle. SDS powder was first weighed into the tube and driven through the constriction into the bottom using a thin stick. Two liquids were then weighed into the tube. The open end of the tube was sealed with parafilm and the tube was placed in a microcentrifuge with this end up so that all components collected in the bottom after centrifugation, leaving the upper portion of the tube clean. Then the tube was quickly sealed with a flame. In this way no component would be decomposed or lost during sealing. High-speed centrifugation of the sample back and forth through the constriction causes thorough mixing and the liquid crystal sample becomes homogeneous.

## RESULTS

### *Phase Equilibria*

Figure 1 gives the phase diagram for the ternary system containing SDS, hexylamine, and water. The magnitude of the lamellar liquid crystal region is quite large. No other liquid crystal region has been found in the system. It is interesting to note that, in terms of SDS concentration, there exists an extremely narrow, isolated, optically isotropic liquid phase spanning about 78 to 95% water, with an SDS content below 1.0%. This region is so narrow that it will appear only as a line in the lower left-hand portion of the phase diagram. A solubility test of the oil-soluble dye Sudan 4 in the three-phase area composed of the three isotropic liquid layers showed that the middle phase, represented by the narrow isolated liquid phase, is probably an O/W-type microemulsion (8). The dye was very sparingly sol-

uble in this layer. No further study of this phase has been attempted.

### *Low-Angle X-Ray Diffraction Results*

For most cases only the first diffraction line was observed although sometimes a much weaker second line was obtained. X-ray diffraction data are typically presented (9–15) for such systems as plots of  $d$ -spacing vs the fraction of water over the fraction of all other components. Results for the lamellar liquid crystalline region from Fig. 1, which contains no heptane, are shown in Fig. 2. In Fig. 3 results are shown for systems where 5% heptane has been added to the hexylamine, while Fig. 4 shows the results obtained with 10% heptane added to the hexylamine.

## DISCUSSION

### *Analysis of Diffraction Data*

It is well known (10–17) that the structure of lamellar liquid crystals of amphiphile–water systems consist of indefinitely expandable,

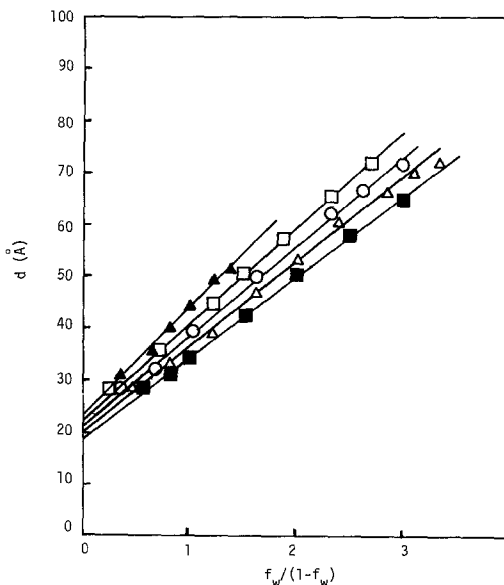


FIG. 2. Interlayer spacing vs fraction of water over the fraction of all other components with no heptane present (System A) for the ratios of SDS/Hex: (▲) 70/30, (□) 60/40, (○) 50/50, (△) 40/60, and (■) 30/70.

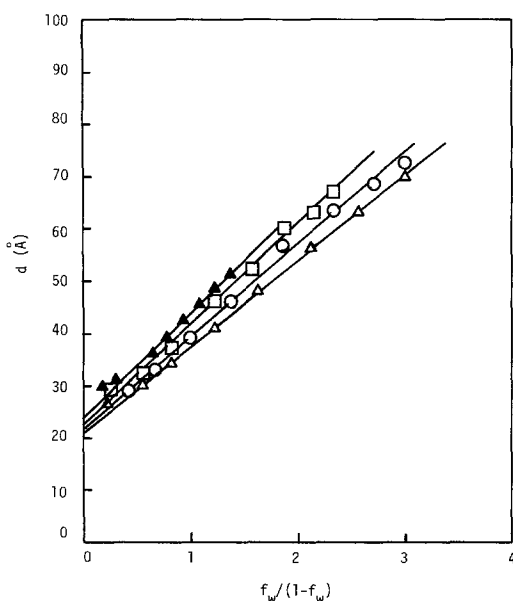


FIG. 3. Interlayer spacing vs fraction of water over the fraction of all other components with  $\text{Hp}/\text{Ha} = 5/95$  (System B) for the ratios of  $\text{SDS}/(\text{Ha} + \text{Hp})$ : ( $\blacktriangle$ ) 70/30, ( $\square$ ) 60/40, ( $\circ$ ) 50/50, and ( $\triangle$ ) 40/60.

parallel double layers of amphiphiles (plus solubilized hydrocarbon, if any) with layers of water intercalated between the amphiphilic bilayers at regularly repeating distances. As a first approximation, one may assume no mutual penetration between the amphiphilic bilayer and aqueous layer. All amphiphilic molecules take such a position that their hydrocarbon chains lie in the interior of the double layer while the polar or ionic groups are anchored at the interface between the bilayer and aqueous layer and interact with water molecules. If hydrocarbon is dissolved into the liquid crystal, it must go into the interior of the amphiphilic double layer. With the above picture of the lamellar liquid crystal structure, it is easy to derive an equation relating the interlayer spacing,  $d$ , to the concentrations of the constituents (9, 16):

$$d = d_0/\phi_0, \quad [3]$$

where  $d_0$  is the thickness of the amphiphilic bilayer, and  $\phi_0$  is the sum of the volume frac-

tions of the substances forming the amphiphilic bilayer. The quantity  $\phi_0$  is given by

$$\phi_0 = \frac{n_{\text{SDS}}V_{\text{SDS}} + n_{\text{Ha}}V_{\text{Ha}} + n_{\text{Hp}}V_{\text{Hp}}}{n_{\text{SDS}}V_{\text{SDS}} + n_{\text{Ha}}V_{\text{Ha}} + n_{\text{Hp}}V_{\text{Hp}} + n_wV_w} \quad [4a]$$

$$= \frac{n_oV_o}{n_oV_o + n_wV_w}, \quad [4b]$$

where  $n_i$  is the number of moles and  $V_i$  is the partial molar volume of component  $i$  and  $n_o$  is the total number of moles and  $V_o$  is the mean partial molar volume of the organic components. The quantity  $\phi_0$  may also be written as

$$\phi_0 = 1 / \left( 1 + \frac{\nu_w}{\nu_o} \frac{f_w}{1-f_w} \right) \quad [5]$$

where  $f_w$  is the weight fraction of water in the system,  $\nu_w$  is the partial specific volume of water, and  $\nu_o$  is the mean partial specific volume of the constituents of the amphiphilic bilayer of the organic components and is given by

$$\nu_o = V_o/M_o.$$

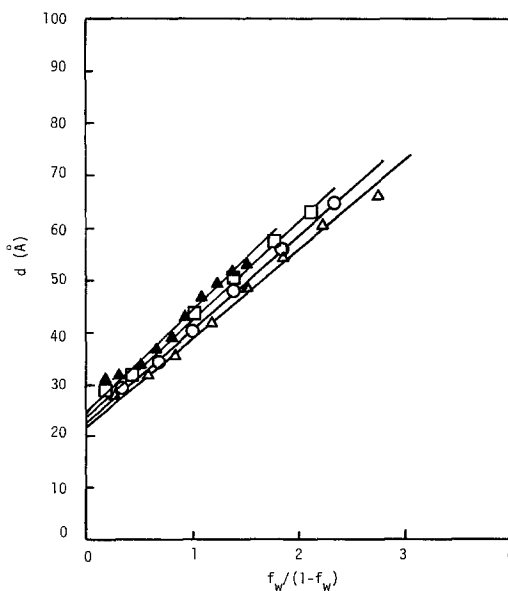


FIG. 4. Interlayer spacing vs fraction of water over fraction of all other components with  $\text{Hp}/\text{Ha} = 10/90$  (System C) for the ratios of  $\text{SDS}/(\text{Ha} + \text{Hp})$ : ( $\blacktriangle$ ) 70/30, ( $\square$ ) 60/40, ( $\circ$ ) 50/50, and ( $\triangle$ ) 40/60.

$M_0$  is the corresponding average molecular weight of the constituents of the amphiphilic bilayer given by

$$M_0 = \frac{n_{\text{SDS}}}{n_{\text{SDS}} + n_{\text{Ha}}} M_{\text{SDS}} + \frac{n_{\text{Ha}}}{n_{\text{SDS}} + n_{\text{Ha}}} M_{\text{Ha}}. \quad [6]$$

Substitution of Eq. [4b] into Eq. [3] gives

$$d = d_0 + d_0 \frac{\nu_w}{\nu_o} \frac{f_w}{1 - f_w}. \quad [7]$$

If the X-ray diffraction measurements are made on systems obtained by adding water to the system at a constant ratio of hexylamine to SDS, and if there is no penetration of the water into the amphiphilic bilayer, or vice versa, then  $d_0$ ,  $\nu_w$ , and  $\nu_o$  all remain constant and a plot of  $d$  versus  $f_w/(1 - f_w)$  should be a straight line the slope of which is  $d_0(\nu_w/\nu_o)$  and the intercept at zero water concentration is  $d_0$ . Figures 2, 3, and 4 give such plots.

However, penetration of water into the amphiphilic bilayer may not be neglected for the present system. One possible reason for this is the fact that water is much more soluble in hexylamine than in medium chain length alcohols (16). There may also exist an appreciable solubility of the SDS in the water layer. To show whether mutual penetration between the amphiphilic double layer and water layer exists, we need to examine Fig. 2 closely. Before doing this, it is necessary to show that the volume of the system is additive so that the data treatment can be made much simpler.

If the volume is additive, we can write

$$\nu = \sum f_i \nu_i^\circ = 1/\rho = \sum f_i / \rho_i^\circ, \quad [8]$$

where  $\nu_i^\circ$  is the specific volume of component  $i$ ,  $\nu$  is the specific volume of the system,  $f_i$  is the weight fraction of  $i$ , and  $\rho$  and  $\rho_i^\circ$  are the densities of the sample and pure  $i$ , respectively. Thus, based on the assumption that volumes are additive,  $\rho$  can be calculated and compared with the experimental values if the density of each component in the system is known. The calculated density should not deviate much from the experimental. This comparison is made on some microemulsion systems instead

of liquid crystals because the high viscosity of the liquid crystalline phase makes density measurements very difficult. Figure 5 shows the variation of the ratio between the experimental and calculated densities with the water weight fraction for some microemulsion systems. It is seen from Fig. 5 that the discrepancy first increases when  $f_w$  is small and then reaches some small and almost constant value. The effect of heptane is to decrease the discrepancy between  $\rho_{\text{ex}}$  and  $\rho_{\text{calc}}$ . As shown in Fig. 6 it seems that the effect of increasing the ratio SDS/Ha (w/w) is also to reduce this discrepancy. The small positive density deviations mean that there is a contractive volume effect upon formation of the microemulsion. The statement that volumes in the microemulsion region are additive is justified. We extend this conclusion to the liquid crystal region with confidence since Fig. 6 shows that increasing the ratio SDS/Ha (w/w) lowers the deviation, and the liquid crystal region appears at higher ratios of SDS/Ha than does the microemulsion region.

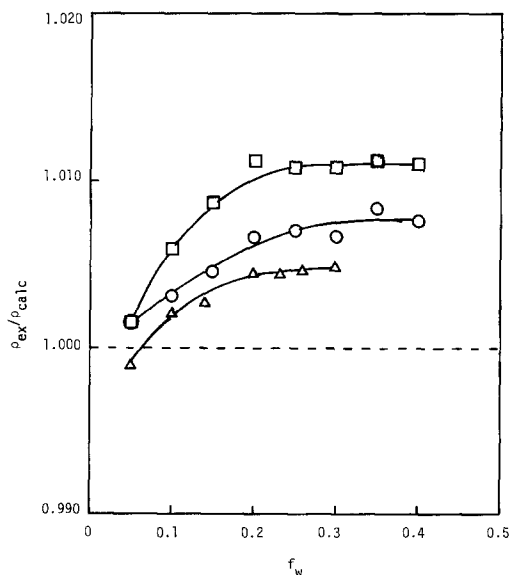


FIG. 5. Ratio of experimental to calculated density,  $\rho_{\text{ex}}/\rho_{\text{calc}}$ , vs weight fraction of water,  $f_w$ , in the microemulsion or  $L_2$  region of the phase diagram for SDS/(Ha + Hp) equal to 20/80 and Hp/Ha: ( $\square$ ) 0/100, ( $\circ$ ) 25/75, and ( $\triangle$ ) 50/50.

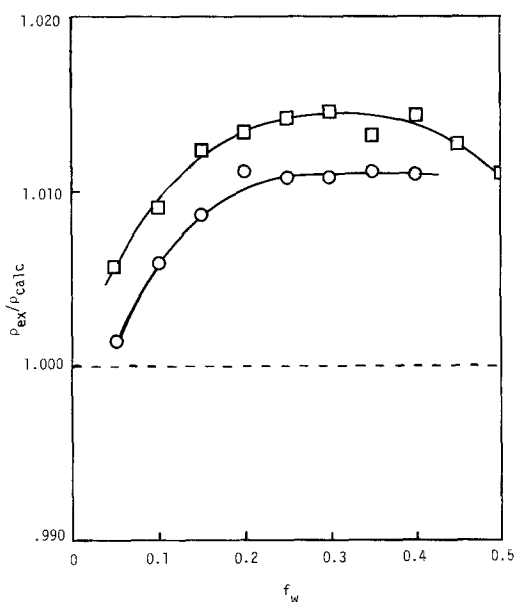


FIG. 6. Ratio of experimental to calculated density,  $\rho_{ex}/\rho_{calc}$ , vs weight fraction of water,  $f_w$ , in the microemulsion or  $L_2$  region of the phase diagram for ratios of SDS/Ha: (□) 10/90 and (○) 20/80 (no heptane present).

Thus in Eq. [7],  $\nu_w/\nu_o$  can be replaced by

$$\frac{1/\sum f'_i/\rho_i}{\rho_w}, \quad [9]$$

where  $f'_i$  is the weight fraction of component  $i$  in the mixture constituting the amphiphilic bilayers (SDS, Ha, and Hp).

If mutual penetration between the amphiphilic bilayer and the water layer in the liquid crystal were negligible, the ratio  $\nu_w/\nu_o$  obtained from the slope of a plot of  $d$  vs  $f_w/(1 - f_w)$  should be close to the value calculated based on the assumption of no penetration and should increase with the increasing ratio of SDS/(Ha + Hp). This should be so because SDS has the highest density, 1.16 g/ml, of any of the components of the system, and the specific volume of the bilayer,  $\nu_o$ , should become smaller when the SDS content increases. Table I compares the experimental with calculated values of  $\nu_w/\nu_o$ , and two important facts are seen. First, the calculated value is always greater than the experimental one. Second,

there is no obvious tendency for  $\nu_w/\nu_o$  to increase with increasing the ratio of SDS/(Ha + Hp), and in some cases it even decreases. Such results would be expected if water penetration into the amphiphilic bilayer occurs.

Considering water penetration into the bilayer and assuming a negligible solubility of the amphiphiles in the aqueous layer, Eq. [7] can be modified as follows. Because of the penetration of water, the actual volume fraction of the amphiphilic bilayer, designated  $\phi_b$ , must include a factor representing the penetration. Thus

$$\phi_b = \phi_0(1 + x), \quad [10]$$

where  $\phi_0$  is the volume fraction of the bilayer without water penetration and  $x$  is a factor giving the effect of this penetration. When there is no water penetration,  $x$  must be equal to zero, so  $\phi_b = \phi_0$ . As a first approximation, we further assume that water penetration into the bilayer is proportional to the water content in the liquid crystal, that is,

$$x = bf_w, \quad [11]$$

where  $b$  is a proportionality constant. Thus

$$\phi_b = \phi_0(1 + bf_w)$$

TABLE I

System A Hp/Ha = 0					
SDS/Ha	30/70	40/60	50/50	60/40	70/30
$(\nu_w/\nu_o)_{ex}$	0.803	0.750	0.749	0.772	0.795
$(\nu_w/\nu_o)_{calc}$	0.853	0.887	0.923	0.963	1.006
$b$	0.060	0.184	0.230	0.245	0.250
System B Hp/Ha = 5/95					
SDS/(Ha + Hp)					
$(\nu_w/\nu_o)_{ex}$		0.744	0.737	0.764	0.748
$(\nu_w/\nu_o)_{calc}$		0.881	0.915	0.958	1.003
$b$		0.187	0.240	0.280	0.316
System C Hp/Ha = 10/90					
SDS/(Ha + Hp)					
$(\nu_w/\nu_o)_{ex}$		0.719	0.772	0.733	0.707
$(\nu_w/\nu_o)_{calc}$		0.877	0.915	0.950	1.000
$b$		0.121	0.181	0.290	0.266

which upon substitution of Eq. [5] becomes

$$= \frac{1 + bf_w}{1 + (\nu_w/\nu_o)(f_w/(1 - f_w))}. \quad [12]$$

Substitute Eq. [12] into Eq. [3] to obtain

$$d = d_0 \left( \frac{1 + (\nu_w/\nu_o)(f_w/(1 - f_w))}{1 + bf_w} \right). \quad [13]$$

Therefore a straight line passing through the origin and with a slope equal to  $d_0$  should be observed if  $d$  is plotted against the quantity in the parentheses and the parameter  $b$  is chosen properly. Figures 7, 8, and 9 show such plots for the three series of liquid crystals corresponding to Figs. 2, 3, and 4. It is seen that, for the present systems, the straight line has an intercept on the  $d$  axis greater than zero if  $b$  is chosen to be zero. This means that water penetration into the bilayer has occurred; that is, a positive value of  $b$  must be chosen to give a zero intercept of the straight line. The  $b$  values for the three series of systems are given in the last line for each system in Table I. Figure

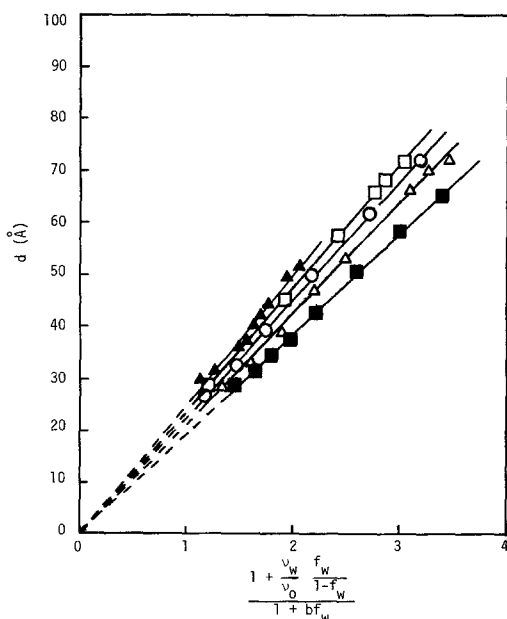


FIG. 7. Interlayer spacing,  $d$ , plotted according to Eq. [13] for System A (no heptane present) with ratios of SDS/Ha: (▲) 70/30, (□) 60/40, (○) 50/50, (△) 40/60, and (■) 30/70.

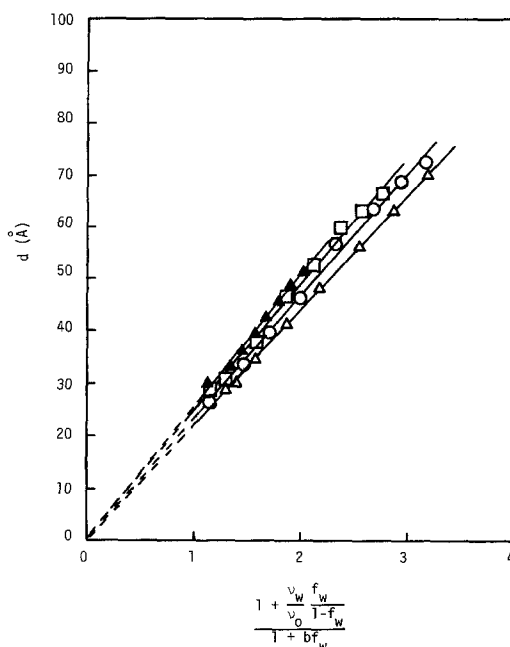


FIG. 8. Interlayer spacing,  $d$ , plotted according to Eq. [13] for System B (Hp/Ha = 5/95) and the ratios of SDS/(Ha + Hp): (▲) 70/30, (□) 60/40, (○) 50/50, and (△) 40/60.

10 shows the thickness of the bilayer at zero water concentration,  $d_0$ , versus the molar ratio of hexylamine to SDS. These  $b$  and  $d_0$  values are obtained from Figs. 2, 3, and 4 using the linear least-squares method.

From Table I it can be seen that, when the molar ratio of SDS to hexylamine is low, the value of  $b$  is small. This value increases rapidly with this ratio at first and then more slowly. This is particularly obvious for the tertiary System A, which contains no hydrocarbon. When the liquid crystal contains a small amount of heptane (System B), the water penetration into the bilayer seems to be enhanced because a larger value of  $b$  must be used in order to make the straight lines in Figs. 7, 8, and 9 pass through the origin. This means the presence of a small amount of heptane enhances the interaction between water and amphiphilic molecules for these systems. A related result has been observed in the microemulsion region, where the addition of a small amount of heptane to the reverse micellar re-



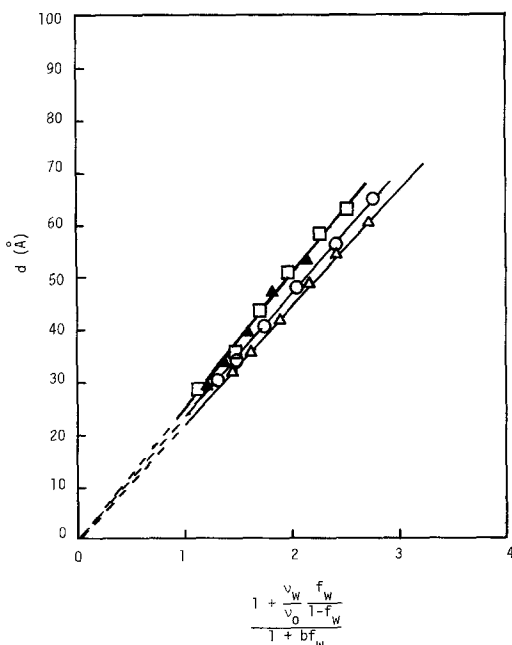


FIG. 9. Interlayer spacing,  $d$ , plotted according to Eq. [13] for System C ( $H_p/H_a = 10/90$ ) and the ratios of SDS/ ( $H_a + H_p$ ): (▲) 70/30, (□) 60/40, (○) 50/50, and (△) 40/60.

gion at a SDS concentration increases the water solubilization into the microemulsion drastically (2). It may be expected, however, that because of the hydrophobic nature of hydrocarbon, a further increase in heptane content will eventually lead to weakening the interaction between water and amphiphile molecules so that the water penetration into the amphiphilic double layer decreases (7). This begins to be observed for System C in which the weight ratio  $H_p/H_a$  is 10/90.

It is obvious from Table I that, for all three series of systems, an increase in SDS concentration causes an increase in water penetration into the bilayer. Since SDS is an ionic surfactant, its interaction with water would be expected to be stronger than that of the polar, but neutral, hexylamine molecule. We will also see this effect in a later section dealing with the average interfacial area per polar group of amphiphilic molecules.

Figure 10 shows the plot of the interlayer spacing at zero water concentration,  $d_0$ , versus

the molar ratio of hexylamine to SDS. The effect of this ratio is pronounced as  $d_0$  decreases almost linearly with an increase in the ratio. Since hexylamine molecules are shorter than SDS molecules, there is more space available for the tails of SDS molecules to move around and assume less extended configurations as the molar ratio of hexylamine to SDS increases. Therefore the thickness of the bilayer on average will decrease.

Figure 10 also shows the effect of solubilized hydrocarbon on the interlayer spacing at zero water concentration. A solubilized hydrocarbon molecule can either locate in the center of the bilayer and move around since it is in a liquid state and highly disordered (7, 15, 19–23) or penetrate into the array of hydrocarbon chains of the amphiphiles. For the former case, an increase in interlayer spacing would be expected. For the latter, little or no increase in interlayer spacing would occur. From Fig. 10 we see that a small amount of solubilized heptane in the liquid crystal causes an increase in interlayer spacing at zero water concentration. That is, there certainly exist nonpenetrating heptane molecules.

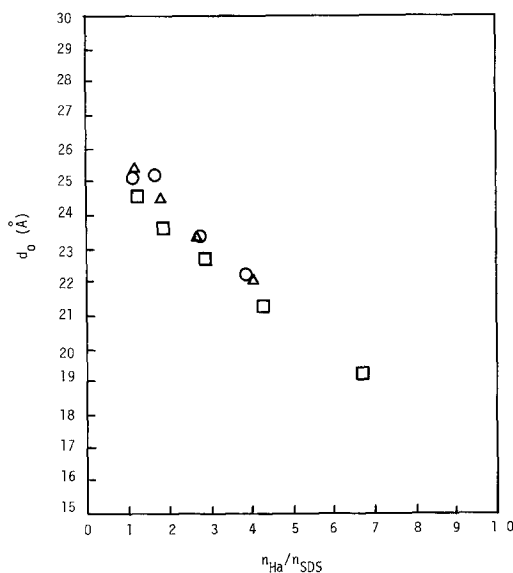


FIG. 10. Bilayer thickness,  $d_0$ , as a function of the molar ratio of hexylamine to SDS,  $n_{Ha}/n_{SDS}$ , for: (□) System A, (△) System B, and (○) System C.

Measuring the interlayer spacing at constant ratios between SDS and hexylamine plus heptane makes data treatment easy because the thickness of the bilayer is constant during the addition of water to the system. We also did the measurement keeping the weight ratio of SDS to water constant and varying the concentration of hexylamine. Although such measurements make data treatment more complicated because the thickness of the bilayer is no longer constant, we can look further into the effect of hexylamine content on the bilayer structure. According to the above analysis, one may expect a decrease in interlayer spacing upon the addition of more hexylamine to the liquid crystal. This is seen from Fig. 11, in which the effect of water concentration is also obvious. However, the more important aspect in making measurements under this condition is to extract some new information from the experimental results. By proposing a linear relation of the thickness,  $d_0$ , of the amphiphilic bilayer to the volume fraction of hexylamine in the bilayer, we will show that it is possible to estimate the thickness of the bilayer of pure SDS or of pure hexylamine.

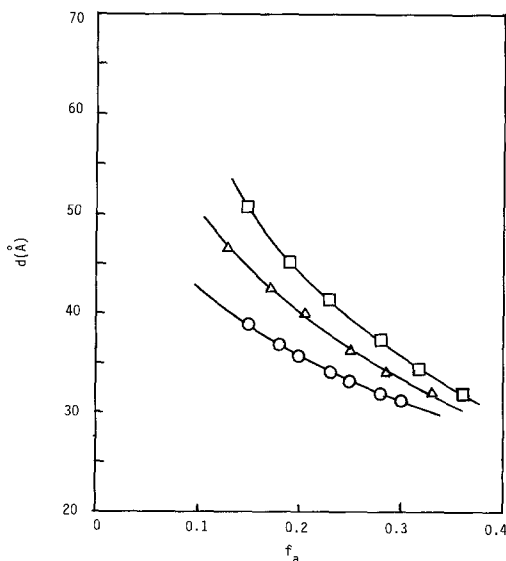


FIG. 11. Interlayer spacing,  $d$ , vs fraction of hexylamine for the ratios of SDS/H<sub>2</sub>O: (□) 30/70, (Δ) 40/60, and (○) 50/50.

For the ideal case, we may assume that neither water penetration into the bilayer nor dissolution of the amphiphiles into the aqueous layer is appreciable. Under the conditions of constant ratio between SDS and water, variation of hexylamine concentration and therefore the molar ratio  $n_{\text{SDS}}/n_{\text{Ha}}$  in the system will cause the thickness of the amphiphilic bilayer,  $d_0$ , to change. In order to relate this variation of  $d_0$  to the concentration of SDS and hexylamine, let us first consider the limiting cases. If there were no hexylamine present, the thickness of the bilayer would be equal to twice the length of the SDS molecules, which may take any particular conformation. We designate this thickness as  $d_{\text{SDS}}^0$ . On the other hand, if the volume fraction of SDS in the double layer were equal to zero, the bilayer thickness,  $d_{\text{Ha}}^0$ , would be twice the length of hexylamine molecules. Their conformation would be associated with the condition at which the extrapolation is made. The following equation satisfies these limiting conditions:

$$d_0 = d_{\text{SDS}}^0 \phi'_{\text{SDS}} + d_{\text{Ha}}^0 \phi'_{\text{Ha}}, \quad [14]$$

where  $\phi'_{\text{SDS}}$  and  $\phi'_{\text{Ha}}$  are the volume fraction of SDS and hexylamine in the bilayer considering only the bilayer. Therefore

$$\phi'_{\text{SDS}} + \phi'_{\text{Ha}} = 1 \quad [15]$$

and

$$d_0 = d_{\text{SDS}}^0 - (d_{\text{SDS}}^0 - d_{\text{Ha}}^0) \phi'_{\text{Ha}}. \quad [16]$$

Substitution of this equation into Eq. [3] where  $d = d_0/\phi_0$  gives

$$d\phi_0 = d_{\text{SDS}}^0 - (d_{\text{SDS}}^0 - d_{\text{Ha}}^0) \phi'_{\text{Ha}}. \quad [17]$$

For the ideal case where no mutual penetration occurs between the bilayer and aqueous layer,  $\phi_0$  is given by Eq. [4]. With the assumption that the volume of the liquid crystal system is additive,  $\phi_0$  and  $\phi'_{\text{Ha}}$  can be calculated readily. Equation [17] should give a straight line if  $d\phi_0$  is plotted versus  $\phi'_{\text{Ha}}$ . Thus the value of  $d_{\text{SDS}}^0$  may be obtained by determining the intercept after extrapolating to zero hexylamine concentration. The slope of such a plot gives  $-(d_{\text{SDS}}^0 - d_{\text{Ha}}^0)$ . Therefore,  $d_{\text{Ha}}^0$  can be obtained either by combination of the intercept with

the slope or by extrapolation to  $\phi'_{\text{Ha}} = 1$ . These results are presented in Fig. 12, where a linear relation does exist if  $\phi'_{\text{Ha}}$  is not taken close to the boundary of the liquid crystal region. From Eq. [17] it is expected that the straight line be independent of the ratio between SDS and water. However, some deviation from this is seen in Fig. 12. The line at the weight ratio SDS/H<sub>2</sub>O = 40/60 is very close to that at SDS/H<sub>2</sub>O = 50/50, but the line with SDS/H<sub>2</sub>O = 30/70 is obviously lower than the other two. This deviation might result from the nonideality of the liquid crystal system due to a different extent of water penetration at different ratios between SDS and water.

Information about the mean interfacial area per polar group of amphiphilic molecules can be derived from the measurement of the interlayer spacing of the liquid crystal if some appropriate approximations are made. Here again we assume that no penetration occurs between the aqueous layer and the amphiphilic bilayer and all hydrocarbon is incorporated within the interior of the bilayer. With these assumptions it is easy to derive an equation to calculate the average area per polar group for the lamellar liquid crystal (16, 17).

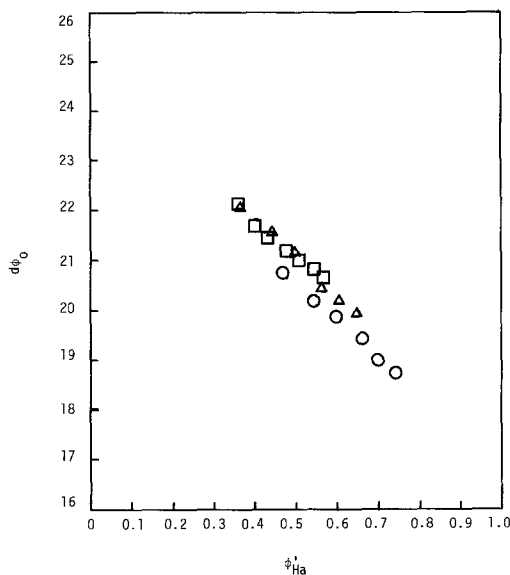


FIG. 12. The quantity  $d\phi_0$  vs  $\phi'_{\text{Ha}}$ , according to Eq. [17] for System A (no heptane present) at the ratios of SDS/H<sub>2</sub>O: (□) 50/50, (△) 40/60, and (○) 30/70.

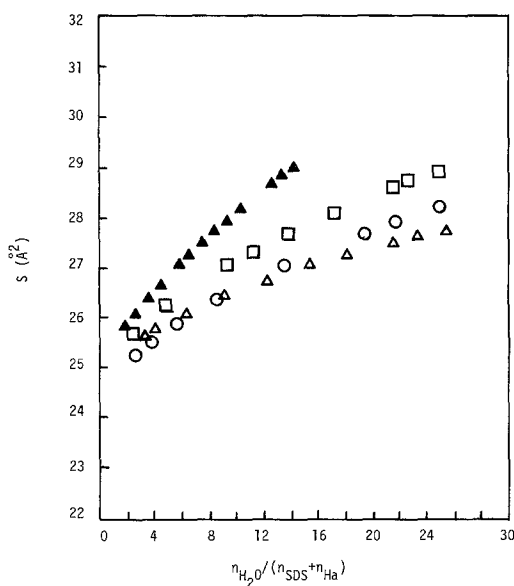


FIG. 13. Calculated mean surface area per amphiphile molecule vs  $n_{\text{H}_2\text{O}}/(n_{\text{SDS}} + n_{\text{Ha}})$  for System A (no heptane present) for the ratios of SDS/Ha: (▲) 70/30, (□) 60/40, (○) 50/50, and (△) 40/60.

$$S = 2M_0(\nu_o + R_H\nu_H + R_w\nu_w)/N_A d, \quad [18]$$

where  $M_0$  is given by Eq. [6], and

$$R_H = f_{\text{Hp}}/(f_{\text{Ha}} + f_{\text{SDS}})$$

$$R_w = f_w/(f_{\text{Ha}} + f_{\text{SDS}})$$

and  $\nu_i$  is the specific volume of component  $i$ ,  $N_A$  is Avogadro's number, and  $d$  is the measured interlayer spacing. The average interfacial area per polar group of amphiphilic molecules versus the molar ratio between water and the sum of SDS plus hexylamine for the three series of systems are presented in Figs. 13, 14, and 15. In these figures the curves were calculated from computer-fitted graphs of  $\log d$  vs  $\log \phi_0$ . From these figures, some conclusions can be drawn. First, the mean interfacial area per polar group of the amphiphiles increases with the molar ratio of water to the amphiphiles. This feature is in agreement with the one generally expected (3, 15). Second, the higher the ratio of SDS to hexylamine, the larger the average interfacial area per polar group. This is reasonable because the inter-

action between SDS and water is stronger than that between hexylamine and water. Increasing the hydrocarbon concentration eventually leads to decreasing the interfacial area. This result is best seen by comparing Fig. 14 with Fig. 15 since the differences between Figs. 13 and 14 are probably indistinguishable within the limits of experimental error. This effect of solubilized hydrocarbon on the interfacial area per polar group may be attributed to the hydrophobic nature of hydrocarbon which weakens the interaction of the polar group of amphiphilic molecules with water (6) so that the interfacial area decreases as hydrocarbon content increases.

### SUMMARY

Phase equilibria have been investigated for the system composed of SDS, hexylamine, water, and heptane. Emphasis has been on the study of the lamellar liquid crystal region by means of low-angle X-ray diffraction. It is possible to evaluate water penetration into the amphiphilic double layer of the lamellar liquid

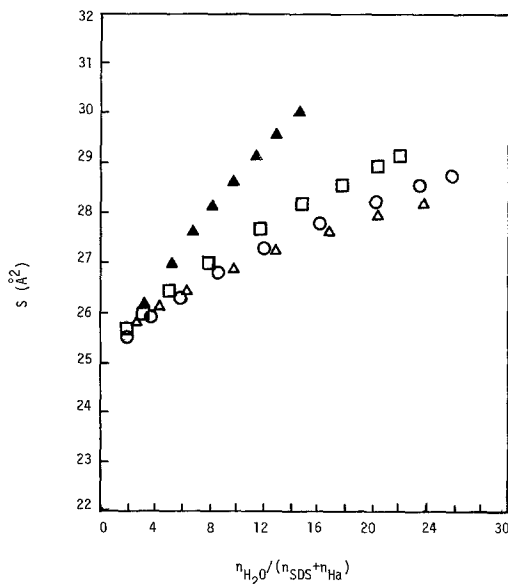


FIG. 14. Calculated mean surface area per amphiphile molecule vs  $n_{H_2O}/(n_{SDS} + n_{Ha})$  for System B (Hp/Ha = 5/95) for the ratios of SDS/(Ha + Hp): (▲) 70/30, (□) 60/40, (○) 50/50, and (△) 40/60.

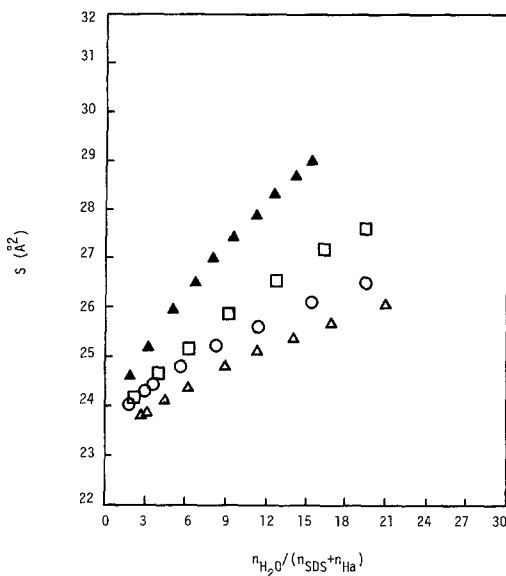


FIG. 15. Calculated mean surface area per amphiphile molecule vs  $n_{H_2O}/(n_{SDS} + n_{Ha})$  for System C (Hp/Ha = 10/90) for the ratios of SDS/(Ha + Hp): (▲) 70/30, (□) 60/40, (○) 50/50, and (△) 40/60.

crystal using a modified equation relating the measured interlayer spacing to the water concentration or amphiphile content. Measurements of X-ray diffraction at a constant weight ratio between SDS and water are made more informative by means of the approximation that the thickness of the amphiphilic bilayer is linearly proportional to the volume fraction of SDS in the bilayer. The average interfacial area per polar group of amphiphilic molecules is also calculated and the results show that this area becomes larger as water concentration increases.

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