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Effects of Solubilized Hydrocarbons on the Structure and the Dislocation Pattern in a Lamellar Liquid Crystal

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The structure and dislocation pattern in a lamellar liquid crystal from water and polyoxyethylene dodecyl ether were studied for the effects of solubilization of large amounts of hydrocarbon using low angle X-ray diffraction and optical microscopy.

The X-ray data showed extremely small changes of interlayer spacings with added aromatic hydrocarbons indicating them to be located within the amphiphilic layer of surfactant and water. Addition of the aliphatic hydrocarbon gave an increase of the lamellar distance equal to or even in excess of the one for non-penetrative addition indicating a change in the direction of the amphiphilic substances.

The lamellar liquid crystal containing only water and surfactant showed a pattern of enhanced presence of focal conic dislocations with increased surfactant concentration for tetraoxyethylene dodecyl ether. For pentaoxyethylene dodecyl ether with a hydrophilic character this trend was observed after enhancing the lipophilic part by addition of hydrocarbon.

INTRODUCTION

Surfactant phase equilibria have a wide scientific and technical importance ranging from the biological association structures to the mechanisms involved in tertiary oil recovery. Studies of them have been numerous in the last two decades.

The equilibria between ionic surfactants, water and more hydrophobic amphiphiles have been studied by Ekwall,[1-3] whose results formed a basis

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for later investigations into structural details of the intermolecular interactions[4–11] and for a systematic approach to the structure of the s.c. microemulsions.[12–18] The systems containing nonionic surfactants have also been investigated by several authors; the HLB-temperature concept by Shinoda[19–23] has later been used to systematize[24] the complex behavior of these systems.

The combination of nonionic surfactants and water give liquid crystals with a special feature; the solubilization of hydrocarbon into their lamellar phases reaches high values at certain temperature ranges. Stable structures with as much as 60% (W/W) of an aliphatic hydrocarbon have been observed.[24] This means a hydrocarbon/emulsifier molecular ratio of 4; a value that is sufficiently high to merit consideration of the stability of such a lamellar structure taking into account the low degree of order for solubilized hydrocarbons.[25]

The present communication contains investigations of such structures using low angle X-ray diffraction to identify the structure of the liquid crystal and to determine the site of the hydrocarbon in the liquid crystal structure. Optical microscopy was used to obtain information about the change of dislocation pattern with hydrocarbon solubilization.

The interest in the structure and energetics of the dislocation patterns in liquid crystals has been revived in later years; numerous contributions form a continuation of the pioneering contributions by Fridel.[26]

The lamellar liquid crystal has attracted special interest since its structure may be considered as a stacking of bilayers each similar to the one forming the central part of a biomembrane. Its dislocations, especially the lecithin/water liquid crystalline phase, have been described.[27–33] The patterns include the well known confocal domains in which the layers coincide with Dupin cyclides or tori and also other linear singularities: edge and seam dislocations, disinclination lines with a rotation of the molecule by 180° and walls where the lamellae change their direction. The energetics of the different dislocation patterns have been analyzed[33] and the forms and structures behind a possible elasticity in the lamellar layers have been evaluated.[33]

The investigations have been limited to water/lecithin systems and focused on the influence of the water fraction on the pattern. This influence is of vital interest for the question of stability of the lamellar phase; much information of the structure of the aqueous part of the phase has also been obtained from different kinds of magnetic resonance investigations.[34–38] These in combination with the fact that the ordering of water close to polar surfaces gives a pronounced repulsive force between layers in liquid crystals[39] and between solids[40–41] make the question of the influence of the aqueous part highly interesting.

So far no investigations on the corresponding influence of solubilized hydrocarbons have been published; the problems of the ordering, penetration and location of the hydrocarbon chains and the pronounced difference between aromatic and aliphatic hydrocarbons justified a first investigation into these phenomena.

EXPERIMENTAL

Materials

Benzene: Fisher, ACS certified thiophene-free.
Hexadecane: Aldrich, 99+ % spectrophotometric grade.
Para-xylene: Aldrich, 99%
Pentaethyleneglycol-dodecylether, (PEGDE), and
Tetraethyleneglycol-dodecylether, (TEGDE), Nikkol, 99+ %
pure (gas chromatography).

Materials of the above mentioned qualities were used without further purification. Doubly distilled water was used for all preparations.

Preparation of samples

The compositions of the liquid crystalline samples were selected to correspond to the intersection points of lines from the water and hydrocarbon verticies (Figures 1–3.) These lines were drawn from the verticies to decimally spaced points on the sides of the triangle. Samples of half a gram total weight were prepared by weighing on a top loading balance. The accuracy of the weighing was ±0.002 g. The surfactant and the hydrocarbon were first weighed and mixed in glass bottles in the ratios of 9 : 1, 8 : 2, 7 : 3, etc. These two components form a homogenous liquid phase in all weight ratios. Predetermined amounts of the liquid mixture and water were then weighed into 3 ml screw-cap vials. The vials containing these samples were then centrifuged (to collect the entire sample at the bottom) and mixed thoroughly on a vibromixer. The centrifugation and the vibromixing steps were repeated twice to ensure good mixing and a final centrifugation got rid of trapped air bubbles. Small amounts of the liquid crystalline materials were then sucked into thin-walled glass capillaries for the X-ray determination of interlayer spacing. The vials containing the samples were then kept at 20°C until they were used for microscopic examination.

Photomicrography

An Olympus-BH polarizing microscope, attached to an automatic exposure camera was used for photomicrography. A Bailey Instruments thermoelectric

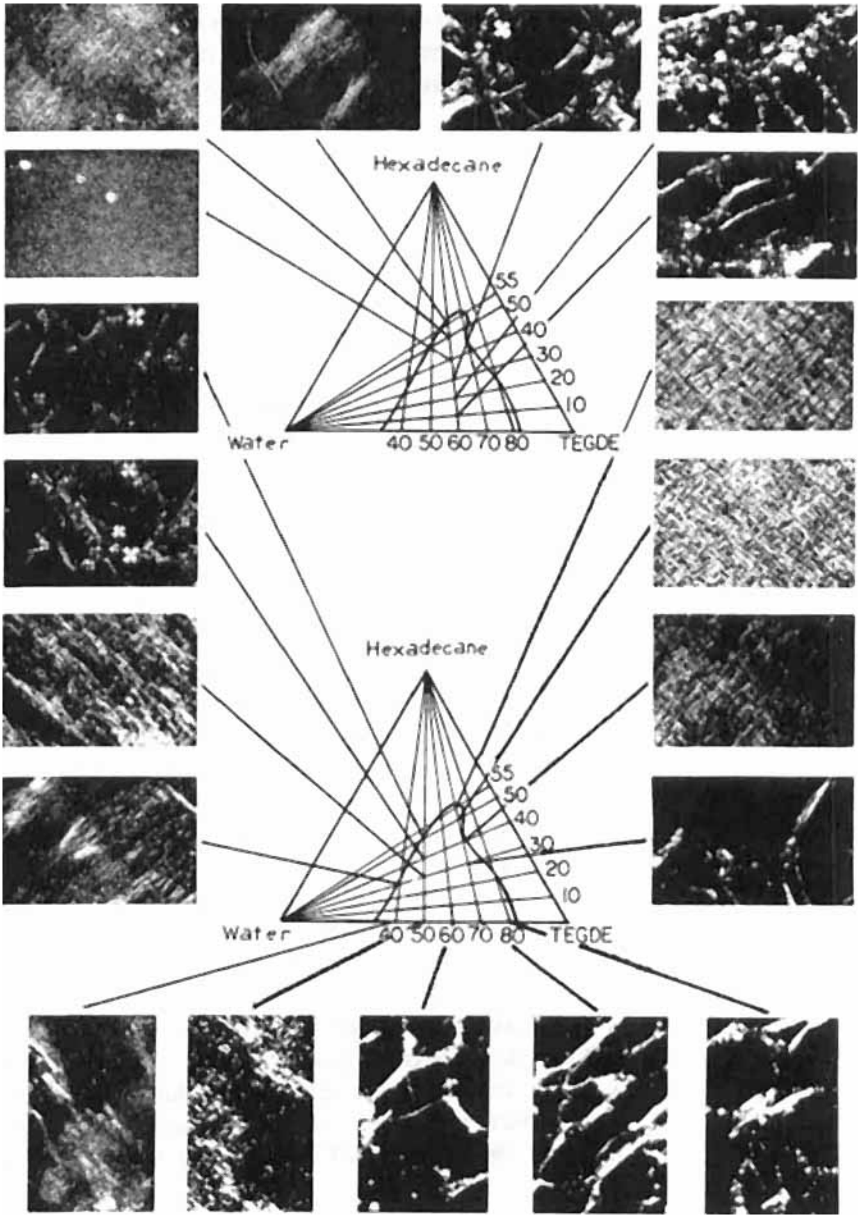

FIGURE 1 Microscopy photographs in polarized light of the lamellar liquid crystal in the system water, tetraoxyethylene dodecyl ether, hexadecane.

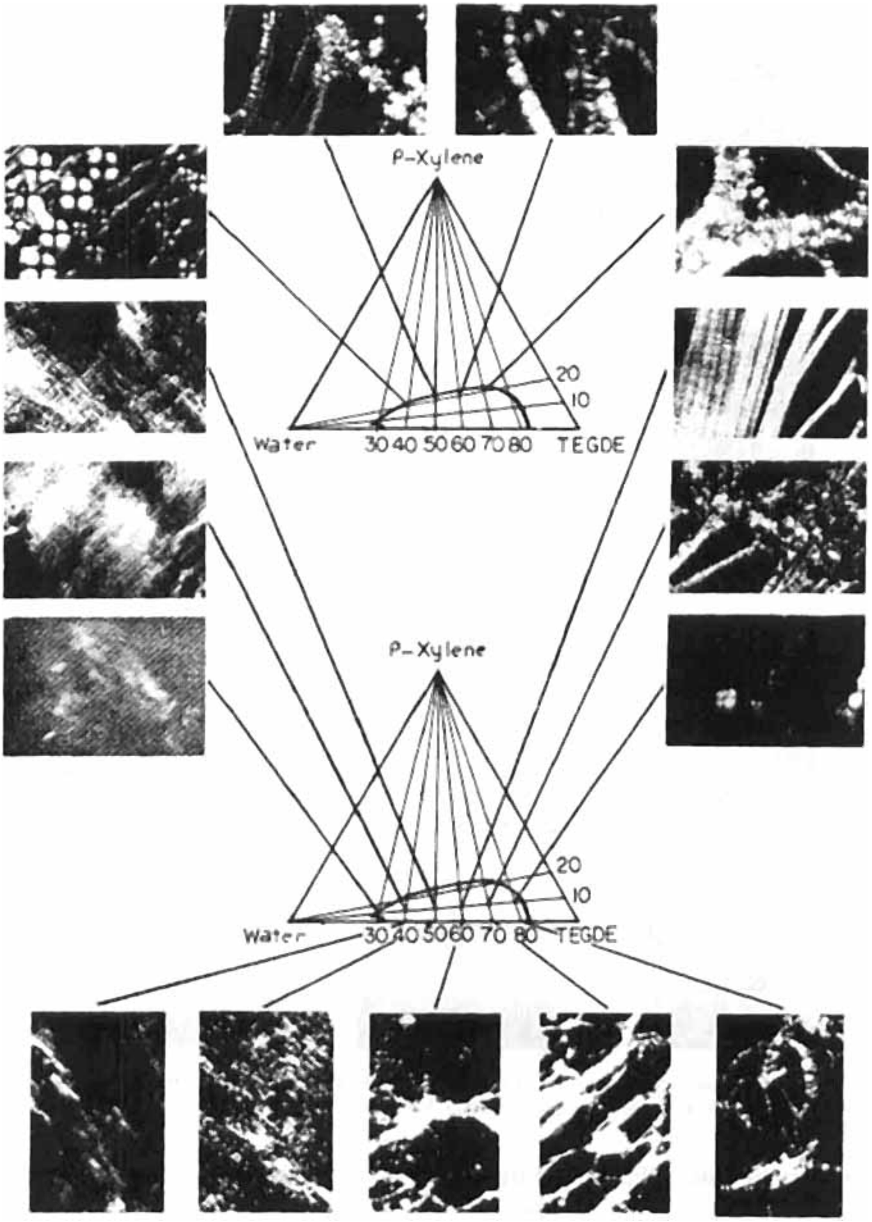

FIGURE 2 Microscopy photographs in polarized light of the lamellar liquid crystal in the system water, tetraoxyethylene dodecyl ether, *p*-xylene.

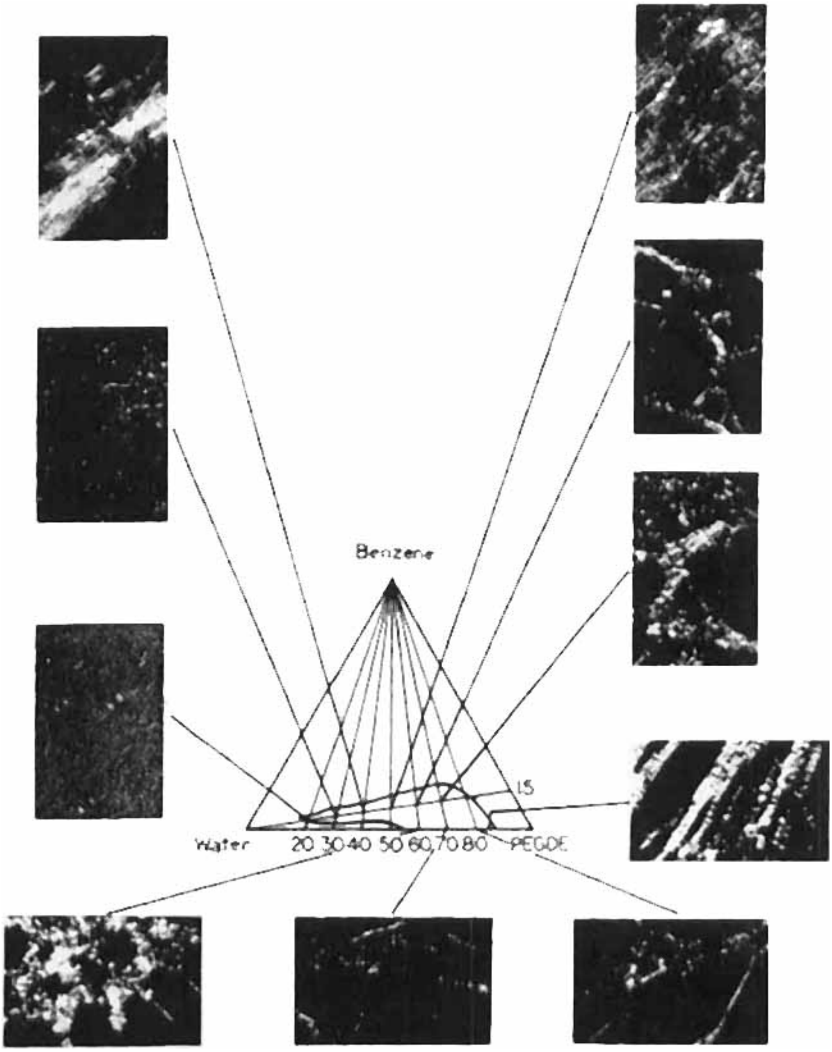

FIGURE 3 Microscopy photographs in polarized light of the lamellar liquid crystal in the system water, pentaoxyethylene dodecyl ether, benzene.

stage with automatic temperature control, calibrated from −40°C to 60°C was used to keep the sample at 20°C during picture taking. Pre-cleaned microscope slides and covers were selected, and they were buffed with lint-free paper tissue immediately before use. The following is a typical description of the procedure for the microscopic observation and photographing of a liquid crystalline sample. A small amount of the sample was transferred with a dropper from the vial onto the glass slide and was immediately covered with the slide cover. The sample was then sheared between the slide and the cover to a thickness of about 5 to 10 microns and was left for a few minutes on the constant temperature stage for relaxation and thermal equilibration. The appearance of the sample was then observed between crossed polarizers oriented at ±45° (with respect to the vertical direction of the prints). A representative region was then selected and photographed at a magnification of 100. The final prints show the samples at an overall magnification of 400.

Determination of interlayer spacing

Interlayer spacing for these lamellar samples was determined by X-ray diffraction (low angle). The bubble-free samples were introduced into special thin walled capillary glass tubes of 0.5 mm or 0.7 mm diameter. The ends of the capillary tubes were then sealed in a flame. In a typical determination the capillary was mounted on the sample holder of a Rich. Seifert low angle (Kiessig) camera. The finest collimators for the X-ray beam were selected (0.3 mm, 0.5 mm, 0.3 mm, 0.5 mm) and the sample-to-film distance chosen was 500 mm or 600 mm. Ni-filtered Cu-radiation was used ($\lambda = 1.542$ Å). After exposure, development and fixing the radius of the circular pattern on the film, for first-order diffraction, was measured and divided by the sample-to-film distance. The quotient of these two quantities is tan (2θ). The interlayer spacing was then obtained by applying Bragg's Law,

$$d = \frac{n\lambda}{2 \sin \theta} \qquad (n = 1, \text{ for first order diffraction.})$$

Phase equilibria

The phase regions were preliminarily determined by titration to obtain the regions of isotropic liquids. The liquid crystalline regions were determined in the same manner by microscopic observation of weighed in samples. The final determinations were made on two- and three-phase samples after long time storage.

RESULTS

This section will report data from the phase analysis, data from the X-ray analysis and from optical microscopy.

Phase regions

The solubilization of hexadecane in the liquid crystalline phase of water and tetraoxyethylene dodecyl ether approximately covered an area of a triangle with the base between 17 and 70% water and with the top at 50% hexadecane and 15% water (Figure 1). Exchanging the aliphatic hydrocarbon with *p*-xylene gave a corresponding area that only reached to 20% hydrocarbon (Figure 2). The maximum solubilization of benzene was in the water/pentaoxyethylene dodecyl ether liquid crystal (Figure 3) similar to the one for tetraoxyethylene and water but the addition of benzene enhanced maximum water content of the liquid crystal. The maximum water solubility with no hydrocarbon was 46%; the addition of benzene to a benzene/pentaoxyethylene dodecyl ether weight ratio of 0.18 almost doubled the maximum solubility of water reaching 80%.

X-ray data

All samples belonged to a liquid crystal with lamellar structure and the interlayer spacing was determined using the Bragg equation. The results are shown in Figure 4 plotted against the water ratio. These plots were linear and permitted extraction to water content 0. The extrapolation was made with a least square's fit to the experimental points.

The pronounced increase of interlayer spacing with addition of the aliphatic hydrocarbon is obvious. An analysis of the phenomenon will be made in the Discussion section; but the increase to more than double the interlayer distance with hydrocarbon addition is a directly observed and conspicious feature of the diagram.

Addition of *p*-xylene, on the other hand, gave only a modest increase of the interlayer spacings; the comparison between spacings of the samples with the hydrocarbon/emulsifier ratio of 1/4 (Figure 5) is illustrative of this point. For pentaoxyethylene dodecyl ether (Figure 6) the values at low water content actually demonstrated a reduction of the distance for extrapolated values. The basis for this behavior is found in the stronger *increase* of distance with added water when the hydrocarbon is present.

Dislocation patterns

The dislocation patterns of the liquid crystalline phase of water and tetraoxyethylene with no hydrocarbon (Figures 1 and 2, bottom rows) showed Malthesian crosses and broad lines at low water content (20 and 30%). With increased water content (40%) the Malthesian crosses disappeared and the pattern consisted of the broad lines with transversal striations and a

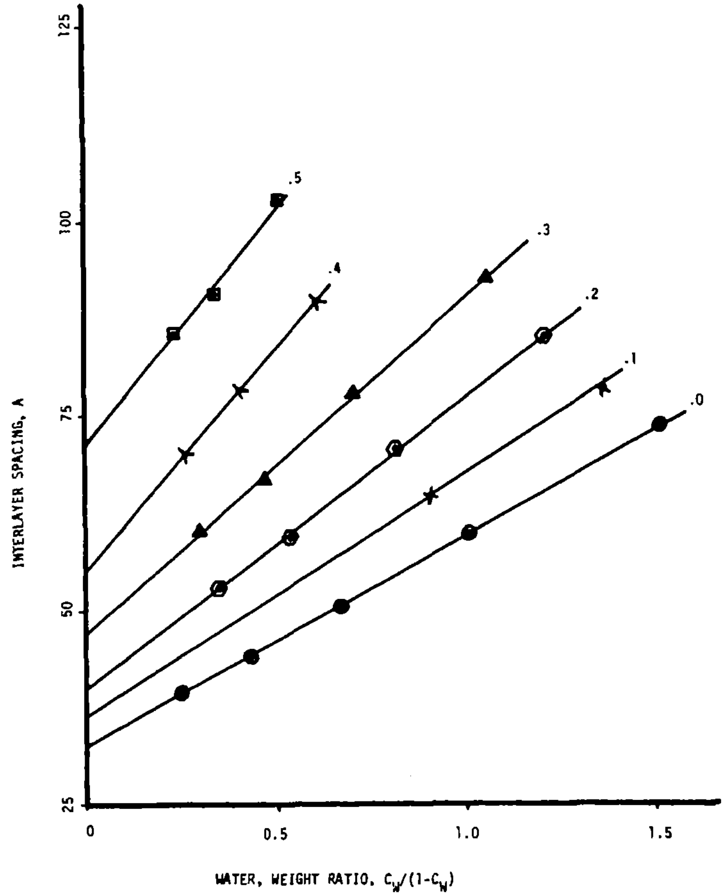

FIGURE 4 Interlayer spacing as function of water weight ratio for the system water, tetraoxyethylene dodecyl ether, hexadecane. Hydrocarbon Fraction 0/(0 + S); ⊙ = 0; × = 0.1; ⊖ = 0.2; ▲ = 0.3; ⅄ = 0.4; ▣ = 0.5.

network of extremely thin lines. Larger water contents (50–70%) left less and less of the broad lines; at 70% water only the thin lines are present.

Addition of hexadecane showed similar changes (Figure 1, photographs from right to left, top row) at the hexadecane/surfactant weight ratio of 0.67 equal to a molecular ratio of 1.07 caused the broad lines to disappear leaving the fine line pattern characteristic of the high water content samples.

The variation of pattern with water content at different hexadecane/surfactant ratios displayed a regular trend. For the series with a hydrocarbon/surfactant ratio below 1 (the four series with lowest hydrocarbon content, Figure 1) increased water content caused changes similar to the ones in the

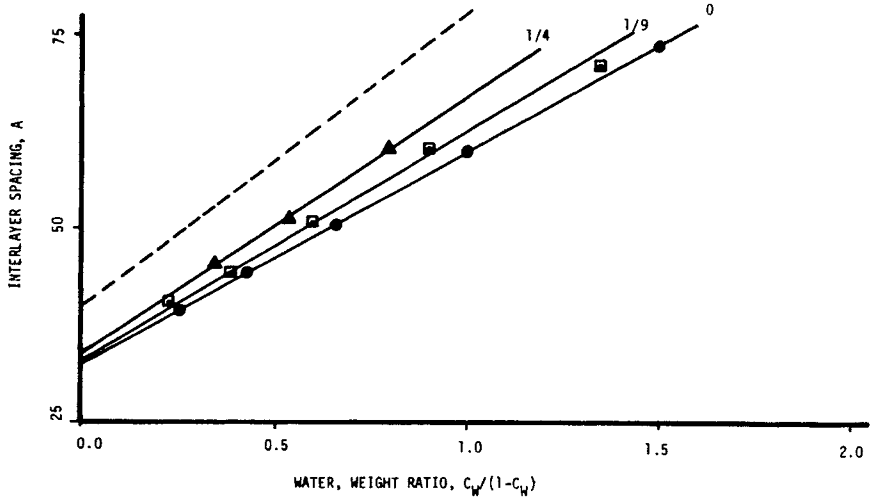

FIGURE 5 Interlayer spacing as function of water weight ratio for the system water, tetraoxyethylene dodecyl ether, *p*-xylene. (Broken line shows for comparison the values for hydrocarbon fraction 0.2 in Figure 4). ⊙ = 0; ▣ = $\frac{1}{9}$; ▲ = $\frac{1}{4}$.

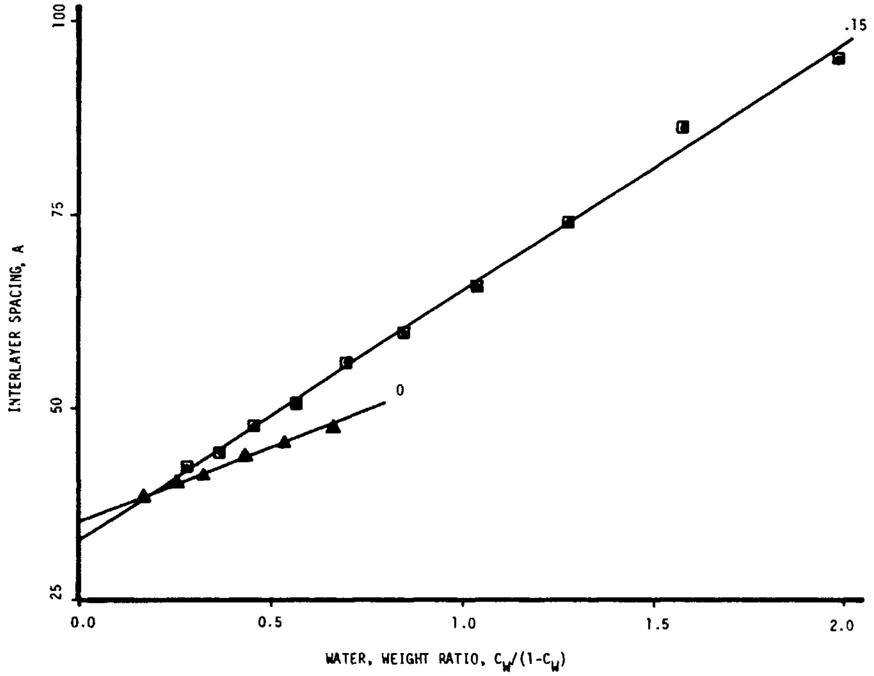

FIGURE 6 Interlayer spacing as function of water weight ratio for the system water, pentaoxyethylene dodecyl ether, benzene. ▲ = 0; ▣ = 0.15.

series without hydrocarbon. For the series with the hydrocarbon/surfactant ratio in excess of one the pattern with frequent focal conics was found at high water concentrations, the fine line pattern in the center and the broad striation pattern at low water concentrations.

In the liquid crystals with aromatic hydrocarbons the hydrocarbon/surfactant weight ratios were small corresponding to molecular ratios less than one (Figures 2 and 3). The change of dislocation pattern with water content was similar to the ones for samples with no hydrocarbon (Figure 2). The series with pentaoxyethylene (Figure 3) gave enhanced numbers of focal conics at *high* water content which means compositions in equilibrium with an aqueous solution with normal micelles. With benzene added higher amounts of water were included into the structure; the dislocation behavior now was similar to the one displaced by tetraoxyethylene dodecyl ether and water (Figures 1, 2).

DISCUSSION

The results gave information about the difference in structural and stability influence by solubilized aromatic and aliphatic hydrocarbons in a lamellar liquid crystalline phase formed by water and a polyoxyethylene dodecyl ether. Two features are conspicuous and deserve comments.

The first one is the fact that the aliphatic hydrocarbon was solubilized to a maximum of 50% whilst the aromatic compounds were limited to less than one-third of that value. The second feature is the combination of benzene and pentaoxyethylene dodecyl ether giving a liquid crystalline structure with a water solubilization maximum more than double (85% H_2O) that of the pure surfactant (40%). The maximum solubilization of the aliphatic hydrocarbon was equal to a molecular hydrocarbon/surfactant ratio slightly in excess of two, 2.1, the corresponding *p*-xylene and benzene ratios were limited to values slightly in excess of one. These values pose a problem of interest in the location and order of the hydrocarbons.

A conservative estimation of the interlayer spacing increment from the addition of hexadecane is obtained from the values extrapolated to zero water content in Figure 4. The maximum increase of interlayer distance is 39 A; the length of two *crystalline* hydrocarbon chains of hexadecane. With the hydrocarbons being liquid and highly disordered[34–38] the picture of a *liquid* hydrocarbon layer of considerable thickness emerges as reasonable.

The reason for the stability of such an arrangement is an intriguing problem. It would be tempting to suggest a mechanism of pairwise packing of the solubilized aliphatic hydrocarbon molecules with the hydrocarbon chains of the nonionic surfactant. There is, however, no evidence for an arrangement of that kind. On the contrary quadru-polar splittings in similar systems[34–38] have demonstrated a pronounced lower order parameter for the solubilized hydrocarbon than the one for the hydrocarbon chains of an amphiphilic mesogen. The order parameter of the solubilized hydrocarbon has been found less by a *factor* of 20.

With no information about the order of the solubilized hydrocarbons, the interpretation of the X-ray results must be limited to information about the sites of different molecules enabling estimations of the molecular interactions leading to the structures. The following part will treat both the water/surfactant interaction and its influence on the hydrocarbon/water-surfactant conditions.

The X-ray data may be used to give indirect information about the location of solubilized hydrocarbons in the structure from the dependence of the interlayer spacing on the content of hydrocarbon and water. Such values are usually presented[42–46] as a plot of the logarithm of the interlayer distance d as a function of the negative logarithm of the volume fraction of one substance. The rationale behind this is an implicit assumption of

$$d_s = d \cdot \phi_s^n$$

in which d_s is the part of the interlayer distance that formally may be ascribed to the solubilized species, d is the total interlayer distance and ϕ_s is the volume fraction of solubilized substance.

Taking the logarithm gives

$$\log d = \log d_s - n \log \phi_s$$

and the slope of the graphic $\log d(-\log \phi_s)$ gives the value of n. A value of n equal to one shows no penetration of the solubilized substance into the layer of the amphiphile; a value of zero shows complete penetration.

This presentation of data has been useful for systems of water and soaps[3] in which the components vary over relatively small concentration ranges and do not reach zero concentration, but is obviously of little use in the present system with large concentration variations commencing at zero. For such systems the following discussion is appropriate.

In the present case the solubilized hydrocarbon reached to zero concentration and the interlayer spacing as function of the water ratio could easily be extrapolated to zero amount. Hence, it was considered of advantage to compare directly the change of interlayer spacing as a function of composition with the theoretical change for a completely non-penetrating substance included into a lamellar liquid crystal with no accompanying change of direction of the amphiphilic molecule. For such a mechanism the interlayer spacing will vary as

$$d_v = d_0/(1 - \phi_v)$$

in which d_v is the actual spacing at the volume fraction ϕ_v of the component and d_o is the interlayer spacing at zero content of the component.

Postulating constant density of the components within the liquid crystalline realm introduces an error of less than 1 % and will enable the calculation of the spacing dependence on the water ratio. The final expression is

$$d = d_o\left[\frac{R_w}{f_0/\rho_o + (1 - f_o)/\rho_s} + 1\right]$$

in which d is the interlayer spacing, R_w is the weight ratio of water, f_o is the weight fraction of oil defined as $f_o = m_o/m_o + m_s$ in which the $m:s$ are weights, the subscripts o and s mean hydrocarbon and surfactant, and ρ_o and ρ_s are the densities of oil and surfactant respectively. This method is being used in the following sections to show the location in the liquid crystalline structure of water and the different hydrocarbons.

Site of water in the structure

A comparison of the variation of interlayer spacing with water content in Figure 4 with calculated values showed the results given in Table I. The values correspond to some penetration of water at zero hydrocarbon and at 0.1 hydrocarbon fraction (counted on hydrocarbon and emulsifier only), changing to a negative penetration at 0.2-0.4 hydrocarbon fraction and a value corresponding to non-penetration at the highest hydrocarbon fraction. The data for hydrocarbon fraction =0.5 is not sufficiently accurate to be discussed but the ones for lower values are.

TABLE I

Change of interlayer spacing with added water

Ratio, $R_{e/c}$, between experimental values and values calculated for nonpenetration.

Water, tetraoxyethylene dodecyl ether, hexadecane

f_0	0	0.1	0.2	0.3	0.4	0.5
$R_{e/c}$	0.88	0.91	1.04	1.04	1.16	1.0

Water, tetraoxyethylene dodecyl ether, p-xylene

f_0	0	0.11	0.25
$R_{e/c}$	0.88	0.94	1.08

Water, pentaoxyethylene dodecyl ether, benzene

f_0	0	0.15
$R_{e/c}$	0.81	1.04

The first conclusion: The presence of hydrocarbon reduced the penetration of water into the liquid crystalline structure. This is immediately evident. The correspondence between the changes in the *minimum* water content of the liquid crystalline phase (Figure 1, right phase limit) also indicated changes of the liquid crystalline structure with the hydrocarbon content.

The solution to the problem of water penetration vs. conformation change with added water at zero hydrocarbon content is less apparent. A formal calculation using the values in Table I at a water percentage of 60% shows a presence of 3 water molecules for each amphiphilic substance within the structure and 24 water molecules between the layers. This value is of reasonable magnitude. The value at the lowest limit of water is only 1 water molecule within the amphiphilic layer and 7 molecules between them; a low but not impossible value of water penetration. The values for pentaoxyethylene dodecyl ether showed the corresponding values 3, 24 (40% water) and 1, 8.5 (14% water). The values may, of course, not be interpreted as exactly reflecting a physical reality. They are, however, of a reasonable magnitude and cannot be used as a proof of a conformation change with compositions in the liquid crystal formed by water and surfactant only.

For samples containing hydrocarbon, the changes in interlayer spacing in excess of the completely non-penetrating case are evidence of either a change in conformation and/or angle of the packing of the amphiphilic molecules.

The assumption of change of the angle between the molecular axis and the planes of the lamellar structure postulates an optically biaxial arrangement. For a uniaxial structure the opening angle of the cone the hydrocarbon chains cover in their precessional movements may be changed. So far most lyotropic liquid crystals[47] have been shown to be of the smectic C structure and it appears probable that the present structure also belongs to this group.

The possibility of conformation change cannot be decided without further investigations, but it appears evident that an enhanced interlayer spacing reflecting an enhanced order of the amphiphilic chains has little probability. An addition of a highly disordered hydrocarbon cannot be expected to enhance the order of the amphiphilic chains. A changed angle for the amphiphilic substances appears more reasonable.

Summarizing it may be concluded that the added water partly penetrated the amphiphilic structure at zero hydrocarbon content; at higher hydrocarbon content a change in structure with added water took place giving enhanced interlayer spacing; reflecting most probably a changed angle between the molecular axis of the amphiphilic substances and the lamellar planes.

The presence of *p*-xylene gave a similar pattern (Table I); the hydrocarbon molecules most probably gave rise to an alteration of the angle between the amphiphilic substance and the plane of the lamellar liquid crystal.

The change of the interlayer spacing with added water for pentaoxyethylene dodecyl ether was conspicious (Figure 6) leading to lower values in the extrapolation region at low water content. For samples containing hydrocarbon the interlayer distance, *extrapolated to zero water*, is less than the corresponding distance for samples with no hydrocarbon. It is essential to realize that this is solely due to the strongly enhanced increment in interlayer spacing at high water content. The values for interlayer spacing ratio (Table I) showed the expected higher water penetration for the pentaoxyethylene ether than for the tetra compound.

Site of hydrocarbon in the structure

The distance change as function of the hydrocarbon content showed a more complex although regular behavior and a plot as function of the hydrocarbon ratio (as in Figure 4) tended to obscure important variations at low hydrocarbon content. The distance plotted as function of hydrocarbon volume fraction is shown in Figure 7.

The results demonstrate the influence of the water fraction on the site of the hydrocarbon. Highest amount of water gave an increase of interlayer spacing that was greater than the theoretical one for nonpenetration (curve 0.61, Figure 7). Reduced water content ($f_w = 0.5$, Figure 7) also gave a greater distance but the difference was smaller. For $f_w = 0.4$ the actual distance was smaller for volume fractions of hydrocarbon less than 0.175 at which composition the trend changed. For $f_w = 0.3$ the corresponding change took place $\phi = 0.3$ and for the curve corresponding to an $f_w = 0$ (extrapolated values) the experimental values were lower for hydrocarbon volume fractions up to 0.6.

The interpretation is obvious. High water content led to conformation or angle changes with hydrocarbon addition giving an increase of the distance in excess of the theoretical one for non-penetration. With lower water content small additions of hydrocarbon gave changes of interlayer spacing less than the calculated one for non-penetration at higher hydrocarbon content hydrocarbon additions led to angle changes.

It is essential to realize that the results do not exclude alteration of the angle of the amphiphile at low water and hydrocarbon content; only they form no proof as was the case for high water and hydrocarbon contents.

The results concerning dislocation patterns ruled out the possibility of using them as a sensitive indication of the stability of the system. Figures 2 and 3 demonstrate a different stability pattern for the penta- and tetraoxyethylene ethers but the dislocation patterns did not differ significantly. Nor did the pattern significantly vary between the systems with aliphatic and aromatic hydrocarbons in spite of the pronounced difference in stability for the systems.

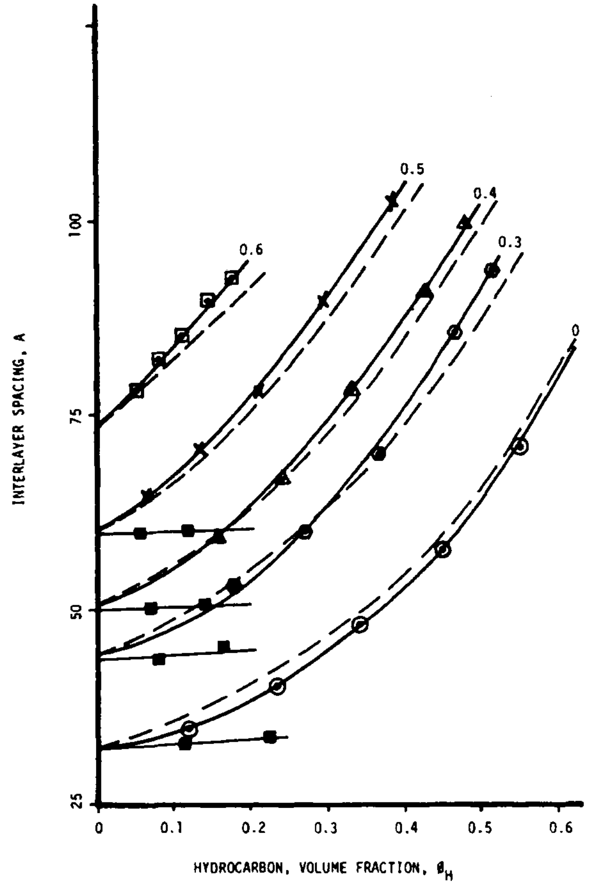

FIGURE 7 Interlayer spacing as function of hydrocarbon volume fraction. Numbers on the curves show water fraction, $w/(w + s)$. ⊙ = 0; ⊙ = 0.3; ▲ = 0.4; × = 0.5; ⊡ = 0.6.

The conclusion must be that the dislocation pattern is not a sensitive means to indicate limits of stability of the liquid crystalline phase.

SUMMARY

X-ray data of a lamellar liquid crystalline phase containing nonionic surfactants gave evidence of different sites for aromatic and aliphatic hydrocarbons solubilized into the structure. They also showed that the presence of large amounts of solubilized water gave rise to conformation changes when hydrocarbon was added to the structure and *vice versa*.

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