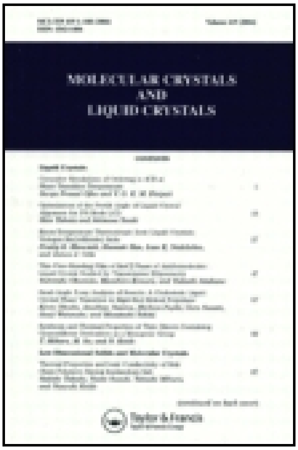

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Lyotropic Liquid Crystals†

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The importance of the structure of solubilized molecules for the structure of lyotropic liquid crystals is illustrated by examples from phase diagrams and NMR investigations of molecular mobility in the liquid crystal.

When the solubilization capacity is exceeded the liquid crystal is dispersed and a pronounced influence on the colloidal stability of the disperse system has been found. The basis for this stabilization is discussed in terms of a strongly modified distance dependence of the Van der Waals attraction potential.

INTRODUCTION

Lyotropic liquid crystals are formed after addition of a solvent to a solid or to a polar liquid. A good illustration to the former phenomenon is the influence of water on a crystalline monoester of glycerol, monolaurin.[1] In the solid state the hydrocarbon chains are in a crystalline close-packing; it is essential to understand that the stability of this crystalline packing is dependent on the network of hydrogen and polar bonds in the central part of the structure (Figure 1). The regular pattern of hydrogen bonds are indicated in the right part of the structure.

Addition of water leads to a disruption of the regular hydrogen bond network. Water forms hydrogen bonds with the hydroxyl groups of the glycerol residue. These bonds are of equal strength to the ones in the solid ester, but the order in the central part of the structure is destroyed and a transition from crystalline order of the hydrocarbon chains to a liquid crystalline order takes place. The order in the liquid crystalline state (Figure 2) may be exemplified by the order parameter[2]

$$S = \langle 3 \cos^2 \theta - 1 \rangle$$

For a soap system the order of a hydrocarbon chain is fairly constant except for the three last carbon atoms toward its end; where the order parameter will rapidly decrease (Figure 3).

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† Plenary lecture presented at the Sixth International Liquid Crystal Conference, Kent State University, August, 1976.

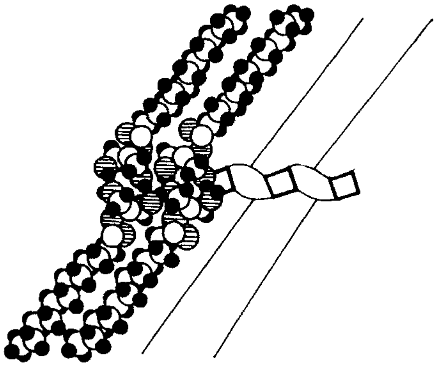

FIGURE 1 The crystalline close-packing of a monolaurin[1] depends on the hydrogen bond network in the central part of the structure for its stability.

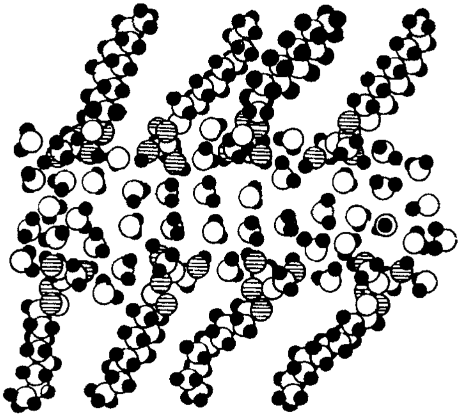

FIGURE 2 Introduction of water destroys the order in the central part of the structure (cf. Figure 7) and the hydrocarbon chains becomes less ordered in the liquid crystalline state.

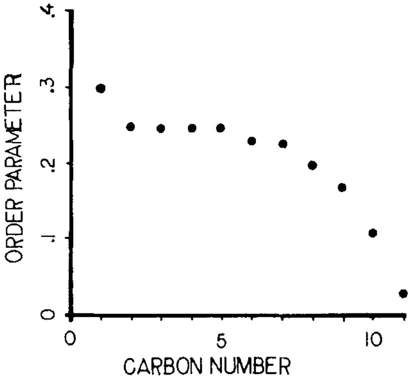

FIGURE 3 The methylene groups of a soap in the liquid crystalline state have a constant order parameter except for the three last ones towards the chain end, which show increasing disorder.

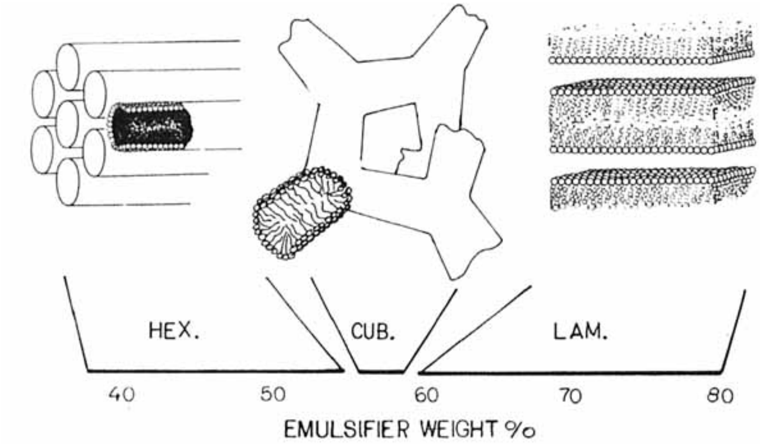

FIGURE 4 A liquid emulsifier, vinyl phenol poly[9] ethylene glycol ether, and water form several liquid crystalline phases at 20°C. Increased account of water gives structures with increased water/amphiphile interface. (Right to left in the figure.)

This case illustrates the common *disordering* at the addition of water to a structure. The opposite phenomenon is also possible; an amphiphilic *liquid* may form a liquid crystalline phase in combination with water. One example is 1-amino octane,[3] the phase behavior of a commercial liquid poly-ethylene glycol nonyl-phenyl ether[4] and water is a more interesting illustration. These two substances form a whole series of liquid crystalline phases with water at 20°C. The phases are shown in Figure 4 illustrating the gradual enhancement of water exposure to the polar groups with increasing water concentration. At low water content a lamellar structure is observed, increasing water content gives a structure of short rods, which are transformed to infinitely long rods in a regular hexagonal packing at high water content.

The lyotropic liquid crystals will solubilize hydrocarbons and amphiphilic substances. The systems formed may at first look highly complex but they actually behave in a regular manner and the general features of the phase diagrams studied by Ekwall[5] may be estimated. The following treatment gives a schematic view of the importance of molecular interactions from the solubilized compound for the association structures in different parts systems.

PHASE DIAGRAMS AND INTERACTIONS WITH SOLUBILIZED MOLECULES

The base for the studies is the pair water/sodium octanoate, a short chain soap. Dissolution of soap in the water gives rise to a molecularly dispersed solution for concentrations below 5% (W/W), which is the critical micellization concentration. The micellar solution accepts a maximum of 40% soap, at concentration above this limit a liquid crystalline phase is formed. Its structure contains a hexagonal array of cyclinders (Figure 4, Hex); a typical "middle phase".

The interaction between hydrocarbons and these two association structures is small; Figure 5 demonstrates a maximum solubilization of a few percent and no difference between aromatic and aliphatic hydrocarbons is observable. This is in complete agreement with the determinations of order parameters[6] of solubilized hydrocarbons. The order parameter of an ethylene group would be of the magnitude 0.05; that of a methyl group in the hydrocarbon would be only 0.005. Introduction of a polar group in the solubilized molecule causes a drastic change of the interaction. The dotted lines in Figure 5 demonstrate the strongly enhanced solubilization of an ester; approximately a magnitude.

An alcohol of corresponding chain length (Figure 6) gives an even stronger solubilization; the lamellar liquid crystalline phase reaches far towards the water corner; in the example the lamellar structure will be stable to a water content of 88%. The reason for this stability is found in the suitable packing conditions of an alcohol and a soap. The small polar group of the alcohol with no long range repulsion forces to the soap nor to itself causes no strains in the lamellar structure and the extremely high stability are illustrated by the order parameter;[6] it shows identical values to these of the parent surfactant for the entire chain.

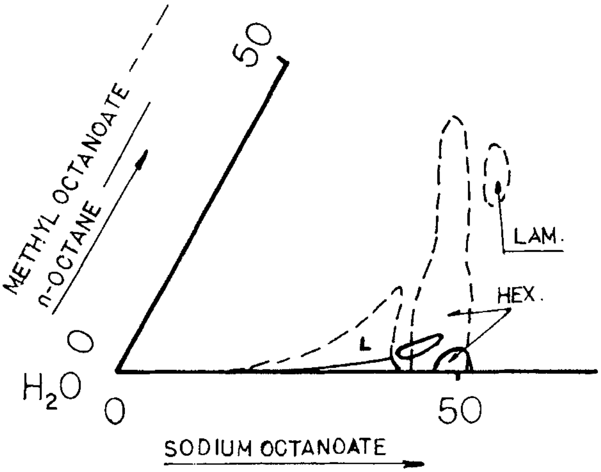

FIGURE 5 The difference in solubilization is pronounced between a hydrocarbon (——) and an ester (- - -) both in an aqueous micellar solution (L) and in a liquid crystalline "middle phase" (cf. Figure 4).

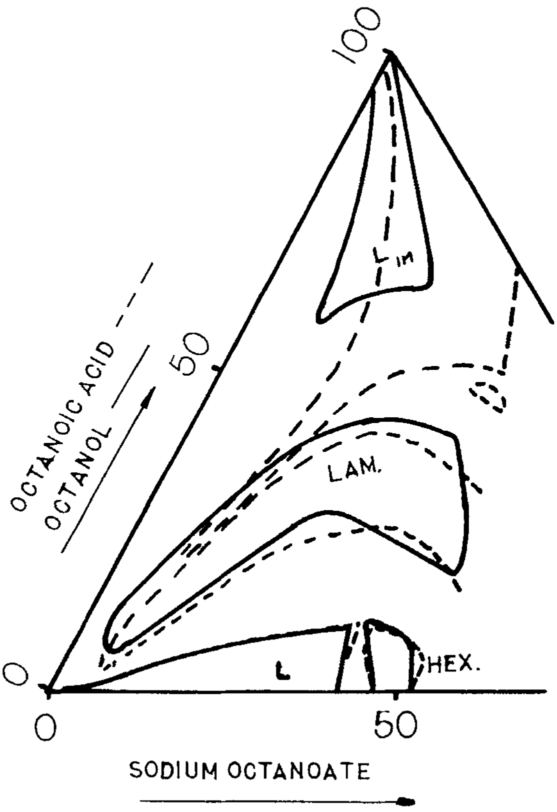

FIGURE 6 The solubilization in the aqueous micellar solution (L), in the "middle phase" (Hex) and in the lamellar liquid crystalline phase (Lam) are similar for *n*-octanol (——) and *n*-octanoic acid (– – – –).

The stability of the lamellar packing with soap, alcohol and water, is also illustrated by the phase equilibria at high water concentrations. The solubility of the alcohol (Figure 7) is small in water at concentrations less than the critical micellization concentration (cmc); at which an increase of the alcohol solubility due to solubilization in the soap micelles is observed. It should however be noticed that the critical micellization is not the lowest concentration at which an association structure is formed. A liquid crystalline phase is formed in equilibrium with the aqueous solution of soap at alcohol concentrations in excess of its solubility in water. The lamellar phase is actually in equilibrium with a more dilute aqueous solution of the soap than the one at the critical micellization concentration, which is a good illustration of ((a), Figure 7) the stability of the lamellar liquid crystalline phase of alcohol and soap.

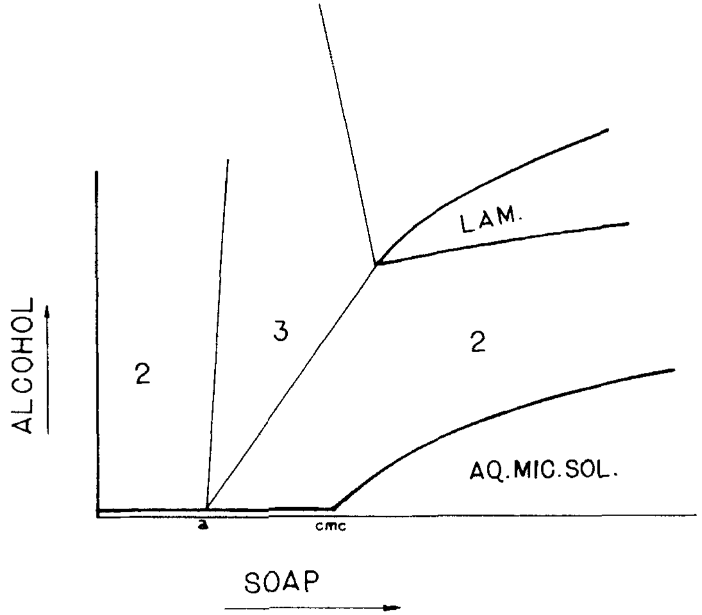

FIGURE 7 The lamellar liquid crystalline phase of soap and a medium chain length alcohol is in equilibrium with an aqueous solution of soap at a concentration (a) lower than the critical micellization concentration (cmc) of the soap.

A carboxylic acid shows a more enhanced interaction with the soap than the alcohol does which is manifested in a pronounced direct solubility of the soap in the liquid acid. Figure 8 shows the solubility of water and sodium octanoate in octanol and in octanoic acid. The alcohol (Figure 8, ——) dissolves the soap only to 2%; further dissolution requires three water molecules per soap molecule according to the solubility line. The acid on the other hand dissolves the soap to 36%, which corresponds to a soap/acid molecular ratio of 0.5.

The reason for the soap solubility is found in the strong hydrogen bond between the acid and the soap as evidence by the changes in infrared spectra.[7] At addition of soap to the acid, the out-of-plane deformation vibration of the carboxylic OH group at 935 cm^{-1} disappears showing the acid *dimers* to be disintegrated. The OH stretching vibrations in the range 3100–2900 cm^{-1} are moved towards lower frequencies and a new absorption is observed at 1900 cm^{-1}. These two modifications of the spectrum are indicative of a hydrogen bond of enhanced strength compared to the one in the acid dimer. The added soap molecules form a liquid compound of soap and acid. The aggregate actually contains four molecules of acid and two molecules of soap[8] and is stable to high dilutions in carbon tetrachloride. Dilution with

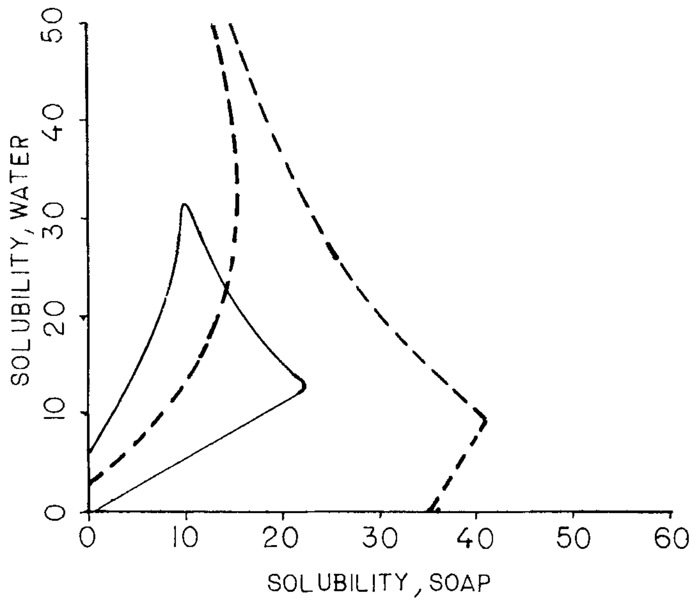

FIGURE 8 Octanoic acid will dissove sodium octanoate to an isotropic liquid (- - -) a combination of water and soap are necessary to bring about solubilization in octanol (——).

water, on the other hand, disintegrates the hydrogen bond at a water concentration of 40% by weight.[9]

This change in the bond strength is also reflected in an interesting manner in the phase equilibria with water and soap. At low water concentrations at which the strong hydrogen bond is present a distinct difference from the phase diagram with alcohol is observed (Figures 6, 8). On the other hand with a disintegrated hydrogen bond at high water concentrations, the phase equilibria with alcohol and acid are extremely similar (Figure 6).

Numerous investigations of such systems[5] have demonstrated the validity of these simple rules; few fundamental investigations as to the reasons for the stability of different association structures has so far been presented.

DISPERSE SYSTEMS

The fact that liquid crystals might be present in disperse systems such as emulsions had been known for about ten years,[10-12] when the first demonstration of their pronounced effect on the stability was published.[13] Several investigations were made to confirm the effect[14,15] and the technical development has been comparatively rapid.[16]

The location of the liquid crystals to the O/W interphase was observed using optical microscopy with polarized light,[17] later determinations with electron microscopy[18] displayed the liquid crystalline pattern with great clarity. Corresponding investigations on foam stability illustrated the possibility to make stable foams from hydrocarbons[19] and could also add to the understanding of the action by defoamers and destabilizers for foams.[20]

The basis of the enhanced stability of disperse systems which contain a liquid crystalline phase has recently been clarified.[19] The main reason for the stability is found in the modification of the distance dependence of the Van der Waals potential. This potential influences the flocculation of emulsion droplets when they have approached each other to a distance less than half the radius between the surfaces. At this distance the hydrodynamic conditions in the zone between the droplets causes a flattening of the part of the drops which is closest to each other and a reasonable model system is two infinite flat surfaces according to Figure 9.

The Van der Waals potential of the droplets without a liquid crystalline phase (A, Figure 10) is

$$V = -\frac{A}{12\pi d^2} \tag{2}$$

in energy units per area unit in which A is the Hamaker constant and d is the distance between the surfaces.

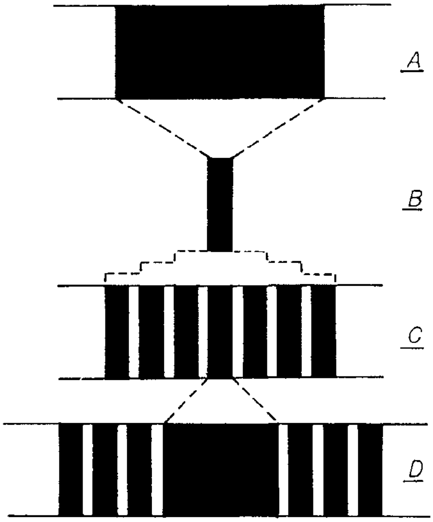

FIGURE 9 The model system used to calculate *VdW* potential during flocculation leads to *B* with a thin oil film between the droplets which bursts at coalescence. *D*. Two water droplets covered with a lamellar liquid crystal and a thick oil film. Flocculation leads to *C* and coalescence involves a stepwise removal of layers to *B* and bust.

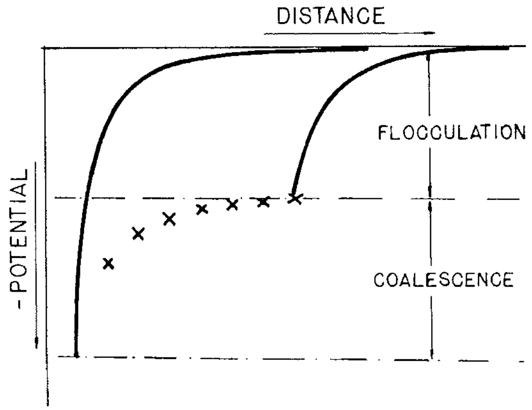

FIGURE 10 The distance dependence of the *VdW* potential is similar for droplets with (right curve) and without a lamellar liquid crystal (left curve) during flocculation (upper part). The presence of a crystal causes a pronounced change during the coalescence (lower part).

The flocculation process for the droplets with liquid crystals (*D*, Figure 9) involves the Van der Waals potential from the complete system of drops and liquid crystals. The ratio between the Van der Waals potential for the droplets covered with a liquid crystal (*D*) and those without one (*A*) gives a fairly complex equation even when the simple formula (2) is used.

$$\frac{V_B}{V_A} = d^2 \cdot \left\{ \sum_{q=0}^{n} \sum_{p=0}^{n} [d + (p + q) \cdot (l + M]^{-2} + \sum_{p=0}^{n-1} \sum_{q=0}^{n-1} [d + 2l + (p + q) \cdot (l + m)]^{-2} - \sum_{p=0}^{n} \sum_{q=0}^{n-1} 2 \cdot [d + l + (p + q) \cdot (l + m)]^{-2} \right\} \qquad (3)$$

As is easily seen there is only a small difference between the two cases. No difference has been found in the flocculation rate for emulsions with and without a liquid crystalline phase.

The potential change during coalescence process is different for the two cases. The droplets with a monomolecular layer of surfactant coalesce over a liquid film and the Van der Waals potential distance dependence is represented by the part of the upper potential curve in Figure 10. This potential dependence means an enhanced driving force for coalescence with reduced thickness of the film. The pressure will in fact be inversely proportional to the cube of the distance. The coalescence over the liquid crystalline phase implies a step-wise removal of the layers between the droplets (Figure 9, *C* – *B*) of the change of Van der Waals potential during this process only the changes in the potential at the surfaces between the water and the liquid crystalline phase are of importance for the coalescence. The expression will be

$$\frac{V_M}{V_F} = m^2 \cdot \left\{ \sum_{p=0}^{n} [m + p(m + l)]^{-2} - \sum_{p=0}^{n} [(p + 1)(m + l)]^{-2} \right\} \tag{4}$$

with the meaning of the symbols as in Eq. (2).

The difference in the distance dependence of the Van der Waals potential is striking (Figure 10). The value of Eq. 3 is entirely governed by terms with small p; removal of the first layer of the many in the liquid crystalline phase changes the potential only to insignificant amounts. (Potential marked by crosses in the COALESCENCE part of Figure 10.) This means that the driving force is almost zero and an extremely slow coalescence should be expected. It appears reasonable to attribute the enhanced dispersion stability mainly to this factor; the enhanced viscosity also means an influence in the same direction.

CONCLUSIONS

The knowledge about lyotropic liquid crystals their solubilization and the behavior of their dispersion has now reached a state in which the systematic phenomenological knowledge appears to be sufficient both for a more basic contribution to the problems and for a wide technological application.

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