Formation of a Liquid Crystalline Phase Between Aqueous Surfactant Solutions and Oily Substances

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The process in which a ternary liquid crystalline (LC) phase containing surfactant, water and oily substance is formed after contact of aqueous surfactant solution and oily substance was investigated by a combination of (i) microscopic observation in polarized light and (ii) penetration of water-soluble or oil-soluble dye into LC phase. The structure of LC phase and the process of its formation were found to be affected by many factors, such as kinds of surfactant, surfactant concentration, alkyl chain length of oil and so on.

Oil is supposed to be gradually incorporated into LC phase with time. The fact that parts of LC phase are projected into the exterior surfactant solution, and that the continuous phase within LC phase is water, suggest the possibility of the dispersion of LC phase into the exterior solution.

The process of the formation of LC phase implies some contribution to oily dirt removal.

Several workers have noted that a ternary liquid crystalline (LC) phase containing surfactant, water and oily substance is formed between aqueous surfactant solution and oily substance when they come into contact with each other in various systems (1-4). Such a formation of LC phase has been discussed with respect to the mechanism of oily dirt removal, and the results of many washing experiments (performed under conditions where LC phases were present) have suggested some contribution of LC phase to detergency (3-7). We have also described elsewhere (8) the detergency performance for cotton and polyester fabrics in both conditions where LC phase is formed and where it is not.

There is a large recent literature on the structure of LC phase appearing in various systems containing surfactants. For example, Friberg and his co-workers (9-11) have described the structure of LC phases formed in various emulsions and foams. Miller, et al. (12-17) have described the phase behavior and the structure of LC phase, microemulsion and other phases, especially with respect to oil recovery and to detergency.

For investigation of the correlation between the LC phase formation and the oily dirt removal, the structure of LC phase formed between surfactant solution and oil after contact is more important than that formed in mixed systems such as emulsions. Miller and his co-workers have also observed the diffusion process of oily substance into aqueous surfactant solution through microemulsion and LC phase (15,18,19).

In this paper we describe the process in which LC phase is formed between surfactant solution and oily substance from the standpoint of the structure of LC phase, especially molecular orientation of surfactant. The dynamic phenomena, which occur after bringing surfactant solution into contact with oil, were observed with a polarizing microscope in various systems. The structure of LC phase in each system was investigated from its optical properties found in polarized light, and also from penetration of water-soluble or oil-soluble dye into LC phase.

EXPERIMENTAL

Materials. Sodium dodecyl sulfate (SDS) and sodium dodecylbenzene sulfonate (DBS), with linear alkyl chains, were obtained from Wako Junyaku Kogyo Co. Sodium dodecylbenzene sulfonate, with a branched alkyl chain, was obtained from Kanto Kagaku Kogyo Co. Various oily substances in a liquid state at room temperature were used as simple models of oily dirt. n-Alkanes, n-fatty alcohols and n-fatty acids with various alkyl chain lengths were obtained form Tokyo Kasei Kogyo Co. (Tokyo, Japan). All surfactants and oily substances were used without further purification of the commercial extra pure grade samples, having purities of at least 95%. Deionized and distilled water was used to prepare the surfactant solutions. Water-soluble and oil-soluble dyes used were Benzopurprine 4B (C.I. Direct Red 2) and Sudan I (C.I. Solvent Yellow 14), obtained from Tokyo Kasei Kogyo Co. and Sigma Chemical Co. (St. Louis, MO), respectively.

Observations with a polarizing microscope. Sample was prepared in a vertical orientation within a glass cell, which has rectangular windows and path length of 1 mm. After pouring aqueous surfactant solution into the cell by half, oily substance was gently added to make the cell filled out. When these two liquids were brought into contact with each other, care was taken to control the disturbance near the solution/oil interface as little as possible. Immediately after contact, the cell was set in a horizontal orientation on the stage of a polarizing microscope (Nikon, OPTIPHOTO-POL), and dynamic phenomena, which occurred in the vicinity of the solution/oil interface, were observed. Similar techniques have been used by Benton et al. (20) to study the dynamic contacting of aqueous surfactant solutions with hydrocarbons. Sample preparations and observations were performed at 20°C. In case LC phase was formed as a layer, the increase of its thickness with time was measured using a micrometer.

The structure of LC phase was investigated by examining the molecular orientation using a sensitive color plate (R=530 nm) inserted between a sample and an analyzer in the crossed-nicols. A birefrigent sample shows a higher order interference color (blue), or a lower order interference color (yellow), depending upon the direction in which the sample is set against the axes of the sensitive color plate (21). In linear hydrocarbon chain surfactants, the refractive index is larger in the direction of long chain axis (22), so that the different interference color can be observed whether hydrocarbon chains are oriented parallel or perpendicular to the one axis of the sensitive color plate. Therefore, molecular orientation of surfactant in

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LC phase can be examined by the color observed using the plate.

Textures found in polarized light were also used for classification of liquid crystal (23). Observation of textures was performed for a small amount taken from LC phase on a slide glass.

Penetration of water-soluble or oil-soluble dye into LC phase. The penetration phenomena of water-soluble or oil-soluble dye into LC phase in the process of its formation were also examined in order to investigate the structure of LC phase. Sample preparations were as follows: 0.2 mol/1 SDS solution colored with Benzopurprine 4B (0.01%) was gently brought into contact with the colorless oil in a vial (System A). On the other hand, oil colored with Sudan I (0.01%) was brought into contact with the colorless 0.2 mol/1 SDS solution (System B). Whether the LC phase formed between SDS solution and oil became dyed or not was examined with time for both systems at 20℃.

FIG. 2. Conditions where a liquid crystalline phase is either formed (LC) or not (N) in the systems of DBS solutions and various oily substances (20℃).

RESULTS AND DISCUSSION

Conditions determining whether LC phase is formed or not. Prior to investigation of the structure of LC phase, the conditions determining its formation were defined. Various combinations of surfactant solutions and oils were brought into contact with each other. The sample was left for 30 min, and then the vicinity of the solution/oil interface was observed with a polarizing microscope (× 100). When a birefrigent phase was found between dark solution phase and dark oily phase in the crossed-nicols LC phase formation was recognized.

Results are shown in Figure 1 for the systems of SDS and in Figure 2 for the systems of DBS, respectively. Conditions where LC phase is formed (LC) and not (N), were defined.

In Figure 1, no change is detected in the vicinity of the interface between SDS solution and n-alkanes having various alkyl chain lengths. On the other hand, LC phase is formed above a certain SDS concentration between aqueous SDS solutions and polar oily substances, n-fatty alcohols and n-fatty acids.

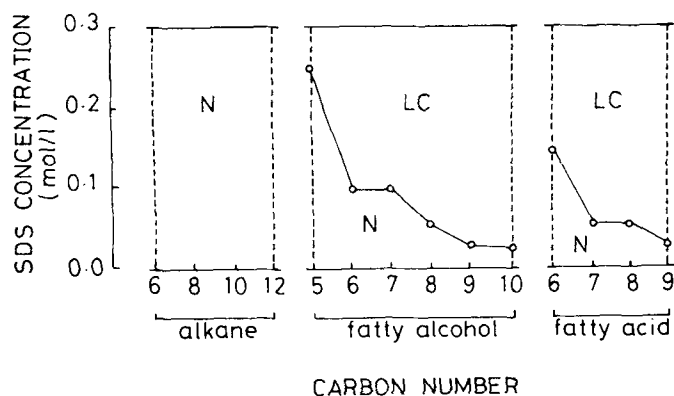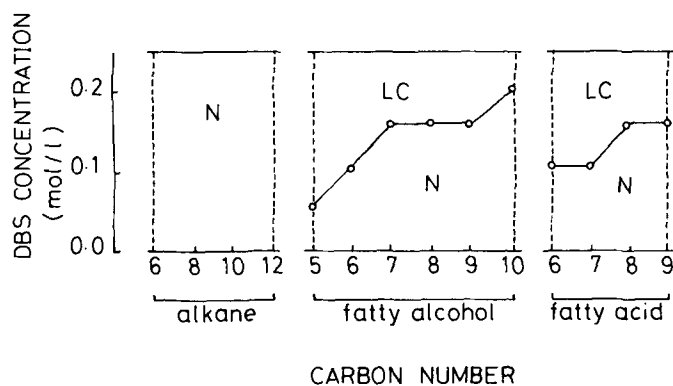It is supposed that whether or not LC phase is formed between SDS solutions and oils after contact is primarily dependent upon whether a mixed adsorbed film containing both SDS molecules and oil molecules is formed or not at the interface. Polar oils, having some surface activity, are supposed to be adsorbed at the interface and form a mixed film with SDS molecules. The mixed adsorbed film might grow to multi-layer, and then successively to LC phase above the critical concentration.

The lowest SDS concentration, at which LC phase formation can be detected between SDS solution and fatty alcohols or fatty acids, is dependent upon the alkyl chain length or carbon number of these oils. The critical concentration is lowered with increasing the carbon number of them. There is no remarkable difference between the system of fatty alcohols and that of fatty acids with respect to the critical concentration.

LC phase is also formed between DBS solutions and polar oils above a certain concentration of DBS, as shown in Figure 2. The critical DBS concentration, however, becomes higher with increasing the carbon number of oils, as opposed to the systems of SDS.

Whether an alkyl chain of surfactant is linear or branched also affected the results. In the case of DBS with a branched dodecyl group, LC phase was not formed between aqueous solutions and all kinds of oils examined. In both systems of linear and branched DBS, spontaneous emulsification often occurred in the vicinity of the interface, whether or not LC phase was formed. The structure of emulsion was not examined.

From these results, it is found that whether LC phase is formed or not between surfactant solutions and oily substances is dependent upon many factors, such as polarity and alkyl chain length of oils, kinds and concentration of surfactants, and so on. It is supposed that the interaction in a ternary system (which contains surfactant, water and oil) is affected by such factors, and that the complicated phenomena (including the formation of LC phase and spontaneous emulsification) result from the interaction in each system.

Microscopic observation of LC phase formation: SDS solution/fatty alcohol systems and the effect of SDS concentration. Figure 3 shows a micrograph of the interface between 0.05 mol/1 SDS solution (left side) and octanol (right side). Formation of LC phase is found in the vicinity of the interface. Because of the vigorous convection in the vicinity of the interface, the LC phase dispersed into the
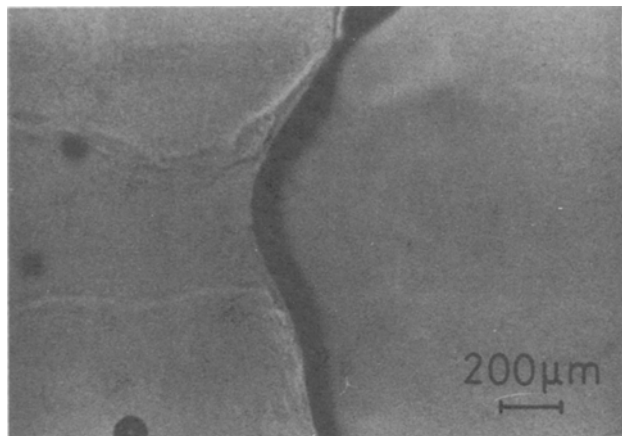
FIG. 1. Conditions where a liquid crystalline phase is either formed (LC) or not (N) in the systems of SDS solutions and various oily substances (20℃).

FIG. 3. Microscopic observation of the interface between 0.05 mol/1 SDS solution and octanol (25 min after contact, crossed-nicols, × 40).

exterior SDS solution, and then disappeared without growing.

At the higher SDS concentrations, the LC phase was formed as a thin layer between SDS solution and octanol as soon as they were brought into contact. Figure 4a shows a typical micrograph of the LC phase formed between 0.25 mol/1 SDS solution (left side) and octanol (right side). By using a sensitive color plate, as mentioned above, the hydrocarbon chains in LC phase were found to be oriented parallel to the interface at first contact in almost all parts of LC phase. Partially different molecular orientations were found in some parts of it. Such partial disorder of the molecular orientation is supposed to be caused by a disturbance which occurs at the time of contact.

After about 10 min many fine drops appeared near the boundary between the LC phase and the exterior SDS solution. From the heterogeneity of the color of the LC phase, the molecular orientation in the LC phase was
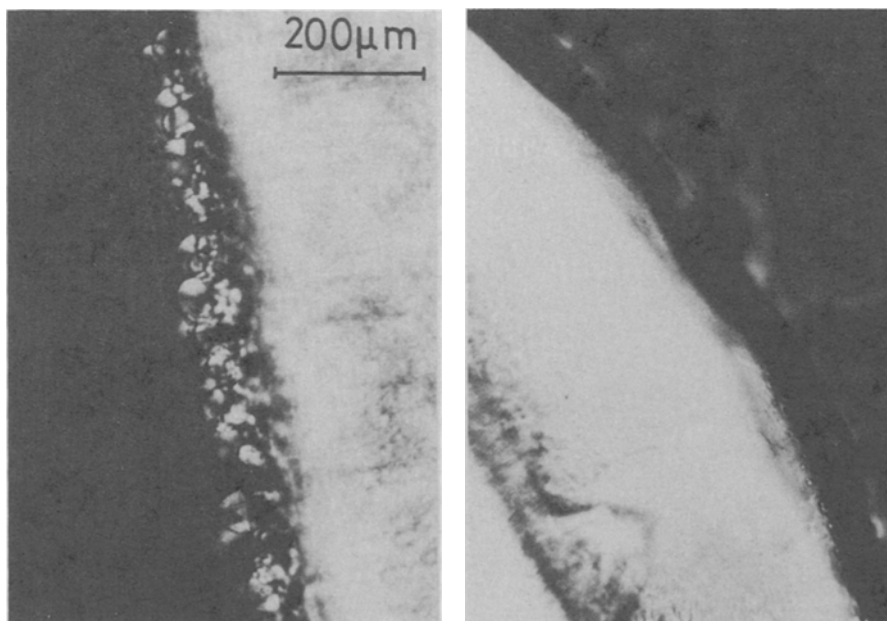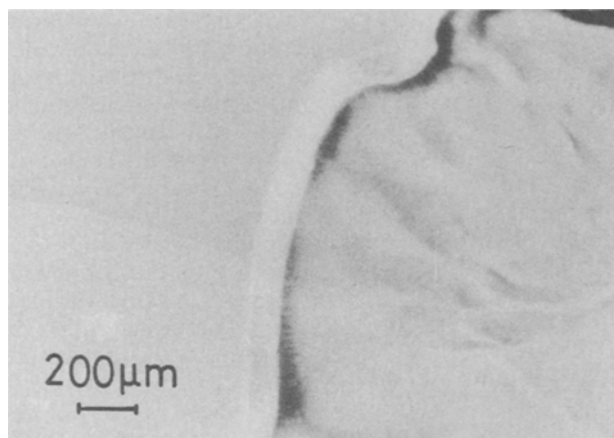

FIG. 4. Microscopic observation in the system of 0.25 mol/1 SDS solution and octanol (crossed-nicols). a) 1 min after contact (× 40); b) after 4 hr, the boundary between a liquid crystalline phase and SDS solution (× 100); and c) after 4 hr, the boundary between a liquid crystalline phase and octanol phase (× 100).

FIG. 5. Oily streak and mosaic textures found in the SDS solution/octanol system (crossed-nicols, X 100).

found to become gradually disordered, probably due to the diffusion of the molecules.

As shown in Figure 4b, many spherulites projecting into the exterior solution appear near the boundary between the LC phase and the solution after 4 hr of contact. From the color of the spherulites, the hydrocarbon chains in them were found to be oriented from the center to the surface. Tube-like structures called myeline figures were also observed. Stevenson (2) has already discussed the formation of myeline figures and anisotropic droplets or spherulites. The structure near the boundary between LC phase and the exterior octanol phase (Fig. 4c) is obviously different from the other side, shown in Figure 4b, which has been in contact with the aqueous solution. These features were observed more clearly after 24 hr of contact.

Figure 5 shows the texture observed in the crossed-nicols in both samples, which are taken from the LC phases left for 4 and 24 hr. Oily streak and mosaic textures, characteristic of the lyotropic liquid crystal of lamellar structure (neat soap) (23), were found.
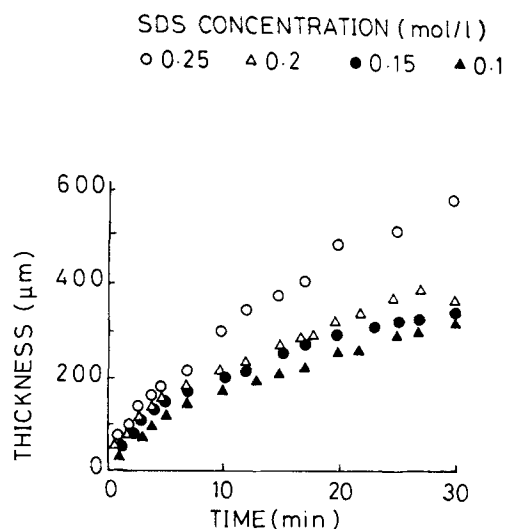
SDS CONCENTRATION (mol/l)

o 0.25   ▵ 0.2   ● 0.15   ▲ 0.1

FIG. 6. Effect of SDS concentration on the thickness of a liquid crystalline phase (20°C).

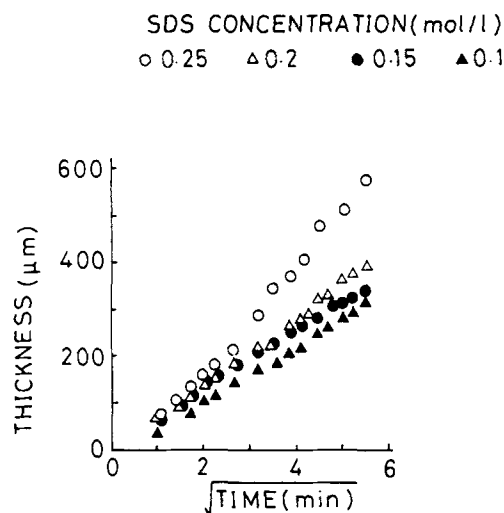SDS CONCENTRATION(mol/l)

o 0.25   ▵ 0.2   ● 0.15   ▲ 0.1

FIG. 7. Replotting of the data in Figure 6. The thickness of a liquid cystalline phase vs square root of time.

When LC phase was formed as a layer, it thickened gradually toward the aqueous phase from the interface of first contact. Figure 6 shows the increase of its thickness with time after contact for the representative case of SDS solution and octanol. LC phase becomes thicker with increasing SDS concentration. These data are replotted against square root of time in Figure 7. Diffusion path theory predicts a linear relationship between the thickness of LC phase and square root of time (18,24). In Figure 7, however, apparent deviations are observed from the linearity. Many complicated factors, such as the effect of convection, are supposed to cause the nonlinearity in this system.

The effect of alkyl chain length of fatty alcohol. Various phenomena were observed in the systems of 0.25 mol/l SDS solution and fatty alcohols of various alkyl chain lengths.

As shown in Figure 8, when pentanol is brought into contact with 0.25 mol/l SDS solution, many spherulites are formed near the interface of solution (left side) and pentanol (right side). From the color of the spherulites, the molecular orientation within them was found to be the same as those observed in the octanol system. The
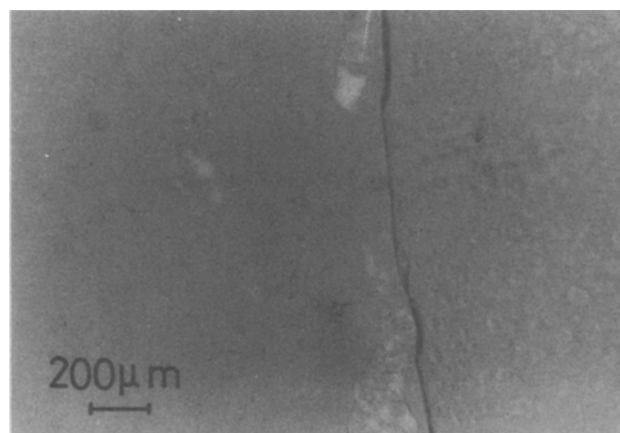

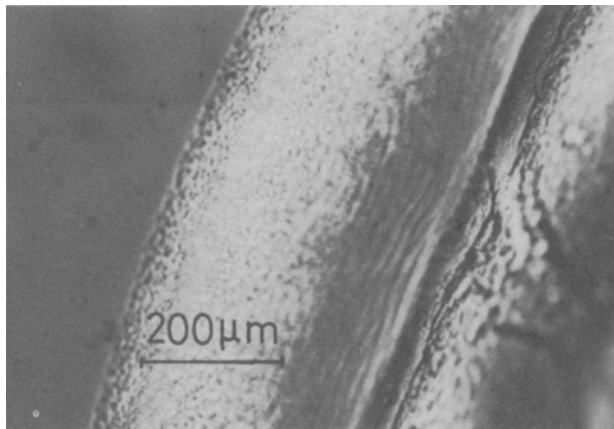FIG. 8. Spherulites formed in the system of 0.25 mol/l SDS solution and pentanol (after 1 min, crossed-nicols, X 40).

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FIG. 9. A liquid crystalline phase formed in the system of 0.25 mol/1 SDS solution and hexanol (after 1 hr, crossed-nicols, ×100).

spherulites moved about near the interface, dispersed into the aqueous solution, and then disappeared. This means that LC phase is broken and dissolved in the surfactant solution.

In the case of hexanol, LC phase is formed as a thin layer between SDS solution (left side) and hexanol (right side) (Figure 9). Striation pattern parallel to the interface is observed in it. The distance between striations is in the range of about 20–30μm. A region of fine drops is also observed on the side of the boundary in contact with the aqueous solution. The region was gradually spread over a wide range in time. From the color of the LC phase, the molecular orientation was found to be parallel to the interface in the region with striation pattern, but perpendicular to the interface in the region of fine drops. It is supposed that the striation pattern observed in the crossed-nicols suggests the existence of a kind of long-range ordered structure. Furthermore, the LC phase was found to contain lamellar structure from the oily streak and mosaic textures similar to those shown in Figure 5. The detailed discussion of its structure needs further investigations. Similar behaviors were observed in the system of heptanol.
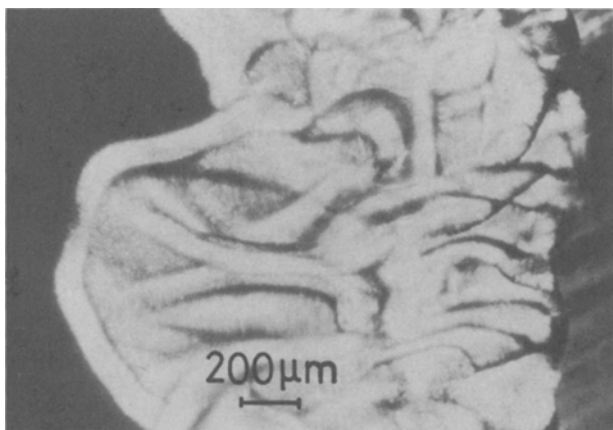
In the case of decanol (Figure 10), LC phase is formed in entangled layers between SDS solution (left side) and oil (right side) with vigorous disturbance immediately after contact. Spherulites were observed near the boundary between the LC phase and the exterior solution, same as in the case of octanol. Oily streak and mosaic textures were also observed.

It is found that LC phases formed in the SDS solution/fatty alcohol systems contain lamellar structures from the characteristic textures; but their whole features are determined by the alkyl chain length of fatty alcohol.

Other systems: Effect of polar group of oily substance. The system of fatty acid was compared with that of fatty alcohol in order to examine the effect of polar group of oil on the process of LC phase formation. In the system of octanoic acid and 0.25 mol/1 SDS solution, similar phenomena were observed to the systems of octanol. Spherulites and myeline figures were observed near the aqueous solution, and textures showed the features of lamellar structure.

Effect of molecular structure of surfactant. When 0.25 mol/1 DBS solution was brought into contact with octanol, disturbance near the interface was more vigorous than that of the SDS systems. It was about 10 min after contact that a stable LC phase was formed. By the color of the LC phase, molecules in the LC phase were found to be oriented parallel to the interface, as in the SDS systems, at the initial stage. At the latter stage, however, the molecular orientation was found to invert from parallel to perpendicular to the interface, from the change of the color. As shown in Figure 11, fan-like texture, which is characteristic of the lyotropic liquid crystal of hexagonal structure (middle soap) (23), is found in both samples left for 4 and 24 hr. These results suggest that the hexagonal structures become dominant at the latter stage in this system.

Molecular shape generally affects the way that molecules pack into hexagonal or lamellar structure (25). Molecular structure of surfactants is supposed to be one of the important factors determining the liquid crystalline structure. The difference of LC structure between SDS and DBS systems might be explained by the poor molecular packing of DBS molecules, as compared with SDS, owing to a benzene ring.
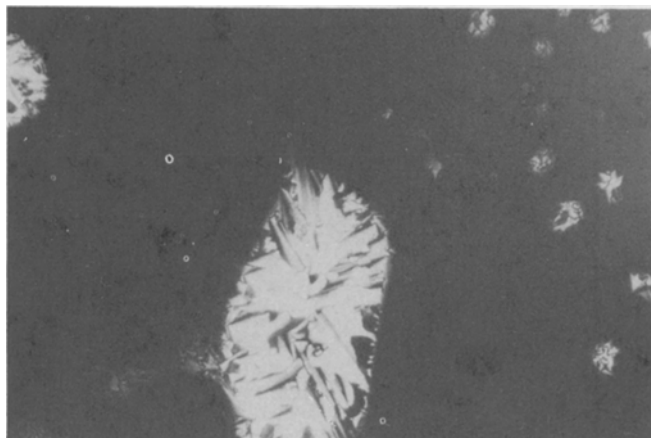

FIG. 10. A liquid crystalline phase formed in the system of 0.25 mol/1 SDS solution and decanol (after 2.5 min, crossed nicols, ×40).

FIG. 11. Fan-like texture found in the DBS solution/octanol system (crossed-nicols, ×100).
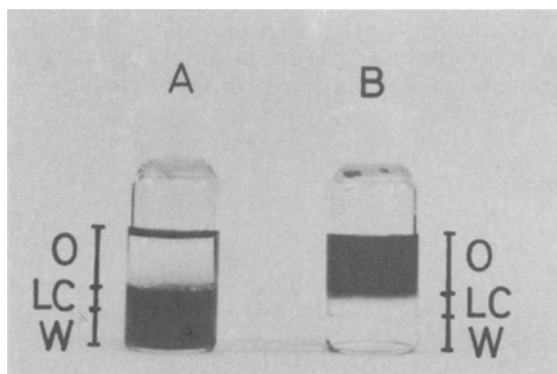
FIG. 12. Coloring of the liquid crystalline phase 24 hr after contact in the systems of (A) 0.2 mol/1 SDS solution = Benzopurprine 4B/octanol, and (B) 0.2 mol/1 SDS solution/octanol = Sudan I.

Penetration of water-soluble or oil-soluble dye into LC phase. Ekwall *et al.* (1) revealed that the LC phase formed between laurate solution and decanol was hydrophilic from the fact that the LC phase was dyed when water-soluble dye was added in laurate solution, but not dyed when oil-soluble dye was added in decanol. However, it is supposed that the hydrophilicity or lipophilicity of the LC phase will change according to the change of its structure in the process of the formation. In order to obtain some information on the structure of LC phase, penetration of water-soluble or oil-soluble dye into LC phase was examined in the systems of SDS solution and fatty alcohol or fatty acid.

The formed LC phase was dyed in the system of SDS solution colored with Benzopurprine 4B and octanol (System A), but not dyed in the system of SDS solution and octanol colored with Sudan I (System B) at the initial stage of its formation. It shows that only water-soluble dye can be dissolved in the LC phase at this stage; namely, the continuous phase within the LC phase is supposed to be water. In other words, the LC phase is supposed to be hydrophilic. This result is consistent with that reported by Ekwall *et al.* (1).

However, it was found that remarkable changes occur in both systems left for longer periods. Figure 12 shows the samples left for 24 hr after contact. In System B, the LC phase becomes gradually dyed from the boundary contact with the colored octanol phase. Penetration of oil-soluble dye into the LC phase occurs. This suggests that incorporation of oil into the LC phase is enhanced as the LC phase is formed, and separated phases of oil, in which oil-soluble dye can be dissolved, appear within the LC phase. On the contrary, at the initial stage of the formation of the LC phase oil is incorporated only as monomolecules to form the liquid crystalline structure, because oil-soluble dye cannot be dissolved in the LC phase.

Moreover, in System A, the octanol phase becomes dyed with time from the boundary contact with the dyed LC phase. This means that the penetration of water-soluble dye into the oily phase occurs. This change is supposed to be caused by the solubilization of water and water-soluble dye in the reversed micelles of SDS, or the W/O emulsification of them, in the oily phase.
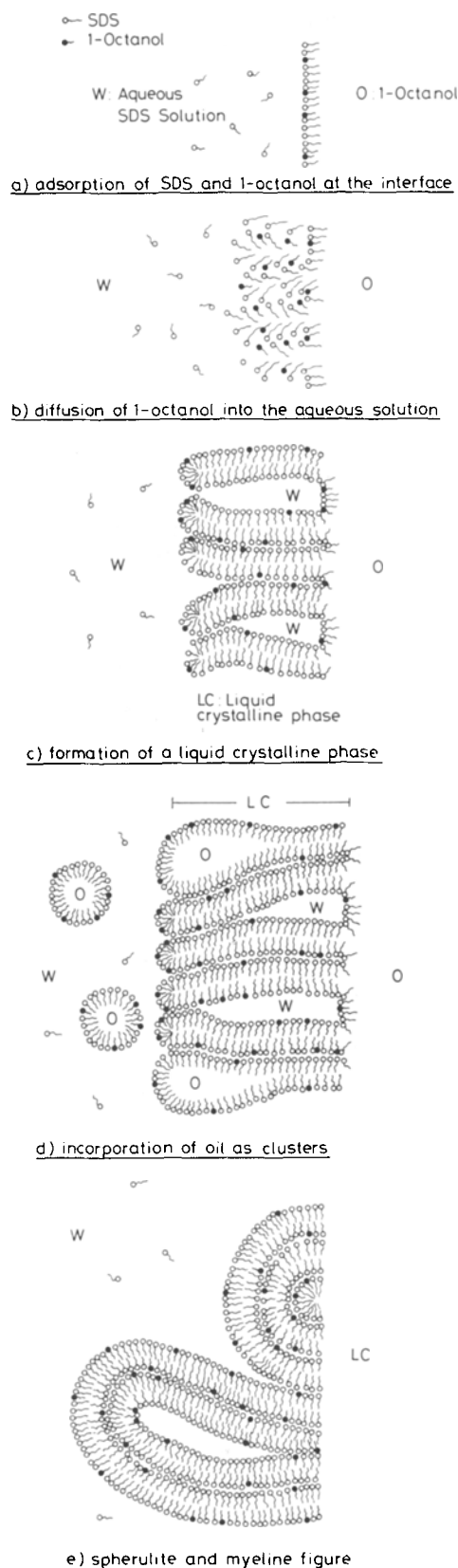
FIG. 13. Schematic illustration of the process of a liquid crystalline phase formation in the system of SDS solution and octanol—a)adsorption of SDS and octanol at the interface; b) diffusion of octanol into the aqueous solution; c) formation of a liquid crystalline phase; d) incorporation of oil into a liquid crystalline phase and emulsification or solubilization of oil; and e) spherulite and myeline figure.

In the systems of other oily substances—hexanol, hexanoic acid and octanoic acid—similar results were obtained.

Process of LC phase formation. From the results obtained above, the process of formation of LC phase is speculated with respect to its structure for the representative case of SDS solution and octanol. Figure 13 shows the schematic illustration of the process of LC phase formation.

When SDS solution comes into contact with octanol initially, the mixed adsorbed film which consists of SDS molecules and octanol molecules is formed (Figure 13a). Diffusion of octanol molecules into the aqueous solution causes the orientation of SDS molecules (Figure 13b). Above a certain SDS concentration a stable layer of LC phase, thick enough to be observed, is formed between solution and oil. At the initial stage of its formation (Figure 13c), the molecular orientation is mainly parallel to the interface of first contact, and water layers exist between the hydrophilic groups of lamellar layers. LC phase at the proceeding stage (Figure 13d) consists of stacks of lamellar layers of SDS and octanol, with the water layers interposed between the hydrophilic groups of the lamellar layers, and separated phases of octanol. At the same time, near the boundary between the LC phase and the aqueous solution, octanol is emulsified or solubilized. As the formation of LC phase is advanced, the molecular arrangement of the lamellar structure becomes disordered because of the diffusion of the molecules. Near the boundary contact with the aqueous solution, parts of LC phase are projected into the solution (Figure 13e), which are the spherulites and the myeline figures.

It is supposed that the basic structure of the LC phase formed between SDS solution and fatty alcohol or fatty acid is similar to that described above.

As mentioned above, the process of LC phase formation includes the incorporation of oil into it and the projection of spherulites and myeline figures into the exterior solution. The latter suggests that since the continuous phase within LC phase is water, LC phase will be dispersed into the solution. Therefore, the process describes the incorporation of oil into the LC phase and the subsequent release of oil into the exterior solution.

Kielman *et al.* (24) have claimed the contribution of LC phase formation to oil removal based on a series of studies which involve diffusion path in surfactant-water-oil systems and detergency performance in the presence of LC phase (26). Detailed discussion on the correlation between the LC phase formation and the mechanism of oily dirt removal needs further investigation, including contact experiments, phase behavior studies and washing experiments. However, our results of the microscopic observations suggest some contribution of the LC phase to detergency.

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