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

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Differential scanning calorimetry (DSC) was applied to determine the composition of a liquid crystalline (LC) phase formed between an aqueous solution of sodium dodecyl sulfate (SDS) and octanol under various conditions. The concentrations of three components, SDS, water, and octanol, contained in the LC phase were determined approximately from the DSC melting peak areas.

The composition of the LC phase varied with time within the LC region in the phase diagram reported in the literature. The change of the octanol concentration in the LC phase was correlated to the process in which octanol is gradually incorporated into the LC phase and then released into the exterior aqueous SDS solution. Increasing temperature facilitated such a process.

Several workers have noted that a liquid crystalline (LC) phase formation between an aqueous surfactant solution and an oily substance makes some contributions to the removal of oily dirt (1-5). In our previous paper (6), we supposed that the process of the LC phase formation consisted of incorporation of oil into the LC phase and the subsequent release of oil from the LC phase into the exterior aqueous solution. The oil concentration incorporated into the LC phase, or the composition of the LC phase, is correlated with how effectively oily dirt is removed.

The composition variation within intermediate phases formed between aqueous surfactant solutions and oily substances has been qualitatively predicted by the use of diffusion paths (7-9). However, only a few experimental results have been reported on the composition of the LC phase (10-11). There has been no systematic information available on the composition of the LC phase formed under various conditions.

Differential scanning calorimetry (DSC) has been used to investigate the interaction and the phase transitions in binary systems composed of nonionic surfactants and water (12-13), the gel structure in ternary systems composed of nonionic surfactants, water, and long-chain alcohols (14-15), and the thermal behaviors of various emulsions (16-17).

In this paper, a new approach is proposed for determining the composition of the LC phase formed between aqueous surfactant solutions and oily substances by application of DSC. It seems reasonable to assume that rapid cooling of the LC phase brings about a frozen phase which keeps the state of mixing of a surfactant, water, and an oily substance in its original LC phase. Based on this assumption, the DSC heating curves of the frozen phase were obtained in order to gather some information on the original LC phase. The composition of the LC phase

was determined from the melting peak area of each component. The change of oil concentration in the LC phase with time was correlated to the process of the oily dirt removal.

EXPERIMENTAL

Materials. The pure anionic surfactant, sodium dodecyl sulfate (SDS) was obtained from Wako Junyaku Kogyo Co. 1-Octanol was obtained from Tokyo Kasei Kogyo Co., and was used as the oily substance. These chemicals were reagent grade materials and used without further purification. The water was deionized and distilled.

Sample Preparations. DSC measurements were made on both sets of samples having known and unknown compositions. The samples having known compositions were prepared by thoroughly mixing known amounts of SDS, water, and octanol. The mixtures were stored at room temperature for 24 hr before sampling for DSC.

The samples having unknown compositions were the LC phases formed between aqueous SDS solutions and octanol. The LC phases were prepared by bringing aqueous SDS solutions and octanol into contact with each other under various conditions.

The optical anisotropy of all samples was examined by use of a Nikon polarizing microscope (Optiphoto-Pol).

DSC measurements. DSC measurements were made on a Seiko Denshi SSC 560. About 1-3 mg of the samples were transferred to the DSC ampoules. The samples were cooled to -50°C at a cooling rate of ca 10°C/min by liquid nitrogen, and subsequently heated from -50 to 30°C at a heating rate of 5°C/min in an atmosphere of nitrogen. Water was used for the temperature and enthalpy calibration.

RESULTS AND DISCUSSION

DSC on the SDS-water-octanol system. First a series of mixtures of known amounts of SDS, water, and octanol was investigated. The compositions of these mixtures are listed in Table 1 with the characterization of those under polarizing microscope. The octanol concentration is held constant in all samples while the SDS concentration is increased with increasing the sample number from O_1 to O_6.

O_1 and O_2 are identified as emulsion by their isotropic appearance. O_3 and O_4 were droplets with slight optical anisotropy and identified as the mixtures of emulsion and liquid crystal. Futhermore, O_5 and O_6 are found to contain lamellar liquid crystal by the characteristic textures [e.g. oily streak and mozaic textures (18)].

DSC heating curves for O_1 -O_6 are given in Figure 1. During heating all these samples show two distinct endothermal peaks, one at about -18°C (melting of octanol) and one at 0°C (melting of ice).

Our DSC method is based on the assumption that rapid cooling of a LC phase brings about a frozen phase which keeps the state of mixing of the components in its original
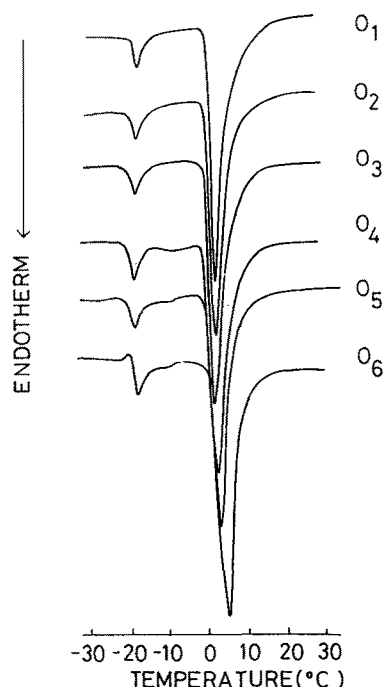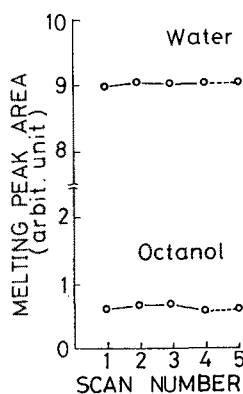
FIG. 1. DSC curves for O_1-O_6.

FIG. 2. Melting peak areas of octanol and water for O_6 on repeated scans. From 1st to 4th scan: cooling rate ca 10°C/min, heating rate 5°C/min; 5th scan: cooling rate ca 3°C/min, heating rate 5°C/min.

LC phase. In order to determine the composition of the LC phase from the DSC thermograms, it is necessary to examine the reproducibility of the thermograms on repeated freezing/melting cycles prior to the detailed investigations.

DSC scans were repeated five times on O_6 as a representative sample. Figure 2 shows the melting peak areas of octanol and water obtained in each scan. As can be seen from Figure 2, the repetition of cooling/heating cycles (from 1st to 4th scan) and a reduction of the cooling rate (5th scan) have no effect on both melting peak areas of octanol and water. The DSC curve was also reproducible on each scan.
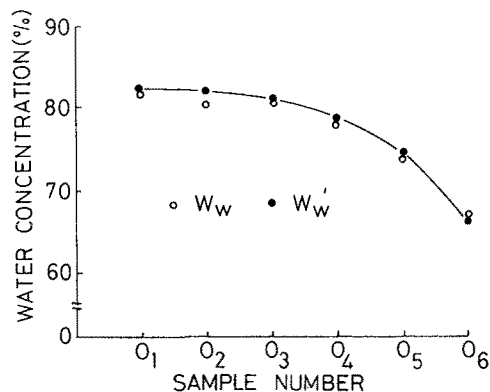

FIG. 3. Comparison of the water concentration calculated from the DSC peak area (W_w) with that shown in Table 1 (W_w') for O_1-O_6.

As shown in Figure 1, the samples O_1-O_3 containing lower SDS concentrations, show no other peaks except for the melting peaks of octanol and water. This result agrees with the fact that these samples are composed of almost only emulsion, i.e., isotropic droplets of octanol and water.

On the other hand, the samples O_4-O_6 containing higher SDS concentrations, show a broad endothermal peak over a wide temperature range between the melting peaks of octanol and water. As mentioned above, these samples contain liquid crystal to some extent. Therefore, the broad endothermal peak detected in the DSC curves for these samples is supposed to be due to the presence of the liquid crystal composed of SDS, water, and octanol.

In addition, a slight exothermal peak is detected below the melting point of octanol in the DSC curves for O_5 and O_6. This peak is probably due to the reorientation of octanol molecules, namely transition from glassy to crystalline state during heating.

From the melting peak areas of octanol and water, the concentrations of each component contained in the mixtures O_1-O_6 were approximately calculated. The area of the broad endothermal peak that may be attributed to the presence of liquid crystal in O_4-O_6 was neglected because it is less than 5% of the total peak area, and also because the composition of the liquid crystal cannot be estimated.

Figure 3 shows the water concentration in each sample. In all samples the water concentration calculated from the melting peak area of water (W_w) is in good agreement with W_w' shown in Table 1.

The octanol concentration in each sample is shown in Figure 4. The octanol concentrations calculated from the melting peak area of octanol (W_o) are compared with W_o' shown in Table 1. The difference between W_o and W_o' is a little larger than that between W_w and W_w'. This result may be attributed to the greater sensitivity of octanol to various factors during cooling and heating. W_o tends to be more or less underestimated than W_o', especially in O_6, which probably contains the largest amount of liquid crystal.

These results support the usefulness of the DSC method proposed in this work. It is concluded that in the SDS-water-octanol system, the concentrations of water (W) and octanol (W_o) in a mixture can be approximately determined from the melting peak area of each

TABLE 1

Mixtures of Known Compositions

Sample no.	Composition (wt %)			Characterization under polarizing microscope	
	water	octanol	SDS		
	W_w'	W_o'	W_s'		
O_1	82.4	17.2	0.4	isotropic	emulsion
O_2	82.0	17.2	0.8	isotropic	emulsion
O_3	81.1	17.2	1.7	droplets, slightly anisotropic	emulsion and liquid crystal
O_4	78.7	17.2	4.1	droplets, anisotropic (thread-like texture)	emulstion and liquid crystal
O_5	74.5	17.2	8.3	anisotropic (thread-like, oily streak, mozaic textures)	contains lamellar liquid crystal
O_6	66.2	17.2	16.6	anisotropic (thread-like, oily streak, mozaic textures)	contains lamellar liquid crystal

FIG. 4. Comparison of the octanol concentration calculated from the DSC peak area (W_o) with that shown in Table 1 (W_o') for O_1-O_6.

FIG. 5. DSC curve for the LC phase formed between 20% aqueous SDS solution and octanol 24 hr after the contact at 20°C.

component, whether liquid crystal exists or not in the mixture. Although SDS shows no remarkable thermal change over the scanning temperature range, the concentration of SDS (W_s) can be determined by deducting W_w and W_o from the total, i.e. 100%. The influences of some phase transitions of liquid crystal, the reorientation of octanol molecules, and enthalpy changes due to mixing are negligible for approximately determining the composition of the SDS-water-octanol mixtures.

Composition of a LC phase formed between aqueous SDS solutions and octanol. When an aqueous SDS solution is brought into contact with octanol under certain conditions, a viscous phase with optical anisotropy (namely a LC phase) appears between the aqueous solution phase and the octanol phase. The composition of the LC phase is unknown. DSC measurements were made on the LC phases formed under various conditions in order to determine the compositions of those.

A typical DSC heating curve for a LC phase is shown in Figure 5. The curve resembles those for the samples O_4-O_6 shown in Figure 1.

As can be seen from Figure 5, the DSC curve of the LC phase shows the respective melting peaks of octanol and water in spite of the remarkable birefrigence detected for the LC phase. Furthermore, the melting point depression is not found for both melting peaks of octanol and water. The DSC curve suggests that the LC phase formed between an aqueous SDS solution and octanol is predominately composed of isotropic domains of octanol and water.

The broad endothermal peak between the melting peaks of octanol and water is similar to those detected in the DSC curves for O_4-O_6, and probably attributed to the ternary liquid crystal composed of SDS, water, and octanol. The area of this broad endothermal peak is less than 5% of the total peak area. These results suggest that a small amount of the real ternary liquid crystal and the isotropic domains of octanol and water constitute the
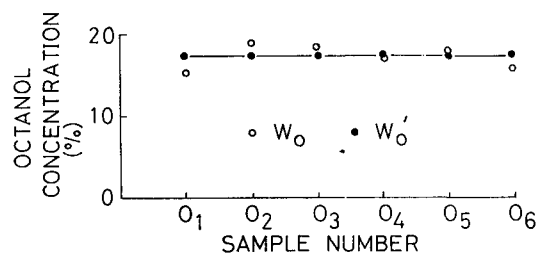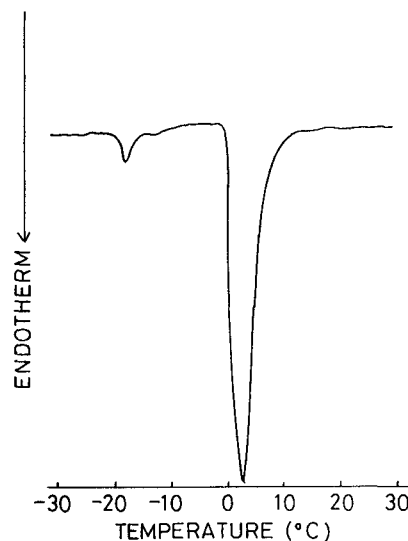
apparent LC phase found between the aqueous solution phase and the octanol phase. This speculation is consistent with the result obtained in the penetration experiment of water-soluble and oil-soluble dyes into the LC phase in our previous paper (6).

As described above, the compositions of the SDS-water-octanol mixtures such as the apparent LC phases can be approximately determined from the melting peak areas of octanol and water. On the other hand, octanol is supposed to be incorporated into the LC phase not only as monomolecules that participate in the constitution of the real liquid crystal, but also as isotropic domains in the process of the LC phase formation. In discussion about how effectively oily dirt is removed through the LC phase formation, the composition of the apparent LC phase containing isotropic domains of octanol and water besides the real liquid crystal seems practically more important than the composition of the real liquid crystal alone. Therefore, it seems worthwhile to determine the composition of the apparent LC phase by the DSC method proposed in this work.

Table 2 shows good reproducibility of the composition of the LC phase formed under a certain representative condition—20% aqueous SDS solution/octanol, 24 hr after the contact at 20°C. Water occupies the largest por-

TABLE 2

Reproducibility of the Composition of the LC Phase Formed Between 20% Aqueous SDS solution and Octanol 24 hr After the Contact at 20°C

Repetition no.	Composition (wt %)		
	Water W_w	Octanol W_o	SDS W_s
1	63.9	14.8	21.3
2	58.8	17.6	23.6
3	60.9	17.2	21.9
Average	61.2	16.5	22.3

tion, ca 61%, of the LC phase. This fact implies that water constitutes a continuous phase within the apparent LC phase. On the other hand, the SDS concentration in the LC phase is ca 22%, a little higher than the initial SDS concentration in the aqueous solution. Namely, SDS is more concentrated in the LC phase than in the exterior aqueous solution.

The composition change of the LC phases formed under various conditions was investigated. In Figure 6, the compositions of the LC phases formed between 5 and 10% aqueous SDS solutions and octanol at 20°C are plotted in the phase diagram for the SDS water-octanol system reported by Kasai et al. (19).

Kielman et al. have predicted the composition of the LC phase formed between two isotropic liquids in the Triton X 100-water-decanol system by application of the diffusion path theory (7). Our work provides the valuable experimental data for the composition of the LC phase formed in the SDS-water-octanol system. As can be seen

from Figure 6, the composition of the LC phase varies with time within the LC region in the phase diagram.

Kasai et al. (19) have supposed that, in the LC region for the SDS-water-octanol system, apparent liquid crystalline phases containing real liquid crystall and isotropic solutions exist. This speculation has been supported by determining the distribution of an inorganic electrolyte between free and bound water in the apparent LC phase. Furthermore, their speculation is consistent with ours on the LC phases formed between aqueous SDS solutions and octanol.

It is supposed that the composition change shown in Figure 6 results from the change in the amounts of real ternary liquid crystal and isotropic octanol and water within the apparent LC phase. It needs further investigations to interpret the present data by use of diffusion paths.

In Figure 7, the octanol concentration in the LC phase shown in Figure 6 is replotted against time. In both SDS concentrations, the octanol concentration in the LC phase is highest about 2 hr after the contract. It decreases steeply, and then remains almost constant with the elapse of time. The change of the octanol concentration in Figure 7 can be interpreted as the result of the incorporation of octanol into the LC phase and the subsequent release of octanol from the LC phase into the exterior aqueous solution. Such a process is correlated to the oily dirt removal via the LC phase formation between aqueous surfactant solutions and oily substances. The steep decrease of the octanol concentration may be attributed to the remarkable growth and the subsequent collapse or dispersion of spherulites and myeline figures which were observed on the boundary between the LC phase and the exterior aqueous solution (6).
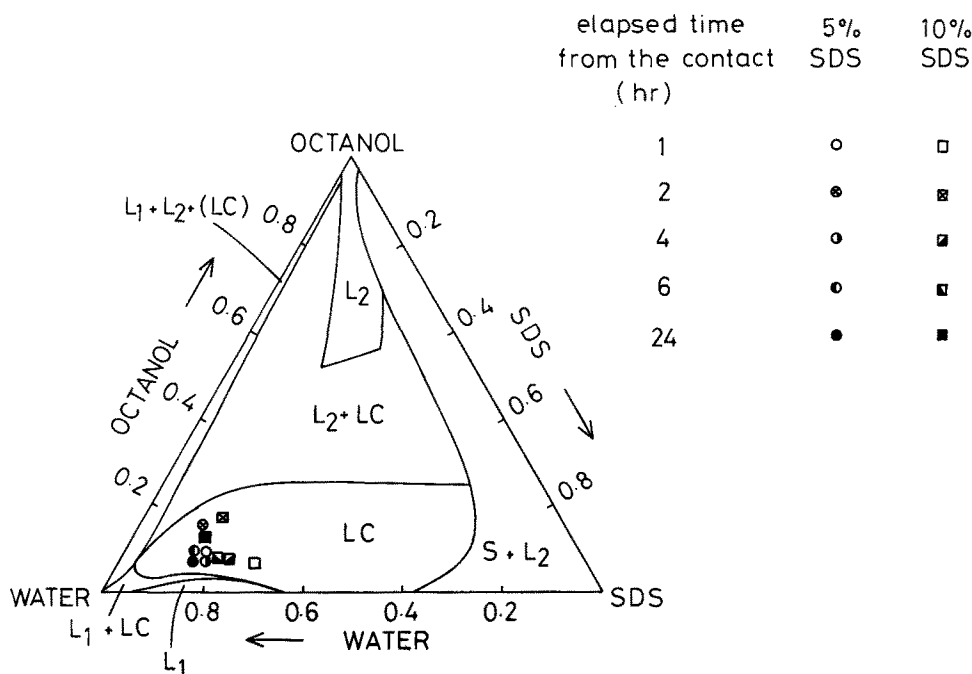

FIG. 6. Composition change of the LC phase formed between 5 or 10% aqueous SDS solution and octanol at 20°C. Plotted in the phase diagram for the SDS-water-octanol system reported in the literature (19). S:solid SDS, LC:liquid crystalline phase, L_1:aqueous SDS solution in which octanol being solubilized, L_2:octanol in which SDS and water being solubilized.
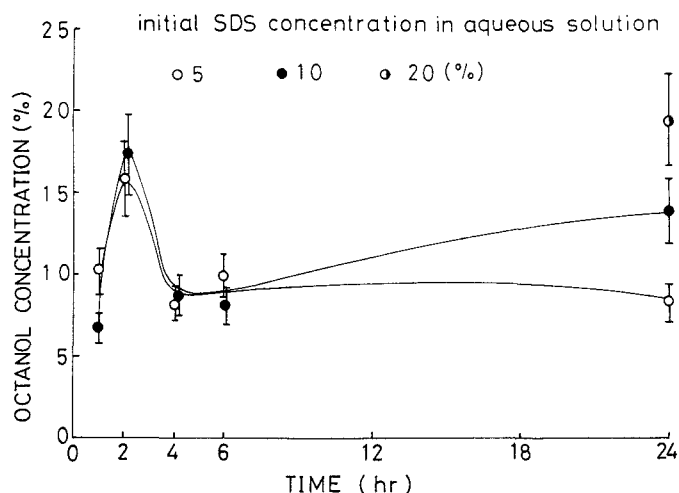
FIG. 7. Octanol concentration in the LC phase formed between 5-20% aqueous SDS solution and octanol at 20°C plotted against the elapsed time from the contract.
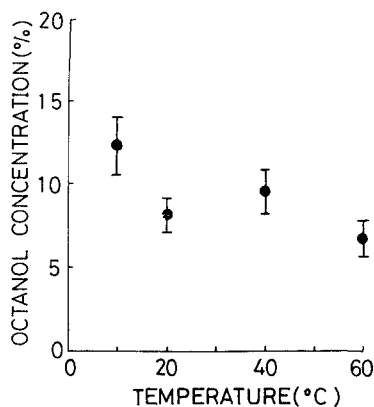

FIG. 8. Octanol concentration in the LC phase formed between 5% aqueous SDS solution and octanol 4 hr after the contact at different temperatures.

Next, temperature effect on the oily dirt removal via the LC phase formation was investigated with respect to the composition of the LC phase. Figure 8 shows the octanol concentration in the LC phase formed between 5% aque-

ous SDS solution and octanol 4 hr after the contact at different temperatures. The octanol concentration in the LC phase decreases with an increase in temperature. This result is supposed to be caused by the facilitated release of octanol from the LC phase into the aqueous solution at higher temperatures.

It can be concluded that the composition of the LC phase formed between aqueous SDS solutions and octanol varies with time and temperature. The change of the octanol concentration in the LC phase with time is correlated to the process of the oily dirt removal. A detailed discussion on the role of real liquid crystal in the oily dirt removal needs further investigations.

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