Complex Formation in a Ternary System Composed of Lauroamphoglycinate, Oleic Acid, and Water

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ABSTRACT: The formation of a complex, composed of lauroamphoglycinate (LG), oleic acid (OA) and water, was investigated, and this system was applied to emulsification. The complex was formed in the water-rich area (more than 90% in this system) at a molar ratio of OA to LG from 1 to 3, where two-phase systems of water and the complex existed. The interaction between LG and OA, both in the aqueous solution and at the interface of liquid paraffin dissolving the OA and LG solution, was studied by pH measurements and interfacial tension measurements, respectively. The results implied that LG and OA were linked stoichiometrically, both in aqueous solution and at the interface, and formed complexes. X-ray diffraction patterns and the strong hydrophobicity showed that the equimolar complex composed of LG, OA, and water was a liquid crystal with a reversed hexagonal structure. The reversed hexagonal liquid crystal was capable of solubilizing a certain amount of liquid paraffin in its alkyl group parts while maintaining its hexagonal structure. These results suggest the possibility to prepare a W/O-type emulsion by using the liquid crystal formed by LG, OA, partial liquid paraffin, and water as the continuous phase. The authors could obtain a stable W/O emulsion without coalescence of the water droplets that contained a substantial amount of water (approximately 90%). Furthermore, various types of emulsions, O/W, W/O, W/O/W, could be prepared by changing the ratio of LG and OA.

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KEY WORDS: Amphoteric–fatty acid system, highly concentrated W/O emulsion, liquid crystal.

Many studies have reported the interaction between surfactants and oily substances, such as higher alcohols and higher fatty acids. There have been some especially interesting studies on mixed systems of cationics–alcohol (1,2), cationics–fatty acid (2,3), anionics–alcohol (2,4–6), and anionics–fatty acid (2,6–8). Most authors have reported vesicular liquid crystal formation and a conditioning effect of the liquid crystal on hair. However, little is known about the mixed system of amphoterics–oily substance. In this paper, the authors describe the formation of a liquid crystal in a mixed system of an amphoteric surfactant, higher fatty acid, and water. There have been some reports (9–11) in which the liquid crystals have been applied to emulsification because it prevents coalescence of the emulsion particles. The surfactants used in these systems were only reported to form liquid crystals that are suitable for the formation of either an O/W or a W/O emulsion. Because these liquid crystal are rigid, a polyalcohol, such as glycerol, is often used during the preparation of emulsions to improve the efficiency of emulsification by softening the system. In the cosmetic industries, however, there are instances where a polyalcohol is said to give a bad feel to the skin. In the authors' system, LG and OA are dissolved in water and an oil, respectively. If a liquid crystal is formed at the oil/water interface, it is possible to prepare an emulsion easily without using glycerol. Using this perspective, the authors attempted to produce emulsions with this system. With this system as emulsifier, various types (W/O, O/W, W/O/W) of emulsions, especially highly concentrated W/O emulsion, could be prepared. This paper describes the properties of the complex and its application as an emulsifier.

MATERIALS AND METHODS

Materials. The amphoteric surfactant and fatty acid used were commercially available (Table 1). A 28.5% aqueous solution of the amphoteric surfactant (pH = 8.4) was lyophilized and used in this study.

Preparation of emulsion. A solution of OA in liquid paraffin (LP) was stirred in a homogenizer (model L, Tokushu Kika Kogyo Co., Ltd., Osaka, Japan) at 5000 rpm, and an aqueous solution of LG was slowly added to form an emulsion at 25°C. The emulsion type was identified by the electric conductivity method.

IR measurement. Infrared spectra were measured with a Fourier-transform infrared spectrophotometer (Qualimatic, Bio-Rad Co., Ltd., Hercules, CA) in the range of 4000–400 cm^{-1} to identify the site of the interaction between LG and OA to form the complex.

X-ray measurement. A Rigaku-Denki RV-3 X-ray diffractometer (Osaka, Japan) was used to characterize the structure of the complex. Because X-ray diffraction of the liquid crystal indicated a peak at a relatively low angle, it was measured from 0° to 5° at a 2θ angle of 1°/min. The surface of the sample was covered with polyethylene film to prevent water in the sample from volatilizing.

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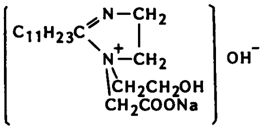
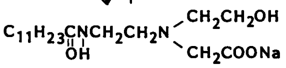
TABLE 1
Amphoteric Surfactant and Fatty Acid Used for Study

	Type	Structure	Abbreviation	Name
Amphoterics	Dodecyl imidazolinium betain		IB	Obazolin-662N Toho chemical Industry Co., Ltd.[a]
		↓↑		
	Lauroamphoglycinate	 $C_{11}H_{23}\underset{OH}{\underset{\|}{C}}NCH_2CH_2N\begin{cases}CH_2CH_2OH\\CH_2COONa\end{cases}$		
Fatty acid	Oleic acid	$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH$	OA	Extraolein90 Nippon Oils and Fats Co., Ltd.[b]

[a] Tokyo, Japan.
[b] Hyogo, Japan.

Interfacial tension measurement. Samples were prepared by carefully pouring a liquid paraffin solution of OA into an aqueous solution of LG. Interfacial tension of the prepared samples was measured at 25°C after 30 min with a Wilhelmy-type Shimadzu ST-1 tensionmeter (Tokyo, Japan).

PH measurement. The pH of the samples was measured at 25°C with a Horiba F-16 pH meter after 20 h of stirring.

RESULTS AND DISCUSSION

Complex formation. A rigid whitish complex was immediately formed on mixing the LG aqueous solution with OA and was separated from water. Figure 1 is a photograph of the complex formed in the system, where the molar ratio of OA

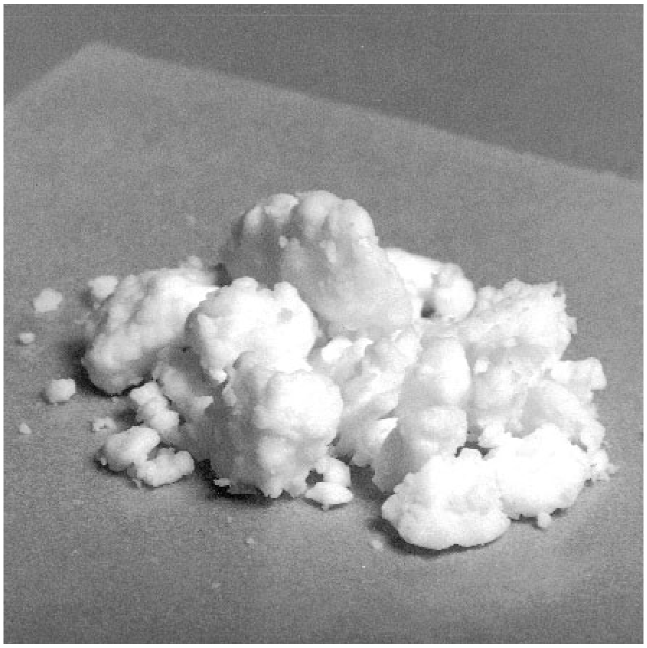


FIG. 1. Photograph of the complex with a molar ratio = 1, formed between the LG aqueous solution and OA.

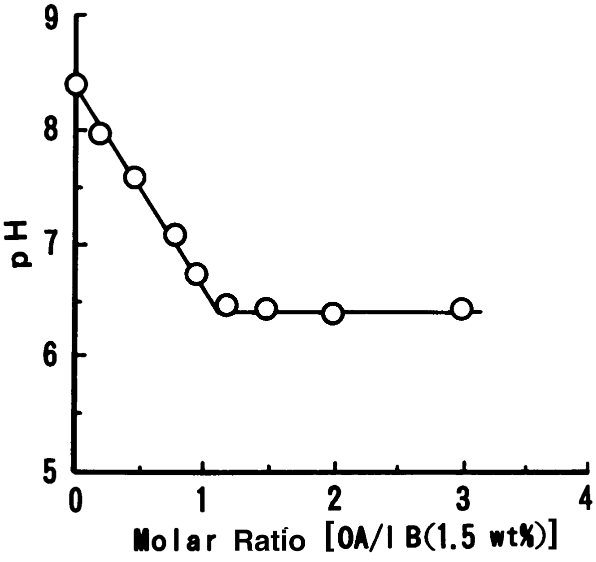


FIG. 2. Changes in pH as a function of the molar ratio of OA to LG (1.5 wt%).

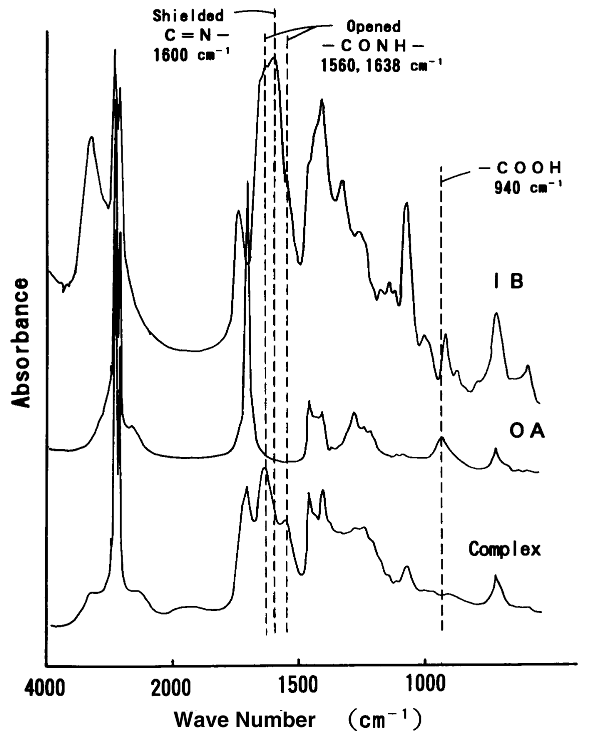


FIG. 3. IR spectra of LG, OA, and the complex with a molar ratio = 1.

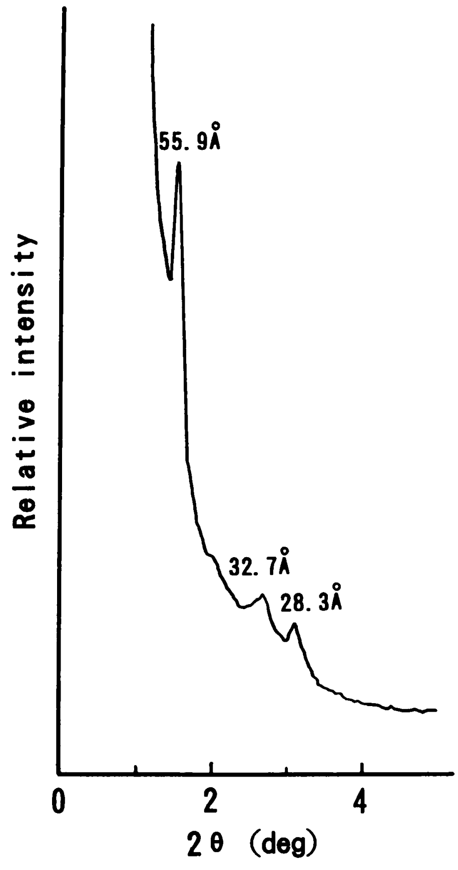


FIG. 4. X-ray diffraction pattern of equimolar complex, formed by LG, OA, and water.

to LG is 1:1 and the amount of water is 95 wt%. This rigid complex was also formed at molar ratios from 1 to 3, had strong hydrophobicity, and showed anisotropy in a microscope under polarized light. At a molar ratio of more than 3, OA was separated from this system as a liquid. Generally, a liquid crystalline phase of surfactants appears at concentrations of more than approximately 40 wt% (9). In the system used, at low concentrations (below 5 wt%) of total LG and OA, liquid crystals were formed. This may be related to the fact that the solubility of water in the liquid crystal is small.

Figure 2 shows the changes of pH when adding OA to a 1.5 wt% LG aqueous solution. Samples with a molar ratio greater than 1 were two-phase systems of water and liquid crystals. The pH values decreased with an increase in the molar ratio and became constant at a molar ratio of about 1. These results indicate that lowering of the pH value is due to an increase in dissociated protons from the carboxyl group of the OA molecule by complex formation.

Figure 3 shows the IR spectrum of the complex with a molar ratio of 1. The IR spectrum of this complex is different from the superposition of the component spectra of the complex. It is already known that LG in solution can adopt both a shielded and open imidazoline ring structure; the absorption of the former appears at 1600 cm^{-1}, and the amido peaks of the latter are at 1638 cm^{-1} and 1560 cm^{-1} (12). The LG peak at 1600 cm^{-1} disappeared upon mixing with OA, indicating that the imidazoline structure of LG in the complex has an open ring. The OH absorption near 940 cm^{-1} of OA also disappeared; therefore, the authors believe that OA combines with LG at the carboxyl group portion of OA. These results showed that OA and LG are combined in aqueous solution to form equimolar ion-pairs that contain a small amount of water and form liquid crystals.

X-ray diffraction was measured to clarify the structure of the liquid crystal. Low-angle X-ray diffraction patterns of the complex at a molar ratio of 1 are shown in Figure 4. Three

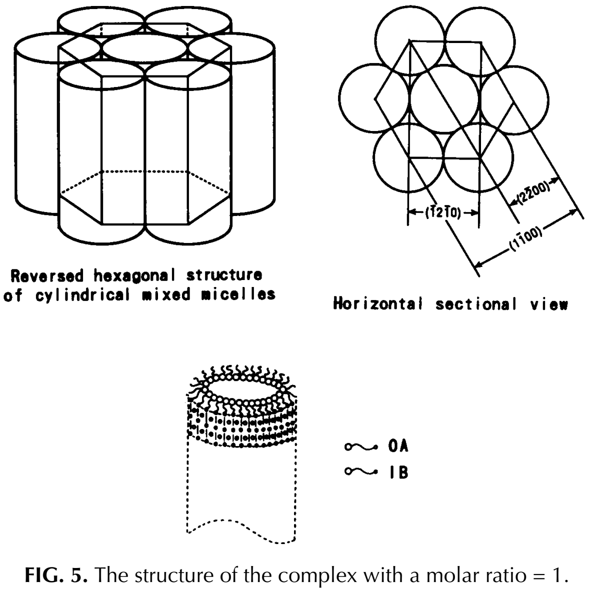


FIG. 5. The structure of the complex with a molar ratio = 1.

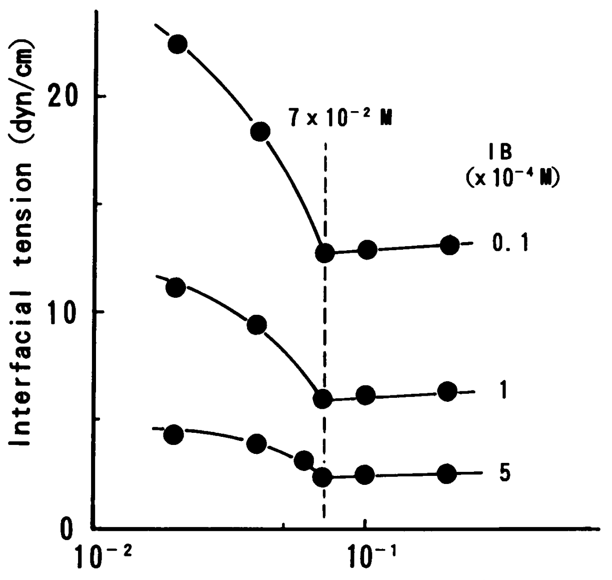


FIG. 6. Relationship between interfacial tension and OA concentration in LP versus LG solutions of various concentrations at 25°C.

clear peaks are observed. It was confirmed from the Bragg spacings at the ratio of $1:1/3^{1/2}:1/2$ that the complex has a hexagonal structure. From the X-ray diffraction results and the strong hydrophobicity, the structure of the liquid crystal was considered to be a reversed hexagon, consisting of cylindrical mixed micelles that are formed at a molar ratio of 1 (Fig. 5). These results suggest that the complexes formed between the LG solutions and OA have a reversed hexagonal structure and that the formation of the complex goes to completion at equimolar composition. Upon adding more OA, OA was solubilized in the hydrophobic portion of the reversed hexagonal structure as an oil up to a molar ratio of 3. At a molar ratio greater than 3, OA was separated from the system, and OA, reversed hexagonal liquid crystals, and water coexisted.

Interfacial tension measurements were conducted to determine whether or not OA and LG combined to form the complex stoichiometrically at the interface between the oil and water also.

Complex formation at oil/water interface. Figure 6 shows the relationship between the interfacial tension for various concentrations of LG below the CMC (8×10^{-4} M) and OA concentration in LP. The interfacial tension between LP and the LG solution was markedly reduced by the addition of OA. This indicates an electrostatic interaction between OA and LG at the LP/water interface. Figure 7 shows the relationship between the interfacial tension and LG concentration when the LG concentrations were varied with a constant OA concentration of 7×10^{-2} M, corresponding to the break point in Figure 6, above which OA is adsorbed to saturation at the LP/water interface.

Gibbs' adsorption isotherm was applied to a curved portion below the concentration of the break points shown in Figures 6 and 7, to obtain the adsorption amounts of LG and OA at the LP/water interface:

$$\Gamma = -1/RT \times d\gamma/d\ln C \qquad [1]$$

where Γ, C, γ, R, and T are surface excess, the concentration, interfacial tension, gas constant, and absolute temperature, respectively. The amount of OA adsorbed was calculated from the slope at an OA concentration of 7×10^{-2} M for the various concentration curves of LG shown in Figure 6. The amount of LG adsorbed was calculated from the slope at various LG concentrations for the curve shown in Figure 7.

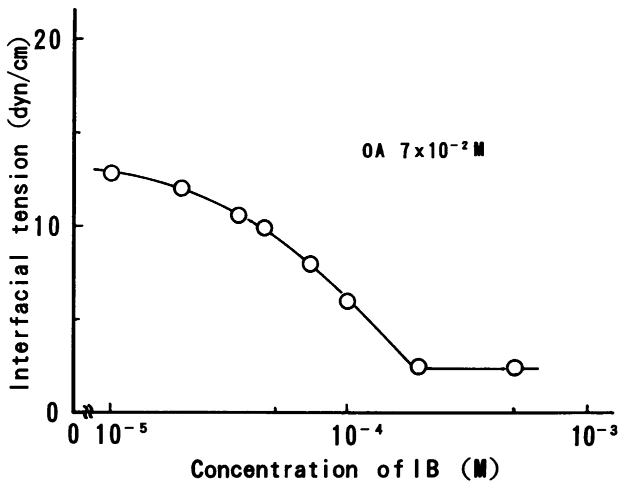


FIG. 7. Relationship between interfacial tension and LG concentration when OA concentration is constant.

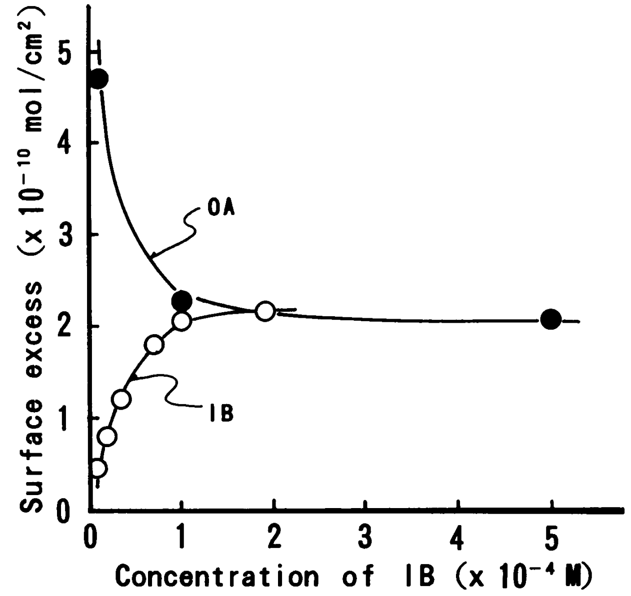


FIG. 8. Adsorption amount of LG and OA at LP/water interface.

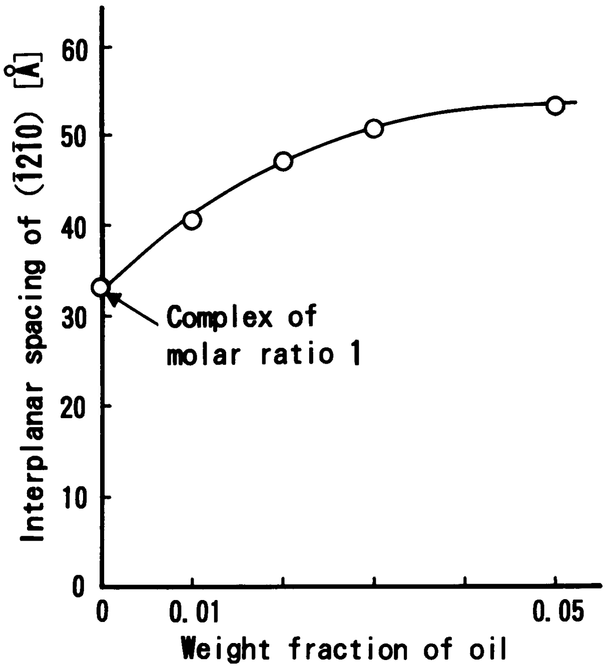


FIG. 9. Effect of LP on the interplanar spacing of the complex with a molar ratio = 1.

The values of the adsorbed amounts of LG and OA, obtained by Gibbs' equation, are plotted in Figure 8. The adsorbed amounts of LG at the LP(OA)/water interface gradually increased with the LG concentration as it was added to the water phase while the OA concentration was constant. On the other hand, adsorption of OA decreased with an increase in the LG concentration, and the surface excess of LG became constant at an LG concentration of more than about 2×10^{-4} M. The results that showed the adsorption ratio of OA to LG to be approximately 1:1 at the LP/water interface, also showed that LG and OA are linked stoichiometrically at the oil/water interface. Thus, the binding power between LG and OA is superior to the solubilizing power of OA in LP.

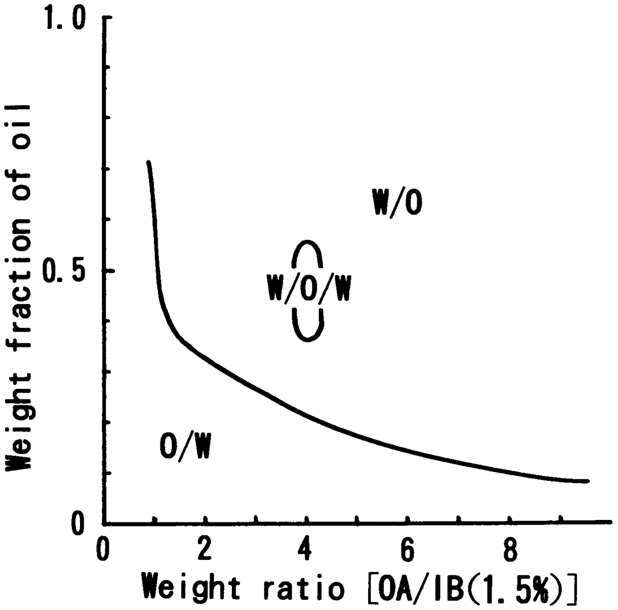


FIG. 10. Diagram of emulsion type for the four-component system consisting of LG, OA, LP, and water.

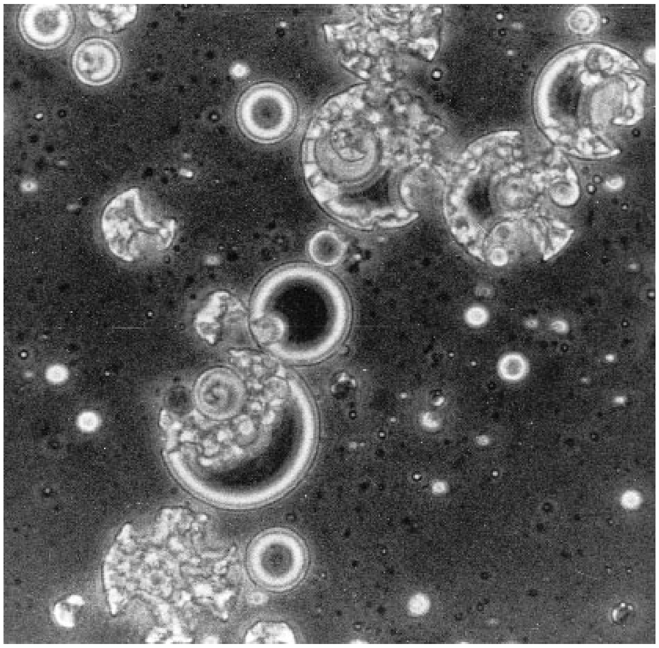


FIG. 11. Photomicrograph (800×) of a W/O/W emulsion prepared from 1.5 wt% LG, 6 wt% OA, 46.25 wt% LP, and 46.25 wt% water.

The effect of LP on the interplanar spacing of the complex with a molar ratio of 1 is shown in Figure 9. The interplanar spacing of the complex with a molar ratio of 1 increased to about 50 Å as the LP concentration increased. The liquid crystal that contained LP had strong hydrophobicity. In the system in which the weight fraction of LP was above 0.05, LP was separated from the system. X-ray measurements confirmed that the structure of the liquid crystal with LP was also a reversed hexagon. The authors expect that this complex can be used as an emulsifier and that the liquid crystal, including partial water and oil, contributes to the stabilization of emulsions.

Emulsifying characteristics of the complex. A diagram of the emulsion type for the four-component system, consisting of LG, OA, LP, and water, is shown in Figure 10. The emulsion type changes depending on the mixing ratio of LG and OA and that of water and LP. The molar ratio of 1, at which LG and OA form ion-pairs, was the boundary of O/W and W/O emulsions. The complex acts as a emulsifier and the emulsion type can be selected because the hydrophile–lipophile balance (HLB) of the complex can be controlled by changing the mixing ratio of LG and OA.

An O/W emulsion, prepared at a molar ratio of less than 1, showed slight anisotropy in a microscope under polarized light that suggested the participation of the liquid crystal in this emulsification. However, it is difficult to state that the liquid crystal dispersed in the system is a reversed hexagonal liquid crystal. It could be a lamellar liquid crystal composed of ion-pairs of LG and OA, and an excess of LG, water, and oil. These must be investigated further.

A W/O emulsion, containing a substantial amount of water (approximately 90 wt%), was formed when prepared at a molar ratio near 9. For an ordinary W/O emulsion, an increase in the internal water phase causes instability of the emulsion because the water droplets coalesce easily. In fact, it has been reported (13) that highly concentrated W/O emulsions were prepared with a variety of low-HLB emulsifiers that decreased in rigidity with time due to the enlargement of the emulsion particles caused by coalescence or by molecular diffusion (called “Ostwald ripening”).

In the prepared emulsions, stability toward the coalescence of water droplets improved somewhat with an increase in the internal water phase. The reversed hexagonal liquid crystal could solubilize LP up to 5 wt%. Because the amount of LP is small in concentrated W/O emulsions, all of it is solubilized into the reversed hexagonal liquid crystal. The continuous phase becomes just a reversed hexagonal liquid crystal phase; the emulsion type in this system is a water-in-reversed hexagonal liquid crystal emulsion. This is the reason why the emulsion is stable against the coalescence of water droplets. In fact, concentrated W/O emulsions with over 90 wt% of the internal phase were stable for one month at 50°C without enlargement of the water droplets due to coalescence and creaming. Water could no longer be dispersed into the reversed hexagonal liquid crystal at more than 90 wt% of internal water phase, and was separated from the system to eventually produce O/W emulsions.

Figure 11 is a photomicrograph of the W/O/W emulsion prepared in the LP/complex/water system. When the W/O/W emulsion is diluted with water, the pits from which water had been ejected remain intact. Thus, this liquid crystal is oriented on the interface between the water and oil and functions as a strong interfacial film. As for the liquid crystal, formed between the amphoteric surfactant solution and fatty acid, and the mechanism of this unique emulsification, the authors will investigate them in detail later.

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