Colloid Polym Sci 273:584–589 (1995)

ORIGINAL CONTRIBUTION

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Phase behavior of sucrose monoalkanoate in a water-long-chain alcohol system

Received: 22 September 1994
Accepted: 14 December 1994

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Abstract Phase diagram of a water/sucrose monododecanoate (SE)/hexanol system was determined at 30 °C. Aqueous micellar, reverse micellar, normal hexagonal liquid crystalline, and lamellar liquid crystalline phases appear in the phase diagram. The change in interlayer spacing and interfacial section area of surfactant in the liquid crystalline phases was investigated by small-angle x-ray scattering. Upon addition of water, the section area and the radius of cylindrical aggregates are almost constant in a hexagonal liquid crystal, whereas the distance between each cylinder is separated on the water-SE axis. The interlayer spacing slightly decreases or is almost unchanged on the surfactant-hexanol axis, because alcohol molecules penetrate into the palisade of bilayers. Although the average section area decreases with increasing alcohol content, each section area of SE and alcohol molecules are kept constant. Since the interfacial section area of alcohol is less than the section area of hydrocarbon chain, the phase transition from lamellar liquid crystal to reverse micelle occurs in an alcohol-rich region.

Key words Sucrose monoalkanoate – lamellar liquid crystal – small-angle x-ray scattering

Introduction

Sucrose monoalkanoates (SE) are unique biocompatible surfactants used in foods, cosmetics, medicines, etc. [1, 2]. They are strongly hydrophilic and forms aqueous micelles over a wide range of compositions in water. Sucrose monoalkanoates also form a hexagonal liquid crystal at high concentration of the surfactant in water. Unlike ordinary nonionic surfactants, SE is hydrophilic even at high temperature [3].

Ordinary polyoxyethylene-type nonionic surfactants do not form reverse micelles in hydrocarbons in the absence of water [4]. On the other hand, due to the strong interaction of hydrophilic parts, sucrose monoalkanoate forms a lamellar liquid crystal or reverse micelles in oil [3, 5]. Although the phase behavior of SE in binary SE-water or SE-oil systems was studied by Herrington [6], that of SE in a ternary water/SE/oil system has not been extensively investigated.

Recently, it was found that SE forms a unique self-organizing structure, reverse vesicles, consisting of closed bimolecular layers in nonpolar media [7–9]. Reverse vesicles are the counter structure of normal vesicles or liposomes formed in water. Reverse vesicles are essentially the dispersion of lamellar liquid crystal swelling a considerable amount of oil in their bilayers. The stability of reverse vesicles is highly dependent on the content of added water

[10]. It is considered that the structure of liquid crystal is related to the stability and the mechanism of the formation of reverse vesicles. Mixtures of SE and polyoxyethylene-type nonionic surfactant or long-chain alcohols are used for the formation of reverse vesicles. However, the whole phase behavior in a water/sucrose monoalkanoate/alcohol system has not been studied extensively.

In this context, we have investigated the phase behavior and the structures of liquid crystals in a water/sucrose monododecanoate/hexanol system by means of phase study and small-angle x-ray scattering (SAXS).

Experimental section

Materials

Two kinds of sucrose monododecanoate were supplied from Mitsubishi Chemical Corporation. L-1695 is a commercial sucrose monododecanoate and its monofatty acid content is above 80%. SM-1200 is a reagent-grade monododecanoate and its monoester content is above 99%. Both surfactants were dehydrated using P_2O_5 under vacuum. L-1695 was used for determining phase diagrams and SM-1200 was used for the SAXS experiment. The phase boundaries of lamellar and hexagonal liquid crystals are almost the same for both systems. Extra-pure-grade hexanol was obtained from Tokyo Kasei Kogyo Co. All the chemicals were used without further purification.

Phase diagram

The phase diagram was constructed on the basis of direct visual inspection of the samples and by polarizing microscopy. All the samples were examined against crossed polaroids for homogeneity and birefringence. Characteristic textures of liquid crystals were detected under the polarizing microscope (Nikon, X2F-NTF-21) [11].

Small-angle x-ray scattering

Interlayer spacing was measured using small-angle x-ray scattering (SAXS), performed on a small-angle scattering goniometer with an 18 kW Rigaku Denki Rotating anode generator (RINT-2500) at ~ 30 °C [4]. The fluid samples were flame-sealed in capillary tubes of 1.5-mm (o.d.). The very viscous samples were lapped by plastic films for the measurement (Mylar seal method). Hexagonal and lamellar liquid crystalline phases are distinguished by the SAXS peaks. The ratios of interlayer spacings from first and second peaks are $1:1/\sqrt{3}$ for hexagonal type and $1:1/2$ for lamellar type, respectively [12].

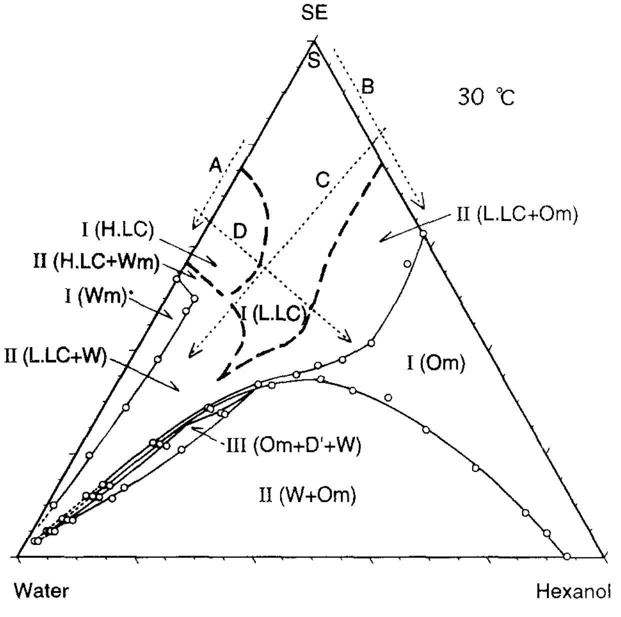
The wide-angle x-ray scattering measurement shows a wide diffuse reflection with a position corresponding to a spacing of 0.45 nm for both hexagonal and lamellar liquid crystals in the present system. This result strongly supports that hydrocarbon chain of sucrose monoalkanoate is in a liquid state [12].

Results and discussion

Phase diagram of a water/sucrose monododecanoate (SE)/hexanol system

Phase diagram of water/SE/hexanol system was determined at 30 °C and the result is shown in Fig. 1. SE is a hydrophilic surfactant and forms aqueous micellar solution phase up to 54% on the water-surfactant axis. In a concentrated region on the surfactant-water axis, a hexagonal liquid crystalline phase (H.LC) is formed. There is a two-phase region between H.LC and a single micellar phase, but the region is not indicated in Fig. 1. In a more

Fig. 1 Phase diagram of water/sucrose monododecanoate (SE)/hexanol system at 30 °C. I, II, and III indicate single-, two-, and three-phase regions, respectively. Wm is an aqueous micellar solution phase and Om is an isotropic alcohol phase. H.LC and L.LC mean hexagonal and lamellar liquid crystals, respectively. S means "solid present" region. The single Om region is extended toward a water apex and forms a three-isotropic-phase region indicated by Om + D′ + W although the Om and D′ phases are connected. W means excess water

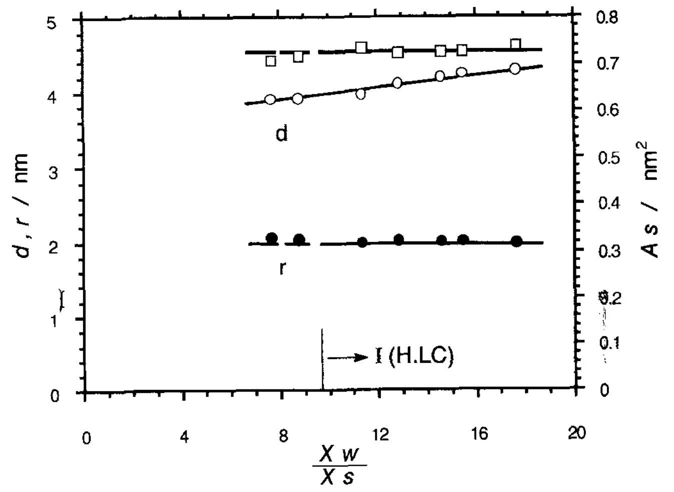


concentrated region, gel phase or solid surfactant are present in the vicinity of the surfactant apex [6], but the boundary was not determined.

SE forms an isotropic solution phase (Om) on a surfactant-hexanol axis. Since SE is a very hydrophilic surfactant, reverse micelles may be present in the Om phase [4]. In the main miscibility gap (Om + W) of the ternary system, a water phase is separated from the reverse micellar solution phase extended from the surfactant-alcohol axis, and three-phase region (Om + D′ + W) appears along the elongated single phase region. The isotropic middle phase (D′) is considered to be a surfactant phase whose structure is different from reverse micellar solution phase, because it coexists with alcohol and water phases. But the D′ and Om phases are continuously connected, as shown in Fig. 1. Although SE is a hydrophilic surfactant, the present ternary phase diagram resembles that of a water/lipophilic polyoxyethylene-type nonionic surfactant/hydrocarbon system [13].

In the concentrated region, a single lamellar liquid crystalline phase (L.LC) is also produced. The L.LC is extended from the surfactant-alcohol axis towards the water apex. The L.LC also forms in a water/ionic surfactant/alcohol system, but the melting temperature for ionic surfactant is usually very high and the L.LC does not appear on the surfactant-alcohol axis [14]. In this ternary water/SE/hexanol system, a H.LC is changed to aqueous micelles on the SE-water axis, whereas the phase transition from L.LC to reverse micelles occurs on the SE-hexanol axis. However, as described before, the boundary between the two-phase regions including H.LC or L.LC is not shown in Fig. 1 because the former region is narrow.

Fig. 2 The changes in interlayer spacing, *d*(○), and radius of cylinder, *r* (●), and interfacial section area per one surfactant molecule, A_s (□), for a hexagonal liquid crystal as a function of water/surfactant molar ratio in a binary water-SE system along the line A in Fig. 1

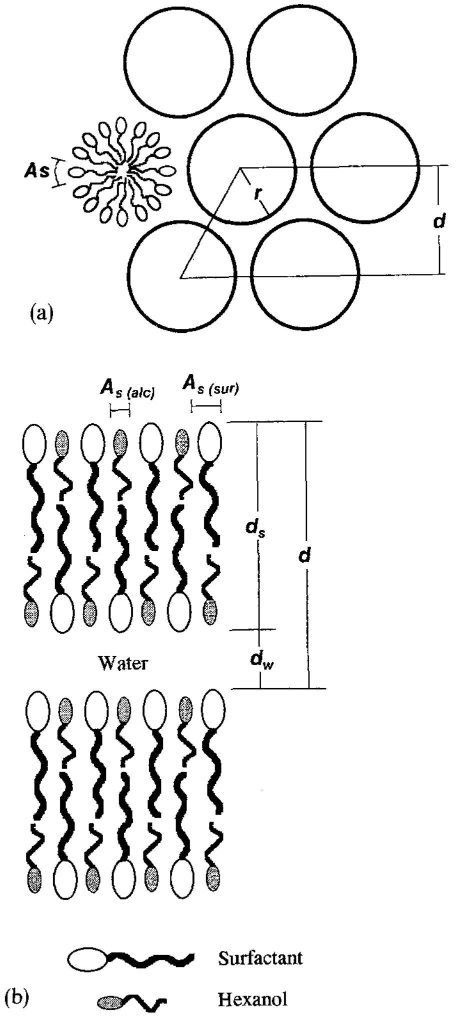


Interlayer spacing of hexagonal liquid crystal in water

The interlayer spacing, *d*, of hexagonal liquid crystal was measured along the line A in Fig. 1 (a binary SE and water system) and the result is shown in Fig. 2. With increasing water content, the interlayer spacing, *d*, slightly increases. In the dilute region, hexagonal liquid crystal changes to aqueous micellar solution phase.

The structures of hexagonal and lamellar liquid crystals are schematically shown in Fig. 3. The H.LC consists of hexagonally packed cylindrical aggregates. The *d* in Fig. 3(a) was measured by SAXS [12]. If one assume that water does not penetrate into the hydrophilic part of surfactant and the volume fraction of cylindrical aggregates is the same as that of SE, then the interfacial section area of one surfactant molecule and the radius of the

Fig. 3 Schematic structures of hexagonal (a) and lamellar (b) liquid crystals



cylinder can be expressed by simple geometrical relation [12] as,

$$A_s = \frac{2M_s}{\rho_s L\, r} \tag{1}$$

$$r = d\left(\frac{2}{\sqrt{3}\pi}\phi_s\right)^{1/2}, \tag{2}$$

where A_s is the interfacial section area per one surfactant molecule, L is the Avogadro constant, d is the measured interlayer spacing, M_s is the molecular weight of the SE (524.7), ρ_s is the density of the surfactant, r is the radius of the cylinder of aggregates, and ϕ_s is the volume fraction of surfactant.

The density of the SE aqueous solution was measured up to 50 wt% of surfactant by a density meter (Anton Paar, model DMA 40). By extrapolation, the density of SE is estimated to 1.19. This value was used for the calculation of the interfacial area of surfactant.

The radius of cylinder is unchanged with increasing water content as is shown in Fig. 2. The plot of A_s versus X_w/X_s is shown in Fig. 2, and we see that the A_s is also unchanged. X_w and X_s are the mole fractions of water and SE, respectively. With increasing water content, the distance between cylinders is gradually separated whereas the radius of the cylinder is almost unchanged. At a certain distance, the hexagonally packed structure cannot be maintained and the hexagonal liquid crystal is turned into aqueous micelles. However, this does not mean that rod micelles are formed in a single isotropic phase region close to a hexagonal liquid crystal region of the binary water – SE system. In fact, there is a cubic phase between a hexagonal liquid crystal and a micellar phase in a shorter-chain SE – water system [15].

Interlayer spacing in a SE – hexanol system

The interlayer spacing was also measured in a binary SE – hexanol system, and the result is shown in Fig. 4. The interlayer spacing, d, is almost unchanged or slightly decreases upon addition of alcohol. It is known that amphiphilic compounds such as long-chain alcohols penetrate surfactant palisade layers and form mixed self-organizing structures. Judging from Fig. 4, most of alcohol molecules form bilayers and d is not increased, because their solubilities are very small in water. In this case, we can assume that the measured interlayer spacing, d, is equal to the bilayer thickness, d_s in Fig. 3(b). Then, we obtain,

$$\frac{A_s d L}{2} = \frac{M_s}{\rho_s}X_s + \frac{M_a}{\rho_a}X_a\,, \tag{3}$$

where M_a and ρ_a are molecular weight and density of alcohol, and X_a is the mole fraction of alcohol. In this case, A_s means the average interfacial section area per one amphiphilic molecule (surfactant and alcohol). When the section area is plotted against the mole fraction of alcohol, the straight lines are obtained as shown in Fig. 4.

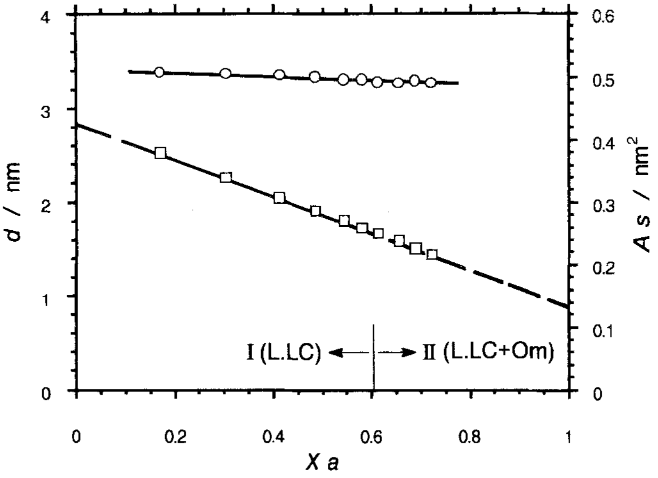


Fig. 4 The change in d (○), and A_s (□) for a lamellar liquid crystal in a binary hexanol-SE (along the line B in Fig. 1) system. It is assumed that surfactant and alcohol form a mixed bilayer

The section area at $X_a = 0$ is approximately 0.43 nm^2. This value corresponds to the section area of one SE molecule and is considerably smaller than that for hexagonal liquid crystal. Judging from Fig. 4, it is considered that each section area of surfactant ($A_{s(\mathrm{sur})}$) and alcohol ($A_{s(\mathrm{alc})}$) is not changed in a mixed lamellar liquid crystal. The section area for alcohol molecule is about 0.13 nm^2 and is considerably smaller than that of straight hydrocarbon chain (0.21 nm^2) [16]. Therefore, alcohol molecules alone cannot form lamellar liquid crystal.

Consequently, whereas the average section area decreases upon addition of alcohol, each interfacial section area of surfactant and alcohol molecules is almost unchanged in the mixed bilayer. It is considered that there is no special interaction between polar head groups to shrink the interfacial section area. Accordingly, we obtain,

$$A_s = A_{s(\mathrm{sur})}X_s + A_{s(\mathrm{alc})}X_a\,, \tag{4}$$

where $A_{s(\mathrm{sur})}$ is the interfacial section area per one SE and $A_{s(\mathrm{alc})}$ that for alcohol. When the average section area approaches that of hydrocarbon chain, the lamellar liquid crystalline structure is not maintained and is changed to reverse micelles as is shown in Fig. 1.

Interlayer spacing of liquid crystals in the ternary system

We also measured the interlayer spacing along the lines C and D in the ternary system in Fig. 1, and the results are

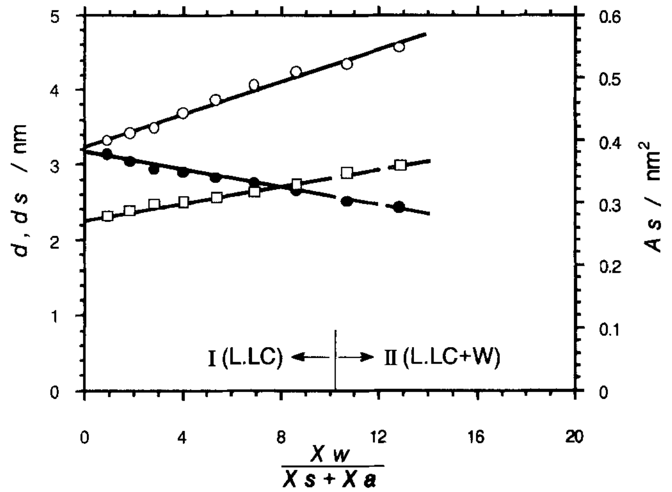


Fig. 5 The change in d (○), A_s (□), and bilayer thickness, d_s (●) for a lamellar liquid crystal along the line C in Fig. 1

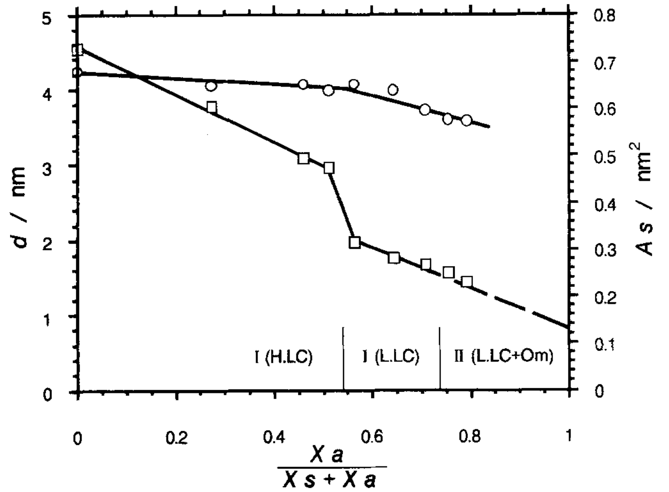


Fig. 6 The change in d (○) and A_s (□) for hexagonal and lamellar liquid crystals along the line D in Fig. 1

shown in Figs. 5 and 6. If the water thickness is represented by d_w and water is considered not to penetrate into bilayers, we obtain

$$\frac{A_s d_w L}{2} = \frac{M_w X_w}{\rho_w (X_a + X_s)} , \tag{5}$$

where ρ_w is the density of water, M_w is the molecular weight of water, and X_w is the mole fraction of water. Since $d = d_s + d_w$, we combine Eqs. (3) and (5), and A_s is calculated by

$$A_s = \frac{2}{dL}\left\{\frac{M_s X_s}{\rho_s (X_a + X_s)} + \frac{M_a X_a}{\rho_a (X_a + X_s)} + \frac{M_w X_w}{\rho_w (X_a + X_s)}\right\} . \tag{6}$$

The change in A_s along the lines C and D were calculated and the results are also shown in Figs. 5 and 6.

For a hexagonal liquid crystal in the ternary system, we assumed that all the surfactant and alcohol molecules participate to form cylinders. Hence, interfacial section area in a hexagonal liquid crystal is calculated by Eq. (1).

With increasing water content along the line C, the average interfacial area per one amphiphile (surfactant + alcohol) is gradually increased and the bilayer thickness gradually decreases. Upon addition of water, the hydrophilic parts of SE are hydrated and tend to separate each other. This causes the increase in the interfacial section area. Actually, SE forms a hexagonal liquid crystal in the absence of alcohol, in which the section area is large. However, this tendency is suppressed by alcohol molecules in the bilayer. Therefore, the bilayer structure remains even in a dilute region. Beyond the single L.LC region along the line C, we observed vesicles, that is, the dispersion of L.LC in water.

On the other hand, on the line D, the interfacial area is decreased with increasing alcohol content, because the area for alcohol molecule is very small. When A_s reaches 0.48 nm^2, phase transition from H.LC to L.LC occurs as is shown in Fig. 6. In the L.LC region, as is still decreased and the extrapolating value (at $X_a = 1$) is approximately 0.13 nm^2, which is the same as that on surfactant-alcohol axis.

Summary

Phase diagram of a water/sucrose monododecanoate (SE)/hexanol system was determined at 30 °C. On the water-SE axis, a liquid crystal of hexagonal type is present in a concentrated region and an aqueous micellar solution phase is observed in a dilute region. On the other hand, a lamellar liquid crystal appears on the hexanol-SE axis and a reversed micellar solution phase is formed in the dilute region. In the main miscibility gap of the ternary system, the reverse micellar solution phase coexists with a water phase. The change in interlayer spacing and interfacial section area of surfactant in the liquid crystalline phases was investigated by small-angle x-ray scattering. Upon addition of water, the section area and the radius of cylindrical aggregates are almost constant in a hexagonal liquid crystal, whereas the distance between each cylinder is separated on the water-SE axis. The interlayer spacing slightly decreases or is almost unchanged on the surfactant-hexanol axis, because alcohol molecules penetrate into the palisade of bilayers. Although the average section area decreases with increasing alcohol content, each section area of SE and alcohol molecules are kept constant.

Since the interfacial section area of alcohol is less than the section area of hydrocarbon chain, the phase transition from lamellar liquid crystal to reverse micelle occurs in an alcohol-rich region.

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