Colloid Polym Sci 279:92–97 (2001)
© Springer-Verlag 2001

SHORT COMMUNICATION

J.-Feng
K. Aramaki
A. Ogawa
T. Katsuragi
H. Kunieda

Phase behavior and solution properties of sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate in water

Received: 15 June 2000
Accepted: 27 July 2000

J.-Feng · H. Kunieda (✉)
Division of Artificial Environments and Systems, Graduate School of Engineering
Yokohama National University
Tokiwadai 79–5, Hodogaya-ku
Yokohama 240–8501, Japan
e-mail: kunieda@ynu.ac.jp

K. Aramaki
Division of Material Science and Chemical Engineering, Faculty of Engineering
Yokohama National University
Tokiwadai 79–5, Hodogaya-ku
Yokohama 240-8501, Japan

A. Ogawa · T. Katsuragi
Mitsubishi Chemical Corporation Research and Development Division, Yokohama Research Center, Kamosida-cho 1000
Aoba-ku, Yokohama 227–8502, Japan

Abstract Sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate (SLGMS) is a conjugated anionic surfactant in which a glycerol residue connects with a hydrophilic sodium succinate and dodecanoate. Aqueous micellar phase (W_m), hexagonal (H_1), bicontinuous cubic (V_1), and lamellar (L_α) phases are successively formed with increasing the surfactant concentration in a binary SLGMS-water system. The Krafft point is below 0 °C. The effective cross sectional area per surfactant molecule, a_s, in the H_1 phase is almost constant, 0.5 nm^2, and the shape of cylindrical micelle is almost unchanged with surfactant concentration. The cmc value of SLGMS measured by means of surface tension, electrical conductivity, and fluorescence probe methods is in the range of $4{\sim}9 \times 10^{-5}$ mol/l that is much lower than that of sodium dodecanoate, 2×10^{-2} mol/l, or SDS, 8×10^{-3} mol/l. Hence, it is considered that the polar glycerol part in the SLGMS acts as a hydrophobic part. The solubilization of oil in the SLGMS solution is much higher than that in the SDS solution and this also suggests that the glycerol and succinic units act as lipophilic moieties.

Key words Phase behavior · Sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate · Conjugated surfactant · Cmc · Krafft point

Introduction

Some ionic surfactants like alkyl polyoxyethylene sulfates, in which an ionic head group and a lipophilic chain are bound with a spacer such as oxyethylene, glycerol, etc., reveal very unique features in aqueous solutions [1]. These compounds may be called conjugated ionic surfactants. Compared with conventional ionic surfactants, Krafft temperatures of the conjugated surfactants are, in general, low and they can be used even in hard water [1, 2]. The cmc is also very low for these surfactants in spite of the fact that these mid-polar groups act as a hydrophilic head group for nonionic surfactants, polyoxyethylene alkyl ethers.

There are many surfactants of the conjugated type in nature, e.g., phospholipids, bile salts, etc., whose conjugated polar parts are glycerol, taurine, etc. The conjugated spacer may also act as a hydrophobic group. For example, the cmc of lysolecithin with C_{12} hydrocarbon chain is much lower than that of sodium dodecanoate although the glycerol group is hydrophilic in monoglyceride [3].

Ester-type surfactants are, in general, easily decomposed by hydrolysis, and may be environment-friendly. Many surfactants related to biological systems have ester-junctions in their molecules. Sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate (SLGMS) is a unique conjugated surfactant with a glycerol residue as a spacer. However, in the past, it has been difficult to obtain the pure compound and the basic physicochemical properties of the aqueous surfactant solutions have not been reported.

In this context, phase behavior and solution properties of SLGMS were investigated by phase study, surface-tension measurement, and small-angle X-ray scattering techniques, etc.

Experimental section

Synthesis of sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate (SLGMS)

Succinic anhydride (34 g, 0.34 mol) was added to 50 g (0.17 mol) of 90% distilled glycerol monolaurate (Riken Vitamin, Tokyo) and they were kept at 120 °C for 90 min to react. The reaction mixture was cooled to room temperature and was dispersed in 300 g of deionized water. Aqueous NaOH solution (1 N) was added to the dispersion to adjust the pH to 7.5. Ethyl acetate (300 g) was added to extract unreacted glycerol monolaurate and glycerol dilaurate. Aqueous HCl solution (3 N) was added to adjust the pH to 2 and oily substance was separated. The oily substance was extracted by adding 250 g of ethyl acetate and the ethyl acetate solution obtained was washed with 125 g of deionized water to remove inorganic salts and it was dried over anhydrous Na_2SO_4. Finally, 61 g of white powder was obtained by evaporating ethyl acetate under vacuum. Yield was 96%.

The compound obtained was checked by elemental analysis. Experimental values: C, 59.05%; H, 8.57%. Theoretical values for $C_{19}H_{34}O_7 \cdot 1/2H_2O$ are C, 59.51%; H, 9.20%.

^{1}H-NMR spectra were recorded in $CDCl_3$ on a JEOL EX270 spectrometer operating at 270 MHz. Chemical shifts were recorded in ppm (δ) relative to tetramethylsilane as internal standard. Chemical shifts observed are at: 0.88 ppm (3H, *t*, $C\mathit{H}_3CH_2$); 1.26 ppm (16H, *s*, $CH_3(C\mathit{H}_2)_8CH_2$); 1.61 ppm (2H, *bs*, $CH_3(CH_2)_8 C\mathit{H}_2CH_2OCO$); 2.33 ppm (2H, *q*, $CH_3(CH_2)_8CH_2C\mathit{H}_2OCO$); 2.66 ppm (4H, *m*, $COOC\mathit{H}_2C\mathit{H}_2COOH$); 4.12 ~ 4.35 ppm (4H, *m*, $COOC\mathit{H}_2CH(OH)C\mathit{H}_2OCO$); 5.29 ppm (1H, *quint*, $C\mathit{H}OH$). No signal from -OH was detected because a small amount of water was contained in $CDCl_3$ and the exchange of the proton took place. Numbers in round brackets indicate the number of proton. Notations: *s*, *bs*, *t*, *q*, *quint*, and *m* indicate singlet, broad singlet, triplet, quartet, quintet, and multi signal, respectively. Protons corresponding to each chemical shift are indicated in italics. The chemical structure of synthesized substance was determined as (3-dodecanoyloxy-2-hydroxy-propyl) hydrogen succinate (LSMSA).

The purity of the obtained LSMSA was checked by gas chromatography. Synthesized product was dissolved in the mixture of pyridine, N,O-bis(trimethylsilyl) acetamide, *N*-trimethylsilylimidazole, and trimethylchlorosilane. This solution was injected to gas chromatograph equipment (Shimadzu, GC-9A). Nitrogen was used as a carrier gas at 60 ml min^{-1}. FID was used as a detector. Temperature was 350 °C at injection and 300 °C at the detector. Column temperature was programmed from 150 °C to 350 °C. Chromatogram peaks attributed to glycerol monolaurate, glycerol dilaurate, and LSMSA were detected and the purity of LSMSA in the product is determined as 96% from the ratio of peak areas.

LSMSA (slightly soluble in water) is dispersed in water and 1 N aqueous NaOH solution equivalent to the acid was added. White powder (sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate; SLGMS) was obtained by freeze-drying process.

Materials

The chemical structure of SLGMS is shown in Fig. 1.

m-Xylene (99%) and *n*-decane (99%) were obtained from Tokyo Kasei Kogyo, Tokyo. Glycerol tri(2-ethylhexanoate) ester (TEH, 97%) from Nisshin Seiyu, Tokyo, was also used. Distilled water was used.

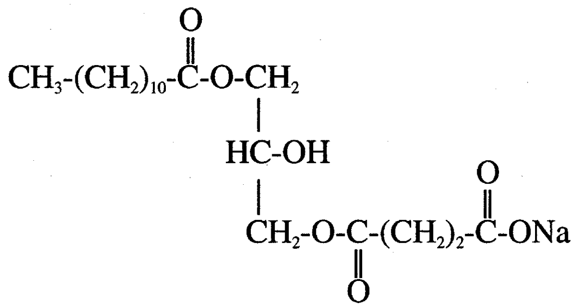

Fig. 1 Chemical structures of sodium (3-dodecanoyloxy-2-hydroxy-propyl) succinate (SLGMS)

Phase diagram

Samples of required compositions were sealed in glass ampoules. They were well shaken and were kept in a thermostat. Phase separation was detected by visual observation. Liquid crystal was detected by crossed polarizers, and its type was identified by small angle X-ray scattering.

Cmc measurement

Surface tension (γ) of aqueous surfactant solution was measured at 25 °C by a Wilhelmy-type surface balance (Kyowa Interface Science, CBVP-Z). A cmc value was determined by a break of a γ-logC (C is molarity.) curve. The cmc was also determined by electrical conductivity measurement performed at 25 ± 0.01 °C with an electrical-conductivity meter (Toa Electronics, Model CM-40S) and fluorescence probe method with a fluorescence spectrophotometer (Shimadzu, RF-5300PC). Pyrene was used as the fluorescence probe and the excitation wave length is 335 nm. The concentration of pyrene in micellar solutions is approximately 10^{-7} mol/l. Intensities of first and third peaks of fluorescence spectrum (I_1 and I_3, respectively) were measured and the I_1/I_3 ratio shows a marked breakpoint when the concentration of surfactant increases, at which the microenvironment of pyrene changes from hydrophobic to hydrophilic and determined as cmc [4].

Solubilization measurement

Aqueous solution of SLGMS (0.075 mol/l) was prepared. The aqueous solutions containing oil in vials were continuously shaken in a water bath at 25 ± 0.01 °C for 48 h to attain equilibrium. Transmittance of light (wave length is 650 nm) through the solutions were measured with a Shimadzu Model UV1200 V spectrophotometer. The transmittance drops sharply when excess oil is separated.

Small angle X-ray scattering (SAXS)

Identification of liquid crystals Interlayer spacing of liquid crystal was measured using small-angle X-ray scattering with an 18 kW Rigaku Denki rotating anode (Rint-2500) at about 25 °C. The samples of liquid crystals were lapped by poly(ethylene terephthalate) films for the measurement (Mylar seal method). The types of liquid crystal were determined by interlayer spacing ratio [5, 6]. For example, the SAXS peak ratio of the hexagonal phase is $1:1/\sqrt{3}:1/2$. The liquid crystal was also identified by means of a polarizing microscope (Nikon, OPTIPHOTO-2).

Calculation of a_s and r_H in the H_1 phase It is assumed that infinitely long cylindrical micelles are packed in a hexagonal array in the H_1 phase as is schematically shown in Fig. 2.

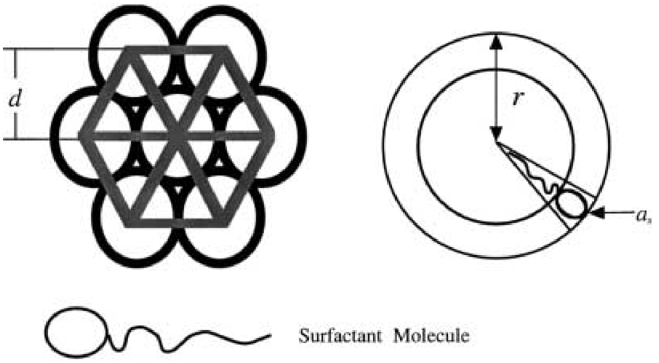

Fig. 2 Schematic representation of the H_1 phase

The radius of cylindrical micelle, r_H, and effective cross sectional area per head group of surfactant at the interface of aggregate, a_s, are calculated by the following geometrical relation [5]:

$$r_H = \left(\frac{2}{\sqrt{3}\pi}\phi_S\right) \qquad (1)$$

$$a_S = \frac{2M_S}{r_H N_A \rho_S} \qquad (2)$$

where d is a measured interlayer spacing, ϕ_s is the volume fraction of surfactant in the system, M_s is the molecular weight of surfactant, ρ_s is the density of the surfactant, and N_A is the Avogadro constant.

Density of SLGMS Density of surfactant was measured at 25 °C by a digital density meter, Anton Paar model DMA40. Since the surfactant is in a solid state, the density of the aqueous solution was measured at various surfactant concentrations. The reciprocals of these values were plotted against surfactant concentration and the density of the pure surfactant in a liquid state was estimated from the intercept at 100% surfactant. As a result, the density of surfactant is estimated to 1.21 (g cm^{-3}), and the molar volume of surfactant is calculated to 309.5 (cm^3 mol^{-1}).

Results and discussion

Phase behavior in a binary surfactant-water system

Figure 3 shows the phase diagram of a binary water-SLGMS system as a function of temperature.

The phase behavior is typical for ordinary water-ionic surfactant systems [7]. As the surfactant concentration increases, an aqueous micellar solution phase (W_m), a hexagonal liquid crystal (H_1), a cubic phase (V_1), and a lamellar liquid crystal (L_α) are successively formed. The cubic phase is considered to be a bicontinuous cubic phase since it is located between H_1 and L_α phase [8]. Although there is a solid-present region at a high surfactant concentration, we did not investigate in detail. Within all the temperature range investigated (above 0 °C), no solid phase was found in the dilute region. Namely, the Krafft temperature for SLGMS is below 0 °C. Since the Krafft temperature is related to melting temperature for a hydrated surfactant, the present conjugated surfactant is hardly crystallized in the presence of water due to the complicated molecular architecture. Note that the Krafft temperature for sodium dodecanoate is around 45 °C [9]. The liquid crystal phases are not melted to an isotropic solution at least up to 120 °C.

Surface tension

The change in surface tension of aqueous solution of SLGMS is shown in Fig. 4.

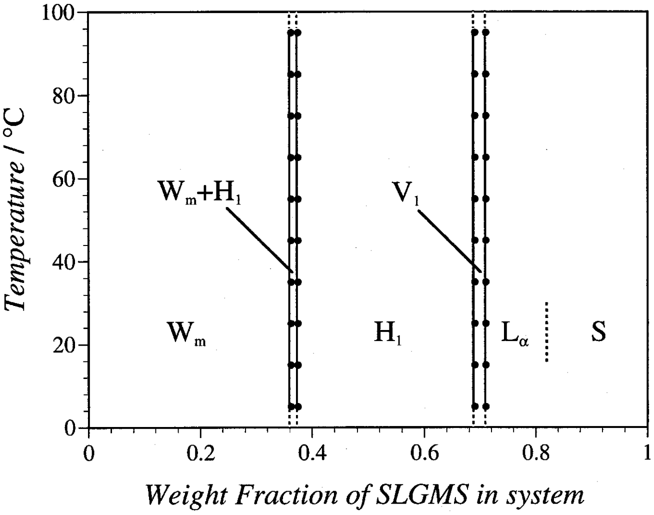

Fig. 3 Phase diagram of SLGMS/water system as a function of surfactant concentration and temperature. H_1 = hexagonal liquid crystalline phase; V_1 = cubic liquid crystalline phase; L_α = lamellar liquid crystalline phase; S is a solid phase

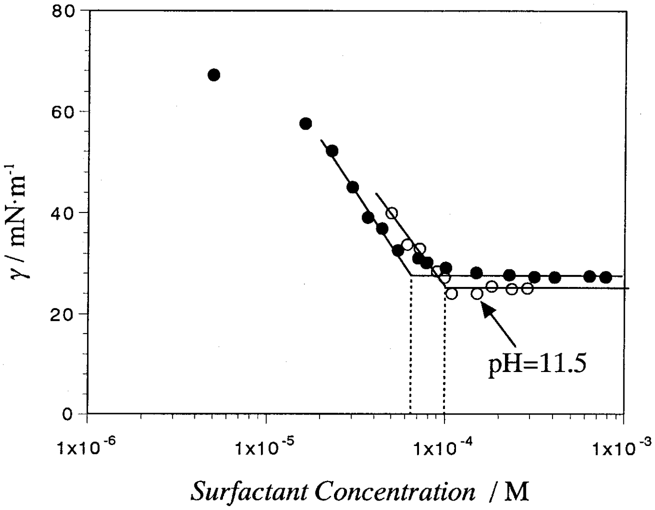

Fig. 4 Surface tension in aqueous solution and NaOH solution (pH = 11.5) of SLGMS at 25 °C

Table 1 Effective area per molecule at air-water interface (a_s), cmc, minimum surface tension at cmc (γ) for various aqueous surfactant solutions

Surfactant	Temperature (°C)	a_s (nm^2)	cmc (mmol/l)	γ (mN/m)	Reference
SDS	25	53	8.2	38.4	[2]
$C_{12}H_{25}OC_2H_4SO_4Na$	25	56	3.9		[20]
$C_{12}H_{25}(OC_2H_4)_2SO_4Na$	25	63	2.9		[20]
$C_{12}H_{25}(OC_2H_4)_3SO_4Na$	50		2.0		[21]
$C_{12}H_{25}(OC_2H_4)_4SO_4Na$	50		1.3		[21]
$C_{11}H_{23}COONa$	25		20		[10]
SLGMS	25	62	0.065	27	

The cmc obtained from the surface tension curve is 6.5×10^{-5} mol/l. This value is lower by two or three orders of magnitude than for sodium dodecanoate (2×10^{-2} mol/l) [10] or for SDS (8×10^{-3} mol/l) [11], which have a C_{12} carbon chain as lipophilic part. It should be noted that the cmc of aqueous solution of SLGMS was also measured by electrical conductivity (4×10^{-5} mol/l) and fluorescence probe method (9×10^{-5} mol/l). We have also measured the cmc in NaOH solution at pH = 11.5, which is also shown in Fig. 4. The measured cmc is 9.8×10^{-5} mol/l. Hence the extremely low cmc of SLGMS is not attributed to by the acidic soap.

The cmc values are compared with those of sodium dodecanoate, $C_{12}H_{25}(OC_2H_4)_nSO_4Na$ and SDS in Table 1.

It is known that the cmc values are depressed by introducing ethyleneoxide groups between the hydrocarbon chain and ionic group [12–14]. The oxyethylene group is hydrated as well as the ionic group. Therefore counter ions distribute not only outside of the ionic group but also in the hydrated oxyethylene group and this results in the decrease in electrical potential at the surfaces of micelle [15]. However, even if such a mechanism works, the decrease in cmc by introducing oxyethylene groups is not large as is shown in Table 1. In the present case, the cmc is drastically decreased by introducing the glycerol and succinic-acid residue so that a different mechanism should be considered. It is known that the cmc for ordinary ionic surfactant becomes half with the increase in one methylene unit in the hydrophobic chain. Compared with sodium dodecanoate, the carbon number increases in the present conjugated surfactant. If the glycerol (C_3) and succinic-acid (C_4) residues act as a hydrophobic part, cmc would be decreased by two orders of magnitude. This may be the reason for the low cmc of SLGMS.

Stability in hard water

The aggregation number of the micelles in an aqueous ionic surfactant solution is finite (about 50–90 for SDS) and the micelles are charged. Therefore, the concentration of the counter ions increases with surfactant concentration and the Krafft point is affected by the surfactant concentration as well as added salt [16, 17]. The Krafft points of ionic surfactants with calcium ions as counter ions are generally higher than room temperature, and therefore they are usually less soluble than corresponding sodium salts. The change in Krafft points for SLGMS, SDS, and sodium dodecanoate as a function of the ratio of divalent cation to surface active anion ($2M^{2+}/R^-$) is shown in Fig. 5.

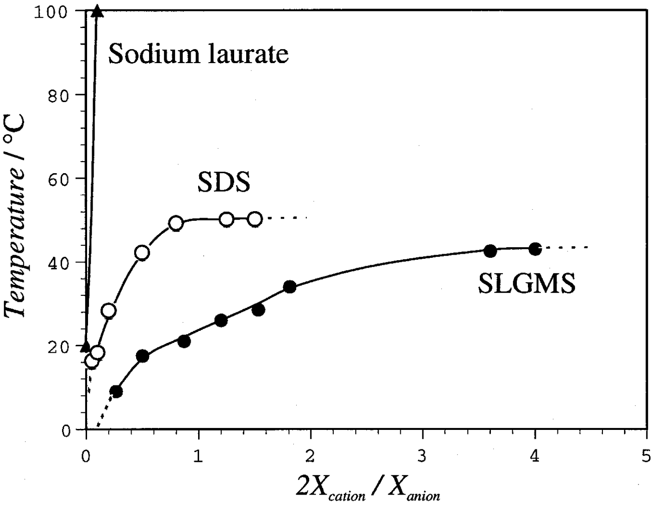

Fig. 5 Effect of added $CaCl_2$ on the Krafft point of 1 wt% aqueous solution of SLGMS and sodium dodecanoate

The Krafft point of SLGMS increases by the addition of divalent cation until the ratio $2M^{2+}/R^-$ reaches nearly 3. Above this concentration at which the sodium ion may be almost completely replaced with the divalent ion, the Krafft point is raised only a little [17]. On the other hand, the Krafft point of SDS increases rapidly compared with SLGMS. Furthermore, the Krafft point of sodium dodecanoate dramatically increases in the presence of a trace amount of divalent cation and the isotropic solution phase does not appear at least below 100 °C. It is also found from Fig. 5 that the Krafft point of SLGMS in pure water is lower than that for the sodium dodecanoate, 20 °C [18]. It is noteworthy that the Krafft point of SLGMS in pure water is below 0 °C, and thus the surfactant dissolves well in the presence of

Table 2 Solubility of oil in aqueous micellar solutions

Oil	Solubility/g mol^{-1}		
	m-Xylene	Decane	TEH
SLGMS	0.92	0.38	0.28
SDS	0.52	0.29	0.20

divalent cations such as Ca^{2+} and can be used in hard water.

Solubilization of oils

The maximum solubilization of oils in the micellar solution is shown in Table 2.

The small-molecular-size oil is more solubilized than large ones. Due to the penetration of small-size oil in the surfactant palisade layer, a marked increase in micellar size takes place and the solubilizing power increases [15]. The solubilization of oil in the aqueous solutions of SLGMS is greater than that of SDS. This is also the evidence for the glycerol and succinic unit as hydrophobic moieties since the solubilization capacity normally increases with the increase in the length of hydrophobic chain.

SAXS measurement in a binary water-surfactant system

Interlayer spacing of H_I phase, *d*, was measured by means of SAXS at 25 °C, and the results are shown in Fig. 6.

With increasing the concentration of SLGMS, the *d* is gradually decreased whereas r_H and a_s are almost unchanged. This indicates that the shape of cylindrical micelles does not change and only distances between the cylinders gradually increases with increasing the surfactant concentration [19].

Since the volume of one surfactant molecule is calculated to be 0.51 nm^3 and the net sectional area of a linear hydrocarbon chain is $0.2 \sim 0.22$ nm^2, the maximum length of surfactant is calculated to be approximately $2.1 \sim 2.3$ nm in their fully extended forms. It is assumed that the hexagonal (H_I) phase consists of infinitely long cylindrical micelles packed in a hexagonal array. Thus, the a_s is calculated by Eq. (2) using the interlayer spacing, *d*, obtained from the SAXS measurement. The a_s is around 0.5 nm^2 in the H_I phase.

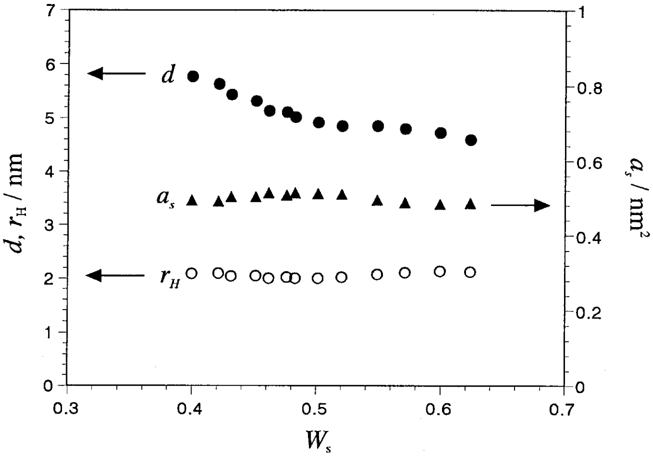

Fig. 6 Change in interlayer spacing (*d*), effective cross sectional area (a_s), and radius (r_H) in the H_I phase as a function of W_s

Summary

The phase diagram of a water/sodium (3-dodecanoyl-oxy-2-hydroxy-propyl) succinate (SLGMS) system was constructed. In the system an aqueous micellar phase (W_m), hexagonal (H_I), bicontinuous cubic (V_I), and lamellar (L_α) phase are successively formed with increasing the surfactant concentration. In H_I phase, the interlayer spacing *d* decreases upon addition of the surfactant concentration. We calculated the effective cross sectional area per surfactant molecule, a_s, in the aggregates using the measured *d* values. The calculated a_s was above 0.5 nm^2.

The properties of the surfactant solution such as surface tension, Krafft point, the cmc, and the solubilization of oil were examined. The cmc values of SLGMS were much lower than that of sodium dodecanoate or SDS. The Krafft point of SLGMS was lower than that for the sodium dodecanoate or SDS. The solubilization for oils in the aqueous SLGMS solution is much more than that in the SDS/water system.

References

1. Hato M, Shinoda K (1973) J Phys Chem 77:378
2. Rosen MJ (1989) Surfactants and interfacial phenomena, 2nd edn. Wiley, New York, chap 1
3. Stafford RE, Fanni T, Dennis EA (1989) Biochemistry 28:5113
4. Turro NJ, Kuo PL, Somasundaran P, Wong K (1986) J Phys Chem 90:288
5. Kunieda H, Shigeta K, Ozawa K, Suzuki M (1997) J Phys Chem 101:7952
6. Fontell K (1974) In:Gray GW, Winsor PA (eds) Liquid crystals and plastic crystals, vol 2. Wiley, New York, chaps 3, 4
7. Laughlin RG (1994) The aqueous phase behavior of surfactants. Academic Press, London, chap 5
8. Jönsson B, Lindman B, Holmberg K, Kronberg B (1999) Surfactants and

polymers in aqueous solution. Wiley, Chichester, chap 3

9. Ogino K, Ichikawa Y (1976) Bull Chem Soc Jpn 49:2683
10. Klevens HB (1953) J Am Oil Chem Soc 30:74
11. Elworthy PH, Mysels KJ (1966) J Colloid Sci 21:331
12. Weil JK, Bistline RG, Stirton AJ (1958) J Phys Chem 62:1083
13. Weil JK, Stirton AJ, Bistline RG, Maurer EW (1959) J Am Oil Chem Soc 36:241
14. Tokiwa F, Ohki K (1967) J Phys Chem 71:1343
15. Shinoda K, Hirai T (1977) J Phys Chem 81:1842
16. Shinoda K, Yamaguchi N (1989) J Phys Chem 93:7216
17. Nakayama H, Shinoda K (1967) Bull Chem Soc Jpn 40:1797
18. Shinoda K, Minegishi Y, Arai H (1976) J Phys Chem 80:1987
19. Kanei N, Imae T, Kihara K, Tagawa T, Kunieda H (1996) J Jpn Oil Chem Soc (J Oleo Sci) 45:849
20. Dahanayake M, Cohen AW, Rosen MJ (1986) J Phys Chem 90:2413
21. Gotte E (1960) 3rd Int Congr Surface Activity Cologen 1:45