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

Abstract  Sodium (3-dodecanoyl-
oxo-2-hydroxy-propyl) succinate  
(SLGMS) is a conjugated anionic  
surfactant in which a glycerol resi-
due connects with a hydrophilic  
sodium succinate and dodecanoate.  
Aqueous micellar phase ($W_m$),  
hexagonal (H$_1$), bicontinuous cubic  
($V_1$), and lamellar (L$_d$) 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, $a_{se}$ 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 conduc-
tivity, and fluorescence probe  
methods is in the range of  
4~9 × 10$^{-2}$ 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 consid-
ered 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 sul-
fates, 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 conjugat-
ed 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$_{12}$ hydro-
carbon 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 decom-
posed by hydrolysis, and may be environment-friendly.  
Many surfactants related to biological systems have  
ester-junctions in their molecules. Sodium  
(3-dodeca-

nolexyloxy-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 physico-
chemical properties of the aqueous surfactant solutions  
have not been reported.

In this context, phase behavior and solution proper-
ties 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 Na2SO4. 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 C12H22O7Na: C, 59.51%; H, 9.20%.

1H-NMR spectra were recorded in CDCl3 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: 0.88 ppm (3H, t, CH2CH2); 1.26 ppm (16H, s, CH2(CH2)17CH2); 1.61 ppm (2H, t, CH2CH2CH2CH2O); 2.33 ppm (2H, q, CH2CH2CH2O); 2.66 ppm (4H, m, COOC6H4CH2COO); 4.12 ~ 4.35 ppm (4H, m, COOC6H4CHOH); 5.29 ppm (1H, q, CH2OH). No signal from -OH was detected because a small amount of water was contained in CDCl3 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) sodium 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.

\[
\text{CH}_3-(\text{CH}_2)_{10}\text{C}=(\text{CH}_2)_{2}\text{O}\text{-CH}_2
\]

\[
\text{HC-OH}
\]

\[
\text{CH}_2\text{-O-}\text{C}-\text{(CH}_2\text{)}_{2}\text{C-ONa}
\]

**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 (Kyoaya Interface Science, CBVP-Z). A cmc value was determined by a break of a γ-log C (C is molarity,) curve. The cmc was also determined by electrical conductivity measurement performed at 25 ± 0.1 °C with an electrical-conductivity meter (Toa Electronics, Model CM-408) and fluorescence probe method with a fluorescence spectrophotometer (Shimadzu, RF-5300PC). Pyrene was used as the fluorescence probe and the excitation wavelength 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 (I1 and I3, respectively) were measured and the I1/I3 ratio shows a marked breakpoint when the concentration of surfactant increases, at which the microenvironement 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 dipped by polyethylene 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√3:1/2. The liquid crystal was also identified by means of a polarizing microscope (Nikon, OPTIPHOTO-2).

**Calculation of a and b in the H1 phase** It is assumed that infinitely long cylindrical micelles are packed in a hexagonal array in the H1 phase as is schematically shown in Fig. 2.