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Formation of intermediate micellar phase between hexagonal and discontinuous cubic liquid crystals in brine/*N*-acylamino acid surfactant/*N*-acylamino acid oil system

Yuji Yamashita [a], Hironobu Kunieda [a], Eiko Oshimura [b], Kazutami Sakamoto [a,*]

[a] *Graduate School of Environment and Information Sciences, Yokohama National University, Tokiwadai 79-7, Hodogaya-ku, Yokohama 240-8501, Japan*
[b] *Amino Science Laboratories, Ajinomoto Co. Inc., 1-1 Suzuki-cho, Kawasaki 210-8681, Japan*

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Abstract

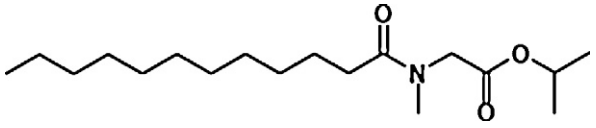
The phase behavior in the brine/sodium *N*-dodecanoyl sarcosinate (Sar)/isopropyl *N*-dodecanoyl sarcosinate (SLIP) system has been investigated by means of phase study, static light scattering, and small-angle X-ray scattering. The liquid crystal phases, hexagonal (H_1) and discontinuous cubic (I_1), melt upon the addition of NaCl, which shows the similar effect to the increasing of temperature. The addition of SLIP to the brine/Sar solution at high Sar concentration induces the phase transition from H_1 to I_1 via the isotropic micellar solution (W_{m2}). The micellar structure in the W_{m2} phase also changes from the wormlike to the globular micelle with SLIP concentration. Adding NaCl reduces the repulsive force between the Sar head groups and simultaneously the space of the solubilized SLIP in the palisade layer, leading SLIP to shift their location further into the micelle core. As a consequence, the hexagonal symmetry breaks into the micelle solution and the liquid crystal order is destabilized entropically.

Keywords: Amino acid derived oil; Acylsarcocinate; Phase behavior; Electrolyte; Micelle structure; Hexagonal phase; Cubic phase; SAXS; Static light scattering

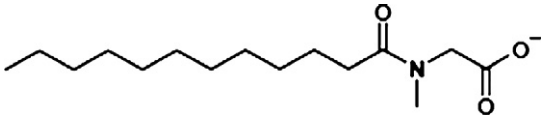
1. Introduction

Development of personal care products requires comprehensive knowledge and experiences of formulating compounds on the basis of phase behavior. In addition, specific properties of the products such as pH and viscosity requires accommodating the consumer's demands and can be controlled commonly by additives such as oils and electrolytes. Novel additives have been created and their properties in surfactant systems are investigated daily to fulfill the consumer's never ending desire. Isopropyl *N*-dodecanoyl sarcosinate (SLIP) is an amphiphilic oil for such purpose, which is derived from acylsarcosinate as shown in Fig. 1. Acylsarcosinates (Sar) are commonly used as mild anionic surfactants for personal-care products in liquid system. The novel function of SLIP is to help solubilize the UV absorbers, or to disperse the UV scattering agents such as the fine-grain TiO_2 [1]. Also, SLIP is expected to be applied to shampoos as an alternate thickener to alkyl-alkanolamides.

In previous papers, we have introduced the effects of SLIP on aggregate structures in various surfactant systems. *N*-acylamino acid ester is classified as amphiphilic or semi-polar oil,



(a)



(b)

Fig. 1. Chemical structure of (a) isopropyl *N*-dodecanoyl sarcosinate (SLIP) and (b) *N*-dodecanoyl sarcosinate (Sar).

* Corresponding author. Present address: Research Center, Shiseido Co. Ltd., 2-2-1 Hayabuchi, Tsuzuki-ku, Yokohama 224-8558, Japan.
E-mail address: kazutami.sakamoto@to.shiseido.co.jp (K. Sakamoto).

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i.e. likely to behave as polar or non-polar oil depend on the occasion. We had found that this semi-polar oil behaves as co-surfactant in the polyoxyethylene-type nonionic surfactant ($C_{12}EO_8$) [1–3] and sodium dodecyl sulfate (SDS) systems [3,4]. Afterwards, however, it was demonstrated that the solubilization sites of SLIP varies with its concentration in a homologous amino acid surfactant system: SLIP penetrates into the palisade layer at its low concentration, but further addition of SLIP leads to the solubilization in the micelle core [4]. The variation of the solubilization sites of SLIP involves the phase transition from hexagonal liquid crystal (H_1) to discontinuous cubic liquid crystal (I_1). This unique solubilization behavior attributes to the balance of amphiphilicity of SLIP and strength of the head group repulsions of Sar. Present study aims to investigate the additional effects of electrolytes on the peculiar phase behavior of the Sar/SLIP system to promote applications of SLIP.

2. Experiments

2.1. Materials

N-dodecanoyl sarcosine (>99%) was purchased from Fluka Chemie GmbH and used as received. The surfactant aqueous solutions were prepared by neutralizing the carboxyl group of dodecanoyl amino acid with sodium hydroxide (NaOH) purchased from Junsei Chemical Co. Ltd. NaOH was added at 2 mol% excess of an equivalent value in order to avoid hydrolysis. Isopropyl *N*-dodecanoyl sarcosinate (SLIP, >96%) was synthesized by conventional esterification of *N*-dodecanoyl sarcosine at Ajinomoto Co. Inc. [1]. Sodium chloride (NaCl) was purchased from Junsei Chemical Co. Ltd.

2.2. Phase diagram

Samples were weighed at required compositions and sealed in glass ampoules. They were well agitated and kept in a thermostat bath at 20 °C for at least one week. Phase states were determined visually with and without a crossed polarizer. Types of liquid crystals were identified by small angle X-ray scattering (SAXS).

2.3. Static light scattering (SLS)

The static light scattering measurements were carried out by using DLS-6000HL (10 mW) with the He–Ne Laser (wave length = 632.8 nm) produced by Otsuka Denki Co., equipped with a water circulating thermostat (RML6S). The solutions were filled in test tubes (diameter = 5 mm) through a microfilter. The refractive indices of the solutions were measured by a refractive meter (Otsuka Denki Co.) at 20 °C.

2.4. Small angle X-ray scattering (SAXS)

The interlayer spacing of liquid crystals was measured by SAXS, performed on a small angle scattering goniometer with a 18-kW Rigaku Denki rotating anode generator (RINT-2500) at about 20 °C. The samples were sealed in a metallic sample holder with plastic film windows (Mylar seal method).

For the micellar solution phase, a quartz capillary tube was used as sample holder. In priori, a blank measurement was performed in order to remove scatterings of the capillary and the surfactant monomer from the total intensity. The Sar aqueous solution at its critical micelle concentration (cmc; 1.5×10^{-2} mol/L [5]) was applied to the blank measurement.

3. Results and discussions

3.1. Phase diagrams of brine or water/Sar/SLIP system at 20 °C

Fig. 2 shows the triangle phase diagrams of (a) brine ($X_{NaCl} = 0.0398$) or (b) water/Sar/SLIP system at 20 °C.

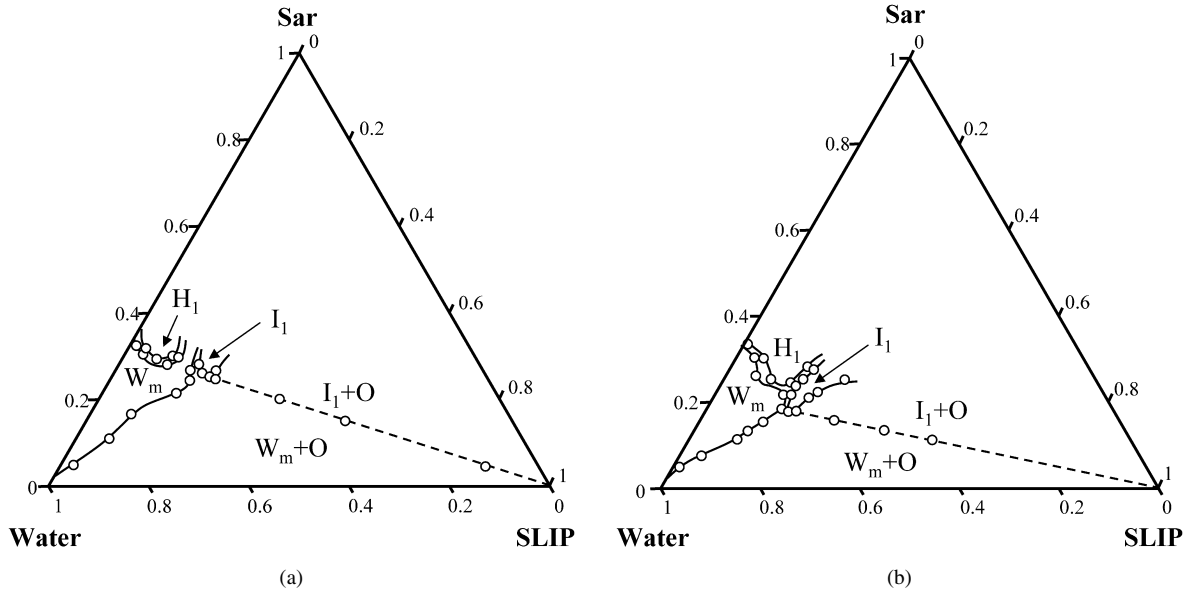

Fig. 2. Triangle phase diagram of (a) brine ($X_{NaCl} = 0.0398$) or (b) water/Sar/SLIP system at 20 °C.