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Formation of wormlike micelles with natural-sourced ingredients (sucrose fatty acid ester and fatty acid) and a viscosity-boosting effect induced by fatty acid soap

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ABSTRACT

We have investigated the formation of a viscoelastic wormlike micellar solution with natural-sourced materials such as sucrose monopalmitate (C_{16}SE) and fatty acid (FA). Zero-shear viscosity of 10 wt% aqueous solutions of C_{16}SE and lauric acid (LA) increased with the increase in the C_{16}SE fraction to a certain level but it decreased after a maximum value. Viscous solutions having almost maximum zero-shear viscosity showed non-Newtonian behavior and had Maxwell-type mechanical properties. When a small fraction of LA of the water/C_{16}SE/LA system was substituted with sodium laurate (SL), the maximum zero-shear viscosity increased by nearly one order of magnitude from the original system due to a decrease in the diffusion constant of the wormlike micelles. With further substitutions of LA with SL, the zero-shear viscosity decreased because the highly hydrophilic fatty acid soap makes elongated micelles shorter.

1. Introduction

It is well known that micelles in aqueous solutions of surfactants grow one-dimensionally by tuning surfactant hydrophobically, and long, flexible aggregates called wormlike micelles are produced. If the scission energy, which is the energy required to break a wormlike micelle into smaller parts, is large enough, the length of the rods can become longer than their persistence length, and the micelles behave like semi-flexible linear polymer chains. Because of entanglement of the wormlike micelles, the wormlike micellar solutions show highly viscoelastic properties. Wormlike micelles are different from polymers because they can break and reform under shear forces as the wormlike micelles are composed of low-molecular-weight molecules.

In order to grow a spherical micelle into a wormlike micelle, the effective head group area of surfactants must be decreased, for example, by adding salts that screen the electrostatic repulsions between the neighboring head groups. Wormlike micelles have been shown to form in some ionic surfactant systems, by the addition of salts [1–6] or in mixed surfactant systems [7–9]. It was also found that several hydrophilic anionic, cationic and nonionic surfactants could form wormlike micelles with a hydrophobic nonionic cosurfactant [10–17].

Nonionic surfactants are not always suitable for forming wormlike micelles when compared to ionic surfactants. Conventional poly(oxyethylene)-type surfactants do not yield wormlike micellar solutions with extensive high viscosity [18], except for poly(oxyethylene) cholesteryl ether [19–21]. Polyol-type surfactants are one type of nonionic surfactants, and one of the more important surfactants of this type is sucrose fatty acid ester. Sucrose fatty acid ester is suitable for use in food or cosmetic products because it is composed of the natural-sourced materials, sucrose and fatty acids. Contrary to the conventional poly(oxyethylene)-type nonionic surfactant, the hydrophilicity of sucrose fatty acid ester does not change with varying temperature, which leads to thermally stable microemulsions [22–24] and liquid crystals [25]. It has been reported that sucrose fatty acid ester shows good performance with respect to wormlike micelle formation with hydrophobic poly(oxyethylene) alkyl ether, glycerol monoalkanoate [26,27] and aliphatic alcohols [28]. In concordance with those previous studies, we report that a highly viscous wormlike micellar solution can be formed with a fatty acid (FA) as a cosurfactant. Such viscous systems, which contain all natural-sourced ingredients, may satisfy industrial demands for use in food and cosmetic

Abbreviations: C_{16}SE, sucrose monopalmitate; FA, fatty acid; LA, lauric acid; SL, sodium laurate.

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products. In addition, having more viscous systems widens the possibility for such applications. Recently, it was reported that adding ionic surfactants to a nonionic sugar surfactant-based wormlike micellar solution leads to a significant increase in its solution viscosity due to an electrostatic excluded volume effect. Ishizuka et al. reported that the viscosity of a sucrose monooleate-based wormlike micellar solution was boosted by adding SDS, DTAB and CTAB [29], and Yamamoto et al. reported a similar phenomenon in a sucrose monopalmitate system as well [30]. In this report, we present data that show that the electrostatic excluded volume effect occurs in a sucrose fatty acid ester + FA wormlike micellar solution by substituting fatty acid with fatty acid soap.

2. Experimental

2.1. Materials

Sucrose monopalmitate (C_{16}SE, monoester content > 95%) was obtained as a gift from Mitsubishi-Kagaku Foods Co., Tokyo. Hexanoic, octanoic, decanoic and lauric acids, and sodium laurate were obtained from Tokyo Chemical Industry, Co. Millipore filtered water was used as a solvent.

2.2. Rheological measurements

Before performing measurements, all samples were homogenized and left in a water bath for at least 48 h to ensure equilibration. Rheological measurements were performed in a stress-controlled rheometer (AR-G2; TA Instruments Co.) at 30 °C, using cone-plates of two sizes, 40 or 60 mm in diameter, each of which had a cone angle of 1°. The geometry depended on the viscosity of the sample.

3. Results and discussion

3.1. Phase behavior and solution viscosity in the water/C_{16}SE/fatty acid (FA) systems

The solution state of the water/C_{16}SE/FA systems at 30 °C was observed as the mixing composition of the sugar surfactant and FA was varied at a constant water weight fraction of 0.9. In the system with lauric acid (LA), an aqueous micellar solution phase was formed below $W_1 = 0.1$, where W_1 is defined as the weight fraction of FA of the total C_{16}SE and FA. Above $W_1 = 0.1$, the system formed a lamellar liquid crystalline phase. In the systems with hexanoic or octanoic acids, a micellar phase was formed in the same range of W_1. In the decanoic acid system, the micellar phase is observed from $W_1 = 0$ to 0.08. The highest viscosity of the micellar solution is given in the lauric and decanoic acid systems. Therefore, we have studied the rheological property of the micellar solution phase in the system with lauric acid and the results are shown in the following section.

The results from measuring the steady shear rate of the water/C_{16}SE/LA system at 30 °C and at various W_1 values are shown in Fig. 1. The weight fraction of water in the entire system was fixed at 0.9. Viscosity was nearly constant at a low shear rate and decreased above a certain shear rate for all of the samples. The point at which the viscosity started to decrease shifted to the lower shear rate when W_1 increased from 0 to 0.04 and changed direction when W_1 was greater than 0.06.

We can obtain a zero-shear viscosity value (η_0) by extrapolating a viscosity curve in Fig. 1 to a shear rate of zero. Fig. 2 is a plot of η_0 for various FA systems against W_1. As can be seen in Fig. 2, the zero-shear viscosity increased with W_1 and then decreased after a maximum viscosity for all of the systems. This type of behavior

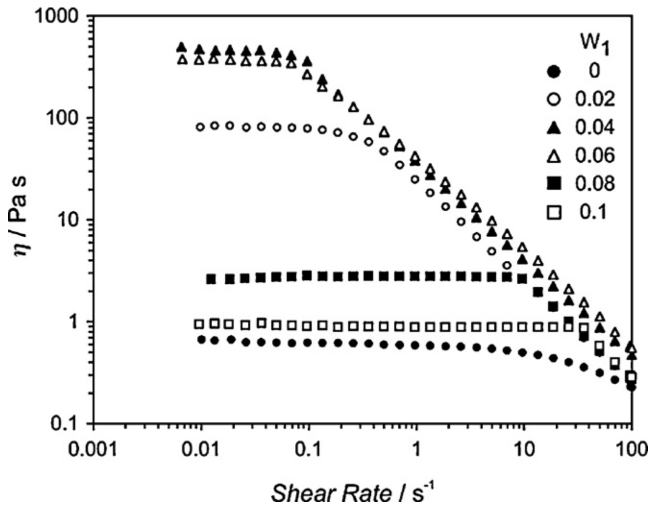

Fig. 1. A plot of viscosity for micellar solutions of the water/C_{16}SE/LA system at 30 °C against shear rate at various weight fractions of LA in total amphiphiles (W_1) is shown. Weight fraction of water in the whole system is fixed at 0.9.

is often observed for mixed amphiphile systems where wormlike micelles are present [15,16,18,28]. The decrease after the maximum can be attributed to either the breaking or branching of micelles [31], or possibly to the two types of mixed micelle formation due to the chain length difference between the sugar surfactant and the fatty acids. Note that the pH values of these aqueous sugar surfactant and fatty acid solutions were above 3.7.

3.2. Viscoelastic properties for the water/C_{16}SE/FA systems

Oscillatory-shear (frequency sweep) measurements were performed on the viscoelastic samples formed around the viscosity maximum. A representative plot of the elastic or storage modulus (G') and the viscous or loss modulus (G'') against oscillation frequency (ω) for the water/C_{16}SE/LA system is presented in Fig. 3. For all of the samples, liquid-like behavior ($G' < G''$) was observed at a region of low frequency, whereas, solid-like behavior ($G' > G''$) was observed at a region of high frequency. This is typical viscoelastic behavior shown by a wormlike micellar solution.

Maxwell-type oscillatory rheological behaviors of viscous micellar solutions can be related to the transient network formed

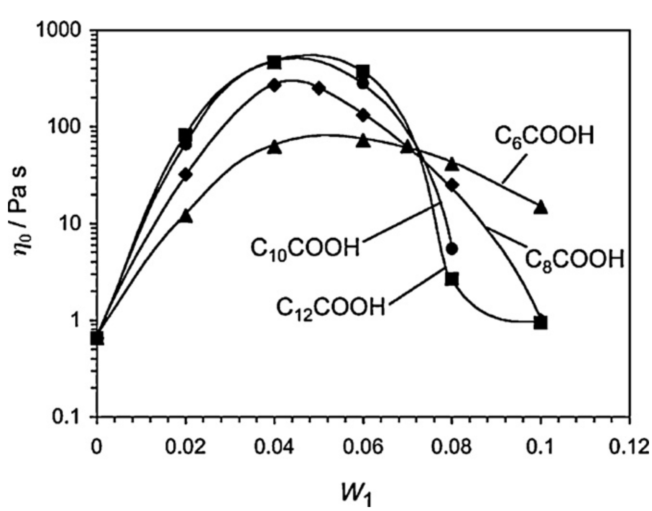

Fig. 2. Variation of zero-shear viscosity (η_0) of the water/C_{16}SE/FA systems as a function of W_1 at 30 °C. Weight fraction of water in the whole system is fixed at 0.9 for all of the systems.