Effect of Alcohols on the Phase Behavior and Emulsification of a Sucrose Fatty Acid Ester/Water/Edible Oil System

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Abstract: The effect of alcohols (ethanol, 1-propanol, propylene glycol, glycerin, sucrose) on the phase behavior and emulsification of sucrose stearic acid ester (SSE)/water/edible vegetable oil (EVO) systems was investigated. Adding sucrose, propylene glycol, and glycerin narrowed the oil-separated two-phase region in the phase diagram of the SSE/water/EVO systems, whereas adding ethanol and 1-propanol expanded the oil-separated two-phase region. Changing the course of emulsification in the phase diagram showed that the size of the oil-droplet particle typically decreased in a system with a narrowed oil-separated region. The emulsification properties of the systems varied with respect to changes in the phase diagram. The microstructure of the systems was examined using small-angle X-ray scattering, and the ability to retain the oil in the lamellar structure of the SSEs was suggested as an important role in emulsification, because the mechanism of the systems was the same as that for the liquid crystal emulsification method.

Key words: glycolipid, liquid crystal, phase diagram, emulsion, small-angle X-ray scattering

1 INTRODUCTION

Lipids are important for life as a source of nutrition and a constituent of organisms. Among them, polar lipids are often amphiphilic and a major constituent of the lipid bilayer of the cell membrane; therefore, they play an important role in signal transduction in vivo. Recently, glycolipids have gained attention because of their unique properties and importance in the cell life; however, the role and behavior of glycolipids in vivo have not been elucidated because of the variety and complexity.

Surface-active agents with a sugar group as the hydrophilic part have been used in many applications in various industries (e.g., food, cosmetic, and medicine) because they are safe for consumers to use and have a lower environmental impact (they are derived from natural raw materials). In recent years, there has been growing interest worldwide in safety and the environment; therefore, sugar surfactants are viewed as an important surfactant. Sucrose fatty acid esters are well known as a sugar surfactant and have been widely used for a long time in industries throughout the world. They are biodegradable and biocompatible and have a broad hydrophilic-lipophilic balance (HLB), which provides a broad selectivity in the degree of esterification because of the eight hydroxyl groups of sucrose, making them suitable for use in cosmetic, pharmaceutical, and food formulations. Because the safety of sucrose fatty acid esters has been evaluated by the Food and Agriculture Organization of the United Nations/World Health Organization Joint Expert Committee on Food Additives, further applications of these esters as emulsifiers, and surfactants for foods, is expected in the future. Therefore, there have been many studies on sucrose fatty acid esters. In particular, important systematic studies were conducted by Kunieda, Aramaki, and Funan. However, studies conducted in the food industry were mostly performed as screening tests based on trial and error because the industrial products of sucrose fatty acid esters are mixtures containing esters with different degrees of esterification and fatty acid composition, and the composition of the food is complex. Therefore, few studies have examined the relationship between the phase behavior and emulsification of sucrose fatty acid esters under practical conditions in the food industry. In particular,
lar, sucrose stearic acid esters (SSE), which are major emulsifiers in food because of their mild taste, have not been systematically studied at the temperatures used in the heated emulsification processes used in industry.

In this study, the phase behavior and emulsification properties of SSEs with different HLB values in water and edible oil systems were examined in a temperature range used in an actual heated emulsification process as a model food emulsion, and the effects of alcohols (ethanol, 1-propanol, propylene glycol, glycerin, sucrose) on the SSEs were investigated to elucidate the mechanism of emulsification by SSEs and to optimize the application of SSEs in the food industry. Furthermore, the investigation was conducted to help determine the behavior and role of glycolipid mixtures in complex living organisms by clarifying the behavior of mixed sucrose esters in food systems.

2 EXPERIMENTAL PROCEDURE

2.1 Materials

SSEs with different HLB values (S-1670, S-1170, S-570; HLB and ester composition shown in Table 1; the chemical structure of sucrose mono stearic acid ester is shown in Fig. 1) were gifted from Mitsubishi-Chemical Foods Corporation (Tokyo, Japan; former company name: Mitsubishi-Kagaku Foods Corporation). The ratio of stearic acid esters and palmitic acid esters in the SSEs was about 7:3. Edible vegetable oil (EVO) (Nisshin Salad Oil; a mixture of soy oil and canola oil) was purchased from Nisshin OilliO Group, Ltd. (Tokyo, Japan). Ethanol (ET), propanol (PR), propylene glycol (PG), glycerin (GL), and sucrose (SC) (reagent grade) were purchased from Nacalai Tesque, Inc. (Kyoto, Japan). All materials were used without further purification. Purified water was prepared using a BarnsteadTM E-Pure™ ultrapure water purification system (Dubuque, USA).

2.2 Determination of the phase diagram

Glass test tubes containing a mixture of the desired compositions of SSE, water or alcohol aqueous solution, and EVO were mixed using a vortex mixer (MyLab TMSLV-6; Seoulin Bioscience Co., Ltd., Seongnam, Korea) and stoppered to prevent sample evaporation. The samples were then heated using a block heater (Heating Block HF-21; Yamato Scientific Co., Ltd., Tokyo, Japan) at 80°C for 20 min. After ensuring the mixtures were homogeneous, they were stored at room temperature for one month to reach an equilibrium state.

Polarizing plates placed on each side of the test tube under a crossed Nicols condition were used to confirm whether the mixtures formed liquid crystalline phases at 65°C. If a uniform liquid crystalline phase formed, the light passed through the polarizing plates because of the birefringence of the liquid crystal structure. The types of liquid crystal phases were identified using small-angle X-ray scattering (SAXS) techniques.

2.3 Small-angle X-ray scattering measurements

SAXS measurements were performed on a Nano-Viewer SAXS instrument (Cu Kα radiation; Rigaku Co., Tokyo, Japan) equipped with a PILATUS detector at a wavelength (λ) of 0.154 nm (30 mA and 40 kV). The samples were poured into Mylar membrane pockets affixed to a U-shaped board (height: 1.5 cm, width: 1.2 cm, depth: 2 mm) using double-sided tape. The temperature of the samples during the measurements was maintained at 65°C using a microscope hot stage (Mettler-Toledo International Inc., Tokyo, Japan) and an FP90 central processor (Rigaku Co., Tokyo, Japan). The peak top was analyzed using Fityk or Igor Pro (Hulinks Inc., Tokyo, Japan), and the lattice spacing was calculated using Bragg’s equation. In addition, the structure of the liquid crystal was assigned using the obtained lattice spacing ratio.

2.4 Preparation of oil in water emulsions

The mixtures of SSE and a water or alcohol aqueous solution were prepared at the desired weight ratios and mixed using a vortex mixer before emulsification. The required amount of EVO was dropped into the mixtures with mechanical stirring using an anchor blade mixer (Mazera Z; Tokyo Rikakikai Co., Ltd., Tokyo, Japan) at a mixing speed of 300 rpm and a constant temperature of 65°C (Uni Cool UC-55; Tokyo Rikakikai Co., Ltd., Tokyo, Japan). After adding the EVO, water or alcohols aqueous solution was

| Table 1 | HLB and ester composition of SSEs. |
|---------|----------------------------------|
| SSE     | HLB  | Ester composition (% w/w) |
|         |      | mono  | di < |
| S-570   |  5   | 30    | 70   |
| S-1170  | 11   | 55    | 45   |
| S-1670  | 16   | 75    | 25   |

Fig. 1 Chemical structure of sucrose mono stearic acid ester (SSE).
added to the mixtures with stirring using an anchor buddle mixer (mixing speed: 300 rpm) at 65°C until the final ratio of SSE and EVO:water or alcohols ag. was 0.03:0.97. The emulsification courses A and B on the phase diagram are shown in Fig. 2. The oil in water (O/W) emulsion for the mixing course was prepared in triplicate. In addition, previous tests showed that ET and PR evaporated during the emulsification at 65°C; therefore the desired weight ratios were maintained by compensating for the evaporated amounts of ET and PR.

2.5 Measurement of particle size distributions

Particle size distributions of the O/W emulsions were analyzed using a laser scattering particle size analyzer (SALD-7100; Shimadzu Co., Kyoto, Japan) with a batch cell unit. The particle size distributions were measured in triplicate by taking three measurements from the same emulsion except for one sample. The volume-based particle mean diameters and 95% confidence intervals (n = 9 or 6) were then calculated from all the results.

3 RESULTS AND DISCUSSION

3.1 Phase diagram

The phase diagrams of the SSE/water/EVO systems and SSE/40 wt% SC aqueous solution (40% SC aq.)/EVO systems showed a one-phase region (I) and a two-phase co-existing region including a separated oil phase (II), as shown in Fig. 3. An SC concentration of 40% was selected for comparison with previous studies.23, 26 The effect of SC on the phase diagram was investigated by comparing the water systems (left side in Fig. 3) and 40% SC aq. systems (right side in Fig. 3). All diagrams of the SSEs with different HLBs (S-1670, S-1170, S-570) show expansion of the one-phase region; in other words, the oil-separated two-phase coexisting region in the 40% SC aq. systems is less than that for the water systems. Moreover, a high HLB, i.e., highly hydrophilic S-1670, shows the largest one-phase region among the SSEs with different HLBs in both the 40% SC aq. and water systems. In addition, the samples are in a gel state and do not flow in the region of high SSE concentration; however, as the concentration of SSE decreases, the fluidity increases and changes from a gel to a sol state (data not shown).

Murakami et al. indicated that the cloud point of decaglycerin monooleic acid ester (DGMO) and polyoxyethylene sorbitan monooleate (MOPS) extensively decreased as the sugar concentration increased, and sugar added to DGMO or MOPS/water/tricapryl acid glyceride systems expanded the liquid crystalline phase region.23, 24 Miyashita et al. revealed that adding SC to MOPS/water/EVO systems at 25°C and to decaglycerol monolaurilester (DGML)/water/EVO systems at 25°C expanded the liquid crystalline phase; the spongious phase region expanded toward lower MOPS contents, and the lamellar phase region expanded toward lower DGML contents, respectively.25 Ikeda et al. clarified that disaccharides, such as D-maltose and SC, enlarged the liquid crystal region more than monosaccharides, such as D-glucose and D-fructose.26 Prasert and Gohtani determined that adding SC to a polyoxyethylene sorbitan monolaurate/water/EVO system had little effect on the phase behavior, but adding SC changed the phase behavior in the polyoxyethylene sorbitan monopalmitate or MOPS/water/EVO systems.27 In our previous studies, even though the hydrophilic group and the hydrophobic group of the amphiphilic substance were different, it was common for the liquid crystal region to expand by adding

![Fig. 2 Emulsification courses on the phase diagrams.](image-url)
sugar to the aqueous phase. This finding suggests that decreasing the oil-separated region and expanding the one-phase region by adding SC to the systems in this study is caused by expanding the liquid crystal region of the SSEs. The liquid crystal phase of the SSEs was presumed to consist of lamellar structures because sucrose fatty acid esters with various fatty acid chain lengths and degrees of esterification form lamellar structures. Additionally, Dave et al. used SAXS to confirm lamellar structures in sucrose laurate or sucrose oleate (high monoester content: high HLB type)/aqueous phase/D-limonene systems containing SC and trehalose at high concentrations. The phase diagram of the SSE/SC aq./EVO system shows a one-phase region and a two-phase coexisting region including a separated oil or water phase, as shown in Fig. 3. The effect of PG and GL on the phase diagrams was compared with that for the water system (upper left side). In both cases, expansion of the one-phase region by adding PG or GL is common, but the expansion is smaller than that for the 40% SC aq. system. The water phase separation for the 50% PG aq. system occurs in a region with high water content. PG may have higher hydrophobicity than GL and sucrose, so the affinity of SSE for water probably decreases because of the change in the liquid crystal structure of SSE caused by PG.

On the other hand, the 10% or 50% ET aq. and 10% or 50% PR aq. systems show a one-phase region and a two-phase coexisting region including a separated oil or water phase, as shown in Fig. 5. The effect of ET and PR on the phase diagrams was investigated with respect to the water system (upper left side). Adding 10% ET or PR expanded the one-phase region, but...
Effect of Alcohols on the Emulsification of a Sucrose Ester System

Fig. 4  Phase diagrams of the W or alcohols aq./SSE(S-1170)/EVO systems at 65°C (top left: water, top right: 40% SC aq., bottom left: 50% GL aq., bottom right: 50% PG aq.).

Fig. 5  Phase diagrams of the W or alcohols aq./SSE/EVO systems at 65°C (top left: water, top middle: 10% ET aq., top right: 50% ET aq., bottom left: 40% SC aq., bottom middle: 10% PR aq., bottom right: 50% PR aq.).
adding 50% ET or PR causes the one-phase region to almost disappear. Dixit et al. indicated that most of the water molecules exist as small hydrogen-bonded strings and clusters in a "fluid" of close-packed methyl groups, with water clusters bridging the neighboring methanol hydroxyl groups through hydrogen bonding in a concentrated alcohol-water mixture, and they suggested an incomplete mixing model at the molecular level. The hydrophobic environment formed by the methyl groups of ET or PR could interact with the hydrophobic moiety of the SSEs, weaken the interaction between the SSEs, promote destruction of the liquid crystal structure and molecular dissolution, and decrease the emulsifying ability of the SSEs. For 10% ET and PR, as well as GL and SC, the liquid crystal region expands, likely because of the decreasing hydrophilicity of the SSEs from hydration of ET or PR. PR (10%) is more hydrophobic than ET (10%); thus, at the same concentration, PR strongly influences the structure of the SSEs, and the three-phase region appears to separate. Therefore, the optimum concentration must be determined in future research.

3.2 SAXS measurements

In this study, only the lamellar liquid crystal is confirmed as a type of liquid crystal structure by the calculated lattice spacing ratios (1:1/2:1:3/1:4), showing that clear peaks are obtained. An example of the S-1670 system is shown in Fig. 6. In the water and S-1670 system, no liquid crystal structure is observed in the region with high water content (water:S-1670:EVO = 7:3:0). However, when SC was added to water, a lamellar liquid crystal structure is confirmed in the same water-rich region (40% SC aq.:S-1670:EVO = 7:3:0). As discussed for the phase diagram, the SAXS results confirm that adding SC helps form a liquid crystal structure (lamellar liquid crystal). The multiple lamellar liquid crystal structures with different lattice spacings (d) in a region with high SSE content are probably due to the presence of sucrose fatty acid ester with different carbon chain lengths from the SSEs. The difference in the d value between the different lamellar liquid crystal structures is about 0.3 or 0.6 nm, which correspond to 2 or 4 times the distance of a single bond between two carbon atoms (about 0.15 nm). In other words, the liquid crystal structure composed of SSE and SPE, or SPE and SPE is considered to coexist with the main lamellar liquid crystal structure composed of SSE and SSE.

Figure 7 shows the relationship between \( X_w \) (left side) and \( d \), and \( X_0 \) (right side) and \( d \), which were calculated from the first peak of the assigned to the lamellar liquid crystal. \( X_w \) is the weight fraction of 40% SC aq. in the 40% SC aq. and SSE systems (results for 40% SC aq.:SSE:EVO = 1:9:0, 3:7:0, 5:5:0, 7:3:0, and 9:1:0), and \( X_0 \) is the weight fraction of EVO in the alcohols aq./S-1170/EVO systems (result from water or alcohols aq.:S-1170:EVO = 5:5:0, 4:4:2, and 3:3:4). For systems with multiple lamellar liquid crystal structures, all values of \( d \) are plotted.

As \( X_w \) increases, \( d \) increases, with a particularly marked increase when \( X_w \) is equal to or greater than 0.7. S-1170 and S-570 have the largest \( d \) values at \( X_w = 0.9 \). The lamellar structure could not be confirmed for S-1670 at \( X_w = 0.9 \). It is presumed that S-1170 and S-570 could maintain the lamellar structure even if the amount of water increases, but S-1670 could not. A two-chain amphiphile, such as a phospholipid, forms a stable lamellar liquid crystal structure. Conversely, Yamada et al. investigated the effect of osmotic pressure on vesicle formation in a di-oleoyl-phosphatidylcholine/water/NaI system and concluded that the osmotic pressure, which is due to the high amount of NaI in the lipid film, induces an unbinding transition, which accelerates vesicle formation from the lamellar structure.
In this study, the S-1170 and S-570 systems maintain the lamellar liquid crystal structure, even in the region with high water content ($X_w = 0.9$). As shown in Table 1, S-1170 and S-570 contain more polyesters, which are more hydrophobic than monoesters. Therefore, the lamellar liquid crystal structure could be maintained, even in the region with high water content, because the hydrophobic interaction between polyesters is strong. However, S-1670 contains more monoesters than polyesters, so the liquid crystal structure changes (to a vesicle or micelle structure) in the region with high water content.

Compared with $X_w$, even if $X_o$ increases, there is no significant change in $d$. This result suggests that water is incorporated as a microdomain in the interlamellar structure, but EVO is not incorporated. In other words, the oil is incorporated as a macrodomain while maintaining the lamellar structure that is constituted by water or alcohols (aq.) and SSEs in this system. This system appears to be close to the emulsification method developed by Suzuki et al., which formed oil in a liquid crystal emulsion. Figure 7 shows a comparison of the $d$ values between the water system and alcohol system: the $d$ value is smaller in the alcohol systems (less than 8 nm) than in the water system (larger than 8 nm). The $d$ value for the 50% PG aq. system is markedly lower at 6 nm or less. As mentioned above, the interlamellar distances are shortened by inhibiting the hydration of the SSEs by hydration of the alcohols. Meanwhile, we hypothesize that PG changes the innerlamellar structure because of the polarity of PG, and consequently, $d$ becomes shorter than the other systems. PG enters the

**Fig. 7** Relationship between $X_w$ (left side) and the lengths of lattice spacing ($d$), and between $X_o$ (right side) and the lengths of lattice spacing ($d$), calculated from the first peak of the peak assigned as lamella liquid crystal.

**Fig. 8** Average values obtained from the results of measuring the mean diameter of oil droplets in the emulsions of the W or 40% SC aq./SSE/EVO systems for each emulsification course (left: Course A, right: Course B). Error bars indicate 95% confidence intervals ($n = 9$ or 6); double asterisks (***) indicate a significant difference in the average value of the water system at the 1% significance level; and the absence of an asterisk indicates no significant difference at the 5% significance level.

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hydrophobic region of the lamellar structure and could closely pack with the fatty acid chain of SSEs. Furthermore, the water separation region of the 10% PG aq. system described in the phase diagram presumably results from a more compact lamellar structure, which is different from the other systems\textsuperscript{200}.

3.3 Emulsification

Figures 8 and 9 show the average values obtained by measuring the mean diameter of the oil droplets in the emulsions for each emulsification course (left: Course A, right: Course B). Figure 8 shows the influence of SC on the systems and the comparison between the SSEs with different HLB values. S-1670, which shows the narrowest separation region in the phase diagram, has the smallest average mean diameter of oil droplets in both courses. The separation region in the emulsification course of the phase diagram for the S-1170 (Course B) and S-570 (Course A) systems narrow by adding SC, and they have significantly smaller average mean diameter for the oil droplets than those for the water systems. Wakisaka et al. revealed that replacing the water with GL in the water/mixture of polyglycerol polyricinoleate and hexaglycerol monolaurate/EVO \textsuperscript{174} system changed the microstructure of the mixed surfactants, and as a result, the mean diameter of the oil droplets of emulsion with optimal liquid crystal structure decreases\textsuperscript{32}. However, in this study, the same microstructure (lamellar liquid crystal structures) is observed regardless of the presence or absence of SC in the SAXS measurements of the courses (S-1170, Course B and S-570, Course A), where the mean diameter of oil droplets changes. Therefore, unlike the result obtained by Wakisaka et al., a relationship between the microstructure and the change in the mean diameter of oil droplets could not be found.

The influence of adding various alcohols to the S-1170 system is shown in Fig. 9. With the 50% ET aq. and 50% PR aq. systems, precipitation and separation occur during the emulsification course; therefore, emulsification is not possible. Lamellar structures with $d = 4.0 - 4.1 \text{ nm}$ are observed from the SAXS measurement of the 50% ET aq. and 50% PR aq. systems \textsuperscript{(data not shown)} in the emulsification courses at room temperature. From the value of $d$, SSE is considered to crystallize on its own and precipitate; as a result, emulsification is not possible\textsuperscript{301}. For the 40% SC system mentioned above, the systems whose separation regions in the emulsification course on the phase diagram are narrowed by adding alcohols show significantly smaller average mean diameter of oil droplets than those of the water systems. However, only Course A of the 10% ET aq. system show large average values of mean diameter of oil droplets, even with no separation area on the course.

The ratio of distances through the oil-separated region to the total distances during the emulsification courses on the phase diagrams was calculated using the values measured from the phase diagrams to confirm the influence of the separation region on the mean diameter of oil droplets. The correlation between the ratio and the mean diameter of oil droplets is shown in Fig. 10. The coefficient of determination ($R^2$) was calculated, as shown in Figure 10 (dashed line), and a high correlation is found between the ratio and the mean diameter of oil droplets, although the result is qualitative. Furthermore, a higher correlation is observed (solid line and $R^2$) by excluding the results for the S-1170 10% ET aq. system.

In describing the SAXS results, if the systems are the same as that considered by Suzuki et al., the mean diameter of oil droplets should depend on the physical stirring force when SSE and EVO are in a fixed ratio\textsuperscript{32}. The correlation between the distances through the oil-separated region and the mean diameter of oil droplets is a reasonable result considering that the physical force is poorly used in the oil-separated region. Suzuki et al. found that adding alcohols such as GL improves the oil uptake capacity of liquid crystals by increasing the liquid crystal forming...
Effect of Alcohols on the Emulsification of a Sucrose Ester System

4 CONCLUSIONS

The effect of alcohols (ethanol, 1-propanol, propylene glycol, glycerin, sucrose) on the phase behavior and emulsification of SSE/water/EVO systems were investigated. Adding sucrose, propylene glycol, and glycerin narrowed the oil-separated two-phase region of the phase diagram of the SSE/water/EVO systems, whereas adding ethanol and 1-propanol expanded the oil-separated two-phase region. By changing the emulsification in the phase diagram, the oil droplet particle size generally decreased in the system with a narrowed oil-separated region. The emulsification properties of the systems varied by changing the phase diagram. The microstructure of the systems was examined using SAXS and the ease of incorporation of macroscopic oil into the lamellar structure of the SSEs was suggested as an important role for emulsification, because the mechanism of the systems was the same as the mechanism for liquid crystal emulsification.

The influence of the interfacial tension on the reducing ability, viscosity, and liquid crystal film viscoelasticity could also affect the emulsification; therefore, further investigation is expected. We hope that the results of this study will be useful for future application research on glycol lipids in the food industry and in the field of biochemistry.

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