Effects of Sugars on the D Phase Emulsification of Triglyceride Using Polyoxyethylene Sorbitan Fatty Acid Ester

Atsushi Murakami1,2, Kazuhiro Fukada3, Yoshimasa Yamano4 and Shoichi Gohtani3*

1 Department of Food Science, The United Graduate School of Agricultural Science, Ehime University
(2393, Ikenobe, Miki-cho, Kita-gun, Kagawa 761-0795, JAPAN)
2 Research and Development Department, Kamada Soy sauce Co., Ltd.
(1-6-35, Hommachi, Sakaide, Kagawa 762-0044, JAPAN)
3 Department of Biochemistry and Food Science, Kagawa University
(2393, Ikenobe, Miki-cho, Kita-gun, Kagawa 761-0795, JAPAN)
4 Institute of OISHISA Science
(Next-Kagawa 101, 2217-44 Hayashimachi, Takamatsu, Kagawa 761-0301, JAPAN)

Abstract: Sucrose, D-glucose and D-maltose were examined for their effects on the hydrophilie-lipophile balance (HLB) of polyoxyethylene sorbitan monooleate (MOPS) and the D phase emulsification of triglyceride by MOPS. With rise in concentration, each was found to decrease HLB of MOPS with reduction in MOPS cloud point. In the phase diagram of the MOPS/aqueous solution/triglyceride three component system, the D phase region was noted to expand with sucrose addition. Regardless of the sugar, an O/D emulsion gel formed at high triglyceride content on adding oil to a 40 wt% aqueous sugar and MOPS mixture. Mean O/W emulsion droplet size subsequent to O/D emulsion gel dilution was ca. 1 μm while with agent-in-oil emulsification, ca. 10 μm. Droplet distribution of the emulsion prepared by agent-in-oil emulsification was broad and that of the emulsion produced by D phase emulsification, narrow. It thus may be concluded that the addition of sugars as the 4th ingredient to a MOPS/water/triglyceride system is a promising means for D phase emulsification in the industry.

Key words: polyoxyethylene sorbitan fatty acid ester, sugar, cloud point, emulsion, D phase emulsification

1 Introduction

Polyoxyethylene sorbitan fatty acid ester, a widely used surfactant in cosmetic production, has been used as a licensed food additive from the 1960s in the United States and 1995 in EU. Polyoxyethylene sorbitan fatty acid esters as food additives in Japan are presently under consideration by the Food Safety Commission of Japan (1). Sagitani et al. noted the addition of polyols to polyoxyethylene sorbitan fatty acid ester/water/oil systems to readily provide fine uniform O/W emulsions (2), the procedure for this process being referred to as D phase emulsification since O/W emulsions can be obtained by the dilution of an oil-in-surfactant emulsion gel (O/D emulsion gel) comprised of concentrated oil droplets surrounded by a surfactant phase (D phase). It thus follows that not only polyol but also sugars, commonly used in food preparation, may function in the same manner as polyols in emulsification since sugar molecules, like polyols, also possess hydroxyl groups.
Accordingly, the present study was conducted to clarify the effects of sugars on D phase emulsification.

Previous examination of the effects of sucrose on the emulsification of a polyglycerin fatty acid ester/water/triglyceride system (3) clearly indicated sucrose to decrease the hydrophilic-lipophilic balance (HLB) of polyglycerin fatty acid ester, resulting in greater hydrophobicity and the production of fine droplet-size O/W emulsions.

The effects of sugars on emulsification of the polyoxyethylene sorbitan monooleate (MOPS)/water/triglyceride system were examined so as to clarify whether these effects on D phase emulsification would be the same as noted for the system previously studied.

2 Experimental

2.1 Materials

Polyoxyethylene (20 oxyethylene units) sorbitan monooleate (MOPS; commercial name, Polysorbate 80 with reported HLB number, 15.0) was from Nikko Chemicals Co. and triglyceride (tricaprylic acid glyceride) from NOF Co. Sucrose and D-glucose were obtained from Wako Pure Chemical Co. D-maltose was from Hayashibara Inc. All materials were used without further purification. De-ionized and then distilled water was used in all cases.

2.2 Methods

2.2.1 Phase diagram and cloud point

Samples differing in composition were placed in test tubes which were then sealed. Homogeneity was brought about using a vortex mixer operated above 90°C. The tubes, after being repeatedly shaken, were stored in a thermostat bath at 25°C. Phase state and the presence of liquid crystals were confirmed by direct visual and/or polarized light microscopy (OLYMPUS, BH-2) at 25°C.

Change in MOPS cloud point with sucrose concentration was noted in each case by visual inspection of 1.0 wt% MOPS aqueous solution.

2.2.2 Preparation of O/D emulsion gel and O/W emulsion

MOPS and water (or aqueous sugar solution) were mixed at a 1:1 using it ration followed by very slow triglyceride addition with stirring at room temperature to produce an O/D emulsion gel with 80 wt% triglyceride content. For O/W emulsion preparation, gradual O/D emulsion gel (5 g) dilution with water (15 g) was carried out with stirring using a magnetic stirrer.

2.2.3 Oil-droplet size distribution

Each O/W emulsion was diluted by excess water and droplet size distribution was determined base on microscope images using computer software, Scion Image (Scion Co.).

3 Results and Discussion

3.1 Phase Diagram

Phase diagrams obtained for MOPS/water/triglyceride and MOPS/aqueous 40 wt% sucrose solution/triglyceride are shown in Fig. 1 (A) and (B), respectively. Figure 1 (A) shows the isotropic surfactant phase (D) to have formed at MOPS with water content above 50 wt% and below 20 wt%, respectively. At MOPS content less than 50 wt%, the oil phase (O) separated out to give a two-phase coexisting region (D + O). At on MOPS to water ratio less than 0.35, a two-phase region consisting of micelle solution and an oil phase (Wm + O) was formed. At triglyceride content below 10 wt%, a liquid crystal phase (LC) could be seen at 42-75 wt% MOPS and 20-58 wt% water content. An isotropic transparent gel (VI) could be seen at 35-55 wt% MOPS content. In the middle of the phase diagram, an isotropic cloudy gel phase (VW) was present.

For the MOPS/aqueous 40 wt% sucrose solution/triglyceride system (Fig. 1 (B)), D phase and (D + O) regions could be seen to spread toward the low MOPS content region more so than in Fig. 1(A). The VW phase and two-phase region consisting of Wm + O disappeared and in place of which, a three-phase region (D + Om + W) appeared at MOPS content below 40 wt%.

The two phase diagrams in Fig. 1 suggest the effects of sucrose on phase behavior to possibly arise from decrease in HLB of MOPS. Reduction in HLB for polyglycerin fatty acid ester by sucrose was previously confirmed (3).

3.2 Effects of Sugars on MOPS Cloud Point

The cloud point of a surfactant is closely related to HLB (4) and thus, in this study, the effects of sucrose, D-glucose and D-maltose on this parameter were examined.

Figure 2 shows MOPS cloud point to decrease with sucrose concentration above 10 wt%, suggesting reduc-
Effects of Sugars on the D Phase Emulsification

In HLB, i.e., greater hydrophobicity of MOPS due to sucrose. The enlarged D phase region in Fig. 1(B) may possibly be due to increased solubility of triglyceride in the D phase owing to higher hydrophobicity of MOPS. With addition of D-glucose or D-maltose instead of sucrose, the cloud point decreased more steeply with sugar content, so that MOPS in D-glucose or D-maltose aqueous solution may be considered more hydrophobic than in sucrose solution.

3.3 O/D Emulsion Gel Formation

In D phase emulsification, the O/D emulsion gel was initially prepared by the slow addition of oil to the D phase with stirring followed by dilution with excess aqueous solution to obtain the O/W emulsion (2). For clarification of the phase transformation process during triglyceride addition to the 1 : 1 mixture of MOPS and aqueous solution to produce the O/D emulsion gel, triglyceride weight fractions of 0.2, 0.4, 0.6, and 0.8 were prepared as shown in A, B, C and D in Fig. 3, respectively. Sample appearance for MOPS/water/triglyceride and MOPS/aqueous 40 wt% sucrose solution/triglyceride is shown in Figs. 4-1 and 4-2, respectively.

It is evident from Fig. 4-1 that a white hard gel is formed at compositions A and B but the oil phase separates out at the oil content above 60 wt% (point C and D) for the MOPS/water/triglyceride system. For the MOPS/sucrose solution/triglyceride system (Fig. 4-2), a turbid liquid was obtained at A with the system in the two-phase region (D + O). With increase in oil content in proceeding from A to C, the sample in Fig. 4-2 became more viscous and translucent. At D, a cloudy transparent O/D emulsion gel could be seen. These findings were essentially the same as in the formation of a transparent gel in the polyoxyethylene sorbitan fatty acid ester/aqueous polyol solution/oil system (2).

The transparency of an O/D emulsion gel is correlated with HLB of the surfactant (5). When glycerin or sorbitol, which lowers the cloud point of nonionic sur-
factants, is added to a nonionic/water/oil system, a transparent O/D emulsion gel is obtained on using more hydrophilic surfactants. With the present system, sucrose lowered the cloud point of MOPS and thus a more clearly transparent gel should be produced on using a more hydrophilic nonionic surfactant than MOPS.

### 3.4 Effects of Glycerin, PEG and Sucrose Compared

The effects of glycerin and polyethyleneglycol (PEG 400) on the phase behavior of nonionic surfactant/water/oil systems reported by Sagitani et al. should be discussed in order so as to clarify the effect of sucrose in the present system. (5)

The addition of glycerin has been shown to enlarge the D phase region in the polyoxyethylene oleyl ether/aqueous solution/liquid paraffin system and increase the cloud point of polyoxyethylene oleyl ether. In the polyoxyethylene oleyl ether/aqueous 80 wt% glycerin solution/liquid paraffin system, a two-phase (D + O) region and O/D emulsion gel formation were previously clearly demonstrated (5). In this study, with

---

**Fig. 3** Schematic Diagram of Triglyceride addition to a 1:1 Mixture of MOPS and Aqueous Phase. Weight Fractions of Triglyceride were 0.2, 0.4, 0.6 and 0.8 as into A, B, C and D, respectively.

**Fig. 4** Photographs of MOPS/Aqueous 40 wt% Sugar Solution/Triglyceride Systems. Weight Ratios of MOPS, Sugar Solution and Triglyceride were 4:4:2 (A), 3:3:4 (B), 2:2:6 (C) and 1:1:8 (D), respectively.
aqueous 70 wt% PEG 400 as an aqueous solution, D phase region enlargement was less and the cloud point decreased. The two-phase region was shown composed of the D phase and water (D+W) since polyoxyethylene oleyl ether was not soluble in aqueous solution of 70 wt% PEG 400, nor could an O/D emulsion gel be obtained by liquid paraffin addition to the D phase containing PEG 400.

The present study confirms the following: 1) sucrose lowers the cloud point of MOPS, 2) sucrose enlarges the D phase region like PEG 400 and 3) two-phase region (D+W) and O/D emulsion gels are formed in the system containing sucrose. The hydrophile-lipophile balance of MOPS in the system of MOPS/aqueous 40wt% sucrose solution/liquid paraffin should thus be essentially the same as that of polyoxyethylene oleyl ether with aqueous 80 wt% glycerol solution + liquid paraffin.

3.5 D Phase Emulsification

To demonstrate potential application of D phase emulsification to the MOPS/aqueous sucrose solution/triglyceride system, comparison was made of droplet size of O/W emulsions prepared by D phase emulsification and agent-in-oil emulsification (6). In the former, MOPS was dissolved in the aqueous phase and oil was slowly added with stirring to produce an O/D emulsion gel with 80 wt% triglyceride, 10 wt% aqueous phase and 10 wt% MOPS. An O/W emulsion was prepared by diluting the O/D emulsion gel as described in 2.2.2. In the latter, MOPS was first dissolved in triglyceride, followed by excess aqueous solution addition with stirring. The final O/W emulsion samples were 2.5 wt% MOPS, 77.5 wt% aqueous phase and 20 wt% triglyceride.

Microphotographs of emulsions obtained by D phase emulsification (A) and agent-in-oil emulsification (B) are shown in Fig. 5. Mean droplet size in Fig. 5 (A) and (B) was ca.1 μm and ca. 10 μm, respectively, thus clearly indicating greater efficiency of D phase emulsification for preparing an O/W emulsion.

3.6 Effects of Each Sugar

For mixtures with 10 wt% MOPS, 10 wt% aqueous sugar solution containing 40 wt% D-glucose or D-maltose and 80 wt% triglyceride, translucent O/D emulsion gel formation was confirmed as shown in Fig. 4-3 and 4-4. Gels containing D-glucose or D-maltose were less transparent than that with sucrose, the difference possibly arising from the hydrophobicity of MOPS in 40 wt% D-glucose or D-maltose solutions compared to 40 wt% sucrose (see Fig. 2). The transparency of an O/D emulsion gel is sensitively influenced by HLB of the emulsifier (5).

Droplet size distribution of O/W emulsions prepared by D phase emulsification was examined. Fine emulsions were obtained for any sugar used. Figure 6 clearly shows droplet size of the O/W emulsion containing D-maltose to be smallest and size distribution to be narrower compared to cases with sucrose or D-glucose.

3.7 Effects of Sucrose Concentration on O/D Emulsion Gel Formation

These effects were examined for 10, 20 and 30 wt% sucrose aqueous solutions. 10 wt% MOPS, 10 wt% aqueous phase and 80 wt% triglyceride samples were prepared. As shown in Fig. 7, no O/D emulsion gel
A. Murakami, K. Fukada, Y. Yamano et al.

could be prepared and the oil phase separated out on using the 10 wt% aqueous sucrose solution. But with the 20 wt% aqueous sucrose solution, a very soft and heterogeneous gel was obtained with the oil still separated out from the gel. The failure to produce an O/D emulsion gel using sucrose solutions below 20 wt% may possibly have been due to the too high HLB of MOPS in the systems. With 30 wt% sucrose aqueous solution, a white O/D emulsion gel was formed and from which, an O/W emulsion was prepared by D phase emulsification. Droplet size, however, exceeded that of the O/W emulsion made with 40 wt% sucrose solution.

4 Conclusion

Examination was made of the effects of sucrose, D-glucose and D-maltose on MOPS cloud point and D phase emulsification of triglyceride by MOPS. Each sugar decreased the cloud point, indicating enhanced hydrophobicity of MOPS. At high triglyceride content, an O/D emulsion gel was prepared by the addition of oil to MOPS and 40 wt% aqueous sugar solution mixtures. Fine O/W emulsions were produced by diluting the O/D emulsion gel. Sucrose should thus serve as the 4th ingredient in a MOPS/water/triglyceride system for preparing food emulsions.

References


