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# Influence of sugar surfactant structure on the encapsulation of oil droplets in an amorphous sugar matrix during freeze-drying

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ABSTRACT

The encapsulation of O/W emulsion droplets in a freeze-dried amorphous sugar matrix was investigated, focusing on the impact of the molecular structure of the emulsifying surfactant. O/W emulsions, containing various surfactants, were freeze-dried in the presence of a sugar. Thirty types of surfactants, including eighteen different sugar surfactants and ten types of commercially available sugar ester mixtures, were used. Linoleic acid methyl ester and trehalose were used as the oil phase and sugar. The amounts of oil droplets encapsulated in freeze-dried amorphous sugar matrix were analyzed by Fourier transform Infrared spectroscopy. Sugar surfactants were generally superior to the other classes of surfactants for oil droplet encapsulation during freeze-drying, and there was the optimum alkyl chain length of the sugar surfactant. Sugar esters generally exhibited greater oil encapsulation than sugar ethers. Larger sugar head group appeared to result in better encapsulation in the case of sugar esters, but the opposite tendency was found for sugar ethers. A limited combination of sugar surfactants (15% sucrose mono- and 85% di-stearate) resulted in the maximum oil droplet encapsulation efficiency although these surfactants are individually quite poor in the encapsulation and other tested combinations did not improve the encapsulation efficiency relative to their individual effectiveness.



## 1. Introduction

O/W emulsion is one of the forms of oil that is frequently used as in foodstuffs. A surface active substance is usually used as an emulsifier, and the characteristics of the surfactant are determinants of the stability of such O/W emulsions. A wide variety of surfactants have been examined for their contributions to emulsion stability, and considerable knowledge and know-how in terms of tuning an O/W emulsion stability are currently available (Benita & Levy, 1993; Capek, 2004; Tadros, Izquierdo, Esquena, & Solans, 2004).

On the other hand, in the case of oily flavoring substances, hydrophobic therapeutic agents, insoluble taste components, and related food additives, it is often necessary to convert them into a solid (powder) form from the viewpoint of the handling and usage. In the case of solidification (powderization), the oily materials are emulsified into O/W emulsions with the aid of a surfactant and then dehydrated in the presence of bulk forming agents. Consequently, the emulsified oil droplets, or oil droplets containing hydrophobic substances, are embedded in the resulting dried bulk matrix. The encapsulation of emulsified oil droplets has been extensively investigated (Corveleyn & Remon, 1999; Desai & Park, 2005; Gharsallaoui, Roudaut, Chambin, Voilley, & Saurel, 2007; Gibbs, Kermasha, Alli, & Mulligan, 1999; Gouin, 2004; Porter, Charman, Williams, Bakalova, & Charman, 1996; Shimada, Roos, & Karel, 1991), in which the spray drying is frequently employed (Anwar & Kunz, 2011; Desobry, Netto, & Labuza, 1997; Gharsallaoui et al., 2007; Hogan, O'riordan, & O'sullivan, 2003). As a result, a close relationship has been found between encapsulation efficiency, emulsion size distribution (Minemoto, Hakamata, Adachi, & Matsuno, 2002; Soottitantawat, Yoshii, Furuta, Ohkawara, & Linko, 2003; Soottitantawat et al., 2005) and types of bulk-forming agent (Matsuno & Adachi, 1993; Moreau & Rosenberg, 1996; Paramita, Furuta, & Yoshii, 2010) as well as drying conditions (Anwar & Kunz, 2011; Desobry et al., 1997; Hansen, Holm, & Schultz, 2004; Jonsdottir, Bragadottir, & Örn Arnarson, 2005).

Oil droplets can be encapsulated via freeze drying. In freeze-drying, the low temperature below the freezing point and the absence of air thoroughly minimize the chemical degradation of labile components (Anwar & Kunz, 2011; Longmore, 1971) although it is reported to cost

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30–50 times more than spray-drying (Desobry et al., 1997). Another merit of freeze-drying is that the amorphous state of encapsulation matrix is easily obtained, even when easy-to-crystallize materials, such as sucrose and trehalose, are used as matrix-formers (Bayram, Bayram, & Tekin, 2005; Drusch, Serfert, Van Den Heuvel, & Schwarz, 2006). The deposition of dried preparations on the dryer wall and consequent yield loss is less likely to occur in the freeze-drying compared with spray drying (Anwar & Kunz, 2011).

It would naturally be expected that the combination of oil phase, surfactant, and matrix materials is essential for the efficiency of oil encapsulation in a dried solid (powder). In our previous study, the characteristics of various types of sugars in the encapsulation of O/W emulsion droplets during freeze-drying were investigated (Imamura et al., 2013). A model O/W emulsion, comprised of linoleic acid methyl ester and sucrose monolaurate as the oil phase and surfactant, respectively, was freeze-dried in the presence of various types of sugar and mixtures, and the amount of oil droplet encapsulated in the dried matrix was determined. The findings indicated that the loss of oil droplets mainly occurred at the primary stage of the freeze-drying process, i.e., during the sublimation of frozen water, and the oil droplets that failed to be encapsulated were segregated on the wall surface of the sample container. The final encapsulation efficiencies for different matrix-formers (sugars) after freeze-drying could be correlated with the glass transition temperatures of sugars in the fully hydrated state ($T_g^*$). Based on these findings, it was possible to optimize oil droplet encapsulation efficiency by combining different types of sugars so as to give a $T_g^*$ of around −50 °C (Imamura et al., 2013).

In the next step, the influence of the molecular structure of the surfactant on oil droplet encapsulation in a freeze-dried matrix of amorphous sugar was investigated in this study. Sugar-derived surfactants were employed in this study, since they would be expected to have a high compatibility with the bulk-forming sugar matrix. Linoleic acid methyl ester (LME) was used for an oil phase, and trehalose was mainly used as a matrix-former, respectively. As emulsifiers, various types of sugar surfactants, with different alkyl chain lengths, sugar head groups, type of bond linking the sugar head group to the alkyl chain, and alkyl chain length, were used as well as other categories of surfactants. The O/W emulsions, emulsified with various surfactants, were freeze-dried and the efficiencies of encapsulation of oil droplets in freeze-dried amorphous sugar matrix were compared. The molecular structure of the sugar surfactant that is the most suitable for the oil droplet encapsulation in freeze-drying was discussed. Furthermore, combinations of different types of sugar surfactants were also investigated for their effect on oil droplet encapsulation in a freeze-dried sugar matrix.

## 2. Materials and methods

### 2.1. Materials

D-(+)-Xylose, xylitol, fructose, α-glucose, trehalose, α-maltose, and sucrose were products of Wako Pure Chemical Industries, Ltd. (Osaka, Japan). Maltotriose, -tetraose, and -pentaose were obtained from Hayashibara Biochemical Laboratories, Inc. (Okayama, Japan). Dextrans with mean molecular masses of 1500 and 40,000 were from Sigma-Aldrich Co. (St. Louis, MO). Twenty four types of surface active substances, including eighteen types of sugar surfactants and seven types of commercial sucrose ester mixtures, were used and are listed in Table 1. *N*ε-lauryl-L-lysine was obtained, following the procedure previously described in our previous study (Koreishi et al., 2009). Namely, *Streptomyces lividans* cells, coding ε-lysine acylase (ELA) originated from *Streptomyces mobaraensis* NBRC (IFO) 13819, were cultivated for 72 h at 30 °C in the same manner as was used in our previous study (Koreishi, Kawasaki, Imanaka, Imamura, & Nakanishi, 2005). Several mL of the cell-free extract obtained from the cultivation were mixed with 50 mL of an aqueous buffer solution containing 500 mM L-lysine

**Table 1**
Sugar surfactants used in this study.

| Surfactant | MW | Abbreviation | Cat. no. |
|---|---|---|---|
| Gum arabic | 240 k–580 k | Gum arabic | 016-00025[a] |
| lauryl trimethyl ammonium chloride | 264 | LTAC | 328-86992[a] |
| lecithin | ~790 | Lecithin | 126-0812[a] |
| Nε-lauryl-L-lysine | 328 | Llysne | –[b] |
| Sodium dodecyl sulfate | 288 | SDS | 191-07145[a] |
| Sucrose caprylate ester | 469 | Sucrose C8 | 494466[c] |
| Sucrose caprate ester | 497 | Sucrose C10 | 252721[c] |
| Sucrose laurate ester | 525 | Sucrose C12 | 324374[c] |
| Sucrose palmitate ester | 581 | Sucrose C16 | 9413A101[d] |
| Sucrose stearate monoester | 609 | Sucrose C18 | –[e] |
| Sucrose stearate diester | 876 | Sucrose C18 | –[e] |
| Sucrose stearate triester | 1143 | Sucrose C18 | –[e] |
| Trehalose caprylate ester | 469 | Sucrose C8 | T459[f] |
| Trehalose caprate ester | 497 | Sucrose C10 | T460[f] |
| Trehalose laurate ester | 525 | Sucrose C12 | T461[f] |
| Trehalose myristate ester | 553 | Sucrose C14 | T464[f] |
| Trehalose palmitate ester | 581 | Sucrose C16 | T465[f] |
| α-Maltose laurate ester | 525 | Maltose C12 | –[g] |
| Palatinose laurate ester | 525 | Palatinose C12 | –[g] |
| n-Octyl-β-D-glucopyranoside | 292 | Glucose C8 ether | 494459[c] |
| n-Decyl-β-D-glucopyranoside | 320 | Glucose C10 ether | 152-483[h] |
| n-Octyl-β-D-maltopyranoside | 455 | Maltose C8 ether | 82494-08-4[h] |
| n-Dodecyl-β-D-maltopyranoside | 455 | Maltose C12 ether | 341-06161[f] |
| Sucrose mono- (80%) + di, tri-laurate (20%) | | L-1695 | –[d] |
| Sucrose mono- (80%) + di, tri-myristate (20%) | | M-1695 | –[d] |
| Sucrose mono- (80%) + di, tri-palmitate (20%) | | P-1670 | –[d] |
| Sucrose mono- (70%) + di, tri-olate (30%) | | O-1570 | –[d] |
| Sucrose mono- (30%) + di, tri-stearate (70%) | | S-570 | –[d] |
| Sucrose mono- (55%) + di, tri-stearate (45%) | | S-1170 | –[d] |
| Sucrose mono- (70%) + di, tri-stearate (30%) | | S-1670 | –[d] |

Supplier: (a) Wako Pure Chemical Industries, Ltd.; (b) Prepared in lab.; (c) Calbiochem Co. (San Diego, CA); (d) Mitsubishi Kagaku Foods Co. (Tokyo, Japan); (e) gifted from Mitsubishi Kagaku Foods; (f) Dojindo Lab. (Tokyo, Japan); (g) gifted from Adachi et al.; and (h) Affymetrix Inc. (Santa Clara, CA).