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Regular Article

Interface tuning and stabilization of monoglyceride mesophase dispersions: Food emulsifiers and mixtures efficiency

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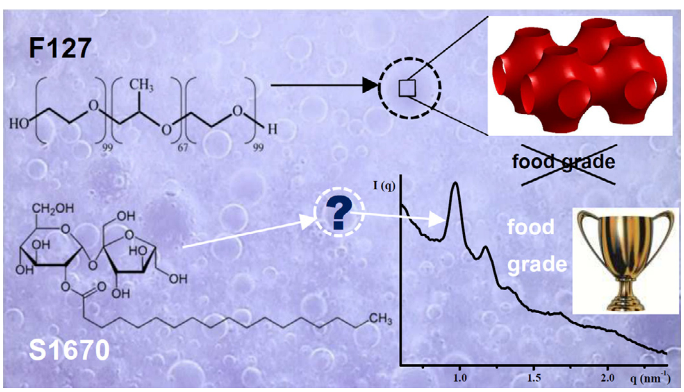
GRAPHICAL ABSTRACT



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ABSTRACT

Several food surfactants were examined as possible efficient emulsifiers for liquid crystalline monolinolein-based particles and as alternative choices to the non-food-grade emulsifier conventionally used Pluronic® F127. We described a food emulsifiers' toolbox, investigating their ability to emulsify mesophases (stabilization capacity, particle size, zeta potential) and their impact on internal nanostructures (from swelling to drastic modifications). Among the selected surfactants, sucrose stearate (S1670) was found to be the best candidate for replacing in a long term F127 as an efficient stabilizer of lipid particles. The emulsification performed by mixing F127 with S1670 or sodium caseinate (NaCas), and S1670/NaCas helped to discriminate their respective role in the particles and so their efficiency for the stabilization. In case of S1670 as co-emulsifier no strong structural modification was observed, while using F127 (25 wt% NaCas) an unexpected hexagonal mesophase was highlighted in self-assemblies. The evolution of zeta potentials by varying the mesophase and the emulsifier also informed about the distribution of co-surfactants in the particles. We thus reported submicronic nanostructured systems (from 100 to 350 nm) that were fully food-grade and possibly contained limonene, with a surface charge from −70 to −5 mV.

1. Introduction

Amphiphilic lipids such as monoglycerides are known to self-assemble when mixed with water. They form inverted mesophases leading to high interfacial area materials with both hydrophilic and hydrophobic subspaces. Hence, such mesophases can be used as

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reservoirs of active compounds of various hydrophobicities. The aqueous part embedded in the continuous hydrophobic medium may be organized in continuous cubic networks, hexagonal phase with water nano-channels or inverse micelles organized in a cubic arrangement. Among nanostructured binary mixtures, those based on monoolein [1–4], monolinolein [5] or phytantriol [6,7] are extensively studied. A fluid isotropic reversed micellar phase L_2, a reversed hexagonal phase H_2, lamellar and reversed bicontinuous cubic phases V_2 ($Pn\bar{3}m$ and $Ia\bar{3}d$ space groups) may be formed depending on temperature, water content or external pressure [8].

Mesophases are thermodynamically stable systems. When swollen by water they can be dispersed in a continuous aqueous phase as particles ideally keeping the structure of the bulk phase with excess of water [5]. Particles of submicron size containing V_2 phases (cubosomes) [9], the H_2 phase (hexosomes) [10], the reversed micellar cubic phase I_2 (micellar cubosomes) [11,12] and the L_2 phase (emulsified micro emulsions - EME) [13,14] are reported. Below room temperature, the emulsification is often easily obtained by adding an apolar component (oil) to the binary system; an oil/monoglyceride ratio is used to relate to the internal structure [14,15]. The destabilization of dispersions is prevented by using emulsifiers. In many studies, the synthetic triblock copolymer F127, consisting in two poly(ethylene oxide) blocks (PEO) separated by a poly(propylene oxide) block (PPO), is used for this purpose. The hydrophobic moieties (PPO) of the polymer are adsorbed at the surface of the particles, whereas the hydrophilic ones (PEO) build a corona that sterically stabilizes the dispersion. Emulsifiers may however interact with the internal structures of particles. Even in the case of F127 [16–18], a weak interaction is found for low F127 contents but colloidal stability is thus strongly reduced. At larger contents, the internal structure may be drastically modified by incorporating F127 [19]. In this context, screening of Pluronics performance was carried out to optimize the stability of the emulsified cubic phases [20]. New classes of steric stabilizers (PEO stearate) for lyotropic liquid crystal dispersions of monoolein and phytantriol were also recently screened [21,22].

The possibility of integrating functional molecules (drugs, foods, aroma) in those nanostructured particles suggests many potential applications like delivery systems [23,24]. Particularly they are promising systems in food industry to improve solubilization and protection of active ingredients, to be used as reactors, to control aroma release or to create structured food products [25,26]. In this context, structural transformations of these particles are notably investigated under conditions of digestion [27]. Although F127 is very efficient for stabilizing lipid mesophases, it cannot be employed for some direct applications because it is not food-grade. This drawback is overcome by searching other emulsifiers to effectively stabilize such particles. Dextran and hydrophobically modified starches are reported to disperse monoolein-based cubosomes [28]. Cellulose derivatives are tentatively used for the replacement of F127 again for stabilizing cubosomes [29,30], as well as mixtures of F127/β-casein used for emulsifying cubosomes and hexosomes [31]. By using hydrophobically modified ethyl hydroxyethyl cellulose the long-term stability as obtained with F127 is not ensured [29], whereas it is demonstrated for only 30 days with hydroxypropyl methyl cellulose acetate succinate [30]. Polysorbate 80 is used to help for the stabilization of glycerol dioleate/diglycerolmonooleate sponge-like particles for months (long-term size data not shown) [32]. The anionic surfactant citrem also stabilizes non cubic particles for three weeks [33]. Partially hydrolyzed lecithin is also used for the emulsification of monolinolein/vitamin E acetate mesophases but a poor degree of structural order is observed [34]. Moreover, the use of F127 often induces undesired vesicles in increasing amount in the sample with larger proportion of polymer [9,10]; the substitution of F127 by other emulsifiers could solve this problem [31].

Our main goals are to propose other emulsifiers being able to efficiently stabilize nanostructured lipid dispersions and to offer complete food-grade systems. In this study, neutral or charged surfactants with low or high molecular weight are used: sucrose stearate and oleate, sodium stearoyl lactylate, sodium caseinate, whey protein isolate, lecithin, and Tween 80. We first tested the ability of those food emulsifiers to disperse and stabilize various mesophases. To specify the framework of possible applications using such lipid-based particles, we tested their stability with time. Dispersions were probed by small angle X-ray scattering in order to determine dispersed mesophases; in case we described any structural modification due to an interaction between emulsifiers and mesophase compounds. The influence of the food emulsifier content on the size and overall charge of particles was observed for different kinds of mesophase. We also studied size variations and internal structure modifications with emulsifier mixtures at different ratios. The study was conducted at room temperature.

2. Experimental

2.1. Materials

Dimodan® U/J (DU) is a commercial-grade form of monolinolein and is supplied by DANISCO A/S (Braband, Denmark). It contains 96% distilled monoglycerides, of which 62% are monolinoleate. *R*-(+)-limonene is purchased from Fluka (purity > 96%). Pluronic® F127 (PEO_{99}-PPO_{67}-PEO_{99}) is provided by BASF. Sucrose stearate (S1670) has a monoester content of 75% and a purity of stearic acid of 70%; sucrose oleate (OWA-1570) has a monoester content of 70% and a purity of oleic acid of 70%. The sugar esters S1670 and OWA-1570 are gifts from Mitsubishi-Kagaku Foods Corporation. Sodium stearoyl-2 lactylate (SSL) is given by Dr. Straetmans Chemische Produkte GmbH. Sodium caseinate salt from bovine milk (NasCas) is purchased from Sigma Aldrich. Whey protein isolate (WPI, Prolacta® 90) is kindly provided by BBA Lactalis Industries where proteins represent 90% of the dry matter. Polysorbate 80 (Tween™ 80) is from Croda Uniquema. Lecithin (Phospholipon® 85G from soybean) is kindly provided by Lipoid GmbH and contains a minimum of 85% phosphatidylcholine. F127, S1670, Tween 80 and OWA-1570 are neutral emulsifiers while SSL, WPI and NaCas are anionic emulsifiers at neutral pH. Pure lecithin is zwitterionic, however Phospholipon® may contain fatty acids with negative charges. The molecular structures of those materials are gathered in Fig. 1. Copolymer F127 usually stabilizes macroemulsions by steric repulsion while charged surfactants should stabilize by electrostatic repulsion. Milk proteins (NaCas and WPI) benefit both stabilizing properties. All chemicals are used without further purification.

2.2. Sample preparation

Ultrapure water (deionized water at 18.2 MΩ cm from a Millipore Milli-Q device) is used for the preparation of all the aqueous dispersions. The mixture forming the dispersed phase is first prepared. The δ weight ratio $\delta = \frac{DU}{DU+oil} \times 100$ represents the percentage of Dimodan U in the dispersed phase. R-(+)-limonene is the oil added at room temperature to DU in order to tune the type of mesophase. The emulsifier is separately dissolved into deionized water. The emulsifier/mesophase content is defined by the β weight ratio $\beta = \frac{Emulsifier}{DU+oil} \times 100$. Except the study conducted to determine the emulsifier content effect on the size, β is kept constant at about 8.