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Regular Article

Demulsification to control solute release from Pickering crystal-stabilized water-in-oil emulsions

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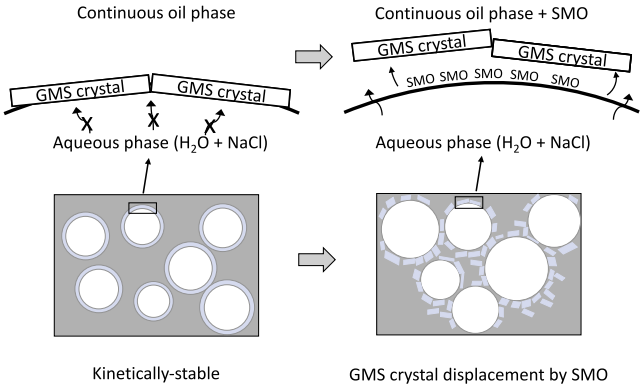
GRAPHICAL ABSTRACT



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ABSTRACT

Controlled demulsification was used to tailor the release of NaCl as a solute from water-in-oil (W/O) emulsion droplets encased in glycerol monostearate (GMS) crystalline shells. Under quiescent conditions at room temperature, the GMS shells behaved as an effective barrier against salt diffusion. A second surfactant, sorbitan monooleate (SMO), added to the emulsion post-preparation to controllably demulsify, resulted in concentration-dependent removal of the interfacially-bound GMS crystals resulting in aqueous droplet coalescence. As a result, NaCl was released from the now-unstable emulsions. Mechanistically, the SMO and GMS demonstrated competitive adsorption for the oil–water interface, with the SMO significantly reducing the displacement energy of the interfacially-bound GMS. Overall, secondary surfactant addition to Pickering emulsions was shown to have important implications for tailoring interfacial composition, and by extension, modulation of the release of solutes from fat crystal-stabilized W/O Pickering emulsions.

1. Introduction

Though most emulsions comprise small-molecule surfactants and/or polymeric substances to assist in emulsion formation and stabilization, particles adsorbed onto the oil-water interface are increasingly being sought for their ability to confer exceptional

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resistance against droplet coalescence in both oil-in-water (O/W) and water-in-oil (W/O) emulsions. Owing to their interfacial entrapment within a deep energy well when wetted by both oil and water [1], the resulting steric hindrance can potentially reduce emulsion sensitivity to pH, salt concentration and temperature [2–4]. Historically, such emulsions have been referred to as Pickering emulsions, as per one of the first reported instances of their existence [5]. Many studies have also explored how surfactants can enhance particle attachment to the oil-water interface [6–8]. With such tools, there is considerable interest in the use of particle-stabilized emulsions for applications that require stability in complex environments such as personal care products, drug delivery, and processed foods [9–11].

A vast array of particles have been explored for emulsion stabilization [12,13]. In this regard, many food-grade particles derived from chitosan, sodium alginate, cellulose, starch and others have been effectively applied to the development of Pickering-type emulsion-based delivery systems [14–16], with a variety of other particles such as cyclodextrin [17], Janus microspheres [18], protein particles [19], solid lipid nanoparticles [20] and microbes [21] also studied for their Pickering emulsion formation and stabilization ability. Pickering emulsions also have been shown to be effective for topical drug delivery [22,23].

Under certain circumstances, the outstanding stability of Pickering particles may pose problems. For example, highly-stable asphaltene-based emulsions that form during bitumen extraction can reduce oil recovery efficiency [24] whereas particle-based emulsions to remove soil contaminants demand effective particle displacement from the interface for recycling [25]. Previous attempts to remove interfacially-bound particles focused on dilution or pH variations have met with limited success as particles in biphasic solutions remain attached to the interface even after phase separation [6,26–29]. Recent efforts at Pickering emulsion destabilization have explored the detachment of particles resulting from competitive behaviour with surfactants at the oil-water interface [30]. The extent to which surfactant displace particles from the interface may give rise to both micro and macro-scale changes in emulsion properties, namely coalescence and phase separation.

In this regard, to our knowledge, there are no published reports on the competitive behaviour of surfactants in controlled release applications involving Pickering-stabilized emulsions, in particular W/O emulsions. The present study explores the release behaviour of NaCl from water droplets encased in glycerol monostearate (GMS) crystalline shells in the presence of sorbitan monooleate (SMO), a surfactant with a similar HLB value. The SMO's concentration-dependent GMS destabilization via competitive displacement is used to alter NaCl release from the dispersed aqueous phase in these emulsions.

2. Materials and methods

2.1. Materials

Canola oil (CO) (acid value ~0.2 mg KOH/g oil) [31] purchased from a local supermarket and stored at room temperature (RT) was used for the oil phase. Deionized (DI) water with a resistivity of >15 MΩ cm (Barnstead E-Pure, Thermolyne, Ottawa, ON, Canada) was used for the aqueous phase. Glycerol monostearate (GMS) (Kolliwax® GMS I, >95 wt%; MW: 358.6 g/mol; HLB = 3.8) was kindly provided by BASF (Ludwigshafen, Germany) and sorbitan monooleate (SMO) (Span®80 S6760, MW: 428.6 g/mol; HLB = 4.3) was purchased from Sigma-Aldrich (Oakville, ON, Canada) (Fig. 1). Distilled glycerol monooleate (GMO) (Dimodan MO90) was obtained from Danisco USA, Inc. (Madison, WI, USA). NaCl was purchased from Fisher Scientific (Nepean, ON, Canada).

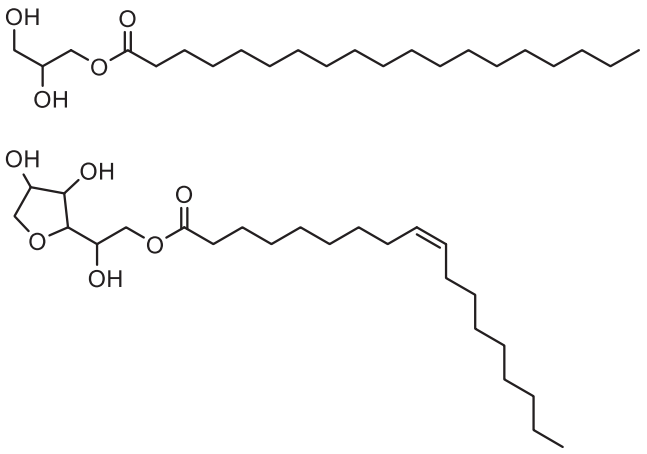

Fig. 1. Skeletal structure of GMS (top) and SMO (bottom).

The oil phase of all emulsions contained 4 wt% GMS in CO and the aqueous phase contained 5 wt% NaCl in water.

2.2. Emulsion preparation

Emulsions (400 g) were prepared by coarse-emulsifying the oil phase (80 wt%) and aqueous phase (20 wt%) with a rotor/ stator mixer (PT 10/35, Kinematica, Inc., Bohemia, NY, USA) for 1 min at 13,000 rpm using a d = 1 cm generator probe. The coarse mixtures were then emulsified in a high-pressure valve homogenizer (APV-1000, Albertslund, Denmark) at a pressure of 65 MPa for 8 cycles. All emulsification runs were performed at >70 °C to ensure that all components were liquid. Emulsions were cooled in an ice-water bath with continuous stirring (500 rpm with a magnetic stirrer) to RT (25.5 °C ± 0.5 °C). This protocol allowed the GMS to effectively emulsify and then crystallize at the oil-water interface [32].

2.3. Droplet size determination

The dispersed droplet size distribution of the emulsions was determined using a Bruker Minispec Mq pulsed field gradient nuclear magnetic resonance (pfg-NMR) unit (Bruker Canada, Milton, ON, Canada). The NMR software version was 2.58 revision 12/NT/XP (Bruker Biospin GmbH, Rheinstetten, Germany) and the water droplet size application was v5.2 revision 4a. The pulsed gradient separation and number of pulse widths were 210 ms and 8 ms, respectively. The oil suppression delay was 85 ms and the magnet gradient strength was 2 T/m. The pfg-NMR field gradient strength was calibrated with $CuSO_4$-doped water (diffusion coefficient = 2.30×10^{-9} m^2 s^{-1} at 25 °C; 1.33×10^{-9} m^2 s^{-1} at 5 °C). For analysis, emulsion samples (height = 1 cm) in glass tubes (ID = 0.8 cm, L = 20 cm) were put in the NMR sample chamber, where the temperature was kept as 5 °C using an external water-bath. Both the volume-weighted geometric mean diameter ($D_{3,3}$) and the breadth of distribution (σ, geometric standard deviation) are reported. Free water was defined as dispersed water droplets sized above the NMR instrumental limit (>500 μm) that had not phase-separated from the emulsion as bulk water. When phase separation was present, the droplet size of the remaining emulsion was measured.

2.4. Contact angle and interfacial tension measurements

The contact angle (θ) value of sessile water droplets on a lipid surface as a function of composition and time were determined via axisymmetric drop shape analysis [33] with a contact angle