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Fat crystal-stabilized water-in-oil emulsions as controlled release systems

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ABSTRACT

Fat crystal-stabilized water-in-oil emulsions were developed as a controlled release matrix for the delivery of salt. Glycerol monostearate (GMS), glycerol monooleate (GMO) and polyglycerol polyricinoleate (PGPR) were used as emulsifiers and hydrogenated canola oil (HCO) was added as a solid fat. Salt release towards an external aqueous phase was measured *via* conductivity as a function of temperature. Following 2 h of release at room temperature, the GMS emulsion had the highest encapsulation efficiency followed by the PGPR-HCO, PGPR-only and GMO–HCO emulsions, respectively. The GMS crystals formed Pickering shells around the water droplets that effectively prevented salt transport whereas in the GMO–HCO emulsion, the presence of partial interfacial HCO crystal coverage resulted in lower retention. All crystal-stabilized emulsions showed rapid release of their salt load upon melting of the surrounding solid fat, while little temperature effect was observed with the PGPR-based emulsions. However, these emulsions were sensitive to the presence of a salt concentration gradient whereas the fat crystal-stabilized emulsions showed little response. Overall, this study demonstrated that the spatial distribution of the stabilizing fat crystals (*i.e.*, interfacial *vs*. continuous phase) as well as the emulsifier type were critical factors controlling salt release patterns.

1. Introduction

Fat crystal-stabilized water-in-oil (W/O) emulsions are seeing increased use as encapsulation and controlled release/delivery matrices for labile, water-soluble compounds such as amino acids, peptides, vitamins, aromas and flavours (Shakeel & Ramadan, 2010; Wu, Ramachandran, Weiner, & Roessler, 2001). Nominally, such emulsions require the presence of an emulsifier to help maintain the stability of the emulsion and incorporated compound. Though fat crystals are integral to the formation and stability of many common emulsions (*e.g.*, butter, margarine, whipped cream and ice cream), judicious tailoring of their properties such as solid fat content and spatial distribution has only been recently explored for release and delivery applications. Notably, Norton and coworkers used fat crystals to stabilize W/O emulsions and the internal aqueous phase of water-in-oil-in-water ($W_1/O/W_2$) emulsions for controlled release of salt and showed that interfacial fat crystal 'shells' encasing individual droplets effectively prevented salt release even in the presence of an osmotic gradient (Frasch-Melnik, Norton, & Spyropoulos, 2010; Frasch-Melnik, Spyropoulos, & Norton, 2010).

There are three recognized modes of W/O emulsion stabilization by fat crystals – Pickering, network and a combination of the two. Pickering fat crystals often consist of a high-melting interfacially-active emulsifier (*e.g.*, glycerol monostearate – GMS) that resides at the oil–water interface and creates a steric barrier between adjacent water droplets thereby hindering droplet collisions, film drainage and coalescence (Binks, 2002; Rousseau, 2000). If the crystals are surface-inactive [*e.g.*, saturated triacylglycerols (TAGs)], their proclivity to reside at the interface will be greatly diminished. *Via* van der Waals interactions, such crystals will form a crystalline network that prevents the diffusion of droplets away from the network and thus contact with neighbouring droplets (Lucassen-Reynders & van den Tempel, 1963). Finally, fat crystals may act as both Pickering and network stabilizers, depending on the presence of an appropriate liquid or solid-state emulsifier to promote interfacial heterogeneous nucleation (Ghosh & Rousseau, 2012; Ghosh, Tran, & Rousseau, 2011). For example, glycerol monooleate (GMO), a emulsifier typically used in the liquid state, has been

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shown to promote the interfacial heterogeneous nucleation of saturated TAG crystals thereby providing both Pickering and network stabilization (Ghosh et al., 2011).

A basic premise of this research was that the spatial distribution of the stabilizing fat crystals in the emulsions studied represented a key factor that could dictate the ability of salt to diffuse from dispersed aqueous droplets towards an external aqueous phase (*e.g.*, water, saliva, *etc.*). The term 'spatial distribution' expresses differences in how the fat crystals are organized within the network. Two extremes herein explored consist of crystals solely interfacially-bound (*i.e.*, not present in the continuous phase) *vs.* those present only in the continuous oil phase, but not wetted by the droplets themselves. In this research, we showed that the mode by which dispersed aqueous droplets are stabilized within W/O emulsions altered the release behaviour of NaCl used as a model aqueous compound. Pickering-stabilized emulsions were formed by interfacial crystallization of surface-active GMS followed by sintering of crystals at the interface (Frasch-Melnik, Norton, et al., 2010; Ghosh et al., 2011). For network stabilization, liquid-state polyglycerol polyricinoleate (PGPR) and solid hydrogenated canola oil (HCO) were used as emulsifier and network stabilizer, respectively. Combined network and Pickering stabilization was achieved by using GMO and HCO. NaCl release from the dispersed water droplets to an external water phase was evaluated as a function of the mode of fat crystal stabilization and temperature.

2. Materials and methods

2.1. Materials

Canola oil (CO) (acid value ~ 0.2 mg KOH/g oil oil) (AOCS Official method Ca 5a-40) was purchased from a local grocery store and stored at room temperature (RT). Deionized water with a resistivity of >15 MΩ-cm (Barnstead E-Pure, Thermolyne, Ottawa, ON, Canada) was used for the aqueous phase. Distilled GMS (Pationic 901, >95 g GMS/100 g) and GMO (Dimodan MO 90®, >92 g GMO/100 g) were kindly provided by Caravan Ingredients (Lenexa, KS, USA) and Danisco (New Century, KS, USA), respectively. PGPR (acid value max. 6 mg KOH/g; iodine value 72–103 g I_2/100 g; saponification value 170–190 mg KOH/g; hydroxyl value 80–100 mg KOH/g) was donated by Nealanders International, Inc. (Mississauga, ON, Canada). GMS (MW: 358.6 g/mol) and GMO (MW: 356.6 g/mol) are small-molecule monomeric emulsifiers consisting of one stearic acid or oleic acid chain esterified to a glycerol backbone, respectively, whereas PGPR is a larger (average MW: 1800 g/mol) polymeric emulsifier, consisting of a complex mixture of partial esters of polyglycerol with linearly esterified ricinoleic acids derived from castor oil (Wilson, van Schie, & Howes, 1998). HCO was purchased from Bunge (Oakville, ON, Canada). It had a capillary melting point of 69.5 °C (AOCS Official Method Cc 1-25) and a free fatty acid content of 0.018 g/100 g oil. The predominant TAG species in HCO were C_{52} (13.3 g/100 g oil), C_{54} (73.6 g/100 g oil), and C_{56} (5.0 g/100 g oil). The critical micelle concentration (CMC) of GMO and GMS is 4.0 g/100 g oil and that of PGPR is 0.5 g/100 g oil (measured in canola oil) (Ghosh & Rousseau, 2009). NaCl was purchased from Fisher Scientific (Nepean, ON, Canada).

2.2. Emulsion preparation

The different oil phase compositions are given in Table 1. W/O emulsions were prepared by pre-mixing the oil phase (80 g/100 g emulsion) with an aqueous phase (20 g/100 g emulsion) in a rotor/stator mixer (PT 10/35, Kinematica, Inc., Bohemia, NY, USA) for 1 min at 27,000 rpm. The aqueous phase contained different amounts of NaCl (0–10 g/100 g aqueous phase). The coarse mixtures were emulsified in a high-pressure valve homogenizer (APV-1000, APV, Albertslund, Denmark) at a pressure of 69 MPa for 6 cycles. Emulsification was performed at >70 °C to ensure that all components were liquid. All emulsions were cooled with continuous stirring (500 rpm with a magnetic stirrer) to RT (25.5 °C ± 0.5 °C), which allowed the GMS and HCO to crystallize and prevent sedimentation of the dispersed phase. This temperature also ensured that the GMO would remain liquid during the experimental timeframe (Ghosh et al., 2011).

Table 1
Continuous oil phase composition of W/O emulsions used for salt release experiments.

Name	Oil phase composition (g/100 g canola oil)	Emulsion stabilization mechanism
GMS	4 GMS	Pickering
GMO–HCO	4 GMO, 10 HCO	Partial Pickering and network
PGPR-HCO	2 PGPR, 10 HCO	Network
PGPR	2 PGPR	Control emulsion

2.3. Emulsion storage stability

Emulsion samples were transferred to glass vials (ID = 2.5 cm, L = 9.5 cm) and stored at 25 °C for 4 weeks. Stability was assessed *via* sedimentation, droplet size and microscopy.

2.4. Sedimentation

Emulsion sedimentation was recorded visually and with a digital camera. Pictures of 6 cm high emulsions in glass vials were taken on days 0, 7, 14 and 30 and the height of the sedimented emulsion layer was recorded.

2.5. Droplet size determination

The dispersed droplet size distribution of the emulsions before and after salt release was determined at 25 °C using a Bruker Minispec Mq pulsed field gradient nuclear magnetic resonance (pfg-NMR) unit (Bruker Canada, Milton, ON, Canada) that allows unimodal characterization of emulsion droplet size distributions *via* restricted diffusion measurement (van den Enden, Waddington, van Aalst, van Kralingen, & Packer, 1990; Li, Cox, & Flumerfelt, 1991). The Minispec Mq 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, 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 = 2.3×10^{-9} m^2 s^{-1} at 25 °C). Emulsion samples (height = 1 cm) were placed in NMR tubes (ID = 0.8 cm, L = 20 cm) for characterization. Droplet sizes were reported as the 2.5th, 50.0th and 97.5th percentile values for a given emulsion droplet size distribution. The 50.0th percentile droplet diameter is also known as the volume-weighted geometric mean diameter or $d_{3,3}$ value (Alderliesten, 1990). As this technique relies on the molecular movement of water molecules within droplets, it detects size increases in the droplets themselves and not their clustering, thereby differentiating coalescence from flocculation/coagulation.

2.6. NaCl release experiments

The release of NaCl from the water droplets towards the external aqueous phase was investigated using a conductivity meter (model HI 98188, Hanna Instrument, Romania) equipped with an