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Aggregation behavior of partially crystalline oil-in-water emulsions: Part II – Effect of solid fat content and interfacial film composition on quiescent and shear stability

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ABSTRACT

Partially crystalline fat globules in oil-in-water emulsions are susceptible to aggregation via partial coalescence. In this study, the role of solid fat content and interfacial composition on the aggregation behavior of a model food emulsion (35 wt% fat, 2 wt% sodium caseinate) was investigated. By displacing adsorbed sodium caseinate from the oil-water interface using Tween 20, we prepared partial coalescence sensitive emulsions with interfacial compositions of mixed sodium caseinate-Tween 20 (0.5 wt% Tween 20) and Tween 20 dominated (≥1.5 wt% Tween 20). Stability was monitored quiescently and under shear over 6 days of storage at 5 °C. Quiescently, the emulsions were stable with 0.5 wt% Tween 20 regardless of solid fat content. At 1.5 wt% or above, stability decreased with increasing solid fat content and Tween concentration. Under steady shear, the aggregation time of emulsions with Tween 20 dominated interfaces decreased with increasing solid fat content whereas for mixed sodium caseinate-Tween 20 emulsions it increased with increasing solid fat content. Cryo-TEM micrographs of the fat globules revealed a relatively smooth surface at low SFC but increasingly rough surface containing protuberances with increasing SFC. Notably, the protuberances were not jagged but rather round indicating that protruding fat crystals may not initiate partial coalescence especially in Tween 20 dominated emulsions. These findings have important implications on how the partial coalescence mechanism changes with solid fat content and interfacial film composition.

1. Introduction

Partial coalescence of fat globules in partially crystalline oil-in-water emulsions has been the subject of on-going research since a mechanism was proposed (van Boekel & Walstra, 1981; Boode, Bisperink, & Walstra, 1991; Boode & Walstra, 1993; Boode, Walstra, & Degrootmostert, 1993). Many factors such as solid fat content, interfacial composition, interfacial film thickness, globule size and viscosity have been identified as affecting the susceptibility of fat globules to partial coalescence (Fredrick, Walstra, & Dewettinck, 2010). These findings have led to an improved understanding of fat globule aggregation in food products such as cream (Hinrichs & Kessler, 1997), ice cream (Goff, Verespej, & Smith, 1999) and whipped toppings (Goff, 1997). More recently, researchers have used emulsions sensitive to partial coalescence as tools to study lipid release during digestion (Golding et al., 2011) and in-mouth texture perception (Benjamins, Vingerhoeds, Zoet, de Hoog, & van Aken, 2009; Dresselhuis, de Hoog, Stuart, Vingerhoeds, & van Aken, 2008).

According to Walstra (2003), partial coalescence occurs when a protruding fat crystal from one fat globule pierces the interfacial film of another globule. This process allows liquid oil to flow between the globules and form a largely irreversible connection between the internal phases of the globules. Complete coalescence is prevented by the presence of a fat crystal network within each fat globule, hence the term partial coalescence. Rupture of the interfacial film by a protruding fat crystal is reported to depend on several factors such as size, shape and protrusion distance of the fat crystals as well as the properties of the interfacial film (Fredrick et al., 2010; Walstra, 2003). However, there is little direct

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evidence, e.g. micrographs, confirming that fat crystal protrusion plays a direct role in film rupture and partial coalescence (Fredrick et al., 2013). The available evidence is even contradictory; for example while trying to confirm the role of fat crystal protrusion in partial coalescence using light microscopy, Boode and Walstra (1993) reported fat crystals protruded from an interface and caused partial coalescence whereas Ergun (2011) reported no crystals protruded. Instead, molten fat pooled at the oil-water interface during temperature cycling resulting in a potential site for globule-globule association.

Although there is some discrepancy around the role of protruding fat crystals in partial coalescence, the role of solid fat content (SFC) is better described. Studies on the effect of SFC on partial coalescence generally report a maximum rate of partial coalescence around 25–35% SFC (Fredrick et al., 2010; McClements, 2007; Walstra, 2003). Others report a less conservative range of 10–50% (Davies, Dickinson, & Bee, 2000). At SFC values below and above these values, the partial coalescence rate decreases due to a lack of fat crystals or a lack of liquid oil respectively. As Fredrick et al. (2010) noted however, the susceptibility to partial coalescence is dependent on many factors in addition to SFC thus deviations from this general rule should be expected.

Partial coalescence can be effectively prevented by adsorbing thick layers of proteins to fat globules (Goff, 1997; Pelan, Watts, Campbell, & Lips, 1997; Segall & Goff, 1999). A thick protein layer provides significant steric stabilization which prevents the close contact between globules necessary for partial coalescence. To induce partial coalescence, low molecular weight surfactants are generally added to displace adsorbed proteins from the interface. Mechanistically, protein displacement may increase the occurrence of partial coalescence due to reduced film thickness (Palanuwech & Coupland, 2003), reduced interfacial film elasticity (Dickinson, Owusu, & Williams, 1993) or the formation of surfactant-rich domains aka “hotspots” within the protein film (Dalgleish, 2006; Walstra, 2003). The latter cause is the result of surfactants adsorbing non-uniformly within the adsorbed protein film (Mackie, Gunning, Wilde, & Morris, 2000).

Our goal in this study was to better understand the combined roles of SFC in emulsions with different interfacial compositions of protein and surfactant ranging from protein only, mixed protein-surfactant and surfactant dominated. Sodium caseinate and Tween 20 were selected for this purpose given the extensive understanding of their effects on partial coalescence (Davies, Dickinson, & Bee, 2001; Davies et al., 2000; Pelan et al., 1997; Thanasukarn, Pongsawatmanit, & McClements, 2006) and the displacement mechanism of adsorbed sodium caseinate by Tween 20 (Woodward, Gunning, Mackie, Wilde, & Morris, 2009).

To determine the susceptibility of the emulsions to partial coalescence, we examined emulsion stability under both quiescent and shear conditions. In part 1 of this study, we reported on the use of a rheological technique to characterize shear-induced aggregation of partially crystalline emulsions (Fuller et al., 2015). Here, this technique was used to measure the effect of different interfacial compositions and solid fat content on the aggregation characteristics of partially crystalline oil-in-water emulsions.

2. Materials and methods

2.1. Ingredients

Sodium caseinate (92.5 wt% protein, 0.8 wt% fat, 4.66 wt% moisture and 3.4 wt% ash) was provided by Fonterra Co-operative Group Ltd (Auckland, New Zealand). Sodium azide, Tween 20 and sodium dodecyl sulfate (SDS) were purchased from Sigma–Aldrich (St. Louis, MO). Hydrogenated palm kernel oil (HPKO) (White Cloud Shortening KL, Goodman Fielder Food Services Ltd, North Ryde, New South Wales, Australia) and refined canola oil (Marsanta Foods, Mt. Wellington, Auckland, NZ) were purchased from a local foodservice supplier. Milli-Q (MQ) water was used in all emulsions.

2.2. Emulsion preparation

Emulsions were prepared following the procedure described in Fuller et al. (2015). Briefly, 2.4 wt% sodium caseinate stabilized stock emulsions containing 42 wt% fat composed of different blends of hydrogenated palm kernel oil (HPKO) and canola oil were first prepared. Fine emulsions were produced by high shear mixing (Ultraturrax T25, Janke & Kunkel GMBH & Co. KG) followed by homogenization at 180–200 bar (Panda, Niro Soavi, Italy). Working emulsions (25 g) containing the final formulation were prepared by diluting stock emulsions with Tween 20 and MQ water. Each emulsion was then placed in a 65 °C water bath for 30 min before cooling the emulsions in ice-water. All formulations contained 2 wt % sodium caseinate and 35 wt% fat with a final pH of 6.85 ± 0.03.

2.3. Particle size analysis

The particle size distribution and mean particle size of emulsions were measured by laser diffraction particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd., Malvern, Worcestershire, UK). Prior to testing, 1 part emulsion was diluted with 4 parts MQ water or 1% SDS solution and gently mixed by hand. The refractive indices used for water, canola oil and HPKO were 1.330, 1.470 and 1.450 respectively. For emulsions prepared from mixtures of fats, the refractive index was adjusted proportionally. The imaginary refractive index of the dispersed phase was set at 0.001.

2.4. Solid fat content

The solid fat content (SFC) of bulk fat was measured by low resolution pulsed nuclear magnetic resonance (NMR) using The Minispec MQ20 (Bruker Optics, GmbH, Rheinstetten, Germany). SFC was determined by the standard direct method using a 90° pulse, 2 s recycle delay time and the standard algorithm supplied by Bruker. Blends of hydrogenated palm kernel oil (HPKO) and canola oil were prepared by gently mixing melted oils at 65 °C. NMR tubes were filled to a height of 35 mm and held at 65 °C for 30 min. Tubes were then stored isothermally at 5 °C for 24 h before analysis. The NMR measurement chamber was cooled to 5 °C to maintain isothermal conditions.

The blends of HPKO and canola oil studied here contained 30, 50, 70 or 100 wt% HPKO and were found to contain 25.0 ± 0.8, 42.8 ± 0.5, 61.9 ± 1.0 and 90.6 ± 0.3% SFC respectively. SFC measurements were made on the bulk fat rather than the emulsified fat because the aqueous phase of the emulsion interferes with the NMR signal (Fredrick et al., 2011; Gribnau, 1992). However, cooling well below the onset crystallization temperature of the emulsified fat as was done here has been shown to result in near complete crystallization of the emulsified fat after 24 h (Fredrick et al. 2011). Therefore, we expect the SFC of the emulsion to be very similar to the bulk fat.

2.5. Adsorbed protein content

Adsorbed protein content was determined by the depletion method. The centrifugation conditions used and method for calculating of the total mean surface area are described in Fuller et al. (2015). Briefly, the emulsions were heated above the melting point of the fat prior to centrifugation to separate the fat