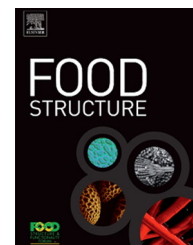


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Kinetic effects on interfacial partitioning of fat crystals



Roja Ergun^a, Richard W. Hartel^{a,*}, Patrick T. Spicer^b

^a Food Science Department, University of Wisconsin-Madison, Madison, WI, USA

^b School of Chemical Engineering, University of New South Wales, Sydney, NSW, Australia

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ABSTRACT

Fat crystals, like other colloidal particles, can influence the stability of food emulsions. Unlike colloidal particles added to form Pickering emulsions, however, crystals form within food emulsion droplets via crystallization and then the crystal wettability determines its ultimate partitioning relative to the oil–water interface. Most descriptions of crystal partitioning assume the final interfacial state of fat crystals can be predicted by key system properties like interfacial tension and contact angle. However, recent work has shown the kinetics of interfacial particle adsorption can be surprisingly slow as a result of variables like particle roughness as well as internal droplet rheology. This work examined the effects of common variables, normally not thought to control crystal partitioning, on the state of crystals in a milkfat emulsion. For example, crystallization dynamics, tuned by varying surfactant adsorption and the crystallization driving force, are found to alter interfacial partitioning of milkfat crystals at oil–water interfaces. Slower crystallization rates increase the likelihood that crystals will leave the droplets by dewetting and reside in the aqueous phase, even with no compositional changes. The tendency of fat crystals to dewet the liquid oil increased as the oil–water interfacial tension, and the contact angle of aqueous surfactant on fat crystals, decreased. Several possible explanations for the results observed are postulated.

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1. Introduction

From cosmetics to food, emulsion stability has great importance in a variety of applications. Due to the positive free energy required to combine two immiscible liquids, emulsions are thermodynamically unstable. Emulsion stabilization occurs by interfacial adsorption of either surfactants, such as food emulsifiers, or colloidal particles, like those added to form Pickering emulsions (Aveyard, Binks, & Clint, 2003; Pickering, 1907). In Pickering systems, the colloid wettability determines the ultimate particle position in the emulsion. If

mostly wetted by either emulsion phase, the particles will reside there, but if significantly wetted by both phases the particles reside at the oil–water interface and stabilize the emulsion against coalescence because of the significant energy required to remove them (Clint & Taylor, 1992). In stark contrast to Pickering emulsions, made by added particles, are systems where colloids form within the emulsion, adjust to find a stable position, and alter the emulsion stability depending on their wettability and fluid environment. In such cases the history of the particles' formation is strongly variable, with a strong influence on the final particle interfacial properties.

* Corresponding author. Tel.: +1 6082631965.

E-mail address: rwhartel@wisc.edu (R.W. Hartel).

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Particle wettability is related to interfacial conditions using Young's equation to describe the three phases of crystal (c), oil (o), and water (w) (Barnes & Gentle, 2005):

$$\gamma_{o/w} \cos \theta = \gamma_{o/c} - \gamma_{w/c} \quad (1)$$

Here, θ is the aqueous phase contact angle on the crystal (Fig. 1) and $\gamma_{o/w}$, $\gamma_{o/c}$, and $\gamma_{w/c}$ are the oil–water, oil–crystal and water–crystal interfacial tensions, respectively. The left-hand term, $\gamma_{o/w} \cos \theta$, in Eq. (1) is known as the adhesion tension, a measure of the relative affinity of the solid phase for the two liquid phases (Bartell & Greager, 1929; Walstra, 2003). Although often used to explain experimental observations of fat crystal effects on emulsion stability, Eq. (1) is based on equilibrium properties of homogeneous systems and may not always describe systems where particle formation, adsorption, and rheological dynamics occur simultaneously.

Boode and Walstra (1993) found that adding surfactant to a partially crystalline emulsion changed the wettability of fat crystals from hydrophobic to hydrophilic, moving crystals outside of the droplets during a 24-h wait. Fig. 1 shows the diagram they use to illustrate different regimes of crystal wetting depending on interfacial conditions. Although useful as a conceptual map, Fig. 1 assumes homogeneous equilibration of the system and that the final state of an emulsion is history-independent. In practice, equilibrium partitioning is reached only after the system passes through a range of dynamic contact angles over a surprisingly long time scale (Kaz, McGorty, Mani, Brenner, & Manoharan, 2012), even in relatively ideal colloidal systems. When particles crystallize within an emulsion, a number of aspects of their immediate environment can occur simultaneously, like emulsifier incorporation into the crystals (Johansson & Bergenstahl, 1992), crystal phase separation (Hartel & Kaylegian, 2001), and droplet rheology evolution (Pawar, Caggioni, Ergun, Hartel, & Spicer, 2012). In addition to foods, petroleum (Ashbaugh et al., 2002; Karanjkar, Lee, & Morris, 2012) and cosmetic (Yang & Hrymak, 2011) emulsions also experience simultaneous crystallization and partitioning, but few kinetic studies of the combined phenomena exist.

Spicer and Hartel (2005) used microscopic observations to study adsorbed surfactant effects on crystallization of

high-melting fat in oil-in-water emulsions. Because the droplets fully solidified, they observed three regimes of behavior by controlling cooling rate, surfactant level, and fat purity: (1) Solidification of the entire droplet, (2) formation and immediate ejection of small crystals from droplets, and (3) simultaneous crystallization and dewetting. Many food systems, however, only partially solidify, resulting in liquid droplets containing some fraction of higher melting fat crystals with potentially variable composition. The relative amount of the crystals, and their interfacial properties, will then determine the emulsion stability (Fredrick, Walstra, & Dewettinck, 2009) and rheology, often contributing strongly to the overall food microstructure (Dickinson, 2010; Rousseau, 2000).

This article examines the fundamental question of how crystallization dynamics and interfacial conditions, as controlled by fat purity, cooling rates, and surfactant levels, affect the final crystal disposition within a milkfat-in-water emulsion. Equilibrated materials were evaluated with bulk measurements and then the dynamic crystal position within the emulsion during crystallization was observed.

2. Materials and methods

2.1. Materials

Anhydrous milk fat (AMF) was obtained from Schreiber Cheese (Green Bay, WI, USA) and stored at 4 °C. All AMF samples were melted at 60 °C prior to use. Sodium dodecyl sulfate (SDS) with purity greater than 98% was obtained from Fisher Scientific (New Jersey, NY, USA). Deionized reverse osmosis water is used in all experiments.

AMF is comprised of a wide range of different triacylglycerols, containing the widest range of both saturated and unsaturated fatty acids (from C4:0 to C18:3) of any known natural fat. Three different components, based on melting point, are generally recognized. High melting milk fat fraction (HMF) is enriched in long-chain saturated fatty acids while low melting milk fat fraction (LMF) contains one long-chain saturated fatty acid and two short-chain or unsaturated acids (Hartel & Kaylegian, 2001). However, the exact composition and melting point depends on fractionation and filtration conditions. The AMF (melting point of 36.2 °C) here was fractionated by a melt fractionation method followed by vacuum filtration to generate distinct high and low-melting fractions with melting points of 44.2 °C and 18.5 °C, respectively. Although exact fatty acid or TAG profile were not measured here, they are expected to follow the fatty acid and TAG profiles found in the literature (Tietz & Hartel, 2000).

2.2. Evaluating crystal position

Fat samples were hand-mixed with aqueous surfactant at 60 °C, producing droplets between 50 and 500 μm in diameter. Droplet size was chosen to aid microscopic observations; the effects of droplet size on these phenomena would be interesting to study, particularly as smaller droplets would be expected to have modified crystallinity and network properties that could influence the results. Microscopic observations were carried out on samples inside flat glass

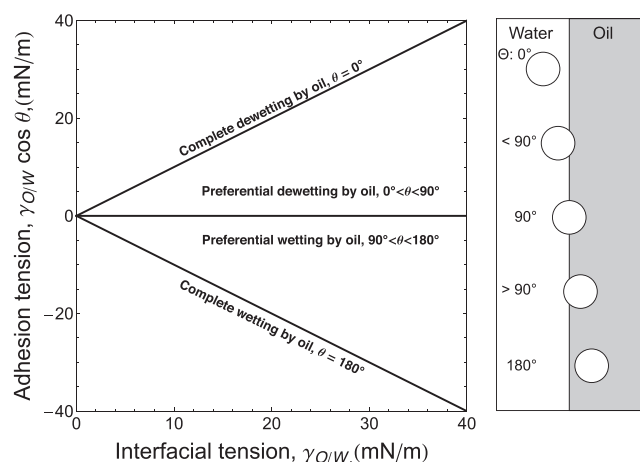


Fig. 1 – An adhesion tension diagram indicating crystal partitioning at an oil–water interface depending on surfactant adsorption (after Boode & Walstra, 1993).

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