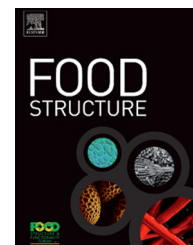


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Kinetic effects on interfacial partitioning of fat crystals



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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.

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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

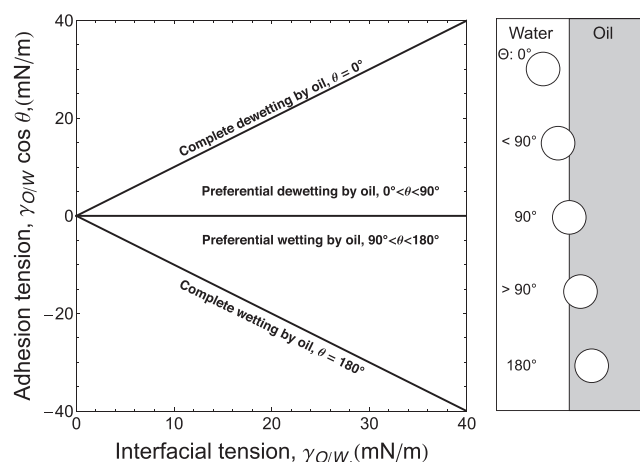


Fig. 1 – An adhesion tension diagram indicating crystal partitioning at an oil–water interface depending on surfactant adsorption (after Boode & Walstra, 1993).

capillaries (Vitrocom, Mountain Lakes, NJ) that were attached to a microscope slide, and sealed at both ends, with glue. A controlled temperature microscope stage (Linkam PE94) was used to cool the samples from 50 to 4 °C at 10, 5, 3, 1, 0.5 and 0.1 °C/min. A Nikon Labophot light microscope (Melville, NY, USA) with Qimaging Qicam camera (Surrey, BC, Canada) was used to determine crystal position at oil–water emulsion interfaces while cooling to crystallize the samples. Observations were performed in duplicate with independent samples. In all cases, unless otherwise specified, we use the word “crystals” here to mean colloidal-scale aggregates of smaller single crystals, or a polycrystalline structure.

2.3. Interfacial measurements

A Krüss DSA100 drop shape analysis system (Krüss, Hamburg, Germany) was used to measure oil–water interfacial tension between the milkfat and 1.6, 2, 4, 6, 8 and 16 mM SDS solutions. The AMF sample, in a glass cuvette, was placed on a hot stage while the surfactant solution was added to the syringe. The system uses images of the surfactant solution drops inside the oil samples to determine drop shape and interfacial tension. Observations were made in triplicate with independent samples. The DSA100 system was also used to measure the equilibrium advancing contact angle of liquid LMF on solid HMF inside of an aqueous surfactant sample (Johansson, Bergenstahl, & Lundgren, 1995). A flat crystal of HMF was placed at the top of a cuvette in contact with 11 ml distilled water. A liquid LMF droplet was injected via syringe onto the crystal bottom surface and allowed to equilibrate. Sufficient 80 mM SDS solution was then injected into the water to obtain a desired concentration, from 1.6 to 16 mM SDS. Images of the three-phase interface were taken until the contact angle stopped changing. Due to the known variability in this measurement (Walstra, 2003), 30–50 replicates were used to report the results for independent samples. Although the order of addition of the surfactant could affect the contact angle measured, here all measurements were made with surfactant added to an existing water–oil–crystal system, consistent with past studies of crystal wetting (Boode & Walstra, 1993).

2.4. Crystallization rate measurements

A Perkin Elmer Differential Scanning Calorimeter (DSC) (Perkin Elmer, Chicago, IL, USA) with Pyris software for Windows was used to obtain cooling thermograms of AMF, HMF and LMF samples. The instrument was calibrated with indium and mercury standards prior to analysis. Dry nitrogen gas was used to purge the thermal analysis system and a mechanical cooler was used for cooling. Fat samples (4–10 mg) were placed into standard DSC aluminum pans at 60 °C. The pans were hermetically sealed and put in the calorimeter with an empty pan used as a reference. AMF samples were cooled from 50 to 4 °C at 0.1, 0.5, 1, 3, 5 and 10 °C/min. Mixtures of HMF and LMF, with LMF levels of 0, 50, 75 and 91% LMF were cooled from 60 to 4 °C at a rate of 1 °C/min. Changes in heat flow during cooling were recorded and performed in triplicate with independent milk fat samples. The crystal fraction formed at any time can be found as the cumulative integral of the energy

curve (Ozawa, 1971; Henderson, 1979). The initial slope of the integrated energy curve was assumed to be proportional to the initial crystallization rate.

3. Results and discussion

The overall goal of this study was to evaluate crystallization and wetting dynamic effects on the position of fat crystals as they form from a molten milkfat emulsion droplet. Interfacial properties between AMF, crystalline fat (HMF) and aqueous phase (SDS solution) were studied. Fig. 2 shows the equilibrium values of interfacial tension between AMF and aqueous surfactant at different SDS concentrations. As expected, as the SDS concentration increased, interfacial tension decreased up to a point. Surface tension at CMC (critical micellar concentration) (8 mM) for SDS was about 4 mN/m with no significant further decrease at higher SDS concentrations. A decrease in the relative contact angle of liquid low-melting milk fat fraction (LMF) on crystalline HMF in a surfactant solution at 22 °C was also observed with increased surfactant concentration (Fig. 3), from 140° to around 80° at the surfactant CMC. The large variability in contact angle, evidenced by the error bar size in Fig. 3, is likely due to surface polarity differences caused by liquid oil impurities that adsorb at the crystal surface (Walstra, 2003).

Using the equilibrium properties determined in Fig. 1, an adhesion tension diagram was plotted (Fig. 4) to predict crystal partitioning at the oil–water interface (Boode & Walstra, 1993; Johansson et al., 1995). Crystals showed a large range of dewetting potential at all the surfactant concentrations due to the contact angle variations observed. Still, distinct trends are discernable. Fat crystals are preferentially wetted by the oil phase below about 6 mM SDS concentration. Above about 6 mM SDS, mixed behavior is seen. Some fat crystals were wetted (preferred oil phase) while others were dewetted by the

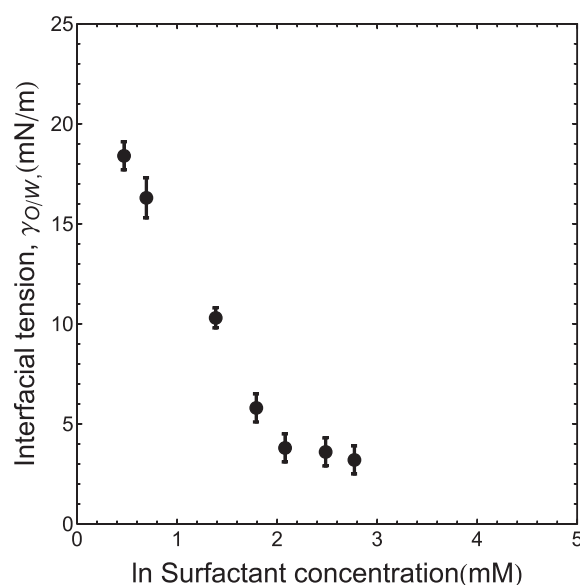


Fig. 2 – Interfacial tension between anhydrous milk fat (AMF) and sodium dodecyl sulfate (SDS) solution at 22 °C. Error bars are standard deviation values with $n > 3$.

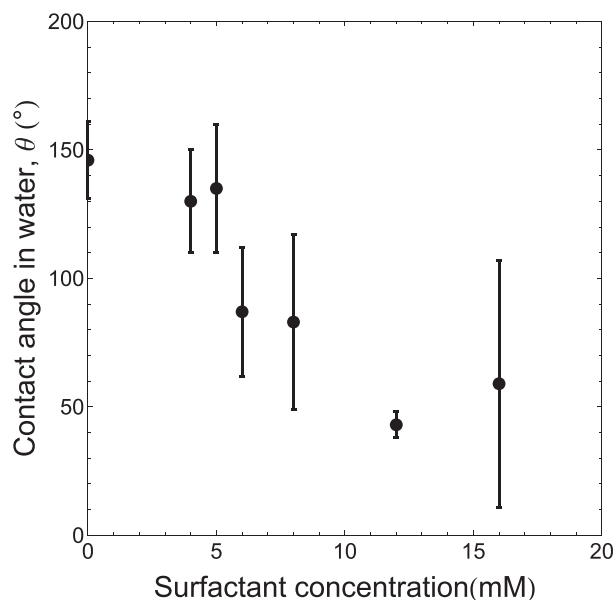


Fig. 3 – Contact angle between a drop of liquid fat (low melting milk fat fraction) on a layer of crystalline fat (high melting milk fat fraction) in aqueous surfactant solution as a function of sodium dodecyl sulfate (SDS) concentration. Error bars are standard deviation values with $n > 30$.

oil phase (preferred aqueous phase), based on the variability of contact angle. At SDS concentrations below 4 mM, all the crystals are expected to remain in the oil phase, whereas above 6 mM SDS concentration, some crystals may remain in the oil phase while some may partition at, or even through, the oil–water interface.

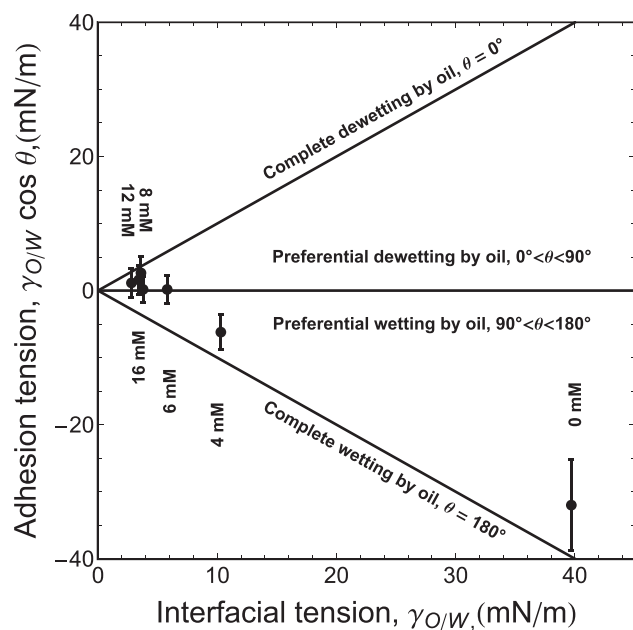


Fig. 4 – Milk fat adhesion tension at four sodium dodecyl sulfate (SDS) concentrations showing the shift from oil wetting to oil dewetting states with surfactant addition.

To demonstrate the effects of interfacial conditions on crystal partitioning, an AMF emulsion in an SDS solution was visualized during cooling on the microscope. The milk fat emulsion was crystallized in 4, 8 and 16 mM SDS by cooling at 0.1 °C/min. The slow cooling rate allows careful study of the effects of surfactant adsorption on the rate of crystalline network formation (Spicer & Hartel, 2005). Representative microscope images of crystal partitioning at an oil–water interface are shown in Fig. 5 at two temperatures during cooling and three different surfactant concentrations. In 4 mM SDS solution, the crystals appear completely wetted by the oil phase; that is, all fat crystals remain within the droplet even though the oil droplet surface has some irregularities. Increasing the SDS concentration to 8 mM shifts some crystals to the oil–water interface, though most remain in the oil droplet. At 16 mM SDS, some crystals are seen to completely exit the droplet as a result of dewetting. As all results in Fig. 5 were obtained with a slow cooling rate, the dominant influence on crystal position was assumed to be interfacial. From Figs. 2 and 3, increased surfactant adsorption both increases fat crystal hydrophilicity and decreases oil–water interfacial tension. Combining these terms in the adhesion tension allows us to compare the equilibrium predictions of Fig. 4 with the dynamic observations in Fig. 5.

At a slow crystallization rate, the adhesion tension diagram accurately describes the partitioning of crystals (Fig. 4). At SDS levels below 6 mM, crystals remain in the oil phase as Fig. 4 predicts. Above about 6 mM SDS concentration, some crystals in Fig. 5 remain in the oil phase while some sit at the oil–water interface. As the SDS concentration increases to 16 mM, some crystals moved completely into the water phase in addition to some that remain in the oil phase and at the oil–water interface. Despite measured contact angle variability, the general effects of surfactant adsorption on crystal wettability can be seen from these results. Increasing the amount of SDS decreases the oil–water interfacial tension and the aqueous phase–crystal contact angle, increasing the tendency of fat crystals to be dewetted from the oil remaining in the fat globule. Although the dynamic emulsion droplet crystallization process was not directly observed here, there are three likely possibilities explaining the effect of added SDS: (1) some fat crystals nucleate at the oil–water interface where SDS can then adsorb onto the crystals, (2) crystals form in the interior and, through convective forces, contact the interface where they are influenced by SDS, and (3) crystals form in the interior but have insufficient mobility (perhaps because of a crystal network) to reach the interface. The first two possibilities would lead to particles leaving the interface under appropriate conditions, while the third would mean the particles remain inside the droplet regardless of the conditions.

Other effects of the SDS, beyond wetting, are also possible. For example, the left-hand images in Fig. 5 show an apparent decrease in the average size of crystalline regions within or around the droplets, indicating a potential effect on crystal growth rates. Even more interestingly, the 16 mM sample appears to produce two populations of crystals. In Fig. 5, the lower left image at 16 °C exhibits crystals that have already exited the droplets, while the droplets themselves contain no crystals at that point. After cooling the sample further to 4 °C, more crystals are now visible inside of the droplets. This

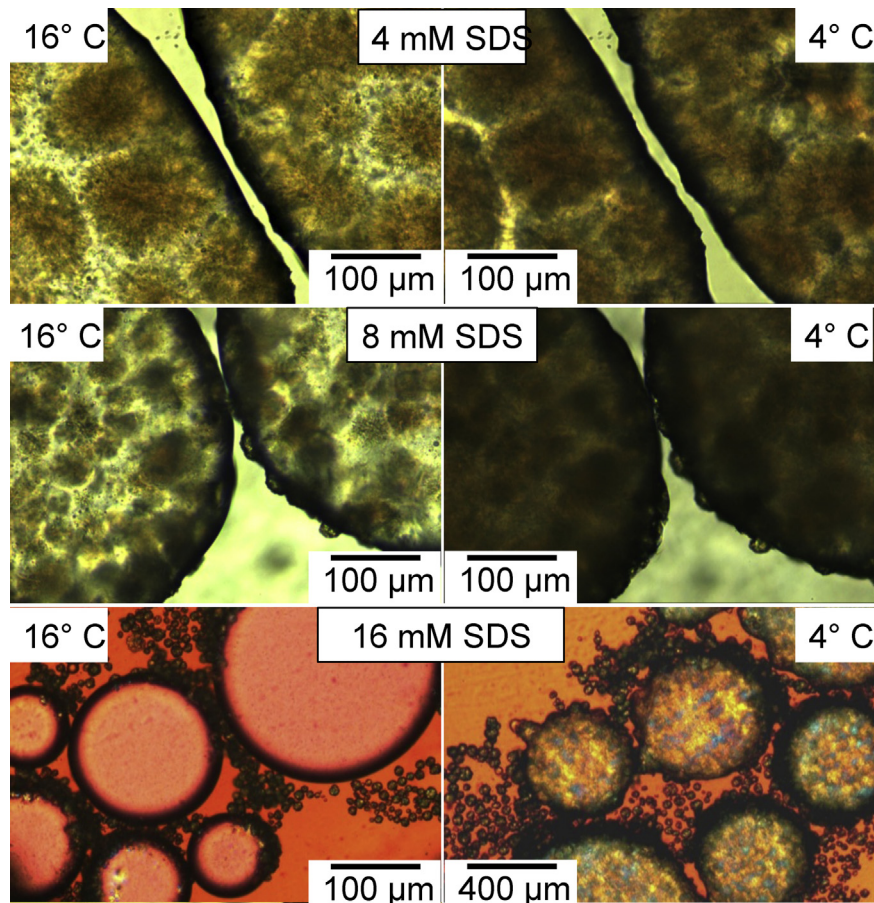


Fig. 5 – Microscope images of fat crystal partitioning for anhydrous milk fat (AMF) crystallized at 4, 8, and 16 mM sodium dodecyl sulfate (SDS) concentrations. All mixtures were cooled at a rate of 0.1 °C/min. Images on the left are at 16 °C while the right-hand ones are the same sample cooled further to 4 °C.

indicates that the two crystal populations produced are dewetted, and wetted, respectively, by the liquid oil either because of compositional differences caused during crystallization, where HMF separates from LMF, or very different effects of surfactant adsorption. In the latter case, permanent incorporation of the SDS into the crystals during fat solidification could deplete the SDS supply, preventing subsequent dewetting. Further study is needed to assess such hypotheses.

In general, slow cooling rates produce results in good agreement with equilibrium predictions, so it is also of interest to probe the impact of faster cooling rates on the equilibrium expectations. Crystallization rate effects on crystal partitioning were studied here by varying cooling rate and the ratio of high to low melting fractions of milk fat. The crystallization rate of AMF as a function of cooling rate was determined from the initial slope of the exothermic peak in DSC heat flow curves, and the expected trend of increased initial crystallization rate with increased cooling rates was observed. Since milk fat generally crystallizes as the β' polymorph (Herrera & Hartel, 2000), polymorphism was not considered a factor in this study. Microscopic study of milkfat droplet crystallization was then performed to check for any deviations from the behavior in Fig. 5. To test this, AMF was emulsified in 16 mM SDS solution, the concentration that exhibited the most

pronounced dewetting behavior in Fig. 5, and crystallized by cooling a sample from 50 °C to 4 °C at 0.1, 0.5, 1, 3, 5 and 10 °C/min on a microscope stage. Fig. 6 shows representative microscope images of fat crystal orientation at the oil–water interface as a function of cooling rate. At 5 and 10 °C/min, oil droplet surfaces were mostly smooth, with few irregularities; all the crystals were completely wetted by the oil phase. As the crystallization rate decreased to 3 and 1 °C/min, some crystals partitioned between oil and water phases, but most crystals were preferentially wetted by the oil phase. As the crystallization rate decreased to 0.5 °C/min, significant numbers of crystals partitioned between oil and water phases and were preferentially dewetted by the oil phase. At the lowest cooling rate studied, 0.1 °C/min, numerous crystals were completely dewetted by the oil phase and individual crystals surrounded the initial fat globule.

Clearly, the position of crystals relative to the oil–water interface depends on crystallization rate and is not just governed by initial interfacial conditions. The adhesion tension diagram (Fig. 4) and the observations in Fig. 5 indicate many of the AMF crystals in 16 mM SDS solution should move into the aqueous phase. However, as demonstrated microscopically, crystals showed a systematically decreased likelihood to leave the oil phase, moving from some totally

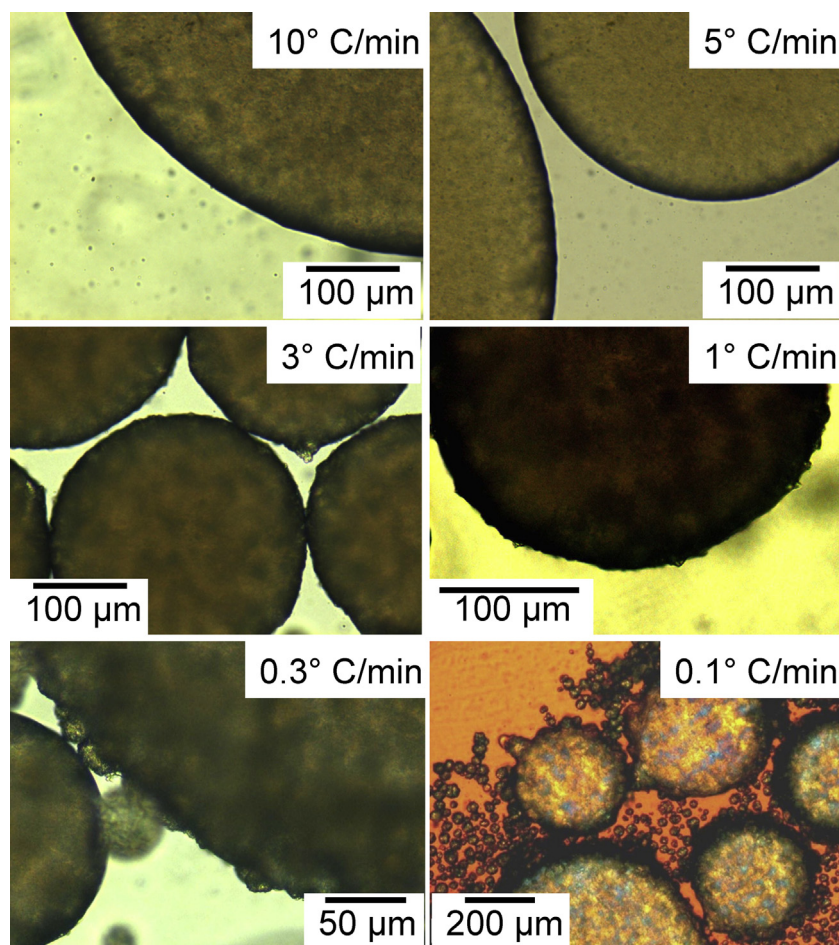


Fig. 6 – Microscope images of fat crystal partitioning as a function of cooling rate for anhydrous milk fat (AMF) crystallized in 16 mM sodium dodecyl sulfate (SDS). All images are at 4 °C.

dewetted crystals to essentially none, as crystallization rate increased. This is a fascinating result, as the initial composition of the system is identical in each case but the wettability of the crystals is clearly modified by producing them at different cooling rates.

Other changes in the crystals are also expected at different cooling rates. For example, smaller and more plentiful crystals are typically produced at faster cooling rates, although we saw no clear evidence of significant size effects here. Milkfat is also a heterogeneous mixture and the inherent separation, of compounds with differing melting points, occurring during crystallization may produce crystals with varying fractions of lipid chain lengths. If successive crystals produced from a mixed droplet have different relative compositions, for example with varying fractions with different molecular polarity or surface activity, it could partially explain the observed shift from dewetted to wetted crystals seen here.

A second method of modifying the crystallization rate is to vary the solids content of the droplets through systematic variation of the LMF to HMF ratio. The rates of crystallization for several LMF–HMF mixtures with 0, 50, 75 and 91% LMF were determined from DSC heat flow curves at 1 °C/min and listed in the caption of Fig. 7 for all the samples studied here. The

crystallization rate decreased with increasing LMF in the mixture, consistent with the approximation of HMF as the solidifying solute in the mixture, with LMF as the solvent. As a result, a decreased HMF level reduced the solution supersaturation and the crystallization driving force, thus decreasing the crystallization rate.

Microscopic observations of the LMF–HMF mixtures crystallizing in the presence of 16 mM SDS allow comparison with the results in Figs. 5 and 6. Emulsions were cooled from 50 °C to about 20 °C at a rate of 1 °C/min, with lower final temperatures required for higher LMF contents. Representative microscope images of crystal position at the oil–water interface as a function of LMF percentage are shown in Fig. 7. For LMF levels of 0 and 50%, Fig. 7a and b, the oil droplet surfaces exhibited few irregularities and all the HMF crystals remained within the oil phase when cooled to 22 °C. At 75% LMF, Fig. 7c, an increase in the surface irregularities was observed although the crystals still seem largely contained by the oil phase with a few appearing to sit at the interface. At the highest level of LMF studied, 91%, some crystals left the oil phase completely, as seen in Fig. 7d. Although slower cooling rates produced the most crystals outside of the emulsion droplets in Fig. 6, here the trend was the opposite, with an increased crystallization

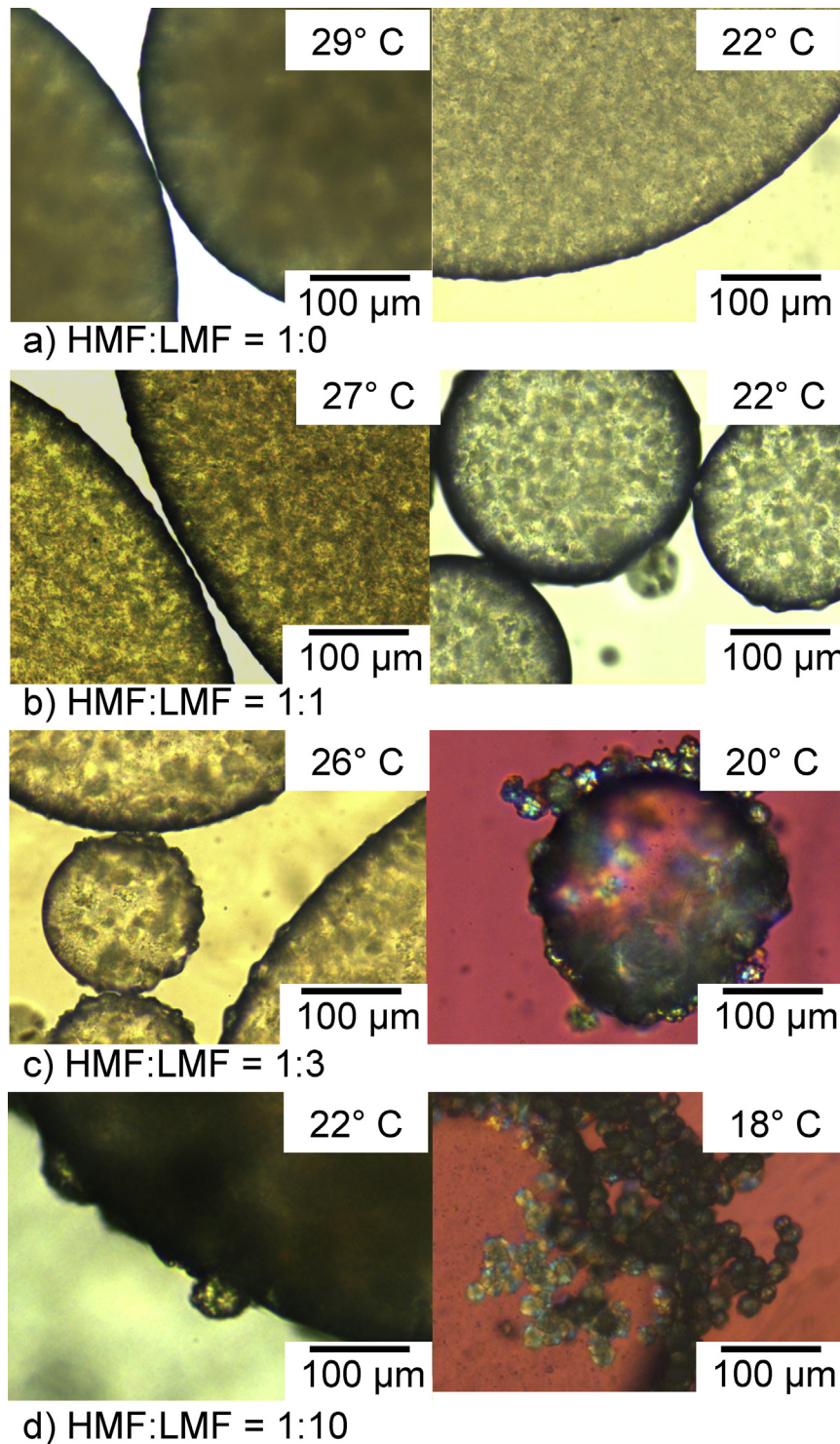


Fig. 7 – Microscope images of fat crystal partitioning as a function of high-melting milk fat fraction (HMF) content relative to low-melting milk fat fraction (LMF). HMF-LMF mixtures at crystallization rates of 2.5 mJ/s (a), 1 mJ/s (b), 0.9 mJ/s (c) and 0.06 mJ/s (d) were crystallized in 16 mM sodium dodecyl sulfate (SDS) solutions cooled at a rate of 1 °C/min.

rate, for high HMF contents, producing crystals that remained within the oil phase (Fig. 7). Clearly the variation in composition drives effects other than just altering crystallization rate and likely impacts rheological and/or interfacial properties of the crystals. For example, increasing solid levels

in droplets produced a power law growth in the elasticity (Pawar et al., 2012), which may impede or fully arrest crystal mobility before they can be moved out of the network. Also possible is that the crystals formed at each HMF level have different amounts of surface-active compounds adsorbed,

resulting in a compositional variation in wettability, which may also explain the different crystalline partitioning seen in Fig. 5 at different temperatures (Tietz & Hartel, 2000).

The observed effects of surfactant level, cooling rate, and solids content indicate that the positioning of crystals at an oil–water interface is more complex for natural fats than predicted by the adhesion tension diagram. While the homogeneous equilibrium predictions for a system that only varies cooling rate are the same, our data indicate other factors must influence the ultimate state of the crystals formed in an emulsion with varying rates and heterogeneous composition. Thus, the adhesion diagram is not sufficient to predict crystal partitioning at the oil–water interface for practical systems, especially when the controlling rate phenomena change significantly. Spicer and Hartel (2005) used variations in the relative rates of crystallization and dewetting to influence crystal state for fully solidified droplets, and here we have shown that for partially crystalline droplets a similar influence can be applied.

4. Conclusion

The partitioning of crystals within an oil-in-water emulsion is governed by the interfacial properties as well as the crystallization dynamics. Increasing the surfactant concentration lowers the oil–water interfacial tension and the contact angle between liquid and crystalline fat, leading to an increased dewetting of fat crystals by oil. The adhesion tension approach predicts such behavior reasonably well, in agreement with past results for systems with surfactant added after crystallization (Boode & Walstra, 1993). However, other variables also determine the final partitioning of milkfat crystals in an emulsion. Increased cooling rates led to a switch, for identical composition systems, from dewetting by oil to complete wetting, possibly because of a change in phase separation kinetics driven by cooling rate variations. Manual compositional changes have a strong influence on dewetting potential in emulsions, as increasing the solid fat content of milkfat mixtures shifted the emulsion from oil dewetting to complete wetting. As the key variables examined here, emulsifier level, cooling rate, and solid content, are all used to control crystallization rates and product quality, it will be worthwhile to build on these results with purer, model systems to better understand how to control and optimize the dewetting behavior of fat emulsions.

Industrial relevance

Fat crystals partitioning through an o/w interface is a well-known, but little-studied, phenomenon. As the basis for the detergent fat fractionation (Lanza) process, it has been known for over 100 years. Also, there are a variety of food processes (for example, bread baking) that are influenced by fat crystal partitioning through an o/w interface. A better understanding of this phenomenon is needed to better control these operations.

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REFERENCES

- Ashbaugh, H. S., Radulescu, A., Prud'homme, R. K., Schwahn, D., Richter, D., & Fetters, L. J. (2002). Interaction of paraffin wax gels with random crystalline/amorphous hydrocarbon copolymers. *Macromolecules*, 35, 7044–7053.
- Aveyard, R., Binks, B. P., & Clint, J. H. (2003). Emulsions stabilized by colloidal particles. *Advances in Colloid and Interface Science*, 100–102, 503–546.
- Barnes, G., & Gentile, I. (2005). *Interfacial science: An introduction* (1st ed.). New York: Oxford University Press.
- Bartell, F. E., & Greager, O. H. (1929). Relation of adhesion tension to liquid absorption. *Industrial and Engineering Chemistry*, 21(12), 1248–1251.
- Boode, K., & Walstra, P. (1993). Partial coalescence in oil-in-water emulsions: 1. Nature of the aggregation. *Colloids and Surfaces A: Physicochemical and Engineering Aspects*, 81(1), 121–137.
- Clint, J. H., & Taylor, S. E. (1992). Particle size and interparticle forces of overbased detergents: A Langmuir trough study. *Colloids and Surfaces*, 65(10), 61–67.
- Dickinson, E. (2010). Food emulsions and foams: Stabilization by particles. *Current Opinion in Colloid Interface Science*, 15, 40–49.
- Fredrick, E., Walstra, P., & Dewettinck, K. (2009). Factors governing partial coalescence in oil-in-water emulsions. *Advances in Colloid and Interface Science*, 153(1), 30–42.
- Hartel, R. W., & Kaylegian, K. E. (2001). Advances in milk fat fractionation. In N. Garti & K. Sato (Eds.), *Crystallization processes in fat and lipid systems* (pp. 381–427). New York: Marcel Dekker.
- Henderson, D. W. (1979). Thermal analysis of non-isothermal crystallization in glass-forming liquids. *Journal of Non-Crystalline Solids*, 30, 301–315.
- Herrera, M. L., & Hartel, R. W. (2000). Effect of processing conditions on crystallization kinetics of a milk fat model system. *Journal of American Oil Chemists' Society*, 77(11), 1177–1187.
- Johansson, D., & Bergenstahl, B. (1992). The influence of food emulsifiers on fat and sugar dispersions in oils: I. Adsorption, sedimentation. *Journal of American Oil Chemists' Society*, 69(8), 705–717.
- Johansson, D., Bergenstahl, B., & Lundgren, E. (1995). Wetting of fat crystals by triglyceride oil and water: I. The effect of additives. *Journal of American Oil Chemists' Society*, 72(8), 921–993.
- Karanjkar, P., Lee, J., & Morris, J. (2012). Calorimetric investigation of cyclopentane hydrate formation in an emulsion. *Chemical Engineering Science*, 68, 481–491.
- Kaz, D. M., McGorty, R., Mani, M., Brenner, M. P., & Manoharan, V. N. (2012). Physical ageing of the contact line on colloidal particles at liquid interfaces. *Nature Materials*, 11, 138–142.
- Ozawa, T. (1971). Kinetics of non-isothermal crystallization. *Polymer*, 12, 150–158.
- Pawar, A. B., Caggioni, M., Ergun, R., Hartel, R. W., & Spicer, P. T. (2012). Arrested coalescence of viscoelastic droplets with internal microstructure. *Faraday Discussion*, 158, 341–350.
- Pickering, S. U. (1907). Emulsions. *Journal of the Chemical Society*, 91, 2001–2021.

- Rousseau, D. (2000). Fat crystals and emulsion stability – A review. *Food Research International*, 33, 3–14.
- Spicer, P. T., & Hartel, R. W. (2005). Crystal comets: Dewetting during emulsion droplet crystallization. *Australian Journal of Chemistry*, 58(9), 655–659.
- Tietz, R. A., & Hartel, R. W. (2000). Crystallization and microstructure of milk fat cocoa butter blends related to bloom formation in chocolate. *Journal of the American Oil Chemists' Society*, 77(7), 763–772.
- Walstra, P. (2003). *Physical chemistry of foods*. New York: Marcel Dekker.
- Yang, D., & Hrymak, A. N. (2011). Crystal morphology of hydrogenated castor oil in the crystallization of oil-in-water emulsions: Part I. Effect of temperature. *Industrial and Engineering Chemistry Research*, 50, 11585–11593.