

Edible Oil-Water Foamulsions Stabilized by Vesicle Network of Sucrose Ester

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ABSTRACT

Foamulsions are tri-phase dispersions consisting of oil, water and gas. The stabilizers of foamulsions are typically single surfactants or their mixtures. However, foamulsions stabilized by molecular surfactants are usually unstable against long term storage. In this work we report that a nonionic surfactant, sucrose stearate C-1807 (HLB = 7), can be a good stabilizer for foamulsions prepared with edible oils such as canola oil and soybean oil. It is found that C-1807 forms spherical vesicles in water which develop further to a vesicle network at concentrations beyond 3 wt.%, increasing significantly the viscosity of the aqueous phase. Normally, the presence of oil is unfavourable for the stabilization of foams, however long-term stable foamulsions can be attained due to the highly viscous continuous phase as well as the presence of vesicles around oil droplets and air bubbles which inhibits their coalescence. The foamulsions are stable against cooling-heating cycles (5 °C to 30 °C) though partially unstable during freeze-thaw cycles (-20 °C to 30 °C). The stabilization of foamulsions by sucrose ester applies to different edible oils, and C-1807 as a non-toxic and biodegradable surfactant may act as a fat replacer in developing healthy foods such as low fat cream or butter.

Keywords: Foamulsions, sucrose ester, vesicles, high stability

1. INTRODUCTION

Foams and emulsions are biphasic fluid dispersions which have a long history of application in daily products as well as in industrial processes.[1] A foam is a dispersion with air dispersed as bubbles in a liquid, while an emulsion is that with a liquid dispersed as droplets in another immiscible liquid.[1] Recently, triphasic dispersions consisting of gas, oil and water named foamed emulsions or foamulsions have attracted attention in which air bubbles and droplets are dispersed in a continuous aqueous phase. [2-6]

Foamulsions are frequently encountered in daily commercial products, such as whipped cream and ice cream, where bubbles and drops are stabilized by protein and milk fat. [7,8] Recently, foamulsions also found applications in oil recovery processes, [9,10] fuel development [11,12] and novel functional material design.[13] Similar to foams and emulsions, foamulsions are thermodynamically unstable and may undergo creaming and coalescence of droplets and drainage and rupture of bubbles. Hence, stabilizers such as a single surfactant [14,15] or a mixture of surfactants [16] are required for their stabilization. Sometimes other additives can also be helpful in the stabilization of foamulsions. For example, when sodium dodecyl sulphate is used to stabilize foamulsions of water and n-dodecane, the presence of perfluorohexane can slow down bubble coalescence.[17] Nevertheless, the mechanism for the stabilization of foamulsions by surfactants is still not completely clear at present, although there are reports that claim that surfactant adsorbs at both oil-water and air-water interfaces to create a pseudoemulsion film between oil drops and air bubbles which is beneficial for stabilization.[14,15] However, even when the pseudoemulsion film is stable, foamulsions stabilized by molecular surfactants are still found to be unstable against long term storage, and in some systems the drainage of water cannot be hindered and the foamulsions last only for tens of hours.[5,6,15]

In order to improve the stability of foamulsions, colloidal particles have been introduced to the systems. For example, Wege and co-workers prepared foamulsions with extraordinary stability by using hydrophobic cellulose microparticles generated

from aqueous solutions of hypromellose phthalate by adjusting the pH of the system.[18] On one hand, the cellulose microparticles adsorb irreversibly at air-water and oil-water interfaces providing steric protection for bubbles and droplets. On the other hand, the accumulation of oil droplets in the Plateau borders of the foam increases the viscosity of the matrix, reducing drainage of water and thus keeping bubbles stable for a long time. Similarly, Wan *et al.* [19] and Li *et al.* [20] have generated stable foamulsions by using glycyrrhizic acid nanofibrils, where the nanofibrils form gels in water to increase the viscosity of the matrix as well as coat the bubbles and droplets to prevent them from coalescence. The foamulsions show gel-like behavior and can be stable for several months. In addition, Patel and co-workers reported foamulsions stabilized by colloidal complexes prepared from a mixture of methylcellulose and tannic acid.[3] The foamulsions prepared are stable for more than 4 weeks and are temperature-responsive owing to the thermally sensitive characteristic of methylcellulose. Compared with foamulsions stabilized by surfactants, the addition of particles greatly enhances their stability and endows a new mechanism for their stabilization. However, the particles mentioned above are either sensitive to pH or require specific conditions to form, which may limit their application.

Sucrose esters (SEs) are non-toxic and biodegradable surfactants usually derived from sucrose and fatty acids through esterification or transesterification reactions.[21] The various origins of plant sources as the headgroup and variable chain length of the fatty acids make it possible to produce SEs with a wide range of hydrophile-lipophile balance (HLB) number.[22,23] SEs have been widely used to stabilize emulsions and foams since the 1950s, especially in food, cosmetic and pharmaceutical products.[24-28] Recently, Zeng *et al.* added sucrose ester S370 to whipped creams (aerated oil-in-water emulsions **stabilized by protein and fat**) and found that 0.05 wt.% induced the formation of a homogeneous fat crystal network which resulted in whipped creams with high firmness and bubble stability.[29,30] However, higher concentrations of S370 led to unstable whipped creams due to replacement of protein

by SE molecules at air-water and oil-water interfaces.[31,32] It is therefore interesting to explore whether SEs alone can stabilize foamulsions.

In this work, we explore the possibility of preparing edible oil-water foamulsions using SE C-1807 which has an intermediate HLB number of 7. At relatively high concentrations, C-1807 forms vesicles in water endowing the aqueous phase with viscoelastic behavior. The viscosity of the solution increases with increasing surfactant concentration. Aqueous-continuous foamulsions can then be prepared using the aqueous solutions with edible oils. The stabilization of foamulsions at different C-1807 concentrations as well as at different oil volume fractions was investigated. In addition, the edible oil-water foamulsions show excellent cooling-heating stability between 5 and 30 °C.

2. EXPERIMENTAL

2.1 Materials

Sucrose stearate (tradenname C-1807, food/cosmetic-grade with 40 wt.% monoester and 60 wt.% di-/tri-/polyesters, HLB no. = 7 quoted by the supplier) was provided as a white powder by Mitsubishi-Kagaku Foods Corporation (Tokyo). Canola oil and soybean oil were purchased from a local store (Wuxi, China). Canola oil (density = 0.9133 g/cm³) [33] is produced by Bunge Canada and soybean oil (density = 0.9157 g/cm³) was from General Reagent, China both with food-grade specifications. Water was treated with a Merck Millipore Pure Water System (China) until a resistivity of 18 MΩ cm was achieved.

2.2 Methods

2.2.1 Preparation and characterization of aqueous C-1807 solutions

Aqueous solutions of C-1807 at required concentrations were prepared by weighing a known mass of C-1807 powder in a sample vessel of diameter 1.8 cm and height 5 cm containing a known volume of pure water. The vessel was placed in a water bath for 30 min at 70 °C until a homogeneous bluish solution was formed. The

prepared surfactant solution was kept in an incubator at 25 °C for further use.

Cryogenic Scanning Electron Microscopy (cryo-SEM) observation was carried out on selected C-1807 solutions in the following way. A small volume of C-1807 solution was pipetted onto a channelled aluminium stub to form a dome and plunged into nitrogen slush for 30 s. The frozen sample was transferred to a Quorum Technologies (PP3000T) preparation chamber at -145 °C. A scalpel was used to fracture the frozen sample exposing a freshly cut surface. The sample was transferred to the cold stage in the SEM instrument (-140 °C) and sublimed at -90 °C for 10 min. Then the sample was transferred back to the Quorum preparation chamber and sputtered with Pt for 60 s at 10 mA. It was then examined with a FEI Quanta 450 SEM at an accelerating voltage of 5 kV.

Surface/interfacial tensions were measured using an OCA-40 interfacial tensiometer (Dataphysics, Germany). For air-water and air-oil tensions, a pendent drop of water or oil was formed in air using a syringe equipped with a blunt steel needle (diameter = 1.83 mm). The profile of the drop was observed and the surface tension was determined by fitting with the Young-Laplace equation. For oil-water interfacial tensions, a rectangular glass cuvette of dimensions 50×30×40 mm was filled with 30 mL of oil, then a pendent drop of water was formed in the oil phase and the measurement was the same as that described above.

Rheological measurements were conducted using a stress-controlled rheometer (Discovery DHR-3, TA Instruments) connected to a temperature-controlled water bath. All measurements were conducted at 25 °C with a stainless steel cone and plate (diameter = 40 mm, cone angle = 2°). The gap between the centre of the cone and the plate was 53 µm. Prior to measurements, a stress sweep was performed at a frequency of 1.0 Hz. A stress value was then chosen to ensure that the sample was in the linear viscoelastic region during the subsequent oscillatory measurements.

2.2.2 Preparation and characterization of foamulsions

A required volume of aqueous C-1807 solution and an edible oil were added to a screw-top glass vial (i.d = 1.8 cm, height = 5 cm). The two phases were aerated and emulsified using an IKA T18 basic homogenizer equipped with an S18N-10G head operating at 11,000 rpm for 2 min. Foamulsions were formed by gently moving the vessel around the head of the homogenizer, during which process the homogenizer brought air into the sample. All experiments were conducted at room temperature (23 ± 2 °C) unless otherwise stated. Photos of the obtained foamulsions were taken immediately after preparation and at different times during storage to visually evaluate their stability. The emulsion type was inferred from the drop test. The over-run of foamulsions is defined as,

$$\text{over-run}(\%) = \frac{V_{total} - V_{initial}}{V_{initial}} \times 100\% \quad (1)$$

where V_{total} is the total volume of the foamulsion after preparation and $V_{initial}$ is the initial volume of the liquids (oil + water). The volume of free oil and water released from an emulsion was also measured, and f_o and f_w are used to assess their stability to coalescence and creaming, respectively. They are calculated from $f = V_t/V_0$ where V_t is the volume of oil (water) released at time t and V_0 is the initial oil (water) volume before homogenization. Optical microscopy images of the prepared foamulsions were taken using a VMX40M microscope equipped with VistarImage software. A small sample (~50 μ L) was diluted with the corresponding aqueous phase (50 μ L) on a glass slide (Thermo Scientific) and then observed under the microscope. The mean droplet diameter and mean bubble diameter were calculated from the image using Image J 1.47v. Fluorescence microscopy images of foamulsions were taken using a Zeiss Axio Imager Z2 fluorescence microscope equipped with eGFP and DAPI filters. The oil phase of the foamulsion was stained using Nile red while the aqueous phase was dyed using Rhodamine.

Rheological measurements and cryo-SEM measurements of foamulsions are similar to those of aqueous C-1807 solutions.

2.2.3 Cooling-heating and freeze-thaw stability of foamulsions

To evaluate the cooling-heating stability of a model foamulsion, the vessels containing freshly prepared foamulsions were stored in a thermostat bath at 5 °C for 22 h and then heated to 30 °C in a water bath for 2 h (one cycle). Photos and optical microscopy images of the foamulsion were taken after each cycle. Every sample experienced three cooling-heating cycles and the experiment was done in triplicate. For the freeze-thaw stability, the foamulsions were stored at -20 °C for 22 h followed by thawing at 30 °C for 2 h (one cycle); three freeze-thaw cycles were conducted for each sample.

3. RESULTS AND DISCUSSION

3.1 Characterization of aqueous C-1807 solutions

A series of C-1807 aqueous solutions at different concentration was prepared and their appearance at 25 °C is shown in Figure 1(a). Bluish solutions were observed at all C-1807 concentrations studied here. The solutions are viscous but can still flow slowly when inclining the vessels, with a small amount of foam formed during stirring of the samples. It has been reported that sucrose stearate can form vesicles at concentrations higher than the critical aggregation concentration.[22,34] Figure 1(b) shows cryo-SEM images of selected concentrations. Small and large spherical vesicles are identified for 1 wt.% aqueous C-1807 solutions, the diameters of which vary between 50 and 600 nm. This is in accordance with the closed vesicles observed by electron microscopy and fluorescence microscopy reported by Ishigami *et al.* [34] and Schenk *et al.* [35] In contrast, in the sample containing 3 wt.% C-1807, a network of vesicles was observed and closed vesicles are visible from the magnified image. The size of these vesicles is difficult to determine as they are highly aggregated and connected to each other.

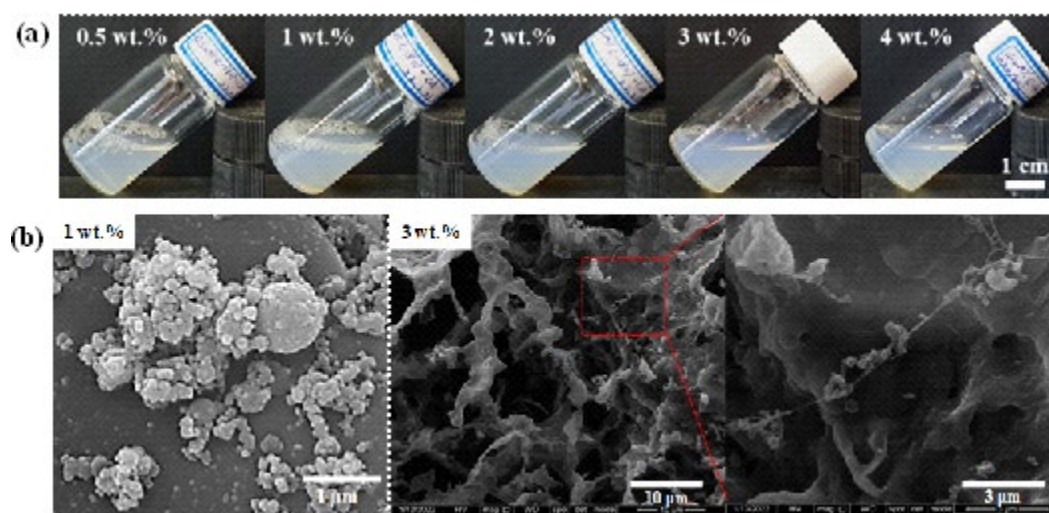


Figure 1. (a) Photos of aqueous solutions of C-1807 in pure water at different concentrations at 25 °C, (b) cryo-SEM images of selected solutions in (a).

The variation of steady shear viscosity of C-1807 aqueous solutions at different concentrations at 25 °C is shown in Figure 2(a). The viscosity of the solution with 1 wt.% C-1807 is lower than 0.01 Pa s and remains nearly constant with shear rate, close to that of pure water. By contrast, the viscosity of the solutions at higher C-1807 concentrations is significantly higher, increasing markedly with surfactant concentration but decreases with increasing shear rate displaying typical shear thinning. These results are consistent with the literature.[36] The increased shear rate disrupts the interactions in the vesicle network and eventually causes disruption thereby decreasing the viscosity. It is worth noting that the viscosity of 4 wt.% C-1807 solution is significantly higher than that of the solution with 3 wt.% C-1807, reflecting a denser 3D network of vesicles. For the frequency sweep for solutions at 3 wt.% and 4 wt.% C-1807, as shown in Figure 2(b), the elastic modulus (G') and viscous modulus (G'') indicate that the dynamic viscoelasticity is almost frequency independent. G' is always higher than G'' , indicative of solid-like behavior. These results indicate that C-1807 solutions at high concentrations are gel-like.

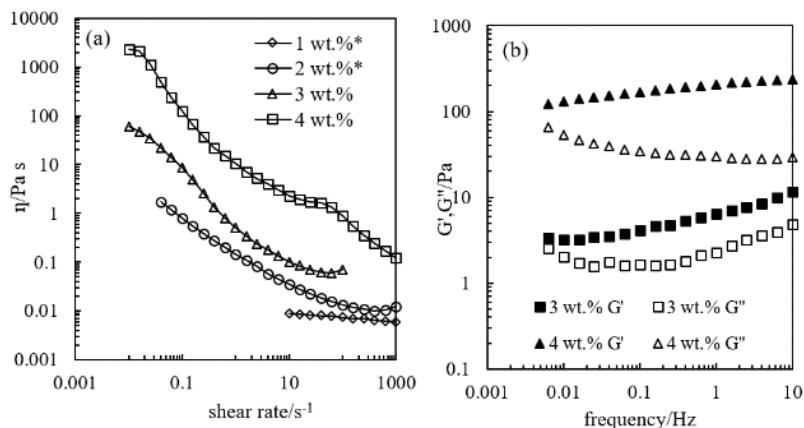


Figure 2. (a) Viscosity of C-1807 aqueous solutions at different concentrations (given) as a function of shear rate at 25 °C, (b) variation of elastic modulus G' and viscous modulus G'' with shear frequency within the linear viscoelastic region for C-1807 aqueous solutions at 25 °C.

3.2 Foamulsions of canola oil stabilized by different concentrations of C-1807

Foamulsions with canola oil dispersed in aqueous solutions of C-1807 at different concentrations at an oil:water volume ratio of 1:1 were prepared and characterized. The appearance of the foamulsions is shown in Figure 3(a). They are water-continuous as confirmed by the drop test immediately after preparation. The foamulsions at C-1807 concentrations lower than 2 wt.% are fluid, whereas those at higher concentrations are gelled and remain immobile when vessels are inverted. Foamulsions prepared at low surfactant concentrations (≤ 1 wt.%) are unstable against long term storage and complete phase separation was observed after two months, as shown in Figure 3(b). By contrast, parallel samples containing 2 wt.% of C-1807 show creaming but no coalescence of droplets after long-term storage. Foamulsions prepared with 3 wt.% C-1807 and higher are completely stable to creaming and coalescence ever after two months of storage. Figure 3(c) shows the over-run of the foamulsions against surfactant concentration. The value at C-1807 concentrations ≤ 1 wt.% is zero indicating that no bubbles are created in the system. However, the over-run shows a gradual increase as the surfactant concentration increases, and an over-run of 35% is obtained in the sample containing 4 wt.% C-1807. The long-term over-run indicates the stability of bubbles against storage. As seen, after two months

the value decreases at all surfactant concentrations except at 4 wt.% C-1807, meaning that bubbles in foamulsions with 2 wt.% and 3 wt.% surfactant are partially destroyed after 2 months of storage.

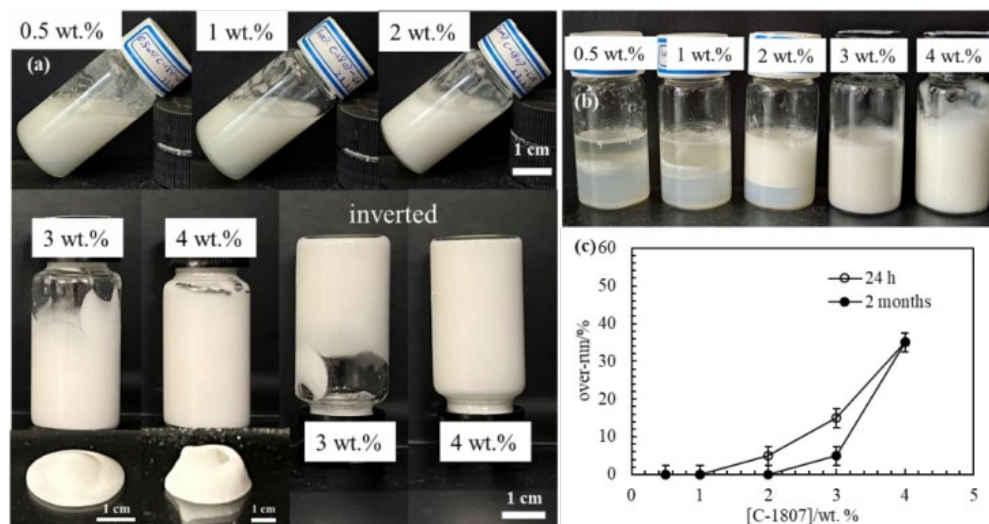


Figure 3. Appearance of foamulsions with canola oil ($\phi_o = 0.5$) stabilized by C-1807 at different concentrations taken (a) 24 h and (b) 2 months after preparation. (c) Over-run of foamulsions vs surfactant concentration **at two times**.

Figure 4(a) presents optical microscopy images of air bubbles and oil droplets in the foamulsions prepared above. No bubbles are observed at 0.5 wt.% C-1807, then an increasing number of bubbles is detected upon increasing the surfactant concentration consistent with the over-run results. Spherical droplets are observed in all cases, with the size gradually decreasing with surfactant concentration indicating an improvement of droplet stability to coalescence. The size of bubbles is slightly larger than that of droplets except at 1 wt.% C-1807 (Figure 4(b)).

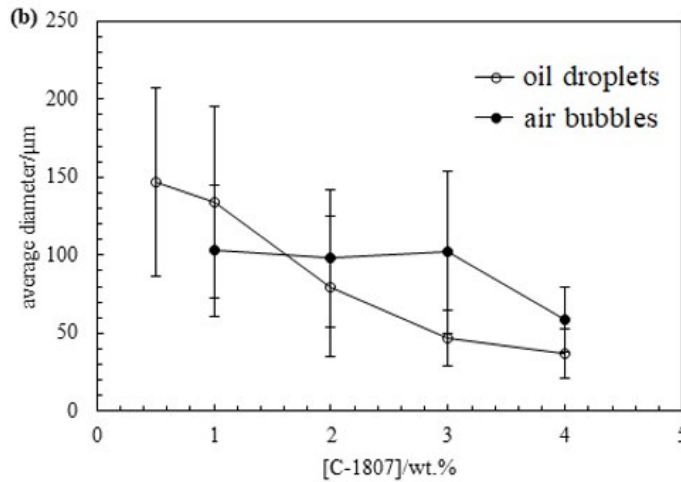
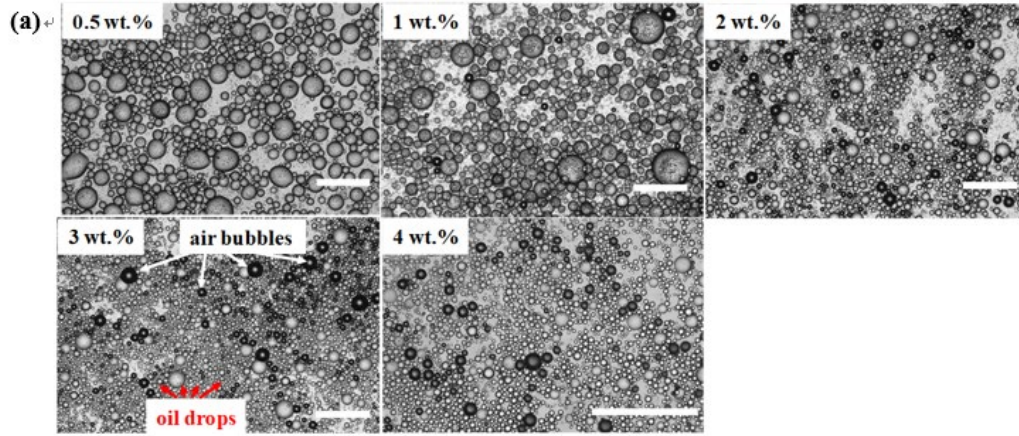


Figure 4. (a) Optical microscopy images of foamulsions with canola oil ($\phi_o = 0.5$) stabilized by different concentrations of C-1807 (given) taken 24 h after preparation, scale bar = 400 μm . (b) Average diameter of oil droplets and air bubbles in foamulsions as a function of C-1807 concentration.

As a comparison, aqueous foams stabilized by different concentrations of C-1807 were prepared using the same protocol. As shown in Figure S1(a), foams are observed on the top of the aqueous phase. The drainage of water was not halted completely until 3 wt.% surfactant. The over-run of the foams is given in Figure S1(b), where 35% - 50% is obtained immediately after preparation. It is worth noting that the over-run of aqueous foams is higher than that of foamulsions at the same C-1807 concentration, as the presence of oil in the latter partially destroys the foams. The reason will be discussed later.

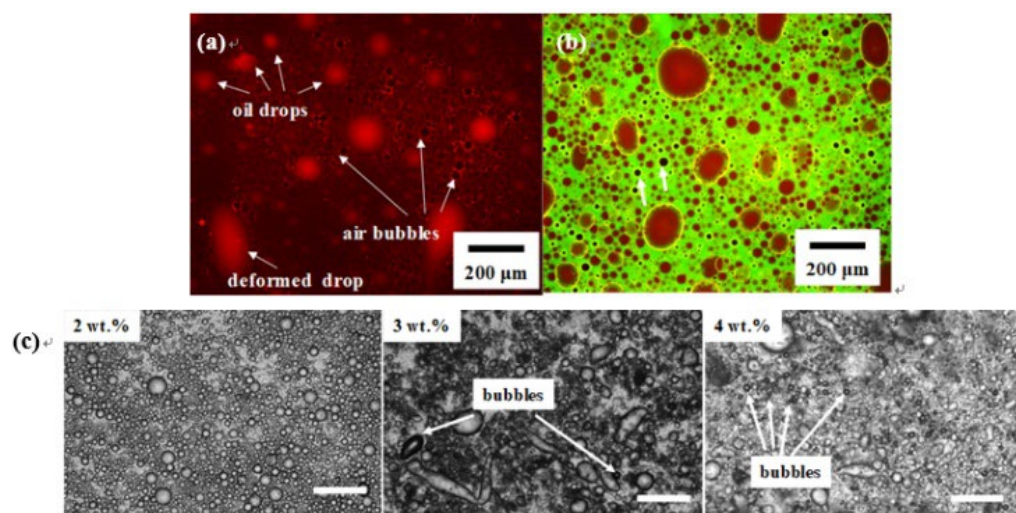


Figure 5. (a), (b) Fluorescence microscopy images of foamulsion stabilized by 3 wt.% C-1807 with the canola oil phase stained by Nile red and the aqueous phase dyed by Rhodamine. (c) Optical microscopy images of foamulsions containing different concentrations of C-1807 after 2 months, scale bar = 400 μm .

Figure 5(a) shows fluorescence microscopy images of a foamulsion stabilized by 3 wt.% C-1807 with the oil phase stained with Nile red. The red oil droplets can be clearly seen, whereas black air bubbles are probably surrounded by surfactant vesicles which are also dyed by Nile red. To clearly distinguish the oil from the aqueous phase as well as the bubbles, both Nile red and Rhodamine were incorporated into a model foamulsion to stain the oil phase and aqueous phase respectively. Red fluorescent oil droplets and black holes with green edges indicated by arrows can be seen in Figure 5(b). The black holes are air bubbles as the hydrophilic portion of the surfactant was stained by Rhodamine. After 2 months of storage, foamulsions with C-1807 lower than 1 wt.% are all destroyed and no bubbles or droplets remain. By contrast, the droplets in foamulsions containing higher concentrations of C-1807 remain stable after long-term storage, although bubbles either disappeared completely or partially as shown in Figure 5(c). It is worth noting that in the samples containing 3 wt.% and 4 wt.% C-1807, non-spherical droplets and bubbles are also observed. Non-spherical droplets and bubbles have been reported in Pickering emulsions[37] or particle-stabilised foams[38], where jammed particles are close-packed on droplet or

bubble surfaces. Here, the non-spherical droplets and bubbles are likely to be covered by a vesicle network which jams at the interface during the **approach** of **several** droplets/bubbles.

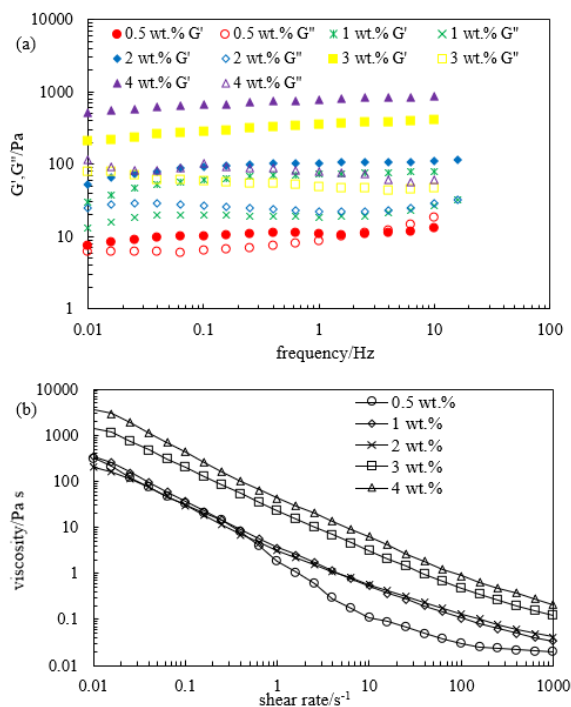


Figure 6. (a) Variation of elastic modulus G' and viscous modulus G'' with frequency for foamulsions of canola oil and water ($\phi_o = 0.5$) stabilized by different concentrations of C-1807 (given) at 25 °C. (b) Viscosity of foamulsions as a function of shear rate at 25 °C. Both are measured 24 h after preparation.

We have determined the rheological properties of the foamulsions as shown in Figure 6(a). Values of G' (elastic modulus) are higher than the corresponding G'' values (viscous modulus) at all frequencies ranging from 0.01 to 10 Hz, indicating high gel strength of these foamulsions. In addition, the G' and G'' values of foamulsions are all higher than that of surfactant solutions at the same concentration, implying that the formation of bubbles and droplets enhances the gel strength of the system. As for the apparent viscosity, the values for foamulsions are significantly higher than those of surfactant solutions especially at low surfactant concentrations, and all foamulsions show shear-thinning behavior as shown in Figure 6(b). The viscosity of foamulsions increases markedly with increasing surfactant concentration,

resembling the trend for aqueous surfactant solutions. This is reasonable since a denser 3D vesicle network is formed at higher surfactant concentrations. The gel-like aqueous phase enhances the gel strength of the continuous phase and is beneficial in preventing oil droplets and bubbles from coalescence. This stabilization mechanism is similar to what we reported for emulsions stabilized by sucrose ester C-1815,^[22] where oil droplets are surrounded by vesicles verified by cryo-SEM.

If foamulsions are to be of use in the food industry, their stability against temperature change is important during storage and transport. Hence, the cooling-heating and freeze-thaw stability of the prepared foamulsions was evaluated. For cooling and freezing, 5 °C and -20 °C were set as the low temperature limits, respectively close to that used in home refrigerators, while 30 °C was selected as the high temperature limit. For cooling-heating cycles the foamulsions prepared at room temperature were cooled to 5 °C (22 h) and then heated to 30 °C (2 h), and this process was repeated three times. The appearance of foamulsions with canola oil droplets stabilized by C-1807 undergoing three cooling-heating cycles is shown in Figure 7(a). It is clear that the foamulsions prepared with 3 wt.% and 4 wt.% surfactant show good stability against cooling and heating. The foamulsion volume remains the same before and after the cycles without any free water or oil released. Figure 7(b) shows optical microscopy images of the foamulsions before and after cooling-heating cycles. The droplets as well as the bubbles remain in the sample with their size much about the same.

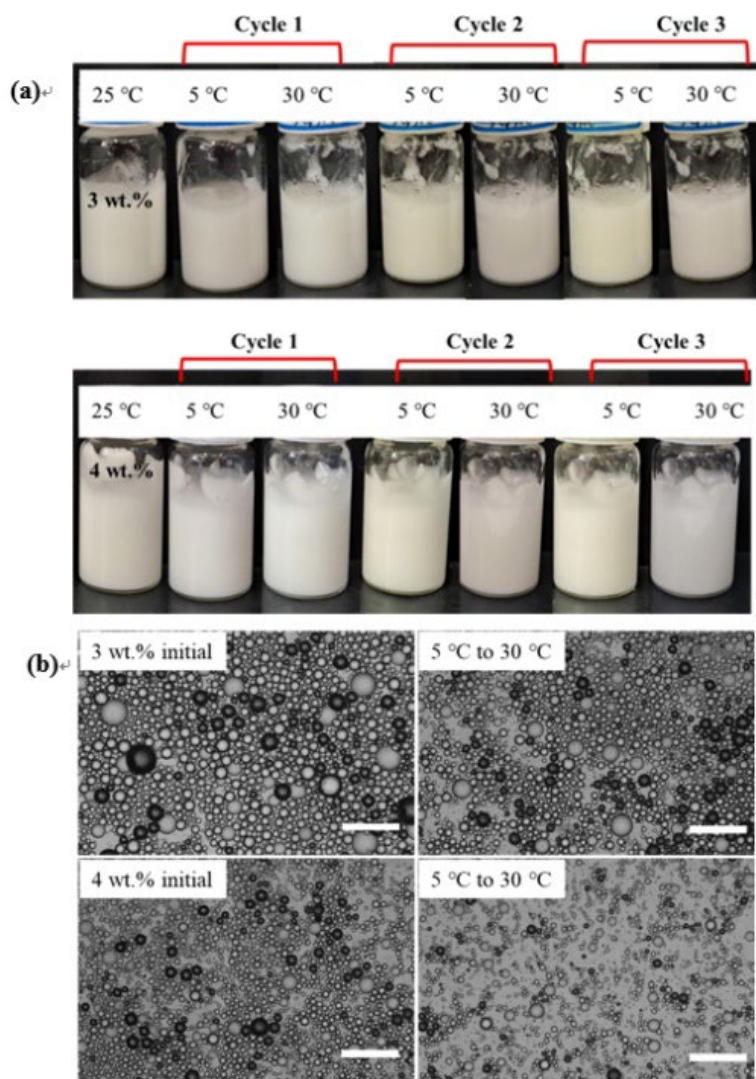


Figure 7. (a) Appearance of foamulsions with canola oil ($\phi_o = 0.5$) stabilized by different concentrations of C-1807 undergoing cooling-heating cycles between 5 °C and 30 °C. (b) Optical microscopy images of the foamulsions (left) before and (right) after three cooling-heating cycles, scale bar = 200 μm .

Regarding the stability against freezing and thawing, the same foamulsions underwent three freeze-thaw cycles (-20 °C/30 °C), and the relevant appearance and micrographs are shown in Figure S2. It can be seen that the foamulsions are partially damaged after the first freeze-thaw cycle with both oil and water released. In addition, the volume of released oil and water increases with the number of cycles, although some residual foamulsion remains after three cycles. The optical micrographs of foamulsions after three freeze-thaw cycles are shown in Figure S2(b), in which both oil droplets and air bubbles can be observed but their size has increased compared

with that before any freeze-thaw process. These results indicate that foamulsions are only partially stable against freeze-thaw cycling.

3.3 Foamulsions with canola oil and 3 wt.% C-1807 at various oil volume fractions

It was noticed that the maximum over-run of foamulsions stabilized by 4 wt.% C-1807 at $\phi_o = 0.5$ reached 35%, and we wondered if it was possible to incorporate more air into them and what the consequence would be on their strength. For this purpose, a series of foamulsions stabilized by 3 wt.% C-1807 and in which the oil volume fraction was varied was prepared. Figure 8 shows the appearance and over-run of these foamulsions. At $\phi_o = 0$ (no oil) only aqueous foams were obtained which showed gel-like characteristics and were stable against long-term storage with no water released after one month of storage. On addition of oil the over-run of foamulsions decreased as less air was incorporated. The optical micrographs shown in Figure S3 indicates that fewer bubbles were generated as the oil volume fraction increases, consistent with the over-run data. After one month of storage, foamulsions with $\phi_o = 0.2$ and 0.6 show some creaming. Nevertheless, all foamulsions are stable to coalescence.

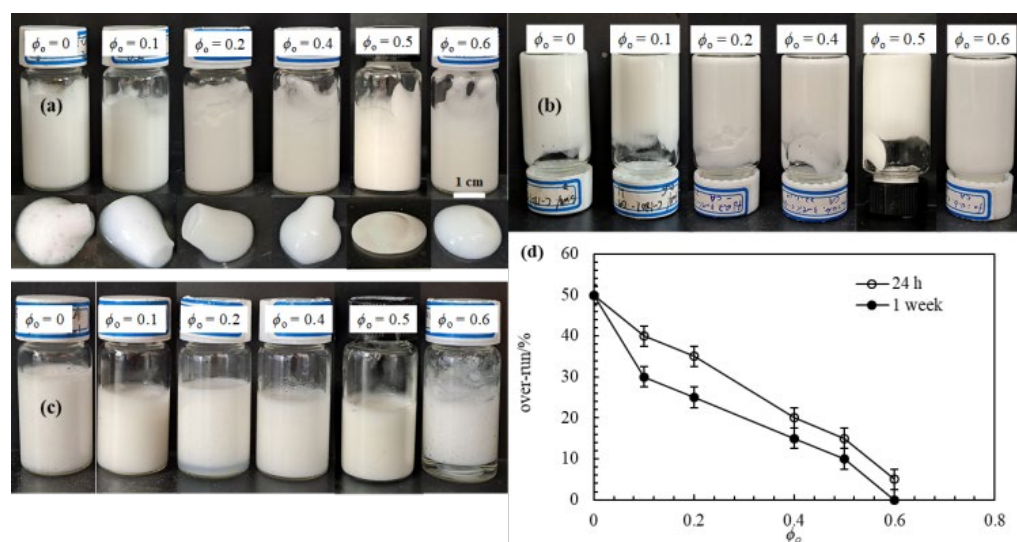


Figure 8. (a) - (c) Appearance of foamulsions with canola oil stabilized by 3 wt.% C-1807 at different oil volume fractions ϕ_o taken (a), (b) 24 h and (c) 1 month after

preparation. (d) Over-run of foamulsions vs oil volume fraction at two times after preparation.

The rheological properties of foamulsions containing different volume fractions of oil are shown in Figure 9. The G' values are higher than the corresponding G'' at all frequencies, indicating that all these samples show gel-like characteristics. It is worth noting that the sample with $\phi_o = 0$ is not a foamulsion but an aqueous foam, and the high strength comes from the aqueous phase alone. For foamulsions, an increase in ϕ_o results in a decrease in G' and G'' , implying that systems with a lower volume fraction of aqueous phase are of lower strength, providing evidence that the high strength of foams and foamulsions derives from the aqueous phase. The apparent viscosity of the foamulsions decreases slightly with increasing oil volume fraction except for the foam without oil which shows the lowest viscosity especially at low shear rates. This implies that the mixture of bubbles and droplets results in more viscous systems and the presence of bubbles is beneficial in increasing the viscosity of foamulsions.

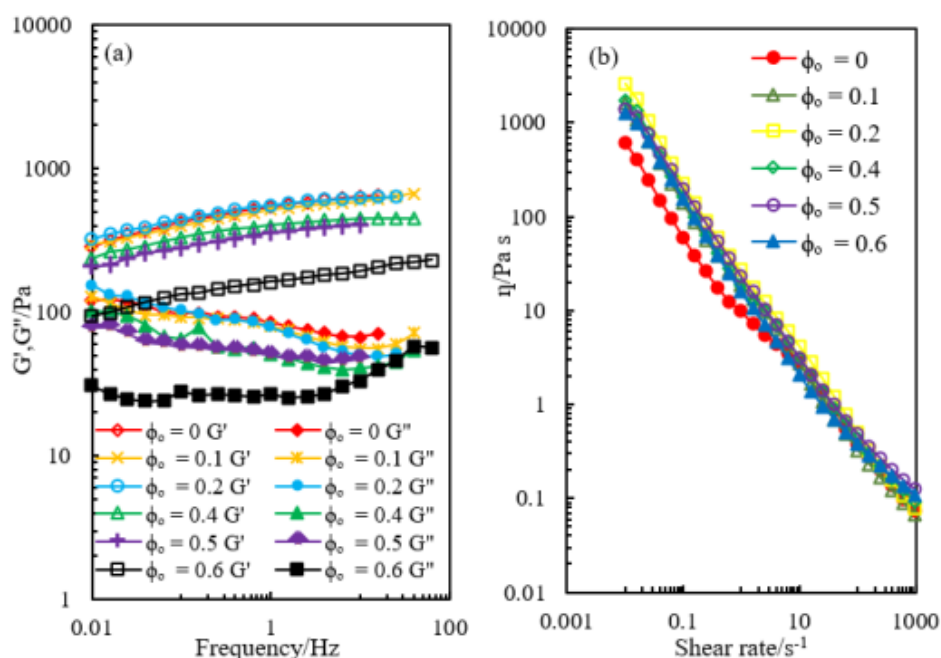


Figure 9. (a) Variation of elastic modulus G' and viscous modulus G'' with frequency of foamulsions with canola oil stabilized by 3 wt.% C-1807 at different oil volume fractions. (b) Viscosity of foamulsions as a function of shear rate for foamulsions in (a) at 25 °C. Both are measured 24 h after preparation.

The results above indicate that the presence of oil is unfavourable for the formation and stabilization of bubbles in foamulsions. It has been reported that oil can act as a defoamer either **by** spreading on the surface of bubbles leading to the thinning of foam films or **by** forming a bridge between the two surfaces of a foam film.[39] However, there are also reports claiming that oil may enhance the stability of foams.[14,15] Whether an oil increases or decreases foam stability may be evaluated by considering the entry coefficient (E), spreading coefficient (S) and bridging coefficient (B) defined below: [40,41]

$$E = \gamma_{aw} + \gamma_{ow} - \gamma_{ao} \quad (2)$$

$$S = \gamma_{aw} - \gamma_{ow} - \gamma_{ao} \quad (3)$$

$$B = (\gamma_{aw})^2 + (\gamma_{ow})^2 - (\gamma_{ao})^2 \quad (4)$$

where γ is the interfacial tension and subscripts w, a, and o represent water, air and oil respectively. When $E > 0$, the oil will invade the air-water interface of the foam, and if $S > 0$, it will spread on the interface dragging underlying water to flow out of the foam film into the Plateau borders. Moreover, if $B \geq 0$, the oil will form a bridge to destroy the foam film eventually.[40,41] We have measured the air-water, oil-water and air-oil interfacial tensions for canola oil in the presence of C-1807 in water. To avoid viscous surfactant solutions, the surfactant concentration was kept below 0.1 wt.% where non-viscous and transparent solutions were obtained. The air-water and oil-water interfacial tensions reach a plateau value above 0.1 wt.% due to aggregation in bulk. The measured air-canola oil interfacial tension (γ_{ao}) is 31.5 ± 0.1 mN/m, in good agreement with that reported by Sahasrabudhe and co-workers.[33] As shown in **Figure 10**, the surface tension-concentration curve of the aqueous surfactant solution tends to a plateau above 0.003 wt.% with the surface tension being 47.6 ± 0.1 mN/m. The interfacial tension between aqueous C-1807 and canola oil (γ_{ow}) has a plateau value of ~ 8.0 mN/m. Consequently, the three parameters at 0.1 wt.% of C-1807 were calculated to be $E = 24.1$ mN/m, $S = 8.1$ mN/m and $B = 1337.5$ (mN/m) **give error bars for all three parameters; in our work (refs. 40 and 41, what do we conclude about**

mechanism of the oil effect when E, S and B were all positive (think we had a table)?. Since they are all positive, it means that oil is not favorable to the stability of foams. This agrees with our finding that adding more oil results in fewer bubbles in foamulsions.

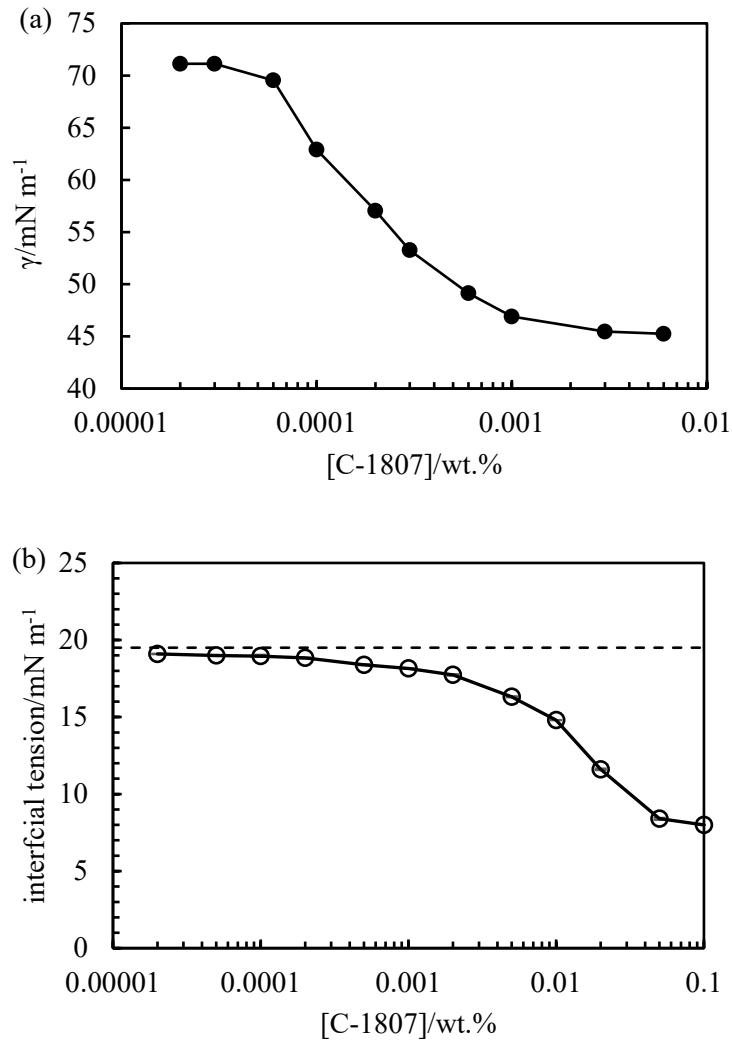


Figure 10. (a) Surface tension of C-1807 as a function of surfactant concentration at 25 °C, (b) interfacial tension between C-1807 aqueous solution and pure canola oil as a function of surfactant concentration; dashed line indicates the bare canola oil-water interfacial tension ($19.5 \pm 0.1 \text{ mN m}^{-1}$). The lines joining the points are a guide to the eye.

(a) I still worry about the shape – it is concave implying a decreasing surface concentration with increased bulk concentration which cannot happen?? Noemally it is convex (surface conc. **increases** with bulk conc.)

To explore the mechanism of stabilization of foamulsions, their microstructure was analysed using cryo-SEM as shown in **Figure 11**. Cavities form after air bubbles burst together with spherical shells of surfactant vesicles. In addition, frozen spherical droplets can also be observed and there is a vesicle network extending between droplets and bubbles. These micrographs reveal that the stability of droplets and bubbles is assured by the vesicle network which prevent them from coalescence. In addition, the viscous aqueous phase retards the drainage of water, which is also beneficial for bubble stability. This mechanism resembles that operating in foamulsions stabilized by saponin glycyrrhizic acid nanofibrils.[19,20] Here the aqueous phase is gelled due to the presence of nanofibrils which enhances foamulsion viscosity reducing creaming of the emulsion and drainage of water. The nanofibrils also coat the droplets and bubbles enhancing their stability to coalescence.

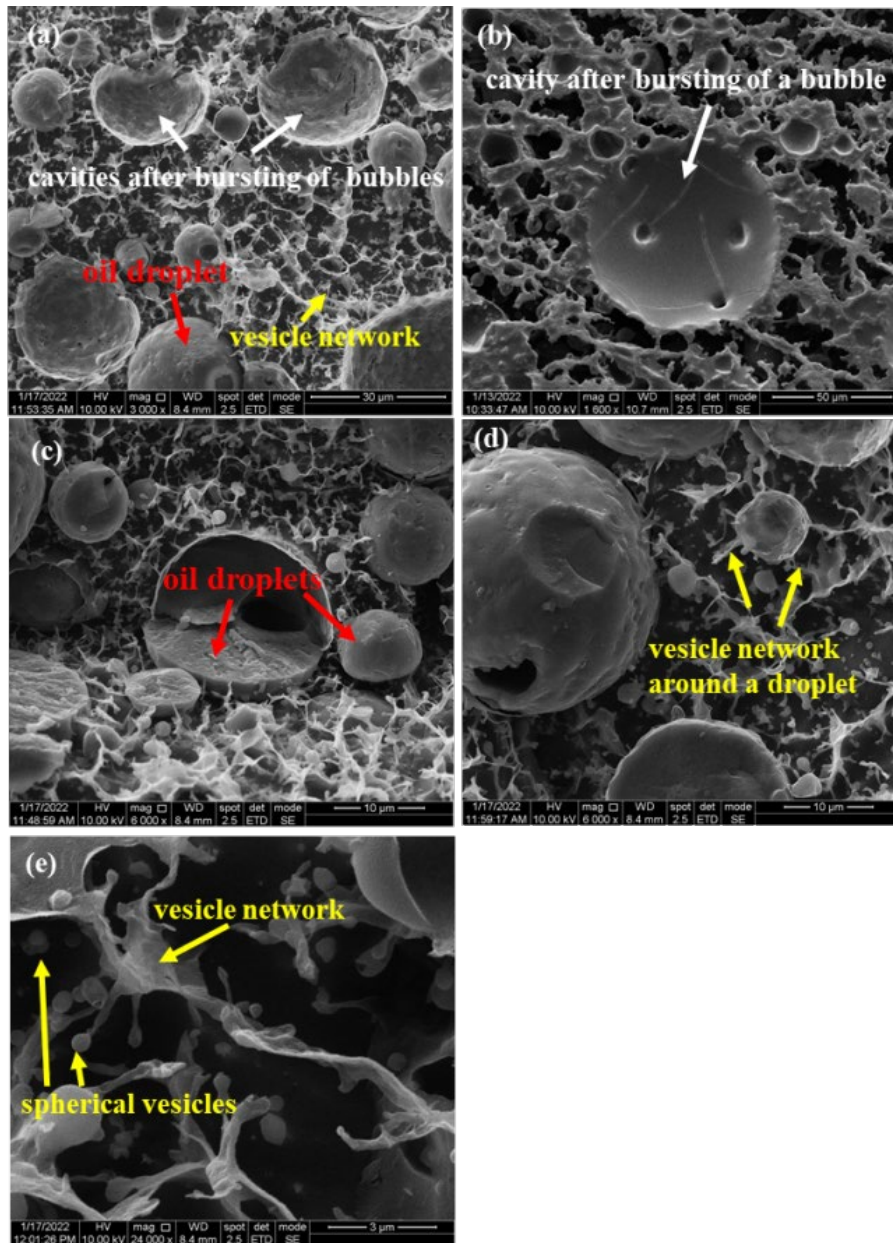


Figure 11. Cryo-SEM images of foamulsions with canola oil ($\phi_o = 0.5$) stabilized by 3 wt.% C-1807 taken 24 h after preparation. (a), (c), (d) and (e) taken from exposed surface of the sample after fracturing, (b) taken from the surface of the frozen sample before fracturing.

3.4 Foamulsions with soybean oil stabilized by C-1807

To evaluate whether the stabilization of foamulsions by C-1807 applies to other edible oils, foamulsions were prepared with soybean oil and are shown in **Figure S4**. Similar to systems with canola oil, stable foamulsions were obtained at 3 wt.% surfactant although they were partially stable to creaming at lower surfactant

concentrations. The optical microscopy images of foamulsions are shown in Figure S5, where both spherical and non-spherical droplets can be observed in all samples together with an increasing number of bubbles as the surfactant concentration increases. The fluorescence microscopy image of a foamulsion depicts the red oil droplets and black air bubbles with red edges due to surfactant adsorption at bubble surfaces. The values of G' and G'' of foamulsions given in Figure S6 confirm their gel-like property. The viscosity of foamulsions with 3 wt.% and 4 wt.% surfactant is comparable to that of foamulsions of canola oil at the corresponding surfactant concentration. Figures S7 to S9 demonstrate that the foamulsions are stable upon cooling-heating cycles, but are only partially stable against freeze-thaw cycles. The amount of oil and water released from the foamulsions is higher than in those of canola oil however. The freezing point of soybean oil is around $-16\text{ }^{\circ}\text{C}$, closing to the experimental temperature. Both the oil phase and the aqueous phase will form crystals, which is more detrimental to the stability of the system upon warming compared with foamulsions with canola oil. That is probably why more oil and water were released from foamulsions with soybean oil.

4. CONCLUSIONS

The hydrophile-lipophile balanced sucrose ester C-1807 forms spherical vesicles in water and a vesicle network at high concentrations, which increased the viscosity of the aqueous phase enabling it to exhibit gel-like characteristics. The vesicle network constructed by C-1807 was able to stabilize oil-in-water emulsions and aqueous foams which enables formation of stable foamulsions at C-1807 concentrations higher than 3 wt.%. The strength and viscosity of the foamulsions increase with increasing surfactant concentration, which makes the foamulsions gel-like and stable upon long term storage. However, an increase in oil volume fraction was unfavorable for the stabilization of foamulsions, especially harmful to stabilization of bubbles, resulting in reduced over-run. The foamulsions are stable against cooling and heating cycles between $5\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$, although only partially stable to freezing and thawing cycles between $-20\text{ }^{\circ}\text{C}$ and $30\text{ }^{\circ}\text{C}$. The stabilization of foamulsions by sucrose ester applies to

different edible oils, and C-1807 as a non-toxic and biodegradable surfactant can potentially be used as a fat replacer to develop healthy foods.

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Conflict of interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Author contributions

Raojun Zheng: Investigation, Data curation, Methodology, Writing – review & editing. **Xin Hu:** Investigation, Data curation. **Chenning Su:** Investigation, Data curation. **Jianzhong Jiang:** Project administration, Supervision, Funding acquisition, Writing-review & editing. **Zhenggang Cui:** Writing-reviewing and Editing. **Bernard P. Binks:** Discussion, Writing-reviewing and Editing.

Appendix A. Supplementary material

Supplementary data to this article can be found online at ?

References I have corrected inconsistencies in these! should vol. no. be in bold?

- [1] L. L. Schramm, Emulsions, foams, and suspensions: fundamentals and applications, Ch.1, (2006) John Wiley & Sons, Weinheim.
- [2] A. Salonen, Mixing bubbles and drops to make foamed emulsions, *Curr. Opin. Colloid Interface Sci.*, 50 (2020) 101381.
- [3] A. R. Patel, E. Drost, T. B. J. Blijdenstein, K. P. Velikov, Stable and temperature-responsive surfactant-free foamulsions with high oil-volume fraction, *Chemphyschem.*, 13 (2012) 3777-3781.
- [4] A. Salonen, R. Lhermerout, E. Rio, D. Langevin, A. Saint-Jalmes, Dual gas and oil dispersions in water: production and stability of foamulsion, *Soft Matter*, 8 (2012) 12135-12135.
- [5] M. Schneider, Z. Q. Zou, D. Langevin, A. Salonen, Foamed emulsion drainage: flow and trapping of drops, *Soft Matter*, 13 (2017) 4132-4141.
- [6] N. Koursari, P. Johnson, M. Parsa, M. Schneider, A. Trybala, V. M. Starov, Modelling of foamed emulsion drainage, *Colloids Surf. A*, 600 (2020) 124915.
- [7] D. W. Stanley, H. D. Goff, A. K. Smith, Texture-structure relationships in foamed dairy emulsions, *Food Res. Int.*, 29 (1996) 1-13.
- [8] T. Truong, N. Bansal, B. Bhandari, Effect of emulsion droplet size on foaming properties of milk fat emulsions, *Food Bioprocess Tech.*, 7 (2014) 3416-3428.
- [9] W. F. Pu, P. Wei, L. Sun, Y. Pu, Y. Chen, Investigation on stabilization of foam in the presence of crude oil for improved oil recovery, *J. Disper. Sci. Technol.*, 40 (2019) 646-656.
- [10] X. M. Liu, Z. Chen, Z. G. Cui, Synergistic effects between anionic and sulfobetaine surfactants for stabilization of foams tolerant to crude oil in foam flooding, *J. Surf. Det.*, 24 (2021) 683-696.
- [11] B. Kichatov, A. Korshunov, A. Kiverin, E. Son, Foamed emulsion - Fuel on the base of water-saturated oils, *Fuel*, 203 (2017) 261-268.

- [12]B. Kichatov, A. Korshunov, A. Kiverin, N. Medvetskaya, Combustion of foamed emulsion prepared via bubbling of oxygen-nitrogen gaseous mixture through the oil-in-water emulsion, *Fuel Processing Technol.*, 186 (2019) 25-34.
- [13]A. Szczurek, V. Fierro, A. Pizzi, A. Celzard, Mayonnaise, whipped cream and meringue, a new carbon cuisine, *Carbon*, 58 (2013) 245-248.
- [14]K. Koczo, L. A. Lobo, D. T. Wasan, Effect of oil on foam stability - Aqueous foams stabilized by emulsions, *J. Colloid Interface Sci.*, 150 (1992) 492-506.
- [15]L. Lobo, D. T. Wasan, Mechanisms of aqueous foam stability in the presence of emulsified non-aqueous-phase liquids - Structure and stability of the pseudoemulsion film, *Langmuir*, 9 (1993) 1668-1677.
- [16]Y. L. Yan, C. Shan, Y. Wang, Q. Deng, Effects of oil on aqueous foams: Electrical conductivity of foamed emulsions, *Chemphyschem.*, 15 (2014) 3110-3115.
- [17]C. Guidolin, N. Jiang, D. Langevin, A. Salonen, One-step generation and characterisation of aerated emulsions using laser diffraction, *Colloids Surf. A*, 641 (2022) 128454.
- [18]H. A. Wege, S. Kim, V. N. Paunov, Q. X. Zhong, O. D. Velev, Long-term stabilization of foams and emulsions with *in-situ* formed microparticles from hydrophobic cellulose, *Langmuir*, 24 (2008) 9245-9253.
- [19]Z. L. Wan, Y. E. Sun, L. L. Ma, F. B. Zhou, J. Guo, S. Q. Hu, X. Q. Yang, Long-lived and thermoresponsive emulsion foams stabilized by self-assembled saponin nanofibrils and fibrillar network, *Langmuir*, 34 (2018) 3971-3980.
- [20]Q. Li, M. Xu, Y. Yang, J. Guo, Z. Wan, X. Yang, Tailoring structure and properties of long-lived emulsion foams stabilized by a natural saponin glycyrrhizic acid: Role of oil phase, *Food Res. Int.*, 150 (2021) 110733.
- [21]Y. Teng, S. G. Stewart, Y.-W. Hai, X. Li, M. G. Banwell, P. Lan, Sucrose fatty acid esters: synthesis, emulsifying capacities, biological activities and structure-property profiles, *Critical Rev. Food Sci. Nutr.*, 61 (2021) 3297-3317.

- [22]X. Hu, B. P. Binks, Z. G. Cui, High internal phase emulsions stabilized by adsorbed sucrose stearate molecules and dispersed vesicles, *Food Hydrocolloids*, 121 (2021) 107002.
- [23]G. Garofalakis, B. S. Murray, D. B. Sarney, Surface activity and critical aggregation concentration of pure sugar esters with different sugar headgroups, *J. Colloid Interface Sci.*, 229 (2020) 391-398.
- [24]L. Osipow, F. D. Snell, M. Ferencz, Stability of emulsions containing sucrose esters, *J. Am. Oil Chem. Soc.*, 35 (1958) 65-68.
- [25]R. Gupta, K. James, F. Smith, Sucrose esters and sucrose ester/glyceride blends as emulsifiers, *J. Am. Oil Chem. Soc.*, 60 (1983) 862-869.
- [26]J. Buck, C. Walker, M. Pierce, Evaluation of sucrose esters in ice cream, *J. Food Sci.*, 51 (1986) 489-493.
- [27]A. Tual, E. Bourles, P. Barey, A. Houdoux, M. Desprairies, J.L. Courthaudon, Effect of surfactant sucrose ester on physical properties of dairy whipped emulsions in relation to those of O/W interfacial layers, *J. Colloid Interface Sci.*, 295 (2006) 495-503.
- [28]A. Szűts, P. Szabó-Révész, Sucrose esters as natural surfactants in drug delivery systems-A mini-review, *Int. J. Pharm.*, 433 (2012) 1-9.
- [29]D. Zeng, Y. Cai, T. Liu, L. Huang, P. Liu, M. Zhao, Q. Zhao, Effect of sucrose ester S370 on interfacial layers and fat crystals network of whipped cream, *Food Hydrocolloids*, 113 (2021) 106541.
- [30]D. Zeng, Y. Cai, T. Liu, L. Huang, Y. Zeng, Q. Zhao, M. Zhao, The effect of sucrose esters S1570 on partial coalescence and whipping properties, *Food Hydrocolloids*, 125 (2022) 107429.
- [31]V. Klang, J. C. Schwarz, N. Matsko, E. Rezvani, N. El-Hagin, M. Wirth, C. Valenta, Semi-solid sucrose stearate-based emulsions as dermal drug delivery systems, *Pharmaceutics*, 3 (2011) 275-306.

- [32] V. Klang, A. Novak, M. Wirth, C. Valenta, Semi-solid o/w emulsions based on sucrose stearates: influence of oil and surfactant type on morphology and rheological properties, *J. Disper. Sci. Technol.*, 34 (2013) 322-333.
- [33] S. N. Sahasrabudhe, V. Rodriguez-Martinez, M. O'Meara, B. E. Farkas, Density, viscosity, and surface tension of five vegetable oils at elevated temperatures: Measurement and modeling, *Int. J. Food Prop.*, 20 (2017) 1965-1981.
- [34] Y. Ishigami, H. Machida, Vesicles from sucrose fatty acid esters, *J. Am. Oil Chem. Soc.*, 66 (1989) 599-603.
- [35] P. Schenk, M. Ausborn, F. Bendas, P. Nuhn, D. Arndt, H. W. Meyer, The preparation and characterization of lipid vesicles containing esters of sucrose and fatty acids, *J. Microencaps.*, 6 (1989) 95-103.
- [36] C. Calahorro, J. Muñoz, M. Berjano, A. Guerrero, C. Gallegos, Flow behavior of sucrose stearate/water systems, *J. Am. Oil Chem. Soc.*, 69 (1992) 660-666.
- [37] S. A. Bon, S. D. Mookhoek, P. J. Colver, H. R. Fischer, S. van der Zwaag, Route to stable non-spherical emulsion droplets, *Eur. Polymer J.*, 43 (2007) 4839-4842.
- [38] A. Bala Subramaniam, M. Abkarian, L. Mahadevan, H. A. Stone, Non-spherical bubbles, *Nature*, 438 (2005) 930-930.
- [39] P. R. Garrett, Defoaming: Antifoams and mechanical methods, *Curr. Opin. Colloid Interface Sci.*, 20 (2015) 81-91.
- [40] R. Aveyard, B. P. Binks, P. D. I. Fletcher, T. G. Peck, C. E. Rutherford, Aspects of aqueous foam stability in the presence of hydrocarbon oils and solid particles, *Adv. Colloid Interface Sci.*, 48 (1994) 93-120.
- [41] R. Aveyard, B. P. Binks, P. D. I. Fletcher, T. G. Peck, P. R. Garrett, Entry and spreading of alkane drops at the air-surfactant solution interface in relation to foam and soap film stability, *J. Chem. Soc. Faraday Trans.*, 89 (1993) 4313-4321.