

Making Good Foams and Emulsions – The Role of Adsorption Layer Properties and Emulsifier Self-Assembly Phenomena

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Most Food products contain oil droplets or air bubbles. These two colloidal entities determine in a significant way sensorial and physical properties of food emulsions and foams. The control and/or modulation of the physical and structural properties of these colloidal entities represents an important task for each manufacturer when producing emulsions and foams which are appreciated by the consumer. In the present work we describe how self-assembly structure formation of low molecular weight emulsifier systems in water influences adsorption layer formation at air-water interfaces and how the established adsorption layer properties are related to the observed stability of single gas bubbles and respective model foams. The investigated emulsifiers are Tween 80, which forms normal micelles in water, and SSL (sodium stearyl lactylate) which forms bilayer structures. Whereas bilayer structure forming emulsifiers, such as SSL, show a low critical aggregation concentration, i.e., a low monomer solubility, leading to slow adsorption rates, micellar structure forming emulsifiers, such as Tween 80, are much better soluble in water leading to faster adsorption rates. We will show that when forming mixed micelles between Tween 80 and SSL the adsorption rate of SSL monomers to water-air interfaces can be increased and the stability of the generated model foam considerably improved with respect to the stability of Tween 80 stabilized foams. BAM experiments show that the increased single bubble and model foam stability is related to the formation of SSL-rich aggregates at the air-water interface. Mixed micelle formation seems to be a potential route to produce foams or emulsions with a better shelf-life.

Keywords: Emulsions, foams, emulsifiers, interface, self-assembly

1 INTRODUCTION

Relevant properties of food emulsions or foams, such as texture, taste or nutritional functionality are essentially determined by colloidal structures, such as oil droplets or gas bubbles, formed during processing, and how these colloids interact with each other. Consumers distinguish without difficulty between 'good' and 'bad' emulsions or foams. Although different product attributes exist which the consumer takes to consciously or unintentionally formulate his preference, it is clear that the production of 'good' emulsions and foams requires the formation of stable, fine and/or monodisperse droplets or bubbles. The energy input usually used during homogenization, the established flow conditions (laminar or turbulent) in the homogenizer, the droplet/bubble deformation and break-up and/or the viscosity of the continuous phase are main factors controlling droplet/bubble size and size distribution [1]. However, one of the most important factors controlling size or stability is the interfacial tension and/or viscoelasticity which is related to the adsorption of amphiphilic molecules to the droplet/bubble interface from the continuous phase [2]. Droplets or bubbles become more deformable as the interfacial tension is lowered, making them easier to disperse. The important timescale for emulsion or foam formation can be sub-

milliseconds. Therefore, the kinetic of adsorption of a surfactant or polymer to the interface is critical for foam and emulsion formation. Moreover, the stabilization of emulsions and foams against coalescence or Ostwald ripening requires specific interfacial properties.

Usually, polymeric emulsifiers, such as whey proteins or caseins, or low molecular weight emulsifiers, such as polysorbates, lecithins, etc., are used to stabilize interfaces in foods. Application of low molecular weight emulsifiers (surfactants) for water-based food systems is often restricted by their low monomer solubility in aqueous media. Beyond a certain emulsifier concentration, called critical aggregation (CAC) or critical micellar concentration (CMC), these emulsifiers form self-assembly structures which themselves are not efficiently adsorbing to interfaces. Emulsifiers are efficiently adsorbing only in their monomeric form. Therefore, if the CAC (or CMC) is very low, only very slow adsorption rates can be attained. An example of self-assembly structures which usually form at very low monomer concentrations (CAC is below 10^{-4} mM), are bilayer structures in vesicles or lamellar crystals. On the other hand, micelle forming emulsifiers have a much higher monomer solubility (CMC is significantly higher than the CAC) and the rate of adsorption from micellar solutions is found to be much faster. If incorporating bilayer forming

emulsifiers into micelles, creating so-called mixed micelles, bilayer forming surfactants could be more efficiently involved in fast adsorption processes.

In the present work we investigated the adsorption phenomena to a water-air interface (i) of the micelle forming emulsifier Tween 80 (is a polysorbate), (ii) of the bilayer forming emulsifier SSL (sodium stearyl lactylate) and (iii) of SSL/Tween 80 mixed micellar solutions. We investigated the general mechanism of micellar promoted adsorption (by means of dynamic surface tension and Brewster Angle Microscopy (BAM)) and show the impact of mixed micelle formation on single bubble stability (by means of the Diminishing Bubble Technique) and foam stability (by means of a model foaming experiment based on sparging gas through a glass frit).

2 MATERIAL AND METHODS

2.1 Methods

Dynamics of surface tension changes in Tween 80, SSL and mixed SSL/Tween 80 solutions was monitored by means of Wilhelmy plate measurements in an appropriate PTFE vessel equipped with a BAM-1 set-up (NFT, Germany) allowing simultaneous capturing of video-sequences corresponding to different stages of the adsorption process. The surface of the studied solutions was rapidly cleaned by aspiration, and, immediately after its mechanical equilibration, the dynamic surface tensions were measured along with video monitoring of the surface layer morphology. The optical scheme of the used BAM-1 is given elsewhere [3].

The Diminishing Bubble Technique was used to follow the stability of a single air bubble immersed in an emulsifier solution. The principle of this experiment is described elsewhere in more details [4, 5]. A microscopic film is formed at the top of a bubble floating at the surface of an emulsifier solution. Because of the pressure difference between the two sides of the film, gas diffuses from the inside of the bubble through the film to the outside air and the bubble shrinks. The bubble is monitored by means of a light microscope and the radius R of the bubble is measured as a function of time. The obtained bubble radius data were normalised and plotted as a function of time (R^3/R_0^3 vs t), where R_0 is the bubble radius at $t = 0$. The slope of this curve allows to estimate the rate of disproportionation and to determine the gas permeability coefficient through the film [4,5]. The emulsifier concentration of the used solution was 2.55 mM.

Foams were generated and analysed by means of the Foamscan TM (from IT Concept, Longessaigne, France). With this instrument the foam formation, stability and drainage can be monitored by conductometric and optical measurements. The

foam is generated by blowing gas (nitrogen) at a flow rate of 40 ml/s through a porous glass frit (0.2 mm) at the bottom of a glass tube where 20 ml of the emulsifier solution is placed. The foam volume is measured over time using a CCD camera. In all experiments 100 ml of foam is generated. Foaming properties were measured at 25°C and a solution pH of 7. The used emulsifier concentration was 2.55 mM.

2.2 Materials

Commercially available SSL (sodium stearyl lactylate; mol. weight 385 g/mole) was purchased from Danisco. Tween 80 (mol. weight: 1312 g/mole; CMC is 0.099 mM (13 mg/l)) of Biochemical purity grade was obtained from Fluka. All chemicals were used without further purification. Milli-Q deionised water was used for the preparation of all solutions. The SSL/Tween 80 mixed micellar solutions were prepared in the following way: The respective amounts of SSL and Tween 80 were placed into a glass volumetric flask, filled with water and stirred vigorously at approximately 60°C. As the mixture was completely clarified, stirring and heating were stopped and the solutions were left to cool down to room temperature. The prepared solutions remain clear (stable) at room temperature for 2 - 7 days, depending on the SSL molar fraction in the mixed solution. Note that a 2.28 mM pure SSL solution is not getting clear and remains opalescent indicating the presence of a considerable amount of large colloidal SSL vesicular or lamellar crystalline particles in the bulk.

3 RESULTS

3.1 Dynamic Surface Tension and BAM measurements

Figure 1 summarizes the dynamic surface tensions measured for pure Tween 80, pure SSL, and mixed solutions at different SSL/Tween 80 ratios. The total amount of emulsifier was kept constant at 2.28 mM, i.e. far above the CMC of Tween 80.

The topmost solid curve shows the dynamic surface tensions of the pure Tween 80 solution. After 5 hours the curve levels off at about 37 mN/m. The fast changes in surface tension at the beginning can be ascribed to the stage of proper adsorption whereas the following slow relaxation is attributed to the additional equilibration processes which may take place within the adsorption layer once the first stage is already finished. As possible processes, either reorientation of the Tween 80 molecules at the interface or surface cluster formation in the adsorption layer can be assumed. Note also that the Tween 80 sample represents a technical sample, although characterised as biochemical grade, so that it does not only consists of one single compound but rather of a mixture of surfactants. Thus, the slow surface tension decrease could also be caused by replacement of lower by higher

surface active compounds in the Tween 80 mixture.

SSL is much less soluble in water than Tween 80 forming lamellar crystalline particles. While a 2.28 mM SSL solution is turbid, the respective Tween 80 solution is clear. Simple SSL titration experiments in which SSL was added to a Tween 80 solution (see Materials) revealed that SSL can be incorporated into the Tween 80 micelles up to 40 mol-% SSL. After addition of more SSL, the solution turns turbid indicating that not all SSL is incorporated anymore into the Tween 80 micelles.

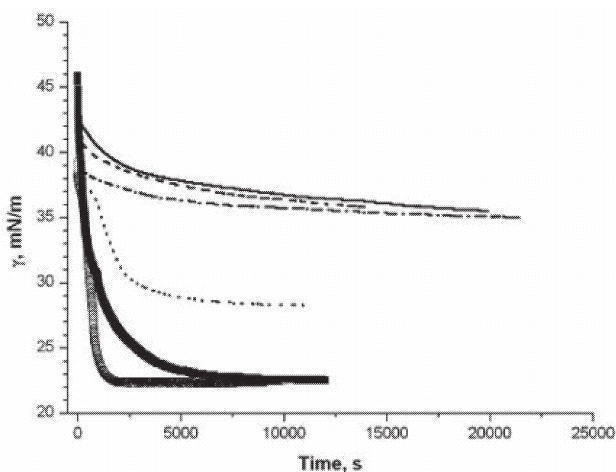


Figure 1: Dynamic surface tensions of SSL/Tween 80 mixed solutions at different bulk molar fractions of SSL: 0 (no SSL added) – solid curve; 0.1 - dashed; 0.2 - dotted-dashed; 0.3 - dotted; 0.4 - bold curve with open symbols; 1.0 (aqueous dispersion of pure SSL) - bold curve with filled symbols.

Figure 1 summarizes also the influence of mixed micelle formation on dynamic surface tension. At a SSL/Tween 80 molar ratio of 0.1 or 0.2 the adsorption is dominated by the adsorption of Tween 80. The shape of the $\gamma(t)$ dependences are almost the same, only the part corresponding to the slow relaxation becomes slightly shorter and the whole curve is shifted slightly to lower γ values. Most probably, these moderate differences reflect a low contribution of SSL molecules to the slow stage of the kinetics and to the final equilibrium adsorption layer structure. The corresponding BAM images are shown in Figures 2a and 2b. It confirms that no significant microscopic interfacial structures are observed at a molar ratio of 0.1. The surface is dominated by the Tween 80 molecules, which do not form aggregates. However, BAM reveals that at a molar ratio of 0.2, domains, which are rich in SSL become visible. They grow and merge with time into large almost spherical microscopic structures.

The situation changes drastically for a SSL/Tween molar ratio of 0.3. The slow stage of adsorption kinetics proceeds now much faster and the equilibrium surface tension of 28.4 mN/m is attained already within 2 hours (see Figure 1), which is considerably lower than observed in the pure Tween

80 system. Moreover, the shape of the surface tension curve obtains a special feature; an inflection point at a value corresponding approximately to the equilibrium tension for the pure Tween 80 solution can be monitored. This point indicates probably the end of the Tween 80 co-adsorption in the mixed system and the onset of its displacement by the higher surface active SSL. Tween 80 is squeezed out from the surface layer leading to a slight deceleration of the surface tension decrease with time (manifested by the inflection point in the $\gamma(t)$ dependence). The corresponding BAM images demonstrate also a considerable difference to the systems with a lower SSL content. Figure 2c shows the shape and number of surface aggregates for a surface age of only 15 sec. It is clearly seen, that the transfer rate of SSL from bulk to the surface is now much faster. It is so fast that the degree of surface coverage (area covered by bright aggregates as compared to the total area) attains a value of at least 25% already within this short time. An almost complete coverage is observed at an adsorption time corresponding to the onset of the plateau region in the $\gamma(t)$ curve.

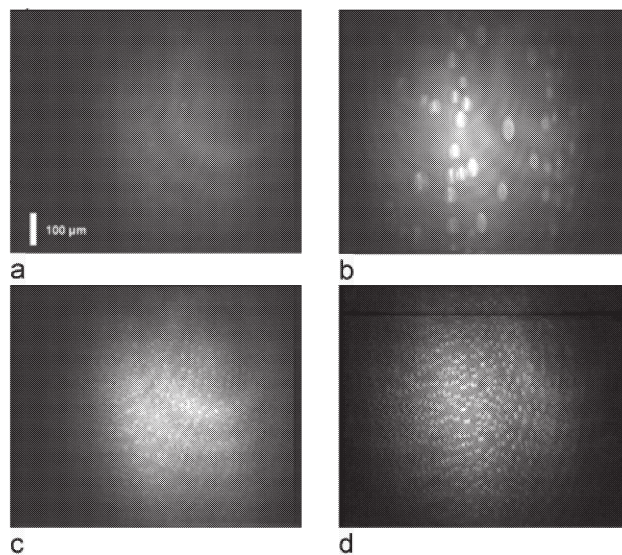


Figure 2: BAM images of layers adsorbed from SSL/Tween 80 mixed micellar solutions at various SSL/Tween 80 molar ratios: a: ratio 0.1 after 30 minutes adsorption; b: ratio 0.2 after 30 minutes; c: ratio 0.3 after 15 seconds; d: ratio 0.4 after 15 seconds

Adsorption from mixed micellar solutions with a SSL/Tween 80 molar ratio of 0.4 is yet faster, and the surface tension reaches equilibrium already within 30 minutes (Figure 1). Note, that this decrease is even faster than observed for the aqueous dispersion of pure SSL at the same total concentration of 2.28 mM. Like for the SSL molar ratio of 0.3, an inflection point is observed at 37 mN/m. However, it is less pronounced due to the faster displacement of Tween 80. The relatively fast surface tension decrease is related to the corresponding rate of surface coverage by insoluble

aggregates. Figure 2d shows the surface layer state after 15 s. The surface coverage is considerably higher than at the molar ratio of 0.3, and reaches a value of approximately 40%. Shape and size of the growing surface aggregates also indicate the rate of their formation: the higher the SSL molar ratio is, the smaller and less regularly shaped are the domains and, therefore, the higher is their growth rate.

In conclusion: SSL alone is only slightly soluble in water. Its solubility can be significantly enhanced by forming mixed micelles with Tween 80. Mixed micelle formation facilitates the formation of the SSL-dominated interfacial layer, since the diffusion of the mixed micelles to the so-called subphase (the layer adjacent to the interface) is faster than the diffusion of the much larger lamellar crystals. Moreover, the micelles disintegrate faster than the lamellar crystals and, therefore, liberate more Tween 80 and SSL monomers which can adsorb to the interface.

3.2 Diminishing Bubble and Foaming Experiments

In this chapter we discuss the effect of mixed micelle formation (i) on the stabilization of a single bubble against Ostwald ripening and (ii) on the stabilization of a model foam using the Foamsan apparatus.

Figure 3 shows the evolution of a single air bubble in the presence of either a Tween 80, SSL or SSL/Tween 80 (molar ratio 0.4) mixed micellar solution. While the gas bubble stabilized with Tween 80 has lost already 50% of its initial volume after around 100 minutes, using SSL alone, the bubble is much more stable. Interestingly, also in the presence of the SSL/Tween 80 mixed micelles the bubble is much more stable than in the presence of pure Tween 80 micelles.

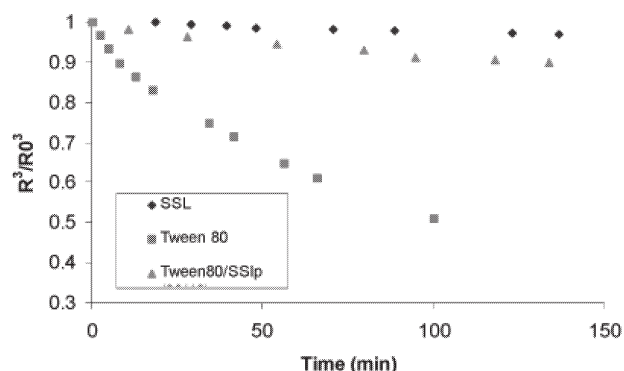


Figure 3: Normalized radius of a single air bubble as a function of time at different aqueous phase compositions; total emulsifier concentration is 2.55 mM.

In Table 1 the gas permeability coefficients are given for the different systems. It can be seen that the gas permeability of a Tween 80 stabilized film formed at the top of the bubble floating at the surface of the emulsifier solution is about 10 times

higher than that of the SSL/Tween 80 stabilized film. This result shows that solubilizing SSL into the Tween 80 micelles at a molar ratio of 0.4 significantly enhances the stability of the thin film and considerably slows down Ostwald ripening of the bubble. Note that the calculated gas permeability coefficient of the mixed micellar film is very close to the value found for the pure SSL dispersion.

Table 1: Gas permeability coefficient K at 25°C obtained for 2,55 mM emulsifier in demineralised water

Emulsifier	K (cm/s)
Tween 80	0.077
SSL	0.001
SSL/Tween 80 (ratio 0.4)	0.008

These findings suggest that solubilizing SSL into Tween 80 micelles should also enhance the stability of a multitude of gas bubbles, i.e., a foam. Figure 4 shows the stability of a foam obtained with equimolar Tween 80, SSL and SSL/Tween 80 mixed micellar solutions. Clearly, the SSL/Tween mixed micellar solution stabilized the foam significantly better than the Tween 80 micelles in absence of SSL. The foam stability obtained with the mixed micellar solution is very similar to the foam stability obtained with the SSL alone.

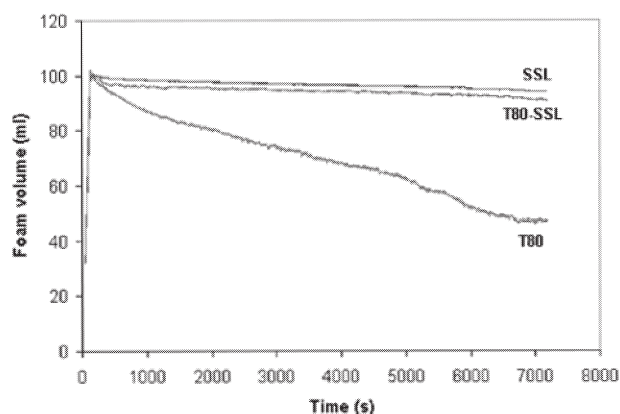


Figure 4: Time evolution of the foam volume obtained after sparging N₂ into a 2.55 mM emulsifier solution. The SSL/Tween mixed micelles had a molar SSL/Tween 80 ratio of 0.4.

4 CONCLUSIONS

The present work showed that surfactant self-assembly phenomena are significantly influencing the macroscopic properties of foams (or emulsions), such as shelf-life, due to their impact on surfactant monomer adsorption to water-air (or water-oil interfaces). Incorporating bilayer forming surfactant monomers, such as SSL molecules, into micellar surfactant self-assembly structures (based on Tween 80) forming mixed micelles enhances both the stability of single air bubbles against Ostwald

ripening and the stability of model foams produced by sparging gas through a glass frit. The mechanism how SSL is stabilizing the interface is not completely clear yet. Our BAM experiments, however, suggest that the SSL molecules, once at the interface, form aggregates which might be responsible for the observed stabilization effect.

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REFERENCES

- [1] Windhab EJ, Dressler M, Feigl K, Fischer P, Megias-Alguacil D: Emulsion processing - from single-drop deformation to design of complex processes and products. *Chemical Engineering Science* 60 (2005) 2101-2113.
- [2] Wilde PJ: Interfaces: their role in foam and emulsion behaviour. *Curr. Opin. Colloid Interface Sci.* 5 (2000) 176-181.
- [3] Grigoriev DO, Leser ME, Michel M, Miller R: in preparation.
- [4] Platikanov D, Nedyalkov M et al., *J. Colloid and Interface Sci.*, 75 (1980) 620.
- [5] Schmitt C, Palma da Silva T, Bovay C, Rami-Shojaei S, Frossard P, Kolodziejczyk E, Leser ME: Effect of time on the interfacial and foaming properties of β -Lactoglobulin/Acacia Gum electrostatic complexes and coacervates at pH 4.2. *Langmuir* 21 (2005) 7786-7795.