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Foam stabilized by large casein micelle aggregates: The effect of aggregate number in foam lamella

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ABSTRACT

In this study, a casein micelle aggregate dispersion (CMAD) with average particle size of 6.7 ± 0.5 μm was prepared using ultracentrifugation, pelleting, milling and redispersion and mixed with a casein micelle dispersion (CMD) with average particle size of 0.13 ± 0.02 μm in varying ratios (0, 25%, 50%, 75% and 100% CMAD, v/v). The effect of particle concentration and size of casein micelle aggregates (CMAs) on foam stability and thin film stability was investigated. Results showed that foam stability increased with increasing bulk concentration of CMAs. The actual aggregate concentration in foam lamella which account for an improved foam stability was well quantified using optical microscopy. Besides, the thin film measurements showed an increase in film rupture times with increasing aggregate concentration in the thin films for diluted dispersions, which confirmed the strong link between aggregate number in foam lamella and corresponding foam stability. At the protein concentration studied (2%), the aggregates did not form a gel network in the lamella but were randomly distributed over the film. The film and foam stabilization by CMAs is ascribed to the fact that they effectively divided the whole film into film elements with smaller radius, resulting in a smaller critical film thickness for film rupture. Another effect is that film drainage can be slowed down by an effective suction pressure in the film due to the curvatures induced by the wetting of hydrophilic particles. In conclusion, aggregated particles of casein micelles around 5–10 μm prepared in this research could be applied to enhance the functional properties of dairy foams.

1. Introduction

Various kinds of particles and aggregates have received lots of attention for applications in food emulsions and foams (Binks, Campbell, Mashinchi, & Piatko, 2015; Fameau & Salonen, 2014; Lazidis et al., 2016; Murray, Durga, Yusoff, & Stoyanov, 2011). Particles or aggregates can be achieved either directly from natural resources or by building up colloidal structures from molecular scale like heat-induced denaturation (protein particles or aggregates) (Rullier, Axelos, Langevin, & Novales, 2009, 2010; Rullier, Novales, & Axelos, 2008), gelation (micro-gel particles) (Schmitt, Bovay, & Rouvet, 2014), fibrillation (fibres) (Oboroceanu, Wang, Magner, & Auty, 2014; Wan, Yang, & Sagis, 2016), surface modification by electrostatic attraction (particle-surfactant complex) (Zou et al., 2016) and so on. They can also be prepared by physical methods like milling or grinding, simply breaking down existing biological structures (Dickinson, 2017). With different preparing method and material, the physicochemical properties (particle size, contact angle, charge, surface roughness and shape etc.) of particles exhibit different properties which will determine their role in foam stabilization or destabilization.

There seems to be an optimal particle size for aggregates to stabilize foam and this optimal size is system-related, ranging from tens of nanometers to a few micrometers. The dependence of foam stability on aggregate size varies for different materials: It could be a few micrometers for casein micelle aggregates (Chen et al., 2016) whereas tens of nanometers for whey protein aggregates (Rullier

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et al., 2010). For the same kind of material, the structure of aggregates also influences the dependence of foam stability on particle size. For example, the particle size that will exhibit high foam stability varied for globular whey protein aggregates (Rullier et al., 2010) and whey protein fibrils (Oboroceanu et al., 2014) as well as whey protein micro-gel (Lazidis et al., 2016; Schmitt et al., 2014). This is probably due to a different surface property: higher surface hydrophobicity (Dombrowski, Dechau, & Kulozik, 2016) or less compact and more asymmetrical and flexible structures (Báez, Moro, Ballerini, Busti, & Delorenzi, 2011) are reported to be advantageous for foam stabilization. It is more difficult to quantify the surface hydrophobicity of protein aggregates which had irregular shapes. However, foam stabilization by solid particles like silica particles is an extensively studied topic (Fameau & Salonen, 2014; Horozov, 2008). Partially hydrophobic silica particles with contact angle, θ, close to 90° can act as a foam stabiliser, whereas very hydrophobic particles (θ > 90°) are used as antifoams through a bridging/de-wetting mechanism (Horozov, 2008). The partially hydrophobic particles with contact angles around 65° and smaller than 90° were found to be optimal for foam stabilization (Ata, Ahmed, & Jameson, 2004; Ata, Ahmed, & Jameson, 2002; Schwarz & Grano, 2005): these particles will adsorb at the air/water interface, while hydrophilic particles remain in the continuous phase of the foam. The adsorption of partially hydrophobic particles at the interface has been found to reduce disproportionation (Stocco, Rio, Binks, & Langevin, 2011; Subramanian, Larsen, & Stone, 2005), or induce structural reinforcement of the film against coalescence (Kaptay, 2003). However, the presence of hydrophilic particles in the continuous phase of a foam has been related to retarded drainage: these particles are suggested to act as a liquid-trapping structural element or to create a jammed structure in the Plateau borders (Guignot, Faure, Vignes-Adler, & Pitois, 2010; Murray & Ettelaie, 2004). Aggregation of particles in the foam network (lamella and Plateau borders) could also occur depending on the bulk concentration and interaction among particles (Carl, Bannuscher, & von Klitzing, 2015), which would further improve foam stability.

Similar to silica particles, the contact angle of protein aggregates determines their location in foam. A previous review reported an improved foam stability due to the presence of protein aggregates without significant differences in the interfacial properties of the air/water interface (Wierenga, van Norél, & Basheva, 2009). However, the dilatational properties were determined only at small deformations and constant frequency, and no large amplitude dilatations which are more sensitive to subtle changes in the microstructure of the interface. Recently, a systematic study of linear and nonlinear surface rheology (Chen et al., 2017) of casein micelle dispersions containing aggregates demonstrated that casein micelles and presumably their aggregates were neither an integral part of the air/water interface, which is in line with researches on other protein aggregates. Therefore, protein aggregates probably stay in the continuous phase, i.e. in the lamella or Plateau borders, similarly to hydrophilic solid particles. A correlation between thin film stability and the foam stability has been reported (Fameau & Salonen, 2014). According to Rullier et al. (2010, 2009, 2008) the thin film stability of dispersions containing aggregates of β-lactoglobulin was dependent on the aggregate size and on the ratio between non-aggregated proteins and protein aggregates. The mobility of aggregates at the film surface was found to be crucial for film stability. A gel-like network formed within the foam film was interpreted from the immobility of aggregates on the film surface. Another important study (Saint-Jalmes, Peugeot, Ferraz, & Langevin, 2005) investigated a casein dispersion with a particle size range between 50 nm and 300 nm. This study showed casein aggregates of a few microns appeared as thick spot-regions within the thin film and indicated that an increase in concentration of the casein aggregates yielded higher film stability. However, the reason why casein micelle aggregates get trapped in the film remains unknown. The effective concentration of aggregates accounting for improved foam stability is not well-quantified. For casein micelle aggregates, there is still no direct proof of a gel network formation by these aggregates in the foam lamella. Besides, the optimum size of casein aggregates for foam stabilization and the location of these aggregates regarding different particle size as well as particle concentration is unclear and need further research.

In the current study, we succeeded in making a dispersion of large casein micelle aggregated particles(CMAD). The casein micelle aggregates (CMAs) had an average particle size of around 10 μm and a unique flat shape which has not been reported before. To obtain more insights of the mechanism leading to ultra-stable foams by these CMAs, a series of samples was prepared by mixing two well-defined systems, i.e. casein micelle dispersions (CMD) and CMAD, in different ratios. This allowed us to investigate the influence of size distribution and concentration of CMAs on their foam stability and thin film stability as well as bulk properties. Samples were characterized for particle size distribution by light scattering and the morphologies of the colloidal particles present in CMD and CMAD by SEM. Foam was produced in two ways: by shaking and by sparging. The microstructure of the foams was visualized using light microscopy and the thin film stability was measured by the thin film balance technique using a Sheludko cell. Correlations between the concentration of CMAs in the bulk and in the foam lamella with foam stability and thin film stability were analyzed.

2. Materials and methods

2.1. Materials

Low-heated skim milk powder NILAC was obtained from NIZO (Ede, The Netherlands). Ultra-pure water (MilliQ Purelab Ultra, Darmstadt, Germany), free of surface active contaminants, was used in all experiments (resistivity>18.2 MΩ-cm, surface tension is 72.26 ± 0.4 mN m^{-1} at 20 °C). Poly-L-lysine hydrobromide 0.01% and Glutaraldehyde 50%, w/w were purchased from Sigma–Aldrich (Steinheim, Germany). Other chemicals were of analytical grade and purchased from Sigma Aldrich (Steinheim, Germany).

2.2. Preparation of casein micelle dispersion (CMD) and casein micelle aggregates dispersion (CMAD)

Skim milk was reconstituted by dissolving NILAC milk powder in MilliQ water (10%, w/w) and stirring overnight at room temperature (RT). Sodium azide (0.02%, w/w) was added as preservative. The reconstituted skim milk was ultracentrifuged (L-60 Beckman Ultracentrifuge, rotor type 70 Ti, Krefeld, Germany) at 100,000 *g* for 90 min at 20 °C, as described elsewhere (Huppertz & de Kruif, 2007). Subsequently the pellets were milled at 30 Hz at 20 °C using a Mixer Mill MM400 (Retch GmbH, Haan, Germany) for different times depending on the samples to be obtained. The ground casein pellets were re-dispersed in milk permeate (2%, w/w). Milk permeate powder was prepared as described by Chen et al. (2016) and reconstituted in MilliQ water (5.76%, w/w) for 30 min. CMD refers to a casein micelle dispersion. This dispersion was prepared by milling casein pellets for 20 min, re-dispersing in milk permeate for 60 h and subsequent homogenization at 40 Pa with a Labhoscop Homogenizer HU 3.0 (Delta Instruments, Drachten, the Netherlands). A dispersion of casein micelle aggregates (CMAD) was prepared by milling pellets for 30 min and redispersing in milk permeate for 3 h at room temperature. The CMD and CMAD were