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Food-grade Pickering stabilisation of foams by *in situ* hydrophobisation of calcium carbonate particles

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ABSTRACT

The aim of this study was to investigate the possibility of stabilising foam bubbles in water by adsorption of calcium carbonate ($CaCO_3$) particles. Because $CaCO_3$ is hydrophilic and not surface-active, particles were hydrophobised *in situ* with several emulsifiers. The used emulsifiers were food-grade and negatively charged at the pH employed. The effect of particle addition on foamability and foam stability of solutions containing either β-lactoglobulin, sodium caseinate, Quillaja, sodium dodecanoate (SD) or sodium stearoyl-2-lactylate (SSL) was studied. It was found that the ability of the emulsifiers to induce surface activity such that the particles are able to adsorb to the air-water interface is related to their structure. The structure needs to consist of a well-defined hydrophobic part and a charged part. Large emulsifiers with a complex structure, such as β-lactoglobulin, sodium caseinate and Quillaja, were able to partially hydrophobise the particles but were not able to act synergistically with the particles to increase the foam stability. Low molecular weight emulsifiers, however, consisting of a single tail with one charged group, such as SD and SSL, adsorbed at the particle surface rendering the particles partially hydrophobic such that they adsorb to the air-water interface. In a subsequent investigation, the pH was changed to a value typical for food products (pH 6–7) and the addition of milk salts on the foamability and foam stability was assessed. Based on these results, the use of food-grade $CaCO_3$ particles hydrophobised *in situ* with food-grade surfactants (SD or SSL) to prepare ultra-stable aqueous foams is demonstrated.

1. Introduction

Aqueous foam is an air in water dispersion. Energy is needed to generate bubbles in the liquid, for example by agitation with a homogeniser or by hand shaking. Because of the thermodynamic instability of foams, ingredients are needed to stabilise the foam. Surfactants and proteins are generally used for this purpose. Through the formation of a surfactant monolayer at the interface with the hydrophobic part directed to the air phase and with the hydrophilic group in the water phase, the interfacial tension is decreased which provides an increased stability against coalescence of bubbles. Drainage of liquid in between the bubbles can be reduced by the formation of interfacial tension gradients which is called the Gibbs-Marangoni effect (Walstra, 2003). However, because of the relatively high free energy of the air-water interface and the resulting high Laplace pressure difference between the inside and outside of the bubbles, it is difficult to completely stabilize foams against disproportionation, coalescence and liquid drainage (Dickinson, 2010).

Through the adsorption of small solid particles to the interface, the stability of foams can be dramatically improved; this is called Pickering stabilisation (Pickering, 1907). Small solid particles can be used for stabilising foams and emulsions, as reviewed by Binks et al. (Aveyard, Binks, & Clint, 2003; Binks, 2002). and by Dickinson (2010, 2011). The contact angle, set by a balance of the solid-air, solid-water and air-water interfacial tensions, determines whether and how the particle adsorbs to the air-water interface. When the contact angle measured into water is smaller than 90°, the particle is partially hydrophobic and is thus only partly wetted by the water phase (Gonzenbach, 2006). In contrast to surfactants, particles are practically irreversibly adsorbed because the energy

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needed to remove the particles from an air-water surface (*ΔG*) can be several orders of magnitude larger than the thermal energy. It has been shown that adsorption of particles to the air-water interface can completely stabilise the bubble against coalescence and disproportionation (Binks & Horozov, 2005).

Air bubbles in water can be stabilised by partially hydrophobic particles. Examples are polymer microrods (Alargova, Warhadpande, Paunov, & Velev, 2004), hydrophobised silica nanoparticles (Binks & Horozov, 2005), polystyrene latex microparticles (Fujii, Iddon, Ryan, & Armes, 2006), particles from hydrophobic cellulose (Wege, Kim, Paunov, Zhong, & Velev, 2008) and ethyl cellulose particles (Jin et al., 2012). The use of many of these particles in food is inhibited because they are not approved for use in food (*e.g.*, hydrophobised silica and polystyrene) or the production of the particles involves the use of solvents (*e.g.*, ethylcellulose particles). On the contrary, a wide range of hydrophilic particles that can be used in food are available (*e.g.*, hydrophilic silica and calcium carbonate). In order to use hydrophilic particles to stabilise bubbles, these particles have to be partially hydrophobised by *ex situ* chemical modification or *in situ* modification with surfactants. Examples of particle-surfactant combinations used for the stabilisation of aqueous foams are crystalline sodium chloride particles with cetyltrimethylammonium bromide (CTAB) (Vijayaraghavan, Nikolov, & Wasan, 2006); Laponite clay particles with either hexylamine (Liu, Zhang, Sun, & Xu, 2009), alkylammonium bromides (Liu, Zhang, Sun, & Xu, 2010), CTAB (S. Zhang, Lan, Liu, Xu, & Sun, 2008), or dodecyltetraoxyethylene ether, $C_{12}E_4$ (S. Zhang, Sun, Dong, Li, & Xu, 2008); alumina particles with short chain carboxylic acids (Gonzenbach, Studart, Tervoort, & Gauckler, 2006a, 2006b, 2007); silica particles with n-amylamine (Arriaga et al., 2012); and calcium carbonate ($CaCO_3$) particles with sodium dodecyl sulphate (SDS) (Cui, Cui, Cui, Chen, & Binks, 2010). However, none of these systems are allowed in food. There are several reviews on food-grade particles for emulsion stabilisation (Berton-Carabin & Schroën, 2015; Dickinson, 2011; Rayner et al., 2014). Examples of food-grade options are protein particles (*e.g.* soy, egg, corn) and polysaccharide particles (*e.g.* cellulose, chitin, starch). However, only few studied have been done on Pickering stabilisation of foam systems.

The aim of this study is to obtain Pickering stabilisation of aqueous food foams, therefore both particles and surfactants should be food-grade. From all the particles studied previously in foams, only cellulose and calcium carbonate particles are food-grade. Calcium carbonate particles were selected as particles to be used in this study because of their successful use with SDS in the stabilisation of foam (Cui et al., 2010). Cui and co-workers studied the use of calcium carbonate particles in combination with three different surfactants to increase the foam stability. They found no synergistic effect on foam stability for $CaCO_3$ particles with the cationic CTAB or with the nonionic surfactant OP-10. This indicates that the $CaCO_3$ particles cannot be surface activated by these cationic or nonionic surfactants. Addition of particles had a synergistic effect on the foam stability of anionic SDS surfactant. However, because SDS is not food-grade, food-grade alternatives need to be found that have the same synergistic effect on foam stability with $CaCO_3$ particles. The use of such a food-grade alternative in combination with $CaCO_3$ particles was studied recently by Binks, Campbell, Mashinchi, and Piatko (2015) and they found that this combination yields ultra-stable foams.

In this study five different emulsifiers that are negatively charged at the relevant pH were selected; β-lactoglobulin (β-lg), sodium caseinate (NaCas), Quillaja, sodium stearoyl 2-lactylate (SSL) and sodium dodecanoate (SD). β-lactoglobulin is a dairy protein present in milk serum. It is a globular protein with its isoelectric point at pH 5.2 (Walstra, Wouters, & Geurts, 2005). Sodium caseinate is made by acidification of casein micelles. It is a random coil protein mixture consisting of α_{s1}-casein, α_{s2}-casein, β-casein, κ-casein and γ-casein of which the α_{s1} and β caseins are most abundant and most surface-active (Fennema, 1996). The caseins contain 35–45% apolar amino acids which make them relatively hydrophobic and their isoelectric point is at pH 4.6 (Walstra et al., 2005). Quillaja is an extract from the inner bark of the tree *Quillaja saponaria* and contains a high concentration of saponins. The properties of Quillaja are variable; the type used in this research is negatively charged at neutral pH because of the presence of a carboxylic acid group with a pK_a value of 3.5 (Y. Yang, Leser, Sher, & McClements, 2013). Sodium stearoyl lactylate is an anionic surfactant consisting of an ester of stearic acid and lactic acid (Kurukji, Pichot, Spyropoulos, & Norton, 2013). Sodium dodecanoate is an anionic surfactant consisting of a sodium carboxylate with a C_{12} chain (Cui, Cui, Zhu, & Binks, 2011). The potential of the emulsifiers to hydrophobise calcium carbonate particles was investigated by measuring the effect of particle addition on the foamability and foam stability of the different foaming agents. As a next step towards practical application, the effect of lowering the pH to around 7 and the addition of salts was studied.

2. Experimental

2.1. Materials

Precipitated calcium carbonate particles ($CaCO_3$) from Tianli Construction Material Co. Ltd. were used. Water was first passed through a reverse osmosis unit and then through a Milli-Q reagent water system. The emulsifiers used were: β-lactoglobulin (β-lg) from DOMO (Hiprotal 35) with 35% protein and a molecular weight of 1.84×10^4 g mol^{-1} (Kontopidis, Holt, & Sawyer, 2004); sodium caseinate (NaCas) from DMV International (EM7) with 90% protein and an average molecular weight of 2.33×10^4 g mol^{-1} (Fennema, 1996); Quillaja from National Starch (Q-Naturale) with 90% saponins, 20% dry matter and a molecular weight of 1.65×10^3 g mol^{-1} (Mitra & Dungan, 1997); sodium stearoyl-2-lactylate (SSL) $C_{24}H_{34}NaO_6$ from Kerry Ingredients (Admul SSL 2012) of 100% purity with a molecular weight of 4.52×10^2 g mol^{-1} and sodium dodecanoate (SD) $C_{12}H_{23}NaO_2$ from Sigma-Aldrich with a purity of >99% and a molecular weight of 222 g mol^{-1}. The critical aggregation (CAC) and micelle (CMC) concentrations of the proteins and surfactants are given in Table 1.

Simulated milk ultra-filtrate (SMUF) was made from three solutions and stored up to a week at 5 °C. The solutions were stored for a maximum of 6 months at 5 °C. 20 mL of each solution was diluted to 500 mL with water before use. Solution 1: 39.5 g KH_2PO_4 (≥98%), 30.0 g $C_6H_5K_3O_7 \cdot H_2O$ (≥99%), 44.8 g $C_6H_5Na_3O_7 \cdot 2H_2O$ (≥99%) and 4.5 g K_2SO_4 (99.5%) were dissolved in Milli-Q water and made to 500 mL. Solution 2: 7.5 g K_2CO_3 (≥99%) and 15.0 g KCl (99.5%) were dissolved in Milli-Q water and made to 500 mL. Solution 3: 33.0 g $CaCl_2 \cdot 2H_2O$ and 16.3 g $MgCl_2 \cdot 6H_2O$ (≥99%) were dissolved in Milli-Q water and made to 500 mL. All the salts were from Sigma-Aldrich except calcium chloride (99%), which was from Fisher Scientific.

2.2. Size distribution of particles

1 wt% of $CaCO_3$ particles was dispersed in Milli-Q water with a high intensity ultrasonic processor (Vibra-cell VC100) with a 20 kV CV18 ultrasonic probe of 2.3 mm diameter for 2 min at 15 W (Sonic & Materials). The sample was diluted in a Hydro 2000SM sample dispersion unit and the particle size distribution was measured using a Malvern Mastersizer 2000 instrument.