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Synergetic interfacial adsorption of protein and low-molecular-weight emulsifiers in aerated emulsions

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ABSTRACT

Whipped creams (aerated emulsions) are a complex emulsion-foam system whose oil-stabilizing potential and aeration capacity are determined by the surface activity of proteins and small surfactants. In this study, the interaction between three low-molecular-weight (LMW) emulsifiers [sodium stearoyl lactylate (SSL), phospholipid (PL), and sucrose ester (SE)] with caseinate was investigated to elucidate the mechanism of formation and stability of whipped creams. Competitive adsorption, interfacial tension, droplet aggregation, viscosity, and morphological variations of the emulsions were examined, and aeration capacity, hardness, and microstructure of whipped creams were measured. The combination of surfactants (0.05−1.0% w/w) with caseinate (0.6% w/w) produced concerted effects on the stability of emulsions. Water-soluble surfactant (SE) adsorbed more strongly than oil-soluble surfactants (SSL and PL) onto oil droplets. The lesser protein adsorption in the SE emulsion enabled a strong foaming activity in the subsequent aeration. Protrusions of triacylglycerol crystals and aggregation of oil droplets into an interactive colloidal matrix with considerable hardness and viscosity were prominently observed in SE creams. On the other hand, shear thinning followed by thickening was observed when PL was added to form the caseinate-based emulsion while no foaming was produced, and SSL, known to form α-gel at the interface, produced no stable foam. The improved emulsion stability yet the propensity to coalesce induced by cooperative actions of casein molecules and hydrophilic surfactant played a crucial role in producing aerated emulsions.

1. Introduction

A whipped cream is an aerated emulsion whose foam structure is stabilized by partially coalesced fat crystals. In the preparation of such products, the pre-emulsion must be quiescently stable prior to whipping but readily subjected to destabilization upon shearing to form a fat network that entraps air bubbles (Goff, 1997). The transformation of the air-free emulsion into an aerated cream matrix involves partial coalescence of oil droplets producing a viscoelastic air-water interface. The construction of the heterogeneous structure depends highly on the amiability of the fat globule membrane (Brooker, Anderson, & Andrews, 1986; Smith, Goff, & Kakuda, 2000).

The thermodynamics of a meta-stable emulsion and the role of the interfacial membrane surrounding the oil droplets have been studied (Maldonado-Valderrama & Patino, 2010). The properties of the interfacial layer depends upon the composition, chemical structure, and the adsorbability of the surfactants (Fernández, Sánchez, Niño, & Patino, 2007). Proteins and low-molecular-weight (LMW) emulsifiers are active surfactants which can adsorb at interface to reduce the interfacial free energy and then facilitate the formation of emulsion (Pugnaloni, Dickinson, Ettelaie, Mackie, & Wilde, 2004). Proteins can form a viscoelastic protective membrane at oil droplet interface due to their amphiphilic structures, providing long-term stability for foams or emulsions via steric and electrostatic stabilization mechanisms (Gunning et al., 2004). LMW emulsifiers are generally composed of a hydrophilic head and one or several hydrophobic tails, which can be classified into three groups according to the charge of the polar head, i.e., non-ionic, ionic, and amphoteric emulsifier. They are more mobile

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and efficient than proteins for lowering the interfacial tension, forming thinner and weaker interfacial layers, which are susceptible to fat droplets coalescence due to lack of steric repulsion (Berton, Ropers, Viau, & Genot, 2011; Dan et al., 2013; Wilde, Mackie, Husband, Gunning, & Morris, 2004).

A whipped cream consists of three incompatible phases where air bubbles are retained by a network of agglomerated fat, which is formed and regulated by a destabilization process. The fat crystals at the oil-water interface are able to pierce the separated interfacial film into a continuous phase thereby forming a stiff crystal network, providing a long-stability of air cells (Fredrick, Walstra, & Dewettinck, 2010). Therefore, the process of partial coalescence is critical to the formation of the structure of a whipped cream, which is highly related to the strength of interfacial membrane. Although the quiescent stability of the emulsion is important before whipping, the fat droplet interface must be sufficiently thin to allow the crystals to hold the droplets together as a clump (Phan, Moens, Le, Van der Meeren, & Dewettinck, 2014).

The co-adsorption of proteins and LMW emulsifiers at the oil-water interface is essential to partial coalescence caused by protein displacement to allow air bubble entrapment during the whipping process (Petrut, Danthine, & Blecker, 2016). The interaction between proteins and LMW emulsifiers in the formation and stability of aerated emulsions has been widely studied in past several years. Munk, Larsen, van den Berg, Knudsen, and Andersen (2014), studying the competitive adsorption of emulsifiers in O/W emulsions, reported that partial displacements of sodium caseinate by LMW emulsifiers reduced fat globule aggregation and improved the emulsion stability. The favored partitioning of high-affinity LMW emulsifiers at the oil-water interface leads to a physically weak fat globule membrane, therefore, an increased tendency of fat crystals to protrude into the continuous phase upon shearing (Petrut et al., 2016). Fredrick et al. (2013) have attributed the susceptibility of fat globules towards coalescence to the physical state of LMW emulsifier at the interface; the improved whipping properties can be achieved by optimizing the composition of the interfacial membrane. The composition of the emulsion interface affects the physicochemical properties of emulsion, which can be manipulated to facilitate coalescence of fat globules (Eisner, Wildmoser, & Windhab, 2005).

The present study compared three LMW emulsifiers having different molecular structures and surface activity for their roles in the formation and stabilization of caseinate-based fully hydrogenated palm kernel oil aerated emulsions. Specifically, an anionic emulsifier (SSL), an amphoteric emulsifier (PL), and a nonionic emulsifier (SE), which are commonly used to aid in air incorporations in emulsions (see structures above), were chosen to study the effect on the oil-water interfacial properties when sodium caseinate was used as a co-emulsifier. The morphology, particle size, rheology, hardness, and aeration capacity of emulsions were specifically examined.

2. Materials and methods

2.1. Materials

Sodium caseinate (90% purity) was obtained from JK Chemical LTD (Beijing, China). Sodium stearoyl lactylate (SSL) was provided by Cardlo Co. (Guangzhou, China). Phospholipid (PL) from soybean was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sucrose ester (SE, consisting of 70% monoester and 30% di- and triesters) were kindly donated by Mitsubishi Chemical Co. (Tokyo, Japan). Fully hydrogenated palm kernel oil (FHPKO) was provided by Yihai Kerry Co. (Shanghai, China). All other reagents were of analytical grade.

2.2. Emulsion preparation

Caseinate (0.6%, w/w) and sucrose (10%, w/w) were dispersed in warm water (60 °C) under continuous stirring until complete dissolution. The solution was then placed in a 4 °C refrigerator for 12 h to ensure full hydration. Hydrophobic emulsifiers (SSL, PL) were separately dispersed in molten FHPKO and hydrophilic emulsifier (SE) was directly dissolved in protein solution. To prepare emulsions, mixtures of FHPKO (25%, w/w) with the protein solution (75%,w/w) containing 0.00%, 0.05%, 0.125%, 0.25%, 0.50%, or 1% (w/w) emulsifiers at 60 °C were blended using Ultra-Turrax (T18, IKA, Staufen, Germany) for 3 min, followed by two-stage high pressure homogenization (150/30 bar) with an AH-2010 homogenizer (ATS Engineering Inc., Ontario, Canada). Emulsions were immediately chilled in ice-water and then stored at 4 °C for 24 h before analysis.

2.3. Measurement of emulsion properties

2.3.1. Interfacial tension

The interfacial tension applicable to the prepared emulsions was measured using a drop tensiometer (DSA100S, Krüss GmbH, Hamburg, Germany) equipped with a pendent drop apparatus. Based on the maximum bubble pressure principle, the measurements probed the diffusion and adsorption kinetics of the surfactants. Corn oil was purified by Florisil adsorbent to remove the surface-active impurities. A value of interfacial tension, $\gamma = 28.6 \pm 0.2$ mN/m, at water-oil interface was deemed acceptable for the test. The interfacial tension was determined at room temperature.

The concentrations of LMW emulsifiers were set at 0.05%, 0.125%, 0.25%, 0.5%, and 1.0% for interfacial tension measurements. The proteins and SE were prepared separately and mixed afterwards. However, for testing the SSL and PL which are oil-soluble surfactants, proteins were dispersed in an aqueous phase and the surfactants in oil. A drop of protein-surfactant solution (about 15 mL) was delivered into an optical glass cuvette which contained purified oil by the automatic sampling system and allowed to stand at the tip of the needle for 30 min. Charged coupled device camera photographed the contour profile of the drop, from which the tension values were calculated using the Drop Shape Analysis software (Krüss GmbH, Hamburg, Germany) automatically.

2.3.2. Particle size

The size of dispersed fat globules was determined by NanoBrook Omni (Brookhaven Instruments, Holtsville, New York, USA). The dispersant refractive index was 1.330 (water), particle refractive index was 1.492, and particle absorption index was 0.001. Prior to each size distribution measurement, emulsions were diluted 1:1000 with deionized water. Measurements were done at least in triplicate.

2.3.3. Apparent viscosity

Steady state flow experiments were performed at 15 °C using a stress controlled DHR3 rheometer (TA Instruments, New Castle, Delaware, USA) with increasing shear rate from 0.01 to 100 s^{-1}. A cone (diameter 40 mm, inclination 4°) was applied to measure the apparent viscosity. All samples were allowed to equilibrate for 3 min before starting the experiment.

2.3.4. Light microscopy

The microstructure of all emulsions were studied by an optical microscope (Leica, DM2700P, Wetzlar, Germany) coupled with a Charge-coupled Device (CCD). One droplet of an emulsion sample diluted with 10-fold phosphate buffer (10 mM, pH 7.0) was placed