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Effect of sucrose ester concentration on the interfacial characteristics and physical properties of sodium caseinate-stabilized oil-in-water emulsions

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ABSTRACT

The effect of sucrose ester (SE) concentration on interfacial tension and surface dilatational modulus of SE and sodium caseinate (NaCas)-SE solutions were investigated. The critical micelle concentration (CMC) of SE was presumed to be 0.05% by measuring interfacial tension of SE solution. The interfacial tension of NaCas-SE solution decreased with increased SE concentration. A sharp increase in surface dilatational modulus of NaCas solution was observed when 0.01% SE was added and a decline was occurred at higher SE level. The influence of SE concentration on droplet size and confocal micrograph, surface protein concentration, ζ-potential and rheological properties of oil-in-water (O/W) emulsions prepared with 1% NaCas was also examined. The results showed that addition of SE reduced droplet size and surface protein concentration of the O/W emulsions. The ζ-potential of the O/W emulsions increased initially and decreased afterward with increased SE concentration. All the O/W emulsions exhibited a shear-thinning behaviour and the data were well-fitted into the Herschel–Bulkley model.

1. Introduction

Food emulsions are consisted of two immiscible liquids (usually oil and water) with one dispersed in another, which are thermodynamically unstable due to flocculation, creaming, coalescence, phase inversion or ostwald ripening (Zhao, Zhao, Yang, & Cui, 2009). Proteins and small molecule surfactants usually coexist in food emulsions as essential emulsifiers. Generally, small molecular surfactants are added to reduce the interfacial tension of the O/W interface (Ferri & Stebe, 2000) and proteins are used to stabilize the emulsion, as their amphiphilic structures provide electrostatic and steric stabilization (Dickinson, 2001).

Sodium caseinate (NaCas), a widely used food ingredient which is produced from milk casein, has been widely used in the formation and stabilization of food emulsions, due to its emulsifying activity and emulsion stability (Dickinson, 1999). In aqueous solution at neutral pH, NaCas contains a mixture of four phosphoproteins: α_{s1}-, α_{s2}-, β- and κ-caseins, which are highly disordered and substantially amphoteric (Liu et al., 2012). All these individual caseins, except for κ-casein, show a strong tendency to adsorb to interface. Therefore, during emulsification using NaCas, a viscoelastic film is established, protecting newly formed droplets against flocculation or coalescence (Sanchez, Rosariorodrigueznino, & Patino, 2005). Sucrose fatty acid ester (SE) is a nonionic surfactant. Due to the hydrophilic sucrose group and the hydrophobic fatty acid group, SE is also widely used in food, medicine and cosmetics for emulsification and foaming (Chansanroj & Betz, 2010; Choi et al., 2011). Garofalakis and Murray (2001) have found that the dilatational modulus of pure SE was affected by the alkyl chain length, and β-lg was found to affect the dilatational properties of SE films even at low concentrations.

Protein–surfactant interactions, especially at the O/W interface, have a great impact on the properties of interfacial film, which further affect the emulsion stability. Nylander, Arnebrant, Bos, and Wilde (2008) have reported that the protein–surfactant interactions can influence the interfacial behaviour of the O/W film. In addition, Palanuwech and Coupland (2003) as well as Rouimi, Schorsch, Valentini, and Vaslin (2005) have reported that the protein–surfactant interactions can affect the stability of emulsions due to the action of competitive adsorption, displacement and complex formation. As a consequence, the relationship between protein–surfactant interactions and the properties of food emulsions is of practical importance. Although protein–surfactant interactions in bulk solution (Garofalakis & Murray, 2001; Lu, Cao, Lai, & Xiao, 2008; Otzen, 2011), and even the interactions between SE and milk proteins have been widely studied (Fontecha & Swaisgood, 1995; Rodríguez Patino, Cejudo Fernández, Carrera Sánchez, & Rodríguez Niño, 2007), the effect of NaCas–SE interactions on interfacial tension and surface dilatational modulus of

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interfacial layers, as well as physical properties of emulsions stabilized by NaCas is still unclear.

Therefore, the objective of this research was to assess the influences of SE concentration on the interfacial characteristics of pure SE and NaCas-SE solutions (i.e., interfacial tension and surface dilatational modulus). The physical properties of NaCas-SE-stabilized emulsions (i.e., droplet size, confocal micrograph, surface protein concentration, ζ-potential and rheological properties) were also investigated. The influences of NaCas–SE interactions on the O/W interfacial characteristics and the physical properties of the O/W emulsion at neutral pH were studied. Moreover, the relationship between NaCas–SE interactions at the O/W interface and physical properties of the O/W emulsion were discussed.

2. Materials and methods

2.1. Materials

NaCas (95 wt.% protein) was obtained from New Zealand Milk Products Co. (Santa Rosa, CA). SE (S1170, consisted of 55% monoester and 45% di-, poly-ester) was donated by Mitsubishi Chemical Co. (Tokyo, Japan). Commercial corn oil was purchased from CR Vanguard (Guangzhou, China). All other reagents were of analytical grade from Guangzhou Reagent Company (Guangzhou, China).

2.2. Emulsion preparation

The emulsion was prepared in deionized water, which contained corn oil (20%), NaCas (1%) and different SE concentrations (0%, 0.01%, 0.03%, 0.05%, 0.08%, 0.10%, 0.20% and 0.30%). The emulsion aqueous phase was prepared by dissolving an appropriate amount of surface-active material (NaCas and SE) in deionized water. Corn oil was added to make a 20% O/W premix. The mixture was stirred at 60 °C for 30 min to ensure complete hydration. Homogenisation was then carried out using a two stage valve homogenizer (APV-1000, Albertslund, Denmark) at 180 bar for the first stage and 20 bar for the second stage.

2.3. Measurement of the dynamic surface properties

2.3.1. Preparation of SE and NaCas-SE solutions

SE and NaCas-SE solutions were prepared by mixing appropriate amount of NaCas (0% or 1%) and SE (0%, 0.01%, 0.03%, 0.05%, 0.08%, 0.10%, 0.20% and 0.30%) with deionized water, and stirred for 60 min at 65 °C to ensure complete dispersion, then cooled to ambient temperature (25 °C) for at least 1 h.

2.3.2. Purification of the corn oil

The corn oil was purified by percolating it through a column packed with Florisil to remove the impurities. Corn oil was deemed acceptable only after the interfacial tension against the deionized water remained constantly at 29 ± 0.5 mN m^{-1} for 30 min.

2.3.3. Measurement of interfacial tension

The interfacial tension (σ) was determined using a fully computer-controlled apparatus DataPhysics OCA20 contact angle meter system (Dataphysics Instruments GmbH, Filderstadt, Germany). Prior to each measurement, a deionized water surface tension measurement was undertaken and compared with standard values to ensure no contamination in the system. A drop of SE or NaCas-SE solution (about 12 ml) was delivered into an optical glass cuvette containing purified oil by the automatic sampling system, and allowed to stand at the tip of the needle for 45 min. Charged coupled device (CCD) camera photographed the contour of the drop, from which the tension values were calculated using the SCA20 software (Dataphysics Instruments GmbH, Filderstadt, Germany) automatically.

2.3.4. Analysis of surface dilatational rheology

An optical contact angle meter, OCA20, with oscillating drop accessory ODG20 (Dataphysics Instruments GmbH, Filderstadt, Germany) was used to determine dynamic interfacial tension (σ) and surface dilatational modulus of SE and NaCas-SE solution-adsorbed films at the O/W interface. The method included a periodic automated-controlled, sinusoidal interfacial compression and expansion performed by decreasing and increasing the drop volume at the desired amplitude ($\Delta A/A$) and angular frequency (ω). The surface dilatational modulus (E) can be described by Eq. (1)

$$E = \frac{d\sigma}{dA/A} = E_d + iE_v \tag{1}$$

The surface dilatational modulus is a complex quantity, which is composed of real and imaginary parts. The real part of the dilatational modulus or storage component is the dilatational elasticity modulus, E_d. The imaginary part of the dilatational modulus or loss component is the surface dilatational viscous modulus, E_v (Lucassen & Tempel, 1972). Measurements were performed in triplicate.

The SE and NaCas-SE solutions were placed in the syringe and a drop of SE or NaCas-SE solution (about 7 μl) was delivered into an optical glass cuvette having purified oil. The OCA20 was used to generate periodical oscillations of a drop of liquid at a chosen amplitude ($\Delta A/A$, 5%) in a frequency of 0.1 Hz. The image of the drop was recorded by CCD camera. The surface viscoelastic parameters (E, E_d and E_v) data, at 60 min after spreading (the dilatational modulus reached a steady-state value), were analysed by the SCA20 software (Dataphysics Instruments GmbH, Filderstadt, Germany) automatically.

2.4. Determination of the droplet size

A Malvern Mastersizer 2000 (Malvern Instruments Ltd., Worcestershire, UK) was used to determine the droplet size of the emulsion. The refractive index and adsorption of the dispersed phase were set as 1.414 and 0.001, respectively, and the refractive index of the continuous phase was 1.330. The emulsion in the sample chamber was diluted 1000-fold with deionized water. The volume surface mean diameter ($d_{3,2}$, μm), volume mean diameter ($d_{4,3}$, μm), dispersion index (span) and specific surface area were calculated by Eqs. (2)–(5), respectively

$$d_{3,2} = \frac{\sum n_i d_i^3}{\sum n_i d_i^2} \tag{2}$$

$$d_{4,3} = \frac{\sum n_i d_i^4}{\sum n_i d_i^3} \tag{3}$$

$$\text{span} = \frac{d(0.9) - d(0.1)}{d(0.5)} \tag{4}$$

$$\text{Specific surface area} = \frac{6}{\rho \times d_{3,2}} \tag{5}$$

where n_i is the number of particles with the same diameter; d_i is the particle size; The d (0.1), d (0.5) and d (0.9) values are average size corresponding to the cumulative distribution at 10% particles/globules, 50% particles/globules and 90% particles/globules, respectively; ρ is the density of the emulsion (Zhao et al., 2009).