Modulating interfacial dilatational properties by electrostatic sodium caseinate and carboxymethylcellulose interactions

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A B S T R A C T

The interactions between sodium caseinate (NaCas) and carboxymethylcellulose (CMC) in aqueous solution influenced by pH and CMC concentration were assessed by visual observation, measuring turbidity, ζ-potential, particle size and rheological tests. Effects of CMC on the interfacial dynamic properties of NaCas were investigated using an automatic pendant drop tensiometer. The results indicated that CMC adsorbed onto NaCas mainly through electrostatic interactions in solution at pH ≤ 5.5. and their interactions revealed a significant influence on the dynamic characteristics of NaCas adsorbed films. For surface pressure (π) and surface dilatational modulus (E) values, they were both changed in response to the presence of CMC in the bulk phase at pH 5.5 and 4. Especially for the E values of films, which showed a continuous increase as function of CMC concentration. However, the presence of CMC in the bulk phase had no significant effect on the adsorption of NaCas molecules at pH 7, indicating the interface was dominated by the protein.

1. Introduction

Proteins and polysaccharides are essential functional ingredients in food industry. A combination of these two biopolymers always used with the purpose of stabilization of emulsions and foams. Being surface-active, proteins typically dominate primary adsorb onto droplets and bubbles, which play a crucial role in the formation and stabilization of emulsions and foams by electrostatic and stericteric effects (Dickinson, 2011). For most polysaccharides that cannot form complex with protein, their effect on emulsion focus on modify textural characteristics of protein-stabilized emulsions (foams) arises from thickening and gelling in the bulk phase, and also led to depletion flocculation (Patino & Pilosof, 2011). While for anionic polysaccharide, extensive electrostatic interactions occurred between protein and polysaccharide especially at protein pI and polysaccharide pKa (Dickinson, 2011). As a result, the properties of protein-stabilized emulsions (foams) system were quite sensitive to the presence of anionic polysaccharides

under conditions of associative protein-polysaccharide interactions (Ganzevles, Fokkink, Van Vliet, Stuart, & Jongh, 2008; Jourdain, Leser, Schmitt, Michel, & Dickinson, 2008; Liu, Zhao, Liu, Kong & et al., 2012).

Besides electrostatic and steric effect, adsorbed layers at liquid interface may also affect emulsion (foam) stability by their elastic behavior (Ganzevles, Zinoviadou, van Vliet, Stuart, & de Jongh, 2006). It has been demonstrated that an electrostatically induced coadsorption of protein with non-surface-active anionic polysaccharides can affect the surface rheological properties (Dickinson, 2011). In a recent study, the mixture of sodium caseinate (NaCas) and a highly sulfated polysaccharide (dextran sulfate) showed a slower decay of interfacial tension and stronger dilatational viscoelastic properties than that produced by protein alone (Jourdain, Schmitt, Leser, Murray, & Dickinson, 2009). These founding was useful to manipulate the adsorption behavior at liquid interfaces and provide reference for food emulsion and foam preparation (Baeza, Sánchez, Patino, & Pilosof, 2005; Liu, Zhao, Liu, & Zhao, 2011).

NaCas has been widely used in the preparation of food emulsions due to its excellent functional and nutritional properties. However, food emulsions stabilized by NaCas alone are extremely

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sensitive to destabilization in acidic condition (Dickinson, 2006). Based on our earlier research (Liu, Zhao, Liu, Kong & et al., 2012), flocculations of NaCas-coated oil droplets were suppressed in the case of acidification by adding CMC, a typical anionic polysaccharide derived from cellulose. The improvement of emulsion stability was mainly assigned to the formation of complex interfacial layers (Liu, Zhao, Liu, Kong & et al., 2012). However, the relationship between interfacial dynamic properties of adsorbed layers and NaCas-CMC interactions are still unknown. The objective of this research was to investigate the mechanism of how interfacial dilatational properties of the mixed NaCas-CMC were influenced by their interactions in the bulk phase, depending on protein/polysaccharide mixing ratio and pH values.

2. Materials and methods

2.1. Materials

NaCas (Alanate 180) was obtained from New Zealand Milk Products Inc. (Santa Rosa, CA). CMC (Ticalose® CMC 2500) was kindly provided by TIC Gums (Maryland, USA). According to the supplier's specification, the protein power contained 91.1 wt% protein (N × 6.38), 3.5 wt% ash, 4.0 wt% moisture, 1.1 wt% fat, and 0.l wt% lactose. The CMC was with an average molecular weight of 250,000 Da, a degree of substitution less than 1.2, and an average degree of polymerization of 1100. Phosphate buffer solutions (PBS) (5 mM, pH 7.0) were made with Milli-Q water. Commercial corn oil was purchased from local supermarket, and all the other reagents were of analytical grade.

2.2. Preparation of NaCas/CMC mixed solutions

Stock solutions of protein and polysaccharide were separately prepared in 5 mM PBS at neutral pH. The mixed solutions within different pH values which contained 1 wt% NaCas and different amounts of CMC (0–0.5 wt%) were prepared by mixing the appropriate volume of each stock biopolymer solutions up to the required concentration and stirred for at least 90 min to make sure completely dissolved. All solutions were prepared in 5 mM PBS buffer using Milli-Q water. The pH was adjusted with 0.1–1 M HCl and NaOH.

2.3. Phase diagram

Aqueous solutions containing 1.0 wt% NaCas and different amount of CMC (0–0.5 wt%) dissolved in 5 mM PBS were prepared, and then the solutions were acidification from pH 7 to 2. After left still overnight at room temperature, the solubility of the complexes was assessed by visual observation as a clear solution, a cloudy solution or a precipitate. A state diagram of pH against CMC concentration was established according to these observations.

2.4. Turbidity measurement

The turbidity of biopolymer solutions and suspensions was evaluated by measuring the optical density at 600 nm using a UV/visible spectrophotometer (Biochrom Ltd., Cambridge, UK). Sample cuvettes were composed of quartz with a path length of 1.0 cm 5 mM PBS was used as the reference.

2.5. ζ-potential and z-average hydrodynamic diameter measurement

ζ-potential and z-average hydrodynamic diameter (D_H) measurements were carried out using Nanoseries ZS instrument (Malvern Instruments Ltd., UK) according to previous report (Liu, Zhao, Liu, Long, Kong & Zhao., 2012). Each sample was diluted with 5 mM PBS within the same pH at a ratio of 1:5, pH was adjusted when necessary. Each measurement was repeated at least five times.

2.6. Rheological tests

Rheological properties test was performed on Haake Rheostress RS600 (Thermo-Scientific, Germany), equipped with a parallel-plate sensor system (PP35 Ti: diameter $\varphi = 35$ mm; gap between plates = 1 mm). A thermostatic Universal Temperature Control (UTC) was used to maintain the temperature at 25 °C.

Rheological behavior of NaCas/CMC mixtures in aqueous solution was achieved by continuous flow conditions. The steps have been described in more detail in previous reports (Liu, Zhao, Liu, Long & et al., 2012). The experimental data were fitted according to the power-law model (Ostwald de Waele model) (Delben & Stefancich, 1997).

$$\tau = K(\dot{\gamma})n$$

where τ is the shear stress (Pa); K is the consistency index (Pa·s); $\dot{\gamma}$ is the shear rate (s^{-1}); n is the flow behavior index (dimensionless) and the exponent n describes the divergence from the Newtonian model.

2.7. Pendant drop method

2.7.1. Interfacial pressure
Interfacial pressure (π) as a function of time were measured for single-component and mixed solutions of protein and polysaccharide using an optical contact angle meter, OCA-20 (Dataphysics Instruments GmbH, Germany). Details of this apparatus are given elsewhere (Caseli, Masui, Furriel, Leone, & Zaniquelli, 2005). The interfacial tension was determined by droplet shape analysis. All results are presented in the terms of interfacial pressure $\pi = \gamma_0 - \gamma$, where γ_0 is the interfacial tension of the solvent, and γ is the measured interfacial tension. Commercial corn oil was used to form oil-water interface. It was purified according to previous method (Liu et al., 2011), and its interfacial tension against the PBS buffer was regarded as γ_0 (24.5 ± 0.5 mN/m).

2.7.2. Interfacial dilatational properties
Interfacial dilatational properties were determined by optical contact angle meter, OCA-20, combined with oscillating drop accessory ODG-20 (Dataphysics Instruments GmbH, Germany). The method involved a periodic automated-controlled, sinusoidal interfacial compression and expansion performed by decreasing and increasing the drop volume at the desired amplitude (ΔA/A) and angular frequency (ω). The surface dilatational modulus (E) derived from the change in interfacial tension (σ), resulting from a small change in surface area.

Each sample was placed in the syringe and allowed to stay for at least 30 min to reach the desired constant temperature. Then a drop was delivered and allowed to stand for 3 h to achieve protein adsorption at the oil–water interface. The dynamic surface viscoelastic modulus (E) was measured as function of adsorption time (t), at 10% of deformation amplitude (ΔA/A) and at 0.1 Hz of angular frequency (ω) within the linear viscoelastic regime. The sinusoidal oscillation for surface dilatational measurements was started 30 s later after the formation of droplets.

All experiments were made at 25 °C. Each solution was diluted with 5 mM PBS within the same pH at a ratio of 1:10 before measurement. The average standard accuracy of the surface pressure