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Effects of milk protein-polysaccharide interactions on the stability of ice cream mix model systems

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ABSTRACT

Polysaccharides (PS) are commonly used as stabilizers in ice cream to improve the structural and textural properties. However, in emulsions, the polysaccharides can interact with the milk proteins, resulting in the thermodynamic destabilization of the emulsion systems. This paper focuses on the effect of the interactions between milk proteins and two gums (carboxymethylcellulose (CMC) and guar gum (GG)) on the stability of ice cream models consisting of 11% skimmed milk powder (SMP) and 10% coconut oil. Parameters such as interfacial tension, fluorescence spectroscopy, zeta-potential, surface adsorption, microstructure, creaming, and rheological properties were determined. Furthermore, the interactions between the proteins and PS attributed to the stability of the emulsions were characterized. The results indicated that the stability of ice cream model emulsions depended on the types and concentrations of polysaccharides. SMP/GG mixed emulsions were distinguished by a higher rate of creaming compared to SMP/CMC mixed models with the same levels of polysaccharides (except for 0.1%). Depletion flocculation was involved in the destabilization of the two SMP/PS emulsion systems. Lower creaming rates above the critical content of phase separation in the SMP/CMC mixed models were related to the attractive interactions between milk proteins and CMC and enhanced apparent viscosity compared to that of SMP/GG systems. These findings provided a theoretical basis for ice cream processing; however, further research is required due to the complex ingredients and reactions involved during ice cream processing.

1. Introduction

Proteins and polysaccharides are two components of ice cream that contribute to the structural and textural properties of the ice cream. Milk proteins (casein and whey protein) are mainly used in ice cream production, and the content of protein is approximately 4%. In the liquid mix of ice cream, part of the protein stabilizes the fat droplets and another part is present in the continuous aqueous phase, which enhances the viscosity of the mix. Polysaccharide stabilizers such as guar gum (GG) and carboxymethylcellulose (CMC) are commonly used in ice cream for viscosity enhancement and water retention. However, micellar casein has shown to be thermodynamic incompatible with some commonly used polysaccharides stabilizers in the ice cream mix (Spagnuolo, Dalgleish, Goff, & Morris, 2005; Vega & Goff, 2005). The instability of the liquid mix becomes an issue for its shelf life. Soft-serve ice cream mix is manufactured commercially and delivered to soft serve retailers. A shelf life of the liquid mix of 14–21 days is often required (Vega, Andrew, & Goff, 2004). Hence, a better understanding of the relationship between milk protein-polysaccharide interactions and the stability of emulsions may improve the design of ice cream formulations because the properties of the final products will partly depend on these macromolecular interactions.

When proteins and polysaccharides are present together in food, the interactions between the proteins and polysaccharide can be segregative or attractive in nature. The formation and stability of dispersed colloidal systems depend on the environmental conditions (i.e., pH, temperature, ionic strength), concentration and the biopolymer ratios (Corredig, Sharafbafi, & Kristo, 2011). Nevertheless, in the same environmental conditions, the polysaccharide type affects system stability. Numerous investigations have reported the behavior of milk protein-polysaccharide interactions in solutions and emulsions (Hemar, Tamehana, Munro, & Singh, 2001; Long et al., 2012; Perez, Carrara, Sánchez, Rodríguez Patino, & Santiago, 2009). Protein–polysaccharide interactions can affect the casein

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micelle diameter, aggregation, microstructure, and phase behavior depending on the polysaccharide type (Hemar et al., 2001; Ji, Corredig, & Goff, 2008; Schorsch, Jones, & Norton, 1999; Spagnuolo et al., 2005). In the case of GG/Na-CN stabilized emulsions, the addition of higher GG can prevent phase separation by forming a strong three-dimensional network (Neirynck, Van lent, Dewettinck, & Van der Meeren, 2007). Long et al. (2012) also reported that even at very low concentrations, GG can induce phase separation through GG/Na-CN interactions. As far as the CMC additions are concerned, the stability of whey protein emulsions against droplet flocculation and creaming depends on the concentration of CMC in the continuous phase and the interactions of the adsorbed protein-polysaccharide at different pH levels (Koupantsis & Kiosseoglou, 2009). The investigation of polysaccharide stabilizers in ice cream mainly focuses on the physicochemical characteristics of ice cream products (viscosity, overrun, texture analysis, melting behavior) and sensory qualities (BahramParvar, Razavi, & Khodaparast, 2010; Soukoulis, Chandrinos, & Tzia, 2008), leaving a gap in terms of the understanding of ice cream mix stability. Limited knowledge exists regarding the relationship between the addition of stabilizers and the phase separation of ice cream mixes (Vega et al., 2004; Vega & Goff, 2005). Furthermore, knowledge of the mechanisms occurring in SMP/PS solutions and coexisting emulsions and the relationship between the two systems, is lacking. This work focused on the interactions between proteins and polysaccharides based on the liquid ice cream mix model system in order to understand the significance of the polysaccharide structure and concentration on the stability of the liquid ice cream mix model system. The ability of charged polysaccharides to associate with milk proteins has been studied by various complementary techniques. This contribution complements previous reports of the biopolymer interactions between SMP and polysaccharides in solution.

2. Materials and methods

2.1. Materials

Coconut oil was purchased from the local market. Skimmed milk powder (SMP, 36% protein content), guar gum and carboxymethylcellulose were supplied by the China Mengniu Dairy (Inner Mongolia, China). 1-Anilinonaphthalene-8-sulfonate (ANS), fluorescein isothiocyanate (FITC) and Nile red were obtained from Sigma–Aldrich Chemical Co. Ltd. (St. Louis, USA). All other reagents were of analytical grade.

2.2. Preparation of the solutions and emulsions

SMP solution (22%, w/w) and PS solutions (0.8%, w/w) were prepared with deionized water by stirring at room temperature for 2 h and stored at 4 °C overnight. The SMP/CMC and SMP/GG solutions were prepared by mixing the appropriate volumes of each double concentrated biopolymer solution to obtain a final SMP concentration of 11% (w/w) and a gum concentration ranging from 0 to 0.4% (w/w), then stirred at room temperature for 1 h to ensure complete mixing.

Oil-in-water emulsions for models typifying ice cream formulations were prepared based on 10% coconut oil, 11% SMP (approximately 4% protein), and different concentrations of guar gum (0–0.4%) or carboxymethylcellulose (0–0.4%). All of the ingredients, except the coconut oil, were dry blended and mixed with water at 55 °C, then the melted coconut oil was slowly added at 7500 rpm with shear emulsifying mixer in 10 min to obtain the coarse emulsion. The pre-emulsions were pasteurized at 65 °C for 30 min, subsequently homogenized with a two-stage single-piston homogenizer using 20 MPa pressure on the first stage and 4 MPa on the second stage, and cooled to 4 °C. The final pH of the emulsions was adjusted to 6.5 using 0.1 M HCl or 0.1 M NaOH. To study the zeta potentials of the emulsions as a function of pH changes, another method of preparation of the emulsions was tested. In the second method, the desired concentrations of PS (0–0.8%) were added to the SMP-stabilized emulsion (20% oil, 22% SMP) after homogenization to obtain the secondary emulsions (10% oil, 11% SMP, 0–0.4% PS). The pH of the emulsions prepared with the two methods was gradually adjusted to 3, 4, 5, 6, 6.5, 7, and 8 using 0.1 M NaOH or 0.1 M HCl. The resulting emulsions were stored at 4 °C for 24 h before analysis.

2.3. Determination of the zeta potential and droplet/particle size

The zeta potentials were determined using a dynamic light scattering technique (Nano-Z, Malvern Instrument, UK). The sample was diluted by pH-matched deionized water at a ratio of 1:100. Three readings were made per sample and each measurement was repeated at least triplicate.

The droplet size distribution and average particle diameter were determined by laser scattering using a Malvern Mastersizer 2000 (Malvern Instruments Ltd, Worcestershire, UK). The refractive indexes of fat and water were 1.47 and 1.33, respectively, with an absorbance of 0.001 and an obscuration value in the range of 10–20%. The average droplet size was characterized by two mean diameters, the surface weighted mean diameter, $D_{3,2}$ and the volume weighted mean diameter, $D_{4,3}$. The $D_{3,2}$ value was used to estimate the specific surface area of freshly made emulsions, and the $D_{4,3}$ value was used to monitor changes in the droplet-size distribution on storage. Before measurement, the emulsions were carefully mixed by turning the containers upside down, and then diluted with water at a ratio of 1:100. All tests were carried out at four storage time points (0, 1, 7, and 21 days). The span, as a measure of the distribution width of the particles in dispersion, was calculated using the following equation:

$$\text{Span} = \frac{d(0.9) - d(0.1)}{d(0.5)} \quad (1)$$

where $d(0.1)$, $d(0.5)$, and $d(0.9)$ are the diameters at 10%, 50%, and 90% cumulative volume, respectively.

In some cases, sodium dodecyl sulfate (SDS, 1%) was used to discriminate between coalescence and flocculation in the emulsion. Flocculation degree (FD %) was measured to describe the tendency to droplet flocculation, regardless of the droplet coalescence (Palazolo, Sobral, & Wagner, 2011). FD % was calculated from the followings equation:

$$\text{FD\%} = \left[\left(D_{4,3} - D_{4,3\ \text{SDS}}\right)/D_{4,3\ \text{SDS}}\right]*100 \quad (2)$$

where $D_{4,3}$ and $D_{4,3\text{SDS}}$ are the volume-weighted diameters, measured in the absence and presence of SDS, respectively.

To determine casein micelle size in the SMP/CMC and SMP/GG solutions, a dynamic light scattering technique (Nano-Z, Malvern Instrument, UK) was used according to Tobin, Fitzsimons, Kelly, and Fenelon (2011).

All results were the average of measurements performed in triplicate, with three readings made per sample.

2.4. The measurement of surface and interfacial tension

The surface and interfacial tensions of the gums alone and in combination with the SMP were measured using the Wilhemy plate method (DCAT 21, Dataphysics, Germany) with plate PT11 at 20 and