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Effect of agave fructans on bulk and surface properties of sodium caseinate in aqueous media

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ABSTRACT

Aqueous systems of agave fructans and sodium caseinate were studied to identify the physical and physicochemical properties of the individual macromolecules and their mixtures. Bulk behavior of agave fructans alone and in mixtures with sodium caseinate systems was similar to that of the density and rheology of monosaccharide solutions. A synergistic surface activity effect was found and attributed to the tendency of agave fructans to associate with sodium caseinate, as was confirmed by the viscosity, zeta potential values and particle size distribution. Their mixture developed properties that make them appealing for applications in foods that are dispersed systems (emulsions and foams) where a large increase in viscosity is not desirable.

1. Introduction

Foods often contain complex mixtures of ingredients, including proteins, lipids and polysaccharides, which are added to control viscosity, form a foam or emulsion or act as water-binding agents (Williams, 2011). The interactions between these ingredients in a mixture can affect the properties, such as stability, flow behavior and texture, of a processed food product.

For example, dairy emulsions contain emulsifying macromolecules to promote stability and viscous or gel-like polysaccharides to increase viscosity or mimic a fatty texture in products reduced in fats and/or sugars (Crispín-Isidro, Lobato-Calleros, Espinosa-Andrews, Álvarez-Ramírez, & Vernon-Carter, 2015; Meyer, Bayarri, Tárrega, & Costell, 2011). Other constituents, like dietary fibers (non-digestible carbohydrates), may interact with these macromolecules to cause either the formation of complexes or a bulk phase separation that modify the characteristics of the final product (Elleuch et al., 2011).

In the last few decades, the food industry has been motivated to develop new products that are low in fat and sugars and high in dietary fiber and prebiotics to meet the demands for easily digestible, healthy foods. Fructans are dietary fibers that have been shown to control glycemia, reduce plasma LDL cholesterol, contribute to satiety and regulate intestinal microbiota with no evidence of toxicity (Carabin & Gary Flamm, 1999). They are one of the most abundant nonstructural polysaccharides found naturally in a wide variety of plants (e.g., agave, asparagus, barley, chicory, dahlia, garlic, Jerusalem artichoke, jicama leek, oat, onion, wheat and yacon) (Praznik, Cieslik, & Huber, 2004) and produced by some species of bacteria (Arvidson, Rinehart, & Gadala-María, 2006). Particularly, fructans obtained from agave have been reported by *in vitro* and *in vivo* studies to have potential prebiotic activity due to their ability to promote the growth of bifidobacteria and lactobacilli, act as immune system activators and contribute other beneficial health functions (Gómez, Tuohy, Gibson, Klinder, & Costabile, 2010; Márquez-Aguirre et al., 2013; Moreno-Vilet et al., 2014). For these reasons, the incorporation of fructans into processed foods is an attractive approach to improving food quality.

Fructans are polysaccharides consisting of one glucose molecule attached to two or more fructose units. Their composition varies among plant species and with geographical region, and their structures are determined by their degree of polymerization (DP).

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For example, inulin-type fructans, mainly obtained from chicory roots, are linear, while levans, found in grasses and grains and produced by fermentation (bacteria and yeast), are the most common form of branched fructans. Agave fructans (AF) with branched and linear linkages ($\beta(2 \rightarrow 1)$ and $\beta(2 \rightarrow 6)$; DP: 3-29) have been reported (López, Mancilla-Margalli, & Mendoza-Díaz, 2003; Praznik et al., 2004).

While linear fructans tend to form gels, branched fructans promote the formation of solutions (Espinosa-Andrews & Urias-Silvas, 2012), properties which are useful in application to new food products. Additionally, it has been reported that levan-type fructans interact with phospholipid membranes, strongly affecting the surface properties of the aqueous mixtures (Vereyken, Chupin, Demel, Smeekens, & De Kruijff, 2001).

Sodium caseinate (SC) is an amphiphilic protein that is used extensively to improve the texture, shelf life and nutritive value of emulsions and foams because it has a high tendency of being adsorbed at air–water and oil–water interfaces (Carrera-Sánchez & Rodríguez-Patino, 2005). SC aggregates are 11–80 nm in diameter and comprise α_{s1}, α_{s2}, β and κ-caseins, which assemble into a micelle according to their hydrophobic and hydrophilic groups (Pitkowski, Durand, & Nicolai, 2008).

Although interactions between SC and various polysaccharides have already been studied (Liu et al., 2012; Neirynck, Van lent, Dewettinck, & Van der Meerena, 2007; Nono, Lalouette, Durand, & Nicolai, 2011; Sosa-Herrera, Berli, & Martínez-Padilla, 2008; Sosa-Herrera, Lozano-Esquivel, Ponce de León-Ramírez, & Martínez-Padilla, 2012), few studies explain how this milk protein behaves with dietary fibers in aqueous systems. A recent study found that increasing the concentration of fructans in yogurt strengthened the protein network and reduced syneresis (Crispín-Isidro et al., 2015). Authors explained these results by suggesting that the added fructans bind water and interact with the milk proteins in the yogurt. This assumption was verified by scanning electron microscopy, which showed that the added AF covered the casein micelles to produce a denser casein network.

Motivated by the functional nutritional properties of AF and the potential outcome of their interaction with SC, we characterize physical and physicochemical properties of AF in aqueous media and in mixtures with SC to identify interactions between macromolecules that produce characteristics that may be of importance for science and the formulation of novel foods. Density, rheology, size distribution, zeta potential of the bulk aqueous system and surface tension at the air–water interface are evaluated.

2. Materials and methods

2.1. Materials

We used commercial samples of AF (4.77 ± 0.09% moisture, Bio Agave, Ingredion de México, S.A. de C.V., Mexico) and SC at 1% (6.9 + 0.2% moisture, Lactonat EN, Lactoprot, Germany). Aqueous samples were prepared by dispersing powders in purified water (E-pura, The Pepsi Bottling Group Mexico, Mexico).

Fructan solutions from 1 to 50% were prepared at 25 °C by dispersion of the powder in purified water using magnetic stirring for 10 min. SC was dispersed for 30 min and then fructans were added and mixed for 20 min more. After that, the systems left to stand for 24 h in a refrigerator, before tests. pH of samples was determined (pH120, Conductronic, Mexico).

2.2. Methods

2.2.1. Density

A digital density meter (DMA38, Anton Paar, Austria) of the oscillating U-tube type was used at a constant temperature of 20 °C for density tests. Data were required to calculate surface tensions.

2.2.2. Rheology

Flow behavior measurements of the bulk aqueous system were performed using a control stress rheometer (MCR 301, Anton Paar, Austria). The rheometer comprises a water bath and a Peltier heating system for accurate temperature control. Steady shear flow tests of AF solutions with different concentrations, and AF-SC mixtures were carried out at 25 °C using a cone and plate (75 mm diameter and 1°) and an up-down shear rate profile between 0.01 and 1000 s^{-1} was applied. Each step included 25 points with 10 s durations. Shear stress and viscosity were recorded as a function of shear rate.

2.2.3. Particle size and zeta potential

The particle size distribution and zeta potentials of the systems were measured using a Malvern Zetasizer (Nano ZS, Malvern, UK) based on dynamic light scattering. The system works according to the principle of phase analysis light scattering. Zeta potential measurement was done according to the principle of laser Doppler electrophoresis. Measurements were made in standard cuvettes using Malvern's dip cell at 25 °C with a refractive index of 1.33 for the dispersant and 1.45 for the biopolymers.

Particle size of the individual biopolymers and those in mixtures with SC at 1% with AF at 1, 3 and 10% (w/w) in aqueous media were measured. Systems with concentrations higher than 10% contained large aggregates and were polydispersed, which prevented accurate particle-size measurements. Distribution of differently sized particles was used to identify types of particles.

2.2.4. Surface tension

Surface tensions at the air–water interface of AF and AF-SC aqueous mixtures were measured using the pendant drop technique (PAT-1, Sinterface Technologies, Germany). In this technique, surface/interfacial tension was calculated from the size and the vertical shape of a drop hanging from the tip of the needle of a syringe that is controlled by a computer. The mathematical treatment of a pendant drop's shape is based on the fundamental equation of capillarity, which relates the interfacial/surface tension to the pressure difference across a surface and to the two principal radii of curvature of the surface at that point (Berry, Neeson, Dagastine, Chan, & Tabor, 2015). The droplet profile was digitized and analyzed through a charge-coupled device camera linked to a video image profile digitizer board connected to a computer. The drop images were continuously visualized on a video monitor, and the drop profiles were processed according to the Laplace equation. The reduction in surface tension was plotted as a function of time. Because adsorption of hydrocolloids is slower than that of small molecules, it may take hours to reach equilibrium. Thus, we assumed pseudo-equilibrium when the tension did not change by more than 0.1 mN/m in 10 min. The maximum concentration of AF used in this test was 40%.

The final surface pressure value was calculated as $\pi_{eq} = \sigma_0 - \sigma_{eq}$, according to Camino, Pérez, Carrera-Sánchez, Rodríguez-Patino, and Pilosof (2009), where σ_0 is the sub-phase interfacial tension (72 mN/m for air/water interface) and σ_{eq} is the interfacial tension of the AF or AF-SC aqueous systems at equilibrium.

All tests were performed in triplicate with the exception of the surface tension tests, which were carried out at least twice. Mean and standard deviation were reported. A two-way analysis of variance was performed ($\alpha = 0.05$).