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Soy protein–polysaccharides interactions at the air–water interface

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Abstract

This work studies the interfacial behavior of mixed soy protein (SP) + polysaccharide (PS) systems to gain knowledge on the interactions between these biopolymers at the air–water interface under dynamic conditions at neutral pH where a limited incompatibility between macromolecules can occur. The PSs used were: hydroxypropylmethylcellulose (HPMC) as surface-active PS; lambda carrageenan (λC) and locust bean (LB) gum as non-surface-active PSs. Protein and PS concentration in the mixed systems were 2% and 0.25%, respectively. The dynamic surface pressure and rheological properties of films were evaluated with a drop tensiometer at 20 °C, pH 7 and ionic strength 0.05 M.

The presence of HPMC and λC greatly increased the surface pressure, surface dilatational elasticity and relative viscoelasticity on the basis of different mechanisms. HPMC competed for the interface with SP, but due to its unusual strong surface activity it could dominate the surface pressure and improve film viscoelasticity. The modification of surface pressure and rheological properties of adsorbed SP films in the presence of λC necessarily suggests the participation of λC+ contaminants at the interface. Pure λC could influence the interface by a complexation mechanism, or indirectly by a depletion mechanism in the vicinity of the interface. In addition surface-active contaminant of λC if strongly bound to the PS could bring some PS molecules at the interface.

LB little affected the surface pressure and rheological properties of SP films even if surface-active contaminants were present in the commercial preparation. Differences in the interaction of λC and LB gum with the protein should be mainly ascribed to different degrees of incompatibility and to the fact that LB is not charged.
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1. Introduction

Proteins due to their amphiphilic character can adsorb at fluid interfaces. The adsorption of proteins at interfaces and other dynamic surface properties—such as film viscoelasticity—are known to play an important role in the formation and stability of food dispersed systems as foams and emulsions (Dickinson & Tanai, 1992). Due to the adsorption at fluid interfaces, protein molecules prevent the recoalescence of previously created bubbles or droplets. In addition, during the protein adsorption the surface or interfacial tension of the air–water or/and oil–water interface decreases which is an important attribute to optimize the input of energy involved in the foaming or emulsification process (Walstra, 1993) and for the production of smaller bubbles or droplets, which is an important factor for the stability of the dispersions.

The use of soy proteins (SP) as functional ingredients in food manufacturing is increasing because of their role in human nutrition and health. The major globulins of SP are conglycinin (7S) and glycinin (11S). Native SP, because of its quaternary and compact tertiary structure has limited foaming (Kinsella, 1979; Utsumi, Matsumura, & Mori, 1997; Yu & Damodaran, 1991) and emulsifying (Kinsella, 1979; Liu, Lee, & Damodaran, 1999) properties. However, structural modifications by chemical methods such as deamidation, succinilation, reduction or denaturation, allowing greater conformational flexibility of protein, may improve its surface behavior and functionality (Carp,

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Wagner, Bartholomai, & Pilosof, 1997; Kim & Kinsella, 1987a, 1987b; Wagner & Guéguen, 1999).

Polysaccharides (PSs) are used in admixture to proteins mainly to enhance stability of dispersed systems. Most high-molecular weight PSs, being hydrophilic, do not have much of tendency to adsorb at the air–water interface, but they can strongly enhance the stability of protein foams by acting as thickening or gelling agents (Dickinson, 2003).

Above the protein isoelectric point thermodynamic incompatibility between the protein and PS generally occurs because of the repulsive electrostatic interactions and different affinities towards the solvent (Tolstoguzov, 1997). In the diluted concentration region protein and PS may coexist in a single phase (miscibility) but in domains in which they mutually exclude one another; above a critical concentration they segregate into different phases.

There are some recent works in conditions of limited thermodynamic compatibility between the protein and PS (i.e. above the protein isoelectric point in the diluted concentration region) that support the evidence of interactions between proteins and PSs at fluid interfaces (Baeza, Carrera Sánchez, Pilosof, & Rodríguez Patino, 2004, 2005; Carp, Bartholomai, Relkin, & Pilosof, 2001; Baeza, Carrera Sánchez, Rodríguez Patino, & Pilosof, 2005). Carp, Bartholomai, and Pilosof (1999) have shown that under conditions of neutral pH where a limited thermodynamic compatibility between SP and xanthan exists, xanthan promoted SP subunits aggregation at the air–water interface in foams based on native SPs, but promoted the basic B-11S polypeptide to be predominating at the interface of denaturated SP foams. Those specific effects should further influence the interfacial and foaming properties of the mixed systems.

In this work we studied the interfacial behavior of mixed SP + PS systems to gain information on the interactions between these biopolymers at the air–water interface in well-defined and controlled experiments under dynamic conditions.

We used hydroxypropylmethylcellulose (HPMC) as surface-active PS and lambda carrageenan (λC) and locust bean (LB) gum as non-surface-active PSs.

Most studies on interfacial and foaming properties of SPs or isolated globulins have been made on native proteins. In spite they allow to understand the structure–function relationship of soy globulins they do not represent commercial isolates available. In this work we are concerning with commercial products that have relevance to real food formulations: a denatured SP isolate and non-surface-active PSs that may contain minor traces of surface-active impurities.

2. Materials and methods

2.1. Materials

A commercial SP isolate (90% protein) from Sambra, Brazil was used. The isolate was denatured as detected by differential scanning calorimetry. Surface hydrophobicity determined with the fluorescence probe 1-anilino-8naphthalene-sulfonate (ANS) was So = 685 (Kato & Nakai, 1980). The PSs used were HPMC called E4M as surface-active PS from Dow Chemical Co., λC a charged PS with three negative charges per two galactoses and LB gum as non-surface-active PS provided by Sanofi Bioindustries, Argentina, all used without further purification.

2.2. Preparation of solutions

Solutions for interfacial studies were prepared by dissolving SP in Milli-Q ultrapure water. The pH and ionic strength were kept constant at 7 and 0.05 M, respectively, by using a commercial buffer solution called Trizma $(CH_2OH)_3CNH_2/(CH_2OH)_3CNH_3Cl$ (Sigma, >99.5%).

All mixed systems had a protein and PS concentration of 2 and 0.25 wt%, respectively.

2.3. Surface pressure and surface dilatational properties

For surface pressure (π) and surface dilatational properties measurements of adsorbed protein films at the air–water interface an automatic drop tensiometer (TRACKER, IT Concept, Longessaine, France) was used as described elsewhere (Rodríguez Patino, Rodriguez Niño, & Carrera Sánchez, 1999). The method involved a periodic automatically 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) (Eq. (1)), its elastic (Ed) and viscous (Ev) components and the phase angle (θ) were derived from the change in surface pressure (π) resulting from a small change in surface area (A). The surface dilatational properties were measured as a function of time, t. The percentage area change was determined (data not shown) to be in the linear region.

$$E = \frac{d\sigma}{dA/A} = \frac{-d\pi}{d \ln A}, \tag{1}$$

$$E = (\sigma_0/A_0)(\cos\theta + i \sin\theta) = Ed + Ev, \tag{2}$$

where σ_0 and A_0 are the strain and stress amplitudes, respectively, θ is the phase angle (degrees) between stress and strain, $\pi = \gamma_0 - \gamma$ is the surface pressure and γ and γ_0 are the surface tension in the presence and in the absence of biopolymers, respectively.

The dilatational modulus is a complex quantity and is composed of real and imaginary parts (Eq. (2)). The real part of the dilatational modulus or storage component is the dilatational elasticity, $Ed = |E|\cos\theta$. The imaginary part of the dilatational modulus or loss component is the surface dilatational viscosity, $Ev = |E|\sin\theta$. The ratio (σ_0/A_0) is the absolute modulus, $|E|$, a measure of the total unit material dilatational resistance to deformation (elastic + viscous). For a perfectly elastic material the stress and strain are in phase ($\theta = 0$) and the imaginary term is

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