

Adsorption dynamics and surface activity at equilibrium of whey proteins and hydroxypropyl–methyl–cellulose mixtures at the air–water interface

Oscar E. Pérez^{a,c}, Cecilio Carrera-Sánchez^b,
Juan M. Rodríguez-Patino^b, Ana M.R. Pilosof^{a,c,*}

^a*Departamento de Industrias, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, Ciudad Universitaria (1428), Buenos Aires, Argentina*

^b*Departamento de Ingeniería Química, Facultad de Química, Universidad de Sevilla, c/Profesor García González 1, 41012 Sevilla, España*

^c*Member of Consejo Nacional de Investigaciones Científicas y Técnicas, Argentina*

Received 1 June 2006; accepted 10 November 2006

Abstract

In this work the competitive behaviour of whey protein concentrate (WPC) and three well-characterized hydroxypropyl–methyl–celluloses (HPMCs), so-called E4M, E50LV and F4M, with different interfacial properties, were studied by measurement of the dynamics of adsorption and surface pressure isotherms. Such differences may be attributed to differences in the molecular weight and degree and molar substitution among the HPMCs. Thus, E4M having the highest molecular weight showed the highest surface activity among the HPMCs. The lower surface activity of F4M, in comparison to E50LV, may be attributed to its lower degree of total substitution. The experiments were performed at constant temperature (20 °C), pH 7, ionic strength 0.05 M and variable concentrations of the components.

The differences observed between mixed systems were according to the relative bulk concentration of biopolymers and molecular structure of HPMC. In the presence of E4M a strong competence for the interface can be observed at short adsorption time. As E4M is more surface active than WPC, the replacement of E4M at the interface by WPC resulted in lower surface pressure. The mixture approached E4M behaviour at longer adsorption time. An additive or synergistic behaviour was observed for celluloses with lower surface activity (E50LV and F4M) at the lowest WPC and HPMC concentrations in the aqueous phase. A depletion mechanism in the vicinity of the interface would predominate in the presence of E50LV and F4M over the competence for the interface, giving rise to a cooperative behaviour. When WPC saturated the interface and the HPMC concentration in the aqueous phase was low enough, WPC dominated the surface pressure at long-term adsorption.

© 2006 Elsevier Ltd. All rights reserved.

Keywords: Hydroxypropyl–methyl–cellulose; Whey proteins; Air–water interface; Interactions; Dynamics of adsorption; Equilibrium surface pressure

1. Introduction

Proteins and polysaccharides are frequently present together in food systems contributing to the stability, texture and shelf life of food products (Singh, Tamehana, Hemar, & Munro, 2003). Proteins contribute to texture and stability mainly throughout their surfactant and gelling properties. Polysaccharides are mainly used for their thickening and

gelling ability arising from their strong hydrophilic character coupled with ion-mediated interactions.

Whey proteins are a significant source of functional protein ingredients for many traditional and novel food products (Mishra, Mann, & Joshi, 2001). The main proteins in whey are β -lactoglobulin (β -lg), α -lactalbumin (α -lac) and bovine serum albumin (BSA), which account for by 70% of total whey proteins. These proteins are responsible for the foaming and emulsifying properties of whey proteins concentrates (WPC). Polymeric surfactants as proteins, which are amphiphilic in nature, are able to

*Corresponding author. Tel.: +54 11 45763377; fax: +54 11 45763366.

E-mail address: apilosof@di.fcen.uba.ar (A.M.R. Pilosof).

constitute a monolayer due to their capacity to orientate the hydrophobic segments to the hydrophobic phase (air or oil) while the hydrophilic segments stay orientated to the aqueous phase (Damodaran, 1996; Dickinson, 1992). The number of segments or monomers making contact with the interface will depend on the molecular flexibility and the polymer affinity for the subphase.

Although much is known about the physicochemical and functional properties of proteins in model systems, predictions of their behaviour in real food systems have not been successful (Bos, Nylander, Arnebrant, & Clark, 1997; Nylander & Ericsson, 1997). The main reasons are the modification of protein during food processing as a consequence of factors such as pH, ionic strength, temperature, shear and interactions with food components. Concerning the last, recent publications on the interactions of whey proteins (mainly β -lg) and polysaccharides at interfaces and in foams suggest that polysaccharides do not only affect the bulk rheology of dispersed systems and therefore their stability, but they strongly influence the properties of interfaces. Furthermore, it was reported that non-surface-active polysaccharides as xanthan or λ -carrageenan may affect the surface pressure and surface dilatational modulus of β -lg films more than the surface-active polysaccharide propylene glycol alginate (Baeza, Carrera-Sánchez, Pilosof, & Rodríguez-Patino, 2004a, b; Baeza, Carrera-Sánchez, Rodríguez-Patino, & Pilosof, 2005a; Baeza, Carrera-Sánchez, Pilosof, & Rodríguez-Patino, 2005b).

Most high-molecular-weight polysaccharides, being hydrophilic, do not have much of a tendency to adsorb at the air–water interface. One distinctly group of surface-active polysaccharides is cellulose derivatives. hydroxypropyl–methyl–cellulose (HPMC) belongs to this family of polysaccharides, which is used in food industry, printing technology and also has pharmaceutical applications because it is non-toxic and possesses good mechanical properties. In the pharmaceutical industry, HPMC is of special interest for controlled drug-release matrixes (Ford, 1999; McCrystal, Ford, & Rajabi-Siahboomi, 1997). In food industry, HPMC is used to improve the quality of baked products (Rosell, Rojas, & Benedicto de Barber, 2001), in gluten free breads (Kobyłański, Pérez, & Pilosof, 2004), for innovative battered food manufacturing, low fat edible coating, etc. (Coffey, Bell, & Henderson, 1995). HPMC applications are based in the methyl substitutions that constitute hydrophobic zones along the cellulose backbone, whereas hydroxypropyl groups are more hydrophilic. The introduction of these hydrophobic groups allows HPMC to behave as a surfactant.

In a recent work (Pérez, Carrera-Sánchez, Rodríguez-Patino, & Pilosof, 2006) the surface pressure isotherms and structural and surface dilatational properties of three HPMCs (called E4M, E50LV and F4M) adsorbed films at the air–water interface were determined. In that work we concluded that HPMC molecules are able to diffuse and saturate the air–water interface at very low concentrations

in the bulk phase. The three HPMCs formed very elastic films at the air–water interface, even at low surface pressures. E4M showed features that make it unique. For instance it showed the highest surface activity, mainly at low bulk concentrations ($<10^{-4}$ wt%). The differences observed in surface activity may be attributed to differences in the hydroxypropyl molar substitution and molecular weight of HPMC. All three HPMCs formed films of similar viscoelasticity and elastic dilatational modulus, which can be accounted for by their similar degree of methyl substitution.

Due to its surface-active character, competitive adsorption of HPMC could occur in mixtures of this polysaccharide and proteins. More recently the study of competitive adsorption of surface-active proteins and polysaccharides is attracting increasing interest (Baeza et al., 2004a; Baeza, Carrera-Sánchez, Rodríguez-Patino et al., 2005a; Baeza, Carrera-Sánchez, Pilosof et al., 2005b; Arboleya & Wilde, 2005) because of the potential synergism of mixed biopolymers at fluid interfaces.

In this work we have studied the competitive behaviour of WPC and three well characterized HPMC, so-called E4M, E50LV and F4M, which exhibited different interfacial properties, by measurement of the dynamics of adsorption and surface pressure isotherms. This paper is part of an extensive study undertaken to obtain information about the thermodynamic and surface dynamic properties (time-dependent interfacial pressure and viscoelastic characteristics) of WPC/HPMC mixed systems at the air–water interface.

2. Materials and methods

2.1. Materials

WPC powder was kindly supplied by Milka Frank, Santa Fe, Argentina. Its composition was: proteins 78.9% (Nx6.25) (Association of Official Analytical Chemist (AOAC), 1980); lactose 5%, ash 4.3% and moisture 5.6%. WPC PAGE-electrophoresis in native conditions was made in a Mini-Protean II dual slab cell system (Bio-Rad Laboratories). Quantification of the protein bands was accomplished by means of Bio-Rad GS-670 imaging densitometry. Bio-Rad Molecular Analyst/PC Molecular Image program allowed the analysis of molecular weight and band intensities under volumetric test option. WPC proteins composition was: β -lg 44%, α -lac 20.1%, BSA 8%. The remainder proteins constituting the minor fraction, were immunoglobulins (Ig) and the proteose-peptone fraction (Mulvihill & Donovan, 1987).

Methocell E4M, E50LV and F4M (food grade) from The Dow Chemical Company were kindly supplied by Colorcon-Argentina and used without purification. Table 1 shows some characteristic properties, such as methyl and hydroxypropyl content, methyl/hydroxypropyl ratio, molar substitution and the degree of substitution, viscosity (20 °C) of 2 wt% solution and molecular weight.

Download English Version:

<https://daneshyari.com/en/article/605939>

Download Persian Version:

<https://daneshyari.com/article/605939>

[Daneshyari.com](https://daneshyari.com)