Colloids and Surfaces A: Physicochem. Eng. Aspects 465 (2015) 1–10

Contents lists available at ScienceDirect

Colloids and Surfaces A: Physicochemical and Engineering Aspects

journal homepage: www.elsevier.com/locate/colsurfa

Impact of hydroxypropylmethylcellulose on whey protein concentrate spread film at the air–water interface: Structural and surface dilatational characteristics

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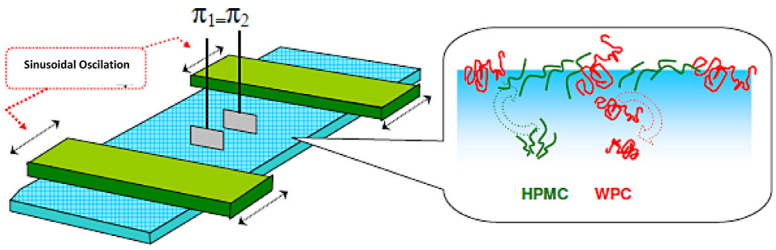
HIGHLIGHTS

- The influence of hydroxypropylmethycellulose on a spread whey protein film was investigated.
- Film structure and elasticity surface dilatational properties data was obtained.
- This fundamental study has practical implications for foamed and emulsified systems design.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 25 June 2014
Received in revised form
11 September 2014
Accepted 15 September 2014
Available online 16 October 2014

Keywords:
Whey protein concentrate
Hydroxypropylmethylcellulose
Air–water interface
Surface tension
Interfacial rheology

ABSTRACT

The static (film structure and elasticity) and dynamic features (surface dilatational properties) of whey protein concentrate (WPC) spread films at the air–water interface, as influenced by three commercial hidroxypropylmethycelluloses (HPMC), i.e., E4M, E50LV and F4M, were studied, at 20 °C, pH 7 and $I = 0.05$ M. To this end a fully automated Wilhelmy-type film balance was used. The results showed a significant influence exerted by HPMC surface active polysaccharides on the WPC film structure. After the polysaccharide addition in the aqueous subphase the π-through area isotherms changed, especially for the highest molecular weight HPMC, as the time increased. Moreover, the presence of HPMC also decreases the surface modulus and the relative viscoelasticity of the WPC protein films. These results can be interpreted in terms of the ability of the polysaccharides to absorb at the air–water interface by itself, penetrate into the spread protein film due to its surface activity and increasing surface pressure. The existence of limited thermodynamic compatibility between the protein and HPMC, occurring in the aqueous phase and at the air–water interface, could be the cause of the observed phenomena, which in turn would be determined by the molecular properties of the cellulose derivative. As mixtures of proteins and polysaccharides are often used in many technological applications, the results presented here should help to improve the processes involved in the formation and stabilization of complex colloidal formulations like foams and emulsion based on these biopolymers.

1. Introduction

Proteins and polysaccharides are natural biopolymers that are used as functional ingredients. Mixtures of proteins and polysaccharides are often used in many technological applications. In many

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http://dx.doi.org/10.1016/j.colsurfa.2014.09.030
0927-7757/

of these applications protein–polysaccharide mixtures are used in the manufacture of processed dispersions [1]. Both proteins and polysaccharides can contribute to the structural, textural and rheological properties of food dispersions in general, and foams and aerated foods, in particular [2–4]. WPC or WPC + HPMC mixtures are complex systems which can be used at an industrial scale in many foams or aerated foods, such as baked, extruded and expanded products, meringue, confectionaries, whipped cream, ice cream, foams based on meat, fish or vegetables [5,6]. Therefore the understanding of the phenomena occurring with these biopolymers at the air–water has technological relevance. In fact, the synergistic effects resulting from blending these biopolymers are of great practical significance for the improvement of many foods formulations, for reducing their cost-price and also to create new functional nano-, micro or macrostructures [4,7]. These nano-microstructures influence the bulk rheology, i.e., the mechanical and flow properties of the dispersion [8] and can be used for encapsulation, protection and delivery of micronutrients. It is increasingly recognized that there is a close relationship between the nature of protein–polysaccharide interactions in aqueous solution and the adsorption behavior of the corresponding biopolymer mixtures at fluid interfaces [9].

Surface active proteins, with hydrophobic and hydrophilic sites, act as polymeric emulsifiers the interfaces [10], this behavior contributes significantly to the interfacial rheological properties and immobilizes proteins in the adsorbed layer. Whey proteins are between those with enormous technological applications. Different whey products are categorized based on their protein concentration, i.e., with whey protein concentrate (WPC) having 30–85% protein and whey protein isolate (WPI) containing >90% protein [11]. WPC and WPI are important ingredients in the manufacture of value added products [12] and also have the advantages of high nutritive value being generally recognized as safe [13]. The major proteins in whey are the globular proteins: α-lactalbumin (α-lac) and β-lactoglobulin (β-lg), bovine serum albumin (BSA). Small amounts of serum albumin and immunoglobulins are also present [14]. These proteins impart functionality to whey [15,16].

Modification of the cellulose chain by attachment of small substituent results in water solubility and thermo-responsive properties [17]. Thus, methylcellulose (MC) and hydroxypropylmethylcellulose (HPMC) are considered the principal cellulose derivatives and they are used in a broad range of applications, in the fields of pharmaceutical and food formulations. Technological applications of HPMC in food industry includes the improvement of quality of backed product [18], for novel battered food developments, film forming agent [19].

The results presented here are part of an integral project undertaken to characterize the behavior of WPC and HPMC in adsorbed monolayers. In previous works we showed the surface pressure isotherms and structural and surface dilatational properties of E4M, E50LV and F4M (three commercial types of HPMC) adsorbed films at the air–water interface [20]; the study of surface dynamic properties as a function of time (surface pressure and surface dilatational properties of these cellulose derivatives) at the air–water [21] and at the oil–water [22] interfaces. Then, the competitive behavior between WPC and the three well characterized HPMCs were studied by measurements of the dynamics of adsorption and surface pressure versus biopolymers bulk concentration isotherms [23]. In a further work, we quantified the competition between WPC and the HPMCs occurring during the dynamic adsorption at the air–water interface by means of dynamic surface tensiometry and the topography of the mixed interface was observed by Brewster angle microscopy. In general the results reflected complex competitive/synergistic phenomena under conditions of thermodynamic compatibility or in the presence of a *depletion mechanism* [24]. The magnitude of the competitive adsorption between these chemical species on the surface dilatational properties at the air–water interface were also explored [25]. In this contribution we are concerned with the analysis of the structural and rheological properties on the spread WPC monolayer at the air–water interface as influenced by three commercial and previously characterized HPMCs.

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) (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 and the proteose-peptone fraction [26].

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 the more relevant physicochemical properties of these HPMCs, 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.

2.2. Surface film balance

The surface pressure (π) measurements vs. trough area (A) were performed on a fully automated Wilhelmy-type balance (KSV 3000, Finland) as described elsewhere [27,28]. The maximum area of the trough between the two barriers was 51.5 cm × 15 cm. Thus, WPC surface film was spread in the form of the solution, to this end aliquots of 400 μl, of the aqueous solutions of WPC (1.6×10^{-4} mg/ml) was spread drop by drop on the aqueous surface, as the procedure followed by [29]. In fact, previous tests pointed out that this method of disposing the protein on the subphase guaranteed its quantitative spreading. The pH and the ionic strength (0.05 M) were kept constant in all the experiments by using 1260 ml of the trizma [$(CH_2OH)_3CNH_2$/$(CH_2OH_3CNH_3Cl)$ (Sigma, >99.5%) buffer solution into the balance trough. Milli-Q ultrapure water pH 7 was always used. To allow complete spreading, adsorption and rearrangements of the protein, 30 min was allowed to elapse before the first measurement was recorded.

To study the effects of the HPMCs addition on the already structured WPC film, i.e., on protein film aged for 30 min, volumes of each polysaccharide solution was added in such an amount to reach a final concentration of 1×10^{-7}%, wt, into the solution bosom which was contained into the through balance. The polysaccharide required high temperature to complete its dissolution, which was the reason why the powders were carefully spread in Trizma buffer at 90 °C. Finally the solutions were kept 24 h at 4 °C to achieve the maximum polysaccharide hydration.

The polysaccharide addition was made by injection of their solutions from behind the balance barriers according to the methodology applied by [27,30]. Subsequent isotherms of these systems were taken at different times: 30 min after WPC spreading, immediately after the HPMCs injection, i.e., 1 h after WPC spreading. Then after 5 h, 24 h and after the compression cycles executed for the rheological analysis (AR), when 28 h had elapsed from the initial protein spreading.