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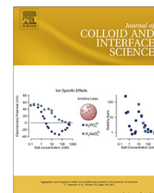

Regular Article

Multistep building of a soft plant protein film at the air-water interface

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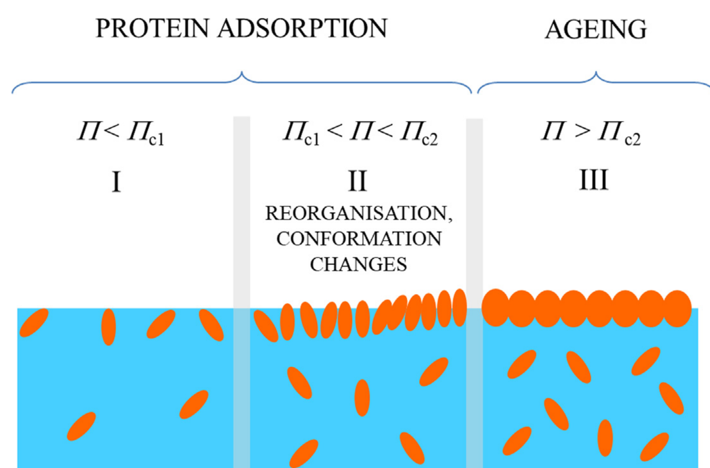
GRAPHICAL ABSTRACT



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ABSTRACT

Gliadins are edible wheat storage proteins well known for their surface active properties. In this paper, we present experimental results on the interfacial properties of acidic solutions of gliadin studied over 5 decades of concentrations, from 0.001 to 110 g/L. Dynamic pendant drop tensiometry reveals that the surface pressure Π of gliadin solutions builds up in a multistep process. The series of curves of the time evolution of Π collected at different bulk protein concentrations C can be merged onto a single master curve when Π is plotted as a function of αt where t is the time elapsed since the formation of the air/water interface and α is a shift parameter that varies with C as a power law with an exponent 2. The existence of such time-concentration superposition, which we evidence for the first time, indicates that the same mechanisms govern the surface tension evolution at all concentrations and are accelerated by an increase of the bulk concentration. The scaling of α with C is consistent with a kinetic of adsorption controlled by the diffusion of the proteins in the bulk. Moreover, we show that the proteins adsorption at the air/water interface is kinetically irreversible. Correlated evolutions of the optical and elastic properties of the interfaces, as probed by ellipsometry and surface dilatational rheology respectively, provide a consistent physical picture of the building up of the protein interfacial layer. A progressive coverage of the interface by the proteins occurs at low Π. This stage is followed, at higher Π, by conformational rearrangements of the protein film, which are identified by a strong increase of the dissipative viscoelastic properties of the film concomitantly with a peculiar evolution of its optical profile that we have rationalized. In the last stage, at even higher surface pressure, the adsorption is arrested; the optical profile is not

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modified while the elasticity of the interfacial layer dramatically increases with the surface pressure, presumably due to the film ageing.

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1. Introduction

Interfacial properties govern many structural and mechanical properties of bulk materials and dispersions. Common examples include the importance of grain-boundaries in the mechanical properties of atomic, molecular and colloidal polycrystals, and of surface actives species in stabilizing foams and emulsions, thanks to their adsorption at air/liquid or liquid/liquid interfaces [1]. Characterizing in details those liquid interfaces is the key to understand and possibly tune the bulk properties of foams and emulsions, which are crucial in a wide range of industrial applications from cosmetics to agrochemistry and pharmacy. There is a wealth of surface active species (e.g. soaps, phospholipids and polymer molecules with different architectures) that spontaneously adsorb at a liquid interface. Proteins, which are amphiphilic compounds made of polar and non-polar amino acid residues, also tend to accumulate at air/water and oil/water interfaces. Understanding and controlling the interfacial adsorption of proteins is important in many industrial fields from food science, to purification and implantable medical devices, for instance. Proteins films are usually characterized by a high viscoelasticity and can undergo a glass or gel transition due to a protein crowding at the interface even for low bulk concentrations of the subphase [2]. Up to now, the majority of detailed studies on interfacial properties of protein films has been conducted with animal proteins. Many works focused on bovine serum albumin, β-lactoglobulin and ovalbumin, which are globular proteins considered as hard proteins, and on β-casein, which is considered as a soft protein prone to conformational changes at the interface and yielding softer interfaces than hard proteins [3].

Interfacial properties of plant proteins have been much less investigated than their animal counterpart [4]. Among vegetable proteins, wheat storage proteins, commonly known as gluten proteins, represent an important part of the occidental people diet. Indeed, many food products traditionally contain wheat flour. In addition, gluten is also used as a texturing agent by the food industry that exploits the unique properties of the viscoelastic network created by these proteins. The interfacial properties of these proteins were also explored to better understand their role in the gas holding capacity of dough, and to determine their potentiality for the development of new products [5]. These studies were performed on either whole gluten proteins [6] or separately on the two main classes of gluten proteins: glutenins, the polymeric proteins, and gliadins, the monomeric ones. Gluten proteins are non-globular proteins that behave as polymers and display a persistence length similar to that of disordered proteins [7]. Their secondary structure is labile and depends of the environment [8] and osmotic pressure [9]. It was established that gliadins are more surface active than glutenins [10] and display at equilibrium lower surface tension at the air-water interface than soy glycinin, casein [11] or bovine serum albumin proteins [12]. Furthermore, gliadins were demonstrated to be very surface active for oil-water interfaces and form highly viscoelastic films [4a]. As a consequence, gliadins were studied to stabilize foams [10a,13] and emulsions [12]. However, the precise mechanism of gliadin adsorption at interface, the structure of the film formed and its rheology are still not well described.

In the present work, we investigate the adsorption of gliadins at the air-water interface from acidic solutions displaying a large range of concentration of proteins, from 1 mg/L to 110 g/L. Solutions are prepared at acidic pH, for which gliadins are the most soluble in aqueous solvent due to their neutral isoelectric point. A combination of tensiometry, dilatational viscoelasticity and ellipsometry measurements is performed as a function of time. A time-concentration superposition is evidenced whatever the subphase concentration and reveals that protein adsorption at the interface is dominated by bulk diffusion. We propose a consistent physical picture of the multistep diffusion-controlled irreversible adsorption of the gliadin proteins at an air/water interface, and discuss our main conclusive results in light of the literature. Overall all our experimental results indicate that gliadin displays a behavior typical of soft proteins.

2. Material and methods

2.1. Material

2.1.1. Gliadin extraction and characterization

Gliadins are extracted from industrial gluten (courtesy of Tereos Syral, France) according to a protocol previously described by some of us [7]. Briefly, gluten powder is mixed with 50% (v/v) ethanol/water solvent and submitted to a continuous rotating agitation for 19 h. After centrifugation, the supernatant is recovered and placed at 4 °C to induce a liquid-liquid phase separation. The light phase, enriched in gliadins, is recovered and freeze-dried. This fraction (labelled S2 in Ref. [7]) is characterized by Sodium Dodecyl Sulfate PolyAcrylamide Gel Electrophoresis, SDS-Page) and size-exclusion high performance liquid chromatography (SE-HPLC). Fig. 1a displays the SE-HPLC profile measured on a TSK G400 SWXL column using the experimental conditions described in Dahesh et al. [14]. The molecular weight (M_w) composition deduced from the profile is 78% gliadins ($25\,000 < M_w < 55\,000$ g/mol), 15% glutenins ($60\,000 < M_w < 400\,000$ g/mol) and 7% albumins-globulins ($M_w \approx 20\,000$ g/mol).

2.1.2. Sample preparation

We use a 50 mM acetic acid aqueous solvent (purity 99%) (pH = 3) to fully solubilize gliadin proteins (gliadins are insoluble at neutral pH). Protein/solvent mixtures of concentration $C = 50$ g/L and higher are put in a rotary shaker overnight at room temperature to allow sample homogenization. They are subsequently filtered with a 0.22 μm cellulose mixed ester membrane. Diluted solutions are prepared from the stock solution at $C = 50$ g/L by dilution with 50 mM acetic acid aqueous solvent to reach the target concentrations.

2.1.3. Bulk sample characterizations

2.1.3.1. Size of the proteins. The hydrodynamic radius of the proteins in a acetic acid solution (50 mM) is characterized by dynamic light scattering (DLS) performed at a wavelength $\lambda = 532$ nm for 6 different scattering angles ranging between 40 and 120°. The number size distribution is dominated by objects with a hydrodynamic radius of 5 nm. This size is consistent with the radius of gyration of gliadins ($3 < Rg < 5$nm) measured by Thomson et al. [15] who modeled gliadins as prolate ellipsoids with an aspect ratio comprised between 4 and 6. We expect that the interfacial properties, as measured in this study, are majorly due to individual gliadins.

2.1.3.2. Dielectric constant and refractive index. The refractive index of the protein solutions in the visible range, n_{bulk}, is measured with

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