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Drainage and critical thickness of foam films from mixed solutions of bovine serum albumin and *n*-dodecyl-*β*-D-maltoside

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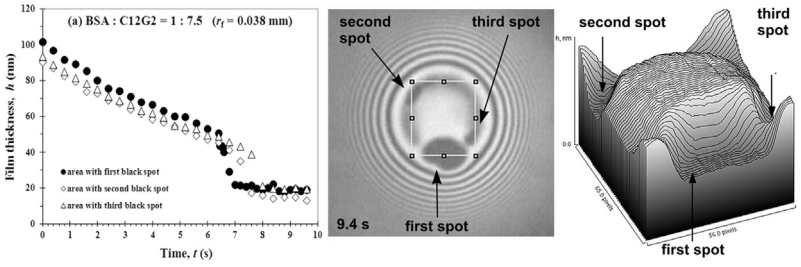
HIGHLIGHTS

- Drainage coefficient α and critical thickness h_{cr} of BSA/$C_{12}G_2$ films are measured.
- The BSA:$C_{12}G_2$ (1:7.5, 1:50) films thin faster than those with pure BSA.
- The film radius and BSA/$C_{12}G_2$ ratio do not change much α in the first spot area.
- h_{cr} values of BSA and mixed films in the spots areas do not differ significantly.
- A big difference is found in h values for the film periphery and other areas.

GRAPHICAL ABSTRACT



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ABSTRACT

Data for the kinetic stability of foam films from "bovine serum albumin" (BSA) solution, or from its mixed solutions with non-ionic surfactant "*n*-dodecyl-*β*-D-maltoside" ($C_{12}G_2$) are presented and discussed based on the specificity of interactions between the components analyzed by tensiometry and fluorescence spectroscopy.

The thickness as a function of time in different areas of BSA or BSA/ $C_{12}G_2$ films formed at different experimental conditions (different molar ratios between protein and surfactant, film radius) is measured interferometrically from a video recording of the film evolution. The thinning velocity presented via drainage coefficient, α, in the areas where first, or other black spots appear, or in other film areas was determined from the lnh (t) dependences up to the critical state (first black spot formation in the film). It is found that BSA film has the slowest thinning and the most regular thickness. The thinning velocity of the both BSA and BSA/surfactant films in the area where first spot appears decreases considerably with increasing of the film radius. The thinning velocity values in other film areas are close to those obtained in areas with spots, but only in the initial period of film drainage. The thinning in these places almost stops around the critical state. In above mentioned different film areas the thicknesses, corresponding to the critical state are measured and compared. It is found that the values of critical thickness in areas with spots are noticeably smaller, than critical thickness in other areas, irrespectively of the film radius and molar ratio of the stabilizers. It means that the value of critical thickness for a protein film can not be obtained as an average value of the thickness values determined in different film areas just before the first black spot formation.

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1. Introduction

The pursuit of people to keep the ecological equilibrium, to produce pure and non toxic foods, stable medical compositions and detergents without allergic effects determines the interest to proteins as stabilizers of foams. The model foam film study is an ideal tool to learn about the forces responsible for foam stability. By this reason foam films (FF) stabilized by different individual proteins (fibrillar or globular) have been subject of many experimental and theoretical studies [1–7]. Low molecular surfactants are used in isolating, purifying and storing of the proteins in the detergents and medicine compositions. That's why in the last years the properties of the films of mixed solutions of proteins and low molecular surfactants are intensively investigated [8–12]. The accent in these studies has been directed to the type, structure and equilibrium film properties at different experimental conditions (protein nature and concentration, electrolyte concentration and pH of the medium). In [8–12] the properties of films from mixed proteins/surfactants solutions have been discussed on the basis of BSA/surfactant interactions in the volume and in adsorption layer depending on the molar ratios between protein and surfactant, as well as on their competitively adsorption. The equilibrium properties of protein FF obtained in the above studies might be of importance for relatively stable foams. Usually, the foams used in the practice are unstable ones. That's why in these cases the film's kinetic (nonequilibrium) parameters as a velocity of thinning and critical film thickness are more important than the equilibrium ones. According to [13] the simultaneous action of hydrodynamic forces and disjoining pressure determines the stages of the FF formation and evolution which are: formation of the thick liquid layer between two mutual approaching slightly deformed bubbles; dimple arising and its out flowing; formation of a plane-parallel film with corrugate surfaces caused by thermal fluctuations; rapidly growing of the corrugations which leads either to the film rupture or to a black spot formation. The latter one is a critical for FF, that's why it is called "critical stage". The optimum averaged film thickness at the moment of rupture, or at black spot formation is referred to as a critical film thickness h_{cr}. Quantitatively, the rate of drainage of liquid from the film is given by velocity of thinning $V = -dh/dt$. It can be evaluated and by two characteristic film thinning times, τ_{0-1} and τ_{1-2}, introduced in [14]: τ_{0-1} is the time from the moment of film formation to reaching of its critical state; τ_{1-2} is the time from the formation of the first black spot to the moment of its expansion to the whole film area, i.e., to black film formation. Theories of film thinning [15–17], equations and approaches for the critical thickness calculation [18–21] have been suggested for films stabilized by low molecular non ionic surfactants. Theoretically, it is found that film thinning velocity depends on the capillary pressure, disjoining pressure acting at different steps of the film evolution, film radius, corrugations of film surfaces and dynamic volume viscosity. The surface tension and disjoining pressure are the major factors controlling the value of the critical thickness. Theoretically predicted dependences of the thinning velocity and critical thickness on the above mentioned parameters have been checked by experimental data of films stabilized by low molecular non ionic and ionic surfactants [16,18–25] obtained by an interferometric method.

According to the literature the quantitative information about the kinetic parameters of protein films is limited. Some qualitative descriptions of the film evolution and velocity of thinning at different experimental conditions (protein and electrolyte concentration, pH of medium, age of the film surfaces before film formation) are given in [2,4,6,7,11]. Although it is difficult to achieve a direct correlation between FF properties and the foam stability in [26–29] attempts for explaining the proteins foam stability based on data of the film thinning, composition of film surfaces, adsorption isotherms of the mixed solutions and the competitive adsorption between the protein/surfactant complexes and free surfactant molecules have been done.

The lack of systematic experimental data for the kinetic parameters of protein films does not permit the adaptation of existing theories of the film thinning and critical thickness to protein films or creating new theories. It can be explained with some experimental difficulties, which have appeared applying of the interferometric method to protein film. They originate from its special manner of thinning due to the high interfacial viscosity which causes nonhomogeneity in the film thickness. The process of protein film evolution distinguishes from that of film stabilized by low molecular surfactant. The protein film thinning is irregular (areas with different thickness are formed sometimes a dimple is trapped in the film), which reveals that the film surfaces are strongly corrugated.

The aim of the presented study was to obtain experimental data for the kinetic parameters of foam films stabilized by "bovine serum albumin" (BSA), or by its mixtures with non-ionic surfactant "*n*-dodecyl-β-D-maltoside" ($C_{12}G_2$).

The aim was realized by (i) determination of the velocity of thinning in different film areas based on the $h = h(t)$ dependences, obtained interferometrically from video recordings of the films evolution; (ii) measuring of the thickness in the same places where the thinning was determined at the moment when first black spot arises.

2. Materials, solutions, experimental conditions and methods

2.1. Materials

The Bovine Serum Albumin (BSA) was purchased from Sigma–Aldrich, USA, protein content 96%. (Mw 67 kDa). The nonionic sugar surfactant *n*-dodecyl-β-D maltoside ($C_{12}G_2$), purity > 99.5%) was purchased from Glycon and used as received.

BSA is a globular protein which molecular structure, volume and interface properties, as well as its interactions with low non ionic molecular surfactants are well studied [4,30–36].

n-dodecyl-β-D maltoside is a well soluble in water, non ionic sugar surfactant with temperature and pH insensitivity. The value of its critical micelles concentration (CMC) is equal to 1.5×10^{-4} M [37]. Its molecule is amphiphilic and it consists of a hydrophobic tail and a hydrophilic head – maltoside unit behaves like a hard disk.

2.2. Solutions

Stock solutions of BSA (1×10^{-5} M) and $C_{12}G_2$ (1.5×10^{-4}; 1×10^{-3} M) were used. They were stored at 5 °C ± 1 °C in a refrigerator. The concentration of stock protein solutions was determined by measuring the optical density A at $\lambda = 280$ nm using $\varepsilon^{1\%}_{1\,cm} = 6.7$ equal to 4.489×10^4 l mol^{-1} cm^{-1}. The working solutions of the individual surfactant were prepared 2 h before each measurement. The working mixed solutions of BSA with $C_{12}G_2$ were prepared a night before each experiment. The pH value of the solutions (4.9) was adjusted by adding of a small amount of 0.1 M HCl.

All experiments were performed at temperature 25 °C ± 1 °C. All glassware was cleaned with concentrated chromic sulphuric acid and rinsed before use with double distilled water.

2.3. Experimental conditions

The investigated films in this study were formed from pure BSA solution with concentration 1×10^{-6} M and from mixed solutions: 1×10^{-6} M BSA + 7.5×10^{-6} M $C_{12}G_2$; 1×10^{-6} M BSA + 5.0×10^{-5} M $C_{12}G_2$ with molar ratio BSA:$C_{12}G_2$ = 1:7.5 and