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# Influence of β-lactoglobulin and its surfactant mixtures on velocity of the rising bubbles

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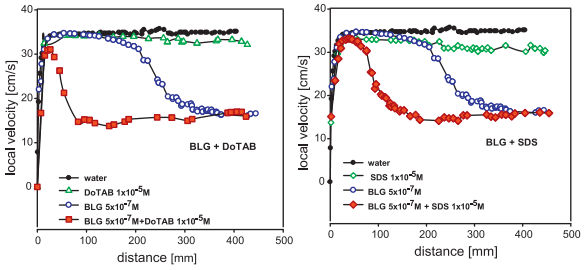
## HIGHLIGHTS

- β-Lactoglobulin alone and mixed with different surfactants were studied.
- The local velocity profiles of rising bubbles in these solutions were analyzed.
- Addition of ionic surfactants to protein solutions caused strong retardation in velocity.
- Mixture of protein and nonionic surfactant had only additive effect.
- Ionic strength of the solution had an effect on the surface activity of the formed complexes.

## GRAPHICAL ABSTRACT

The addition of smallest amounts of ionic surfactants to solutions of β-lactoglobulin leads to a strong retardation of the rising bubble velocity, which can be explained by the high surface activity of the complexes formed between BLG and the surfactants.

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## ABSTRACT

The rising velocity of air bubbles in surfactant solutions is a sensitive measure for the formation of a dynamic adsorption layer (DAL) at the bubble surface. Due to a certain surface coverage by adsorbed species the bubble surface starts to become immobilized and the rising velocity is retarded. There is a large difference in the retardation effect in presence of the protein β-lactoglobulin (BLG) alone and its mixed solutions with surfactants. In presence of added surfactants BLG forms complexes, which adsorb and retard the bubble rising velocity according to their respective surface activity and adsorption kinetics. While the nonionic surfactant $C_{12}$DMPO does not show significant increase in retardation effects as compared to BLG alone, the ionic surfactants SDS and DoTAB form highly surface active complexes and change the rising velocity much stronger.



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## 1. Introduction

Mixtures of proteins and surfactants are widely studied due to their major industrial applications in food processing (from sponginess of bread to proper consistency of mayonnaise), pharmacology, or formulations for hair and body cosmetics, such as shampoos and creams. The formation and stabilization of foams and emulsions depend on the interfacial properties of these mixtures, i.e. the variations of interfacial tension, the bulk and surface rheological behaviour, and the adsorption dynamics, which can be drastically different as compared to those of the single components [1]. From a physical point of view, surfactants and proteins adsorb at interfaces, reducing the respective interfacial tension. While low molecular weight surfactants in most formulations are responsible for foam/emulsion formation thanks to a quick adsorption at the bubble/drop surface, the high-molecular weight proteins stabilize them on longer time scales, forming elastic and often electrically charged interfacial networks [2]. Different methods like dynamic and equilibrium surface tension measurements, dilational and shear rheology, ellipsometry, etc., were used to understand the adsorbed layers of proteins and their mixtures with surfactants [1,3–8]. Interactions of proteins with ionic surfactants such as the anionic sodium dodecyl sulfate (SDS) or cationic cetyl trimethyl ammonium bromide (CTAB) have been described in detail in literature [5]. It was clearly shown that proteins interact with ionic surfactants which lead to formation of complexes. Even in the case when the net charge of the protein and the charge of the surfactant are both negative (or positive), there are local counter charges available on the protein chain so that an electrostatic interaction with the surfactants is possible. After charge compensation due to the binding of ionic surfactants, with increasing surfactant concentration the protein/surfactant complexes start to interact with further surfactant molecules mostly via hydrophobic interaction. In protein solutions containing non-ionic surfactants a complex formation happens exclusively via hydrophobic interactions. A general overview on complex formation between proteins and different types of surfactants was given in [9].

The motion of bubbles in a liquid is strongly affected by the adsorption of surface-active species at the bubble surface and, therefore, has been used as a sensitive tool for investigating the adsorption layer formation in surfactant solutions under dynamic conditions. As proteins also adsorb at liquid/gas interfaces, measurements of the rising bubble velocity in solutions of protein and protein–surfactant mixtures can provide information about their influence on the formation of adsorption layers under dynamic conditions. Generally, the presence of an adsorbed layer retards the mobility of a bubble surface [10–13] and, thereby, the velocity of the rising bubble can be lowered by more than 50% [13–15]. When a bubble grows at the tip of a capillary immersed in a surfactant solution an adsorption layer is formed over the entire bubble surface. The degree of adsorption coverage over the bubble surface in the moment of bubble detachment is determined by the surfactant surface activity and its bulk concentration, the adsorption kinetics and the rate of bubble growth (bubble surface expansion). At low surfactant concentrations the adsorption coverage can be lower than at equilibrium, however, it is a uniform coverage [13,15]. After bubble detachment a non-uniform distribution of surfactants along the bubble surface (dynamic structure of the adsorption layer – DAL) starts to develop [10,12–16], as a result of the viscous drag exerted by the continuous liquid medium on the bubble surface. The formation of a DAL over the surface of a rising bubble means that the adsorption coverage tends to a minimum at the upstream pole of the moving bubble, while at the rear pole it becomes higher than the equilibrium value. This gradient of surface concentration corresponds to a surface tension gradient which causes a reduction of the fluidity of the bubble surface (Marangoni effect). In turn, the immobilization of the bubble surface leads to an increase of the hydrodynamic drag exerted by the liquid on the bubble surface so that the velocity of the bubble decreases. When the bubble moved with a constant (terminal) velocity (steady state conditions) it is an indication that the dynamic architecture of the adsorption layer (DAL) has been established. In solutions of classical surfactants the time-scale of the DAL establishment over the surface of a rising bubble depends on the surfactant type and its solution bulk concentration [14–20]. It was shown in [21,22] that also in solutions of the protein bovine serum albumin (BSA) the velocity of a rising bubble can be lowered significantly as the result of protein adsorption at the bubble surface. However, as far as we know, there is no investigation on bubble motion in protein–surfactant mixtures and this is the topic of this paper.

The present manuscript deals with the investigation of rising air bubbles in solutions containing the protein β-lactoglobulin (BLG), one of the three surfactants SDS, DoTAB, $C_{12}$DMPO, or respective protein/surfactant mixtures at different mixing ratios. We measured the velocity profiles of air bubbles as a function of the distance from the origin or alternatively of the rising time, and discuss qualitatively the differences observed for pure BLG and its mixtures with an ionic or a non-ionic surfactant. The velocity profiles are discussed in terms of adsorbed amounts and their impact on the immobilization of the surface of a rising bubble.

## 2. Experimental method

The bubble rising velocity profiles were determined in a glass square column of cross section area 40 × 40 mm and 50 cm height. A capillary with an inner diameter of 0.075 mm fitted to the column bottom was used to form single bubbles at a controlled time intervals. The time of bubble formation ($t_f$) at the capillary tip was 1.6 sec and the bubble diameter in distilled water was 1.48 ± 0.01 mm. A digital camera (MotiCam) and a stroboscope illumination were used to record images of rising bubbles. The special software ImageJ was used to analyze the video recordings. More details about the experimental set-up and the data analysis procedure can be found elsewhere [14–17]. The reagents used were dodecyl trimethyl ammonium bromide (DoTAB) and sodium dodecyl sulfate (SDS) both purchased from Fluka (Switzerland). The non-ionic surfactant dodecyl dimethyl phosphine oxide ($C_{12}$DMPO) was synthesized in our lab following the protocol given in [23]. BLG was purchased from Sigma–Aldrich (90% pure). The stock solutions were prepared by dissolving the protein in Milli-Q water used for the preparation of the solutions had a surface tension of 72.4 mN/m at 22 °C and a conductivity 0.05 μS/cm. All experiments were carried out at room temperature of 22 °C, and the pH of all studied solutions was 6.2.

## 3. Results

The velocity of the bubble is determined from the capillary tip till the top level of liquid at regular intervals. This gives us the velocities at regular distances from the capillary tip, which when plotted against the distance or time gives us local velocity profile (LVP).

Fig. 1 presents sequences of images of bubbles rising in BLG solutions of different concentrations. All photos were recorded at an identical distance of 100 mm from the capillary orifice. As the pictures were recorded at an identical frequency of the stroboscopic illumination (100 Hz), a smaller distance between subsequent positions of the rising bubble illustrate clearly that the bubble velocity decreases with increasing BLG concentration. Note also, that the shape deformation of the bubbles also decreases with increasing BLG concentration.

Quantitative data on the influence of the BLG concentration on the bubble motion are presented in Fig. 2 as the dependences of

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