

SIMULATION OF DYNAMICS OF ADSORTION OF MIXED PROTEIN-SURFACTANT ON A BUBBLE SURFACE

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Abstract

The dynamics of adsorption of mixed protein-surfactant on a bubble surface is simulated mathematically. The model for the adsorption dynamics is developed based on the Ward-Tordai equation combined with the Frumkin adsorption isotherm. The simultaneous equations are solved using the Newton method for iteration. Base case adsorption and diffusion parameter values for the simulation were sourced from literature. It was found that protein arrives on the surface at a later time than surfactant. At this later time, the protein replaces the surfactant resulting in depletion of surfactant on the surface. There is, however, less protein adsorbed in the presence of more surfactant in the bulk. In contrast, more protein stays in the subsurface layer under these conditions. In addition to the base case simulation and a comparison to the experimental data available in the literature, a parametric study was performed to explore the effects of varying adsorption and diffusion parameters. The parametric study varying the protein surface affinity revealed that below a certain critical affinity, protein tends not to replace surfactant on the surface, even though the affinity of protein remains higher than that of surfactant. Therefore, protein molecules need to have sufficiently high affinity to displace surfactant molecules from the surface. Another parametric study setting a fixed protein surface affinity and varying relative diffusivity and surface affinity of surfactant (for a specified maximum possible surface capacity of surfactant) concluded that with high relative diffusivity and low surfactant affinity (relative to protein), the displacement of surfactant on the surface is more likely to occur.

Keywords: adsorption, mixed protein-surfactant, frumkin isotherm, Ward-Tordai equation

1. INTRODUCTION

Mixtures of protein and surfactant have a practical significance in industry, for example in the stabilisation of emulsions and foams [1]. Moreover, these mixtures can be found easily in biological systems, such as blood serum which contains of human serum albumin (HSA) and a number of compounds including low-molecular weight surface active molecules [2]. Proteins are often mixed with low-molecular weight surfactants to improve the quality of foam produced. The ability of proteins to unfold at the interface generates films with high surface elasticity and provides steric resistance to avoid coalescence of films [3]. As a consequence, studies on the adsorption phenomena of mixed protein-surfactant have significant practical as well as scientific importance. Many works attempt to determine the behaviour of adsorption of protein-surfactant mixtures. Those studies [2, 4–7] describe both the adsorption isotherms and adsorption dynamics of mixed protein-surfactant on the liquid-gas interfaces based on experimental data. On the other hand, studies on mathematical modelling to predict the adsorption behaviour of mixed protein-surfactant on the liquid-gas interfaces are less common. Nevertheless, studies of this nature have a significant importance for the design of a process involving the adsorption of mixed protein-surfactant, such as foam fractionation or emulsification.

The adsorption isotherms and adsorption dynamics of protein and surfactant mixtures in the previous studies [5, 6, 8] were determined based on the experimental data of equilibrium surface tension and dynamic surface tension, respectively. Such analysis as was performed of the equations governing adsorption behaviour was done primarily with a view to extract parameter values from the available experimental data. However, so far a thorough parametric simulation study, elucidating detailed behaviour of adsorption dynamics, has not been developed in previous studies. When a robust simulation of dynamics of adsorption of mixed protein-surfactant is made available,

it will save the resource associated with carrying out a multitude of laboratory experiments to determine the dynamics of adsorption. The mathematical simulation can be developed using the model of adsorption dynamics and also the adsorption isotherm of mixed protein-surfactant on the liquid-gas interfaces developed in the previous studies.

ADSORPTION DYNAMICS OF MIXED PROTEIN-SURFACTANT AT GAS-LIQUID INTERFACES

The equation of state of the surface layer then can be presented as follows [9]:

$$-\frac{\Pi\omega_0}{RT} = \ln(1 - \theta_p - \theta_s) + \theta_p \left(1 - \frac{\omega_0}{\omega_p}\right) + \alpha_p \theta_p^2 + \alpha_s \theta_s^2 + 2\alpha_{ps} \theta_p \theta_s \tag{1}$$

where $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 is the surface tension of the solvent, γ is the surface tension of the solution, R is the gas law constant, T is the temperature, $\theta_p = \Gamma_p/\omega_p$ is the protein surface coverage fraction, Γ_p is the total adsorption of protein, ω_p is the average molar area of the adsorbed protein molecules, $\theta_s = \Gamma_s/\omega_s$ is the surfactant surface coverage fraction, Γ_s is the molar area of the adsorbed surfactant, ω_s is the surface concentration of surfactant, ω_0 is the molar area of the solvent, α_p is the intermolecular interaction parameter of protein, α_s is the intermolecular interaction parameter of surfactant, α_{ps} is a parameter describing the interaction between the protein and surfactant mixture. The adsorption isotherm of the protein is then derived as:

$$b_p C_p = \frac{\theta_p}{(1-\theta_p-\theta_s)} \exp[-2\alpha_p \theta_p - 2\alpha_{ps} \theta_s] \tag{2}$$

where C_p is the concentration of the protein in the subsurface layer and b_p is the equilibrium adsorption constant of protein.

The adsorption isotherm equation for the surfactant is analogous as follows:

$$b_s C_s = \frac{\theta_s}{(1-\theta_p-\theta_s)} \exp[-2\alpha_s \theta_s - 2\alpha_{ps} \theta_p] \tag{3}$$

where C_s is the concentration of the surfactant in the subsurface layer and b_s is the equilibrium adsorption constant of surfactant.

Adsorption dynamics of both protein and surfactant towards the gas-liquid interface follow Fick’s equation[10, 11]. The Laplace transformation of the diffusion equation results in a general dynamics of adsorption equation on a liquid-gas interface as proposed by Ward and Tordai [12]. The equation describes the evolution of surface concentration due to transfer from the subsurface as follows:

$$\Gamma_p(t) = \sqrt{\frac{D_p}{\pi}} \left[2C_{pb} \sqrt{t} - \int_0^t \frac{C_p(\tau)}{\sqrt{t-\tau}} d\tau \right] \tag{4}$$

$$\Gamma_s(t) = \sqrt{\frac{D_s}{\pi}} \left[2C_{sb} \sqrt{t} - \int_0^t \frac{C_s(\tau)}{\sqrt{t-\tau}} d\tau \right] \tag{5}$$

where D_p and D_s are diffusion coefficients of protein and surfactant in the solvent, respectively, C_{pb} and C_{sb} are the bulk concentrations of protein and surfactant, respectively and τ is a dummy integration variable.

The first term on the right hand side of the equation represents the diffusive transport to the surface. This diffusion is mitigated by a reduction in diffusive driving force as surfactant and/or protein on the surface builds up, which is presented by the second term of the right hand side of the equation. The Ward-Tordai equation presented in Equations 4—5 is applicable on a planar interface. This shape of interface is selected as in common applications such as foam fractionation, polyhedral bubbles with nearly planar films occur in the system, due to low fraction of liquid [13].

DIMENSIONAL ANALYSIS OF THE EQUATION OF ADSORPTION DYNAMICS

A dimensional analysis is carried out upon the equations of dynamics of adsorption of mixed protein-surfactant which are Equations 2, 3, 4 and 5. The dimensionless form of the equations governing the dynamics of adsorption involves dimensionless groups that we call D , Γ_{m2} , κ_p , κ_s and c_b , precise definitions of which will be given shortly. The resulting dimensionless equations are as follows.

Dynamics of protein adsorption:

$$\theta_p(t') = \sqrt{\frac{1}{\pi}} \left[2\sqrt{t'} - \int_0^{t'} \frac{c_p'(\tau')}{\sqrt{t'-\tau'}} d\tau' \right] \quad (6)$$

Adsorption isotherm of protein:

$$c_p'(t') = \frac{\theta_p(t')}{\kappa_p(1-\theta_p(t')-\theta_s(t'))} \exp[-2\alpha_p\theta_p(t') - 2\alpha_{ps}\theta_s(t')] \quad (7)$$

Dynamics of surfactant adsorption:

$$\theta_s(t') = c_b \frac{\sqrt{D}}{\Gamma_{sm} \sqrt{\pi}} \sqrt{\frac{1}{\pi}} \left[2\sqrt{t'} - \int_0^{t'} \frac{c_s'(\tau')}{\sqrt{t'-\tau'}} d\tau' \right] \quad (8)$$

Adsorption isotherm of surfactant:

$$c_s'(t') = \frac{\theta_s(t')}{\kappa_s(1-\theta_p(t')-\theta_s(t'))} \exp[-2\alpha_s\theta_s(t') - 2\alpha_{ps}\theta_p(t')] \quad (9)$$

And the equation of state:

$$\Pi^r = -\ln(1 - \theta_p - \theta_s) + \theta_p \left(1 - \frac{\omega_s}{\omega_p} \right) + \alpha_p \theta_p^2 + \alpha_s \theta_s^2 + 2\alpha_{ps} \theta_p \theta_s \quad (10)$$

where $\Pi^r = \Pi\omega_0/(RT)$ is the dimensionless surface pressure, $\theta_p = \Gamma_p/\Gamma_{pm}$ is the dimensionless surface concentration of protein (i.e. the coverage fraction), $\theta_s = \Gamma_s/\Gamma_{sm}$ is the dimensionless surface concentration (coverage fraction) of surfactant, $\Gamma_{pm} = 1/\omega_p$ and $\Gamma_{sm} = 1/\omega_s$ are the maximum surface concentration of protein and surfactant respectively (both measures of surface capacity), $t' = (D_p t)/(\Gamma_{pm}/C_{pb})^2$ is the dimensionless time, $c_p' = C_p/C_{pb}$ is the dimensionless bulk concentration of protein at the layer next to the surface, $c_s' = C_s/C_{sb}$ is the dimensionless bulk concentration of surfactant at the layer next to the surface, C_{pb} and C_{sb} are the initial bulk concentration of protein and surfactant respectively, $\kappa_p = b_p C_{pb}$ and $\kappa_s = b_s C_{sb}$ are the dimensionless adsorption equilibrium constant of protein and surfactant, respectively (both measures of surface affinity), $c_b = C_{sb}/C_{pb}$ is the relative bulk concentration, $D = D_s/D_p$ is the relative diffusivity and $\Gamma_m = \frac{\Gamma_{sm}}{\Gamma_{pm}} = \omega_p/\omega_s$ is the relative capacity which is equivalent to the ratio between molar areas of protein and surfactant.

2. METHODS AND PARAMETER VALUES

The parameters used in the simulation are obtained from a study by Miller et al. [5] using Bovine β - lactoglobulin (BLG) protein and nonionic decyl dimethyl phosphine oxide (C₁₀DMPO) surfactant. Those parameters are listed in Table 1. The parameters from the study by Miller et al. were set as a base case when the simulation involved variation of the material parameters such as diffusion constant of surfactant D_s (or analogously D in dimensionless

form), surface capacity of surfactant Γ_{sm} (or analogously dimensionless Γ_m), adsorption coefficient of surfactant, b_s (or analogously κ_s) and adsorption coefficient of protein, b_p (or analogously κ_p).

Table 1: The values of base case parameters used in the simulation of adsorption dynamics.

Variable name	Symbol	Value	Unit
Diffusivity of protein	D_p	5×10^{-11}	$\text{m}^2 \text{s}^{-1}$
Diffusivity of surfactant	D_s	4×10^{-10}	$\text{m}^2 \text{s}^{-1}$
Bulk concentration of protein	C_{pb}	1×10^{-3}	mol m^{-3}
Bulk concentration of surfactant	C_{sb}	1×10^{-2}	mol m^{-3}
Gas constant	R	8.3144621	$\text{J mol}^{-1} \text{K}^{-1}$
Temperature	T	298	K
Molar area of solvent	ω_0	3.5×10^5	$\text{m}^2 \text{mol}^{-1}$
Molar area of protein	ω_p	4.4×10^6	$\text{m}^2 \text{mol}^{-1}$
Molar area of surfactant	ω_s	2.5×10^5	$\text{m}^2 \text{mol}^{-1}$
Surface capacity of protein	Γ_{pm}	2.27×10^{-7}	mol m^{-2}
Surface capacity of surfactant	Γ_{sm}	4.00×10^{-6}	mol m^{-2}
Protein interaction parameter	α_p	0.4	
Surfactant interaction parameter	α_s	-0.25	
Protein-surfactant interaction parameter	α_{ps}	0.075	
Protein adsorption constant	b_p	1.4×10^3	$\text{m}^3 \text{mol}^{-1}$
Surfactant adsorption constant	b_s	21.9	$\text{m}^3 \text{mol}^{-1}$

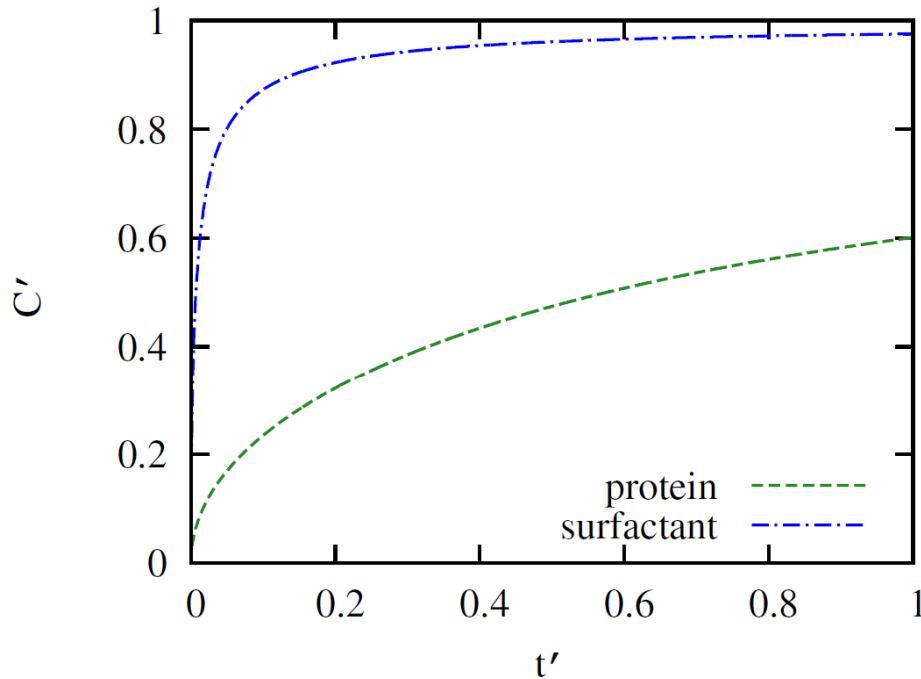


Figure 1: Dimensionless subsurface concentration as a function of dimensionless time observed at dimensionless parameters of: $\kappa_p = 1.4$, $\kappa_s = 0.219$, $\mathcal{D} = 8$, $\Gamma_m = 17.6$, $c_b = 10$.

3. RESULTS AND DISCUSSION

This study examines the adsorption dynamics of mixed protein-surfactant on a bubble surface in a situation typical of a foam fractionation process. A parametric study was also carried out to explore the effect of varying adsorption and diffusion parameters.

Competition between protein and surfactant molecules on the surface

Figure 1, corresponding to the base case parameter values, shows the comparison between the dimensionless subsurface concentration of protein and the dimensionless subsurface concentration of surfactant at base case. This simulation was carried out using these values of dimensionless groups: $\kappa_p = 1.4$, $\kappa_s = 0.219$, $D = 8$, $\Gamma_m = 17.6$, $c_b = 10$. Since the diffusivity coefficient of surfactant is higher than the diffusivity coefficient of protein, surfactant is more rapidly transferred to the subsurface. At early time, there is therefore more surfactant adsorbed on the surface. Due to the faster diffusion (high D), and also lower surface affinity (viz. the low value of the parameter κ_s), surfactant reaches its final concentration in the subsurface faster than protein. The subsequent arrival of additional protein in the subsurface provides more protein molecules to adsorb to the interface while there is limited further change of surfactant concentration in the subsurface. As protein has a relatively higher surface affinity (measured by the values of κ_p vs. κ_s), protein molecules compete strongly with surfactant molecules on the surface. Therefore, protein molecules replace surfactant molecules on the surface resulting in lower surface concentration of surfactant as presented in Figure 2. This overshoot phenomenon also occurs in the adsorption of mixed surfactants as reported by Mulqueen et al. [14].

Figure 3 shows the growth of the surface pressure with the addition of protein in the bulk solution where the values of the dimensionless groups are: $\kappa_p = 1.4$, $\kappa_s = 0.219$, $D = 8$, $\Gamma_m = 17.6$, $c_b = 10$. The time scale of this figure is taken up to five units, longer than the time scale of Figures 1 and 2 which is up to one unit. The longer time scale in Figure 3 has been selected to show the final surface pressure is approached on that time scale. The surface pressure is higher in the presence of protein and surfactant in the bulk solution compared to the surface pressure resulting from pure surfactant or pure protein solution.

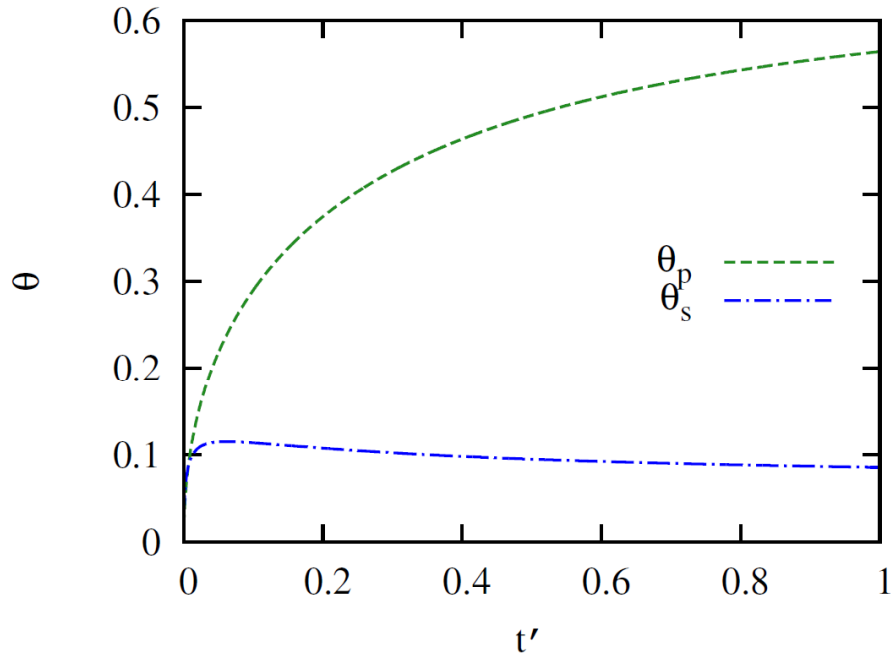


Figure 2: Surface coverage as a function of dimensionless time observed at dimensionless parameters of: $\kappa_p = 1.4$, $\kappa_s = 0.219$, $\mathcal{D} = 8$, $\Gamma_m = 17.6$, $c_b = 10$.

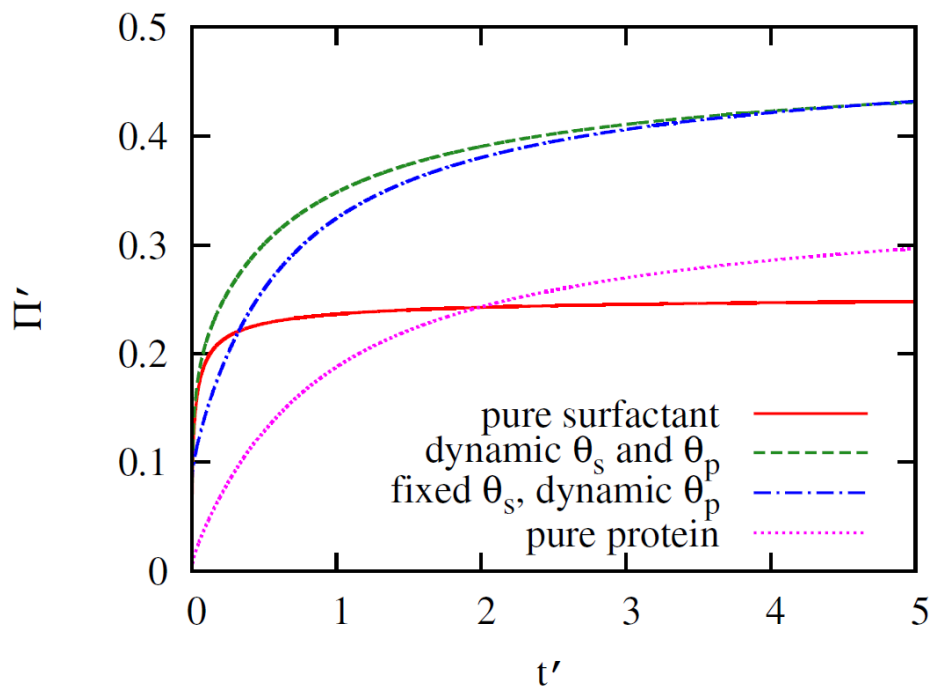


Figure 3: Dimensionless surface pressure as a function of dimensionless time at various protein-surfactant composition using dimensionless parameters of: $\kappa_p = 1.4$, $\kappa_s = 0.219$, $\mathcal{D} = 8$, $\Gamma_m = 17.6$, $c_b = 10$ (solid line: pure surfactant; dashed line: dynamic protein and dynamic surfactant surface concentration; dotted line: dynamic protein and fixed surfactant surface concentration; dashed-dotted line: pure protein).

For a fixed amount of surfactant on the surface (dashed-dotted line), which was set to be the final surface concentration of surfactant in the presence of protein ($\theta_s = 0:0728$), in general, lower surface pressure occurs compared to that obtained from simulation of dynamic concentrations of protein and surfactant on the surface. This happens since the fixed surfactant surface concentration is mostly lower than the dynamic surface concentration, the only exceptions being at very early times and at the final time. Although difficult to resolve on the scale of the graph, at very early time, the surface pressure is higher in the case of fixed surface coverage of surfactant due to finite surfactant concentration on the surface initially. By contrast, in the dynamic case, the surface concentration of surfactant has to grow from zero at very early times. At final time, of course the surface pressure of those both cases will be equal since by that time the dynamic surface concentration of surfactant reaches its final value that is equal to the selected fixed surface concentration.

The graph also indicates that protein concentration on the surface is able to increase (and thereby influence surface pressure) even with the presence of significant surfactant on the surface. Protein with its higher affinity is able to compete with surfactant to adsorb on the surface.

Effect of surfactant concentration on the adsorption

Figure 4 presents the profiles of subsurface and surface concentration of protein and surfactant. The simulations were performed at the following conditions: $K_p = 1.4$, $K_s = 0.219$, $D = 8$, $\Gamma_m = 17.6$, $c_b = 0-100$.

It is obvious in Figure 4 that the surface coverage of surfactant increases with the addition of surfactant in the bulk solution. At early time the surface coverage of surfactant increases dramatically up to a maximum point. Beyond the maximum point, the surface coverage of surfactant decreases due to the presence of protein arriving on the surface. Surfactant reaches its maximum surface coverage faster at higher surfactant bulk concentration. The maximum surface coverage of surfactant with the presence of protein is somewhat lower than the final surface coverage achieved by the adsorption of surfactant on its own. Equation 9 shows that the presence of protein reduces the amount of surfactant adsorbed on the surface. That occurs because there is a smaller denominator on the right hand side of the equation due to the inclusion of protein surface concentration which does not appear in the equation for pure surfactant. This then makes the numerator (i.e. surfactant surface concentration) likewise smaller.

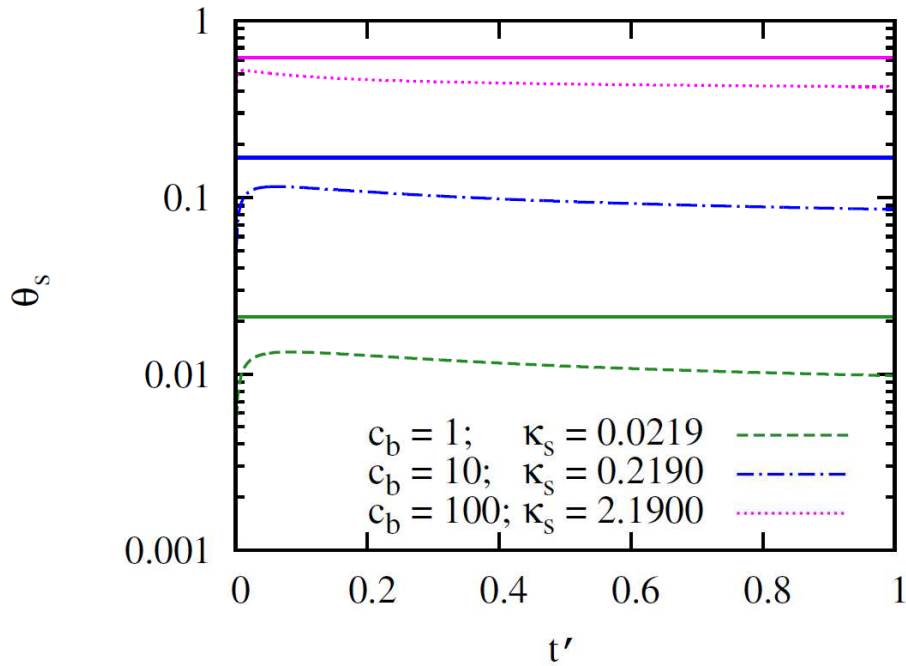


Figure 4: Surface coverage of surfactant as a function of dimensionless time at various bulk concentrations of surfactant where $\kappa_p = 1.4$, $\kappa_s = 0.0219 - 2.19$, $\mathcal{D} = 8$, $\Gamma_m = 17.6$, $c_b = 1 - 100$ (solid line is the final surface concentration of surfactant at respective bulk concentrations in the absence of protein).

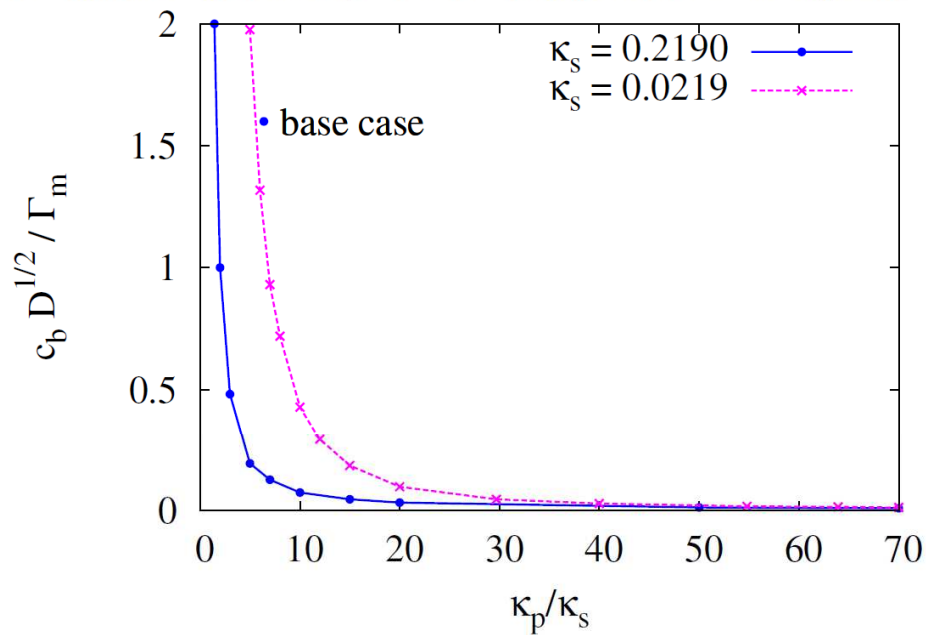


Figure 5: Phase diagram showing the region of surfactant displacement by protein. The parameters used in this simulation range as follows: $\kappa_p = 0 - 15.33$, $\kappa_s = 0.219$, $\mathcal{D} = 1 - 10$, $\Gamma_m = 1 - 1260$, $c_b = 10$ (solid line) and $\kappa_p = 0 - 1.53$, $\kappa_s = 0.0219$, $\mathcal{D} = 1 - 10$, $\Gamma_m = 1 - 200$, $c_b = 1$ (dashed line). The base case was at $\kappa_p = 1.4$, $\kappa_s = 0.219$, $\mathcal{D} = 8$, $\Gamma_m = 17.6$, $c_b = 10$. The displacement of surfactant occurs in the region above and to the right of the curve.

Identification of region where surfactant displacement occurs

A parametric study was carried out to identify the region of surfactant displacement. The result of the parametric study is shown in Figure 5. This parametric study was carried out using parameters in the following ranges: $\kappa_p = 0 - 1.53$, $\kappa_s = 0.219$, $\mathcal{D} = 1 - 10$, $\Gamma_m =$

1—1260, $c_b = 1$ —10. The displacement of surfactant occurs in the region above and to the right of the curve in that figure.

In practical cases of adsorption of mixed protein-surfactant, it is most likely that there is displacement of surfactant by protein. The displacement results in an overshoot of the curve of surface coverage of surfactant. The displacement of surfactant can be avoided when the affinity of protein is not sufficiently large compared to the affinity of surfactant. Small relative diffusivity and large relative capacity also result in the removal of the overshoot. However very significant changes in relative diffusivity and/or relative capacity about our base case values would be needed to eliminate surfactant displacement (taking also our base case $\kappa_s = 0.219$, $\kappa_p = 1.4$ and $c_b = 10$ as considered here).

Figure 5 also shows that the critical protein surface affinity for surfactant displacement to occur is sensitive to the surface affinity of surfactant: data are for $\kappa_s = 0.0219$, $\kappa_p = 0$ —1.53, $D = 1$ —10, $\Gamma_m = 1$ —200, $c_b = 1$. With low (absolute) surfactant affinity, displacement of surfactant is less likely to happen even though the surface affinity of protein is relatively high. Therefore, the boundary between surfactant displacement and no surfactant displacement in the graph depends not only on relative surface affinities, but also depends on the (absolute) surface affinities. A small κ_s needs a massive κ_p/κ_s to displace surfactant, whereas larger κ_s will exhibit surfactant displacement with more modest κ_p/κ_s .

Reducing c_b is also an option for avoiding surfactant displacement, but the most straightforward experimental way of doing that – namely reducing surfactant concentration in the mixture – might impact upon foam quality. Moreover changes in surfactant concentration also affect the value of κ_s and hence the ratio κ_p/κ_s .

4. CONCLUSIONS

Simulations of dynamics of adsorption of mixed protein-surfactant have been carried out using base parameters of the adsorption of mixed BLG protein and C10DMPO non-ionic surfactant. The simulation studies the displacement of surfactant by protein and the effect of surfactant bulk concentration on the adsorption. This study also reports the comparison between the simulation results and the experimental data obtained from literature. Parametric studies were also conducted to examine the effect of protein affinity and the effect of molecular size on the adsorption.

The simulation results show that protein arrives on the surface at a later time than surfactant. At early time surfactant dominates the surface. However, as the protein reaches the surface, it tends to replace the surfactant and reduces the concentration of surfactant on the surface. Surfactant, therefore reaches a maximum surface concentration following which it depletes in competition with protein. There is also less protein adsorbed with more surfactant in the bulk solution. The smaller amount of protein adsorbed on the surface moreover results in more protein molecules in the subsurface. The displacement of surfactant is more likely to occur at high relative diffusivity and low surface affinity (relative to protein affinity) of surfactant. Higher surface coverage is also achieved with higher surface affinity of surfactant.

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