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Interfacial rheology of mixed layers of food proteins and surfactants

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ABSTRACT

Mixed protein–surfactant adsorption layers at liquid interfaces are described including the thermodynamic basis, the adsorption kinetics and the shear and dilational interfacial rheology. It is shown that due to the protrusion of hydrophobic protein parts into the oil phase the adsorption layers at the water–hexane interface are stronger anchored as compared to the water-air surface. Based on the different adsorption protocols, a sequential and a simultaneous scheme, the peculiarities of complexes between proteins and added surfactants are shown when formed in the solution bulk or at a liquid interface. The picture drawn from adsorption studies is supported by the findings of interfacial rheology.

1. Introduction

The conformational changes of protein molecules due to the interaction with surfactants in an aqueous bulk solution are different from those at an interface. In the aqueous bulk the resulting complexes take a conformation that has a maximum of the hydrophobic groups screened by hydrophilic groups toward the solvent water. This conformation is certainly a function of the architecture of the amino acids of the protein and the kind of interacting surfactant. Any changes in the solvent properties, such as by adding salt or ethanol, the pH and/or temperature variations, can lead to changes in the structure of the resulting protein/surfactant complexes.

Adsorbed at an interface, proteins usually unfold and take an optimum conformation such that the hydrophobic parts of the molecule attach at the interface while the hydrophilic parts get in an optimum contact with the aqueous phase. When surfactants are added to the system, they start interacting with the protein molecules in their adsorbed state, which can lead to complexes of quite different structure, i.e., providing the interface with different properties.

The theoretical and experimental tools made available during the recent five years provide a better access to more details of mixed protein/surfactant adsorption layers. Emphasis was paid to the route of adsorption (simultaneous versus sequential route) as well as to the kind of interface (water/air and water/oil interface).

This contribution starts with a brief overview of the most recent state of art of the theoretical description of mixed adsorption layers. Then, the progress made in dilational and shear rheology of interfacial layers is discussed, including a protocol that allows a sequential adsorption route for a pre-adsorption of proteins and a subsequent adsorption of surfactants. Finally, most recent experimental findings are summarized with emphasis on peculiarities in the water/oil interfacial properties.

2. Thermodynamic and Kinetic Models of Adsorption Layer

The various theoretical models for the adsorption behaviour of proteins and protein-surfactant mixtures were summarized recently in [1–3]. During the last decade these models have been refined and we want to show the most recent state of the art briefly here.

For mixture of a protein with a non-ionic surfactant the approximation was used that the molar area of a solvent molecule (ω_S) is almost identical to the area occupied by one segment of an adsorbed protein molecule (area increment ω_{0P}). On the basis of a Frumkin-type

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adsorption model this leads to the following equation of state for protein/non-ionic surfactant mixtures [2]:

$$-\frac{\Pi\omega_0^*}{RT} = \ln(1-\theta_P-\theta_S) + \theta_P(1-\omega_0/\omega_P) + a_P\theta_P^2 + a_S\theta_S^2 + 2a_{PS}\theta_P\theta_S, \quad (1)$$

where the quantity $\omega_0^* = (\omega_{0P}\theta_P + \omega_{0S}\theta_S)/(\theta_P + \theta_S)$ accounts for small differences between ω_{0P} and the maximum possible molar area of the surfactant molecule ω_{0S}, Π is the surface pressure, R is the gas law constant, T is the temperature, a_P, a_S and a_{PS} are the parameters relevant to the pair interactions between protein molecules, surfactant molecules and protein-surfactant cross-interactions, respectively.

It is assumed that protein molecules can adsorb in a number of states n of different molar area, varying between a maximum ω_{max} and a minimum molar area ω_{min}. The quantity $\Gamma_P = \sum_{i=1}^{n}\Gamma_{i,P}$ is the total adsorption of proteins in all n states ($1 \le i \le n$). $\theta_P = \omega_P\Gamma_P = \sum_{i=1}^{n}\omega_P\Gamma_{i,P}$ is the total surface coverage by protein molecules. In this model, the protein molecules have the average interfacial molar area ω_P with $\omega_i = \omega_1 + (i-1)\omega_0$, $\omega_1 = \omega_{min}$ and $\omega_{max} = \omega_1 + (n-1)\omega_0$.

The adsorption isotherm of protein molecules for mixtures of a protein with a non-ionic surfactant was obtained in [2,3]:

$$b_{j,P}c_P = \frac{\omega_P\Gamma_{j,P}}{(1-\theta_P-\theta_S)^{\omega_1/\omega_P}}\exp\left[-2a_P\left(\omega_{1,P}/\omega_P\right)\theta_P - 2a_{PS}\theta_S\right]. \quad (2)$$

Here θ_S is the surface coverage by surfactant molecules. Moreover, it was assumed that all the adsorption equilibrium constants for the protein $b_{j,P}$ are the same.

Eqs. (1) and (2) assume that the adsorption takes place as a single layer. With increasing bulk protein concentration c_P, many proteins tend to form bilayers or multilayers at liquid interfaces. To describe such a multilayer adsorption it was assumed that the coverage of any subsequent (jth) layer is proportional to the adsorption equilibrium constant b_{P2} and the coverage of the previous layers:

$$\Gamma \approx \Gamma_P\sum_{j=1}^{r}\left(\frac{b_{P2}c_P}{1+b_{P2}c_P}\right)^{j-1}. \quad (3)$$

This includes also the assumption that the formation of any additional layer does not affect the surface pressure significantly, as discussed in detail in [1].

Many experiments have shown that up to a certain protein concentration c_P^*, the surface tension decreases significantly and then levels off, although the adsorption further increases. This was explained by a condensation (aggregation) of the protein molecules in the surface layer. With Γ^* and Π^* being the respective values of adsorption and surface pressure corresponding to this 'critical' bulk concentration c_P^*, it is assumed that the distribution of protein molecules over the conformations and the adsorption isotherm for protein are the same as in the 'pre-critical' regime, while the equation of state becomes dependent on a new parameter n_a, which is the aggregation number of protein molecules:

$$\Pi = \Pi^*\left(1 + \frac{1}{n_a}\frac{\Gamma-\Gamma^*}{\Gamma^*}\right). \quad (4)$$

Eqs. (2)–(4) refer to the protein 'subsystem' only. To account for the presence of the surfactant, the equations have to be coupled with the adsorption isotherm for the surfactant 'subsystem'. In particular, for a Frumkin-type surfactant [4] we have:

$$b_Sc_S = \frac{\theta_S}{(1-\theta_P-\theta_S)}\exp[-2a_S\theta_S - 2a_{PS}\theta_P]. \quad (5)$$

Here b_S is the adsorption equilibrium constant for the surfactant molecules. In dedicated experiments it was shown that the surfactant molar area ω_S and the corresponding adsorption Γ_S depend on the surface pressure Π and the total surface coverage θ [5]:

$$\omega_S = \omega_{S0}[1-\varsigma\Pi(\theta_P+\theta_S)], \quad (6)$$

with $\theta_S = \Gamma_S\omega_S = \Gamma_S\omega_{S0}[1-\varsigma\Pi\theta]$. The parameter ς is called the intrinsic compressibility of surfactant molecules in the surface layer and can be interpreted for example by changes in the tilt angle of the adsorbed molecules upon surface layer compression, accompanied by an increase in the surface layer thickness. Other models for the surfactant subsystem were developed; in particular, mixtures of a protein with reorientable surfactants were considered in [6].

If the adsorption of protein molecules takes place in absence of any surfactant then all parameters relative to the surfactant vanish from Eqs. (1)–(6).

For mixtures of a protein with an ionic surfactant the corresponding theoretical equations are quite similar to those obtained for non-ionic surfactants; however, we typically do not have only a competitive adsorption between the two single compounds but also between protein-surfactant complexes, formed due to electrostatic interaction, and any free (unbound) surfactant molecules [3]. Assuming a protein molecule has m ionized groups, it can interact with up to m counter-charged ionic surfactant molecules to form complexes. The corresponding equation of state of the surface layer for the protein–surfactant complex remains the same as Eq. (1) with the subscript P now referring to the protein/surfactant complex, while the adsorption isotherm for this complex differs from Eq. (2) only in that the left-hand side becomes $b_{1,P}(c_P^m c_S)^{1/(1+m)}$ to account for the complex formation. Also, for the ionic surfactant unbound by the protein, assuming the Frumkin ionic model is valid, the left-hand side of Eq. (5) becomes $b_S[c_S(c_S+c_C)]^{1/2}$ (see [7]), where c_c is the inorganic (1:1) salt (or counterion) concentration.

Based on these thermodynamic models, the adsorption kinetics and dilational visco-elasticity can be determined, assuming that the transport of molecules to and from the interface is based on diffusion. The temporal evolution of the adsorption $\Gamma_k(t)$ of each component k is governed by a set of Fick equations with the corresponding model equations used as the boundary conditions at the interface. The implementation of this approach could be based either on the solution of the corresponding Ward and Tordai-type equations [8] as shown in [9], or on direct numerical integration similar to what was done in [10] for mixtures of two surfactants. The resulting mathematics is too extensive to be presented here; the reader can refer to the mentioned original work for the detailed explanation of the computation procedures.

The surface dilational visco-elasticity is a quantity determined by the diffusion controlled exchange of matter and the corresponding equation of state, and hence an independent source of information for the dynamic behaviour of interfacial layers. For mixed adsorption layers a rather complex expression for the visco-elasticity modulus can be derived, as discussed in detail in [11]. This approach was successfully used for the description of the rheological characteristics of mixtures of the whey protein β-casein (BCS) with the anionic sodium dodecyl sulphate (SDS) and cationic dodecyl trimethyl ammonium bromide (DoTAB) surfactants [4].

3. Experimental tools

3.1. Dilational Rheology by Oscillating Drop Method

In recent years, several interesting studies on interfacial rheology were reported, mostly based on oscillating bubble/drop methods. This methodology has been implemented both on drop profile and capillary pressure tensiometers, and is available for most commercial instruments [12]. In the range of low frequencies (<~0.2 Hz), one can determine the dynamic surface elasticity from measuring the respective