



Historical perspective

Thermodynamics, interfacial pressure isotherms and dilational rheology of mixed protein–surfactant adsorption layers

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ABSTRACT

Proteins and their mixtures with surfactants are widely used in many applications. The knowledge of their solution bulk behavior and its impact on the properties of interfacial layers made great progress in the recent years. Different mechanisms apply to the formation process of protein/surfactant complexes for ionic and non-ionic surfactants, which are governed mainly by electrostatic and hydrophobic interactions. The surface activity of these complexes is often remarkably different from that of the individual protein and has to be considered in respective theoretical models. At very low protein concentration, small amounts of added surfactants can change the surface activity of proteins remarkably, even though no strongly interfacial active complexes are observed. Also small added amounts of non-ionic surfactants change the surface activity of proteins in the range of small bulk concentrations or surface coverages. The modeling of the equilibrium adsorption behavior of proteins and their mixtures with surfactants has reached a rather high level. These models are suitable also to describe the high frequency limits of the dilational viscoelasticity of the interfacial layers. Depending on the nature of the protein/surfactant interactions and the changes in the interfacial layer composition rather complex dilational viscoelasticities can be observed and described by the available models. The differences in the interfacial behavior, often observed in literature for studies using different experimental methods, are at least partially explained by a depletion of proteins, surfactants and their complexes in the range of low concentrations. A correction of these depletion effects typically provides good agreement between the data obtained with different methods, such as drop and bubble profile tensiometry.

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1. Introduction

Mixed systems of proteins and low molecular weight surfactants play a crucial role and are very important in many technologies, such as food industry, cosmetics, pharmacology and medicine, coating processes and oil recovery. A good example is the stabilization of the structure of many emulsions and foam-based food products which contain mixtures of proteins and surfactants. Important aspects regarding mixed protein/surfactants solutions are: their capability to lower the interfacial tension and the rate of its lowering; the adsorbed amount; the possibility to change their conformation during and after adsorption; the thickness of the adsorbed layer; the dilational and shear elasticity and viscosity; and the interaction between the adsorbed molecules. The physicochemical properties of the mixtures of polymers and proteins with ordinary surfactants at liquid/gas and liquid/liquid interfaces were reviewed in [1–24], while there exist hundreds of original publications dealing with mixtures of proteins (or polymers) with surfactants of various nature. Among these, the publications [25–96] with important experimental and theoretical results for such mixed solutions are especially worth mentioning.

There are several experimental methods and techniques which can give information about these mixtures, for example optical methods, such as ellipsometry to determine the layer thickness or spectroscopic methods to determine lateral mobility and conformational changes. Very important data regarding the values of the static and dynamic interfacial tension of protein/surfactant mixed solutions can be obtained using various experimental techniques. The dynamics of interfacial tension is studied with regard to the dilational and shear interfacial deformation, which provides insight into the viscoelastic rheological characteristics of mixed adsorption layers. The interfacial rheology provides the best information on mixed adsorption layers at fluid interfaces. Small local changes or fluctuations in the interfacial area are essential for the stabilization of emulsions and foams, due to ongoing dynamic processes in these systems.

The conformational changes of protein molecules due to the interaction with surfactants in an aqueous bulk solution can be different from those at an interface. The addition of surfactants and increase of their concentration can lead to the formation of complexes with quite different structure and influence on the adsorption layer composition. Any changes in the solvent properties, such as the amount of added salt, the pH and temperature variations, also can lead to changes in the structure of the protein/surfactant complexes. Surfactant molecules can gradually displace the protein or polyelectrolyte molecules from the interfacial layers due to a competitive adsorption mechanism or a more complex orogenic displacement as it was discussed in [2–8,10,14,34,35,65,66,68,71].

Many studies have shown that the influence of ionic surfactants on the properties of mixtures is essentially different from that of non-ionic surfactants, because ionic surfactants can interact with the free charges existing in the protein molecules. This results in a significant hydrophobization of the complexes as compared to the individual protein molecules.

To form mixed protein/surfactant interfacial layers two different experimental routes were proposed: a sequential and a simultaneous adsorption [91,92]. These two routes of adsorption layer formation provide important information about the structure of protein/surfactant mixed interfacial layer. The properties of such layers at the solution/oil interface can differ significantly from those at the solution/air interface. This is mainly caused by the specific interaction between the hydrophobic parts of the protein molecules and the surfactant's hydrocarbon chains with the oil molecules [1,2,13,23,24,69,73,83,87,90,96,91,95]. Differences in orientation, molecular areas, or the degree of unfolding of the protein molecules can be expected at solution/oil interfaces. In [97] a theoretical model was developed to describe the adsorption of surfactants at aqueous solution/oil interfaces which took the mentioned influences into account. This model is presented here in a form

generalized for the adsorption of protein/surfactant mixtures at the solution/oil interface.

Due to the practical importance of polyelectrolytes and proteins adsorbed at fluid interfaces there is significant progress in the development of theoretical models for the equilibrium and dynamic behavior of their adsorption layers. A theory for the adsorption from mixed solutions was developed in [74,75] for mixtures of a protein with non-ionic and ionic surfactants, respectively. All these theoretical models were based on the theory for individual protein solutions presented in [98]. This theory makes it possible to describe the interfacial tension, adsorbed amount, adsorption layer thickness, and the dilational characteristics in a wide concentration range in good agreement with experimental data. The theoretical models proposed for the adsorption of mixtures of proteins and surfactants and the refined experimental methods developed mainly during the recent 10 years provide much more details of the resulting mixed adsorption layers at solution/air as well as solution/oil interfaces [12,15,22,74,75,78,80–90,95,96].

This review starts with the theoretical description of protein and protein/surfactant mixed adsorption layers. Then, an overview of recent experimental results is presented which emphasizes the peculiarities observed at solution/oil interfaces. Also the progress achieved in understanding the dilational viscoelasticity of mixed interfacial layers is discussed while shear rheology is not included here.

2. Theory

2.1. Individual protein solutions

For protein solutions the thermodynamic adsorption models are comparatively simple when compared with statistical models, and can be used for the formulation of the equations of state and adsorption isotherms. The thermodynamic model for the adsorption of protein used in this review was proposed in [98]. In what follows, we present the main equations of this theory and its subsequent extensions.

The equations of state and adsorption isotherm for the components in a mixture derived from the expressions for the chemical potentials in the solution bulk and in the interfacial layer are [98]:

$$\Pi = -\frac{RT}{\omega_0} \left[\ln \left(1 - \sum_{i \geq 1} \theta_i \right) + \ln f_0^s \right] \quad (1)$$

$$K_i x_i = \frac{\theta_i f_i^s}{\left(1 - \sum_{i \geq 1} \theta_i \right) (f_0^s)^{n_i}} \quad (2)$$

In these expressions the subscript “i” refers to the respective component of the mixture. Note, in the present model different adsorption states of molecules are considered as different components. Here, Π is the interfacial pressure, R is the gas law constant, T is the temperature, ω_0 and ω_i are the molar area of the solvent and component or state i , Γ_i is the adsorption, $\theta_i = \Gamma_i \omega_i$ is the interfacial coverage, x_i^s is the molar fraction, $n_i = \omega_i / \omega_0$ and the superscript ‘s’ refers to the interface. The parameters $K_i = (x_i^s / x_i^\alpha)_{x_i^\alpha \rightarrow 0}$ are the distribution coefficients at infinite dilution. For non-ideal enthalpy in the framework of the regular solution theory the activity coefficients f_i^{sH} are determined by the expressions:

$$RT \ln f_k^{sH} = \sum_i \sum_j \left(A_{ik}^s - \frac{1}{2} A_{ij}^s \right) \theta_i \theta_j \quad (3)$$

The coefficients $A_{ij}^s = U_{ij}^s + U_{ji}^s - 2U_{ij}^s$, U_{ii}^s and U_{ij}^s are the energies of interaction between the species, and the superscript ‘H’ refers

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