

2. THERMODYNAMICS OF ADSORPTION OF SURFACTANTS AT THE FLUID INTERFACES

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2.1. Introduction

The thermodynamics and dynamics of interfacial layers have gained large interest in interfacial research. An accurate description of the thermodynamics of adsorption layers at liquid interfaces is the vital prerequisite for a quantitative understanding of the equilibrium or any non-equilibrium processes going on at the surface of liquids or at the interface between two liquids. The thermodynamic analysis of adsorption layers at liquid/fluid interfaces can provide the equation of state which expresses the surface pressure as the function of surface layer composition, and the adsorption isotherm, which determines the dependence of the adsorption of each dissolved component on their bulk concentrations. From these equations, the surface tension (pressure) isotherm can also be calculated and compared with experimental data. The description of experimental data by the Langmuir adsorption isotherm or the corresponding von Szyszkowski surface tension equation often shows significant deviations. These equations can be derived for a surface layer model where the molecules of the surfactant and the solvent from which the molecules adsorb obey two conditions:

- (i) not interaction between adsorbed molecules
- (ii) equal molecular areas at the interface.

In a number of cases, deviations from the Langmuir behaviour can be explained by a break of the former condition, for example by the presence of interactions between adsorbed molecules [1-14] or differences in the molecular areas [15-19].

The adsorption isotherm and the equation of state for adsorption layers proposed by Frumkin [1] describe the adsorption of low molecular weight surfactants rather well, provided the systems to be described deviate only slightly from an ideal (Langmuir) behaviour. Reasonable agreement between theory and experiment was found when interactions between all components in the system were taken into consideration [13, 14, 20]. However, the intermolecular interaction parameters which can be estimated from a comparison of experimental data with the isotherms do not always correlate with the properties of the surfactants or solvents. Often they have to be regarded simply as matching parameters. A better understanding of the physical reasons for deviations between experimental data and theoretical models should result from new models for the adsorption isotherm and the corresponding equation of state. In our opinion, such new models should account for the effects of, e.g., the size of the surfactant or protein molecules, molecular reorientation within the surface, dimerisation, cluster formation, etc.

Differences in the molecular area are of obvious relevance in mixed monolayers, where larger molecules have a larger partial molar area than smaller ones. Such differences lead to a situation where the smaller molecules are increasingly preferentially adsorbed with increasing surface pressure, even in the absence of any surface interactions [16]. In adsorption layers consisting of a single surface-active compound similar effects can occur if, due to the asymmetry in different adsorption states the molecules can occupy different areas [3, 4, 15, 19, 21, 22]. The fraction of molecules which are in the state characterised by a particular partial molar area depends on the surface pressure. In a thermodynamic study by Joos and Serrien [21] it was shown that if the molecule possesses, say, the two modifications 1 and 2, with different partial molar surface areas ω_1 and ω_2 (in absence of intermolecular interactions) their ratio in the surface layer obeys the equation

$$\frac{x_2^s}{x_1^s} = K_{12} \exp\left[\frac{\Pi(\omega_1 - \omega_2)}{RT}\right], \quad (2.1)$$

where K_{12} is a constant, R is the gas law constant, T is the temperature, $\Pi = \gamma_0 - \gamma$ is the surface pressure, γ_0 and γ are the surface tension of solvent and solution, respectively, $x_i = m_i / \sum m_i$ are the molar fractions, and m_i are the numbers of moles of the i^{th} state. If $\omega_1 > \omega_2$, then with increasing Π the concentration of modification 2 in the surface layer increases. Equation (2.1) is the analytical expression for the general physico-chemical principle of Braun-Le Châtelier, applied by P. Joos [19] to adsorption layers of surfactants or proteins. It shows that the surface pressure acts as a self-regulation mechanism of the adsorption layer. This model cannot only be used in many cases as an alternative to the known equations based on the intermolecular interaction concept, but it can also predict new effects [21-26]. Recently it was shown [22, 23] that a "superdiffusion" kinetics of octylphenyl polyethylene glycol ethers may be described by a model assuming two different orientations of the polyethylene glycol chain, i.e. flat and normal oriented molecules, depending on the interfacial pressure. Corresponding equations for the adsorption and surface layer state were derived recently for surfactants and proteins displaying a change in the partial molar area with increasing surface pressure due to orientation changes [24-31].

Thus, deviations from the ideal Langmuir isotherm can be caused both by intermolecular interactions, which result in an enthalpy of mixing, and by area differences between molecules, which produce a non-ideal entropy of mixing [18]. For a simple case where the interactions are of the Frumkin type and the partial molar areas of solvent and surfactant are constant the entropic effect of area differences results in typical features of macromolecular adsorption, e.g., a steep initial increase of adsorption ("high affinity" adsorption) and a very slow rise once the surface is approximately half filled [18].

These estimates oversimplify both the enthalpic effects of interaction and the entropic effects of size differences. First, interactions between adsorbed molecules as described by Frumkin type models do not allow for the formation of dimers or larger aggregates in the surface layer which can occur in practice. Equations of state for monolayers showing such two-dimensional aggregation have been proposed for various models [32-42]. Second, proteins differ from surfactants in more than just the size. For proteins, surface denaturation can take place, leading to their unfolding at the surface, at least at low surface pressures. The partial molar surface area for proteins, in contrast to surfactants, is large and variable. The interrelation between the

protein denaturation process at the surface and the activity of the solvent molecules (typically water) was demonstrated by Ter-Minassian-Saraga [43], while Joos [17] showed that the degree of surface denaturation decreases with increasing surface pressure. Joos and Serrien [21], in deriving Eq. (2.1), demonstrated that the surface pressure controls both the composition and the thickness of a protein surface layer. This concept was further developed for an arbitrary number of different modifications of protein molecules at a surface [26].

Various models discussed so far have all been formulated in the framework of a two-dimensional solution theory among which the equation proposed by Butler [44] is the earliest example. One of the aims of this chapter is to demonstrate the general principle of deriving equations of state and adsorption isotherms on this basis. By this method most of the existing relationships can be obtained, for ideal and non-ideal surface layers of single or mixed surfactants. Equations will also be derived from this general principle resulting from models which consider interfacial reorientations [24-26] or aggregations [35, 41]. Moreover, introducing relatively simple corrections (taking into account the mean activity of ions [2, 5] and introducing the electrochemical potential [45-47]) one can apply this approach also to ionic surfactants and polyelectrolytes. The adsorption behaviour of the solutions of proteins and their mixtures with surfactants can also be satisfactorily described in the framework of this general approach [26]. In this chapter we analyse the dependence of the shape of isotherms on the parameters of the theoretical model. Also selected examples will be described to demonstrate the principle application of these new models to experimental surface tension isotherms for particular surfactants. However, a systematic analysis of the adsorption characteristics of various surfactants and complete homologous series will be presented in Chapter 3.