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Fast estimation of the equilibrium adsorption constants of ionic surfactants with account for ion-specific effects

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HIGHLIGHTS

- Knowledge on the surfactant's molecular structure.
- Energy of adsorption on the surfactant's hydrophilic head tabulated.
- Calculation of the equilibrium adsorption constant.

GRAPHICAL ABSTRACT
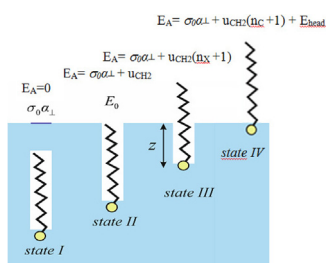
ABSTRACT

Understanding the factors contributing to the adsorption of surfactants to interfaces, without the need to carry out lengthy and meticulous experiments on every new surfactant system, is a pressing need in both industrial and academic research. A large group of the most widely used surfactants have aliphatic chains for their hydrophobic tails. Yet the variations in the length of the tail, the nature of the hydrophilic group, and the nature of the counterion (for ionic surfactants) make the exact adsorption capacity hard to predict.

We present here a simple procedure for the fast and accurate estimation of the adsorption capacity of this large collection of surfactants by parameterizing the separate contributions of their components. We report the determination of the contribution from the polar heads by a model where it is the only free parameter and linear fits to experimental data. Uncertainty from experimental variations is decreased by fitting the results to another linear dependence for a series of homologous surfactants with different tail lengths where the incremental contribution of the tail is well established. The contributions from eight different polar heads (DMPO, DEPO, SO_4^-, OH, COOH, COO^-, NH_3^+, and $N(CH_3)_3^+$) are tabulated, as are contributions from 15 counter-ions (for ionic surfactants). The results allow immediate estimation of the adsorption strength of nearly 300 surfactant systems, for many of which the adsorption constants are not known. Comparisons of the calculated constants of randomly selected surfactant systems against their experimentally measured values yielded deviations of only about $3.5 \pm 2\%$. Such quick calculation of a surfactant's adsorption constant based only on its molecular structure is a powerful tool for quantitative screening and cost-benefit analysis of surfactants for designing many industrial processes, including flotation of mineral particles, pharmaceutical foam fractionation, and de-emulsification in the oil industry. We point out techniques for expanding this method to other types of surfactant systems as well.

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1. Introduction

It is well-known that water-soluble surfactants adsorb on the *air/water* (or *oil/water*) interface thus reducing the surface/interfacial tension. The process is usually described by a proper model-dependent equation of state coupled with interpretation of an adsorption isotherm to determine the values of the model parameters [1–5]. However, multiple adsorption models exist and researchers are often confused which one is suitable for their particular investigation [6,7]. For example, when the model of Frumkin is applied, it often results in negative values of the interaction parameter, corresponding to "van der Waals repulsion" between the adsorbed molecules [6]. The latter result is inconsistent because this parameter can have only positive values according to the theory [1]. Another common challenge is the large number of the matching parameters in the adsorption models, resulting in many "excellent" but non-unique "agreements" between experiment and theory, each one with different values for the same adsorption parameters. Landau noticed: "Any not too wild theory can be fitted to the experimental data, provided that it contains enough undetermined constants". An analysis of the basic adsorption models (Langmuir–Frumkin and Volmer) was made in Refs. [8,9] indicating how their non-realistic assumptions lead to significant over-estimation of the cross-sectional area of a surfactant on the fluid interface compared to experiments. (The model of Langmuir–Frumkin assumes localized adsorption of the surfactant molecules on the interface boundaries (air/water and oil/water), while in reality molecules move tangentially once they are adsorbed. The model of Volmer assumes non-localized adsorption, however, it is formulated for adsorption on a line, instead of on a surface.) The model of Helfand–Frisch–Lebowitz (HFL) [9,10] was proclaimed as the most realistic one as it assumes rigid discs floating on a fluid interface (air/water and oil/water). The latter was additionally improved in Ref. [9] by including a Baxter sticky potential [11]. Yet, even this most realistic adsorption model [9] operates with 4 free matching parameters, which still gives some non-determinacy of the results. For this reason new ways for decreasing the number of the matching parameters were sought in the literature [12]. The most important parameter, which is responsible for the adsorption capacity of one surfactant molecule, is its equilibrium adsorption constant, which always has been a matching parameter in every adsorption model.

We present, in this work, a procedure for the calculation of the equilibrium adsorption constant of simple surfactant molecules at the *air/water* interface. It is based on the theories of Ivanov proposed in Refs. [8,9,13] which account for the effect of counterions and contain only two matching parameters for the contributions from different parts of a molecule (the contribution from the hydrophilic head and the incremental contribution from methylene groups in the hydrophobic tail). The effect of counter-ions (for ionic surfactants), which is independent of the type of surfactant, has been determined previously. Contributions from incremental length of the aliphatic tail have been calculated before, but we find that value correlates with the value of the polar head contribution. Here we use novel analysis to determine the contribution of the polar head and corresponding adsorption energy per methylene group, as the only free parameters, which can be determined from linear fits to experimental data, within the limit of the latest advances of the Davies adsorption model [8,9,13,14]. By using a linear fit over a series of homologous surfactants, we eliminated the effects of experimental variations, thus tabulating the adsorption energy of a number of hydrophilic heads and the related adsorption energy per methylene group from the surfactant's hydrocarbon tail. From these tabulated values one can easily calculate the equilibrium adsorption constant of both ionic
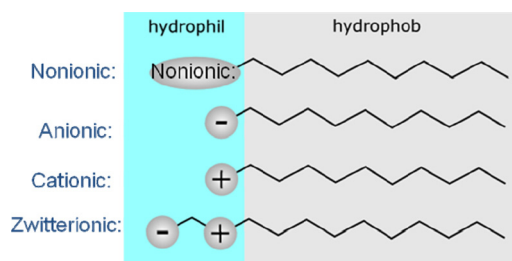

Fig. 1. Basic types of surfactant molecules with a polar head (left) and a straight hydrocarbon tail (right), which readily adsorb on the air/water or oil/water interfaces.

and nonionic surfactants. We propose ways in which the technique could be extended to other classes of surfactants which would enable making an extensive database of different surfactant molecules and their corresponding equilibrium adsorption constants. The latter can be used to predict the effect of surfactants in the design of industrial solutions related to the stability of foams and emulsions in foods, oil extraction, flotation of mineral particles, etc.

2. Theory

Shown in Fig. 1 are the basic types of surfactant molecules consisting of a polar head and a straight aliphatic hydrocarbon tail. Once the surfactant is dissolved in water its molecules diffuse everywhere in the aqueous space.

When they touch the air/water or oil/water interface, the hydrocarbon tail protrudes across the interface in the hydrophobic phase thus reducing its energy. In such a way the surfactant displaces a certain number of surface water molecules, which become bulk water molecules resulting in additional reduction of the free energy of the system. The reduction of the energy of the system by means of adsorption of one molecule is called adsorption energy. The hydrophilic head has a certain contribution to the overall adsorption energy as well. The larger the adsorption energy, the stronger the surfactant is. In this way the adsorption energy can be used as a measure for the adsorption capacity of a certain surfactant. However, the adsorption energy is present in every adsorption model by means of the equilibrium adsorption constant. For non-ionic surfactant molecules (no charge) the following relation between the adsorption energy and the equilibrium adsorption constant exists [13]:

$$K_s = \delta_s \exp\left(\frac{E_A}{k_B T}\right) \qquad (1)$$

where K_s is the equilibrium adsorption constant (has units of length), $\delta_s = l_{CH_2}/(u_{CH_2}/k_B T)$ [13] is the adsorption length, $l_{CH_2} = 0.126$ nm is the length of one CH_2 group, $u_{CH_2}/k_B T$ (which has a value close to unity) is the dimensionless contribution to the adsorption energy of one methylene group in the tail, k_B is Boltzmann constant, and T the is absolute temperature, E_A is adsorption energy of one surfactant molecule. Eq. (1) can be presented in the form:

$$\ln \frac{K_s}{\delta_s} = \frac{E_A}{k_B T} \qquad (2)$$