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How to determine the adsorption energy of the surfactant's hydrophilic head? How to estimate easily the surface activity of every simple surfactant?

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ABSTRACT

A definite way to determine the adsorption energy of the surfactant's hydrophilic head on the air water interface is presented. For this purpose, the Davies adsorption theory and the most advanced version of Helfand–Frish–Lebowitz adsorption theory were applied to the surface tension isotherms of homologous series of sodium alkyl sulfate ($CnH_{2n+1}SO_4Na$, $n = 7–12$), thus deriving the equilibrium adsorption constant, the cross-sectional area of the surfactant molecule, the interaction coefficient and the cohesion constant versus the number of the carbon atoms into the alkyl sulfate molecule. Thus, the total adsorption energy of each particular homolog was calculated in line with the latest development of the adsorption theory, thus calculating the dimensionless adsorption energy of the hydrophilic head E_{head}/k_BT. In our particular case (SO_4^-) we calculated $E_{head}/k_BT = -2.79$, which indicates the strong propensity of the SO_4^- to be surrounded by water molecules. The procedure for calculation E_{head}/k_BT does not depend on the charge of the hydrophilic head. Similarly, we calculated E_{head}/k_BT of another six well known in the literature hydrophilic heads (COOH, OH, DMPO, DEPO, $N(CH_3)_3^+$, and NH_3^+), indicating that the adsorption energy of the CH_2 group depends slightly on the type of the hydrophilic head, but it affects substantially the adsorption energy of the whole surfactant molecule. Finally, we defined and validated a parameter called adsorption capacity of surfactants with simple molecular structure, for easy estimation of their surface activity. Linear dependence between the CMC of ionic surfactants and their adsorption capacity was established.

1. Introduction

The adsorption of amphiphilic molecules on air/water or oil/water interfaces is an old problem, which has been intensively investigated and written about in the literature for many years. Thus, variety of different adsorption models appeared in the literature [1–14] – they usually describe the surface activity of the surfactants (ionic and nonionic) by four parameters – the equilibrium adsorption constant, the cross-sectional area of surfactant molecule on the interphase boundary, the intermolecular interaction coefficient, and one additional parameter (valid only for ionic surfactants), whose physical meaning depends on specificity of the applied adsorption model. They are usually matching parameters, which are obtained by means of application of one of the adsorption models on the surface tension isotherm of given surfactant. However, different adsorption models give often different values of the same parameters, when they are applied to the same adsorption isotherm. For this reason they often contradict trying to get rid of the problem by additional modeling and assumptions. Therefore, we need to know if there is any definite way to easily estimate the surface activity of the different surfactants. If yes, we do not need any experimental data to choose the best surfactant among many of them. With this work, we certainly state that such easy estimation of the surfactants' surface activity is possible.

We can state after careful analysis of many surface tension isotherms, that the most variable adsorption parameter of the surfactants with simple molecular structure is the equilibrium adsorption constant (see Section 2), which is directly related with the adsorption energy of the surfactant molecule. Hence, the surface activity of every surfactant is mostly related with its adsorption energy. The latter is related with the structure of the surfactant's molecule. We must note that this very old idea dating back to Traube's rule from 1890s [15]. It states empirically that for every extra CH_2 group in the surfactant molecule, the surface

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activity approximately triples. The most, which the scientists achieved on this topic [7] during the whole 20th century, was to derive the value of the adsorption energy per methylene group in the surfactant's hydrocarbon tail, thus estimating how the surface activity of the surfactant molecule should increase upon the gradual lengthening of the hydrocarbon tail. Fortunately, significant advance of the theory of the equilibrium adsorption constant was achieved recently by Ivanov et al. [1]. They succeeded to take into consideration the effect of the terminal CH_3 group of the surfactant molecule and the displaced surface water by the surfactant during its adsorption, on the equilibrium adsorption constant. Only the energy of adsorption of the surfactant's hydrophilic head remained as undetermined parameter, which should be investigated in future. Moreover, the problem about the energy of the adsorption of the surfactant's hydrophilic head remained somehow omitted in the literature nevertheless of its importance. This is one of the main tasks of the present work. We show here bellow how to determine the energy of the adsorption of the hydrophilic head of the surfactant molecule on air/water interface. For this purpose we use combination of the adsorption models of Davies [7] and Ivanov (advanced model of Helfand–Frish–Lebowitz) [1,13], which in our opinion are the most realistic ones. We apply our approach to find out the adsorption energies of seven different hydrophilic heads, thus tabulating them. Finally, we show useful for us procedure for easy estimation with precision of about 98.5% the surface activity of every surfactant with simple molecular structure.

2. Theory

We will make s short presentation of the last development of the theory of surfactant adsorption and surfactant's equilibrium adsorption constant [1,13,14,16]. Therefore, we will describe our procedure about the calculation of the energy of adsorption of surfactant's hydrophilic head.

2.1. Adsorption model of Ivanov based on Helfand–Frish–Lebowitz theory of chaotically floating discs on fluid interface

2.1.1. Theory for nonionic surfactants

It is widely accepted that the Gibbs adsorption isotherm is valid for every kind of adsorption layer, which is in thermodynamic equilibrium with its species in the bulk. Thus, for non-ionic surfactant the latter takes the following form:

$$\Gamma_s = -\frac{1}{k_B T}\frac{d\sigma}{d\ln C_s} \tag{1}$$

where Γ_s is surfactant adsorption on the fluid interface, k_B is Boltzmann constant, T is absolute temperature, σ is the surface tension of the fluid interface in contact with the aqueous surfactant solution, and C_s is surfactant's bulk concentration.

Helfand et al. [6] developed the following equation of state valid for solid discs, moving chaotically in a plane:

$$\frac{\pi^s}{k_B T} = \frac{\Gamma_s}{(1-\alpha_0\Gamma_s)^2} \tag{2}$$

where $\pi^s = \sigma_0 - \sigma$ is surface pressure of the adsorption layer, σ_0 is the surface tension of the fluid interface in contact with the pure solvent (water), and α_0 is a real area occupied by one disc. Eq. (2) accounts only for the hard-core part of the interaction between the moving discs. To account for non-hard-core part of the interaction, Eq. (2) should be modified as follows [14]:

$$\frac{\pi^s}{k_B T} = \frac{\Gamma_s}{(1-\alpha_0\Gamma_s)^2} - B_{\text{attr}}\Gamma_s^2 \tag{3}$$

where B_{attr} is attraction constant related with the pair interaction between neighboring adsorbed surfactant molecules. The respective adsorption isotherm can be obtained by integrating Gibbs equation for non-ionic surfactant ($d\pi^s = k_B T\Gamma_s d\ln C_s$), where π^s is substituted from Eq. (3):

$$K_s C_s = \frac{\Gamma_s}{1-\alpha_0\Gamma_s}\exp\left[\frac{\alpha_0\Gamma_s(4-3\alpha_0\Gamma_s)}{(1-\alpha_0\Gamma_s)^2} - 2B_{\text{attr}}\Gamma_s\right] \tag{4}$$

where K_s is the equilibrium adsorption constant and C_s is surfactant's bulk concentration. The essence of Eqs. (3) and (4) is how to model the attraction constant B_{attr}. It has been clearly shown in Refs. [1,14], that it is most appropriate to use for this purpose the "sticky" potential of Baxter [17]. In a such a case $B_{\text{attr}} = 4\alpha_0\beta$, where $\beta = u_0/k_B T$ is the dimensionless potential between two surfactant molecules in contact (called here contact potential), while u_0 is "sticky potential" as has been formulated by Baxter. The latter remains implicit constant in Eqs. (3) and (4) as they are formulated here before. The contact potential β should have only positive values (β), corresponding to attraction between neighboring molecules. Unfortunately, when Eqs. (3) and (4) are applied to real surface tension isotherms, the result from the fitting procedure is often negative value of β. For this reason a new more general theory (model of Ivanov), with the same hard-core part as Eqs. (3) and (4) was derived in Refs. [1,14]:

$$\frac{\pi^s}{k_B T} = \frac{\Gamma_s}{(1-\alpha_0\Gamma_s)^2}\times\frac{2}{1+R_\beta};\quad R_\beta = \sqrt{1+16\beta\frac{\alpha_0\Gamma_s}{1-\alpha_0\Gamma_s}} \tag{5}$$

$$K_s C_s = \frac{\Gamma_s}{(1-\alpha_0\Gamma_s)}\left(\frac{2}{1+R_\beta}\right)^{\frac{1+8\beta}{4\beta}}\times\exp\left[\frac{\alpha_0\Gamma_s(4-3\alpha_0\Gamma_s)}{(1-\alpha_0\Gamma_s)^2}\times\frac{2}{1+R_\beta}\right] \tag{6}$$

Eq. (5) has been derived by means of the heuristic simplification procedure of Hemmer and Stell [18] (for gas of spheres interacting by means "sticky potential"), but adjusted for the 2D case. Accordingly, Eq. (6) was derived by means of Gibbs adsorption isotherm and Eq. (5). The validation of Eqs. (5) and (6) [14] showed positive value of the contact potential β in contrast to Eqs. (3) and (4).

2.1.2. Theory for ionic surfactants

In contrast to the non-ionic surfactants, the ionic ones dissociate to surface active ion (co-ion), adsorbing on the fluid interface and counter-ion, which forms diffuse later close to the fluid interface. Both of them have equal contribution to the surface tension of the surfactant solution. The researchers add very often inorganic salts to the aqueous solutions of the surfactants, to increase their surface activity. For this reason the Gibbs adsorption isotherm takes the following general form for such a case:

$$\Gamma_s = -\frac{1}{k_B T}\frac{d\sigma}{d\ln x} \tag{7}$$

where $x = a_s(a_s + a_{\text{salt}})$, a_s is activity of the surfactant solution, while a_{salt} is the activity of the added salt (if added). There are two approaches of modeling the layer of counter-ions [13] – the model of Stern, and the model of partial penetration of counter-ion into the surfactant adsorption layer. It was proven that the second one is closer to the reality. Therefore, the model of Ivanov was derived assuming that the counter-ions penetrate partially into the adsorption layer. Hence, it can be expressed by the following set of adsorption isotherm and equation of state: