

Adsorption and structure of the adsorbed layer of ionic surfactants[☆]

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Available online 24 July 2006

Abstract

Our goal in this study was to investigate theoretically and experimentally the adsorption of ionic surfactants and the role of different factors in the mechanism of adsorption, the adsorption parameters and the structure of the adsorbed layer. We used available literature data for the interfacial tension, σ , vs. concentration, C_s , for sodium dodecyl sulfate (SDS) in three representative systems with Air/Water (A/W), Oil/Water (O/W) and Oil/Water + 0.1 M NaCl (O/WE) interfaces. We derived 6 new adsorption isotherms and 6 new equations of state (EOS) based on the adsorption isotherms for non-ionic surfactants of Langmuir, Volmer and Helfand–Frisch–Lebowitz (HFL) with interaction term $\beta\theta^2/2$ in the EOS, $\theta = \alpha\Gamma$ being the degree of coverage, with Γ — adsorption and α — minimum area per molecule. We applied Gouy equation for high surface potentials and modified it to account for partial penetration of the counterions in the adsorbed layer. The equations were written in terms of the effective concentration $C = [C_s(C_s + C_{el})]^{1/2}$, where C_s and C_{el} are, respectively concentrations of the surfactant and the electrolyte. We showed that the adsorption constant K was model independent and derived an equation for the effective thickness of the adsorbed layer, δ_s . We found also that the minimum area per molecule, α , is larger than the true area, α_0 , which depends on the adsorption model and is a function of the adsorption Γ . The interaction term $\beta\theta^2/2$ in the Langmuir EOS was found to be exact for small $\beta \ll 1$, but for the Volmer EOS it turned out to be only a crude approximation. Semi-quantitative considerations about the interaction between adsorbed discrete charges revealed that at A/W interface part of the adsorbed surfactant molecules are partially immersed in water, which leads to decreased repulsion and increased adsorption Γ . At O/W the larger adsorption energy keeps the surfactant molecules on the surface, so that the electrostatic repulsion is stronger, which translates into negative β 's, larger α 's and smaller adsorption. The addition of electrolyte partly screens the repulsion at O/W, leading to decreased α and increased adsorption. We determined K , α and β by a three-parameter fit. The constant K was found to be model independent and smaller for A/W than for O/W, because of the smaller adsorption energy. The values of α were larger for O/W than for A/W and decreased for O/W upon addition of electrolyte in agreement with the theory. For the Volmer model α was smaller than for Langmuir's model and both were found to increase with decreasing Γ — again in agreement with the theoretical predictions. It turned out that θ never exceeds 0.5 i.e. the adsorbed layer is never saturated. We tried to determine which adsorption model gave better results by calculating theoretically the Gibbs elasticity, but it turned out that when the results were plotted vs. an experimental variable, say C , all curves collapsed in a single one, which coincided with the respective experimental curve. This means that it is impossible to determine the adsorption model by using only interfacial tension data.

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[☆] Based on paper presented at the Symposium “Surfactants in Solution” (Fortaleza, June 2004) and the XVII ECI Conference (Loughborough, June 2005).

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1. Introduction

The ionic surfactants play an important role in many processes of practical importance, such as formation of emulsions and foams, flotation, wetting, etc. Biological ionic surfactants play also an important role in living organisms. This is the reason for the intense interest for more than a century in their properties and behavior. Detailed information about the structure of the adsorbed layer became even more important after the creation of the DLVO theory for the stability of dispersions and the development of methods for studying the kinetics of adsorption. The problem is that in both cases one needs to know the distribution of the ions in the diffuse layer, while the experimental methods usually give the overall adsorption of the surfactant.

Such detailed information is available through the theory of adsorption of ionic surfactants. The first and the most important breakthrough in this direction was made by Gouy [1], who derived an equation, relating the potential of the diffuse electrical layer with its charge. Davies [2] used the equation of Gouy to derive an expression for the contribution of the diffuse layer, $\Delta\sigma_{\text{el}}$, to the equation of state of a monolayer. It was also used, along with the Boltzmann equation, for the derivation of a simple adsorption isotherm of ionic surfactants [3]. In a similar way Haydon and Taylor [4,5] derived another equation for ionic surfactants based on the Volmer adsorption isotherm. Lucassen-Reynders [6] proposed an alternative approach for derivation of the adsorption isotherm, based on the Butler equation for the chemical potential, but in her approach the diffuse layer was not accounted explicitly. The latter problem was resolved by Borwankar and Wasan [7], who proposed to use the adsorption isotherms for non-ionic surfactants, but to replace in them the bulk surfactant concentration, C_s , by the subsurface concentration C_{ss} , which is related to C_s by the Boltzmann equation.

During the last years there has been an explosion of interest and publications on this important subject. One possible reason for this is the advent of computer calculations, which made easy the fitting of multi-parameter functions and thereby accounting for more effects than it was possible only a few years ago. The new theoretical developments were related mainly to accounting for new physical effects. Kalinin and Radke [8] introduced counterion binding to the adsorbed surfactant ions (the Stern adsorption layer). This process was assumed to be accompanied by dehydration of both ions, which leads, roughly speaking, to the formation of a complex. These authors also introduced two

molecular condensers to account for the different sizes of the dehydrated adsorbed counterions and the freely moving hydrated counterions from the diffuse layer.

Kralchevsky et al. [9] investigated the problem regarding the thermodynamic compatibility of adsorption isotherms for ionic surfactants and counterions, and derived expressions for electrolytes of various valences. Later, they applied the proposed approach to a comparative study of the van der Waals and Frumkin isotherms [10], and to mixtures of ionic–non-ionic [11,12] and anionic–zwitterionic [13] surfactants.

Mulqueen and Blankshtein [14] simplified the theory by disregarding all other effects besides the molecular condenser (the Stern layer). Warszynski et al. [15] accounted for the adsorption of the counterions, for the difference in sizes between the surfactant ions and the counterions, for the Stern layer and for the electrostatic interaction between the adsorbed ions. Fainerman and co-workers [16,17] as well as Liggieri et al. [18] took another direction — they extended the theory of Lucassen-Reynders by including reorientation effect and surface aggregation.

All these models have physical basis and are reasonable. One trouble we see with them is that besides the three adsorption parameters, typical for the non-ionic surfactants (adsorption constant K , minimum area per molecule, α , and interaction parameter, β) they usually involve at least one more parameter. In most cases this makes the fits better, but it is sometimes hard to imagine from the obtained data how are the adsorption parameters related and how they depend on other properties of the system. Another problem with the multi-parameter fits, which we will demonstrate in Section 4, is that the adsorption parameters may combine in such a way that the experimental data are fitted perfectly, but the calculated values of the parameters may change significantly, depending on the theoretical model used. The situation does not improve much if, in order to decrease the number of free parameters, one uses for some of them (say, for the ionic size) data from other sources, since it may turn out that these values are different from the true values of the respective quantities in the adsorbed layer.

That is why we took a somewhat different approach. We did not want to prove or disprove an adsorption model, but were looking mainly for qualitative physical insight in the adsorption process and the structure of the adsorbed layer. Toward this aim we selected a very simple experimental system and considerably simplified the theory in the hope that this will permit more thorough analysis of the theory and the experimental data and will

shed more light on the meaning of the adsorption parameters and the factors affecting them. What interested us can be illustrated by the questions provoked by the three curves in Fig. 1: (i) Why is the adsorption at Air/Water interface at larger concentrations much larger than at Oil/Water interface, in spite of the fact that the adsorption energy is smaller; (ii) What is so special about the neutral electrolyte NaCl, that makes the adsorption isotherm looks so different from that for the system without added electrolyte. Both problems have been studied by other authors, but we found their answers incomplete or unsatisfactory.

To achieve our goals we decided to study only systems with sodium dodecyl sulfate (SDS) as surfactant and NaCl as electrolyte. The reason was that the adsorption behavior depends strongly on the structure and the sizes of the hydrophobic tail and the ionic head as well as on the charge and polarisability of the counterions. We wanted to avoid these additional effects which could complicate and even hamper the understanding of some basic facts. The SDS is a much studied surfactant and the solvated Na^+ ion has small enough polarisability (0.079 \AA^3) to allow neglecting the van der Waals interactions with the interface or with the ionic heads of the adsorbed surfactant. At the same time we selected three systems with interfaces Air/Water, Oil/Water and Oil/Water + NaCl to study the effects of the hydrophobic phase and of the electrolyte. We carefully checked the available experimental data and used only those which exhibited complete coincidence with another set of data with the same or similar system.

On the theoretical side our approach was different. We processed the experimental data using several isotherms, based on different models, in order to reveal how the adsorption parameters depended on the model and how reliable the obtained data were. Moreover, the variation of the parameters with the model considered sometimes provides important physical information. Our goal was greatly facilitated by the finding that all data for the surface pressure, $\Delta\sigma$, vs. the adsorption, Γ , could be fitted perfectly by a second-order polynomial. This means that it is necessary to keep only the effects, giving sizable contribution up to terms of the order of Γ^2 . Our estimates showed that such term stems only from the molecular condenser. However, we accounted for the

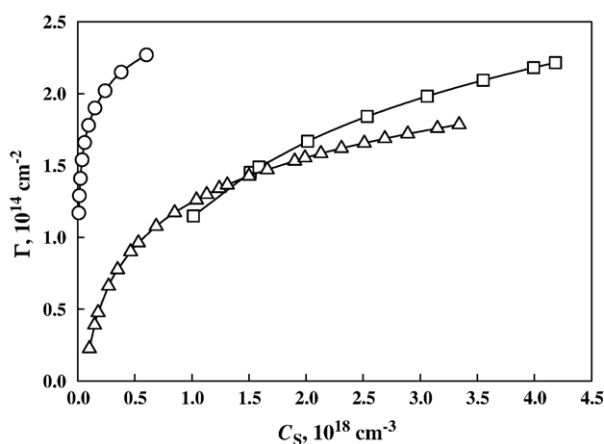


Fig. 1. Adsorption, Γ , vs. surfactant concentration, C_s , for solution of SDS at the interfaces A/W, (squares), O/W (triangles), and O/W + 0.1 M NaCl (circles).

fact that if the coverage of the surface by surfactant ions is not complete, part of the counterions from the diffuse layer can penetrate between the ionic heads in the adsorbed monolayer. Hence, we modified accordingly the Gouy equation (see Eq. (2.5)). We used also an alternative model, without any condenser, which is valid for low degrees of surface coverage. In addition, by using the fact that the surface potential in these systems was always higher than 100 mV, we succeeded in simplifying considerably the Gouy equation. This made the derivation of the adsorption isotherms for ionic surfactants easy and we succeeded to obtain several adsorption isotherms and equations of state based on the isotherms for non-ionic surfactants of Langmuir [19], Volmer [20] and Helfand–Frisch–Lebowitz [21], all of them for the cases with and without molecular condenser. The use of these isotherms (and some others) allowed us to amass the data summarized in Tables 1 and 2. The comparison of the data, obtained by different methods and for different systems, coupled with our theoretical analysis of the adsorption parameters, allowed us to reach some physical conclusions.

The paper is organized as follows. In Section 2.1 we formulate and analyze the basic equations related to the adsorbed and the diffuse layers. In Section 2.2 we present several known adsorption isotherms and equations of state, which are used in Sections 2.3 and 2.4 to derive the respective functions for ionic surfactants. Under certain conditions the equations could be simplified. This allowed us in obtaining analogs for ionic surfactants of the well known equations of Langmuir, of Szyszkowski and of Temkin. Section 3 is devoted mainly to the analysis of the adsorption parameters for non-ionic surfactants, but most of the conclusions hold for ionic surfactants as well. In Section 3.1 a new equation for the adsorption thickness δ_s is derived. In Section 3.2 it is shown that the minimum area per molecule α is by no means a constant, but decreases with increasing adsorption 4 times for the model of Langmuir and 2 times for the model of Volmer. Similar analysis is performed in Section 3.3 for the interaction parameter β , where it is shown that Langmuir–Frumkin equation correctly accounts for weak interactions, whereas the respective term is never correct for the van der Waals equation. The effects of the discreteness of the surface charges are discussed in Section 3.4, where it is shown that they can lead to immersion of a fraction of the surfactant molecules which results in smaller values of α at the Air/Water interface than at the Oil/Water interface, as well as to a decrease of α with added electrolyte. This probably explains the trends of the respective curves in Fig. 1. The analysis of the numerical data in Section 4 largely confirms the theoretical conclusions. The results and the conclusions are summarized in Section 5.

2. Model and basic equations

In Section 2.1 we formulate the models and basic equations for the adsorbed surfactant layer and the diffuse electrical layer. In Section 2.2 we show how to relate the non-electrostatic and electrostatic contributions to the surface equation of state and to the adsorption isotherm. The main equations for non-ionic surfactants are summarized. They are used in Section 2.3 to derive

the adsorption isotherms and in Section 2.4 to derive the surface equation of state for ionic surfactants.

2.1. Model of the adsorbed and diffuse layers

We assume that the surfactant ions adsorb at the interface air/water (or oil/water) with the centers of the ions being at a distance $z=z_0$ from the interface, see Fig. 2. Due to thermal fluctuations this distance is slightly larger than the radius of the ionic head. The number of molecules per unit area (the surfactant adsorption) is Γ and each molecule occupies an area of $1/\Gamma$. The minimum possible area per molecule is denoted by $\alpha=1/\Gamma_\infty$, where Γ_∞ is the maximum possible adsorption. If the surfactant head groups are aligned in a plane (as shown in the figure) and can be considered as solid spheres, the minimum area is very close to $\alpha_0=\pi r_0^2$, where r_0 is the cross-sectional radius of the head group (in fact α_0 contains a numerical factor, close to unity, which depends on surface packing).

However, as we will show later, α can be rather different from α_0 , since α depends on the adsorption model and the interaction between the adsorbed surfactant molecules. The charge per unit area for the adsorbed layer is:

$$Q_a = -\Gamma e_0 = -e_0 \theta / \alpha; \quad \theta = \Gamma / \Gamma_\infty = \alpha \Gamma \quad (2.1)$$

where e_0 is the unit charge and θ is the degree of surface coverage. The surface charge is compensated by the charge of the diffuse layer, Q_{dl} (per unit area), formed predominantly of counterions. The distribution of the counterions is assumed to be governed solely by the electrostatic potential ψ . Indeed, our calculations (paper in preparation [22]), based on London equation for intermolecular interaction, show that the non-electrostatic adsorption energy of the Na^+ counterions is of the order of $0.05kT$ for air/water interface. This value is too small for the counterions to be considered as specifically adsorbed. Nevertheless, due to the electrostatic potential, the counterions can penetrate into the adsorbed layer, as illustrated in Fig. 2. To account for the finite size of the counterions, one usually assumes that they cannot come closer to the adsorbed surfactant ions than at a distance d_c , which is approximately equal to the sum of the radii of the surfactant ionic head and the counterion. In other words, one assumes that the adsorbed layer and the diffuse layer form a molecular condenser of thickness d_c . The plane $z=z_d=z_0+d_c$ is called the Helmholtz plane and the potential in it, denoted by ψ_d , is called the potential of the diffuse layer.

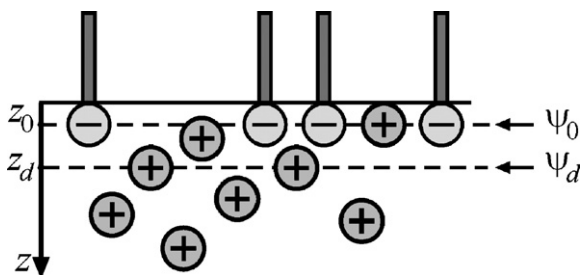


Fig. 2. Model of the adsorbed layer with diffuse layer. Some of the counterions penetrate in the adsorbed layer, beyond $z=z_d$.

The charge Q_{dl} is obtained by integrating Boltzmann distribution for all ions over z from z_d to infinity. The result, found first by Gouy [1], is:

$$Q_{dl} = \frac{4e_0}{\kappa_0} \sqrt{C_t} \sinh\left(\frac{e_0 \psi_d}{2kT}\right); \quad \kappa_0^2 = \frac{8\pi e_0^2}{\epsilon kT}; \quad (2.2)$$

where $C_t=C_s+C_{el}$ is the total electrolyte concentration i.e. the sum of the concentrations of the surfactant, C_s , and the added electrolyte, C_{el} , and κ_0 is that part of the Debye parameter κ (with ϵ being the dielectric constant), which is independent of the electrolyte concentration (for water $\kappa_0^2 \approx 1.769 \times 10^{-6} \text{ cm}^2$).

Although Eq. (2.2) is based on integration of the charge distribution, which in turn is proportional to the local ion concentration, $C(z)$, for non-ideal solutions the local concentrations $C(z)$ must be calculated not from the simple Boltzmann equation, but from the condition for equilibrium between the diffuse layer and the bulk solution:

$$\bar{\mu}_{dl} = \mu^0 + kT \ln C(z) + Ze_0 \psi(z) = \mu^0 + kT \ln a = \mu, \quad (2.3)$$

where a is activity, $\bar{\mu}_{dl}$ and μ are the electrochemical and the chemical potentials, respectively, Z is the valency and μ^0 is the standard chemical potential. Therefore, if the solution is not ideal, C_s and C_{el} must be replaced by the respective activities, a_s and a_{el} .

We do not intend to discuss the derivation and the meaning of the Gouy equation, since in [9] there is excellent analysis of the electrostatic and thermodynamic foundations of the theory of the adsorption of ionic surfactants. We would like only to mention the main assumptions made when deriving Eq. (2.2): (i) The surface charge of the adsorbed layer is supposed to be smeared uniformly over the surface; (ii) The ions in the diffuse layer are point charges, not interacting directly with each other; and (iii) The dielectric constant ϵ has its bulk value. The first assumption that the charge of the adsorbed layer is uniformly spread over the surface $z=z_0$ means that all surfaces parallel to the solution surface must be equipotential. This is true at distances z much larger than the ion diameter. However, close to the interface the potential distribution is much more complex, since the field lines are not perpendicular to the interface, as they should be according to Gouy theory. This deformation of the field leads at least to two effects: (i) The potential in close proximity to the interface is smaller than it would be in the absence of field deformation, which affects the electrostatic adsorption energy [3,23]; and (ii) There is residual repulsion between the adsorbed ions, not accounted for in the Gouy theory. We have ignored the first effect, which seems to be small [23], but we believe that the second one affects the minimum area per molecule, α , and could explain its dependence on the electrolyte concentration and the nature of the hydrophobic phase in contact with the water (air or oil) (see Section 3.4).

The relation between ψ_d and ψ_0 can be established by means of the Gauss theorem, which yields:

$$\Psi_0 - \Psi_d = M\theta; \quad M = \frac{4\pi d_c e_0^2}{\alpha \epsilon kT} \approx 17.8 \quad \Psi = \frac{e_0 \psi}{kT} \quad (2.4)$$

The numerical estimate $M=17.8$ was obtained with the values $d_c=0.6$ nm, $\alpha=0.30$ nm² and $\varepsilon=81$. Since ψ_0 is of the order 150–200 mV (see [3,9]) and $kT/e_0 \approx 25$ mV, Ψ_0 is of the order of 6 to 8. Then, this estimate means that Ψ_d will become zero, i.e. the diffuse layer will disappear, at $\theta=0.4$ to 0.5. This conclusion results from the assumption that none of the counterions can penetrate into the adsorbed layer. In reality, at small θ all counterions can do so, but at $\theta=1$ all counterions must stop at $z=z_d$. We do not see a way to account rigorously for this continuous transition between these two states and will use an approximate calculation, akin to the kinetic derivation of the Langmuir isotherm. Imagine, as sketched in Fig. 3, that all adsorbed ions per unit area are grouped on the left hand side and cover an area θ . If a counterion hits this part of the surface, its potential at the moment of collision will be ψ_d . For the ions, hitting the other part of the area, $1-\theta$, the potential at collision will be ψ_0 . Hence the total charge of the diffuse layer per unit area can be represented as:

$$Q_{dl} = \theta Q_{dl}^d + (1-\theta)Q_{dl}^0, \quad (2.5)$$

where the superscripts d and 0 mean that the respective charges. Q_{dl} are calculated from the Gouy Eq. (2.2) with ψ_d and ψ_0 respectively. This model could be called “partial condenser model” since Eq. (2.5) accounts for the penetration of part of the counterions inside the adsorbed layer.

As already mentioned, Ψ_0 is normally between 6 and 8, then the argument of the hyperbolic sine in Eq. (2.2) is between 3 and 4, so that the following approximation can be safely used:

$$\sinh(\Psi/2) \approx \frac{1}{2} \exp(\Psi/2). \quad (2.6)$$

The numerical estimate shows that the error of this approximation is of the order of 0.1% for $\Psi=6$ and does not exceed 2% even for $\Psi=4$. This approximation has been used previously by several authors (see e.g. [3–5]). By using this approximation in Eq. (2.2), along with Eq. (2.4), one finds

$$Q_{dl}^d = Q_{dl}^0 e^{-M\theta} \quad (2.7)$$

Because of the large value of M , this result means that the term with Q_{dl}^d in Eq. (2.5) can be neglected, unless θ is very small. By setting the sum $Q_a + Q_{dl}$ equal to zero, one finds then

from Eqs. (2.1), (2.2) and (2.5) the relation between the potential Ψ_0 and the surface coverage θ :

$$\theta = a\sqrt{C_t}(1-\theta)e^{\Psi_0/2} \quad a = \frac{2\alpha}{\kappa_0} \quad (2.8)$$

For the model without condenser one must set $\theta=0$ in the right hand side of this equation. The respective equations for the two cases can be described by a single equation:

$$\theta = a\sqrt{C_t} \left(1 - \frac{3-n}{2}\theta\right) e^{\Psi_0/2} \quad (2.9)$$

where the difference between the two models is accounted for by the number n : it is $n=1$ for the model with condenser and $n=3$ for the model without condenser (for brevity we will call them sometimes Model 1 and Model 3, respectively). Eq. (2.9) is a generalized form of the Gouy equation, valid for high surface potentials.

2.2. Adsorption isotherms and equations of state of non-ionic surfactants

The diffuse layer affects the free energy of the system and thereby — its interfacial tension, σ . On the other hand, even if the surfactant is not charged, it still affects σ . Therefore, one must relate these two effects. To achieve this, Davies [2] represented the surface pressure $\Delta\sigma = \sigma_p - \sigma$ (which is the difference of the interfacial tensions, σ_p and σ , without and with surfactant) as the sum of two terms: the non-electrostatic contribution, $\Delta\sigma_{NIS}$, which is calculated from the equation of state of the respective non-ionic surfactant (NIS) and the electrostatic contribution, $\Delta\sigma_{el}$, due to the diffuse electric layer. He derived an equation for the latter, based on Gouy Eq. (2.2):

$$\Delta\sigma_{el} = \frac{8kT\alpha}{\kappa_0} \sqrt{C_t} \left[\cosh\left(\frac{e_0\psi_d}{2kT}\right) - 1 \right] \quad (2.10)$$

For high potentials the factor in square brackets can be replaced by $1/2\exp(\Psi_0/2)$ (see Eq. (2.6)), which, in turn, can be found from Eq. (2.9). For $n=3$ (no condenser) this leads to the very simple result:

$$\Delta\sigma_{el} = 2\Gamma kT \quad (2.11)$$

Borwankar and Wasan [7] proposed an alternative approach for combining the electrostatic and the non-electrostatic contributions to $\Delta\sigma$, namely, to use the adsorption isotherm of the non-ionic surfactant, but to replace in it the equilibrium bulk concentration, C_s , by the subsurface concentration C_{ss} i.e. by the concentration at $z=z_0$, determined by the electric field.

The somewhat obscure notion of “subsurface concentration” can be visualized in the following way. Imagine that the capability for non-electrostatic interactions of the charged species in the bulk of the solution is somehow switched off. Then the species will adsorb only under the action of the potential ψ_0 and in the plane z_0 they will have (subsurface) concentration C_{ss} .

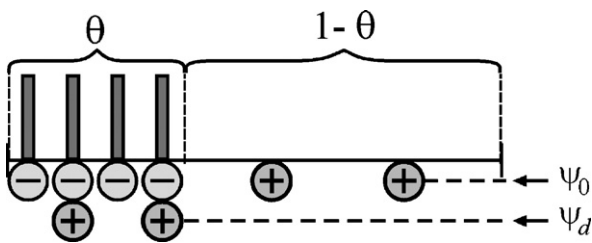


Fig. 3. Model of partial penetration of the counterions in the adsorbed layer which is represented as two portions: in the covered portion, with area θ , the counterions can reach only potential ψ_d , whereas in the free portion, $1-\theta$, they can go to the plane of the adsorbed layer, with potential ψ_0 .

Although then the ionized species are in the plane $z=z_0$, one says that they are located in the sublayer or at the subsurface i.e. these notions denote a state, rather than a position in space. Now, if the non-electrostatic interaction capabilities of the species, already adsorbed at the subsurface, are switched on, the species will redistribute under the action of the respective non-electrostatic adsorption energies — it is customary to say that then the species go from the subsurface onto the surface, although this process does not involve significant change in the spatial position of the ionic head of the surfactant. For the amphiphilic surfactant molecule this imaginary process roughly means that the molecule is in the subsurface layer when its ionic head is already in the plane $z=z_0$ but its hydrocarbon part is still immersed in the water — then the adsorption process from the subsurface onto the surface consists in bringing the hydrocarbon part into the upper phase, air or oil. For this reason the adsorption of the species from the subsurface onto the surface is described by adsorption isotherms valid for non-charged species. The notion of “subsurface” is often used also in the theory of the kinetics of adsorption. The difference with the case of equilibrium adsorption, considered above, is that the molecules (ions) are brought to the subsurface not only by long range (electrostatic) forces, but also by diffusion and/or convection. The subsurface concentration for non-ionic surfactants is calculated by solving the appropriate (convective) diffusion equation. For ionic surfactants one must account also for the role of the electric potential both on the adsorption process and the mass transfer.

The subsurface concentrations C_{ss} are connected with the bulk concentrations C_s of the respective ions and the potential in the adsorbed layer ψ_0 and can be calculated from Boltzmann's equation:

$$C_{ss} = C_s e^{-\psi_0} \quad (2.12)$$

where for non-ideal solutions C_s must be replaced by the bulk activity, a_s (see Eq. (2.3)).

Since both approaches are related to the surface behavior of a non-ionic surfactant, we will start by a brief presentation of several equations of state (EOS) and the respective adsorption isotherms (AI) of non-ionic surfactants. The adsorption isotherm $\theta = \theta(C_s)$ relates the degree of surface coverage θ (i. e. the adsorption Γ) with the surfactant concentration C_s . The equation of state, $\pi_s = \pi_s(\theta)$, relates the degree of surface coverage θ with the dimensionless surface pressure $\pi_s = \alpha \Delta \sigma / kT$. Each of these functions, $\theta = \theta(C_s)$ and $\pi_s = \pi_s(\theta)$, can be derived in principle independently by the methods of the statistical thermodynamics. However, if one of them is known, the other one can be calculated by means of the Gibbs adsorption isotherm, which for a one-component system reads:

$$\frac{d\pi_s}{d\ln C_s} = \theta \quad (2.13)$$

To obtain the adsorption isotherm, one must differentiate π_s over θ and integrate the result.

We will use in this article mainly two EOS and respectively — two isotherms, but will occasionally discuss briefly a few more.

Here we will only formulate the respective equations (for details see [24]) and will postpone to Section 3 the discussion of the models they are based upon. All of these isotherms contain three parameters: the adsorption constant K_s , the minimum area per molecule, α , and the interaction constant, β . The latter two, α and β , participate both in the EOS and the adsorption isotherm and are closely related to the model used. The term with the interaction constant β is usually inserted in the same way in all equations, using at best intuitive considerations. Therefore, what really makes the difference between the models are the terms, containing α , which account for what is called hard core interaction. That is why we will call the models (and the EOS and the isotherms following from them) by the names of the authors, who proposed first the isotherm with hard core interaction.

The most popular isotherm is that of Langmuir, describing localized adsorption:

$$K_s C_s = \frac{\theta}{1-\theta} e^{-\beta\theta} \quad (2.14)$$

which can be obtained by integrating the Gibbs equation along with the Langmuir EOS (as modified by Frumkin):

$$\pi_s = -\ln(1-\theta) - \frac{\beta\theta^2}{2} \quad (2.15)$$

The term $-\beta\theta^2/2$ (respectively, the factor $\exp(-\beta\theta)$ in Eq. (2.14)) was proposed by Frumkin [25] by analogy with the attractive term in the van der Waals equation; that is why in the literature this isotherm is usually called the Frumkin isotherm.

The second most popular isotherm, that of Volmer, refers to non-localized adsorption:

$$K_s C_s = \frac{\theta}{1-\theta} \exp\left(\frac{\theta}{1-\theta} - \beta\theta\right) \quad (2.16)$$

It is based on an equation of state, proposed by Volmer [20] and later generalized (to account for the intermolecular interaction) and integrated by de Boer [26]:

$$\pi_s = \frac{\theta}{1-\theta} - \frac{\beta\theta^2}{2} \quad (2.17)$$

It is often called either isotherm of Volmer–de Boer or of van der Waals, since the respective surface equation of state (Eq. (2.17)) is an exact two-dimensional analog of the three dimensional van der Waals equation. In reality, without the interaction term Eq. (2.17) is an exact equation for adsorption on a line, but not on a surface [21,27].

The third EOS, proposed by Helfand, Frisch and Lebowitz [21], HFL for short, is not popular, but deserves attention, since it is an almost exact EOS for freely moving hard discs on a fluid interface. By analogy with Eqs. (2.15) and (2.17) we will add to the hard core part of the HFL equation an interaction term:

$$\pi_s = \frac{\theta}{(1-\theta)^2} - \frac{\beta\theta^2}{2} \quad (2.18)$$

By substituting this into Eq. (2.13) and integrating, we obtain the respective HFL adsorption isotherm:

$$K_s C_s = \frac{\theta}{1-\theta} \exp \left[\frac{\theta(3-2\theta)}{(1-\theta)^2} - \beta\theta \right] \quad (2.19)$$

In all adsorption isotherms above, the adsorption constant can be presented as:

$$K_s = \alpha \delta_s \exp \left(\frac{E_a}{kT} \right) \quad (2.20)$$

where E_a is the adsorption energy, and the quantity δ_s has the meaning of thickness of the adsorbed layer. These quantities are discussed in more detail in Section 3.1.

2.3. Adsorption isotherms of ionic surfactants

We will apply now the procedure of Borwankar and Wasan, outlined in Section 2.2, to derive the adsorption isotherms of ionic surfactants, corresponding to the isotherms of Langmuir, Volmer, and Helfand–Frisch–Lebowitz (HFL). This will be done by substituting in each isotherm the subsurface concentration C_{ss} from Eq. (2.12) for the surfactant concentration C_s and expressing the factor $\exp(-\Psi_0)$ by means of Eq. (2.9). This derivation involves only a little of easy algebra. We will do it simultaneously for models 1 and 3 and for all three isotherms. The results read:

$$\text{Langmuir model : } KC^{2/3} = \frac{\Gamma}{(1-\theta)^{1/n}} \exp \left[-\frac{\beta\theta}{3} \right] \quad (2.21)$$

$$\begin{aligned} \text{Volmer model : } KC^{2/3} \\ = \frac{\Gamma}{(1-\theta)^{1/n}} \exp \left[\frac{\theta}{3(1-\theta)} - \frac{\beta\theta}{3} \right] \end{aligned} \quad (2.22)$$

$$\text{HFL model : } KC^{2/3} = \frac{\Gamma}{(1-\theta)^{1/n}} \exp \left[\frac{\theta(3-2\theta)}{3(1-\theta)^2} - \frac{\beta\theta}{3} \right] \quad (2.23)$$

Here K 's are new adsorption constants, related to the respective constants K_s for non-ionic surfactants:

$$K = \left(\frac{4 K_s}{\kappa_0^2 \alpha} \right)^{1/3} \quad (2.24)$$

The presence of κ_0 accounts for the electric field. Note that K does not depend on α , since K_s in Eq. (2.20) is proportional to α . This makes the new adsorption constants less dependent on the model.

Another important feature of these results is that C is in fact an effective concentration:

$$C = \sqrt{C_s C_t}, \quad (2.25)$$

For non-ideal solutions the concentrations C_s and C_t must be replaced by the respective activities, a_s and a_t . This makes the treatment of solutions with excess electrolyte identical to that for systems without excess electrolyte. This was found first by Fainerman and Lucassen-Reynders, see for example Ref. [17].

Finally, the isotherms (2.21)–(2.23) reveal that for ionic surfactants the adsorption will not depend on C_s , as it is for non-ionic surfactants, but on $C_s^{2/3}$ (or $C^{2/3}$). Then the Henry equation will not read $\Gamma = K_s C_s$, but will become:

$$\Gamma = KC^{2/3} \quad (2.26)$$

The last equation was first derived by Davies and Rideal [3]. It is however virtually never valid under normal experimental conditions. As our numerical results in Section 4 show, the dependences $\Gamma = \Gamma(C^{2/3})$ and $\sigma = \sigma(C^{2/3})$ have much simpler behavior than $\Gamma = \Gamma(C)$ and $\sigma = \sigma(C)$. Because of this the variable $C^{2/3}$ is very important and we will sometimes use for it the special notation ζ .

Our treatment of the experimental data (see Section 4) revealed that the ionic surfactants never reach a complete coverage, $\theta = 1$, at the critical micellar concentration (cmc). This suggests that some approximate forms of Eqs. (2.21)–(2.23), valid for $\theta < 1$ might be useful. In particular, it is useful to present them in the form of Langmuir adsorption isotherm, since this allows obtaining in simple form the dependence $\theta = \theta(C)$.

For the Langmuir Eq. (2.21) for Model 1 (with condenser) it is sufficient to assume $\beta\theta/3 < 1$, which can be valid even for $\theta \approx 1$, provided that β is small enough. Then one can make the transformation

$$(1-\theta) \exp \left(\frac{\beta\theta}{3} \right) \approx \left(1-\theta + \frac{\beta\theta}{3} \right) \quad (2.27)$$

which leads to:

$$K\zeta = \frac{\Gamma}{1-G_{L1}\theta}; \quad G_{L1} = \frac{1}{3}(3-\beta) \quad (2.28)$$

This equation can be solved to yield $\theta(\zeta)$ and can be also presented in Langmuirian coordinates $1/\Gamma$ vs. $1/\zeta$:

$$\frac{1}{\Gamma} = \alpha G_{L1} + \frac{1}{K\zeta} \quad (2.29)$$

If $1/\Gamma$ is plotted vs. $1/\zeta$ and the plot is linear, one can easily determine K . For α one must know β from other data.

The Langmuir isotherm for $n=3$ (no condenser) must be elevated in power 3 and then one can apply the same approximation as for Model 1 (but in this case one must have $\beta\theta < 1$). This yields:

$$K^3 C^2 = \frac{\Gamma^3}{1-G_{L3}\theta}; \quad G_{L3} = 1-\beta \quad (2.30)$$

This result can be written also in Langmuirian coordinates by dividing it by Γ^2 and rearranging:

$$\frac{1}{\Gamma} = \alpha G_{L3} + \frac{\Gamma^2}{K^3 C^2} \quad (2.31)$$

Again K and possibly α (if β is known) can be determined by plotting $1/\Gamma$ vs. Γ^2/C^2 . It is not possible to easily obtain from Eq. (2.31) the explicit function $C(\theta)$, but this can be achieved by using a different approximation for Model 3 in Eq. (2.21): if θ is small, one can write

$$(1-\theta)^{1/3} \approx 1-\theta/3 \quad (2.32)$$

and then linearize the exponential term in Eq. (2.21). The adsorption isotherm obtained and its Langmuirian plot then coincide with Eqs. (2.28) and (2.29), but with

$$G_{L3}^* = G_{L3}/3 \quad (2.33)$$

instead of G_{L1} .

Similar approach can be applied to the isotherms of Volmer and HFL. Naturally, in this case one must linearize not only the factor $\exp(-\beta\theta)$ but the whole exponent. The final results for the coefficients G for Volmer isotherms are (for $n=1$ and $n=3$):

$$G_{V1} = \frac{1}{3}(4-\beta) \quad G_{V3} = 2-\beta \quad (2.34)$$

and for the HFL isotherm:

$$G_{H1} = \frac{1}{3}(6-\beta) \quad G_{H3} = 4-\beta \quad (2.35)$$

All approximate equations (except Eq. (2.30)) can be presented by a single equation if one uses the notation G_{Mn} , where M stands for adsorption model (L, V or H) and n as usual denotes 1 or 3:

$$K\zeta = \frac{\Gamma}{1-G_{Mn}\alpha\Gamma} \quad (2.36)$$

This equation can be solved with respect to Γ to provide an explicit dependence of Γ on the effective concentration C (please recall that $\zeta = C^{2/3}$):

$$\Gamma = \frac{K\zeta}{1 + \alpha G_{Mn} K \zeta} \quad (2.37)$$

It differs from the usual Langmuir isotherm for a non-ionic surfactant in three respects: (i) Since it is valid for adsorption of ionic surfactants (even in the presence of excess electrolyte), Γ depends on $C^{2/3}$, rather on C ; (ii) By using different expressions for G_{Mn} , one can apply it both to localized and non-localized adsorption; and (iii) The interaction between the surfactant ions is partially accounted for through the parameter β , contained in G_{Mn} .

The approach used above to derive the adsorption isotherms of ionic surfactants can be modified to lead to expressions for the dependence of the surface potential Ψ_0 on the adsorption Γ and the surfactant concentration C . In fact, Eqs. (2.8) and (2.9) are such equations, but they contain both C and θ , which are not independent. To avoid complicated equations, we will consider only two particular cases which are usually the most important: (i) $C_{el}=0$ i.e. $C_t=C_s$, and (ii) $C_{el} \gg C_s$ i.e. $C_t=C_{el}$. In case (i) one can eliminate C_s by means of Eq. (2.12) and any of the adsorption isotherms for non-ionic surfactants. The result will depend, of course, on the adsorption model used. For the Langmuir model after simple algebra one obtains:

$$\exp(2\Psi_0) = \frac{K_s}{a^2} \frac{\theta(1-\theta)}{(1-\frac{3-n}{2}\theta)^2} \exp(\beta\theta) \quad (2.38)$$

The respective equations for the Volmer and HFL models are the same as Eq. (2.38), but the right hand side must be multiplied by the factors

$$\exp\left(-\frac{\theta}{1-\theta}\right) \text{ or } \exp\left[-\frac{\theta(3-2\theta)}{(1-\theta)^2}\right]$$

respectively.

In case (ii) one must simply replace in Eq. (2.8) C_t by C_{el} . In this case the expression for Ψ_0 is independent of the adsorption model.

It is not possible to derive exact explicit dependence of Ψ_0 on the effective surfactant concentration C . Rather good approximate expressions for $\Psi_0(C)$ can be obtained by substituting for θ either $\theta(\zeta)$ from Eq. (2.37) or from the virial expansion of θ vs. ζ from Eq. (2.53) below.

2.4. Equations of state for ionic surfactants

In order to derive the equations of state, corresponding to the adsorption isotherms for ionic surfactants obtained in Section 2.3, we must use an appropriate form of the Gibbs adsorption isotherm. Although this problem is discussed in several papers and books (see e.g. [3,16,24]), it is usually done to the extent needed by the authors. We will try to carry out slightly more systematic analysis, which will shed light on some of our approximations.

For charged species in an external electrical field the Gibbs equation reads (at constant temperature T):

$$\frac{d\sigma}{kT} = -\sum_i \Gamma_i d\bar{\mu}_i \quad (2.39)$$

where $\bar{\mu}_i$ is the surface electrochemical potential of the i -th component. At equilibrium it must be equal to the respective bulk chemical potential μ_i (see Eq. (2.3)) and can be replaced by it.

To simplify notations we will analyze only the case of interest to us: a 1–1 ionic surfactant in the presence of 1–1 neutral electrolyte, having common cation with the surfactant. Typical system is a solution of SDS and NaCl. We will use the subscript 1 for the surfactant ion, subscript 2 for Na^+ and subscript 3 for Cl^- . The respective concentrations are $C_1=C_s$; $C_2=C_s+C_{el}$ and $C_3=C_{el}$, where C_{el} is the concentration of NaCl.

At high negative surface potential the concentration of Cl^- at and near the interface will be very low, so that one can assume $\Gamma_3=0$. Then the condition for electroneutrality will be $\Gamma_1=\Gamma_2=\Gamma$ and the Gibbs Eq. (2.39) becomes:

$$\frac{d\sigma}{kT} = -\Gamma(d\mu_1 + d\mu_2) \quad (2.40)$$

The condition for equilibrium in the bulk requires

$$\mu_1 + \mu_2 = \mu_{tot} \quad (2.41)$$

where μ_{tot} is called *total chemical potential* of the surfactant [28,29], which depends on its total activity $a_{s,tot}$. Then the sum

of the two differentials in Eq. (2.40) must give $d\mu_{\text{tot}}$ and the product of the activities of the ions, $a_1 = \gamma_1 C_1$ and $a_2 = \gamma_2 C_2$, is:

$$a_1 a_2 = \gamma_1 \gamma_2 C_1 C_2 = a_{s,\text{tot}} \quad (2.42)$$

where γ_1 and γ_2 are the respective coefficients of activity of the ions 1 and 2. Since the individual coefficients cannot be determined and therefore the activities a_1 and a_2 are unknown, one introduces the average activity a :

$$a_{s,\text{tot}} = a_1 a_2 = \gamma_1 \gamma_2 C_1 C_2 = a^2 = \gamma^2 C_1 C_2 \quad (2.43)$$

with average coefficient of activity $\gamma^2 = \gamma_1 \gamma_2$, which is calculated from the Debye–Hückel theory.

Therefore, Eq. (2.40) can be written as

$$\frac{d\sigma}{kT} = -2\Gamma d\ln a \quad (2.44)$$

In summary, if the surfactant $C_{12}H_{25}SO_4Na$ is considered as a single species, the interfacial tension σ depends on the total activity $a_{s,\text{tot}}$ of the surfactant molecule. Then the right hand side of Eq. (2.40) is $-\Gamma d\ln a_{s,\text{tot}}$, i.e., there is no factor 2. If however the ions $C_{12}H_{25}SO_4^-$ and Na^+ are considered as separate species, each with an average activity a , then the factor 2 must be used as in Eq. (2.44). Two limiting cases are of greatest interest [3]: (i) $C_{\text{el}} = 0$, i.e. $C_2 = C_1 = C_s$ and $a = \gamma C_s$; (ii) $C_{\text{el}} \gg C_s$ i.e. $C_2 = C_{\text{el}}$ and $a = \gamma \sqrt{C_s C_{\text{el}}}$.

If in a given experiment $C_{\text{el}} \gg C_s$ and $C_{\text{el}} = \text{const}$, then Eq. (2.44) becomes

$$\frac{d\sigma}{kT} = -\Gamma d\ln a_s \quad (2.45)$$

This follows also from Eq. (2.40) with $d\mu_2 = 0$. In the general case one must use $a = \gamma \sqrt{C_s(C_s + C_{\text{el}})}$.

It is convenient to write the Gibbs adsorption Eq. (2.44) in dimensionless form (compare with Eq. (2.13) for non-ionic surfactants):

$$\frac{d\pi_s}{d\ln C} = 2\theta \quad (2.46)$$

Eliminating C between this equation and the adsorption isotherms in Section 2.3, one can easily obtain the equation of state corresponding to a given model. The result can be written in compact form by using the factor n , but the equations are more clear if one writes them separately for $n=1$ and $n=3$. The resulting equations for the Langmuir model with $n=1$ and $n=3$, respectively, are:

$$\begin{aligned} \pi_s &= -3\ln(1-\theta) - \frac{\beta\theta^2}{2} \quad (n=1) \\ \pi_s &= -\ln(1-\theta) + 2\theta - \frac{\beta\theta^2}{2} \quad (n=3) \end{aligned} \quad (2.47)$$

For the Volmer model one has:

$$\begin{aligned} \pi_s &= \frac{\theta}{1-\theta} - 2\ln(1-\theta) - \frac{\beta\theta^2}{2} \quad (n=1) \\ \pi_s &= \frac{\theta}{1-\theta} + 2\theta - \frac{\beta\theta^2}{2} \quad (n=3) \end{aligned} \quad (2.48)$$

(We will not quote the results for the isotherm of HFL, since we will not use them, the more so that the one for $n=1$ is rather cumbersome.)

After expansion in series of θ and keeping the terms up to θ^2 , all four equations above can be expressed in the form:

$$\pi_s = 3\theta - \frac{B\theta^2}{2} \quad (2.49)$$

The linear term has coefficient 3 (instead of 1, as it is for non-ionic surfactants) because of the electrostatic contribution. The virial coefficient B has different forms depending on the model. Using again subscripts L_n and V_n to denote Langmuir 1 or 3 or Volmer 1 or 3 one can present the results as:

$$\begin{aligned} B_{L1} &= \beta - 3 & B_{L3} &= \beta - 1 \\ B_{V1} &= \beta - 4 & B_{V3} &= \beta - 2 \end{aligned} \quad (2.50)$$

A glance at the expressions for the coefficients G_{L_n} and G_{V_n} above (see Eqs. (2.34) and (2.35)) will convince the reader that they are simply connected with the coefficients B in Eq. (2.50). The general formula is:

$$B_{Mn} = -(4-n)G_{Mn} \quad (2.51)$$

It is interesting to check to what form of the adsorption isotherm the expansion (2.49) corresponds. It can be done by differentiating Eq. (2.49) and substituting $d\pi_s$ in Eq. (2.46). Simple integration yields

$$KC^{2/3} = \Gamma e^{-\frac{\beta\theta}{3}} \quad (2.52)$$

Rather surprisingly, expansion in series of the EOS does not correspond to similar expansion for the adsorption isotherm. This explains our finding (see Section 4), that the EOS is much better represented as expansion in series with respect to ζ than the adsorption isotherm.

Nevertheless, we will try to find such an expansion of θ , since for many purposes explicit dependence $\theta = \theta(C)$ is needed. One way to achieve this is to expand the exponent in Eq. (2.52), and to represent θ as series in terms of ζ :

$$\theta = A_1 \zeta + A_2 \zeta^2 \quad (2.53)$$

(note that $\zeta = C^{2/3}$) and to determine the coefficients A_1 and A_2 . This leads to:

$$A_1 = \alpha K; \quad A_2 = \frac{B}{3} (\alpha K)^2 \quad (2.54)$$

The expansion $\theta(\zeta)$ can be substituted into Eq. (2.49) to yield (keeping only the terms up to ζ^2):

$$\pi_s = 3\alpha K \zeta + \frac{B}{2} (\alpha K)^2 \zeta^2 \quad (2.55)$$

Another way to obtain a similar result is to substitute in Eq. (2.46) Γ from the Langmuirian type of Eq. (2.36) and to

integrate with respect to ζ . The result is a generalized form of Szyszkowski's equation, valid for ionic surfactants:

$$\pi_s = \frac{3}{G_{Mn}} \ln(1 + \alpha G_{Mn} K \zeta) \quad (2.56)$$

where the specific expression for G_{Mn} depends on the adsorption model. By expanding the logarithm in Eq. (2.56) in series one finds

$$\pi_s = 3\alpha K \zeta - \frac{3G_{Mn}}{2} (\alpha K)^2 \zeta^2 \quad (2.57)$$

The comparison of the coefficients B_{Mn} and G_{Mn} reveals, that Eqs. (2.55) and (2.57) are indeed identical.

Eq. (2.52) can be represented in a different form by taking its logarithm:

$$\Gamma = A_T + B_T \ln C \quad (2.58)$$

with

$$A_T = -\frac{3}{B\alpha} \ln \frac{K}{\Gamma}; \quad B_T = -\frac{2}{B\alpha} \quad (2.59)$$

The quantity A_T is not a true constant, since it depends on the variable Γ . However, variation in Γ of almost an order of magnitude corresponds to variations in $\ln(\Gamma)$ of only a few percents, so that A_T can be safely considered as a constant. Eq. (2.58) is the Temkin isotherm [30], which is widely used for adsorption of gases on heterogeneous surfaces. It is applicable to moderate adsorptions, since it obviously fails at $C \rightarrow 0$. Davies and Rideal [3] managed to derive it only for potentials smaller than 25 mV and for a high concentration of neutral electrolyte. Our derivation is valid for high potentials (which means also high surfactant concentrations) with no limitations on the electrolyte concentration. The electric field enters the equation through the constants K , B and α .

3. Analysis of the adsorption parameters

For many purposes the adsorption parameters K , α and β can be considered as empirical constants, which are determined experimentally. If, however, more detailed information is sought for the adsorption process and the adsorbed layer, theoretical expressions for these parameters are needed. There are such expressions in the literature, but in many cases they are approximate and sometimes wrong.

In Sections 3.1–3.3 we derive for non-ionic surfactants the expressions for K (including also the adsorption thickness, δ_s), α and β and analyze them. Most of the results are new and some of the conclusions are surprising. These results are not directly applicable to ionic surfactants, but many of the conclusions are valid also for ionic surfactants and will be used in Section 4 for data interpretation. Section 3.4 is devoted to qualitative analysis of the electrostatic interactions between the adsorbed surfactant molecules and their effect on the adsorption isotherm.

3.1. Adsorption constant and thickness of the adsorbed layer

We will start the discussion with a brief summary of the theory of localized adsorption of neutral spherical molecules on solid surfaces from the book of T. L. Hill [31], adapted to our notations. For brevity we will confine ourselves with the case of low coverage, when

$$\theta = K_s C_s. \quad (3.1)$$

It can be rigorously shown that the Langmuir isotherm is valid if each molecule is adsorbed on a point center, where its energy is $u(0)$ if the energy in the bulk of the solution is assumed to be zero. The molecule can perform harmonic oscillations in three directions, x , y and z , if these are the normal coordinates. It is possible to separate the energy $u(0)$ from the vibrational energy. Since the motion along the coordinate z , normal to the surface, is usually different from that along the surface, it is convenient to present the three-dimensional partition function of the adsorbed molecule as (see Eq. (7.18) in Hill):

$$q = q_{xy} q_z e^{-u(0)/kT} \quad (3.2)$$

From Eqs. (4.26) and (7.4) of Hill [31] one can deduce the standard chemical potentials in the bulk, μ_0^b , and at the surface, μ_0^s :

$$\frac{\mu_0^b}{kT} = \ln \Lambda^3; \quad \Lambda = \frac{h}{(2\pi mkT)^{1/2}} \quad (3.3)$$

$$\frac{\mu_0^s}{kT} = -\ln q$$

where m is the mass of the molecule, h is Planck's constant, Λ is the de Broglie thermal wavelength.

From the condition of equilibrium between the bulk and the surface

$$\mu_0^s + kT \ln \theta = \mu_0^b + kT \ln C_s \quad (3.4)$$

and Eq. (3.1) one finds

$$K_s = e^{-\frac{\mu_0^s - \mu_0^b}{kT}} \quad (3.5)$$

The comparison with the definition (2.20) of K_s reveals, that if $\mu_0^b - \mu_0^s$ is considered as adsorption energy, E_a , then one must assume $\delta_s = 1$. If Eqs. (3.2) and (3.3) are used for the standard chemical potentials, the expressions for K_s acquires the form

$$K_s = \Lambda^3 q_{xy} q_z e^{E_a/kT} \quad (3.6)$$

where we have set $-u(0) = E_a$.

This result (along with Eq. (2.20)) suggests that for the Langmuir model

$$\delta_s = \frac{\Lambda^3 q_{xy} q_z}{\alpha} \quad (3.7)$$

Therefore, only part of the difference of the standard chemical potentials, $\mu_0^b - \mu_0^s$, namely, $-u(0)$, is equal to the adsorption energy E_a and the remaining part contributes to δ_s .

With non-localized adsorption the molecules vibrate in the z direction, but in the x – y direction they move freely. Applying the same procedure as for obtaining the equation of state of ideal gas, one can show that for the Volmer equation

$$K_s = \alpha A q_z e^{E_a/kT} \quad (3.8)$$

By applying the standard procedures one can calculate the vibrational partition function q_z . For our purposes it is, however, more instructive to derive directly the adsorption isotherm for an ideal adsorbed layer, which will give us also an expression for δ_s . Let $u(z)$ be the potential energy of a spherical molecule, vibrating around the position $z=z_0$ of the minimum of the energy. If the potential well is deep enough, it can be approximated by a parabola:

$$u(z) = u(z_0) + \frac{u''(z_0)}{2}(z-z_0)^2 \quad (3.9)$$

where $u''(z_0)$ is the second derivative at $z=z_0$. By using the Boltzmann equation for the molecular distribution and the Gibbs definition for the adsorption Γ , one has

$$\Gamma = C_s \int_{-\infty}^{+\infty} (e^{-\frac{u}{kT}} - 1) dz \approx \sqrt{\frac{2\pi kT}{u''(z_0)}} e^{E_a/kT} C_s \quad (3.10)$$

where $E_a = -u(z_0)$ and the last expression in Eq. (3.10) is valid for strong adsorption. Comparing the result with Eqs. (3.1) and (2.20) one finds

$$\delta_s = \sqrt{\frac{2\pi kT}{u''(z_0)}} \quad (3.11)$$

It is more convenient to eliminate $u''(z_0)$ from the result. By setting in Eq. (3.9) $u=0$ one can find the distance l_0 between z_0 and the plane at which $u=0$. This allows writing from Eq. (3.9) $u''(z_0) = 2E_a/l_0^2$, so that Eq. (3.11) becomes:

$$\delta_s = l_0 \sqrt{\frac{\pi kT}{E_a}} \quad (3.12)$$

We will apply now the same procedure to derive δ_s for surfactant molecules. Since, however, they are not spherical, formulating the dependence of the energy on the distance, $u(z)$, requires derivation of this dependence. Hence, before we apply the approach presented above to the calculation of the adsorption constant of amphiphilic surfactant molecules, a brief discussion of their adsorption energy seems pertinent.

The adsorption energy E_a can be calculated by finding the change in free energy involved in the transfer of a molecule from the water phase to the upper hydrophobic phase (W and H, respectively in Fig. 4). We will consider a surfactant with a paraffinic chain with n_c carbon atoms, length per $-\text{CH}_2-$ group $l_1 \approx 0.126$ nm, radius of the paraffinic chain $R_c = 0.26$ nm, cross-sectional area $A_c \approx 0.21$ nm², and lateral area (along the chain) pertaining to one $-\text{CH}_2-$ group $A_1 \approx 0.21$ nm² (all data are based on the geometrical parameters of the paraffinic chain as determined by Tanford [32]). Let w_c be the energy of transfer of one $-\text{CH}_2-$ group. The energy of transfer of the top part (the $-\text{CH}_3-$ group), is larger than w_c because of its slightly larger area — we will

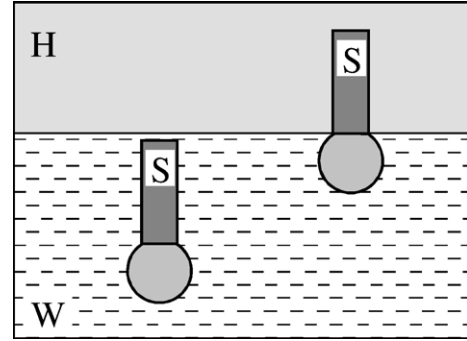


Fig. 4. Transfer of the surfactant molecule (S) from the bulk of the water phase (W) onto the interface with the hydrophobic phase (H).

account for this approximately by adding an additional area A_c for the methyl group. Another effect, usually neglected, is that when the molecule is adsorbed, a portion of the interface, of area A_c (with energy $\sigma_{HW}A_c$) disappears from the interface. Since the polar head remains immersed in the water phase, it should not contribute to the adsorption energy, at least in the case when only short range interactions are effective and there is no change in hydration of the polar head. The overall balance of energy leads to:

$$E_a = w_c n_c + (w_s + \sigma_{HW})A_c = E_0 + w_c n_c \quad (3.13)$$

where $E_0 = (w_s + \sigma_{HW})A_c$ is that part of the adsorption energy, which is independent of the chain length. Equation similar to Eq. (3.13) was postulated by Davies and Rideal [3] based on experimental data. However, unlike us, they ascribed E_0 to the adsorption energy of the polar head. The term pertaining to the hydrophobic chain can also be written as $w_1 l$, where l is the chain length and $w_1 = w_c/l_1$ is the energy of transfer per unit length.

We proceed now with the calculation of the adsorption thickness, δ_s , of amphiphilic neutral molecules. We will follow basically the same approach as for spherical molecules above but will assume that the energy $u(z)$ depends on the degree of immersion of the molecule (see Fig. 5). For simplicity we assume that the adsorbing molecule is always perpendicular to the interface. Eq. (3.13) and the expression $w_c n_c = w_1 l$ suggest to represent the energy as:

$$\begin{aligned} u &= 0 & z > l \\ u &= -E_a + w_1 z & \text{at } z \leq l \end{aligned} \quad (3.14)$$

with $E_a = E_0 + w_1 l$.

Using again the Boltzmann equation for $C_s(z)$ and the Gibbs definition of Γ , one obtains

$$\Gamma = \int_0^l [C_s(z) - C_s] dz \approx \frac{kT}{w_1} e^{E_a/kT} C_s \quad (3.15)$$

In the second step we have assumed strong adsorption. The comparison with Eq. (2.20) gives for the “thickness” of the adsorbed layer

$$\delta_s = \frac{kT}{w_1} = l \frac{kT}{E_c} \quad (3.16)$$

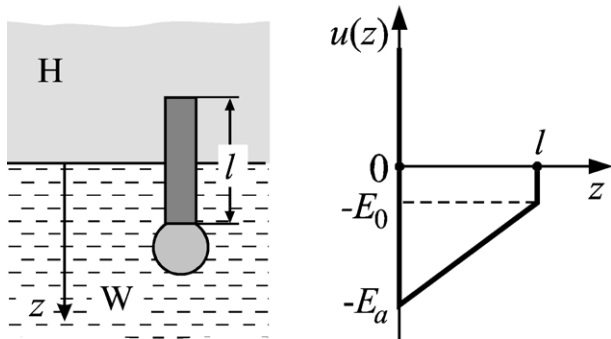


Fig. 5. A partially immersed surfactant molecule. The dependence of the energy $u(z)$ on the immersion depth is shown on the right. $E_0=(w_s+\sigma_{HW}) A_c$ is the energy jump at the moment when the upper part of the molecule touches the interface and E_a is the total adsorption energy.

where $E_c=w_c n_c=w_l l$. The last expression in Eq. (3.16) underlies the similarity of this result with the result of Eq. (3.12) for oscillating spherical molecules. Indeed both l_0 and l are the distances at which $u=0$ and the variations in the energy at these distances are E_a and E_c respectively. The only difference is the missing square root in Eq. (3.16), which is due to the fact that the motion is not oscillatory. When deriving Eq. (3.16) we have neglected two terms, both smaller than unity. The larger one was $(l/\delta_s)\exp(-E_a/kT)$. With realistic values of the parameters in it we found that it was of the order of 10^{-4} and was indeed negligible.

Since $w_1=w_c/l_1$, the numerical values of δ_s can be obtained from the values of w_c , quoted by Tanford [32]: 5.75×10^{-21} J and 4.35×10^{-21} J for O/W and A/W respectively. The result is $\delta_s=0.087$ nm for O/W and $\delta_s=0.116$ nm for A/W. This is about 10 times less than the suggestion of Davies and Rideal [3], who hypothesized that δ_s must be of the order of the length l of the surfactant molecule. Such a difference in the value of δ_s is equivalent to a difference of 2–3 kT i.e. to 2 to 3 times the adsorption energy of a $-\text{CH}_2-$ group. We believe that our result can be checked by processing appropriately the data, obtained from interfacial tension isotherms at different temperatures, T , such as those in Ref. [33], provided that the adsorption energy does not change with T .

The calculation of the adsorption constant K and the thickness of the adsorbed layer δ_s are much more complicated for ionic surfactants. Our preliminary results (paper under preparation [22]) suggest that they depend also on the van der Waals interaction of the ions in the diffuse layer with the interface and on the discreteness of the surface charges.

3.2. Minimum area per molecule

Probably the most controversial adsorption parameter is the minimum area per molecules, α , which most authors assume equal to the true area per molecule $\alpha_0=\pi r_0^2$, where r_0 is the radius of the cross-section of the hydrophilic head. For localized adsorption this will be approximately true, if the adsorbed molecules are closely packed, as assumed by Langmuir in his kinetic derivation of the adsorption isotherm — see Fig. 6a (in fact for hexagonal packing $\alpha_0=1.1\pi r_0^2$). It is obvious however,

that the above assumption fails when the molecules are disordered and/or undergo Brownian motion. For non-localized adsorption one often assumes $\alpha=2\alpha_0$ which is 1/2 of the inaccessible area $4\alpha_0$ (Fig. 6b), i.e. the area where the center of the colliding molecule cannot penetrate (the factor 1/2 accounts for the fact that this area “belongs” to both molecules). This value of α is approximately true only for small surface coverage.

We propose below a simple way to find the exact dependence of α on Γ for Langmuir and Volmer equations, based on the fact, that α in the HFL equation of state (Eq. (2.18)) is the true area per molecule, α_0 . That is why we will denote $\alpha_0\Gamma$ in this equation by θ_0 , and will use here the notations θ_L and α_L , θ_V and α_V for the equations of state of Langmuir and Volmer, respectively. All three EOS (with $\beta=0$) can be written as (see Eqs. (2.15), (2.17) and (2.18)):

$$\frac{\Delta\sigma}{\Gamma kT} = f_M(\theta_M)$$

where f_M is a function of θ_M and M stands for Langmuir, Volmer and HFL. Since the left hand sides do not depend on the model, the right hand sides must be equal. This leads to:

$$-\frac{1}{\theta_L} \ln(1-\theta_L) = \frac{1}{1-\theta_V} = \frac{1}{(1-\theta_0)^2} \quad (3.17)$$

For small θ one can expand the above expressions in series and by keeping only the linear terms in the expansions one finds

$$\alpha_L = 2\alpha_V = 4\alpha_0 \quad (3.18)$$

which is valid of course only for $\theta \ll 1$. The second equation in Eq. (3.17) can be solved easily and leads to the exact relationship for the Volmer model:

$$\frac{\alpha_V}{\alpha_0} = 2 - \theta_0 \quad (3.19)$$

which for $\theta_0 \ll 1$ gives, of course, the result from Eq. (3.18). The exact relation between θ_L and θ_0 from Eq. (3.17) can be found only numerically and the obtained dependence of α_L/α_0 vs. θ_0 is

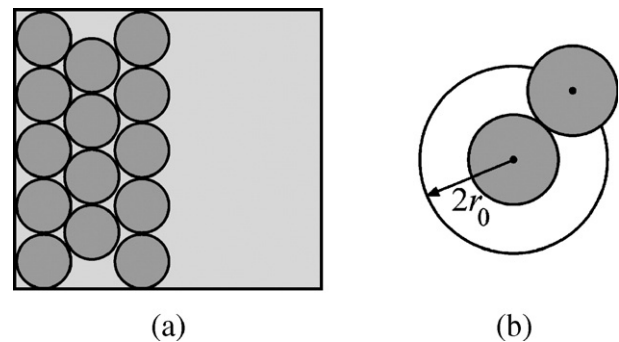


Fig. 6. Schematic representation of: (a) close hexagonal packing of ordered molecules. The area per molecule is $1.1\pi r_0^2$; (b) inaccessible area of two colliding freely moving discs at the interface. The inaccessible area $4\pi r_0^2$ is the area inside the large circle.

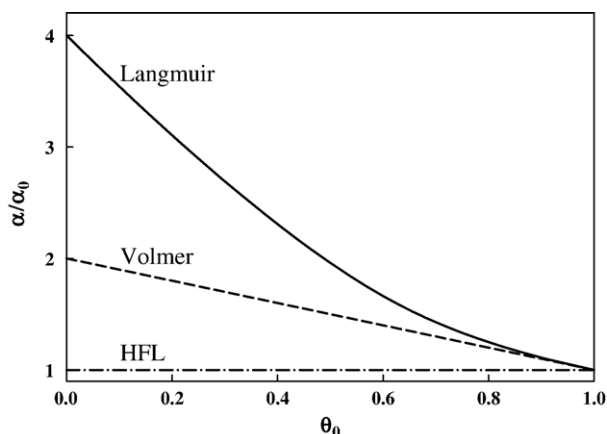


Fig. 7. Dependence of the minimum area per molecule α on the true surface coverage $\theta_0 = \alpha_0 \Gamma$ for the isotherms of Langmuir (full line), Volmer (dashed line), and Helfand–Frisch–Lebowitz (dash-dot line); see Eqs. (3.17) and (3.19).

shown in Fig. 7. The asymptotic behavior of the exact solution at $\theta_0 \rightarrow 0$ is obtained by expansion of θ_L / θ_0 in series of θ_0 ¹:

$$\frac{\alpha_L}{\alpha_0} = 4 - \frac{14}{3} \theta_0 \quad (3.20)$$

The derivation of the asymptotic form at $\theta \rightarrow 1$ is more tricky. At $\theta \rightarrow 1$ one can postulate $\theta_0 = 1 - \varepsilon$ and $\theta_L / \theta_0 = 1 + \delta$ where $\varepsilon \ll 1$ and $\delta \ll 1$. Then, by keeping in the left hand side only the leading terms in ε and δ , from the first and the third term of Eq. (3.17) one obtains:

$$\varepsilon - \delta = \exp\left(-\frac{1}{\varepsilon^2}\right) \quad (3.21)$$

All derivatives of the exponential function in the right hand side are 0 at $\varepsilon = 0$, so that its expansion in series around $\varepsilon = 0$ (i.e. around $\theta_0 = 1$) is identically zero for $\varepsilon \ll 1$. We thus obtain $\varepsilon = \delta$. This result written in the original coordinates α_L / α_0 and θ_0 reads:

$$\frac{\alpha_L}{\alpha_0} = 2 - \theta_0 \quad (3.22)$$

which coincides with Eq. (3.19). This fact explains why the exact solutions for α_V / α_0 and α_L / α_0 in Fig. 7 merge already around $\theta_0 = 0.7$ – 0.8 .

The results from this section suggest several important conclusions: (i) The area per molecule, determined by using a model isotherm, is not a true physical constant, but depends on the model used and the adsorption Γ ; (ii) No matter what the model is, if the fit gives more weight to the larger θ values, the determined value of α will be close to α_0 ; and (iii) If the fit is sensitive to the entire

¹ After this paper was submitted for publication we became aware of a recent paper of A.I. Russanov (Colloids Surfaces A 239 (2004) 105–111) who had ideas similar to ours about the dependence of the minimum area per molecule α on the adsorption Γ . By using a different approach he also found for Langmuir model the limiting values 4 and 1 at $\theta_0 \rightarrow 0$ and $\theta_0 \rightarrow 1$ respectively. For the initial slope at $\theta_0 \rightarrow 0$ he obtained however -6.616 instead of our value $-14/3$ (see Eq. (3.20)).

concentration range, it may lead to the necessity to consider α as a variable.

3.3. The interaction constant

The third parameter in the adsorption isotherms, the interaction constant β , also poses serious problems for correct interpretation of the data. It was already mentioned that the introduction of the factor $\exp(-\beta\theta)$ by Frumkin is an ad hoc assumption made by analogy with the attractive term in the van der Waals equation. In fact, at least for adsorption on solid surfaces where one can speak of adsorption centers and localized adsorption, the Langmuir–Frumkin Eq. (2.14) is a direct corollary from the Bragg–Williams approximation, since it coincides with Eqs. (14)–(47) in [31], which were derived by means of this approximation. Note, however, that according to this equation one must have

$$\beta = -\frac{c_n w}{kT} \quad (3.23)$$

(where w is the interaction energy between two adsorbed molecules and c_n is the number of closest neighbors) i.e. β is the dimensionless interaction energy with all c_n closest neighbors, rather than with only with one of them, as it is sometimes assumed.

Rigorous expression for β for non-localized adsorption, valid for small surface coverage, can be derived by using the theory of the virial expansion for real gases (Chapter 15 in [31]). By analogy with Eqs. (15.12) and (15.23) of Hill, for $\theta < 1$ the surface equation of state for non-localized adsorption can be written as a series expansion with respect to Γ , the first two terms giving:

$$\begin{aligned} \frac{\Delta\sigma}{\Gamma kT} &= 1 + B_2 \Gamma \\ B_2 &= -\frac{1}{2} \int_0^\infty \left(e^{-\frac{w(r)}{kT}} - 1 \right) dA \end{aligned} \quad (3.24)$$

If one neglects the difference in the linear terms (due to the electric field) the comparison of Eqs. (3.24) and (2.49) yields the relation between the second virial coefficient B_2 , and the coefficients B and α :

$$B_2 = \frac{B\alpha}{2} \quad (3.25)$$

The interaction energy $w(r)$ (with r being the distance between the centers of the molecules) can be represented reasonably well by the function:

$$\begin{aligned} w(r) &= +\infty \text{ for } 0 < r < 2r_0; \\ w(r) &= -\frac{L}{r^6} \text{ for } 2r_0 < r < \infty \end{aligned} \quad (3.26)$$

where L is the constant in London's equation of intermolecular interaction [34]. For an interface $dA = 2\pi r dr$. For $r < 2r_0$ the integrand in Eq. (3.24) is -1 and for $r > 2r_0$ in most cases

$|w(r)/kT| < 1$ and the exponent can be expanded in series. Keeping the linear term and performing the integration one obtains:

$$B_2 = 2\pi r_0^2 - \frac{\pi}{4kT} \frac{L}{(2r_0)^4} = 2\alpha_0 + \frac{w\alpha_0}{kT} \quad (3.27)$$

In the last step we have used the relation between the contact energy w and the London constant: $L = -(2r_0)^6 w$. By expanding in series the Volmer Eq. (2.17) and comparing with Eq. (3.24) one finds

$$B_2 = \alpha_V - \frac{\alpha_V \beta_V}{2}$$

The comparison of this expression with Eq. (3.27) shows that the first term in the right hand side of Eq. (3.27) leads to the known result $\alpha_V = 2\alpha_0$ (which confirms again that it is valid only for small coverage) and the attraction constant is:

$$\beta_V = -\frac{w}{kT} \quad (3.28)$$

The comparison with Eq. (3.23) suggests that this value of β is c_n times smaller (between 6 and 4 depending on the packing geometry) than it is for the Langmuir model.

This dramatic difference in the values of β between Langmuir and Volmer models is most probably apparent. Indeed, in the Langmuir model one assumes that all neighboring molecules are situated on the respective centers, so that if all of them are occupied, the total interaction energy is $c_n w$. Conversely, the integration over r , used when deriving Eq. (3.28), means that all molecules, which are at a distance r , can interact with the central molecule. On the entire perimeter of the inaccessible area (see Fig. 6.b) one can fit 6 molecules. Hence, it turns out that the total interaction energy should not be very different for the two models. These considerations are supported by the virial expansions of the two Eqs. (2.15) and (2.17):

$$\begin{aligned} \text{Langmuir model: } \frac{\Delta\sigma}{\Gamma kT} &= 1 + \frac{1}{2}(1 - \beta_L)\alpha_L \Gamma \\ &= 1 + [2\alpha_0 - \beta_L(2\alpha_0)]\Gamma \end{aligned} \quad (3.29)$$

$$\begin{aligned} \text{Volmer model: } \frac{\Delta\sigma}{\Gamma kT} &= 1 + \frac{1}{2}(2 - \beta_V)\alpha_V \Gamma \\ &= 1 + [2\alpha_0 - \beta_V\alpha_0]\Gamma \end{aligned} \quad (3.30)$$

where we have used the values $\alpha_L = 4\alpha_0$ and $\alpha_V = 2\alpha_0$ at $\theta_0 \rightarrow 0$. These two equations become identical if

$$2\beta_L = \beta_V \quad (3.31)$$

This confirms the conclusion above that the difference in the attraction terms between Langmuir and Volmer models is not as big as it looks from Eqs. (3.23) and (3.28). This is also confirmed by the experimental data in Table 2.

The next question deserving analysis is to what extent accounting for the interaction only through the term $\beta\theta^2/2$ in the EOS is correct. The analysis for localized adsorption is facilitated by the fact that a much more accurate EOS based on the so-called

quasi-chemical approximation (QCA) exists (Hill [31], Eq. (14.62)):

$$\pi_s = -\ln(1-\theta) - \frac{c_n}{2} \ln \left[\frac{\beta_n + 1 - 2\theta}{(\beta_n + 1)(1-\theta)} \right] \quad (3.32)$$

where

$$\beta_n = \sqrt{[1 + (4/c_n)\theta(1-\theta)]\beta} \quad (3.33)$$

(the original expression for β_n contains instead of β a factor $[1 - \exp(-w/kT)]$, which we linearized as w/kT to introduce β). The first term in the right hand side of Eq. (3.32) is the usual Langmuirian term and the second one accounts for the interaction between closest neighbors. The precision of this approximation can be estimated by the fact that it leads to a much better value for the critical temperature than the Frumkin equation.

In order to compare Eqs. (3.32) and (2.15), we expanded the interaction term (the second in the right side in Eq. (3.32)) in series and kept the terms up to θ^5 . After long and tedious calculations we obtained:

$$\begin{aligned} \pi_s &= -\ln(1-\theta) - \frac{\beta\theta^2}{2} + \frac{\beta^2\theta^3}{c_n} - \frac{\beta^2(3c_n + 10\beta)\theta^4}{4c_n^2} \\ &+ \frac{\beta^3(4c_n + 7\beta)\theta^5}{c_n^3} + \dots \end{aligned} \quad (3.34)$$

This result suggests two important conclusions: (i) The Langmuir–Frumkin Eq. (2.15) accounts accurately for the interaction up to the second virial coefficient; (ii) More importantly, only in the second virial coefficient the interaction contribution is proportional to β , whereas in the third virial coefficient it is proportional to β^2 , and so on. This means that if $\beta < 1$, it is legitimate to sum up all repulsive terms of the virial expansion (the sum gives the term $-\ln(1-\theta)$), but to keep only the term with the second virial coefficient (proportional to β) from the interaction contributions. Hence, the Langmuir–Frumkin equation is exact if $\beta < 1$, provided that the adsorption is really localized.

The situation with the contribution of the interaction term is less clear, to say the least, with the equation of Volmer (van der Waals). To check this, we derived an equation which accounts exactly for the terms, linear in β , by using a procedure proposed by Hemmer and Stell [35]. The result (valid for adsorption on a line) is:

$$\pi_s = \frac{\theta}{1-\theta} - \beta \frac{\theta^2}{(1-\theta)^2} \quad (3.35)$$

It is obvious that Eq. (2.17) can be obtained only if one neglects θ in the denominator of the second term in the right side of Eq. (3.35). This means that the van der Waals equation has at least two limitations as far as the interaction parameter is concerned: (i) It is valid not only for small β (as the Langmuir–Frumkin equation is) but also for small θ ; and (ii) If one expands the second term in the right side of Eq. (3.35) in series in θ , it is obvious that all virial coefficients will contain terms linear in β . Therefore it is not legitimate to proceed as one can do it with localized

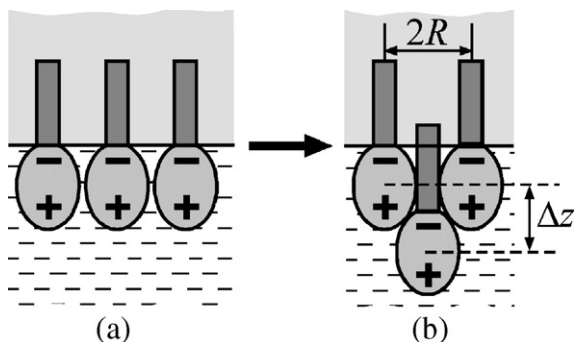


Fig. 8. Expulsion of a surfactant molecule from the adsorbed layer. The combination of surfactant ion and the counterion is modeled as a dipole. In position (a) all dipoles lie in the same plane, which leads to repulsion. To decrease the repulsion, the middle molecule enters deeper into the water phase, as shown in position (b). This is opposed by the adsorption energy, which pulls the molecules up. The result of these opposite effects is that the middle molecule will reach equilibrium at a distance Δz from its initial position.

adsorption, namely, to sum up all the terms corresponding to repulsion (this sum leads to the first terms in the right hand sides of Eqs. (2.17) and (2.18)), but to keep only one of the attraction terms, $\beta\theta^2$, if β is small enough [27]. Hence, the situation with respect to the correct expression for the intermolecular interactions for non-localized adsorption is far from clear.

3.4. Role of charge discreteness

The theoretical results in Sections 3.1–3.3 reveal how cautious one must be when extracting molecular information from interfacial tension data. It should be obvious that the data interpretation is full of pitfalls and reliable data can be obtained only by using sound theoretical basis even for non-ionic surfactants. With ionic surfactants the situation is much more complicated, since the previous theoretical results refer to molecules interacting only through short range forces, effective at close contact between the molecules, whereas the interaction between ions is determined above all by long range electrostatic forces between discrete charges. We believe that the main shortcoming of the Gouy Eq. (2.2) and all theories, based on it (including ours) is the neglect of the discreteness of the charges. That is why such theories cannot explain the main intriguing effect, which we mentioned in the Introduction: the fact that in spite of the lower adsorption energy at Air/Water interface, the adsorption of ionic surfactants at higher concentration is considerably larger than at Oil/Water interface. A complete analysis of the effect of charge discreteness can be carried out only on the basis of a comprehensive theory, which to the best of our knowledge has not been created yet. Warszynski et al. [15] tried to formulate the basis of such theory, but due to mathematical difficulties, they eventually used a two-dimensional analog of the Debye–Hückel equation. That is why in this section we will put forward some qualitative considerations, which could explain not only the difference in adsorption at Air/Water and Oil/Water interfaces, but also some other intriguing effects, which were found while processing the experimental data in Section 4.

We will consider a simplified picture of the electrostatic pair interactions at the interface. Imagine that each adsorbed surfactant

ion has a counterion, opposite to it and situated at a distance $1/\kappa$, where κ is the Debye parameter. This couple forms a dipole with dipole moment $\mu_d = e_0/\kappa$. If all dipoles are aligned in a plane parallel to the interface, the repulsion between them will try to push some of them out of the plane. This process is illustrated in Fig. 8 for three dipoles whose axes lie in a plane perpendicular to the interface. The interaction energy of the expelled dipole with its 6 neighbors is:

$$u_d = 6 \frac{\mu_d^2}{\varepsilon R^3} \frac{1-2Z^2}{(1+Z^2)^{5/2}} \quad (3.36)$$

where $Z = \Delta z/R$, ε is dielectric constant and the other notations, Δz and R , are clear from Fig. 8. To obtain the total energy, u_{tot} , one must add to u_d the transfer energy of the hydrophobic tail, defined by Eq. (3.14). The equilibrium position Z_{eq} of the expelled surfactant is determined by the condition $du_{\text{tot}}/dZ=0$, leading to

$$W = f(Z_{\text{eq}}); \quad W = \frac{\varepsilon R^4 w_1}{6 \mu_d^2}; \quad f(Z) = \frac{3Z(3-2Z^2)}{(1+Z^2)^{7/2}} \quad (3.37)$$

The function $f(Z)$ is plotted in Fig. 9, along with two possible values of the parameter W . In case 1 with $W=W_1$ the condition for equilibrium is not fulfilled, which corresponds to a single layer, as in Fig. 8.a. In case 2 (with $W=W_2$) Eq. (3.37) has two roots, corresponding to two extrema. More detailed analysis of the function $u_{\text{tot}}(z)$ showed however that the smaller root corresponds to a maximum of u_{tot} and only the larger one, denoted in Fig. 9 by Z_{eq} , corresponds to a minimum of u_{tot} i.e. to equilibrium. In the case with W_2 , part of the surfactant molecules will be expelled and the adsorbed layer will become rough, in fact it will become a bilayer (see Fig. 8.b). Such surface

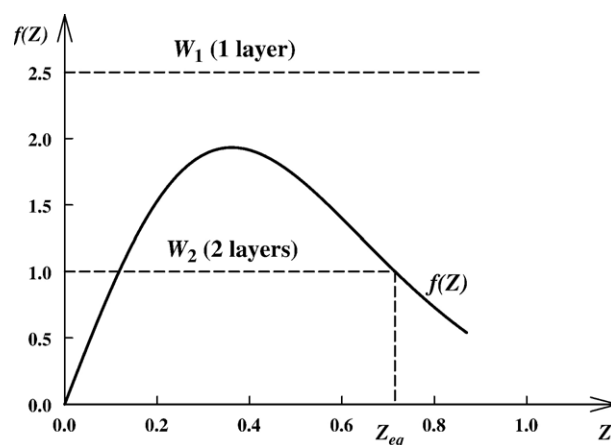


Fig. 9. Plot of the function $f(Z)$ from Eq. (3.37). Two cases, corresponding to two values of the quantity W from Eq. (3.37) are considered: $W=W_1$, which is larger than the maximum of $f(Z)$ and $W=W_2$, which is smaller than the maximum. Since the line W_1 does not intersect the curve $f(Z)$, Eq. (3.37) has no solution, which corresponds to molecules aligned in one plane, as in Fig. 8.a i.e. to a single adsorbed layer. For $W=W_2$ Eq. (3.37) has two solutions but the smaller one corresponds to maximum of the total energy, u_{tot} , so that only the solution, denoted by Z_{eq} gives the equilibrium immersion depth of the expelled molecules (see Fig. 8.b), which form in fact a second adsorbed layer.

roughness was experimentally observed by Lu et al. [36] by neutron scattering. In such bilayer the decreased repulsion will lead to smaller area per molecule, α , and increased adsorption Γ . The area per molecule will be intermediate between the cross-sectional areas of the ionic head and the paraffinic chain. Another peculiarity of such configuration is that there will be two surface potentials, corresponding to the two adsorbed layers. The theory of the diffuse layer must be altered accordingly.

The monolayer configuration will be favored by the factors, leading to larger values of W (see Eq. (3.37)). Indeed, larger R corresponds to a smaller adsorption, smaller repulsion and monolayer structure, which is expected. At the Oil/Water interface W is larger than at Air/Water (since, the transfer energy per unit length, w_1 , is larger), which suggests that at the Oil/Water interface it is more likely to have a monolayer structure.

The structure of the adsorbed layer affects also the value of the minimum area per molecule, α . When the surfactant ions form a monolayer and the counterions are not very close to them (small electrolyte concentration) not all field lines are closed on the counterions and there is direct repulsion between the surfactant ions (see Fig. 10.a). This must lead to larger area per molecule, α , and decreased adsorption which is in agreement with the observed lower adsorption of the surfactants at the interface oil/water. Adding electrolyte will bring the counterions closer to the surfactant ions thus attracting more field lines, decreasing the repulsion and consequently — decreasing also the area per molecule (see Fig. 10.b). Our results in Section 4 show that this is the main effect of the electrolyte and it is one of the reasons for the stronger adsorption in the presence of added salt.

Another consequence of this concept is that for ionic surfactant α has no clear physical meaning (as it has in most cases with non-ionic surfactants). Indeed, at Oil/Water interface α is more likely determined by the electrostatic repulsion, rather than by the true size of the ionic head. At the surface Air/Water α will depend on the degree of immersion of the surfactant molecules. A problem for ionic surfactants is also how to discriminate between α and β , since both quantities are related to the free energy of interaction between discrete charges. This viewpoint is confirmed by the data in Section 4, showing that the variations in α and β are correlated.

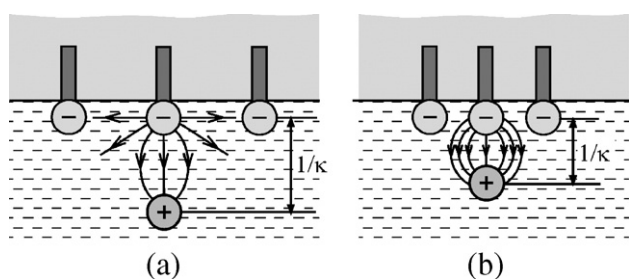


Fig. 10. Sketch of the electrostatic interactions in the adsorbed and diffuse layers: (a) low electrolyte concentration — the counterion is far away from the adsorbed layer; the repulsion and the distance between the adsorbed molecules are large; (b) high electrolyte concentration — the counterion is closer, it captures most of the field lines, and the repulsion and the distance between the adsorbed ions are smaller.

4. Data processing and analysis

In this Section 4 we apply the theoretical results from Sections 2 and 3 to the analysis of the experimental data. In Section 4.1 we explain how we selected the data for the experimental check of the theory and how the two- and three-parameter fits were performed and tested. In Section 4.2 the main numerical results are analyzed and compared with the theoretical predictions.

4.1. Data processing

We tried to check the isotherms, the equations of state and the concepts, outlined in the previous sections as thoroughly as possible. Since the surface tension measurements involve only two of the main experimental variables, namely σ and C (which includes both the surfactant and the electrolyte concentrations, C_s and C_{el}), we calculated the adsorption Γ by means of the Gibbs adsorption isotherm (Eq. (2.44)):

$$\frac{d\sigma}{\ln C} = -2\Gamma kT \quad (4.1)$$

We used also the suggestion of Rehfeld [37] to interpolate the experimental dependence $\sigma(C_s)$ by means of the empirical formula

$$\sigma = a_0 + a_1 \ln C_s + a_2 (\ln C_s)^2 \quad (4.2)$$

which we also applied to the effective concentration $C = [a_s(a_s + a_{el})]^{1/2}$, where a denotes activity. This allowed us to check four models by using both $\theta = \theta(C)$ and $\pi_s = \pi_s(\theta)$ (Langmuir and Volmer models, each with and without molecular condenser, i.e. with $n=1$ and $n=3$ respectively; they are denoted shortly as L-1, L-3, V-1 and V-3). We believe that the HFL isotherm with interaction, Eq. (2.19), needs a deeper analysis of the interaction term and for now we postpone its use for data analysis for the future. For the time being we will use only the Volmer isotherm as model for non-localized adsorption. We analyzed mainly the adsorption isotherm (AI) $C = C(\Gamma)$ and the equation of state (EOS), $\Delta\sigma = \Delta\sigma(\Gamma)$, but we also checked the dependence $\Delta\sigma = \Delta\sigma(C)$. Because of the presence of fractional powers in our equations, to avoid difficulties with the dimensions, we used as dimensions cm^{-3} for concentrations and cm^{-2} for adsorptions.

To simplify the discussion we decided to study only three model systems, all of them with sodium dodecyl sulfate (SDS) as surfactant at Air/Water, Oil/Water and Oil/(Water + added electrolyte NaCl), denoted hereafter for short as (A/W), (O/W) and (O/WE). We used literature data for $\sigma = \sigma(C)$, but checked carefully their reliability. With this goal in mind in Fig. 11 the data of Rehfeld [37] for A/W are compared with those of Hines [38] and the data of Motomura et al. [39] are compared with those of Rehfeld [37] for *n*-heptadecane. It is obvious that the coincidence of the curves is perfect. Haydon and Taylor [4] obtained four isotherms with 0.05, 0.1, 0.25 and 0.5 M NaCl. To simplify the discussion we will use only the curve for 0.1 M NaCl which has more experimental points than the others. Moreover, the plot in Fig. 12 shows that the four curves practically coincide, so that the data obtained with one of them should be representative of all. We finally decided to process the following data: for A/W we selected the data of Rehfeld [37] at

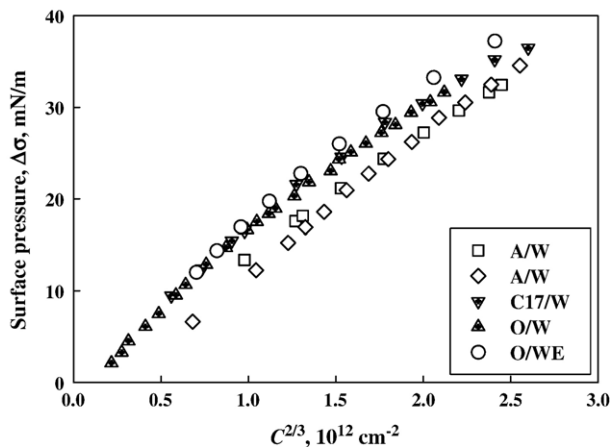


Fig. 11. Surface pressure $\Delta\sigma$ vs. $C^{2/3}$ at A/W, O/W and O/WE. The values of $\Delta\sigma$ for A/W are from Refs. [37] (squares) and [38] (diamonds), those for O/W are from Ref. [39] for hexane (C6, crossed triangles up) and from Ref. [37] for *n*-heptadecane (C17, crossed triangles down), and for O/WE (0.10 M NaCl) are from Ref. [4] (Petroleum ether, circles).

25 °C and $\sigma_p = 71.8$ mN/m; for O/W — the data of Motomura et al. [39] for hexane at 30 °C and $\sigma_p = 50.2$ mN/m, and for O/WE — the data of Haydon and Taylor [4] for petroleum ether as the oil phase at 20 °C and $\sigma_p = 50.9$ mN/m. The equations of state of these systems, i.e. the curves $\Delta\sigma$ vs. Γ , are plotted in Fig. 13.

All curves in Figs. 11 and 13 exhibit perfect fits of $\Delta\sigma$ with quadratic polynomials in terms of $C^{2/3}$ or Γ with standard deviation $r^2 > 0.999$. This fact is the reason for our decision to neglect all effects, leading to contributions of the order of θ^3 and higher. Before we discuss the numerical results, we must point out that our theory is not valid for very low adsorptions. There are several reasons for it, the main ones being: (i) the use of the approximation for high surface potentials (see Eq. (2.6)); (ii) the identification of the adsorption Γ in the Gibbs Eq. (2.44), which includes also the adsorption of the amphiphilic surfactant ion *in the diffuse layer*, with the adsorption Γ in the adsorption isotherms (Eqs. (2.21)–(2.23)), which is only the adsorption of the surfactant *in the adsorbed layer*, at $z = z_0$ — this difference is

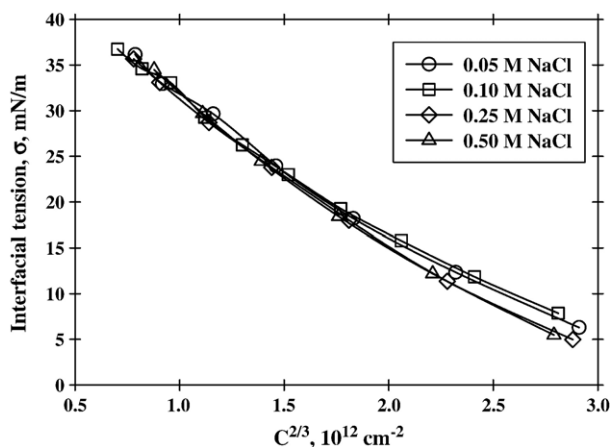


Fig. 12. Interfacial tension, σ , vs. $C^{2/3}$ for four O/W systems with $C_{el} = 0.05, 0.10, 0.25$ and 0.50 M. Data from Ref. [37].

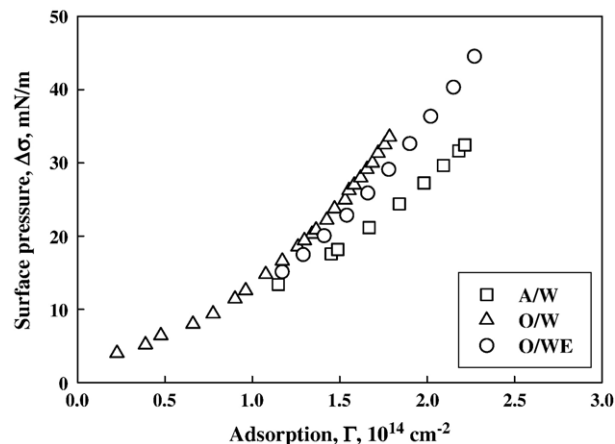


Fig. 13. Surface pressure, $\Delta\sigma$, vs. adsorption, Γ . The adsorption, Γ , is calculated by means of Eqs. (4.1) and (4.2).

negligible for moderate and high adsorptions [40], but may become sizable at small adsorptions [41]; (iii) the use of the Rehfeld formula (4.2), which obviously fails for $C \rightarrow 0$; and (iv) the neglect of the potential due to adsorption of hydroxyl ions, since even the pure interfaces have their own potential (which can be as high as 70–80 mV [42]) — this effect may play a role at small adsorptions.

Every approximate theory leads to false results, when it is applied under conditions, where its premises are not fulfilled. Accordingly, when our fits of σ vs. $C^{2/3}$ or Γ are extrapolated to C or Γ equal to zero, they lead to interfacial tension values σ_0 , which differ from the known values for the pure liquids, σ_p , by several mN/m. For this reason the values of $\Delta\sigma$ in Figs. 11 and 13 were calculated not with σ_p , but with the respective extrapolated values σ_0 . We checked the role of the difference between σ_p and σ_0 in the data processing and it turned out to be small. This effect seems to be of little practical significance, since all data for the systems without added electrolyte which we found were for surfactant concentrations above 10^{-4} M and obeyed quite well our theory. Davies and Rideal [3] also observed that “the lower theoretical limit to Γ for long chain ions is not significant”.

It is well known that the more free parameters a theory contains, the less unambiguous the results are. Although our theory involves apparently the minimum possible number of parameters (only three: K , α and β) we still tried to use, whenever possible, linear fits to obtain more reliable data, at least for some parameters. With non-ionic surfactants at sufficiently low concentrations all functions exhibit linear behavior in appropriate coordinates. A well known example is the linear adsorption isotherm of Henry: $\theta = K_s C_s$. According to Eqs. (2.21)–(2.23) and (2.47)–(2.48), the analog of Henry’s law for ionic surfactants must be:

$$\Gamma = KC^{2/3}; \quad (4.3)$$

and the equation of state for low concentrations must become:

$$\Delta\sigma = 3kT\Gamma = 3kTKC^{2/3} \quad (4.4)$$

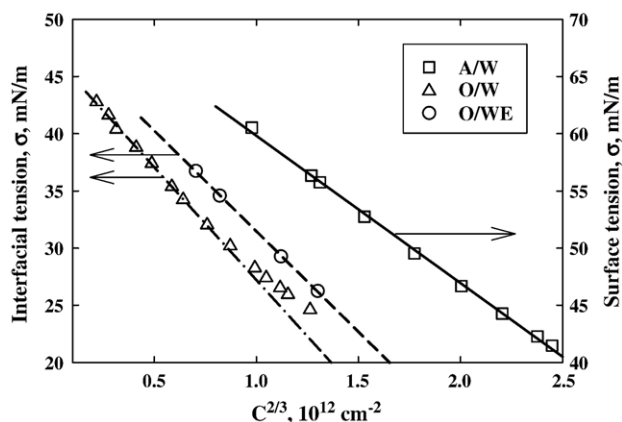


Fig. 14. Interfacial tension vs. $C^{2/3}$ plots for the systems A/W (squares, right axis), O/W and O/WE (See Eq. (4.4)).

However, as we noticed in Section 2 (see Eq. (2.51)), the virial expansion of $\pi_s(\theta)$ corresponds to exponential dependence of $\zeta(I)$. That is why it should not be surprising that, Eq. (4.3) was found to be inapplicable with sufficient precision. On the contrary, the data $\Delta\sigma$ vs. $C^{2/3}$ exhibit good linear relationship in a rather wide concentration range so that the second Eq. (4.4) could be used — in fact for A/W the isotherm $\sigma(C^{2/3})$ is linear almost up to the cmc. This is confirmed by the plots in Fig. 14. The calculated values of K from these plots for the three systems are listed in the first column of Table 1. As one would expect the adsorption constant for O/W is larger than for A/W.

We calculated the product $B\alpha$, i.e. the second virial coefficient (see Eq. (3.25)), for $\Delta\sigma$ vs. Γ , in three different ways. The first one was by linear plot based on Temkin Eq. (2.58) (see Fig. 15). These data are listed in the second column of Table 1. The second method was based on Eq. (2.49) and the values of the second virial coefficient were determined from the quadratic fits of the curves in Fig. 12. The results, listed in the third column of Table 1, are very close to those obtained from the Temkin equation.

The situation is more complicated with the third method, based on the so-called Langmuir plot of the experimental data — see Eq. (2.29) and Fig. 16, where the data for $n=1$ are presented. With the exception of the first 2–3 points for the very low concentrations (not shown), the straight lines are almost perfect. The fit with $n=3$ for A/W (not shown) is almost as good as the fit with $n=1$. However, the Langmuir plot with $n=3$ for O/W is linear only for high adsorptions and for O/WE it never leads to a straight line. According to Eqs. (2.28), (2.29) and (2.51) from the slopes one

Table 1
Values of the adsorption constant, K , and the product $B\alpha$, as obtained from the best fits of the experimental data using equations, specified in the first row

Method	$\sigma(C^{2/3})$, Eq. (4.4)	Temkin, Eq. (2.57)	Virial expansion, Eq. (2.49)	Langmuir plot, Eq. (2.29)
Quantity	K	$-B\alpha \times 10^{14}$	$-B\alpha \times 10^{14}$	$-B\alpha \times 10^{14}$ K
A/W	112	2.58	2.65	2.6 139
O/W	155	4.47	4.63	4.5 227
O/WE	143	3.78	3.8	3.8 240

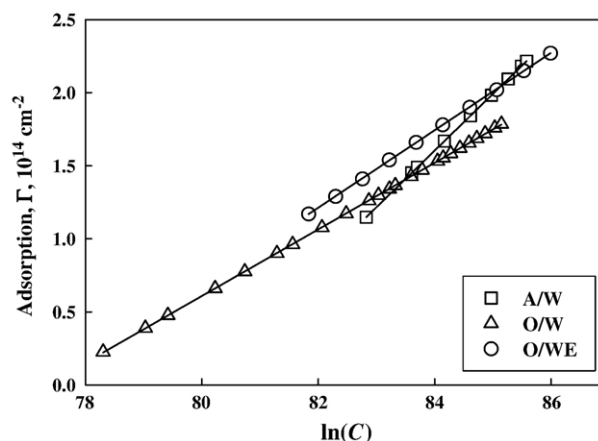


Fig. 15. Temkin plots for the systems A/W, O/W and O/WE (see Eq. (2.57)).

can determine K and from the intercepts $-B\alpha$. The results for $B\alpha$, presented in Table 1, are quite close to those obtained by the other two methods. However, those for K are larger than the ones obtained from surface tension data (the first column), but are close to the respective values in Table 2, obtained by three-parameter fit. This difference with the values of K in column 1 of Table 1 might be due to the approximations involved in the derivation of the equations. The different validities of the Langmuir plots for models 1 and 3 are probably also due to the approximations used: model 1 requires $\beta\theta/3 \ll 1$, whereas for model 3 the requirement is more stringent, i.e. $\beta\theta \ll 1$. Besides, from the data in Table 2 one can see that for O/W and O/WE the parameter β is considerably larger for model 3 than it is for model 1.

The calculated values of $B\alpha$ by these methods are in pretty good agreement, but since these plots give a single value of $B\alpha$ for a given system, no information can be obtained from them for α and β separately. On the other hand, β and α depend on the adsorption model and to understand the process of adsorption one needs information about them. In order to determine α and β separately we performed three-parameter fits of the adsorption isotherms and of the equation of state of Langmuir and Volmer for the two models: with $n=1$ (with condenser) and with $n=3$

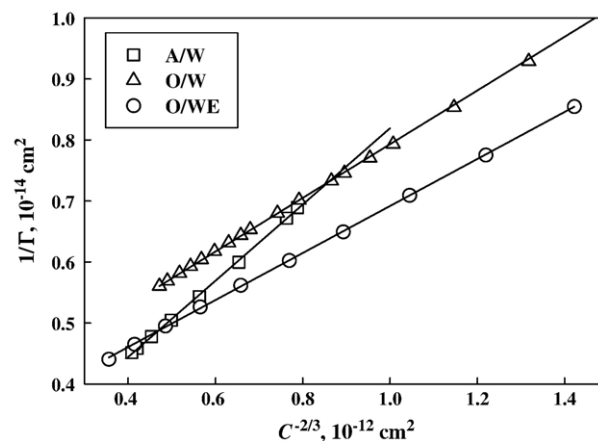


Fig. 16. Langmuir plots for the systems A/W, O/W, O/WE with $n=1$ (see Eq. (2.29)).

Table 2

Values of the adsorption parameters: adsorption constant K , minimum area per molecule, α , and interaction parameter, β , as obtained from 3-parameter fits by using different adsorption isotherms (AI) and equations of states (EOS)

System	Parameter	Langmuir				Volmer				Langmuir		Volmer		QCA	$\Delta\sigma - \Delta\sigma_{cl}$		Langmuir	Volmer
		$n=1$		$n=3$		$n=1$		$n=3$		AI; $n=3$		AI; $n=3$		$n=3$	L-3	V-3	No field	
		AI	EOS	AI	EOS	AI	EOS	AI	EOS	Low	High	Low	High	EOS	EOS	EOS	AI	AI
A/W	K	124	–	133	–	122	–	126	–	116	153	110	146	–	–	–	–	–
	α (nm ²)	0.28	0.29	0.35	0.36	0.23	0.24	0.25	0.26	0.41	0.32	0.30	0.23	0.35	0.35	0.25	0.28	0.20
	β	3.0	3.1	0.4	0.4	4.5	4.4	2.0	1.8	1.4	–0.5	3.3	0.6	–0.2	1	2.3	–4.5	–5
O/W	K	217.0	–	235.0	–	212.0	–	220.0	–	182	330	185	263	–	–	–	–	–
	α (nm ²)	0.37	0.40	0.45	0.49	0.30	0.33	0.33	0.36	0.55	0.28	0.39	0.28	0.47	0.47	0.34	0.39	0.31
	β	0.4	1.2	–2.0	–1.4	1.1	2.1	–1.3	–0.3	–0.9	–8.4	0	–5	0.33	–2.7	–2.2	–8.6	–8.8
O/WE	K	212.0	–	227.0	–	209.0	–	216.0	–	–	–	–	–	–	–	–	–	–
	α (nm ²)	0.28	0.27	0.34	0.34	0.27	0.22	0.25	0.25	–	–	–	–	0.33	0.37	0.24	0.24	0.20
	β	–1.4	–1.7	–3.3	–3.5	–1.1	–1.5	–3.2	–3.5	–	–	–	–	0.31	–2.5	–1.9	–10	–10
Column number		1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17

See text for details.

(no condenser). All fits were excellent, with standard deviation $r^2 > 0.999$. The errors in determining K and α were between 1 and 5%, but the error in β was between 20% and 150%. Typical fits are shown in Figs. 17 and 18 and the values of the adsorption parameters obtained are listed in Table 2, columns 1 to 8 (the extrapolated values σ_0 , corresponding to $C=0$, are not shown).

We fully agree with S. Brunauer [43] who warned in his famous book that the good fit of the experimental data is by no means a guarantee for the validity of a given adsorption model. That is why we expended considerable efforts in checking and analyzing the reliability and the meaning of the data. In this subsection we will summarize only a few general observations, related to the data obtained and the fitting procedure. Some effects, having important physical significance, will be discussed in more details in the next subsection.

The values of the adsorption constant K differ from system to system, but are almost the same for all models for a given system – they are always smaller for A/W and approximately equal for O/W and O/WE. The values of α and β , obtained by fitting the adsorption isotherm and the equation of state for a given substance, are very close in the framework of the same model, but

vary from model to model (α varies much less than β). The models with $n=1$ lead to slightly smaller values of α than those with $n=3$. The Volmer model always leads to smaller α 's than the Langmuir model. The values of α for O/W are larger and those for A/W and O/WE are smaller and close to each other. The values of β vary widely, but are always correlated with the α 's: in the framework of a given model a larger α corresponds to a larger positive β or to a smaller (in absolute value) negative β .

We subjected our fitting procedure to additional tests of reliability. A possible drawback of the fitting procedure is the dependence of the parameters' values on the concentration interval where the fit is performed. To check if such effect was present we divided the experimental data for A/W and O/W into two equal fractions (there were not enough points for the system O/WE), which we called “low concentrations” and “high concentrations”, and fitted them separately for the adsorption isotherms of models L-3 and V-3 (we called “average” the values obtained from the complete fit over all the data, columns 1–8 in Table 2). Columns 9–12 of Table 2 reveal the effect of the degree of coverage on α , discussed in Section 3.2 — the “low” values of α are larger than the respective “average” values in columns 3 and 7 from the overall fit. These results seem to point out also

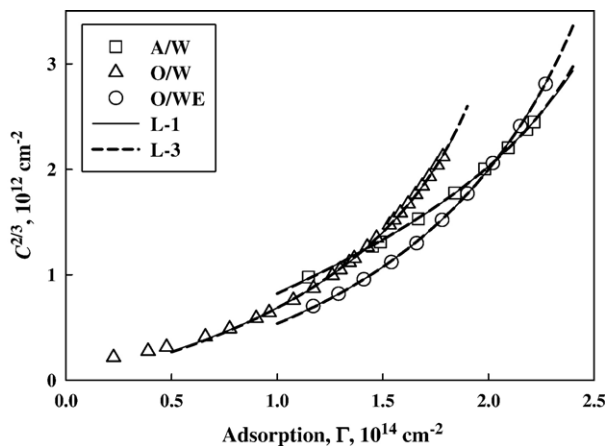


Fig. 17. Fits of the adsorption isotherms for A/W, O/W and O/WE systems with models Langmuir-1 (full lines) and Langmuir-3 (dashed lines) (see Eq. (2.21) with $n=1$ and $n=3$).

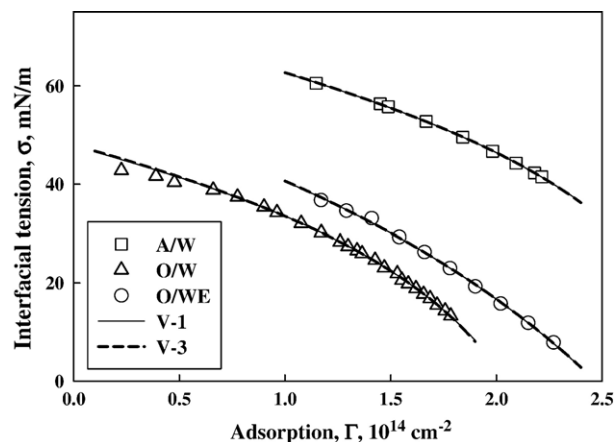


Fig. 18. Fits of the equations of state for A/W, O/W and O/WE systems with models Volmer-1 (full lines) and Volmer-3 (dashed lines) (see Eq. (2.48)).

that our fitting procedure gives more weight to the high concentrations, since the “high” values of α are closer to the “average” values. These data should not be taken, however, too seriously, because of the small number of experimental points in one portion, for example, for A/W there are only 4 points.

A similar dependence on the degree of coverage is observed with the values of the constant K which must be model independent (see Section 3.1 and the comment after Eq. (2.24)) and should be a true constant for a given system. However, if a free parameter is assumed constant during the fitting procedure, but in fact it is variable, the fit will lead to some average value for this quantity, but the results for some other quantities might be compromised. In our case α must depend on Γ (see Section 3.2), i.e. it is variable, but we considered it as a constant. This might be the reason why the values of K , determined by the three-parameter fit are different from the values obtained by the linear fits in Fig. 14. The situation might be similar with the high values of K in Table 1, obtained by fitting all the data in the Langmuir plot.

We tested the Langmuir model by fitting the data with the equation of state in quasi-chemical approximation since it is supposed to account more correctly for the interaction constant β . We used Eq. (3.32) with $c_n=6$ and accounted for the electric field for model 3 by adding in the right hand side a term 2θ . The results in column 13 must be compared with the respective results for model L-3 in column 4 — they reveal that the α 's are almost the same, but the β 's are dramatically different and they are always almost zero in the quasi-chemical approximation.

The data from the fits and the additional checks seem to indicate that the values of α and K may not be absolutely exact, but are reliable and at least qualitatively point to real effects in the right direction. More puzzling are the large variations of β : from 4 to -2.8 . Fortunately, the effect of these variations on the adsorption isotherm is much smaller than it looks. A glance at Eqs. (2.49) and (2.50) reveals that β enters the second term in the right hand side through the coefficient B (the relation between B and β is given by Eq. (2.50)). However, the variation of B with the model is much smaller than that of β . For example, for the system O/W β varies from 0.4 to -2 , but the respective variation of B is only from -2.6 to -3.3 , with an average value of -3 i.e. B changes only by about 10%. The parameters α and B participate always as a product in the virial coefficient of the EOS, which has a single value for a given system and is, therefore, model independent. This means that the product $B\alpha$ must be constant for a given system i.e. the variations in α must be accompanied by opposite variations in B and for that matter in β . As discussed above, this is confirmed by the data in Table 2.

4.2. Data analysis

In spite of the problems with fitting, mentioned in the previous subsection we believe that the data for K and α (and with some reservations — those for β) are reasonable and can be used for discussing the differences between the investigated systems and the role of the various factors on the adsorption parameters and the structure of the adsorbed layer. Of course, one should not insist on exact numerical values, but confines oneself mostly with the qualitative trends indicated by the results.

To confirm this viewpoint, we tried to answer the following question: Do the determined values of α in Table 2 really reflect, at least qualitatively, the variations of this adsorption parameter, induced by the electric field. To check this we proceeded in the following way. According to the concept of Davies (see text in Section 2.2 preceding Eq. (2.10)), $\Delta\sigma = \Delta\sigma_{\text{NIS}} + \Delta\sigma_{\text{el}}$, where $\Delta\sigma_{\text{NIS}}$ is the contribution of the same surfactant in non-ionized form. For $n=3$ the term $\Delta\sigma_{\text{el}} = 2\Gamma kT$ (see Eq. (2.11)) is the only contribution of the electric field. To remove the effect of the electric field it should be then enough to subtract $\Delta\sigma_{\text{el}}$ from the experimental values of $\Delta\sigma$. The right hand side of the resulting equations coincides with the EOS of Langmuir and Volmer for non-ionic surfactants (cf. Eqs. (2.47) and (2.48) for $n=3$ with Eqs. (2.15) and (2.17)). Hence, we fitted $\Delta\sigma - \Delta\sigma_{\text{el}}$ by means of Eqs. (2.15) and (2.17). If the concept of Davies were entirely correct, the result should have given the same value of α for the A/W, O/W and O/WE systems. This value should be close or even equal to the area of the cross-section of the SO_4^{2-} ion, found to be around 0.30 nm^2 in [9]. The comparison of the results (columns 14 and 15 in Table 2) with those ensuing from the three-parameter fit of the full EOS for $n=3$ (columns 4 and 8) reveals a good coincidence of the values of α . Besides, the values of α are different for the three systems and are not equal to 0.30 nm^2 .

This confirms that the values of α , determined by the three-parameter fit, have real physical meaning and indeed depend on the electric field. Another way to check this is to fit the experimental adsorption data $\Gamma = \Gamma(C)$ by means of the Langmuir and Volmer adsorption isotherms for non-ionic surfactants in Eqs. (2.14) and (2.16) i.e. to neglect altogether the electric field. The results for α in columns 16 and 17 of Table 2 are relatively close to the values with $n=1$ of the respective adsorption isotherms (columns 1 and 5) but the values of β obtained seem unreasonable — they are largely negative (even for A/W β is negative and very large: -4.5 and -5 for the two models, respectively).

One result, which seems to be beyond doubt, is that the Volmer isotherm leads always to lower α values than the Langmuir isotherm. This is in agreement with the discussion in Section 3.2, although we considered there only non-ionic surfactants. The observed variation of α with the degree of coverage, revealed by the differences between the “low”, “high” and “average” values of α in Table 2 (columns 1–8 and 9–12), is also in agreement with the theoretical predictions: indeed, the α 's are always smaller for the “high” values, as anticipated in Section 3.2.

The larger values of α and the negative values of β (indicating repulsion) at O/W can be explained by the concept of charge discreteness and the competition between charge repulsion and adsorption energy (see Section 3.4): the larger adsorption energy at O/W pulls the molecules up, which leads to repulsion between the charged surfactant heads. The correlation of α and β is also understandable in the framework of this concept — a more negative β means a stronger repulsion and thus a larger area α .

One might be tempted to explain the increased area per molecule at O/W by intercalation of oil molecules between the hydrophobic chains of the surfactant molecules. Such explanation is plausible, because it is akin to the well known explanation for the difference in thermodynamic properties of paraffins with odd

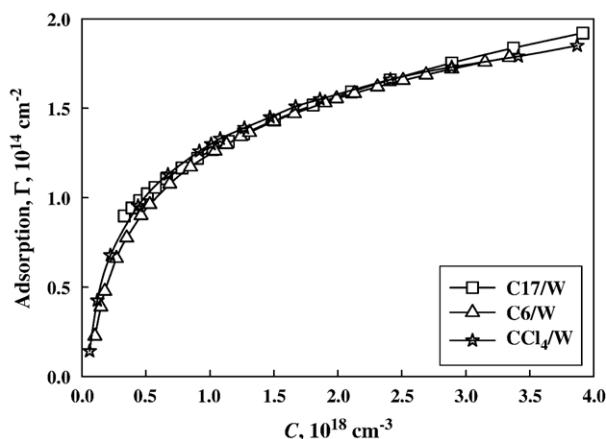


Fig. 19. Adsorption isotherms of SDS at different interfaces. The adsorptions, Γ , are calculated by means of Eqs. (4.1) and (4.2) with data from Refs. [39] (hexane, C6) and [37] (*n*-heptadecane, C17, and tetrachloromethane, CCl_4).

and even numbers of carbon atoms, which is ascribed to the different interactions between the molecules. To check this hypothesis we calculated the adsorption isotherms $\Gamma(C)$ of SDS at interfaces with different oils. Fig. 19 exhibits almost perfect coincidence of the adsorption of SDS at O/W interface with oils with different chain lengths and different sizes and shapes of the molecules, including the perfectly spherical molecule of CCl_4 . This speaks in favor of our explanation that the increased area per molecule is due to electrostatic interaction between the ionic heads.

As explained below, we have no serious reasons to select unambiguously one of the four models as the correct one. Nevertheless, we give preference to the model of Volmer with $n=1$ (with condenser) for the following reasons: (i) The finite size of the counterions (accounted for through the molecular condenser) is probably immaterial at low θ , but it is important at larger θ , especially as $\theta \rightarrow 1$; hence, we think that model 1 (with condenser) is closer to reality than model 3; and (ii) The Volmer equation always leads to values of α closer to the real values α_0 , than the Langmuir equation does (see Section 3.2).

If one takes the values of α for the model Volmer-1 and one plots the respective θ vs. the effective concentration $C = (a_s a_t)^{1/2}$, one sees from Fig. 20 that the degree of coverage, θ , for A/W is smaller than for O/W. This shows that the puzzling effect of much stronger adsorption Γ at A/W (demonstrated in Fig. 1) at high concentrations, in spite of the lower adsorption energy, is due mostly to the lower value of α , which decreases the hindrance between the adsorbed molecules, thus promoting adsorption. The same figure shows that even at the cmc θ hardly exceeds 0.5, which, in turn, shows why the virial expansion of π_s up to θ^2 works. This also explains why the plots σ vs. $\ln C$ (not shown) are not linear close to the cmc.

With the exception of the Langmuir-3 model, the values of α for the interface A/W are smaller than the supposed area of the $-\text{SO}_4^-$ group, 0.30 nm^2 , but are larger than the cross-sectional area of the hydrocarbon chain, 0.21 nm^2 . This intermediate value of α can be explained by, and speak in favor of, our hypothesis of partial immersion of the surfactant molecules at A/W (see Section 3.4).

The value of α for the system O/WE (with 0.1 M NaCl) is considerably smaller than it is for O/W. As explained in Section 3.4, this is possible if the increased concentration of counterions is sufficient to attract almost entirely the electric field, created by the surfactant ions, thus decreasing the electrical repulsion and the area per molecule. The area per molecule at O/WE is only slightly larger than that for A/W which may again mean partial immersion of the surfactant molecules. It is noteworthy that the decrease of α , caused by the electrolyte, occurs almost entirely already at 0.05 M NaCl and does not change significantly with further increase of C_{el} . This fact, along with the minor effect of the electrolyte on the adsorption constant K (see Tables 1 and 2) explains why in Fig. 12 the curves for all systems O/WE practically coincide, when plotted as σ vs. $C^{2/3} = (a_s a_t)^{1/3}$, in spite of the ten-fold increase of C_{el} (from 0.05 M to 0.50 M).

Sometimes the increased adsorption with added electrolyte is ascribed to the change in the bulk activity of the surfactant which transforms the surfactant ion-counterion pair in an almost neutral molecule. Such effect certainly exists, but we believe that the process is more complicated. Our direct calculations showed that the role of the activity coefficient in the adsorption isotherm was minor. Therefore, other factors must be more efficient in controlling the adsorption in the presence of electrolyte. We believe that these are: (i) the decrease of α ; and (ii) the increase of the effective concentration by the added electrolyte. Indeed, the latter effect is equivalent to increasing C_s , since instead of $C_s^{2/3}$, the adsorption becomes dependent on $C_{\text{el}}^{1/3} C_s^{1/3}$. The latter product is not exactly equivalent to mere increase of the surfactant concentration but nevertheless it brings $C = (C_s C_{\text{el}})^{1/2}$ to higher values than C_s , if $C_{\text{el}} > C_s$. That is why, when plotted vs. the effective concentration, as in Fig. 11, the curves for A/W, O/W and O/WE are quite similar, opposite to their appearance when plotted only vs. surfactant concentration, C_s , as in Fig. 1.

The situation with the adsorption constant K is much simpler. True, for reasons, already discussed in Section 4.1, we obtained larger values of K from the three-parameter fit than from the dependence of σ vs. $C^{2/3}$ (which we believe are closer to reality). Nonetheless, all calculated values of K have correct qualitative

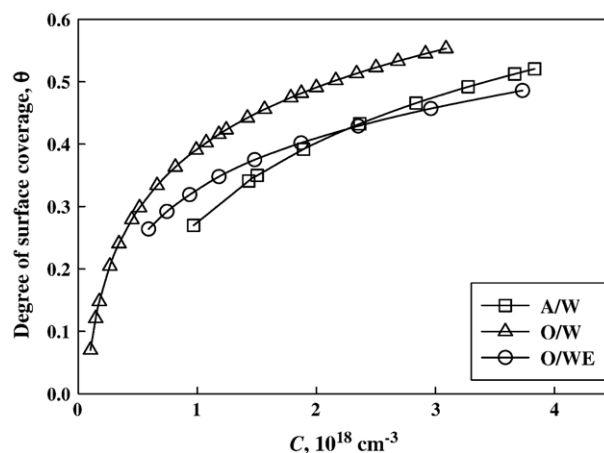


Fig. 20. Degree of surface coverage, $\theta = \alpha \Gamma$ vs. concentration, C , calculated for Volmer-1 model.

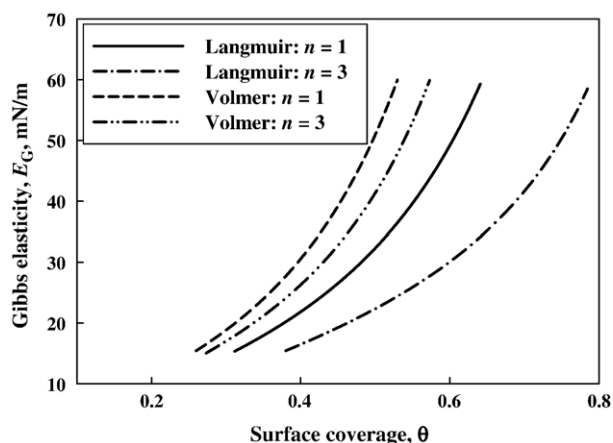


Fig. 21. Gibbs elasticity, E_G , vs. surface coverage, θ , calculated for the system A/W from four models.

physical behavior. For example, they turned out to be approximately the same for all models (see Table 2) as they must be. Indeed, by virtue of the definition of K through Eq. (2.24), it does not contain α and β , so that it must be model independent. The adsorption constant must be larger for O/W than for A/W due to the larger adsorption energy, which was always the case with all of our data. The calculated K 's were affected slightly by the addition of electrolyte, which can act in various ways. These effects are rather complicated and will be the subject of another paper [22].

In spite of the large variations, the value of β also exhibits in some respects a behavior which is in agreement with the theoretical prediction. The β 's are always positive for A/W, which is known to be due to attraction between the hydrocarbon tails [24]. For O/W they are either negative or are small, when they are positive, which speaks of repulsion. Incidentally, it is often assumed in the literature that for O/W $\beta=0$, since there could be no attraction between the hydrocarbon tails in the oil — if it is so the negative values of β' , found by us for O/W, should be due to pure repulsion. They are also negative for O/WE, which is probably due to the fact that at small distances between the surfactant ions (i.e. small α 's) even a weak field can provoke considerable forces. Rather surprisingly, the positive β 's obey reasonably well the relation (3.31), namely, $\beta_L = \beta_V/2$ found by us in Section 3.3.

We expended considerable efforts to find which isotherm (Langmuir or Volmer) and which model (with condenser, $n=1$ or without, $n=3$) were more realistic. The best parameter for such check seemed to be the ζ -potential, which must be close to ψ_0 . According to Eq. (2.38) Ψ_0 cannot give indication about the adsorption isotherm, but it can, in principle, reveal which model, 1 or 3, is effective, since plotted vs. θ the Ψ_0 -potential must continuously increase for $n=1$ and go through a maximum for $n=3$. Unfortunately, the available data [44,45] quoted in [8] are for very low concentrations, lower than the lowest in the data we have used.

Another way to perform such check is to calculate a given quantity from several models by using the respective adsorption parameters and then to compare the curves, obtained from the different models, with the experimental dependence of the same

quantity against an appropriate experimental variable. The model leading to closest coincidence with the experimental dependence must be the most accurate. To realize this check we calculated theoretically the Gibbs elasticity E_G , which can be found from Eqs. (2.47) and (2.48) and the definition:

$$\varepsilon = \frac{d\pi_s}{d\ln\theta} \quad \text{with} \quad \varepsilon = \frac{\alpha E_G}{kT} \quad (4.5)$$

We calculated E_G by using the adsorption parameters from Table 2 for the different models and compared the results with the “experimental” values, calculated from the experimental data $\sigma = \sigma(\Gamma)$ (see Fig. 13) and the equation:

$$E_G = -\frac{d\sigma}{d\ln\Gamma} \quad (4.6)$$

When we plotted the results from the model isotherms for A/W as a function of $\theta = \alpha\Gamma$ for the four models, we obtained four different curves (Fig. 21). However, when we plotted the same results for E_G as a function of an experimental variable, Γ or C , they collapsed in a single curve, which practically coincided with the “experimental” values, calculated by means of Eq. (4.6) and the experimental data (see Fig. 22). The same happened with the data for O/W, but the respective curves in Fig. 22 were of course different. It is easier to understand the reason for this result if one treats in the same way the equations of state (2.47) and (2.48). If one plots $\Delta\sigma = kT\pi_s/\alpha$ vs. θ , the four equations will lead of course to four different curves (for simplicity we assume $\beta=0$). If however in each of these equations one replaces θ by $\alpha\Gamma$ and for α one uses the numerical value, obtained for the respective model, then $\Delta\sigma$ will become function only of Γ . If the model and the fitting procedure were correct, the resulting dependence of $\Delta\sigma$ on Γ should coincide with the original experimental curve.

Therefore, the above calculations of E_G are a proof of the self-consistency of our theory and numerical calculations, but at the same time they indicate that it is impossible to reach definite conclusions about the adsorption model and the structure of the adsorbed layer by using only surface tension data and theoretical adsorption isotherms or equations of state. Obviously, additional

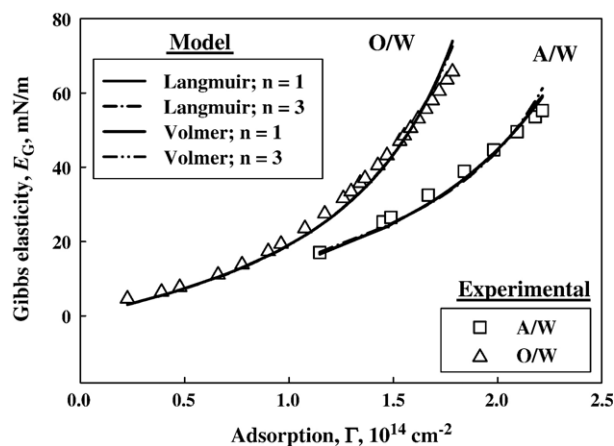


Fig. 22. Gibbs elasticity, E_G , vs. the adsorption, Γ , calculated from four models for the systems A/W and O/W. All four curves for a given system coincide. The symbols denote the experimental values for the respective system.

experimental data are needed in order to understand more deeply the adsorption of ionic surfactants. The use of data for different systems should also help, e.g., data for surfactants with different ionic heads and larger or polyvalent counterions can lead to larger deviations from ideality and this may provide additional information about the model. For this reason we insist that some of the conclusions we reached might be valid only for the surfactant and the electrolyte considered, i.e., SDS and NaCl.

However, above all a new theory, accounting for the discreteness of the surface charges, is needed. Our data seem to indicate beyond doubt that the minimum area per molecule, α , is not a property of the surfactant molecule, as it is, at least approximately, for non-ionic surfactant. It is simply a measure of the hindrance, exerted by the adsorbed molecules against the adsorption of new molecules. Hence, it is a property of the specific system and as we showed it can depend on several factors such as type of the hydrophobic phase and presence of electrolyte. A theory of discrete ion interactions in the adsorbed layer will in fact give the free energy of the system as a whole and it is not clear beforehand how it can be subdivided into separate contributions to α and to an interaction term, analogous to β . The difficulties lying ahead are enormous, but the outcome might be worth the effort.

5. Summary and conclusions

Our goal in this study was to investigate both theoretically and experimentally the adsorption of ionic surfactants and the role of different factors (more precisely — the nature of the hydrophobic phase and the neutral electrolyte) on the mechanism of adsorption, the adsorption parameters and the structure of the adsorbed layer. We used available data about the interfacial tension, σ , vs. surfactant concentration, C_s , for sodium dodecyl sulfate (SDS) in three representative systems: Air/Water (A/W), Oil/Water (O/W) and Oil/Water + 0.1 M NaCl (O/WE). The NaCl was chosen since the Na^+ has a very low polarisability thus one cannot expect that it will interact strongly by van der Waals forces with the interface or the adsorbed surfactant ions.

In order to check the role of the adsorption model we derived 6 new adsorption isotherms (AI) and 6 new equations of state (EOS) based on the adsorption isotherms for non-ionic surfactants of Langmuir, Volmer and Helfand–Frisch–Lebowitz (HFL) with interaction term $\beta\theta^2/2$ in the EOS, $\theta = \alpha\Gamma$ being the degree of coverage, with Γ — adsorption and α — minimum area per molecule. We used for this derivation a modified Gouy equation (Eq. (2.9)), valid for high surface potential, ψ_0 accounting for partial penetration of the counterions in the adsorbed layer or neglecting the penetration — we called the respective AI and EOS models 1 and 3. The AIs were written in terms of the effective concentration $C = [C_s(C_s + C_{\text{el}})]^{1/2}$, so that they could be applied without modification to systems with concentrations of surfactant C_s and of electrolyte C_{el} . From the general form of the AIs we derived approximate equations, analogous to the equations of Temkin, Langmuir (for non-interacting molecules) and Szyszkowski.

In order to be able to analyze more precisely the adsorption data, we carried out in Section 3 a theoretical analysis of the adsorption parameters. We showed that the adsorption constant K is proportional to an effective thickness of the adsorbed layer, which is of

the order of 0.1–0.2 nm and is determined by the energy of transfer of the surfactant hydrophobic tail from the water into the hydrophobic phase (Eq. (3.16)). The so-called minimum area per molecule, α , was shown to be larger than the true area α_0 and is a function of Γ , rather than a constant. It turned out that this function depends on the adsorption model and α/α_0 can vary from 4 to 1 for the Langmuir model and from 2 to 1 for the Volmer model (see Eq. (3.19) and Fig. 7). The analysis of the interaction constant β in Section 3.3 showed that the interaction term $\beta\theta^2/2$ in the Langmuir EOS is exact for small $\beta \ll 1$, but for the Volmer EOS it is only a crude approximation without serious theoretical basis.

Semi-quantitative considerations about the interaction between discrete charges in Section 3.4 revealed that at A/W the adsorbed surfactant is partially immersed in the water, which leads to decreased repulsion and increased adsorption Γ . At O/W the larger adsorption energy maintains the surfactant molecules on the surface and the electrostatic repulsion is stronger, which translates into negative β , larger α and smaller adsorption. The addition of electrolyte partly screens the repulsion at O/W, leading to decreased α and increased adsorption.

The EOS $\Delta\sigma = \Delta\sigma(\Gamma)$, where $\Delta\sigma$ is the two-dimensional surface pressure, is fitted perfectly with a second-order polynomial in Γ , which means that only two constants can be determined precisely. We still tried to determine K , α and β by a three-parameter fit (see the data in Table 2). The constant K , which must be model independent according to Eq. (2.24), indeed turned out to be the same for all models, but is smaller for A/W than for O/W, because of the smaller adsorption energy. The second virial coefficient B_2 has a single value for a given system, independently of the model. Since it is equal to $B\alpha/2$, where B is a linear function of β , the constants α and β must be correlated. We found that it is really the case, but the variations of α with the model were weaker. The values of α were (for a given model) always larger for O/W than for A/W and decreased for O/W upon addition of electrolyte. All this is in full agreement with the concept of electrostatic repulsion between the ions. For the Volmer model α was smaller than that for the Langmuir model and both were found to increase with decreasing Γ — again in agreement with the theoretical predictions. When plotted as θ vs. C , (Fig. 20), the AIs for A/W, O/W and O/WE look very similar, which means that the main reason for the observed large differences in $\Gamma(C_s)$ are the different values of α . It turned out also that θ does not exceed 0.5 i.e. the adsorbed layer is not saturated, which explains the good fit of the EOS with a second-order polynomial in Γ .

We tried to determine which adsorption model gave the best results by calculating the theoretical values of the Gibbs elasticity by using the adsorption parameters determined for each model, but it turned out that when the results are plotted vs. an experimental variable, say C or Γ , all curves collapse in a single one, which coincides with the respective experimental curve. This means that it is impossible to determine the adsorption model by using only interfacial tension data.

Acknowledgment

This work was supported by Unilever (Trumbull, USA). We benefited from discussions and advice from numerous members

of the Laboratory of Chemical Physics and Engineering, Faculty of Chemistry, University of Sofia. We would like to acknowledge specially the invaluable help with numerical calculations and preparation of the manuscript of Dr. K. Marinova, Dr. S. Tcholakova and Mrs. M. Paraskova.

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