

Ionic surfactants on fluid interfaces: determination of the adsorption; role of the salt and the type of the hydrophobic phase

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Abstract

In this work we describe a simple thermodynamic method for determination of the adsorption (amount per unit area) of ionic surfactant. The latter is obtained from the interfacial tension isotherm measured in the presence of arbitrary (and fixed) concentration of inorganic electrolyte. Polynomial fit of the interfacial tension versus the logarithm of the mean ionic activity is combined with the Gibbs adsorption equation written in a form suitable for arbitrary content of salt. This procedure is an extension of the approach of Rehfeld [J. Phys. Chem. 71 (1967) 738]. We have performed measurements with sodium dodecyl sulfate (SDS) on water/air and water/oil (*n*-hexadecane and Soybean Oil) boundaries, at different salt concentrations (10 and 150 mM NaCl). Wilhelmy plate method was used for the water/air measurements; for water/oil we applied drop shape analysis with pendant drops. The obtained isotherms, together with literature data, are processed and the adsorption is determined. The results are compared and discussed in view of the role of the salt and the type of the hydrophobic phase. On oil/water boundaries the adsorption is always lower than that on air/water surface; addition of inert electrolyte increases the adsorption.

We analyze theoretically the asymptotic behavior of the adsorption as a function of the solute concentrations in the limit of high surface coverage. The treatment is based on models existing in the literature (Langmuir isotherm with account for the counterion binding, as formulated by Kalinin and Radke [Colloids Surf. A 114 (1996) 337]; the activity coefficients were taken into consideration in the frames of the Debye-Hückel theory). The obtained asymptotic functional dependence of the adsorption is used for fitting of data. The agreement is always good, in the concentration region below and near the critical micellization concentration (CMC). From the fits we determine the limiting adsorption at maximum coverage (i.e., at saturation); therefrom, the degree of coverage of the interface with surfactant is estimated. It turns out that at the CMC the coverage is lower than about 90%. Thus, we confirm literature results for absence of saturation with ionic surfactants at the CMC. The dependence of the surface coverage upon the mean ionic activity is rather insensitive toward the type of the fluid interface (air/water, oil/water with different hydrocarbons), and the salt concentration.

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1. Introduction

The adsorption of ionic surfactants on fluid interfaces is a topic of considerable interest, in view of its importance for the stability of disperse systems, such as foams (which in-

clude air/water surfaces) and emulsions (in which there are oil/water interfaces). The macroscopic properties of these liquid dispersions (stability, rheology, etc.) are largely determined by the amount of surfactant adsorbed on the fluid boundaries.

While the surface (air/water) and interfacial (oil/water) tensions can easily be measured by means of convenient experimental methods, it is often a challenge to obtain the

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surfactant adsorption (Γ_s , number of molecules per unit area). On air/water surfaces, direct measurement of Γ_s was implemented with radiotracer techniques [1–4]; the latter allow one to determine the radioactivity of the surface when it is covered with labeled surfactant. Another method, again for air/water interfaces, is the neutron reflection [5,6]; it involves fitting of the measured reflectivity profile with a calculated profile for a simple structural model (such as, e.g., a single layer of homogeneous composition, containing surfactant [6]). Lu et al. [6] discussed the reproducibility and the possible errors in the neutron reflection method (associated also with contingent impurities of the surfactant, sodium dodecyl sulfate (SDS)).

In the literature, the measured values of Γ_s were compared with the adsorption obtained by differentiation of the surface tension isotherm according to the Gibbs adsorption equation. Tajima et al. reported good agreement between radiotracer data and the thermodynamically determined Γ_s from the isotherm of σ , for SDS without added salt [1], in the presence of excess NaCl [2], and at different intermediate concentrations of NaCl [3]. In the general case [3], the application of the Gibbs equation required knowledge of two slopes of σ , one versus the surfactant concentration, and one versus the salt. Those studies [1–3] confirmed the appropriateness of the Gibbs isotherm for ionic surfactants in the presence of arbitrary salt concentration.

Thomas and co-workers [5,6] demonstrated that neutron reflection from air/water surface covered by SDS (in absence of salt) gave values of Γ_s close to other literature data and to their own results from the isotherm of σ . At the same time, there is a discrepancy with the findings of Tajima et al. [1–3] about the trend in the adsorption at increasing surfactant concentration. According to Tajima, Γ_s reaches a constant value (saturation) at concentrations of SDS significantly below the critical micellization concentration (CMC) – at about 3×10^{-3} M [1]. In contrast, the neutron reflection measurements proved that the adsorption did not exhibit saturation up to concentrations well above the CMC [5]. The latter conclusion holds for alkyl trimethylammonium bromides [5], as well as for sodium dodecyl sulfate (SDS) [6]. Evidently, a reliable method for determination of the surfactant adsorption (Γ_s) and its concentration dependence will help to resolve this controversy.

Rehfeld [7] proposed that the isotherm of σ versus the surfactant concentration, c , be fitted with a polynomial in powers of $\ln c$

$$\sigma = z_0 + z_1 \ln c + z_2 (\ln c)^2 + \dots \quad (1)$$

(here z_0, z_1, z_2, \dots are numerical coefficients). He explored the simple case of ionic surfactant (SDS) without added salt, when the Gibbs equation specifies that

$$\Gamma_s = -\frac{1}{2RT} \frac{d\sigma}{d \ln c} \quad (2)$$

Thus, the combination of Eqs. (1) and (2) yields Γ_s directly (in the concentration region below the CMC). Rehfeld [7]

used this approach to calculate the adsorption of SDS at the CMC (without added salt), and to compare the air/water surface with different oil/water interfaces. It was established that the area per molecule at the CMC was larger on hydrocarbon/water boundaries ($45\text{--}51 \text{ \AA}^2$ for n -saturated alkanes, and even larger for polar and unsaturated oils), than on air/water boundary (43.9 \AA^2).

Lu et al. [5,6] also used a polynomial fit of σ (Eq. (1)) up to the second power of $\ln c$, again for ionic surfactant without added inorganic electrolyte. It was pointed out that the polynomial fit increased the accuracy of the calculation of Γ_s considerably (in comparison to just taking the slope, Eq. (2)) [5]. However, such a refined procedure required high quality of the raw data [5].

In this work we combine the approach of Rehfeld (Eqs. (1) and (2)) with the more general case of Gibbs adsorption equation written in a form suitable for arbitrary concentration of added inorganic salt. Thus, from the isotherm of σ measured at fixed salt content one can obtain the amount of surfactant per unit area (Γ_s) physically adsorbed on the interface. The proposed procedure is suitable both for air/water and for oil/water boundaries. Comparison of data reveals the influences of the type of the fluid interface (air/water; oil/water), and the presence of inert electrolyte. We also explore the asymptotic behavior of Γ_s at high concentrations. Plots of Γ_s in an appropriate scale allow determination of the limiting adsorption at maximum coverage (Γ_∞), in the frames of the Langmuir adsorption model. The calculated degree of surface coverage, $\theta = \Gamma_s/\Gamma_\infty$, leads to important conclusions: (I) at the CMC the interface is not completely covered by surfactant, with θ_{cmc} of about 0.8–0.9. This supports the findings of Thomas and collaborators [5,6]; (II) for different systems, containing adsorbed SDS on air/water and oil/water interfaces in the presence of various amounts of NaCl, the concentration dependence of θ lies on a “master curve”. The latter curve encompasses both our measurements and literature data for SDS. In other words, although the adsorption Γ_s is different, the degree of surface coverage does not essentially depend on the type of the system.

2. Theory

2.1. Procedure for determination of the adsorption

We consider a system containing ionic surfactant and inorganic electrolyte with a common counterion, such as, e.g., sodium dodecyl sulfate (SDS) and NaCl. All ions are monovalent. The Gibbs adsorption equation (at constant temperature) reads:

$$d\sigma = -\tilde{\Gamma}_s d\mu_s - \tilde{\Gamma}_c d\mu_c - \tilde{\Gamma}_{\text{co}} d\mu_{\text{co}} \quad (3)$$

where σ is the equilibrium interfacial tension; the subscripts designate the surfactant ions (“s”), the counterions (“c”), and the co-ions (“co”); $\tilde{\Gamma}_i$ ($i = s, c, \text{co}$) represent the Gibbs ad-

sorption excesses, which include both the quantities physically adsorbed on the interface (Γ_i), and the excesses from the diffuse part of the electric double layer (Γ_i^{diff}): $\tilde{\Gamma}_i = \Gamma_i + \Gamma_i^{\text{diff}}$; μ_i are the chemical potentials; $d\mu_i = kT d \ln a_i$, where a_i are the ionic activities in the bulk solution, and kT is the thermal energy.

In systems without added inorganic salt, the surfactant concentrations needed for the isotherm of σ are usually below 0.01 M, so the difference between activity and concentration may be neglected [5,8,9]. On the other hand, in systems containing excess inorganic salt and ionic surfactant with concentration below the CMC, the ionic activities a_i far away from the interface are well represented by the relation (cf. Ref. [8]):

$$a_i = \gamma_{\pm} c_i \quad (4)$$

where γ_{\pm} is the mean activity coefficient, and c_i is the concentration of the i th ion in the bulk of the solution. The activities can be regarded as effective concentrations of the ionic species [8]. When the electrolyte is 1:1 valent, the coefficient γ_{\pm} is well described by the following semi-empirical formula (stemming from the Debye-Hückel theory with account for the finite size of the ions) [10,11]:

$$\lg \gamma_{\pm} = -\frac{A\sqrt{I}}{1 + Bd_i\sqrt{I}} + bI$$

Here I is the ionic strength; for NaCl solutions at 25 °C, $A = 0.5115 \text{ M}^{-1/2}$, $Bd_i = 1.316 \text{ M}^{-1/2}$ (the “ion diameter” d_i is a mean value for the respective couple of ions), $b = 0.055 \text{ M}^{-1}$.

In the case when σ is measured as a function of the surfactant concentration at constant concentration of salt, one has $d\mu_{\text{co}} \approx 0$ and $da_s \approx da_c$ (neglecting small changes in the activity coefficient). Then, Eq. (3) becomes:

$$\begin{aligned} d\sigma &= -kT \left(\frac{\tilde{\Gamma}_s}{a_s} + \frac{\tilde{\Gamma}_c}{a_c} \right) da_s \\ &= -kT \left\{ \left(\Gamma_s + \Gamma_s^{\text{diff}} \right) \frac{a_s + a_c}{a_s a_c} + \frac{\tilde{\Gamma}_{\text{co}}}{a_c} \right\} da_s \end{aligned} \quad (5)$$

The second equality follows from the condition for total electroneutrality of the double layer: $\tilde{\Gamma}_c = \tilde{\Gamma}_s + \tilde{\Gamma}_{\text{co}}$. It is natural to assume that the co-ions do not physically adsorb on the interface [3], so $\tilde{\Gamma}_{\text{co}} = \Gamma_{\text{co}}^{\text{diff}}$, and we can use the results of the classical Gouy-Chapman theory for the diffuse layer contributions to $\tilde{\Gamma}_i$ (see e.g. Eq. (11) in Ref. [12]):

$$\frac{\Gamma_{\text{co}}^{\text{diff}}}{\Gamma_s^{\text{diff}}} = \frac{c_{\text{co}}}{c_s} = \frac{a_{\text{co}}}{a_s} = \frac{a_c - a_s}{a_s} \quad (6)$$

Eq. (4) was utilized to write Eq. (6) in terms of activities. Replacing $\tilde{\Gamma}_{\text{co}}$ in Eq. (5) with $\Gamma_{\text{co}}^{\text{diff}} = \Gamma_s^{\text{diff}}(a_c - a_s)/a_s$ from Eq. (6), we derive:

$$d\sigma = -kT \left\{ \Gamma_s \left(\frac{1}{a_s} + \frac{1}{a_c} \right) + \frac{2\Gamma_s^{\text{diff}}}{a_s} \right\} da_s \quad (7)$$

Simple estimate shows that the term with Γ_s^{diff} in Eq. (7) is negligible. Indeed, from Ref. [12]:

$$\Gamma_s^{\text{diff}} = \frac{2c}{\kappa_c \sqrt{I}} \left\{ \exp \left(-\frac{\phi_d}{2} \right) - 1 \right\} \quad (8)$$

where c is the surfactant concentration, $\kappa_c = 0.001338 \sqrt{\text{cm}}$ (besides, $\kappa_c \sqrt{I} = \kappa$ is the inverse Debye screening length), and ϕ_d is the dimensionless electric potential at the onset of the diffuse layer. One writes $\phi_d \equiv Z_s e \Psi_d / (kT)$, where Z_s is the valency of the surfactant ion (-1 for DS^-), e is the electronic charge, and Ψ_d is the respective electric potential; thus, $\phi_d > 0$. The term enclosed in the braces (Eq. (8)) is always between -1 and 0 . As an example, let us assess Γ_s^{diff} for surfactant concentration of $8 \times 10^{-3} \text{ M}$ (the CMC of SDS) and $I = 0.1 \text{ M}$. Eq. (8) gives $|\Gamma_s^{\text{diff}}| < 9.3 \times 10^{11} \text{ cm}^{-2}$. The adsorption Γ_s around the CMC is of the order of $2 \times 10^{14} \text{ cm}^{-2}$ for SDS [6,7], so we conclude that $|\Gamma_s^{\text{diff}}| \ll \Gamma_s$ under typical conditions.

For the sake of convenience, we introduce the auxiliary notation:

$$a_t \equiv a_c = a_s + a_{\text{co}} = \gamma_{\pm}(c + c_{\text{salt}}); \quad a \equiv a_s = \gamma_{\pm} c \quad (9)$$

(c_{salt} is the concentration of inorganic electrolyte). In these terms, the quantity “mean ionic activity”, c^* , used in Refs. [9,13] and in the plots below, is $c^* = \sqrt{aa_t}$. Now, with $da = da_t$, Eq. (7) acquires the form

$$\Gamma_s = -\frac{1}{kT} \frac{d\sigma}{d \ln(aa_t)} \quad (10)$$

Eq. (10) suggests a procedure for determination of the adsorption, Γ_s (the amount of ionic surfactant physically adsorbed on the interface, per unit area), from the isotherm of σ , in the case when the system contains arbitrary concentration of indifferent electrolyte. We represent the concentration dependence of the interfacial tension as a polynomial

$$\sigma = z_0 + z_1 \ln(aa_t) + z_2 [\ln(aa_t)]^2 + z_3 [\ln(aa_t)]^3 \quad (11)$$

(Eq. (11) is a generalization of Eq. (1)). Experimental data are fitted with Eq. (11), and differentiation is applied to the fitting polynomial according to Eq. (10).

2.2. Asymptotic behavior of the adsorption at large surfactant concentrations

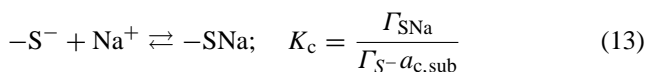
A theoretical model, widely used in the literature and proven to be adequate for description of ionic surfactant adsorption [8,12,14], is the Langmuir/Frumkin model, which assumes existence of a limiting maximum adsorption, Γ_{∞} , reached asymptotically at high concentrations. It should be mentioned that Γ_{∞} is a model parameter, not a quantity attainable in experiment. The isotherm of Γ_s as a function of the surfactant concentration is usually represented in terms of $\theta = \Gamma_s / \Gamma_{\infty}$ (degree of surface coverage), and has

the form [8]

$$\frac{\theta}{1-\theta} \exp(-\beta\theta) = K_s a_{s,\text{sub}} = K_s a_s \exp(-\phi_0) \quad (12)$$

Here β is a parameter accounting for the lateral interactions within the interface, K_s is the adsorption constant, and $a_{s,\text{sub}}$ is the surfactant activity in the sub-surface layer (the region in the volume phase directly adjacent to the interface). In the frames of the model adopted in Ref. [8], the sub-surface and the surface are at the same plane $x=0$. The activity $a_{s,\text{sub}}$ depends on the dimensionless electric potential at the sub-surface, $\phi_0 = Z_s e \Psi_0 / (kT)$ (where Ψ_0 is the sub-surface potential). Below we discuss the dependence of Γ_s on the concentration at high coverages, as predicted by Eq. (12), and use it for data processing.

An essential point in the theory is to consider the counterion binding [8,12]. We accept the view [12] that the free counterions at the sub-surface (they are in the volume phase) rest in equilibrium with counterions attached to the charged heads of the surfactant ions (S^-) which reside on the interface:



For the sake of definiteness, the counterions are designated as Na^+ ; Γ_{SNa} and Γ_{S^-} in Eq. (13) are the adsorptions of the respective species, K_c is the equilibrium constant for the adsorption of counterions, and $a_{c,\text{sub}}$ is the counterion activity in the sub-surface layer, $a_{c,\text{sub}} = a_c \exp(\phi_0)$. In addition, $\Gamma_s = \Gamma_{SNa} + \Gamma_{S^-}$ from the material balance of the surfactant. Let us denote the “degree of surface dissociation” by α , with $\alpha = \Gamma_{S^-} / \Gamma_s$. Then, from Eq. (13) we have

$$\alpha = \frac{1}{1 + K_c a_c \exp(\phi_0)} \quad (14)$$

The value of α is expected to be small, less than 0.10, as stated in Ref. [12], or 0.15–0.20 according to Ref. [15], so it seems reasonable to approximate Eq. (14) as $K_c a_c \exp(\phi_0) = 1/\alpha$.

The electrostatic double layer theory gives a relation between the surface charge and the surface potential (see e.g. Eq. (4.15) in Ref. [8]). In our notation, this relation reads:

$$\alpha \Gamma_s = \frac{4\sqrt{a_c}}{\kappa_c} \sinh\left(\frac{\phi_0}{2}\right) \approx \frac{2\sqrt{a_c}}{\kappa_c} \exp\left(\frac{\phi_0}{2}\right) \quad (15)$$

In the right-hand side of Eq. (15) we replace the hyperbolic sine with exponent because the surface potential is usually large in the presence of adsorbed ionic surfactant, especially at high concentrations. Evidence for this comes from zeta-potential measurements on air/water [12] and oil/water [16] interfaces. In the former case $|\zeta| \sim 150$ mV [12]; in the latter case $|\zeta| \sim 240$ mV [16] (for SDS without added salt). A value of $|\Psi_0| > 60.4$ mV corresponds to $\phi_0 > 2.34$, which ensures that the approximation in Eq. (15) has an error of less than 10%. In the presence of inert electrolyte the magnitude of the ζ -potential decreases [17], but this may be attributed to shrinking of the ionic atmosphere and concomitant decrease

of the electric potential at the “shear plane” where the ζ -potential is measured (rather than to decrease of Ψ_0).

In any case, within the range of validity of the simplified Eq. (15), it can be combined with the counterion-binding model, Eq. (14), and with the Frumkin isotherm, Eq. (12), to yield:

$$\frac{\theta^{5/3}}{1-\theta} \exp(-\beta\theta) = K_s \left(\frac{2K_c}{\kappa_c \Gamma_\infty} \right)^{2/3} a_s a_c \quad (16)$$

We expand the left-hand side of Eq. (16) for small values of the parameter $\delta = 1 - \theta$, i.e., at high surface coverage:

$$\frac{1}{\delta} = \left(\frac{5}{3} - \beta \right) + K_s \exp(\beta) \left(\frac{2K_c}{\kappa_c \Gamma_\infty} \right)^{2/3} a_s a_c + O(\delta) \quad (17)$$

This result is useful in the form (invoking the notation of Eq. (9)):

$$\begin{aligned} \frac{1}{\delta} &= \chi + P a a_t + O(\delta), \quad \text{or} \quad \Gamma_s \\ &= \Gamma_\infty \left\{ 1 - \frac{1}{\chi + P a a_t} + O\left[\frac{1}{(a a_t)^3} \right] \right\} \end{aligned} \quad (18)$$

where χ and P are constant numerical coefficients. Eq. (18) defines the asymptotic dependence of the adsorption upon the concentrations of surfactant and salt at high surface coverage (i.e., close to the CMC). The latter region corresponds to high concentration of surfactant (large values of the product $a a_t$). Discarding the terms $O[1/(a a_t)^3]$ in the right-hand side of Eq. (18), we are left with a rational function which represents the asymptote up to the terms $O[1/(a a_t)^2]$ inclusive. Note that Eq. (18) can be cast into a form of a series expansion in powers of $1/(a a_t)$:

$$\Gamma_s = \Gamma_\infty \left\{ 1 - \frac{1}{P a a_t} + \frac{\chi}{P^2 (a a_t)^2} + O\left[\frac{1}{(a a_t)^3} \right] \right\} \quad (19)$$

Integration of Eq. (10) in the case when Γ_s is given by Eq. (19) provides an asymptotic formula for the concentration dependence of the interfacial tension, σ , at high $a a_t$:

$$\begin{aligned} \sigma &= \text{const.} - kT \Gamma_\infty \{ \ln(a a_t) \\ &+ \frac{1}{P a a_t} - \frac{\chi}{2P^2 (a a_t)^2} + O\left[\frac{1}{(a a_t)^3} \right] \} \end{aligned} \quad (20)$$

Eq. (20) contains an unknown integration constant.

Fits of data for Γ_s for particular systems demonstrate that Eq. (18) is very well satisfied (see below). Such fits give the opportunity to determine the limiting adsorption at full coverage of the interface, Γ_∞ . Therefore, one acquires information about the structure of the adsorption layer, and the fraction of the interface that is covered by surfactant at any value of Γ_s . As an alternative, one can use also Eq. (20) and fit σ ; Γ_∞ will stand as one of the adjustable parameters. Our experience shows that with Eq. (20) the correlation coefficient is appreciably lower than that when Γ_s is fitted with Eq. (18) (this largely depends on the quality of the experimental data).

In the present work we will not discuss the values of the constants χ and P obtained from the fits because (I) the accuracy in determination of χ is low (χ enters the third term in the expansion of Γ_s versus $1/(aa_t)$ – Eq. (19)); (II) P includes several physical parameters of the adsorption layer, which cannot be separated by a single fit of Γ_s .

3. Experimental

Different authors have determined surface [1–4,7,18–20] and interfacial [7,21] tension isotherms of SDS using different oils, varying the salt content and temperature. There are some data indicating different adsorption at water/air and water/oil interfaces [7]. The adsorption could change substantially from interface to interface, that is why it is not recommended to transfer directly information about the physical properties of the layers from air/water to oil/water surfaces.

We measured the water/air and water/oil (*n*-hexadecane and Soybean Oil) interfacial tensions of SDS solutions containing 10 mM NaCl and 150 mM NaCl. Our aim was to obtain the *equilibrium isotherms* of SDS, $\sigma(c)$, and use these data for determination of the adsorbed amount, Γ_s , by means of thermodynamic relations. Information about the adsorption, Γ_s , and the factors affecting it, is very useful for emulsification, since the emulsion stability is basically determined by the degree of coverage of the interfaces by surfactant [22].

3.1. Materials

We measured the surface tension of aqueous solutions of the ionic surfactant sodium dodecyl sulfate (SDS, product of Acros, USA). The surfactant was used as received (special measures to avoid the influence of impurities are described below). All solutions were prepared with deionized water from a Milli-Q purification system (Millipore, USA). Additionally, the prepared aqueous solutions contained inorganic electrolyte sodium chloride (NaCl) with concentration 0.01 or 0.15 M. The used NaCl (product of Merck, Germany) was preliminarily roasted at 500 °C for 3 h to remove any organic contaminations.

As oil phase we used hexadecane (C16) and soya bean oil (SBO). Hexadecane was purchased from Merck, Germany, and was purified by applying 2–3 consecutive passes through a column filled with Silica gel (Merck, Germany) and activated magnesium silicate (Florisil[®], Sigma-Aldrich, Germany) adsorbent. The interfacial tension of purified hexadecane against pure water was 54.0 ± 0.5 dyn/cm, a value which is close to the one determined by Goebel and Lunkenheimer [23]. SBO is a commercial product for food application. SBO was purified by passing through a column filled with adsorbents bentonite (Teokom, Bulgaria) and activated magnesium silicate (Florisil[®], Sigma-Aldrich, Germany). Up to three consecutive passages were applied in order to obtain

oil that was free of substances decreasing its interfacial tension against water with more than 0.2 dyn/cm for 30 min. It is worth mentioning that the interfacial tension of the used SBO had increased with more than 7 dyn/cm after the purification. The value of the interfacial tension of the *purified* SBO was 30.5 ± 0.5 dyn/cm, which is close to that of other pure food-grade oils (~ 31 dyn/cm [24]).

3.2. Methods

3.2.1. Measurement of surface tension

The air–water surface tension, σ_{AW} , of the used aqueous solutions was measured by the Wilhelmy plate method. The measurements were performed by means of a digital tensiometer Krüss K10ST (Krüss GmbH, Hamburg, Germany) at 23.3 ± 0.3 °C, using a sand-blasted glass plate or a platinum plate. Before each measurement, the used plate was cleaned by immersion in sulfo-chromic acid, followed by abundant rinsing with deionized water. The platinum plate was additionally heated to red color in a flame.

All surfactant solutions were prepared 1–2 days before the measurement. Sodium dodecyl sulfate is known to hydrolyze to dodecyl alcohol (dodecanol) in water [6,25–28]. The presence of dodecanol is known to affect significantly both the dynamic and equilibrium surface tension of the solutions [20,27,28]. That is why we took special care to remove the dodecanol possibly present in these solutions: The solutions were poured in the measuring vessel through several clean plastic pipettes. Application of several plastic pipettes was adopted after the “two-tips” procedure suggested by Denkov et al. [29]. This procedure prevents the direct transfer of the surface, and the dodecanol adsorbed on it, from the original solution to the solution used for the measurements. Since dodecanol is very surface active, it can be removed either by surface aspiration, as done by Lunkenheimer [27], or by a prevention of the surface transfer, as done by the pipettes procedure. It is worth mentioning that we did not apply any recrystallization of the used surfactant sample, since it turned out that the dodecanol in the purchased surfactant was in very low concentration, impossible to be decreased further by recrystallization. Moreover, we performed all measurements in presence of at least 0.01 M NaCl in the surfactant solutions and, as shown by Kralchevsky et al. [30], this substantially diminishes the adsorption of the possibly present dodecanol. Furthermore, the obtained results and trends fully comply with the results obtained with best purified samples published in the literature (see below).

The kinetics of the surface tension relaxation for all solutions was followed during at least 20 min. The signal of the tensiometer was recorded and stored on a PC. The equilibrium value of σ_{AW} was determined from the intercept of the plot σ_{AW} versus $t^{-1/2}$ [31]. Since all measured solutions contained at least 0.01 M NaCl, it is reasonable to assume that the barrier to surfactant adsorption is suppressed, and to use the asymptote for diffusion-controlled adsorption, $\sigma \sim t^{-1/2}$ [31,32].

3.2.2. Measurement of interfacial tension

The interfacial tension of the studied solutions was measured by applying the drop shape analysis to pendant drops. The measurements were performed at $23.3 \pm 0.5^\circ\text{C}$ on a Drop Shape Analysis System DSA 10 (Krüss GmbH, Hamburg, Germany). Both pendant oil drops in water solutions and pendant water drops in the oil phase were formed and used for the measurements. No detectable differences were found between the values of the interfacial tension for these two configurations.

Pendant drop of one of the phases was formed on the tip of a metal capillary immersed in the second phase, e.g., oil drop in water solution, or aqueous drop in the oil phase. The outer phase was loaded in a glass cell with plane-parallel optical front and back windows. Purity of the used oil phases was checked before each measurement by determination of the interfacial tension against pure water upon drop surface expansion and/or compression: constant surface tension after compression indicated that the oil was surface chemically pure.

As for the surface tension measurements, the kinetics of the interfacial tension relaxation was followed during at least 20 min. The equilibrium value of σ_{OW} was determined from the intercept of the plot σ_{OW} versus $t^{-1/2}$ [31]. The density of the used oil phases, which was necessary for the interfacial tension determination, was measured by means of a density meter DMA48 (Paar Scientific, UK).

4. Experimental results and discussion

4.1. Surface (air/water) and interfacial (oil/water) tension isotherms

The measured surface tension isotherms of SDS in the presence of two different NaCl concentrations, 0.01 and 0.15 M, are shown in Fig. 1. For comparison, the values ob-

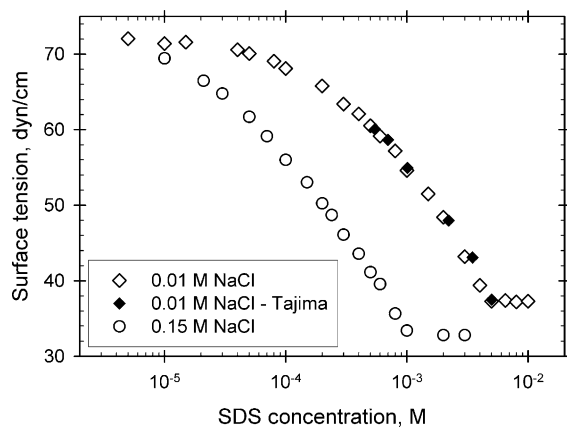


Fig. 1. Surface tension isotherms of SDS in the presence of NaCl at different concentrations: 0.01 M (empty diamonds), and 0.15 M (empty circles). For comparison, data of Tajima [3] in the presence of 0.01 M NaCl are also plotted (full diamonds).

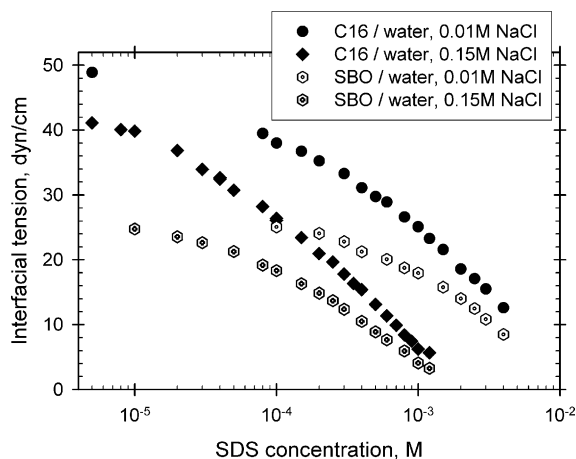


Fig. 2. Interfacial tension isotherms of SDS at hexadecane (C16)/water and soybean oil (SBO)/water interfaces in the presence of 0.01 and 0.15 M NaCl.

tained by Tajima [3] for the surface tension, σ_{AW} , of SDS solutions containing 0.01 M NaCl are also displayed. The experimental values of Tajima coincide fairly well with our measurements. No minimum is observed in the CMC region, which is an evidence for a satisfactory surfactant purity.

The obtained interfacial tension isotherms of SDS on water/hexadecane and water/SBO boundaries in the presence of 0.01 and 0.15 M NaCl are shown in Fig. 2. Both the surface (Fig. 1) and the interfacial (Fig. 2) tensions of the solutions are lower in the presence of higher electrolyte concentration, as has to be expected [32,33]. The effect is due mainly to the electric double layer (the existence of electrostatic contribution to the surface pressure). The critical micellization concentration, CMC, decreases upon addition of more salt: from CMC = 5 mM SDS in the presence of 10 mM NaCl (without oil) to 1 mM SDS with 150 mM NaCl (without oil) – Fig. 1. Note that the CMC is 8.1 ± 0.1 mM SDS without inert electrolyte [7,33]. The same trend in the CMC is observed for the systems with C16 and SBO (Fig. 2).

4.2. Data treatment

The isotherms in Figs. 1 and 2 were processed to give the surfactant adsorption, Γ_s . For that purpose, Eqs. (10) and (11) were applied (cf. the procedure described in Section 2.1). One has a choice to use the polynomial, Eq. (11), up to the second or the third power of $\ln(aa_t)$. In general, this depends on the quality of the available data for σ . As a rule, for very good data the full form of the function, Eq. (11), including the third-power term, should be preferred, and gives higher correlation coefficient of the fit. On the other hand, if there is appreciable scattering of the experimental points, or if they are few, truncated polynomial up to the second power of $\ln(aa_t)$ is a better option. Our isotherms from Figs. 1 and 2 were fitted with the full Eq. (11).

Examples of these fits for two isotherms, one of surface tension and one of interfacial tension, are shown in Fig. 3, together with the determined coefficients in the polynomial

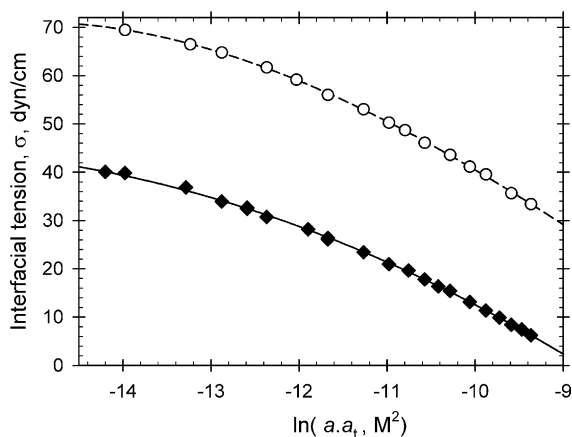


Fig. 3. Interfacial tension isotherms of SDS at air/water (empty circles) and hexadecane (C16)/water (full diamonds) interfaces in the presence of 0.15 M NaCl. The solid lines are best fit curves, according to Eq. (11). The respective best fit equations read: air/water, 0.15 M NaCl (dashed line): $\sigma = 0.0553(\ln(aa_t))^3 + 1.0150(\ln(aa_t))^2 - 7.0346(\ln(aa_t)) - 76.0594$; $r^2 = 0.9997$. C16/water, 0.15 M NaCl (solid line): $\sigma = 0.0401(\ln(aa_t))^3 + 0.7174(\ln(aa_t))^2 - 6.9933(\ln(aa_t)) - 89.1414$; $r^2 = 0.9992$.

equation. It is worth underlining that the correlation coefficient of the fits, r^2 , is better than 0.999. The calculated adsorption, Γ_s (according to Eq. (10)), is presented in Fig. 4. The latter figure includes all systems investigated by us (Figs. 1 and 2), as well as results from processing of isotherms taken from the literature [7,20,21]. There are several interesting observations regarding the data in Fig. 4.

If the system contains inorganic salt, the adsorption of surfactant, Γ_s , depends only on the mean ionic activity $c^* = \sqrt{aa_t}$, and the salt concentration per se is unimportant. Note that the curves $\Gamma_s(c^*)$ for 0.01 and 0.15 M NaCl coincide in the cases of air/water and SBO/water interfaces, and lie very close in the case of C16/water interface (Fig. 4). Fainerman et al. [9,13] paid attention to the fact that several isotherms

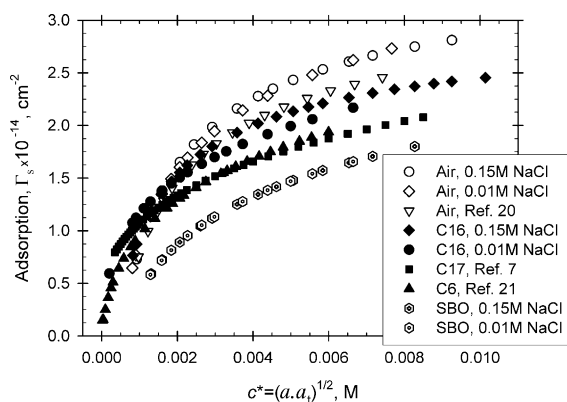


Fig. 4. Determined adsorption, Γ_s , at different interfacial boundaries: air/water, hexadecane (C16)/water, heptadecane (C17)/water (data from Ref. [7]), hexane (C6)/water (data from Ref. [21]), and soybean oil (SBO)/water in the presence of different amounts of NaCl. Data of Rehfeld [7], Hines [20], and Motomura et al. [21] were obtained in absence of additional inorganic electrolyte.

of σ , each with different amount of salt, converge together when plotted as functions of c^* , thus simplifying the effect of the added salt (the surfactant is salted-out to the interface [13]). The authors of Refs. [9,13] did not discuss in detail the adsorption, Γ_s . At the same time, it has been mentioned that some precise details of the adsorption process remain unaccounted for in the scale c^* [34].

From our Fig. 4 it is evident that the complete absence of inert electrolyte in the solution of SDS leads to lower values of Γ_s , compared to the systems with salt at the same c^* . The curves for air/water, C6/water and C17/water boundaries without salt lie below those for the respective systems containing NaCl. So, the mere presence of inorganic salt (at levels above 10 mM) is likely to promote the adsorption of SDS. Perhaps, the reason for this effect is connected with enhanced electrostatic screening in the double layer and decreased repulsion between the surfactant ions.

Remarkable is the fact that the adsorption, Γ_s , is lower on oil/water interfaces (for C6, C16, C17, and even lower for SBO), than on water/air boundary (Fig. 4). This result can only be rationalized if one pays attention to the fact that the lateral interactions between the adsorbed molecules take part in governing Γ_s , together with the standard free energy of adsorption (the latter is dominated by the hydrocarbon tails). Indeed, the adsorption free energy of the tails is slightly higher on oil/water interfaces [35], which would favor larger values of Γ_s . Explanation of the observed peculiarity of lower Γ_s on oil/water boundary may be sought in lateral interactions between the heads, influenced by out-of-plane fluctuations. On oil/water interface, since the hydrocarbon tails of the surfactant ions are pulled more strongly into the oil, the fluctuations of protrusion will be suppressed and consequently, the lateral electrostatic repulsion between the charged heads will be stronger. Thus, the surfactant chemical potential will rise and the adsorption will eventually be lower.

Next, we determined the limiting adsorption at maximum saturation of the interfaces, Γ_∞ , applying the asymptote at high concentrations, Eq. (18). Data for Γ_s (those from Fig. 4) were fitted with the rational function $y = A(1 - 1/(B + Cx))$, where y stands for Γ_s , x denotes the product aa_t , and A , B , C are the constants (see Eq. (18)). Since Eq. (18) is an asymptote, the experimental points selected for the fit are those with the highest values of aa_t from the data set. Fig. 5 presents the respective plot, in which the theoretical curve (the rational function, Eq. (18)) passes through several points with the largest aa_t (smallest $1/(aa_t)$), and deviates from the experimental data at lower aa_t ; such a behavior is normal for an asymptote. Note that the dependence of Γ_s versus $1/(aa_t)$ in Fig. 5 is non-linear, because the function (Eq. (18)) contains terms $\sim 1/(aa_t)^2$, cf. Eq. (19).

The extrapolation to $1/(aa_t) \rightarrow 0$, $\Gamma_s \rightarrow \Gamma_\infty$ was performed as indicated in the sample graph shown in Fig. 5. The fits are always good in the concentration interval just below the CMC (the inset in Fig. 5 displays the correlation coefficient, 0.99991, for the 7 points fitted). The obtained values of Γ_∞ are listed in Table 1. The comparison of

Table 1

Determined adsorption at maximum saturation of the interface, Γ_∞ , the corresponding area per molecule, $A_\infty = (\Gamma_\infty)^{-1}$, and the surface coverage at the CMC, $\theta_{\text{cmc}} = \Gamma_s^{\text{cmc}}/\Gamma_\infty$

System	Γ_∞ (10^{14} cm $^{-2}$)	A_∞ (\AA^2)	θ_{cmc}
Air/water 0.15 M NaCl, 23 °C	3.142	31.92	0.89
Air/water 0.01 M NaCl, 23 °C	3.142	31.82	0.87
Air/water, no salt, 25 °C, Ref. [20]	2.871	34.84	0.86
C16/water 0.15 M NaCl, 23 °C	2.656	37.65	0.91
C16/water 0.01 M NaCl, 23 °C	2.647	37.78	0.91
C17/water no salt, 25 °C, Ref. [7]	2.437	41.04	0.84
C6/water no salt, 30 °C, Ref. [21]	2.424	41.26	0.80
SBO/water 0.01 and 0.15 M NaCl, 23 °C	2.298	43.51	0.72 (0.01 M NaCl); 0.75 (0.15 M NaCl)

different systems reveals that the trends already mentioned for Γ_s apply to Γ_∞ as well: addition of salt increases Γ_∞ (in a threshold manner from 0 to 0.01 M NaCl); on oil/water interfaces Γ_∞ is lower than on air/water surface (in addition, there is no difference between hexane and heptadecane); the lowest limiting adsorption belongs to SBO.

Once we know Γ_∞ , the degree of surface coverage can easily be found: $\theta = \Gamma_s/\Gamma_\infty$. Table 1 displays the values of θ at the CMC of the studied systems. Impressive is the fact that no value is higher than 0.91; for hydrocarbon/water interface without salt $\theta_{\text{cmc}} < 0.85$. These findings indicate absence of saturation of the surface layer up to the CMC, in full agreement with the results reported by Thomas and co-workers [5,6].

In Fig. 6 we plot the surface coverage, θ , evaluated at concentrations below the CMC, in the scale versus the mean

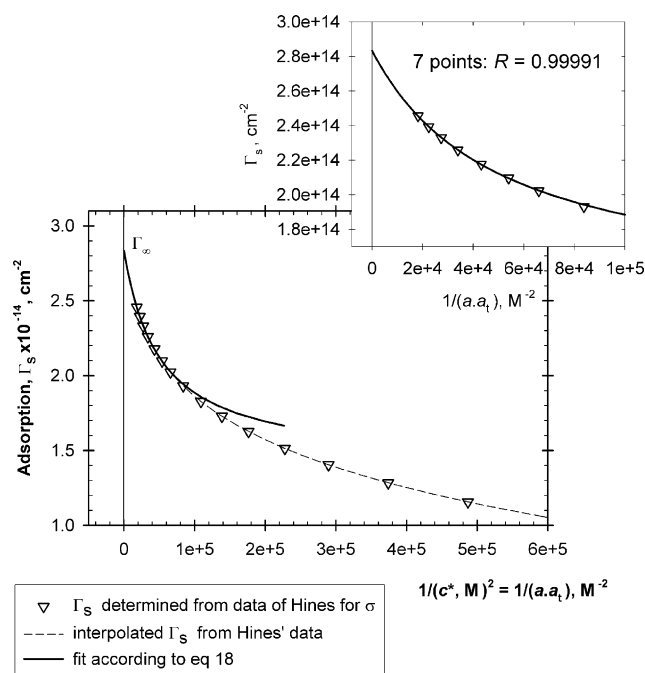


Fig. 5. Determination of the limiting adsorption of fully saturated layer, Γ_∞ , from the data of Hines [20] for SDS on air/water interface, applying the asymptotic relation at high concentrations, Eq. (18). The inset shows in a larger scale the region of high aa_t , and the fit drawn through seven experimental points.

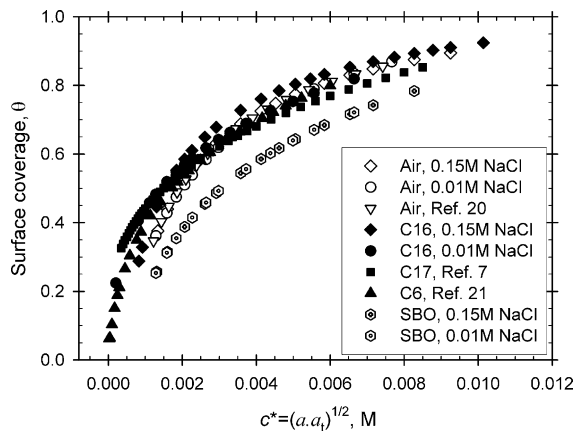


Fig. 6. Surface coverage as a function of $c^* = (aa_t)^{1/2}$ for different water interfaces.

ionic activity, $c^* = (aa_t)^{1/2}$. All data lie very close to a “master curve” for the particular ionic surfactant, SDS, with the exception of the soybean oil. Therefore, (I) the dependence $\theta(c^*)$ is rather insensitive to the type of the hydrophobic phase (air/water, hydrocarbon/water); only major changes in the composition of the oil can affect θ , such is the case of SBO (a commercial product which is basically a mixture of fatty acid glycerides); (II) $\theta(c^*)$ is not significantly influenced by addition of inorganic electrolyte.

5. Concluding remarks

In this work we formulate a simple thermodynamic procedure for determination of the adsorption of ionic surfactant (Γ_s) from the interfacial tension isotherm, measured in the presence of arbitrary (and fixed) concentration of inorganic electrolyte. Polynomial fit of the interfacial tension, σ , versus the logarithm of the surfactant concentration has been used in the literature. We modify it and fit σ versus the logarithm of the squared mean ionic activity (that is, aa_t), which procedure is based on the Gibbs adsorption equation written in a form suitable for arbitrary content of salt.

We have performed measurements with sodium dodecyl sulfate (SDS) on air/water and oil/water boundaries, at different salt concentrations. The obtained isotherms, together with literature data, are processed and the adsorption is

determined. The results are compared and discussed in view of the role of the salt and the type of the hydrophobic phase. On oil/water boundaries the adsorption is always lower than that on air/water surface. To suggest a qualitative explanation, we hypothesize that since the hydrocarbon tails of the surfactant ions are pulled more strongly into the oil, the fluctuations of protrusion may be suppressed and consequently, the lateral electrostatic repulsion between the charged heads will be stronger (a factor that obstructs the adsorption). Addition of inert electrolyte increases the adsorption of surfactant in the scale $\Gamma_s(c^*)$ only in a threshold manner, from 0 to 0.01 M NaCl. Higher amounts of salt do not affect Γ_s if c^* is the same, which simplifies the influence of the electrolyte. In particular, one can foresee results for σ and Γ_s in a certain range of salt concentrations without carrying out measurements.

We analyze theoretically the asymptotic behavior of the adsorption as a function of the solute concentrations in the limit of high surface coverage. The treatment is based on models existing in the literature (Langmuir isotherm with account for the counterion binding). The obtained asymptotic functional dependence of the adsorption, $\Gamma_s \sim 1/(\chi + Paa_t)$, is used for fitting of data. The agreement is always good, in the concentration region below and near the critical micellization concentration (CMC). By extrapolation of the fits, we determine the limiting adsorption at maximum coverage (i.e., at saturation), Γ_∞ . Therefrom, the degree of coverage of the interface with surfactant is estimated, $\theta = \Gamma_s/\Gamma_\infty$. It turns out that at the CMC the degree of coverage is lower than about 90% in all studied cases. Thus, we confirm literature results for absence of saturation with ionic surfactants at the CMC. The dependence of the surface coverage upon the mean ionic activity, $\theta(c^*)$, is rather insensitive toward the type of the fluid interface (air/water, oil/water with different hydrocarbons), and the salt concentration. Only a major change in the composition of the oil (e.g., switching to fatty acid esters) can affect $\theta(c^*)$.

An alternative way of processing equilibrium interfacial tension data in systems containing ionic surfactant and salt is to apply the counterion-binding model directly, that is, to fit isotherms of σ versus the surfactant concentration, c , at fixed concentrations of salt, c_{salt} . Such a procedure has been implemented in Refs. [8,12]; the model includes several adjustable parameters which have to be found simultaneously from the fit (Γ_∞ , the adsorption constants of the surfactant ion and the counterion, the interaction parameter). In order to achieve a reliable model fit, the best way is to have a set of several curves $\sigma(c)$, measured at different c_{salt} . Kralchevsky et al. [8] pointed out that the set of data should contain experimental points for both high and low surfactant concentrations, and for both high and low salt concentrations. If the latter requirement is not satisfied, the merit function of the fit exhibits a flat shallow minimum [8], and therefore, it is practically impossible to determine the adjustable parameters with sufficient accuracy. For this reason, the ion-binding model provides reliable results only when applied to a comprehensive set of

carefully selected experimental data. On the other hand, often a single curve $\sigma(c)$, measured at one concentration of electrolyte, is only available. Then, the ion-binding model is not likely to work well, in the sense that the results will be ambiguous even if the fit is good. It will then be more instructive to apply the simpler approaches described in the present paper, namely: (I) to take a purely thermodynamic relation, Eq. (10), and determine the adsorption Γ_s from the fit of σ with Eq. (11), without invoking any model; and (II) to apply the asymptote at high coverage, Eqs. (18) and (19), and find a single parameter, Γ_∞ , which is useful because it provides information about the degree of surface coverage.

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