Adsorption of Ionic Surfactants on Water/Air Interface: One More Transformation of the Gibbs Equation

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The adsorption of ionic surfactants on the water/air or water/hydrocarbon interface is considered. One form of the well-known Gibbs equation takes into account the surface excess of the amphiphilic ion in the compact layer, or monolayer, Γ_2^m (2D adsorption), and the differential of the electrical potential of this layer. This expression is modified using some simplifying assumptions. The dependence of the surface tension, σ, on the activity of the amphiphilic ion, a_2, degree of gegen-ions binding in the compact layer, β, and Γ_2^m is transformed into the following relationship:

$$-\frac{d\sigma}{RTd\ln a_2} = \Gamma_2^m \left\{ 2-(1-\beta)\frac{d\ln\Gamma_2^m}{d\ln a_2}\left[\frac{1}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{1+t}} - \frac{2b}{RT}\Gamma_2^m\right]\right\}.$$

Here $\Gamma_2^{m\infty}$ denotes the Γ_2^m value at complete filling of the adlayer, $t = -1$, 0, or +1 for the two-phase model of partition, for immobile or mobile monolayer respectively, b is the cohesion constant; both the long-tailed ion and the gegen-ion are single-charged. The usefulness of the proposed equation is discussed.

Keywords: water/air interface, adsorption of ionic surfactant, surface tension, adsorption in the monomolecular layer, degree of gegen-ions binding.

УДК 541.18.04

INTRODUCTION

The adsorption of surfactants on the water/air interface was a matter of numerous experimental and theoretical studies during many decades. Main regularities are reflected in well-known books [1–8]; for more detailed consideration, a set of exhaustive review papers is available [9–13]. Related problems are the adsorption at water/hydrocarbon interfaces and the behavior of insoluble monolayers on the water surface.

The Gibbs theorem (famous equation 508) [14] for a two-component system gives the relation between the surface tension, σ, chemical potential of the surface-active agent, μ_2, and its surface excess, Γ_2, at constant temperature:

$$-d\sigma = \Gamma_2 d\mu_2. \tag{1}$$

(The dividing surface may be lined in such a manner that the surface excess for water, Γ_1, will be equal to zero.) The adsorption causes the decrease in σ, while the chemical potential of the surfactant is a function of its activity in the bulk phase: $\mu_2 = \mu_2^{\circ} + RT\ln a_2$. Hence,

$$-d\sigma = \Gamma_2 RTd\ln a_2. \tag{2}$$

Here R is the gas constant and T is the absolute temperature. For diluted solutions of non-electrolytes with expressed surface activity, equation (2) holds true also for concentrations. For long-tailed ionic surfactants, such as sodium alkylsulfates (sulfonates) or alkyltrimethylammonium chlorides (bromides), which behave as strong electrolytes in water, $d\mu_i = RTd\ln(a_+a_-) = 2RTd\ln a_\pm$. If we use suffixes "2" and "3" for the surface-active agent and the gegen-ion, respectively, the Gibbs equation should be written in the following form:

$$-d\sigma = \Gamma_2 RTd\ln a_2 + \Gamma_3 RTd\ln a_3. \tag{3}$$

In solutions of an ionic surfactant without any additives, $\Gamma_2 = \Gamma_3$. In diluted solutions, $a_3 = a_2 = c_2$. If the solution is extremely diluted, the real equilibrium concentration in the bulk phase should be in some cases estimated taking into account the adsorption. In relatively concentrated solutions, the ionic activity coefficients should be introduced to estimate the a_2 value for the given concentration c_2, and around the critical micelle concentration, *cmc*, the σ value becomes constant despite further increase in c_2.

The influence of H^+ and HO^- ions on the equilibrium in the two-component water–surfactant system is shown to be insignificant [11]. Recently, the discussions concerning the acidity/basicity of the water surface have been resumed. Probably, it is possible to reconcile the negative zeta-potential value of air bubbles [15] and even of the water surface modified by long-chain alcohols [16] with the positive χ-potential of the pure water surface against the aqueous bulk. The viewpoint of the author of the given article is reflected in a book chapter [17].

On the other hand, on addition of a constant large excess of an indifferent surface-inactive salt, such as NaCl, the concentration of gegen-ions becomes practically constant despite varying the surfactant concentration. Thus, the value $d\ln a_3 = da_3/a_3$

should be equated to zero, and the Gibbs equation for the ionic surfactant obeys the "1-form" and looks as that for the non-ionic one: $-d\sigma = \Gamma_2 RTd\ln c_2$.

If the concentration of the indifferent salt is commensurable with that of the ionic surfactant, the Davies equation [18] is suitable in terms of concentrations:

$$-d\sigma = \Gamma_2 RT\left(1+\frac{c_2}{c_2+c_{salt}}\right)d\ln c_2. \tag{4}$$

All of the above equations allow calculating the Γ_2 values using the experimentally obtained dependence of σ on a_2 or c_2. These data may be used for estimating the *cmc* value [2–4, 6] and some other parameters of the surfactant micelles formed in the bulk [19].

However, in a general case this Gibbs excess does not coincide with the excess in the monolayer (dense, or compact layer), i.e., with the 2D adsorption, which we denote as Γ_2^{m}.

Meanwhile, some experimental methods "sense" just the last-named value [10, 20–24], and it seems to be worthwhile obtaining expressions that would connect the $d\sigma/d\ln a_2$ (or $d\sigma/d\ln c_2$) function with the Γ_2^{m} values. Some attempts have already been reported in literature, e.g., by Hall, Pethica, and Shinoda [25, 26].

RESULTS

2D adsorption and the electrostatic term

The driving force of the adsorption process in the systems under consideration is the urge of the hydrocarbon chains towards the water surface, which results in σ decrease. Thus the charged groups of the amphiphile ions are also gathered in the same place. The interfacial region is totally neutral, but the thin monolayer is certainly charged, taking into account the Volta potential measurements on the water/air [27] or water/hydrocarbon [28] interfaces in the presence of ionic surfactants and the electrophoretic effect for air bubbles [29] and oil droplets [30] covered by the same amphiphiles.

It means that the charged head groups of the surface-active ions in the monolayer are incompletely neutralized by gegen-ions; the rest part of the latter is distributed in the diffuse part of the double electrical layer (DEL). In such a case, the amphiphile ion in the diffuse part of the DEL plays the role of a simili-ion, and its Gibbs excess in this region, Γ_2^d, is negative. For the total Gibbs excess, Γ_2, (5) is valid.

$$\Gamma_2 = \Gamma_2^m + \Gamma_2^d. \tag{5}$$

It means that for diluted monolayers the reciprocal Γ_2 value, unlike Γ_2^m, cannot provide the desirable exact information on the area that accounts for one surfactant ion, even if the orientation of the amphiphilic ion within the monolayer and the area directly occupied by it are correctly predicted.

The diffuse part of the DEL may be rather extended. For instance, at the ionic surfactant concentration 10^{-4} M (hereafter, 1 M = 1 mol dm^{-3}) in the absence of other (foreign) electrolytes the Debye length equals to 30 nm.

The formation of the DEL is automatically accounted by (1)–(4) [7]. However, the utilization of Γ_2^m instead of Γ_2 demands the introduction of the electrical item. Such an approach was developed in a plenty of papers for both soluble and insoluble ionic surfactants, on water/air or water/hydrocarbon interfaces [28–37]. (For insoluble monolayers, Γ_2^m should be replaced by the interfacial concentration, and only gegen-ions are present in the underlying pure aqueous phase.) Several aspects were matters of discussion [35, 36] and re-consideration [37], and the authors of some papers came to similar conclusions following somewhat different ways [9, 37]. Basing on equation (23) in the paper by Bell, Levine, and Pethica [34], the following expression may be written:

$$-d\sigma = RT\Gamma_2^m d\ln a_2 + RT\Gamma_3^m d\ln a_3 + q_s d\Psi. \tag{6}$$

Here, q_s stands for the surface charge density and Ψ is the electrical potential of the compact monolayer (i.e., of the Stern layer) against the bulk aqueous phase. In fact, the last term is a substitute for $RT(\Gamma_2^d d\ln a_2 + \Gamma_3^d d\ln a_3)$. The validity of such approach follows also from more recent works [8, 27]. Designating the degree of gegen-ion binding in the monomolecular adlayer, Γ_3^m/Γ_2^m, as β, one obtains:

$$\begin{aligned}-d\sigma = {} & RT\Gamma_2^m d\ln a_2 + RT\beta\Gamma_2^m d\ln a_3 + \\ & + (z_2\Gamma_2^m + z_3\beta\Gamma_2^m)Fd\Psi.\end{aligned} \tag{7}$$

Here F is the Faraday constant, z_i are ionic charges; $z_3 = -z_2$. Therefore:

$$\begin{aligned}& -\frac{d\sigma}{RTd\ln a_2} = \\ & = \Gamma_2^m\,[1+\beta\frac{d\ln a_3}{d\ln a_2}+(1-\beta)\frac{z_2F}{RT}\frac{d\Psi}{d\ln a_2}].\end{aligned} \tag{8}$$

In the absence of an inert salt, $c_3 = c_2$ and $dc_3 = dc_2$. This is, however, not true for ionic activities. Strictly speaking, the ratio $d\ln a_3/d\ln a_2$ is equal to $(f_2f_3dc_2 + c_2f_2df_3)/(f_2f_3dc_2 + c_2f_3df_2)$ and in a general case is not unity. But for relatively diluted surfactant solutions (below *cmc*), the assumption $d\ln a_3 = d\ln a_2$ seems to be reasonable.

The Ψ value is actually a kind of Galvani potential, unavailable for direct experimental determination. It is caused by ionic head groups of the amphiphile and by the gegen-ions, but the orientation of dipoles of water molecules and of long hydrocarbon tails also makes its contribution into the resulting electrical potential of the surface.

Usually, the equations of the DEL were used for decoding the $d\Psi$ value. For example, Hachisu [37] demonstrated that the electrostatic term of the equation of state of soluble ionized monolayers takes the form proposed by Davies, irrespective of the presence or absence of foreign neutral salts; this expression in given below in SI units:

$$\int_0^{\Psi_0} q_s d\Psi = \sqrt{\frac{32(RT)^3\varepsilon_r\varepsilon_0 c}{F^2}} \times \left(ch\frac{F\Psi_0}{2RT} - 1 \right). \tag{9}$$

Here ε_r is the relative permittivity, ε_0 is the absolute permittivity of vacuum, c is the concentration of the ions in the bulk, and Ψ_0 is the surface potential. The square root in mJ m^{-2} units equals to $6.03\sqrt{c}$, if c is expressed in M. The binding of gegen-ions by the monolayer was not expected [37], as in other early studies [1].

However, the Gouy equations are known to be invalid for relatively high electrical potentials. Moreover, the inter-ionic interactions in the diffuse layer and the ion sizes should be taken into account for more detailed considerations. Recently, Pethica and his colleagues reported failure of the Gouy model even under conditions where it is expected to be most applicable [38].

Also, it should be taken into account that quantum-chemical calculations for common surface-active ions *in vacuo* reveal some distribution of the head group charge to the rest of the diphilic ion, first of all, to the neighboring methylene group [39, 40]. In *n*-dodecylsulfate anion, the effective charge of the head group is found to be –1.13, whereas at the first CH_2 group and the hydrocarbon chain it is +0.18 and –0.05, respectively. The effective charges for *n*-dodecyltrimethylammonium cation are +0.73, +0.16, and +0.11, respectively [39]. If this is also true for the water/air or water/oil interface, it may influence, to some degree, the structure of the monolayer. Namely, it may weaken the cohesion of polymethylene chains and enhance the hydration of the region of first methylene groups. The abovementioned orientation of water dipoles may also, to a greater or lesser extent, govern the Ψ values.

In past decades, some detailed equilibrium models have been constructed, and several fruitful approaches have been developed [8, 11, 27, 41–47]. Here we propose a simple scheme, which allows obtaining a simple equation.

The main idea consists in excluding the $d\Psi$ value from (8). This may be done using the equilibrium constant of the amphiphile ion partition between the bulk and the compact monolayer. Hence, the choice of the adsorption isotherm is of key significance.

In this paper, we consider the adlayer of the ionic amphiphile with the bound gegen-ions as a two-dimensional electrolyte solution “without the condition of electroneutrality being fulfilled” [27]. This layer is treated as a monomolecular one, without distinguishing between the (probable) difference in the positions of ionic head groups and gegen-ions. In other words, the concept of the existence of the triple electrical layer [43] is ignored in our simplified model. At the same time, the possible formation of stable associates between oppositely charged ions in the monomolecular layer is not taken into account, and the ionic activity coefficients in this two-dimensional solution are not used.

Contrary to the common micelles of ionic surfactants in the bulk, the β values of monolayers presumably vary within a wide range of limits, depending on the degree of the surface coverage. Indeed, the 2D adsorption of the very first portions of the amphiphilic ions does not require a substantial binding of gegen-ions, because the equilibrium is provided just by the hydration of the rare charges. On the contrary, if the monolayer is filled by charged head-groups, the latter must be neutralized to a high extent.

Equations of the adsorption isotherm of the amphiphilic ion and the transformations of (8)

The applicability of different types of equations describing the adsorption of ions on water/air and water/hydrocarbon interfaces has been already considered in earlier publications [33, 47]. Three approaches are examined in the present study: (i) the Henry model, (ii) the simple model of Langmuir adsorption, and (iii) the model of the mobile Langmuir monolayer. In all these cases, the equilibrium constant is expressed in terms of the Boltzmann distribution and, in fact, varies along with the Ψ value. It should be regarded as a partition coefficient under given concentration conditions.

(i) Regarding the monomolecular adlayer (in fact, the Stern layer) with the thickness δ as a second phase, one can write the condition of the partition equilibrium in the following manner:

$$a_2 \exp(-\frac{\Phi_2 + z_2 F\Psi}{RT}) = \Gamma_2^m \delta^{-1}. \tag{10}$$

Actually, (10) converts into the “normal” Henry equation at Ψ = const. Assuming that the Stern adsorption potential, Φ_2, and the δ values are constant and converting (10) to the logarithmic form, one obtains after differentiating:

$$\frac{z_2 F}{RT}\frac{d\Psi}{d\ln a_2} = 1 - \frac{d\ln\Gamma_2^m}{d\ln a_2}. \tag{11}$$

Then (8) may be re-arranged to the following form:

$$-\frac{d\sigma}{RTd\ln a_2} = \Gamma_2^m\,[2 - (1-\beta)\frac{d\ln\Gamma_2^m}{d\ln a_2}]. \qquad (12)$$

The Henry model is usually used for very diluted systems, owing to the limited capacity of the monolayer.

(ii) Using the Langmuir model of the monomolecular adsorption:

$$a_2\exp(-\frac{\Phi_2 + z_2F\Psi}{RT}) = \frac{\Gamma_2^m}{\Gamma_2^{m\infty} - \Gamma_2^m}, \qquad (13)$$

and performing the above procedure, one obtains:

$$\frac{z_2F}{RT}\frac{d\Psi}{d\ln a_2} = 1 - \frac{d\ln\Gamma_2^m}{d\ln a_2}\times\frac{1}{1-(\Gamma_2^m/\Gamma_2^{m\infty})}, \qquad (14)$$

and

$$-\frac{d\sigma}{RTd\ln a_2} = \Gamma_2^m[2 - \frac{d\ln\Gamma_2^m}{d\ln a_2}\times\frac{1-\beta}{1-(\Gamma_2^m/\Gamma_2^{m\infty})}]. \qquad (15)$$

Here $\Gamma_2^{m\infty}$ denotes the Γ_2^m value at complete filling of the adlayer.

(iii) Finally, following Haydon and Taylor [33], the de Boer equation for the mobile monolayer may be applied:

$$a_2\exp(-\frac{\Phi_2 + z_2F\Psi}{RT}) = \frac{\Gamma_2^m}{\Gamma_2^{m\infty} - \Gamma_2^m}\exp\frac{\Gamma_2^m}{\Gamma_2^{m\infty} - \Gamma_2^m}. \qquad (16)$$

Accordingly, equations (17) and (18) may be obtained:

$$\frac{z_2F}{RT}\frac{d\Psi}{d\ln a_2} = 1 - \frac{d\ln\Gamma_2^m}{d\ln a_2}\times\frac{1}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^2}, \qquad (17)$$

$$-\frac{d\sigma}{RTd\ln a_2} = \Gamma_2^m\{2 - \frac{d\ln\Gamma_2^m}{d\ln a_2}\times\frac{1-\beta}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^2}\}. \qquad (18)$$

Of course, (14) and (17) are inapplicable when $\Gamma_2^m \to \Gamma_2^{m\infty}$. As for (11), which results from the two-phase model, it transforms formally into the Nernstian form if the dependence Γ_2^m on a_2 tends to the plateau and $d\Gamma_2^m / d\ln a_2$ works for zero. This corresponds to the equality of the electrochemical potential of the amphiphile in the bulk phase and monolayer pseudo-phase under conditions of complete filling of the latter. At the same time, the Henry model is known to be able to describe the adsorption isotherm mainly in diluted systems, at least, for adsorption of neutral molecules.

Taking into account the character of the surfactant monolayer on the water/air or water/hydrocarbon interface at low coverage of the interface, (16)–(18) seem to be most pertinent. It cannot be excluded, however, that when Γ_2^m approaches $\Gamma_2^{m\infty}$, the model of immobile monolayer (13)–(15) may be more appropriate. For the two-phase partition model, (10)–(12) should be used.

In those equations, the Φ_2 value for simplicity is assumed to be the same at adsorption on both pure aqueous interface and the dense layer of the surfactant, where the cohesion interactions between the hydrocarbon tails, generally speaking, may be rather strong.

In the case of the water/oil interface, the assumption Φ_2 = const may be true [48]. (In this paper, we do not consider some more sophisticated approaches [49].) However, for the water/air interface, the correction for cohesion seems to be necessary. This approach can be traced back to 1925 [50, 51] and is expressed via the Frumkin isotherm. So, Φ_2 may be presented as a sum of a constant value Φ_2^0 and a variable contribution that is a function of the monolayer filling:

$$\Phi_2 = \Phi_2^0 - 2b\Gamma_2^m. \qquad (19)$$

Therefore, in a general form the proposed equation for the water/air interface should be given as follows:

$$-\frac{d\sigma}{RTd\ln a_2} = \qquad (20)$$
$$= \Gamma_2^m\left\{2-(1-\beta)\frac{d\ln\Gamma_2^m}{d\ln a_2}\left[\frac{1}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{1+t}} - \frac{2b}{RT}\Gamma_2^m\right]\right\}.$$

Here, $t = -1$, 0, or +1. In any case, the ionic activity coefficients should be evaluated using some reasonable equation [6].

Hence, in order to calculate the β values for each surfactant concentration having the surface tension isotherm and direct Γ_2^m determinations, three parameters, $\Gamma_2^{m\infty}$, b, and t are to be estimated. The last one obviously depends on the degree of filling the monolayer. If this degree is around several percents, the difference between the two forms of the isotherm disappears.

The $\Gamma_2^{m\infty}$ value may be determined directly via neutron reflection, ellipsometry, or second harmonic generation (SHG) techniques. However, different $\Gamma_2^{m\infty}$ values for the same surfactant are often available in literature. In order to verify $\Gamma_2^{m\infty}$, the experiments with a large excess of an indifferent electrolyte can be used. The same data, along with other approaches described in literature, may be used to evaluate the cohesion constant.

The equations in the presence of the indifferent (foreign) salt

If adding of an inorganic surface-inactive salt, e.g., NaCl, provides a large constant excess of gegen-ions, equation (3) reshapes into:

$$-d\sigma = RT\Gamma_2 d\ln a_2 + RT\Gamma_3 d\ln a_3 + RT\Gamma_4 d\ln a_4. \qquad (21)$$

Here, suffix “4” denotes the simili-ion, i.e., Cl^- in the case of sodium *n*-dodecylsulfate and Na^+ in the case of *n*-dodecyltrimethylammonium chloride (bromide). From the electroneutrality principle it follows that $\Gamma_2 + \Gamma_4 = \Gamma_3$. If an excess of the indifferent salt is fixed and large enough, then $d\ln a_3 = 0$ and $d\ln a_4 = 0$. On the one hand, it is reasonable to expect that simili-ions are absent from the charged monolayer [25]. Hence, $\Gamma_4 = \Gamma_4^d$. On the other hand, it is reasonable to expect that $\Gamma_2^d = \Gamma_4^d c_2 / c_4$ [25], and thus $-\Gamma_4^d >> -\Gamma_2^d$. If the latter term is negligible, then $\Gamma_2 \to \Gamma_2^m$. Placing this equation to Eq. (6), and taking into account that $-d\sigma = \Gamma_2 RT d\ln a_2$ at $c_2 << c_4$, one obtains $d\Psi \to 0$.

Cohesion is assumed to be independent of electrostatics. Therefore, an expression for b can be derived combining equations (13) or (16) with (19):

$$\frac{2b}{RT} = \frac{1}{\Gamma_2^m[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{1+t}} - \frac{d\ln c_2}{d\Gamma_2^m}. \tag{22}$$

At the fixed bulk ionic strength, f_2 = const. In the presence of a large excess of a foreign salt, the diffuse layer is condensed. For instance, in 0.1 M NaCl solution, the Debye length at $T = 298$ K is around 1 nm. The interfacial charge is largely screened. Also, the β values may increase as compared with those in entire surfactant solutions due to some additional adsorption of gegen-ions.

Usefulness of the proposed equation

At a definite surfactant concentration, the surface tension isotherm reaches plateau ($d\sigma = 0$) as a result of micelle formation. Naturally, this state of equilibrium is beyond the shape of our model. Under such conditions, the structure of the water/air interface may be rather complicated. For instance, for *n*-tetradecyltrimethylammonium bromide it was shown, using neutron reflection, that at $c_2 = 50$ *cmc* the surfactant is totally absent in a 2–3 nm-thick region below the completed monolayer, but a further layer is formed by the adsorbed micelles [52].

In (12), (15), (18), and (20), the lhs approaches $2\,\Gamma_2$. For simplicity, let us consider it to be exactly equal to $2\,\Gamma_2$ (which is true if $a_2 = a_\pm$):

$$\Gamma_2^m - \Gamma_2 = -\Gamma_2^d = \\ = \frac{1-\beta}{2} \times \frac{d\Gamma_2^m}{d\ln a_2}\left[\frac{1}{[1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{1+t}} - \frac{2b}{RT}\Gamma_2^m\right]. \tag{23}$$

On the one hand, the coincidence of Γ_2^m and Γ_2 means that $\Gamma_2^d = 0$ and hence the concentration of the diphilic ion in the diffuse part of the DEL is the same as in the bulk phase. This contradicts the recognized scheme of ion distribution near the charged layer. Within the framework of our simple model, this might take place if $\beta = 1$, i.e., if the monolayer consists of a neutral surface-active salt. This, in turn, is incompatible with the electrokinetic data, because significant values of zeta-potential on the water/air and water/oil interfaces have been observed even at high c_2 values [29, 30]. (The DEL caused by orientation of dipoles cannot produce the electrokinetic effect.)

On the other hand, even if the difference between Γ_2^m and Γ_2 is very small and β is close to unity, the Ψ values may still be substantial. Rough estimates made using the Gouy formula demonstrate that for the bulk concentration of 0.01 M, the value $|\Psi| = 50$ mV may be reached at $q_s = 8.3$ charges per 100 nm^2. If the “molecular area” is 0.40 nm^2, this corresponds to $\beta = 0.97$, etc. Probably, in such cases the accuracy of the experimental data hinders distinguishing between Γ_2^m and Γ_2. Hence, utilization of (20) or (23) may lead to uncertain results.

Under such conditions, $-\Gamma_2^d << \Gamma_2$. This is in line with the viewpoint of Gilányi et al. [53]. However, their estimate of $\beta \approx 0.2$–0.3 for some alkali metal *n*-decylsulfates, even at high coverage of the monolayer [53], differs substantially from the values of $\beta \approx 0.8$ for sodium *n*-dodecylsulfate and *n*-decylsulfates reported by other authors [43, 54]. The approach proposed by Aleiner and Us’yarov leads even to the β value of 0.94 to 0.97 [55].

In 1997, Thomas and co-workers reported a concise overview of the experimental methods of studying the degree of gegen-ions binding, known at that time [56, 57]. Direct measurements via the neutron reflectivity technique demonstrated that in the case of both insoluble monolayers based on docosyl sulfonate (with tetramethylammonium ions in the water phase) and adlayers of tetramethylammonium *n*-dodecylsulfate, a fraction of the gegen-ions remains in the diffuse layer [56, 57]. For instance, for the latter type of monolayers, at c_2 = *cmc*, $\beta = 0.78 \pm 0.10$ [56, 57].

Equations (20), (23) are more useful for small and medium surfactant concentrations when the 2D layer is enough diluted. Under these conditions, some conclusions concerning the values of β and Γ_2^m / Γ_2 may be deduced.

First, let us consider electrometric measurements. Though the Ψ value is experimentally unavailable, it makes a substantial contribution to the corresponding Volta potential, which can be measured, for instance, using the vibrating plate technique [27]. In sodium *n*-dodecylsulfate solutions within the range of 10^{-6} to 10^{-4} M, the ΔV value gradually becomes more and more negative, until the decrease reaches 60 mV. At a further increase in sodium *n*-dodecylsulfate concentration, the change of the Volta potential occurs in an opposite direction, and from 10^{-4} to 4×10^{-3} M it becomes 120 mV higher [27]. The expressed decrease in the σ value and the rise of the surfactant adsorption occurs just in this concentration range [27]. Thus, the positive contribution of the dipoles to the ΔV value overcomes that of the Ψ value [27], though the latter remains negative as detected by electrophoresis. As the adsorption of the n-$C_{12}H_{25}OSO_3^-$ ions obviously occurs monotonously, it is also natural to assume that in extremely dilute solutions the adsorption of amphiphilic anions is accompanied by modest binding of gegen-ions (relatively small β values), but further penetration of the surface-active agents into the monolayer may be realized only together with some increasing fractions of Na^+ ions. In addition, a subsequent rise in the c_2 value results in screening of the interfacial charge. (In contrast, the adsorption of non-ionic surfactants is accompanied by a monotonous change in ΔV, caused by dipole molecules [27]. In the presence of NaCl (at c_4 = 0.01 M and even more so at c_4 0.1 M) the ΔV is much less negative and practically independent on c_2 [27].)

If the electrical potential of the Stern layer becomes less negative along with the increase in the adsorption of the anionic surfactant, the most logical explanation is the increase in the β values. The choice of the $\Gamma_2^{m\infty}$ value within some reasonable limits may influence the results of calculations via (20) and (23), but the general character of the dependences remains the same. In the light of the above argumentation, the model that does not presume the gegen-ion binding in the monolayer seems to be less adequate.

Small β values at adsorption of amphiphile ions from extremely dilute solutions, without foreign electrolytes, resemble, to some extent, the formation of mixed ionic – non-ionic surfactant micelles in the bulk water. Indeed, both direct and indirect estimates allow assuming that at low fractions of ionic surfactants the degree of gegen-ion binding by the micellar pseudophase is low [58].

The proposed equations may be utilized to explain some contradictions observed in the experiments with radioactive indicators. More than half a century ago, those tools were already used in verifications of the Gibbs equation for ionic surfactants. In a pioneering study, it was concluded that a so-called "2-form" of the Gibbs equation for an anionic surfactant sodium di-*n*-octyl sulfosuccinate ($-d\sigma = 2\Gamma_2 RTd\ln c_2$) does not hold in diluted solutions [59]. To explain the absence of factor "2", the protonation of the SO_3^- group in the interfacial region was supposed to take place [59]. In such a case, the "1-form" is quite logical, similarly to the adsorption of non-ionic surfactants. The invalidity of the "2-form" for another anionic surfactant, sodium stearate, was also reported [60]. However, the analysis of the total body of the data obtained with low energy beta-emitters, such as ^{3}H, ^{14}C, ^{22}Na, and ^{35}S, allows concluding that the deviations from the "2-form" take place only in extremely diluted solutions of ionic surfactants. Excellent coincidence with the theory was reported at medium concentrations [2–4, 61].

Simplified explanation may be as follows. In dilute solutions, the diffuse part of the DEL is very extended, while the measurements with the radioactive tracers reflect the concentrations mainly within a relatively thin layer. Hence, a value close to Γ_2^m is registered. The latter is by definition higher than Γ_2 (5). On the contrary, in relatively concentrated solutions, where Γ_2 approaches Γ_2^m and the diffuse region is compressed, the measurements allow to obtain the total Γ_2 value [10].

In the case of non-ionic surfactant, the DEL electrical layer is absent and the Γ_2 values estimated via the radioactive indicators always coincide with those obtained by processing the surface tension isotherm (2). The same situation is observed for ionic surfactants at the foreign salt excess [62], because of dramatic compression of the diffuse part of the DEL.

In extremely diluted solutions of an ionic surfactant without salt addition, at $c_2 \to 0$, the adsorption is feebly marked, thus $\Gamma_2^m << \Gamma_2^{m\infty}$, and the cohesion is less significant. If the increasing Γ_2^m vs. a_2 curve is, at first approximation, approaching linearity, then the product $(d\ln\Gamma_2^m / d\ln a_2)\times[(1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{-1-t}$ is close to unity. In other words, $d\Psi/d\ln a_2 \to 0$: see (11), (14), and (17). This may occur when $\Psi \to 0$; indeed, in an extremely diluted monolayer the contribution of the electrostatic term into the surface pressure is expected to be small [1, 37].

Otherwise, $d\Psi/d\ln a_2 \to 0$ and $(d\ln\Gamma_2^m / d\ln a_2)\times\{[(1-(\Gamma_2^m/\Gamma_2^{m\infty})]^{-1-t} - 2b\Gamma_2^m/RT\}\approx 1$ may correspond to the turning point of the Ψ vs. $\ln a_2$ dependence, due to the increase in gegen-ion binding and shielding of the interfacial charge. In the particular case of anionic surfactants, the ΔV value first drops and then exhibits a minimum mainly owing to the increasing contribution of dipoles of the terminal CH_3 groups [27], but this cannot exclude the presence of the Ψ minimum as well. The zeta-potential at the water/air interface exceeds 200 mV in 5×10^{-5} M solution of *n*-hexadecyltrimethylammonium bromide, then rises to ca. 300 mV, and at 2.5×10^{-4} M the dip of curve becomes evident [29]. Note, that the *cmc* value of this surfactant equals 0.001 M.

Hence, in both cases. (7), (8), (20) and (23) can be reduced to:

$$\Gamma_2^m \approx \Gamma_2 \frac{2}{1+\beta}. \tag{24}$$

$$-\Gamma_2^d \approx \Gamma_2^m \frac{1-\beta}{2}. \tag{25}$$

If an experimental method used for independent Γ_2 estimation gives, in fact, Γ_2^m, then one receives the virtual "(1 + β)-form" of the Gibbs equation. This allows explaining the apparent invalidity of the Gibbs equation, if the radioactivity data reflect mostly the 2D adsorption.

On the other hand, some authors explain the results of earlier works with anionic surfactants by the existence of impurities [10], e.g., Ca^{2+} ions [10]. Indeed, it was demonstrated that such effects might be significant [63]. Unfortunately, the radiotracer data for extremely diluted solutions suitable for numerical processing are quite few.

In a limiting case, if $\beta \to 0$, the Γ_2^m value is ca. two-fold higher than the Γ_2 value, calculated from the surface tension isotherm (24). Poberezhniy et al. have already demonstrated it in a somewhat more complicated way by using the formulae of the DEL [9, 64, 65]. At such small c_2, the σ values approach that of pure water.

For a cationic surfactant with a bulky head group, the combination of surface tension and SHG methods resulted in a "1.28-form" form of the Gibbs equation [24]. The authors ascribe this phenomenon to formation of ion pairs with Br^- ions [24]. In such a case, however, this phenomenon might be of a universal character for a variety of surfactants. Alternatively, one may assume that an unusual type of the amphiphile may cause low β values (23), and then $-\Gamma_2^d$ is commensurable with Γ_2, despite estimates arising from the common DEL model.

The method of neutron reflection gives rather the values of Γ_2^m than of Γ_2 [10]. However, in numerous papers where the corresponding data were reported [10, 21, 22], the Γ_2^m values for both cationic and anionic surfactants practically coincide with those of Γ_2, obtained from the surface tension with proper precautions, even long before the plateau of the adsorption isotherm is reached. As a rule, extremely diluted solutions were not examined. Probably, the sole exception were the data demonstrating the errors caused by the presence of the traces of Ca^{2+} ions in solutions of perfluorinated anionic surfactants [10] and Aerosol OT [10].

CONCLUSIONS

Either of the proposed equations (20) or (23) may be used to process surface tension isotherms if the amount of the ionic surfactant in the monolayer may be determined by an independent experimental method. Any of those equations is applicable, first of all, to low and medium concentrations, where the difference between Γ_2^m and Γ_2 exceeds the experimental uncertainty. To the best of the author's knowledge, such equation has not been used anywhere yet. However, all necessary prime assertions may be found in literature, in particular, in papers and reviews cited in the list of references below. Equations (6)–(8), (10), (13), and (16) are based on dividing the total effect into the electrostatic and "non-electrostatic" contributions. Of course, such approach is conventional and sometimes even misleading [66], but it is most widely used and often helpful. Alternatively, the structure and composition of surfactant layers at the air/water interface are now studied using molecular dynamics and other theoretical approaches [67].

ACKNOWLEDGEMENTS

The author expresses his gratitude to Professors A.I. Rusanov and O.G. Us'yarov (St. Petersburg State University) and V.O. Cheranovskii (Kharkov V. Karazin National University) for helpful discussions of some aspects of the problem, to Professor C. Reichardt (Philipps University of Marburg) for regular information interchange, and to Professor W.T. Ford (Oklahoma State University) for sending the paper by I. Langmuir, ref. [50], which was otherwise unavailable for the author.

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Received 04.11.13

Реферат

Рассмотрена адсорбция ионного ПАВ на границе раздела вода/воздух и вода/углеводород. Одна из форм хорошо известного уравнения Гиббса учитывает поверхностный избыток амфифильного иона в плотном слое, или монослое, Γ_2^m (2D адсорбция), и дифференциал электрического потенциала этого слоя. Это выражение было модифицировано с использованием некоторых упрощающих допущений. Зависимость поверхностного натяжения, σ, от активности

амфифильного иона, a_2, степени связывания противоионов в плотном слое, β, и Γ_2^m преобразована к следующему виду:

$$-\frac{d\sigma}{RTd\ln a_2}=$$

$$=\Gamma_2^m\left\{2-(1-\beta)\frac{d\ln\Gamma_2^m}{d\ln a_2}\left[\frac{1}{\left[1-\left(\Gamma_2^m/\Gamma_2^{m\infty}\right)^{1+t}\right]}-\frac{2b}{RT}\Gamma_2^m\right]\right\}.$$

Здесь $\Gamma_2^{m\infty}$ обозначает значение Γ_2^m в условиях полного заполнения адслоя, $t = -1$, 0 или 1 для двухфазной модели распределения, неподвижного и подвижного монослоя соответственно, b – когезионная константа; длинноцепочечный ион и противоион однозарядны. Обсуждается применимость предложенного уравнения.

Ключевые слова: граница вода/воздух, адсорбция ионного ПАВ, поверхностное натяжение, адсорбция в мономолекулярном слое, степень связывания противоионов.