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

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Abstract—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, $\Gamma_2$ (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, $\sigma$, on the activity of the amphiphilic ion, $a_2$, degree of gegen-ions binding in the compact layer, $\beta$, and $\Gamma_2$ is transformed into the following relationship:
\[
\frac{d\sigma}{RT d\ln a_2} = \Gamma_2^m \left\{ 2 - (1 - \beta) \frac{d\ln \Gamma_2^m}{d\ln a_2} \frac{1}{(1 - (\Gamma_2^m / \Gamma_2^\infty))^{1/t}} - \frac{2b}{RT} \Gamma_2^m \right\}.
\]

Here $\Gamma_2^\infty$ denotes the $\Gamma_2^m$ value at complete filling of the adlayer, $t = -1, 0, +1$ 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

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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, $\sigma$, chemical potential of the surface-active agent, $\mu_2$, and its surface excess, $\Gamma_2$, at constant temperature:
\[
-d\sigma = \Gamma_2 d\mu_2.
\]

(The dividing surface may be lined in such a manner that the surface excess for water, $\Gamma_1$, will be equal to zero.) The adsorption causes the decrease in $\sigma$, while the chemical potential of the surfactant is a function of its activity in the bulk phase: $\mu_2 = \mu_2^0 + RT \ln a_2$. Hence,

\[
-d\sigma = \Gamma_2 RT d\ln a_2. \quad (2)
\]

Here $R$ is the gas constant and $T$ is the absolute temperature. For diluted solutions of non-electrolytes with expressed surface activity, Eq. (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, $d\mu_i = RT \ln (a_i a_i) = 2RT \ln a_i$. 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:

\[
-d\sigma = \Gamma_2 RT d\ln a_2 + \Gamma_3 RT d\ln a_3. \quad (3)
\]

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

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coefficients should be introduced to estimate the $c_2$ value for the given concentration $c_2$, and around the critical micelle concentration, $cmc$, the $\sigma$ 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 $\chi$-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: $-\sigma = \Gamma_2 R T d \ln c_2$.

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:

$$-d\sigma = \Gamma_2 R T \left(1 + \frac{c_2}{c_2 + c_{salt}}\right) d \ln c_2.$$  \hspace{1cm} (4)

All of the above equations allow calculating the $\Gamma_2$ values using the experimentally obtained dependence of $\sigma$ 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 $\Gamma_2^m$.

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 $\Gamma_2^m$ 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 $\sigma$ 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 surfactant 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, $\Gamma_2^d$, is negative. For the total Gibbs excess, $\Gamma_2$, (5) is valid.

$$\Gamma_2 = \Gamma_2^m + \Gamma_2^d.$$  \hspace{1cm} (5)

It means that for diluted monolayers the reciprocal $\Gamma_2$ value, unlike $\Gamma_2^m$, 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 $\Gamma_2^m$ instead of $\Gamma_2^d$ 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, $\Gamma_2^m$ 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 Eq. (23) in the paper by Bell, Levine, and Pethica [34], the following expression may be written:

$$-d\sigma = RT \Gamma_2^m d \ln a_2 + RT \Gamma_2^d d \ln a_1 + q_d d \Psi.$$  \hspace{1cm} (6)

Here, $q_d$ stands for the surface charge density and $\Psi$ 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 $RT (\Gamma_2^d d \ln a_2 + \Gamma_2^d d \ln a_1)$. The validity of such approach follows also from more recent works [8, 27].