

## Surface Tension and Surface Potential of Na *n*-Dodecyl Sulfate at the Air–Solution Interface: Model and Experiment

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Surface potential vs concentration isotherms of Na *n*-dodecyl sulfate (SDDS) adsorbed at the air–solution interface, measured using the vibrating plate method at various concentrations of added salt, exhibit a pronounced minimum. The results of surface tension measurements indicate that the minimum occurs within the concentration range that corresponds to the transition from the Henry regime of adsorption for low surface coverages to the one typical for adsorption of amphiphiles at high surface coverages. We proposed a simple model of adsorption of ionic surfactants at air–fluid interfaces based on the assumption that surfactant headgroups and counterions can adsorb in the Stern layer at the same Helmholtz plane. The electric potential in the electric double layer was calculated according to the Gouy–Chapman model for the diffuse part of the double layer and a modified Stern model for the inner layer with corrections for the discrete charge effects. The total potential drop across the interface was assumed to consist of two contributions: (i) the potential drop in the diffuse and compact double layers, negative for *n*-alkyl sulfate ions adsorbed at the air–solution interface, and (ii) a positive contribution due to the effective dipole moment of adsorbed surfactant molecules attributed mainly to the terminal CH<sub>3</sub> groups. Our model correctly describes the dependence of the surface tension and surface potential of SDDS solution on its concentration and the amount of added salt.

### Introduction

Understanding of the interfacial behavior of ionic surfactants at air–liquid and liquid–liquid interfaces is very important for a variety of colloidal phenomena like surface tension, thin film stability, micellization, foamability, etc. It is widely recognized that adsorption of ionic surfactants is strongly influenced by electric properties of an interface. However, the theoretical description of all electrical phenomena occurring at the interface during adsorption is complicated and still far from being complete. When the ionic surfactant molecules are adsorbed at the fluid–fluid interface, the electric double layer (EDL) is built and the double layer potential is determined by the charge of the surfactant molecules. The buildup of the double layer hinders the adsorption of subsequent surfactant molecules and facilitates adsorption of counterions in the double layer. The detailed description of these processes requires information on some basic properties of the electric double layer at the air–solution interface. The structure of the interface, thickness of the Stern layer where adsorbed surfactant headgroups are located, degree of penetration of the Stern layer by counterions, distribution of the electric dipole moments in adsorbed layer, and its dielectric properties determine the electric properties of air–ionic-surfactant solution interface. Most of these properties are difficult to measure, so there are rather scarce accessible data to formulate a correct model of the adsorption of ionic surfactant at a solution surface. The combination of surface tension and surface potential measurements at a solution interface can provide some insight necessary to develop and verify such a model.

Despite numerous experimental works on adsorption of ionic

surfactant, there is only a limited number of papers on the theoretical description of the adsorption. Davies and Rideal<sup>1</sup> and later Borwankar and Wasan<sup>2</sup> adjusted the Frumkin adsorption isotherm (Langmuir in case of Davies and Rideal) by considering the ionic interactions in the diffuse part of the electric double layer in terms of the Gouy–Chapman theory. They assumed that the surfactant ions were adsorbed in the Stern layer<sup>3</sup> and the counterions remained in the diffuse part of the electric double layer. They obtained the dependence of the surface tension on the ionic surfactant concentration in solution applying the Gibbs adsorption equation. Their result corresponded to the surface equation of state for ionized monolayers obtained by Hachisu.<sup>4</sup> On the basis of this approach, Dukhin et al.<sup>5–8</sup> developed the theory of adsorption kinetics of ionic surfactants at fluid interfaces that has been recently extended by several authors.<sup>9–11</sup> However, as it was shown by Kalinin and Radke,<sup>12</sup> this simple model of adsorption regarding all counterions remaining in the diffuse part of the double layer largely overestimates the diffuse layer potential. The latter can be measured by electrokinetic methods.<sup>13,14</sup> Also, the surface potential measured with the vibrating plate technique at low surface coverages at air–SDDS solution interface<sup>15</sup> is much lower (less negative) than that predicted by the theory of Borwankar and Wasan.

To resolve this discrepancy, Kalinin and Radke<sup>12</sup> developed a new model of ionic surfactant adsorption at the fluid–fluid interface. Their model allows counterion binding to the surfactant ion already present in the Stern layer. They adopted Grahame's<sup>16</sup> concept of the triple layer with adsorbed counterions located at the inner Helmholtz plane (IHP) while adsorbed surfactant headgroups remain at the interface. The hydrated counterions in the diffuse part of the double layer could approach the interface only at the distance of the outer Helmholtz plane (OHP). Although their model seems to be more suitable for the

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charged insoluble monolayers, they successfully described data concerning the dependence of the surface tension at the air–aqueous-SDDS and oil–aqueous-SDDS interfaces on the SDDS and NaCl concentration in the aqueous phase. The diffuse layer potential predicted by their model agrees better with the experimentally measured values than those calculated using the model of Borwankar and Wasan.<sup>2</sup>

The interpretation of the electric potential drop across a vapor–liquid or liquid–liquid interface was established initially by Schulman and Rideal<sup>17</sup> and summarized afterward by Davies and Rideal<sup>1</sup> and Gaines.<sup>18</sup> Some improvements introduced later concerned various ways of discerning components of the interfacial potential drop, evaluating the effective dipole moments of hydrophilic and hydrophobic parts of an adsorbed molecule,<sup>19,20</sup> and assessing local dielectric permittivities<sup>21–24</sup> in various parts of the adsorbed layer. Most of the surface potential evaluations were done for insoluble monolayers.

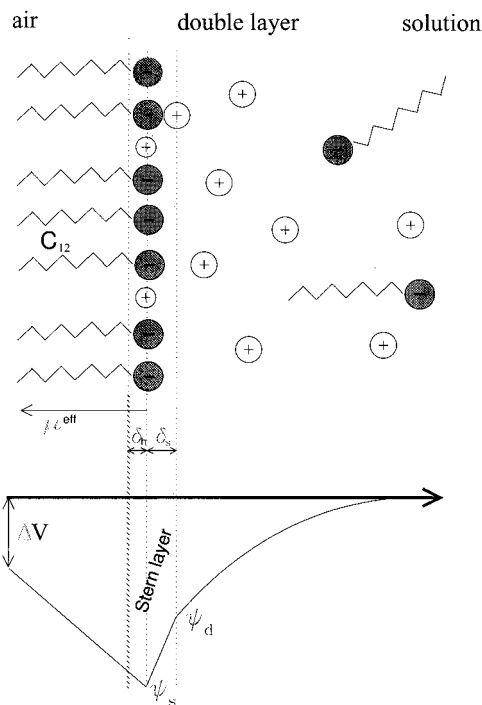
In our paper, we propose the model of adsorption of ionic surfactants at the air–solution interface, which is alternative to the model developed by Kalinin and Radke.<sup>12</sup> Our approach is based on the idea of Levine, Mingins, and Bell<sup>25</sup> of the penetration by counterions of the plane where surfactant headgroups are adsorbed. Thus, the counterions can adsorb at the same Helmholtz plane as the surfactant headgroups contributing to the total surface charge. According to the recent experimental evidence from the low-angle neutron scattering<sup>26,27</sup> as well as from computer simulations,<sup>28,29</sup> that type of model should adequately describe adsorption of soluble ionic surfactants and counterions at the air–solution interface.

The total potential drop across an interface is assumed to consist of two contributions: (i) the potential drop in the diffuse and compact parts of the electric double layer, negative for *n*-dodecyl sulfate ions adsorbed at the air–solution interface, and (ii) the potential drop due to the effective dipole moment of adsorbed surfactant molecules, assumed positive and attributed mainly to the terminal CH<sub>3</sub> group.

We describe by our model experimental data, existing in the literature and obtained by us, for the surface tension and surface potential vs surfactant concentration isotherms for SDDS at the air–solution interface. The measurements of surface potential were performed at various additions of salt. In the next sections, we introduce our model of ionic surfactant adsorption and compare it with other models available in the literature then we compare the experimental results with predictions resulting from various models of ionic surfactant adsorption.

### Model of Adsorption of Ionic Surfactants

The main principle of our model is presented in Figure 1. The adsorption of surfactant ions leads to the formation of the electric double layer at the air–solution interface. Surfactant headgroups, assumed to be negatively charged, are adsorbed at the interface in the Stern layer. The counterions are able also to adsorb in the Stern layer at the same Helmholtz plane like the headgroups. Both ions in the Stern layer preserve their freedom: there is no complex formation with a single surfactant headgroup, and hence an adsorbed counterion can be shared by several headgroups. Thus, the Stern layer can be considered as a two-dimensional electrolyte without the condition of electroneutrality being fulfilled. Surfactant headgroups and counterions in the Stern layer may be partially or totally dehydrated, which is represented in Figure 1 by the difference in size of ions in the Stern layer and in the bulk. The hydrated counterions in the diffuse part of the EDL can approach the interface at the distance  $\delta_s$  equal to the thickness of the outer part of the Stern layer (cf. Figure 1).



**Figure 1.** Model of adsorption of ionic surfactant at air–solution interface.

The total charge in the Stern layer determining the diffuse layer potential is the sum of charges of the adsorbed negative surfactant headgroups and positive counterions

$$\sigma = z_s F \Gamma_s + z_c F \Gamma_c \quad (1)$$

where  $\sigma$  is the surface charge density,  $\Gamma_s$  is the surface concentration of the surfactant in the Stern layer,  $\Gamma_c$  is the surface concentration of the counterions in the Stern layer,  $F$  is the Faraday constant, and  $z_s$  and  $z_c$  are the valencies of surfactant ions and counterions, respectively. For the sake of simplicity we consider a simple system with  $z_c = |z_s| = 1$ .

The diffuse layer potential can be determined from the formula

$$\psi_d = \frac{2kT}{e} \sinh^{-1} \left( \frac{\sigma e}{2\epsilon_0 \epsilon_s k T \kappa} \right) \quad (2)$$

where  $e$  is the elementary charge,  $k$  is the Boltzmann constant,  $T$  is the temperature,  $\epsilon_0$  is the vacuum dielectric permittivity,  $\epsilon_s$  is the dielectric constant of the solution, and  $\kappa$  is the Debye–Hückel reciprocal length. The Stern potential can be found from

$$\psi_s = \psi_d + \frac{\sigma \delta_s}{\epsilon_0 \epsilon_s} \quad (3)$$

where  $\epsilon_s$  is the dielectric constant in the Stern layer. The quotient  $C_s = (\epsilon_0 \epsilon_s) / \delta_s$  is usually referred to as the capacity (per unit area) of the outer part of the Stern layer.

The mean electrostatic potential at the adsorption plane (Stern layer) expressed by eq 3 differs from the local potential at the center of an adsorbed ion. This is due to the fluctuation of the distribution of ions caused by the presence of an ion of a finite size at a given point at the adsorption plane. This fluctuation, which is also known as the discreteness-of-charge effect, was discussed extensively by Levine et al.<sup>25,30–32</sup> and seems to account for a variety of phenomena that are in contradiction with the predictions of the classical Gouy–Chapman–Stern

double layer theory.<sup>30</sup> As an ion approaches the interface during the adsorption process, it feels local electrostatic potential rather than the average one, so it is necessary to account for the discreteness-of-charge effect formulating a model of adsorption of ionic surfactants. At a given point at the adsorption plane, the total potential can be expressed as

$$\psi_{\text{tot}}^{\pm} = \psi_s + \psi_{\text{doc}}^{\pm} \quad (4)$$

where  $\psi_{\text{doc}}^{\pm}$  is the correction to the mean potential accounting for the discreteness-of-charge effect for the positive and negative ions in the adsorbed layer, respectively. The computation of this correction at the air–water interface is a quite complicated task involving the solution of a Fredholm integral equation.<sup>31</sup> This makes it difficult to apply directly to the problem of adsorption of ionic surfactants where the effective fitting algorithm is required. Thus, as a first approximation of the influence of the discreteness-of-charge effect on the adsorption of ionic surfactants, we used a simplified approach proposed by Levine, Mingins, and Bell<sup>25</sup> based on a “cutoff” approximation to the fluctuation potential  $\psi_{\text{doc}}^{\pm}$ . This approach is limited to low electrolyte concentrations when the screening effect of ions in the diffuse double layer on the interaction between ions located in the Stern layer can be neglected. The application of a “cutoff” approximation leads to the analytical formulas that can be directly applied in the fitting procedure of the theoretical model to experimental data.<sup>25</sup>

$$\psi_{\text{doc}}^{+} = -\frac{\pi\sigma_{+}^2}{3\epsilon_0\epsilon_{z+}e} \left( r_{\beta+}^3 [1 + P] + \frac{a_{+}^3}{8} [1 - 6L] \right) - \frac{\sigma_{-}a_{-}}{4\epsilon_0\epsilon_{|z_{+}|}} [1 + H] \quad (5)$$

where  $r_{\beta+} = (e/(\pi\sigma_{+}))^{1/2}$  is the radius of the cutoff disk,  $\sigma_{+} = F\Gamma_c$ ,  $\sigma_{-} = -F\Gamma_s$ ,  $a_{+}$ , and  $a_{-}$  are the mean charge densities and radii of positive and negative ions adsorbed (radius of the headgroup in case of surfactant ions),  $P$ ,  $L$ , and  $H$  are functions of the cutoff disk and ionic sizes as well as of dielectric permittivities, derived in ref 25 and listed in the Appendix. The respective correction for the discreteness-of-charge effect for negative ions can be found by exchanging the role of  $\sigma_{+}$ ,  $\sigma_{-}$ ,  $a_{+}$ , and  $a_{-}$  in eq 5.

To evaluate the discreteness-of-charge effect for high electrolyte concentrations, we applied an approximation proposed by Levine and Robinson.<sup>32</sup>

$$\psi_{\text{doc}} = -2\sigma \frac{\delta_h \delta_s}{\epsilon_h \delta_s + \epsilon_s \delta_h} \frac{1 + \frac{\epsilon_s}{\epsilon_c \delta_s}}{1 + \frac{\epsilon_s}{\epsilon_c \delta_s} \frac{\epsilon_h \delta_s}{\epsilon_h \delta_s + \epsilon_s \delta_h}} \quad (6)$$

where

$$\kappa_e = \kappa \cosh\left(\frac{e|\psi_d|}{kT}\right)$$

is the “local” Debye–Hückel parameter and  $\delta_h$  and  $\epsilon_h$  are the thickness and the dielectric permittivity of the inner part of the Stern layer, respectively. Although eq 6 was derived to describe the discreteness-of-charge effect at the metal–solution interface, it leads to the overestimation of the effect and, as it was pointed out by Hunter,<sup>33</sup> can be a good approximation when applied to

the dielectric–solution interface. In both eqs 5 and 6, the potential due to the image charges is taken into account.

The surface concentration of the surfactant and the counterion adsorbed in the Stern layer can be obtained from the balance equation between respective adsorption and desorption fluxes in equilibrium.<sup>34</sup>

$$\frac{c_s}{\alpha_s} \exp\left(\frac{e\psi_{\text{tot}}^{-}}{kT}\right) (1 - \theta_s - \theta_c) = \theta_s \exp(-2H_s \theta_s) \quad (7)$$

and

$$\frac{c_c}{\alpha_c} \exp\left(-\frac{e\psi_{\text{tot}}^{+}}{kT}\right) (1 - \theta_s - \theta_c)^{g_{sc}} = \theta_c \quad (8)$$

where  $c_s$  is the bulk concentration of surfactant molecules,  $\theta_s = \Gamma_s/\Gamma_{s\infty}$  is the relative surfactant surface coverage,  $\Gamma_{s\infty}$  is the limiting surfactant surface coverage corresponding to the closed packed monolayer of surfactant molecules at the interface,  $\alpha_s$  is the “surface activity” coefficient of the surfactant being a measure of the free energy of the adsorption after subtracting the contribution of the electric interaction,  $H_s$  is the Frumkin interaction parameter accounting for the attractive lateral interactions among the adsorbed surfactant tails,  $c_c$  is the bulk concentration of counterions,  $\theta_c = \Gamma_c/\Gamma_{c\infty}$  is the relative counterion surface coverage,  $\Gamma_{c\infty}$  is the limiting surfactant surface coverage,  $\alpha_c$  is the “surface activity” coefficient of the counterion being a measure of counterion penetration into the Stern layer, and  $g_{sc} = \Gamma_{s\infty}/\Gamma_{c\infty}$ .

The term in the second bracket at the left-hand side of eqs 7 and 8 accounts for the “surface exclusion” effect due to the finite size of the headgroups and counterions in the Stern layer. For the limiting case of  $\psi_{\text{tot}}^{\pm} = 0$  and  $H_s = 0$ , eqs 7 and 8 describe the Langmuir adsorption isotherm of the binary mixture of surface-active species of different molecular area.<sup>35</sup>

The surface concentrations of the surfactant molecules and counterions in the Stern layer can be found from eqs 2–8 by numerical solution using the Newton–Raphson algorithm.<sup>36</sup>

The total surface concentration of the surfactant and all ions present in the system has to take into account also the adsorption in the diffuse part of the double layer. The latter can be computed according to

$$\Gamma_{-} = \Gamma_s + \int_0^{\infty} (c_{-}(x) - c_{-b}) dx \quad (9)$$

$$\Gamma_{+} = \Gamma_c + \int_0^{\infty} (c_{+}(x) - c_{+b}) dx \quad (10)$$

where  $\Gamma_{-}$  and  $\Gamma_{+}$  are the surface concentrations of all anions and all cations present in the solution

$$c_{-}(x) = c_{-b} \exp(e\psi(x)/kT)$$

and  $c_{-b}$  are the local concentration in the double layer and the bulk concentration of all anions in solution (surfactant ions and coions of any added salt),

$$c_{+}(x) = c_{+b} \exp(-e\psi(x)/kT)$$

and  $c_{+b}$  are the local concentration in the double layer and bulk concentration of all cations in solution, and  $x$  is the distance from the interface. Note that, as the electric potential in the double layer is negative, the adsorption in the diffuse double layer of the surfactant and all coions is also negative due to the electric repulsion, since  $c_{-}(x) < c_{-b}$ . The potential distribution

in the double layer can be calculated according to

$$\psi(x) = \frac{4kT}{e} \tanh^{-1} \left( \tanh \left[ \frac{e\psi_d}{4kT} \right] \exp(-\kappa x) \right) \quad (11)$$

To compare the results of the theoretical model with the experimental surface tension data, we calculated it by integration of the Gibbs adsorption equation, which for the ionic surfactant solution assumes the form

$$d\sigma = -RT \left( \sum_i \Gamma_-^i d \ln a_-^i + \sum_j \Gamma_+^j d \ln a_+^j \right) \quad (12)$$

where activities of all anions  $a_-$  and all cations  $a_+$  can be found, based on their bulk concentrations, by applying the Robinson–Stokes formula.<sup>37</sup>

The electric potential drop across the air–solution interface is assumed as consisting of two terms (cf. Figure 1).

$$\Delta V = N_a \Gamma_s \frac{\mu_{\perp}^{\text{eff}}}{\epsilon_0 \epsilon_t} (\Gamma_s) + \psi_s \quad (13)$$

where  $\mu_{\perp}^{\text{eff}}$  is the normal to the interface component of the effective dipole moment per one molecule of surfactant adsorbed,  $N_a$  is Avogadro's number, and  $\epsilon_0 \epsilon_t$  is the effective dielectric permittivity of the adsorbed layer. The first term in eq 13 accounts for the dipolar contribution to the interfacial potential and, as the only term, is responsible for the measured potential drop across the air–solution interface for nonionic surfactants. It consists of several contributions, such as (i) the dipole moment resulting from the disordering of water molecules at the interface around adsorbed molecules, (ii) the dipole moment introduced by the adsorbed headgroups, and (iii) the dipole moment introduced by the hydrocarbon chains.<sup>1,19–24</sup> All these contributions are undiscernible under most experimental conditions and therefore we can express the dipolar contribution to the interfacial potential in terms only of its effective value per adsorbed molecule. The quotient  $\mu_{\perp}^{\text{eff}}/\epsilon_0 \epsilon_t$  is in general a function of the surfactant concentration. It is widely recognized that at the low surface concentrations the surfactant tails are mostly oriented parallel to the interface; thus, the dipole moment of the hydrocarbon chain attributed mainly to the terminal methyl group does not contribute to the effective dipole moment. For high surface concentrations, surfactant tails tend to orient themselves perpendicular to the interface, contributing to the effective dipole moment. However, this effect is diminished by the increase of the local dielectric constant in the tail region from  $\epsilon_t = 1$ , when the interface is uncovered by hydrocarbon chains, to  $\epsilon_t \approx 2$  for the compact hydrocarbon layer. Thus, as a first approximation, we assume that  $\mu_{\perp}^{\text{eff}}/\epsilon_0 \epsilon_t$  is independent of surfactant surface concentration.

If the surface activity parameter for the counterion adsorption  $\alpha_c$  tends to infinity, that means counterions will not penetrate the Stern layer. If we additionally neglect the discreteness of charge, the model of Borwankar and Wasan<sup>2</sup> is reproduced.

As far as a structure of the adsorbed layer is concerned, our model represents the other limiting case in the description of the adsorption of ionic surfactants when compared with the model of Kalinin and Radke.<sup>12</sup> Contrary to their model, we assumed penetration of the plane of the adsorbed headgroups by counterions. The counterions preserve their freedom of thermal motion in the adsorbed layer and can be shared by several headgroups. The counterion “surface activity” parameter  $\alpha_c$  is a measure of the free energy change of the transfer of counterion from the bulk to the Stern layer. If the electric

interactions (including image forces) are correctly separated, it should account for the specific interactions with the adsorbed surfactant headgroups in the mean field approximation and changes in hydration of counterions upon transfer from the bulk to the surface layer,<sup>38</sup> as well as the interaction with the OH<sup>−</sup> groups adsorbed at the air–water interface.<sup>39</sup>

The direct comparison of these two models is difficult, as both contain some parameters that are hard to measure in practice. The experimental results concerning the influence of counterions on the surface tension of some ionic surfactants suggest at least partial penetration of the adsorption plane;<sup>40</sup> however, much more work has to be done to be able to unequivocally compare the models. The simultaneous measurements of the surface tension and surface potential in static and if possible dynamic conditions may provide some insight into which of these models of adsorption of ionic surfactant and under what experimental conditions better describes the system studied. In the subsequent paragraph, we present some results of this type of experiment.

## Experimental Section

Surface tension measurements were performed by the du Noüy ring method with an automatic tensiometer, Lauda TE-1M. All the necessary requirements to obtain the reliable results with this method for soluble monolayers were satisfied.<sup>41</sup>

Most of the surface potential ( $\Delta V$ ) measurements were performed using the vibrating plate method. The computer driven surface potential meter (KSV 1000 SPD) provided by KSV (Helsinki, Finland) was used for the experiments. The electrode was in the shape of the disk (2 cm diameter and 0.5 mm thickness) and was vibrating at a constant frequency of 90 Hz. More details of the experimental procedure are given elsewhere.<sup>42</sup>

The surface potential of the SDDS solution was determined relative to the surface potential of the pure supporting electrolyte (or water if no salt was added to a solution).

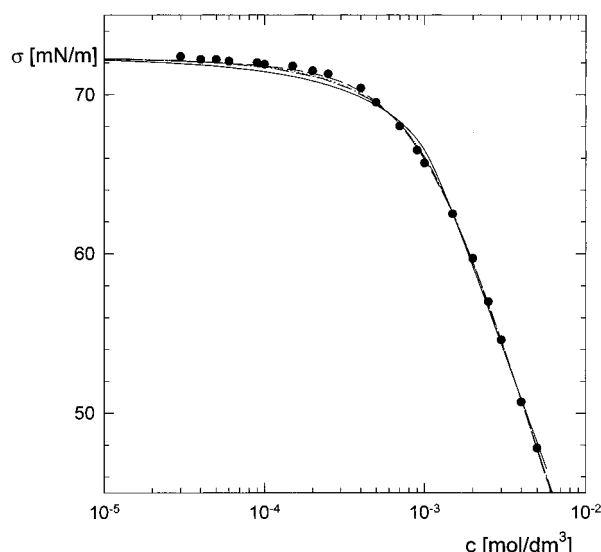
$$\Delta V = \Delta V_i - \Delta V_0 \quad (14)$$

where  $\Delta V_i$  was the surface potential measured in the presence of SDDS and  $\Delta V_0$  was the surface potential measured for the reference solution. First, the reference solution was placed in a Petrii dish underneath the vibrating plate, and after zero adjustment, it was replaced by the solution of desired SDDS concentration. The electrode was constantly vibrating during the measurements. Special care was taken not to make any disturbance of the apparatus zero level during the solution's replacement. A constant distance between the vibrating electrode and solution surface of  $1 \pm 0.5$  mm was maintained. The measurements' reproducibility was better than  $\pm 5$  mV. All surface potential measurements were taken after time sufficient to equilibrate the system after a new surface was formed.

Some measurements of the electric surface potential were performed with the radioactive electrode with an <sup>241</sup>Am  $\alpha$ -emitter. The solution samples of 25 mL were measured in Petrii dishes. The air gap was carefully adjusted to a width of 1–2 mm. The measurements were performed in the supporting electrolyte to provide the conductivity required for a potentiometric measurement. The compensation voltage across the air gap was measured against the silver/silver chloride electrode with a high impedance electrometer.

Sodium *n*-dodecyl sulfate was received from Merck. Prior to the measurements, the surfactant stock solutions were carefully purified either by continuously shaking the stock





**Figure 2.** Dependence of surface tension of aqueous SDDS on its concentration in solution, no NaCl added: (circles) experimental data; (lines) fits to theoretical models of adsorption of ionic surfactants, (solid line) BW model, (dashed line) KR model, (dash–dotted line) WBLF model without discreteness-of-charge effect, (dotted line) WBLF model with discreteness-of-charge effect taken into account. The experimental error corresponds to the size of circles. Best fit parameters are given in Table 1.

solution with charcoal during several days or by an automated purification procedure in a surface purification apparatus.<sup>43,44</sup> The surfactant solutions's grade of purity was judged according to the criteria of "surface chemical purity" proposed by one of us previously.<sup>45,46</sup>

Sodium chloride supplied by Merck of suprapure grade was used as received. The solutions were prepared in triple distilled water. The measurements were carried out at room temperature,  $22 \pm 2$  °C.

## Results and Discussion

Figure 2 presents the experimentally measured dependence of surface tension of SDDS solution on surfactant concentration (circles) together with the best-fit curves to three different theoretical models of ionic surfactant adsorption. The solid line represents the fit of the experimental data to the model of Borwankar and Wasan (BW), the dashed lines show the fit to the model of Kalinin and Radke (KR), and the dash–dotted lines show the fit to the model proposed in this paper (WBLF). As it can be seen, the BW adsorption model provides the poorest fit to the experimental data. It is better illustrated in Table 1, which shows the best-fit parameters together with the goodness of fit expressed in terms of

$$s = \sqrt{\frac{\sum_{i=1}^m (\sigma_{\text{ex}}(c_i) - \sigma_{\text{ev}}(c_i))^2}{f_g}} \quad (15)$$

where  $\sigma_{\text{ex}}(c_i)$  is the measured surface tension at a given concentration,  $\sigma_{\text{ev}}(c_i)$  is the surface tension calculated according to the model adsorption isotherm,  $m$  is the number of experimental points, and  $f_g$  is the number of degrees of freedom defined by

$$f_g = m - n - 1 \quad (16)$$

where  $n$  is a number of fitted parameters.

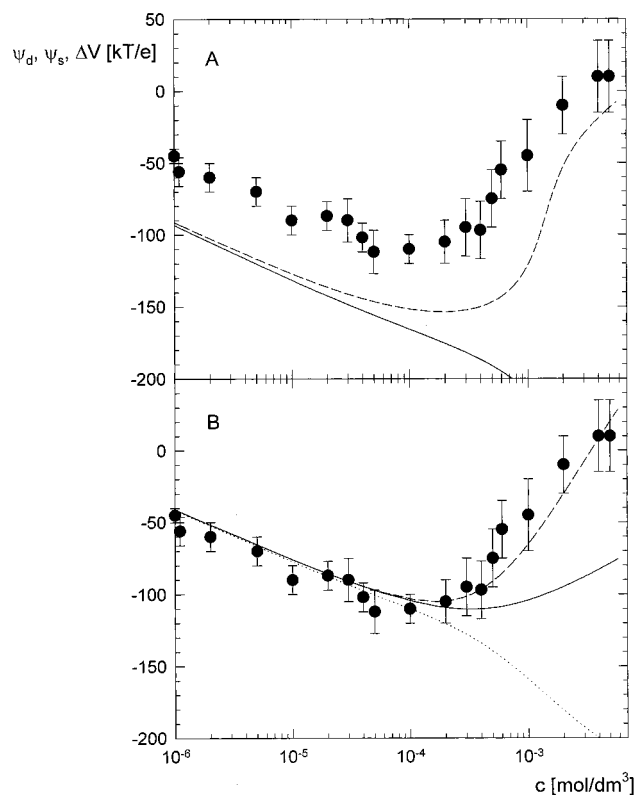
The goodness of fit of the experimental results to two other models of the adsorption of ionic surfactants is comparable (cf. Table 1). To describe our data in terms of the KR model, we had to use a slightly higher surfactant–counterion complexation constant (which is the inverse of  $\alpha_c$ ) than that reported in ref 12. Other parameters are very close to the values obtained by Kalinin and Radke. In the fitting procedure of the experimental data to the adsorption model proposed in this paper, we assumed a fixed value of the limiting adsorption of surfactant ions at the interface  $\Gamma_{\infty} = 6.4 \times 10^{-10}$  mol/cm<sup>2</sup>. It is equivalent to the limiting area per molecule of 0.26 nm<sup>2</sup>, which according to the crystal structure analysis,<sup>47,48</sup> corresponds to the size of the sulfate headgroup hydrated by 1/2 of a water molecule on average. The "surface activity" parameter of the Na<sup>+</sup> counterion, which according to our model of adsorption, is a measure of the ability of counterions to penetrate the layer where the headgroups are located and in this respect corresponds to the complexation constant of the KR model, is almost 2 orders of magnitudes higher. It indicates that, according to our model, the transfer of counterions from the diffuse layer to the Stern layer at the air/solution interface is energetically less favorable. There is no difference in the fit quality when, in our model, the discreteness-of-charge is taken into account using eq 5; however, the values of the fitting parameters are modified. The introduction of discreteness-of-charge lowers the value of the surfactant's surface activity parameter, and thus, makes the surface activity closer to one of the nonionic surfactant with the same hydrocarbon chain length. Provided the electric and "nonelectric" contributions to the free energy of adsorption are properly separated the surface activity parameters obtained for an ionic surfactant and nonionic one with the same hydrocarbon chain length should have comparable values since the main contribution to the adsorption free energy is due to the hydrophobic effect dependent on the length of surfactant chain. The discreteness-of-charge further increases the value of the "surface activity" parameter for the Na<sup>+</sup> counterions. Since by themselves, i.e., without adsorbed surfactant, counterions are rather repelled from the surface layer (the surface tension of the salt solution is higher than for pure water), the latter value,  $\alpha_c$ , should be high. However, neither of the studied models can correctly describe the negative (relative to adsorption of water) adsorption of inorganic electrolyte at the air–solution interface in the absence of ionic surfactant.

Figures 3 and 4 present the comparison between measured interfacial potential using the vibrating plate technique (solid circles) and those calculated (dashed lines) according to the various models of adsorption using the best fit of the model to the surface tension isotherm. As Figure 3A shows, the BW model of adsorption not only gives the poorest fit to the surface tension vs concentration isotherm but also largely overestimates (in the sense of absolute value) the interfacial potential. Although the BW model can describe the observed interfacial potential dependence on the SDDS concentration in solution qualitatively (with  $\mu_{\perp}^{\text{eff}}/\epsilon_1 = 0.35$  D), it fails to give the correct quantitative description. This finding is in agreement with the observation of Kalinin and Radke reported in ref 12. On the contrary, the two other models provide a correct quantitative description of the experimental results. Figure 3B presents the comparison between the experimentally observed interfacial potential and that calculated according to the KR model of adsorption using the best fit parameters listed in Table 1. Figure 4 shows the same comparison but for the WBLF model without the discreteness-of-charge effect taken into account (Figure 4, part A) and including this correction (Figure 4, part B).

**TABLE 1: Best-Fit Parameters of the Models of Adsorption of Ionic Surfactants to the Experimental Surface Tension Isotherm of SDDS with No Salt Added, Presented in Figure 2**

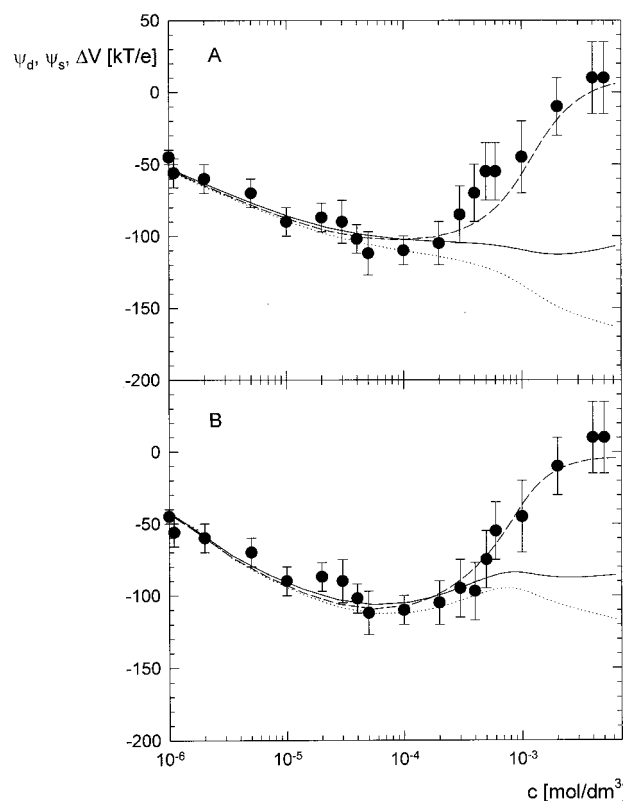
parameter	BW model	KR model	WBLF model	WBLF model with discreteness of charge, eq 5
$\alpha_s$ [ $10^{-5}$ mol/dm <sup>3</sup> ]	$0.49 \pm 0.03$	$10.9 \pm 0.5$	$6.5 \pm 0.8$	$1.1 \pm 0.18$
$\Gamma_{\infty}$ [ $10^{-10}$ mol/cm <sup>2</sup> ]	$2.55 \pm 0.05$	4.5 (fixed <sup>3</sup> )	6.4 (fixed)	6.4 (fixed)
RTH <sub>s</sub> [kJ/mol]	$7.8 \pm 0.2$	$4.1 \pm 0.2$	$9.5 \pm 0.6$	$11.0 \pm 0.6$
$\alpha_c$ [mol/dm <sup>3</sup> ] <sup>b</sup>		$0.009 \pm 0.002$	$0.58 \pm 0.1$	$2.7 \pm 0.1$
$C_{in}$ [ $\mu$ F/cm <sup>2</sup> ]		$265 \pm 40$		
$C_{out}$ [ $\mu$ F/cm <sup>2</sup> ]		$300 \pm 50$	$77 \pm 10$	$110 \pm 10$
$\Gamma_{\infty}/\Gamma_{c\infty}$			$1.0 \pm 0.05$	$1.0 \pm 0.1$
$\delta_1$ [nm] <sup>c</sup>				$0.15 \pm 0.02$
$\mu_{\perp}^{eff}/\epsilon_t$ [D]	0.35	0.30	0.24	0.19
$s$ [mN/m]	0.49	0.23	0.24	0.24

<sup>a</sup> Value suggested in ref 12. Fitting this value gives very small improvement of  $s$ . <sup>b</sup>  $\alpha_c$  is the inverse of the equilibrium constant  $K_{Na}$  introduced in ref 12. <sup>c</sup> According to the suggestions in ref 25, the dielectric constant was assumed to be 30 in the region of headgroups.



**Figure 3.** Dependence of the diffuse layer potential, Stern potential, and interfacial potential of aqueous SDDS on its concentration in solution (with no NaCl added) calculated based on the best fit to the theoretical model of adsorption to the surface tension data from Figure 3 and the experimental data for the interfacial potential obtained by the vibrating plate method (circles): (A) results of the BW model; (B) results of the KR model; (solid line) the diffuse layer potential  $\psi_d$ ; (dotted line) the Stern potential at the plane of adsorbed headgroups  $\psi_s$ ; (dashed line) the interfacial potential  $\Delta V$ .

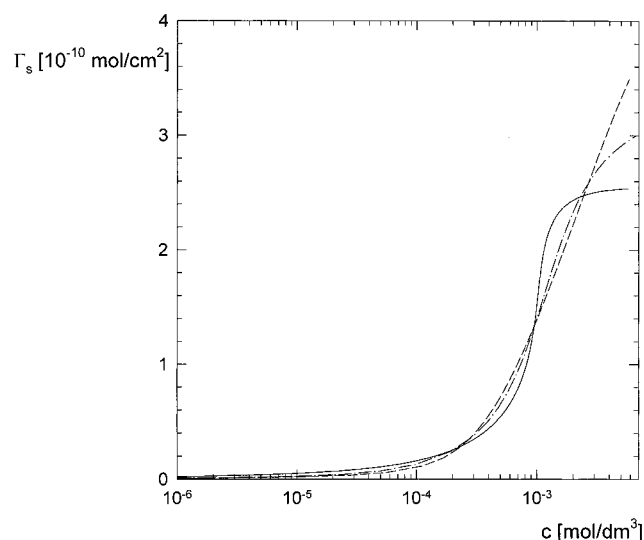
By analyzing the results presented in Figures 3 and 4 one can distinguish two separate regimes in the interfacial potential vs SDDS concentration isotherm. The interfacial potential in the descending part of the isotherm for solution of low concentration is determined mainly by the electric double layer potential. As it is shown in Figure 5, where the dependence of the surface concentration of the SDDS at the interface on its bulk concentration is presented, the descending branch of the surface potential isotherm (below  $10^{-4}$  M SDDS) corresponds to the Henry regime of adsorption when the interface is scarcely covered by surfactant molecules. For higher SDDS concentrations, the adsorption steeply increases with SDDS concentration and the positive dipolar contribution to the interfacial potential



**Figure 4.** Same as in Figure 3. (A) Results of the WBLF model without discreteness-of-charge effect; (B) WBLF model with discreteness-of-charge effect taken into account.

starts to determine the shape of the ascending branch of the isotherm. Thus, the presence of the minimum in the interfacial potential vs concentration isotherm should be an universal feature for anionic surfactants with paraffinic hydrocarbon chains and was observed previously<sup>49</sup> for the homologous series of sodium *n*-alkyl sulfates at the air–solution interface.

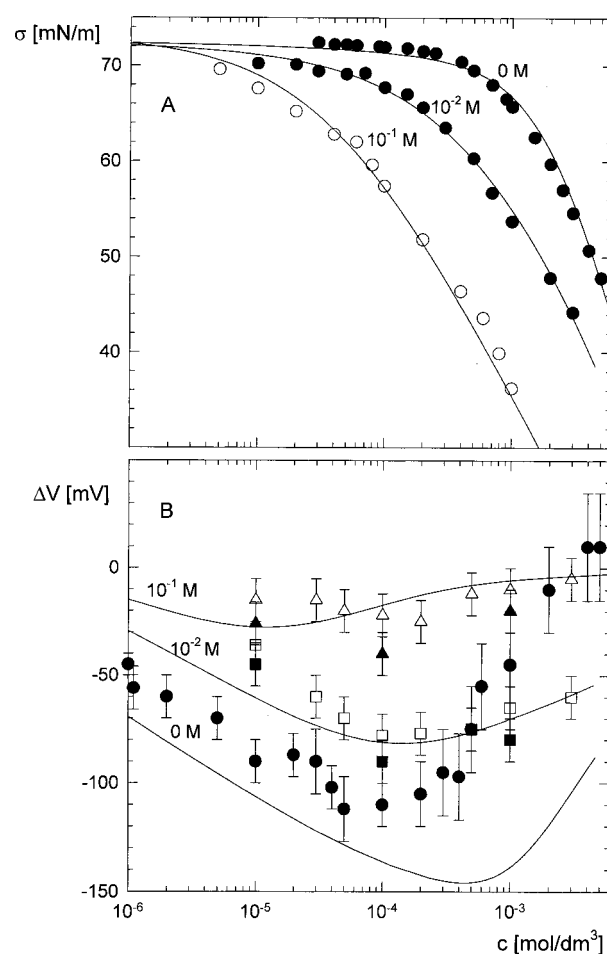
The KR model of adsorption predicts lower values of the diffuse layer potential and of the Stern potential at the air–solution interface than the model proposed in this paper (cf. solid and dotted lines in Figures 3 and 4). The value of the effective dipole moment to obtain the best fit to our experimental data of the surface potential is slightly larger for the KR model ( $\mu_{\perp}^{eff}/\epsilon_t = 0.30$  D) than for our model ( $\mu_{\perp}^{eff}/\epsilon_t = 0.24$  D without and  $\mu_{\perp}^{eff}/\epsilon_t = 0.19$  D with the discreteness-of-charge effect taken into account). However, it is worth noting that if we assume that the local dielectric constant in the adsorbed layer  $\epsilon_t$  is equal to its value for bulk hydrocarbon (i.e.,  $\epsilon_t = 2$ ), the resulting effective dipole moment ranges  $\mu_{\perp}^{eff} = 0.38 - 0.60$  D. This



**Figure 5.** Dependence of the surfactant ion surface concentration on SDDS bulk concentration calculated according to theoretical models using best-fit parameters given in Table 1: (solid curve) BW model; (dashed curve) KR model; (dot-dashed curve) WBLF model of adsorption.

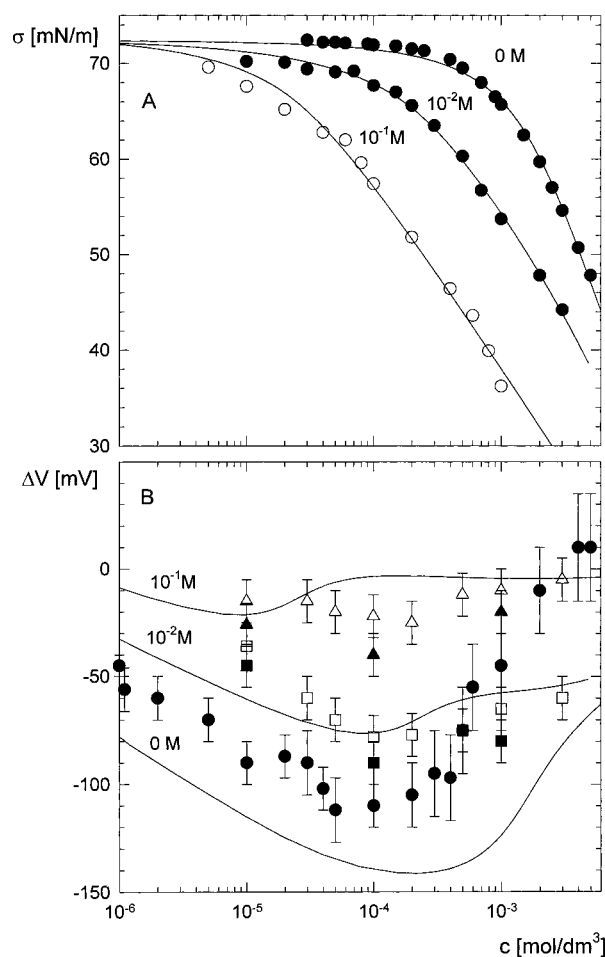
corresponds well to the dipole moment of the terminal methyl group of the hydrocarbon chain in orientation perpendicular to the surface ( $\mu = 0.4 \text{ D}^{50}$ ).

Next, we made an attempt to extend our approach to describe the surface tension and surface potential isotherms of SDDS solution for the various additions of NaCl. We fitted two theoretical models, KR and WBLF, to the experimental SDDS isotherms measured for various concentrations of NaCl added to the solution. The experimental data for the surface tension for 0 and  $10^{-2} \text{ M}$  were obtained by us the data for  $10^{-1} \text{ M}$  NaCl, but with undetermined purity of SDDS, were reported elsewhere.<sup>51</sup> Then, we compared the theoretical values of the interfacial potential calculated using best-fit parameters with the experimentally measured values using vibration plate and radioactive electrode techniques. The results are presented in Figures 6–8. In case of both models being applied, KR and WBLF, with no discreteness-of-charge potential taken into account, we failed to describe both surface tension and surface potential vs concentration isotherms for all electrolyte concentrations studied with the same set of parameters. The parameters that properly described the surface tension isotherm with addition of salt largely overestimated the values of the interfacial potential when no salt was added to the SDDS solution, although the fit to the surface tension isotherm was still tolerable (cf. Figures 6 and 7). The values of the best-fit parameters obtained by fitting to the experimental points for all salt concentration shown in Figures 6 and 7 are reported in Table 2. However, if we took into account the correction for the discreteness-of-charge for no added salt calculated according to eq 5 and in the presence of salt computed using eq 6, we got much better agreement with the experimentally measured interfacial potentials. The results are shown in Figure 8, and the best-fit parameters are given in Table 2. Thus, our result may suggest that introduction of the discreteness-of-charge effect into a model of adsorption of ionic surfactants is important for proper description of the adsorption of ionic surfactant at a fluid–fluid interface. More work should be done to find more exact formulas valid for the broad range of electrolyte concentrations and suitable for the fitting procedures of experimental data to theoretical models.



**Figure 6.** Experimental dependence of surface tension (A) and interfacial potential (B) of aqueous SDDS on its concentration in solution for various additions of NaCl together with best-fit lines to the KR model of adsorption of ionic surfactant. Best-fit parameters are given in Table 2. Data for the surface tension of SDDS in  $10^{-1} \text{ M}$  NaCl for (open circles) taken from ref 51. Experimental data for interfacial potential (circles) 0 M NaCl, (squares)  $10^{-2} \text{ M}$  NaCl, and (triangles)  $10^{-1} \text{ M}$  NaCl measured with the vibrating plate (filled symbols) and radioactive electrode (open symbols) methods.

As it can be seen from Figures 6–8, addition of salt to the surfactant solution drastically lowers its surface tension. Upon addition of 0.1 M NaCl, the surface tension isotherm is shifted more than a decade toward lower concentrations of SDDS. This is the effect of the screening of the interfacial charge by very thin diffuse double layer and also a result of neutralization of the surface charge of adsorbed ionic surfactant molecules by counterions adsorbed in the Stern layer. The adsorbing surfactant molecule “feels” the interface as being almost neutral, and thus the surface activity of the ionic surfactant approaches the surface activity of the nonionic surfactant with the same hydrocarbon chain length. This idea is supported by our results for the interfacial potential in the presence of NaCl. Upon addition of salt, the interfacial potential decreases (in a sense of absolute value). For  $10^{-1} \text{ M}$  and higher concentrations of NaCl, the interface is almost neutral ( $\Delta V \approx 0$ ). The residual presence of the minimum in the surface potential isotherm due to the competition of ionic and dipolar contribution to the interfacial potential drop can still be observed when an excess of salt is added to the SDDS solution. Neglecting the dependence of the effective dipole moment on the average orientation of a surfactant molecule at the interface (i.e., dependence of the effective dipole moment on surfactant surface concentration)

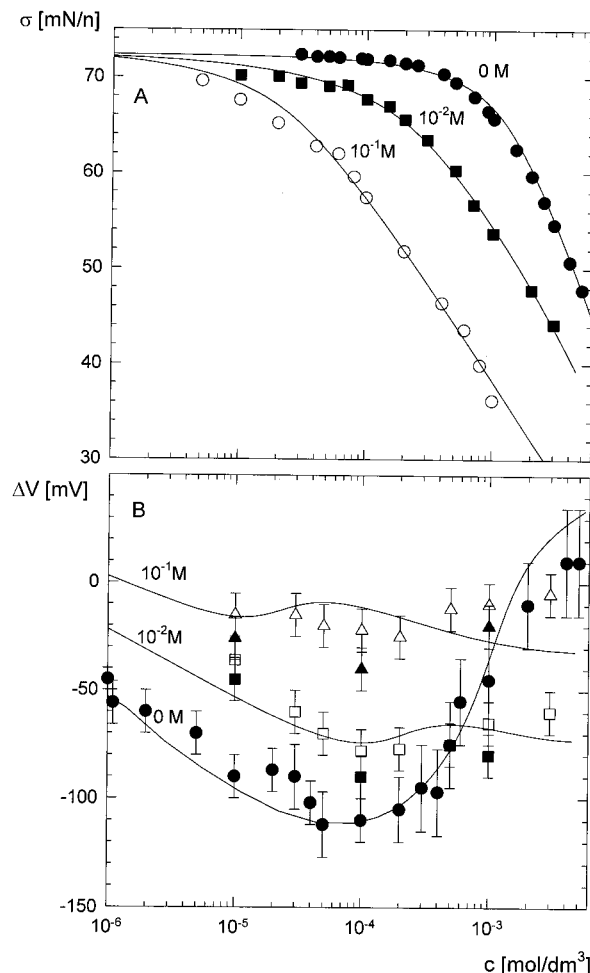


**Figure 7.** Same conditions as in Figure 6 but the experimental data are fitted to the WBLF model of adsorption without the discreteness-of-charge effect taken into account.

may account for the discrepancy between the measured interfacial potentials and theoretical ones at high surfactant and electrolyte concentration in solution. At these conditions the surfactant surface concentration is at its maximum leading to the maximal contribution of the hydrocarbon chains to the effective dipole moment. The other possible reason for this discrepancy is the approximation used to account for the discreteness-of-charge effect.

## Conclusions

The experimental results concerning the surface tension and interfacial potential vs concentration isotherms of SDDS solutions at various salt additions were presented. The most important features of these results are a strong influence of the added salt on the surface tension of SDDS at an air–solution interface and the existence of a minimum in the interfacial potential isotherms at around  $10^{-5}$ – $10^{-4}$  mol/dm<sup>3</sup> at all ionic strengths of the solution studied. We attempted to describe the experimental results in terms of three theoretical models of adsorption of ionic surfactants at the air–solution interface. The first model, proposed by Davies and Rideal and modified by Borwankar and Wasan assumes that the surfactant headgroups are adsorbed in the Stern layer while the counterions remain in the diffuse part of the double layer. This model not only gives the poorest fit to the surface tension vs concentration isotherm of SDDS at air–solution interfaces but also does not enable one to predict quantitatively the interfacial potential dependence.



**Figure 8.** Same conditions as in Figure 6 but the experimental data are fitted to the WBLF model of adsorption with the discreteness-of-charge effect taken into account.

**TABLE 2: Best-Fit Parameters of the Models of Adsorption of Ionic Surfactants as Obtained from the Experimental Surface Tension vs Concentration Isotherms for SDDS for Various Concentrations of Added Salt, Presented in Figure 4**

parameter	KR model	WBLF model	WBLF model with discreteness of charge, eqs 5 and 6
$\alpha_s$ [ $10^{-5}$ mol/dm <sup>3</sup> ]	$1.8 \pm 0.5$	$2.5 \pm 0.8$	$1.7 \pm 0.6$
$\Gamma_{\infty}$ [ $10^{-10}$ mol/cm <sup>2</sup> ]	4.5 (fixed)	6.4 (fixed)	6.4 (fixed)
$RTH_s$ [kJ/mol]	$7.9 \pm 0.3$	$10.3 \pm 0.6$	$10.5 \pm 0.6$
$\alpha_c$ [mol/dm <sup>3</sup> ]	$0.19 \pm 0.08$	$2.5 \pm 0.3$	$3.5 \pm 0.2$
$C_{in}$ [ $\mu$ F/cm <sup>2</sup> ]	$265 \pm 40$	$77 \pm 10$	$125 \pm 20$
$C_{out}$ [ $\mu$ F/cm <sup>2</sup> ]	$300 \pm 50$		
$\Gamma_{\infty}/\Gamma_{\infty}$		$0.92 \pm 0.1$	$0.90 \pm 0.06$
$\delta_l$ [nm]			$0.12 \pm 0.02$
$\mu_{eff}/\epsilon_t$ [D]	0.22	0.20	0.19
$s$ [mN/m]	0.68	0.52	0.51

On the contrary, the other models studied, i.e., one suggested by Kalinin and Radke and the model proposed by us, which allows for counterion penetration into the Stern layer, describe much better the surface tension and interfacial potential isotherms of the SDDS air–solution interface. In particular, we could explain in terms of these models the presence of a minimum in the interfacial potential vs concentration isotherm as a result of the competition of two contributions to the interfacial potential. The first one, of ionic origin, is due to adsorption of negative surfactant ions in the Stern layer. The resulting negative charge at the interface can be partially neutralized by a simultaneous adsorption of counterions. The



effect of neutralization increases with the addition of inorganic salt. The second, positive contribution is of dipolar character. According to experimental results presented in this paper, it seems to originate mainly from the orientation of dipoles of the terminal methyl group of hydrocarbon surfactant's tails.

At a low concentration of SDDS, when the interface is barely covered by surfactant and the tails are mostly oriented parallel to the interface, the ionic contribution prevails and the interfacial potential decreases with surfactant concentration. For high concentrations, when the interface is covered to a large extent by surfactant, the concentration of its tails is significant and, moreover, the surfactant molecules tend to orient themselves perpendicular to the interface. In that region of surfactant concentrations, the positive dipolar contribution starts to dominate and the interfacial potential increases. The same can be observed also when an excess of salt is added to aqueous SDDS, but as a result of the partial neutralization of the interfacial charge by  $\text{Na}^+$  counterions, the interfacial potential is higher (less negative).

The existence of the minimum in the interfacial potential vs concentration isotherms of anionic surfactants with paraffin hydrocarbon chains should be a universal feature as opposed to nonionic surfactants where the interfacial potential is a monotonic function of surfactant concentration.

When enough salt is added to the solution, the interface is almost neutral and thus the surface activity of the ionic surfactant approaches the activity of a comparable nonionic surfactant with the same hydrocarbon chain length.

We were unable to describe by our model or by that developed by Kalinin and Radke the surface tension and interfacial potential isotherms for the whole studied range of NaCl addition to SDDS solution with a consistent set of parameters when the discreteness-of-charge effect was not taken into account. The probable reason for it is that the adsorbing ion "feels" local potential not the average one that is described by the Stern–Grahame theory of the double layer. The preliminary results presented in this paper concerning the modification of the model of adsorption of ionic surfactants by taking into account local fluctuation potential due to the discreteness-of-charge seems to support this hypothesis. However, the applied formulas to describe the discreteness-of-charge effect are only approximate and a more accurate approach is required to account for this effect in the theory of adsorption of ionic surfactants.

The simultaneous or parallel measurements of surface tension and surface potential on the same experimental system in equilibrium and, if possible, in dynamic conditions can provide necessary information for our understanding of the mechanism of adsorption of ionic surfactants at air–liquid and liquid–liquid interfaces.

## Appendix

For the sake of convenience, we introduce the quantities

$$f_1 = \frac{\epsilon_s - 1}{\epsilon_s + 1}$$

and

$$f_2 = \frac{\epsilon_s - \epsilon}{\epsilon_s + \epsilon} \quad (\text{A1})$$

the dimensionless variables  $\bar{x} = \delta_1/r_\beta$ ,  $\bar{x}' = \delta_s/r_\beta$ ,  $\bar{s} = 2\delta_H/a_+$ ,  $\bar{s}' = 2\delta_s/a_+$ ,  $\bar{y} = \delta_H/a_-$ , and  $\bar{y}' = \delta_s/a_-$ , and the functions

$$p(\bar{x}) = (1 + 4\bar{x}^2)^{3/2} - 8\bar{x}^3 - 3\bar{x} \quad (\text{A2})$$

$$l(\bar{s}) = \frac{4}{3}(1 + \bar{s}^2)^{3/2} - 2(1 + \bar{s}^2)^{1/2} + \frac{1}{2(1 + \bar{s}^2)^{1/2}} - \frac{4}{3}\bar{s}^3 \quad (\text{A3})$$

$$h(\bar{y}) = 2(1 + 4\bar{y}^2)^{1/2} - 4\bar{y} - \frac{1}{(1 + 4\bar{y}^2)^{1/2}} \quad (\text{A4})$$

Then we define

$$P = f_1 p(\bar{x}) + \sum_{m'=1}^{\infty} \sum_{m=m'-1}^{m'+1} [2 - (m' - m)^2] f_1^{m'} f_2^{m'} p(m\bar{x} + m'\bar{x}') \quad (\text{A5})$$

The function  $L$  is defined by eq A5 by replacing  $p(\bar{x})$  and  $p(m\bar{x} + m'\bar{x}')$  by  $l(\bar{s})$  and  $l(m\bar{s} + m'\bar{s}')$ , respectively. Analogously, the function  $H$  can be obtained by substituting  $p(\bar{x})$  and  $p(m\bar{x} + m'\bar{x}')$  with  $h(\bar{y})$  and  $h(m\bar{y} + m'\bar{y}')$ . To derive a formula for the fluctuation potential for anions, one has to exchange the role of  $a_+$  and  $a_-$  in the definition of dimensionless variables.

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