

Effect of Nonionic Admixtures on the Adsorption of Ionic Surfactants at Fluid Interfaces. 1. Sodium Dodecyl Sulfate and Dodecanol

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The main target of this study is to develop a theoretical method for determining small contents of dodecanol in samples of sodium dodecyl sulfate (SDS) by a detailed analysis of surface-tension isotherms. As a tool for our analysis, we employ the van der Waals model. Its application to data for alkanols and anionic surfactants gives an excluded area per adsorbed molecule equal to the geometrical area of the molecular cross section and adsorption energies consonant with Traube's rule. Because the dodecanol and SDS have different excluded areas, we extended the van der Waals model for the case of a two-component adsorption layer, with account for the counterion binding in the Stern layer. General expressions for the surface free energy, two-dimensional equation of state, surface chemical potentials, adsorption isotherms, and surface dilatational elasticity are derived. The experimental surface-tension isotherms are fitted by varying only one adjustable parameter. The model was successfully tested against data for solutions of SDS with a known content of dodecanol. Knowing the parameters of the model, we computed various properties of the surfactant adsorption layer. The results show that the presence of a small amount of dodecanol leads to a considerable increase of the total adsorption and surface elasticity. Even a relatively small (0.2 mol %) fraction of dodecanol in SDS may lead to a predominant content (up to 86 mol %) of dodecanol in the mixed adsorption layer. We applied the model for determining unknown contents of dodecanol in SDS samples at different stages of purification. The addition of NaCl may lead to a significant reduction in the mole fraction of dodecanol in the adsorption layer. The developed theoretical model and computational procedure are also appropriate for a quantitative analysis and computer modeling of the adsorption from other mixed ionic–nonionic surfactant solutions, at both air–water and oil–water interfaces.

1. Introduction

The advance in the theory of adsorption from solutions of ionic surfactants^{1–10} allows a detailed analysis and computer modeling of the interfacial properties. Effects, such as the reduction of the interfacial tension, increase of the surface electric charge density, development of electric double layer, and binding of counterions in the Stern layer^{5–10} can be taken into account. Recent reviews can be found in refs 11–13. The processing of experimental surface tension isotherms by means of an adequate

theoretical model can be rather informative. It can be applied for a theoretical description and computer modeling of equilibrium and dynamic surfactant adsorption layers and of the properties of thin liquid films formed from the respective solutions. To achieve that, one has to first determine the adsorption constants as adjustable parameters from the best fit of experimental data. Having these parameter values, and running the respective computer program, one can obtain information about numerous properties of the system just “by pressing a button”. Say, for each combination of surfactant and salt concentrations one can calculate the surface tension, the adsorption of every specific component, the surface electric potential, the surface dilatational elasticity,^{7–9} the thickness of the equilibrium foam and emulsion films formed from the respective solution, and so forth.

Although it is easy to formulate the above program, the latter is not so easy to be realized because of specific difficulties. One of them is that the samples of ionic surfactants, used not only in industrial applications but also in scientific studies, as a rule contain some admixtures of nonionic surfactants. The latter could essentially affect the surface tension and the other interfacial properties, but their removal (the surfactant purification) demands considerable efforts. A typical example is the presence of dodecanol in the samples of sodium dodecyl sulfate (SDS); see refs 14–24. In such a situation, there are two

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alternative ways to compare theory and experiment: (i) to purify the surfactant (to remove the admixtures), and (ii) to determine the contents of the admixtures and to account for their presence in the theoretical model.

Below we follow the second way, which is closer to the needs of the industrial practice and simplifies the experimental work at the cost of a more sophisticated model and computer program. In part 1 of this series (the present paper), we investigate the system SDS + dodecanol. The availability of a considerable amount of data for this system is helpful for the development and test of the theoretical model. In part 2 of this series,²⁵ we present new experimental data and apply the developed model to solutions of sodium dodecylbenzene sulfonate (DDBS), which usually contains an admixture of unsulfonated dodecylbenzene. DDBS is a typical representative of the linear alkylbenzene sulfonates (LAS), the world's largest-volume synthetic surfactant, used in numerous industrial applications.²⁶

This paper is organized as follows. In section 2 we consider the application of the van der Waals model to fit data for alkanols and anionic surfactants and find that the determined excluded area per adsorbed molecule is equal to the geometrical area of the molecular cross section and that the obtained adsorption energies are consonant with Traube's rule. The physical adequacy of this model gives us the certitude to apply it for analysis of unknown contents of dodecanol in SDS samples. Because the dodecanol and SDS have different excluded areas per molecule, in section 3 we extend the van der Waals model to the case of a two-component adsorption layer, with account for the counterion binding. General expressions for the surface free energy, two-dimensional equation of state, surface chemical potentials, and the adsorption isotherms of SDS, dodecanol, and counterions are derived. The results of our model are liable to experimental verification, which, however, is out of the scope of the present article that is devoted to the theory and its testing against available surface tension data. Thus, in section 4 the model is tested against data for solutions of SDS with a known content of dodecanol, and various properties of the surfactant adsorption layer are computed. In section 5 we apply the model for determining unknown contents of dodecanol in SDS samples and investigate the effect of an inorganic electrolyte (NaCl) on the mole fraction of dodecanol in the adsorption layer. The procedure for estimating the experimental errors is described in the Appendix.

2. Minimal Area per Molecule in the van der Waals Model

As already mentioned, our aim is to develop a theoretical model, which allows determination of the unknown concentration of dodecanol in a given sample of SDS from

the best fit of the surface tension isotherm. A criterion for the quality of the fit is not only the standard deviation of the theoretical curve from the experimental points but also whether the obtained values of the adjustable parameters are in agreement with their physical meaning. To check whether the van der Waals model provides a physically adequate theoretical description, in the present section we compare the minimal area per molecule, computed from fits of surface tension isotherms, with the values of this quantity estimated by molecular-size considerations. First we separately consider the simpler cases of normal alcohols and pure SDS (without dodecanol).

2.1. Minimal Area for Alkanols at Air–Water Interface. First of all, the definition and the value of the minimal area per molecule can be different in different theoretical models of surfactant adsorption. Below we compare the Frumkin²⁷ and van der Waals²⁸ models.

The adsorption model of Frumkin corresponds to *localized* adsorption, that is to two-dimensional lattice statistics in the Bragg–Williams approximation.²⁸ In the framework of this model, the adsorption isotherm and the two-dimensional equation of state for a single-component nonionic surfactant are (see, e.g., refs 7 and 12)

$$Kc = \frac{\alpha\Gamma}{1 - \alpha\Gamma} \exp\left(-\frac{2\beta\Gamma}{kT}\right) \quad (2.1)$$

$$\pi_s = -\frac{kT}{\alpha} \ln(1 - \alpha\Gamma) - \beta\Gamma^2 \quad (2.2)$$

Here K is an adsorption constant, k is the Boltzmann constant, T is the temperature, c is the bulk surfactant concentration, Γ is the surfactant adsorption at the phase boundary, π_s is the two-dimensional (surface) pressure ($\pi_s = \sigma_0 - \sigma$), σ_0 and σ are the interfacial tensions of the pure water and the surfactant solution, α is the minimal possible area (excluded area) per molecule at the interface, which accounts for the hard-core interactions between the adsorbed surfactant molecules (in our previous papers^{7–9} we have used the notation $\Gamma_\infty = \alpha^{-1}$), and the rest of the interactions between them are taken into account by the parameter β . For *oil*–water interfaces, the fits of data usually yield $\beta \approx 0$, whereas for *air*–water interfaces $\beta > 0$ is commonly obtained; the value of β in the latter case is being attributed to the van der Waals attraction between the hydrocarbon tails of the surfactant molecules across air.^{1,3} Equations 2.1 and 2.2 describe the dependence $\pi_s = \pi_s(c)$ in a parametric form: $\pi_s = \pi_s(\Gamma)$, $c = c(\Gamma)$.

The van der Waals adsorption model, termed also the Hill–de Boer model,^{28–30} is derived assuming *nonlocalized* adsorption of the two surfactant species.^{28,31,32} The respective relation between subsurface concentration and surfactant adsorption is

$$Kc = \frac{\alpha\Gamma}{1 - \alpha\Gamma} \exp\left(\frac{\alpha\Gamma}{1 - \alpha\Gamma} - \frac{2\beta\Gamma}{kT}\right) \quad (2.3)$$

$$\pi_s = kT\Gamma/(1 - \alpha\Gamma) - \beta\Gamma^2 \quad (2.4)$$

The meaning of the parameters in eqs 2.3–2.4 is similar

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Table 1. Adsorption Parameters for Normal Alkanols Determined from the Fits in Figure 1

$C_n\text{OH}$	Frumkin fit, ³⁷ eqs 2.1–2.2			van der Waals fit, eqs 2.3–2.4			eq 2.8
	E	$\hat{\beta}$	α (\AA^2)	E	$\hat{\beta}$	α (\AA^2)	α (\AA^2)
$C_3\text{OH}$	3.987	0.32	29.06	3.167	0.4262	18.14	20.26
$C_4\text{OH}$	4.512	1.20	28.40	3.545	3.508	22.86	20.45
$C_5\text{OH}$	5.742	1.04	29.06	4.896	3.510	24.10	20.58
$C_6\text{OH}$	6.388	2.08	28.56	6.118	2.999	20.99	20.68
$C_7\text{OH}$	7.783	1.60	27.73	7.397	3.151	20.95	20.75
$C_8\text{OH}$	8.491	2.74	27.40	8.242	4.455	19.61	20.81
$C_9\text{OH}$	10.01	2.40	27.40	10.08	2.868	17.95	20.85
$C_{10}\text{OH}$	10.65	3.60	27.73	10.29	6.750	22.53	20.89
av			28.17			20.89	20.66

to those in eqs 2.1–2.2. In both cases the adsorption parameter K can be expressed in the form³³

$$K = \alpha \delta \exp\left(\frac{\Delta\mu^{(0)}}{kT}\right) \quad (2.5)$$

where δ is the length of an adsorbed molecule (in direction normal to the interface) and $\Delta\mu^{(0)}$ is the standard free energy of adsorption of a molecule from an ideal dilute solution in an ideal adsorption layer. It is convenient to introduce the dimensionless parameters

$$E = \frac{\Delta\mu^{(0)}}{kT}, \quad \hat{\beta} = \frac{2\beta}{\alpha kT} \quad (2.6)$$

The molecular length, δ , which enters eq 2.5, can be estimated by means of molecular-size considerations. After Tanford,^{34,35} one can estimate the molecular length of a normal alkanol, with n carbon atoms as follows

$$\delta(n) = (0.154 + 0.1265n + 0.29) \text{ nm} \quad (2.7)$$

where the last additive, 0.29 nm, stands for the diameter of the OH group.³⁶

Both the Frumkin model, eqs 2.1–2.2, and the van der Waals model, eqs 2.3–2.4, contain three unknown parameters, E , $\hat{\beta}$, and α , which have to be determined as adjustable parameters from the best fit of experimental data for π_s vs c . As an example, Table 1 presents the data for the parameters E , $\hat{\beta}$, and α , determined for normal alkanols alternatively by applying the Frumkin and van der Waals models. We are using the experimental data and the Frumkin's fit from Figure 3.1 and Table 3.1 in the chapter by Fainerman et al.³⁷ The latter figure collects data obtained in different studies.^{38–44} We fitted the same

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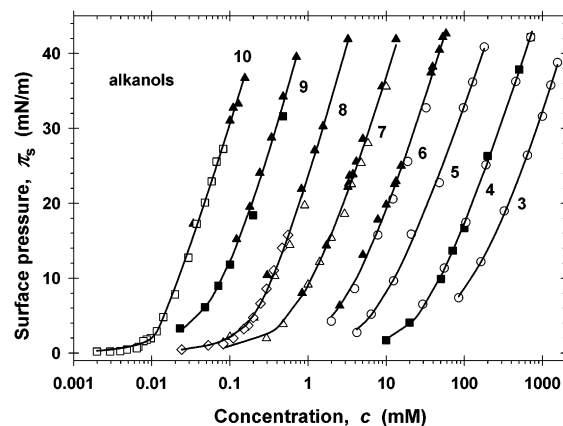


Figure 1. Equilibrium surface pressure, π_s , vs bulk concentration, c , of normal alkanols, from propanol to decanol (the number of carbon atoms, from 3 to 10, is shown at the curves). The data are from Figure 3.1 in ref 37 and are due to different authors: (○) from ref 38, 20 °C; (▲) from ref 39, 20 °C; (△) from ref 40, 25 °C; (◇) from ref 41, 25 °C; (■) from ref 42, 20 °C; (□) from refs 43 and 44, 25 °C. The theoretical curves are drawn as explained in the text; the model parameters are listed in Table 1.

data by means of the van der Waals model, see Figure 1; the determined E , $\hat{\beta}$, and α are also listed in Table 1. The fit with the Frumkin model has practically the same standard deviation as that with the van der Waals model, and the computed curves almost coincide with those shown in Figure 1. Note that the adjustable parameters in Table 1 are computed by fitting separately the isotherm for each individual alkanol. (An alternative way is to simultaneously fit the $\pi_s(c)$ isotherms for all alkanols, see below.) The last column contains the values of the minimal (excluded) area per molecule, calculated by means of the Tanford approach, as the ratio of the volume, v , and length, l , of the hydrocarbon tails of the alkanols^{34,35}

$$\alpha(n) = \frac{v(n)}{l(n)} = \frac{(0.0274 + 0.0269n) \text{ nm}^3}{(0.154 + 0.1265n) \text{ nm}} \quad (2.8)$$

Two details should be mentioned. (i) In ref 37, the values of K are given for the Frumkin's fit. The respective values of E in Table 1 are calculated from K and α with the help of eqs 2.5–2.7. (ii) Part of the data in Figure 1 are obtained at 20 °C, whereas another part are obtained at 25 °C. For that reason, the theoretical curves $\pi_s(c)$ are drawn at an intermediate temperature, 22.5 °C.

The most important result in Table 1 is that the minimal area per molecule, α , calculated by means of the van der Waals model agrees well with the values of α calculated by means of Tanford's eq 2.8; compare the last two columns of Table 1. In particular, the average value from the van der Waals fits, $\alpha = 20.89 \pm 2.23 \text{ \AA}^2$ is close to the respective average $\alpha = 20.66 \text{ \AA}^2$ stemming from the Tanford formula. On the other hand, the α values obtained from the Frumkin fit are considerably greater.

The values of α and $\hat{\beta}$ in Table 1, obtained from the fits, are rather scattered. This can be overcome by an improvement of the procedure of data processing. In fact, Figure 1 contains 125 experimental points, which are fitted by 8 theoretical curves each of them drawn by variation of 3 parameters; that is a total 24 adjustable parameters. On the other hand, we found that the same set of 125 points can be excellently fitted by using only three adjustable parameters, as follows.

We use again the van der Waals model, eqs 2.3 and 2.4, but this time the excluded area, α , is determined by Tanford's eq 2.8. In addition, we use the expressions

$$E(n) = E_0 + nE_1 \quad (2.9)$$

$$\hat{\beta}(n) = n\hat{\beta}_1 \quad (2.10)$$

Equation 2.9 is related to Traube's rule,⁴⁵ which has been interpreted by Langmuir;⁴⁶ see refs 1 and 47 for details. In particular, E_1 is the work (in kT units) to bring one CH_2 group from the body of the solution into the surface region. Likewise, E_0 is a similar adsorption work, but related to the headgroup.¹ Equation 2.10 reflects the fact that the energy of interaction between two adsorbed surfactant molecules is expected to be proportional to their chain lengths. With the help of eqs 2.3, 2.4, and 2.8–2.10, we fitted all 125 experimental points in Figure 1 by using only three adjustable parameters: E_0 , E_1 , and $\hat{\beta}_1$. The theoretical curves agree excellently with the data: the standard deviation is $\Delta\sigma = 0.78$ and 0.70 mN/m, respectively, for the fits with 3 and 24 adjustable parameters. From the best fit we determine

$$E_0 = 0.3286 (=193.8 \text{ cal/mol});$$

$$E_1 = 1.025 (=604.5 \text{ cal/mol}) \quad (2.11)$$

$$\hat{\beta}_1 = 0.6077 (=358.4 \text{ cal/mol}) \quad (2.12)$$

The above value, $E_1 = 604.5$ cal/mol, agrees well with the result $E_1 \approx 600$ cal/mol obtained by Langmuir.⁴⁶ In addition, the dimensionless value, $E_1 = 1.025$, is close to the classical result of Traube: $E_1 \approx \ln 3 = 1.099$.

From another viewpoint, knowing the values of only three parameters, E_0 , E_1 , and $\hat{\beta}_1$ (eqs 2.11 and 2.12) and using eqs 2.3, 2.4, and 2.8–2.10, one can predict the surface tension and adsorption of any of the alkanols in Figure 1, for any concentration in the range below the surface phase transition.

One of the conclusions from the present subsection, which is important for our following analysis, is that (at least for alkanols) the parameter excluded area, α , in the van der Waals model, eqs 2.3 and 2.4, can be identified with the cross-sectional area of the adsorbed molecule determined by molecular-size considerations (by eq 2.8 for alkanols). In the next subsection we show that this conclusion is valid also for some ionic surfactants.

It should be noted that the processed literature data refer only to alkanols which exhibit a pronounced solubility in pure water (their bulk concentrations are plotted along the abscissa in Figure 1). We could not find such data for dodecanol, which has a very low solubility in pure water. Nevertheless, the established applicability of the Tanford formula, eq 2.8, for $3 \leq n \leq 10$, makes this equation appropriate for estimating the excluded area $\alpha(n)$ also for $n > 10$. (Note that for all $n \geq 10$, eq 2.8 predicts the same $\alpha(n) \approx 21 \text{ \AA}^2$.)

2.2. Minimal Adsorption Area for Ionic Surfactants. First of all, let us compare the value of the minimal (excluded) area per dodecyl sulfate ion, DS^- , determined from the best fit of surface tension isotherms, with the size of the sulfate headgroup. We determined the radius, r_{SO_4} , of the SO_4^{2-} ion in water from data for the equivalent conductivities and the known "hydrated" radii, r_i , of other

Table 2. Values of r_{SO_4} Computed from Literature Data for r_i and $\Lambda_i^{(0)}$ for Various Ions

ion	$\Lambda_i^{(0)}/z_i$, refs 49 and 50 ($\Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$)	r_i , ref 36 (\AA)	r_{SO_4} , eq 2.14 (\AA)
K^+	73.52	3.3	3.04
Cs^+	77.20	3.3	3.19
Mg^{2+}	53.06	4.3	2.85
Ca^{2+}	59.47	4.1	3.06
Cl^-	76.34	3.3	3.16
Br^-	78.10	3.3	3.23
I^-	76.80	3.3	3.18
NO_3^-	71.44	3.4	3.04
		Average:	3.09 ± 0.11

ions, as follows. The equivalent conductivity, $\Lambda_i^{(0)}$, of a given ion can be estimated from the expression^{48,49}

$$\Lambda_i^{(0)} = \frac{z_i e^2 N_A}{6\pi\eta r_i} \quad (2.13)$$

where z_i is the ionic valence, " e " is the electronic charge, N_A is the Avogadro number, and η is the viscosity of water. By using eq 2.13 we get

$$r_{\text{SO}_4} = \frac{\Lambda_i^{(0)}/z_i}{\Lambda_{\text{SO}_4}^{(0)}/z_{\text{SO}_4}} r_i \quad (2.14)$$

For the sulfate ion we have⁴⁹ $1/2\Lambda_{\text{SO}_4}^{(0)} = 79.8 \Omega^{-1}\cdot\text{cm}^2\cdot\text{mol}^{-1}$. In the last column of Table 2 we list the values of r_{SO_4} calculated by means of eq 2.14 using values of $\Lambda_i^{(0)}$ from refs 49 and 50 and values of r_i from ref 36.

On the other hand, in ref 9 we fitted simultaneously 11 surface tension isotherms of SDS (obtained^{51–53} at 11 fixed concentrations of NaCl) by means of the van der Waals model, and from the best fit we obtained $\alpha \equiv \Gamma_\infty^{-1} = 29.8 \text{ \AA}^2 = \pi r_{\text{SO}_4}^2$, from where we find $r_{\text{SO}_4} = 3.08 \text{ \AA}$; supposedly the excluded area per SDS molecule is determined by the sulfate headgroup. The latter value of r_{SO_4} agrees excellently with the average value of r_{SO_4} in Table 2. In addition, the above value of α is close to the value 28 \AA^2 given in ref 54 and quoted by Tajima et al.⁵¹ for the "cross-sectional area for a hydrated sulfate ion." Because the determined r_{SO_4} is slightly smaller than r_{NO_3} (Table 2), and it is known³⁶ that the hydration number of the NO_3^- ion is 0, then one could expect that the hydration number of the SO_4^{2-} ion is also 0. (The hydration number is the number of water molecules bound to a given ion in aqueous solution.³⁶)

A third example for coincidence of the excluded area, α , determined by a van der Waals fit of surface tension data, with the value of α obtained by molecular-size considerations, is the result obtained in the second part of this study, ref 25, for the anionic surfactant sodium dodecyl benzene sulfonate (DDBS). Thus, from the surface-tension fit we obtain²⁵ $\alpha = 35.55 \text{ \AA}^2$, which equals the area of a circle of diameter $2r = 6.73 \text{ \AA}$. On the other hand, it is known⁵⁵ that the outer diameter of the benzene ring is

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(47) Adamson, A. W.; Gast, A. P. *Physical Chemistry of Surfaces*, 6th ed.; Wiley-Interscience: New York, 1997.

Table 3. Comparison of the Excluded Area per Molecule, α , Determined by van der Waals Fits of Surface-Tension Data and by Molecular-Size Considerations (details in the text)

molecule/ion	α from surface tension fits (\AA^2)	πr^2 from molecular size (\AA^2)	molecular diameter, $2r$ (\AA)
paraffin chain	20.9	21.0	5.17
SO_4^{2-}	29.8	30.0	6.18
benzene ring	35.6	35.3	6.7

exactly 6.7 \AA . The latter diameter is greater than the diameter of the sulfonate (and sulfate) ion, $2r \approx 6.2 \text{\AA}$ (see Table 2), and for that reason the excluded area for a DDBS molecule in the adsorption layer is determined by the size of the benzene ring.

2.3. Discussion. In summary, we have three cases (see Table 3) in which the excluded area per molecule, α , determined by van der Waals fits of surface-tension data, coincides with the geometrical area

$$\alpha = \pi r^2 \quad (2.15)$$

where r is a cross-sectional radius determined by molecular-size considerations. Most probably, this coincidence is not occasional. The results (Table 3) indicate that the van der Waals' two-dimensional equation of state provides an adequate description of surfactant adsorption layers, at least in the case of "two-dimensional gas", that is before the appearance of a phase transition in the adsorption layer. Note that the statistical derivation of the van der Waals equation implies that α accounts for the hard-core interactions (related to the molecular size), while β takes into account the forces of longer range.²⁸ For this reason, α is expected to be independent of the density of the "two-dimensional gas".

The result that $\alpha = \pi r^2$ calls for some discussion, because in the literature one can find another expression, $\alpha = 2\pi r^2$; see eq 16.14 in ref 28. It should be noted that the latter expression is derived with the help of the essential approximation that the energy of molecular interaction, U , is pairwise additive, that is

$$U(\mathbf{r}_1, \mathbf{r}_2, \dots, \mathbf{r}_N) \approx \sum_{1 \leq i < j \leq N} u(|\mathbf{r}_i - \mathbf{r}_j|) \quad (2.16)$$

where u is the interaction energy for an isolated couple of molecules and \mathbf{r}_i is a position vector. The latter approximation is accurate only for sufficiently low concentrations (adsorptions, $\alpha\Gamma \ll 1$), when the terms with the third and higher order virial coefficients in the expansion of the surface pressure, π_s , are negligible. However, at higher concentrations, the contribution of the higher-order virial coefficients becomes considerable. (It is not occasional that the best equation of the state for a gas of hard spheres, that by Carnahan & Starling, is derived by summing-up the whole virial expansion; see refs 56 and 57.) From this viewpoint, the results in Table 3 indicate that the van der Waals model provides a correct description of the surfactant adsorption layer, including the range of high surface concentrations.

In addition, we applied the van der Waals model to fit available experimental data (like those collected in ref 3) for SDS adsorption at the oil-water interface. For various hydrocarbons we obtained $\alpha \approx 40 \text{\AA}^2$, which is markedly greater than the value $\alpha \approx 30 \text{\AA}^2$ for SDS at the air-water

interface. The result $\alpha \approx 40 \text{\AA}^2$ could be attributed to the fact that oil molecules can penetrate between the hydrocarbon tails of the adsorbed surfactant molecules, as established by Lu et al.⁵⁸ by neutron reflection. It seems that the cohesion between the chains of the surfactant and the intercalated oil is strong enough to prevent the expulsion of the oil molecules upon compression of the adsorption layer. Thus, for an oil-water interface, the excluded area per adsorbed SDS molecule seems to be determined by the cross section of the hydrocarbon chains with bound oil molecules. The latter is greater than the cross section of the sulfate headgroups.

The finding that $\alpha \approx \pi r^2$ can be utilized in two ways. First, when processing experimental data by means of the van der Waals model, one may check whether α , obtained from the fit, satisfies the relationship $\alpha \approx \pi r^2$, where the radius r is determined by molecular-size considerations; this could serve as a criterion for reliability of the fit (see, e.g., section 4.3 below). Second, if a fit with many unknown parameters is to be used, the relationship $\alpha \approx \pi r^2$ can be applied to determine some of them and thus to reduce the number of adjustable parameters. The latter potential applications of the van der Waals approach motivated us to extend the model to the case of a more complex system which is frequently encountered in the experiment and practice (the next section).

3. Two-Component van der Waals Model for an Ionic-Nonionic Surfactant Mixture

3.1. Basic Equations. Our purpose is to extend the van der Waals model, see eqs 2.3 and 2.4 above, to describe theoretically the adsorption of two surfactants, one ionic (like SDS) and one nonionic (like dodecanol), in the presence of added nonamphiphilic electrolyte (like NaCl). As in our previous papers,⁷⁻⁹ we will use the following numbering of the species: component 1, a surfactant ion (say, dodecyl sulfate, DS^-); component 2, a nonamphiphilic counterion (Na^+); component 3, a nonamphiphilic co-ion (Cl^-); component 4, a nonionic surfactant (dodecanol).

Irrespective of the fact the target of our paper is the adsorption of SDS + dodecanol at an air-water interface, the proposed model is applicable to both anionic and cationic surfactants and to both air-water and oil-water interfaces.

The ionic valence is $Z_i = (-1)^i$, $i = 1, 2, 3$. The subsurface activity of the i th ionic species in the solution, a_{is} , is defined by the equation⁵⁹

$$a_{is} = a_{i\infty} \exp\left(-\frac{Z_i e \psi_s}{kT}\right) \quad (3.1)$$

$$i = 1, 2, 3$$

which stems from the constancy of the electrochemical potential throughout the electric double layer. $a_{i\infty}$ is the bulk activity of this component, e is the electronic charge, ψ_s is the surface electric potential, k is the Boltzmann constant, and T is the temperature. The bulk activity is related to the respective concentration, $c_{i\infty}$, by means of the formula $a_{i\infty} = \gamma_{\pm} c_{i\infty}$, with γ_{\pm} being the activity coefficient; see eq 5.1 below.

The surface pressure, $\pi_s = \sigma_0 - \sigma$ ($\sigma_0 =$ interfacial tension of the pure water), can be expressed in the form^{1,2,7}

$$\pi_s = \pi_a + \pi_d \quad (3.2)$$

$$\pi_d = \frac{\epsilon}{4\pi} \int_0^\infty dx \left(\frac{d\psi}{dx}\right)^2$$

(56) Carnahan, N. F.; Starling, K. E. *J. Chem. Phys.* **1969**, *51*, 635.

(57) Balescu, R. *Equilibrium and Nonequilibrium Statistical Mechanics*; Wiley: New York, 1975.

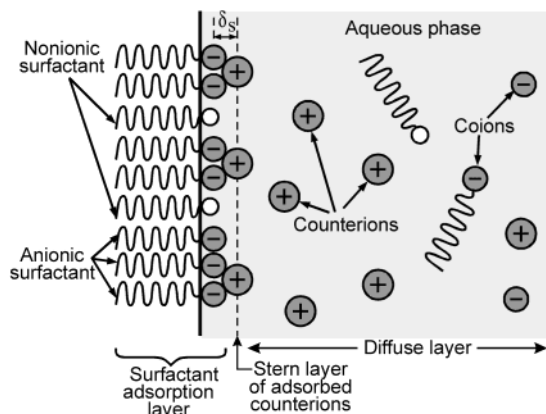


Figure 2. Sketch of the electric double layer in the vicinity of a mixed adsorption monolayer of an anionic and a nonionic surfactant, like SDS + dodecanol. The diffuse layer contains free ions involved in Brownian motion, while the Stern layer consists of adsorbed (immobilized) counterions; δ_s is the distance between the Stern layer and the plane of the headgroup charges.

where π_d is the contribution of the diffuse electric double layer, whereas π_a is the contribution of the adsorption layer consisting of surfactant molecules/ions adsorbed at the interface, as well as of the counterions bound in the Stern layer (Figure 2). In eq 3.2, ψ is the electrostatic potential, x is a coordinate normal to the interface, and the coordinate origin, $x = 0$, is located at the boundary between the Stern and diffuse layer. The surface tension can be also expressed as a sum of analogous contributions: $\sigma_s = \sigma_a + \sigma_d$, where $\sigma_a = \sigma_0 - \pi_a$ and $\sigma_d = -\pi_d$. Likewise, the total adsorption of the i th component, $\bar{\Gamma}_i$, can be presented as a sum, $\bar{\Gamma}_i = \Gamma_i + \Lambda_i$, where Γ_i and Λ_i are contributions due to the adsorption and diffuse layers, respectively.^{2,7} Of course, for the nonionic surfactant we have $\Lambda_4 = 0$. On the other hand, the nonamphiphilic coion (Cl^-) is not expected to be present in the adsorption layer, and therefore $\Gamma_3 = 0$; see ref 7 for details.

In accordance with the interfacial thermodynamics, developed by Gibbs,⁶⁰ and extended by Boruvka and Neumann,⁶¹ the adsorption layer can be treated as a separate surface phase with its own surface excess free energy, F_s , and fundamental thermodynamic equation; see ref 32 for a recent review. Let us denote by

$$N_i = A \Gamma_i \quad (i = 1, 2, 4) \quad (3.3)$$

the number of molecules of the i th species in the adsorption layer of area A . Then, if the function $F_s = F_s(T, A, N_1, N_2, N_4, \psi_s)$ is available, one can deduce theoretical expressions for the surface pressure, π_a , and the surface chemical potentials, μ_{is} , as follows (see, e.g., ref 32)

$$\pi_a = - \left(\frac{\partial F_s}{\partial A} \right)_{T, N_1, N_2, N_4, \psi_s} \quad (3.4)$$

$$\mu_{is} = \left(\frac{\partial F_s}{\partial N_i} \right)_{T, A, N_j \neq N_i, \psi_s} \quad (i = 1, 2, 4) \quad (3.5)$$

The surface electric charge is given by a version of the Lippmann equation³⁵

$$e(Z_1 N_1 + Z_2 N_2) = \left(\frac{\partial F_s}{\partial \psi_s} \right)_{T, A, N_1, N_2, N_4} \quad (3.6)$$

3.2. Expression for the Surface Free Energy. Our model is based on the following major assumptions: (i) We are dealing with a *nonlocalized* adsorption of *interacting* surfactant molecules (both ionic and nonionic) with different minimal areas per molecule. Such an assumption corresponds to a van der Waals type equation of state for the surfactant species.^{28,32} (ii) The counterions bind to the headgroups of the ionic surfactant in the surface monolayer, that is a *localized* adsorption of counterions takes place. Such an assumption corresponds to the Stern isotherm of counterion binding.^{1,7,32} (iii) In general, we may assume that the surface electric potential, ψ_s , in the plane of the bound counterions (the Stern layer) is not identical with the electric potential, ψ_h , in the plane of the headgroups of the adsorbed surfactant ions; the distance between these two planes is denoted by δ_s (Figure 2). In correspondence with the above three assumptions, the surface free energy can be expressed as a sum of three terms

$$F_s = F_{1,4} + F_2 + F_{el} \quad (3.7)$$

The meaning of the three terms in the right-hand side of eq 3.7 is as follows: First, $F_{1,4}$ is the free energy of a two-dimensional binary mixture of nonlocalized interacting molecules. According to Gurkov et al.,⁶² $F_{1,4}$ can be expressed in the form

$$\frac{F_{1,4}}{kT} = -N_1 \ln \left(\frac{eAq_1}{N_1} \right) - N_4 \ln \left(\frac{eAq_4}{N_4} \right) - (N_1 + N_4) \ln \left[1 - \frac{\alpha}{A}(N_1 + N_4) \right] - \frac{\beta}{kTA} (N_1 + N_4)^2 \quad (3.8)$$

see also refs 28 and 32. Here, by definition, $\ln(e) = 1$; $q_i = q_i(T)$ is the statistical partition function for the respective molecule; α and β are the average excluded area per molecule and the mean interaction parameter, which are defined as follows⁶²

$$\alpha \equiv \alpha_{11} X_1^2 + 2\alpha_{14} X_1 X_4 + \alpha_{44} X_4^2 \quad (3.9)$$

$$\beta \equiv \beta_{11} X_1^2 + 2\beta_{14} X_1 X_4 + \beta_{44} X_4^2 \quad (3.10)$$

where

$$X_i = \frac{N_i}{N_1 + N_4} = \frac{\Gamma_i}{\Gamma_1 + \Gamma_4} \quad (i = 1, 4) \quad (3.11)$$

is the mole fraction of the respective surfactant in the adsorption layer, α_{ij} and β_{ij} are constant parameters, whose meaning is analogous to α and β in the van der Waals equation of state, eq 2.4, that is the α values are excluded areas and the β values are interaction parameters; see section 4.2 for a more detailed discussion.

Further, F_2 in eq 3.7 accounts for a localized (Langmuirian type) adsorption of counterions, say Na^+ , on the

(58) Lu, J. R.; Li, Z. X.; Thomas, R. K.; Binks, B. P.; Crichton, D.; Fletcher, P. D. I.; McNab, J. R.; Penfold, J. *J. Phys. Chem. B* **1998**, *102*, 5785.

(59) Kirkwood, J. G.; Oppenheim, I. *Chemical Thermodynamics*; McGraw-Hill: New York, 1961.

(60) Gibbs, J. W. *The Scientific Papers of J. W. Gibbs*; Dover: New York, 1961; Vol. 1.

(61) Boruvka, L.; Neumann, A. W. *J. Chem. Phys.* **1977**, *66*, 5464.

ionic-surfactant headgroups. Consequently, F_2 can be expressed in the form (see Table 4 in ref 32)

$$\frac{F_2}{kT} = -N_2 \ln(q_2/N_2) + (N_1 - N_2) \ln(N_1 - N_2) - \frac{N_1 \ln N_1}{N_1} \quad (3.12)$$

where q_2 is partition function for a separate bound counterion. Finally, F_{el} accounts for the electrostatic energy

$$F_{el} = Z_1 e N_1 \psi_h + Z_2 e N_2 \psi_s \quad (3.13)$$

Having in mind that $Z_2 = -Z_1$, and using the expression for a plane-parallel condenser

$$\psi_h - \psi_s = \frac{4\pi Z_1 e \delta_s}{\epsilon_s A} (N_1 - N_2) \quad (3.14)$$

(ϵ_s = dielectric permittivity in the Stern layer), we can bring eq 3.13 into the form

$$F_{el} = Z_1 e \psi_s (N_1 - N_2) + \frac{\beta_e}{kTA} (N_1^2 - N_1 N_2) \quad (3.15)$$

where

$$\beta_e \equiv 4\pi Z_1^2 e^2 \frac{\delta_s}{\epsilon_s} \quad (3.16)$$

3.3. Surface Equation of State and Surface Chemical Potentials. By differentiating eq 3.7, in accordance with eqs 3.4 and 3.8–3.15, we arrive at a van der Waals type surface equation of state, viz.

$$\frac{\pi_a}{kT} = \frac{\Gamma_1 + \Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{\beta}{kT} (\Gamma_1 + \Gamma_4)^2 + \frac{\beta_e}{kT} (\Gamma_1^2 - \Gamma_1 \Gamma_2) \quad (3.17)$$

where α , β , and β_e are defined by eqs 3.9, 3.10, and 3.16. For a single nonionic surfactant ($\Gamma_1 = \Gamma_2 = 0$), eq 3.17 reduces to the conventional van der Waals equation, eq 2.4, in terms of Γ_4 . Moreover, for $\beta_e = 0$ eq 3.17 reduces to the respective result by Gurkov et al.⁶²

Likewise, by differentiating eq 3.7 in accordance with eqs 3.5 and 3.8–3.15, we deduce the following expressions for the surface electrochemical potentials

$$\frac{\mu_{1s}}{kT} = \frac{\mu_{1s}^{(0)}}{kT} + \ln\left(\frac{\alpha_{11}(\Gamma_1 - \Gamma_2)}{1 - \alpha(\Gamma_1 + \Gamma_4)}\right) + \frac{(2\alpha_{11} - \alpha)\Gamma_1 + (2\alpha_{14} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2}{kT}(\beta_{11}\Gamma_1 + \beta_{14}\Gamma_4) + \frac{\beta_e}{kT}(2\Gamma_1 - \Gamma_2) + \frac{Z_1 e \psi_s}{kT} \quad (3.18)$$

$$\frac{\mu_{2s}}{kT} = \frac{\mu_{2s}^{(0)}}{kT} + \ln\left(\frac{\Gamma_2}{\Gamma_1 - \Gamma_2}\right) - \frac{\beta_e \Gamma_1}{kT} + \frac{Z_2 e \psi_s}{kT} \quad (3.19)$$

$$\frac{\mu_{4s}}{kT} = \frac{\mu_{4s}^{(0)}}{kT} + \ln\left(\frac{\alpha_{44}\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)}\right) + \frac{(2\alpha_{14} - \alpha)\Gamma_1 + (2\alpha_{44} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2}{kT}(\beta_{14}\Gamma_1 + \beta_{44}\Gamma_4) \quad (3.20)$$

where the standard chemical potentials are defined as follows

$$\mu_{is}^{(0)} = -kT \ln(\alpha_{ii} q_i) \quad (i = 1, 4) \quad (3.21)$$

$$\mu_{2s}^{(0)} = -kT \ln(q_2)$$

Finally, by differentiating eq 3.7 in accordance with eqs 3.8–3.15, and $Z_2 = -Z_1$, we obtain the Lippmann equation (3.6).

3.4. Adsorption Isotherms. The adsorption isotherms can be derived by setting the obtained expression for the surface chemical potentials μ_{is} equal to the bulk chemical potential of the respective species in the subsurface layer, that is, *equilibrium* between surface and subsurface is assumed²⁸

$$\mu_{is} = \mu_{is}^{(0)} + kT \ln(a_{is} \delta_i \alpha_{ii}) + \frac{Z_i e \psi_s}{kT} \quad (3.22)$$

Here, the activity of the respective molecule/ion in the subsurface layer, a_{is} is scaled with the volume per molecule in a dense (saturated) adsorption layer, $v_i = \delta_i \alpha_{ii}$, where δ_i is the length of the respective adsorbed molecule. In terms of the subsurface activity, a_{is} , eq 3.22 can be applied not only to quasistatic processes but also to dynamics of adsorption under diffusion control. For the nonionic surfactant we have $a_{4s} = c_{4\infty}$, where $c_{4\infty}$ is the respective bulk concentration. Next, substituting eqs 3.18 and 3.20 into eq 3.22, we derive the adsorption isotherms for the respective surfactant species

$$K_1 a_{1s} = \frac{\alpha_{11}(\Gamma_1 - \Gamma_2)}{1 - \alpha(\Gamma_1 + \Gamma_4)} \exp\left[\frac{(2\alpha_{11} - \alpha)\Gamma_1 + (2\alpha_{14} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2}{kT}(\beta_{11}\Gamma_1 + \beta_{14}\Gamma_4) + \frac{\beta_e}{kT}(2\Gamma_1 - \Gamma_2)\right] \quad (3.23)$$

$$K_4 a_{4s} = \frac{\alpha_{44}\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} \exp\left[\frac{(2\alpha_{14} - \alpha)\Gamma_1 + (2\alpha_{44} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2\beta_{14}\Gamma_1 + 2\beta_{44}\Gamma_4}{kT}\right] \quad (3.24)$$

where $a_{4s} = c_{4\infty}$, and the adsorption constants are defined as follows

$$K_i = \alpha_{ii} \delta_i \exp(E_i), \quad E_i \equiv \Delta\mu_i^{(0)}/(kT) \quad (3.25)$$

Likewise, combining eqs 3.19 and 3.22, we deduce a generalized form of the Stern adsorption isotherm for the counterions

$$K_2 a_{2s} = \frac{\Gamma_2}{\Gamma_1 - \Gamma_2} \exp\left(-\frac{\beta_e}{kT} \Gamma_1\right) \quad (3.26)$$

(62) Gurkov, T. D.; Kralchevsky, P. A.; Nagayama, K. *Colloid Polym. Sci.* **1996**, *274*, 227.

which reduces to the conventional Stern isotherm for $\beta_e = 0$ ($\delta_s = 0$ in Figure 2); see eq 3.16. Moreover, in view of eq 3.26, one can check that for $\beta_e = 0$ eq 3.23 reduces to the van der Waals type adsorption isotherm for the case when only one ionic surfactant is present ($\Gamma_4 = 0$); cf. Table 1 in ref 7. In a similar way, one can deduce (as a special case) the van der Waals adsorption isotherms in Table 2 of ref 7 by setting the excluded areas identical: $\alpha_{11} = \alpha_{14} = \alpha_{44} = \Gamma_\infty^{-1}$.

The Gibbs adsorption equation, which should be satisfied by any thermodynamic model, can be expressed in the form⁷

$$\frac{d\pi_a}{kT} = \Gamma_1 d \ln a_{1s} + \Gamma_2 d \ln a_{2s} + \Gamma_4 d \ln a_{4s} \quad (3.27)$$

$$T = \text{constant}$$

In eq 3.27 we substituted π_a from eq 3.17 and the activities a_{is} , $i = 1, 2, 4$, from eqs 3.23, 3.24, and 3.26, and we obtained that eq 3.27 is identically satisfied, as it must be. Another way to check the correctness of the derived theoretical expressions is to verify whether the Euler equation⁷

$$\frac{\partial \Gamma_i}{\partial \ln a_{js}} = \frac{\partial \Gamma_j}{\partial \ln a_{is}} \quad (3.28)$$

$$i \neq j; i, j = 1, 2, 4$$

is satisfied. Equation 3.28 is a corollary from the fact that $d\pi_a$ in eq 3.27 is a total differential. In view of the form of the above adsorption isotherms, it is more convenient to use another version of eq 3.28, viz.

$$\frac{\partial \ln a_{is}}{\partial \Gamma_j} = \frac{\partial \ln a_{js}}{\partial \Gamma_i}$$

$$i \neq j; i, j = 1, 2, 4 \quad (3.29)$$

To derive eq 3.29 we have made a Legendre transformation in eq 3.27 from variables (a_{1s} , a_{2s} , a_{4s}) to variables (Γ_1 , Γ_2 , Γ_4). Substituting a_{1s} , a_{2s} , and a_{4s} from eqs 3.23, 3.24, and 3.26 into eq 3.29, we verified that the latter Euler's type relationship is satisfied by the adsorption isotherms derived in our model.

3.5. The Full Set of Equations. Our final goal is to obtain a full set of equations for calculating the surface tension as a function of the bulk surfactant and salt concentrations, $\sigma = \sigma(a_{1\infty}, a_{2\infty}, a_{4\infty})$. For the nonionic component we have $a_{4\infty} = c_{4\infty}$. Then seven unknown variables remain, σ , ψ_s , a_{1s} , a_{2s} , Γ_1 , Γ_2 , and Γ_4 , and we need a set of seven equations for their determination. Five equations are provided by eq 3.1 for $i = 1, 2$, and by the adsorption isotherms, eqs 3.23, 3.24, and 3.26. The necessary two additional equations are the surface equation of state, eq 3.30, and the Gouy equation, eq 3.31 (see, e.g., ref 7)

$$\sigma = \sigma_0 - \pi_a - \frac{8kTI}{\kappa} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \quad (3.30)$$

$$\Gamma_1 - \Gamma_2 = \frac{4I}{\kappa} \sinh\left(\frac{\Phi_s}{2}\right) \quad (3.31)$$

where π_a is given by eq 3.17, I is the ionic strength of the solution, and κ and Φ_s are the Debye parameter and the dimensionless surface potential, defined as follows

$$\kappa^2 = \frac{8\pi e^2 I}{\epsilon kT}, \quad \Phi_s = \frac{Z_1 e \psi_s}{kT} \quad (3.32)$$

with ϵ being the dielectric constant of water. For the considered system of an ionic and a nonionic surfactant, in the presence of an added nonamphiphilic electrolyte, the van der Waals type model, developed in the present section, contains 10 unknown parameters: E_1 , E_2 , E_4 , α_{11} , α_{14} , α_{44} , β_{11} , β_{14} , β_{44} , and β_e (see eq 3.25 for the definition of E_j). In the next section it is demonstrated that for the system SDS + NaCl + dodecanol we can determine in advance nine of these parameters from available data or relationships. Thus, in section 4.3 we apply a fit of experimental data using *only one* adjustable parameter, viz., α_{44} .

An alternative model of the adsorption from mixed ionic–nonionic surfactant solutions was published by Mulqueen and Blankschtein.⁶⁴ It is based on a molecular-thermodynamic approach, which is developed in a preceding study.⁶⁵ In particular, their expression for π_a , adapted to our system and notations, reads (see eq 5 in ref 64)

$$\frac{\pi_a}{kT} = \frac{\Gamma_1 + \Gamma_4}{1 - (\alpha_{11}\Gamma_1 + \alpha_{44}\Gamma_4)} + \frac{\pi(r_1\Gamma_1 + r_4\Gamma_4)^2}{[1 - (\alpha_{11}\Gamma_1 + \alpha_{44}\Gamma_4)]^2} - \frac{\beta}{kT}(\Gamma_1 + \Gamma_4)^2 \quad (3.33)$$

where r_j is the radius of a hard disk of area α_{jj} ($j = 1, 4$). Equation 3.33 is to be compared with our eq 3.17, without the term $\propto \beta_e$. Having in mind the definition of α , eq 3.9, one sees that only the last term, that proportional to β , is identical in the two models. The second term in the right-hand side of eq 3.33 has no counterpart in our eq 3.17. In other words, these are two different models, both of them accounting for the hard disk interactions through the α values, and for the forces of longer range through the β values. In the special case of a single-component system, our model reduces to the common van der Waals model, while this is not the case with the model in refs 64 and 65. There are also some differences in the treatment of the electrostatic effects. For example, an energy of binding of counterions in the Stern layer is not considered in ref 64, which is equivalent to set $E_2 = 0$ in our eqs 3.25–3.26.

4. Comparison of the Two-Component van der Waals Model with Experimental Data

4.1. Determination of the Parameter β_e . The parameter β_e is proportional to the distance, δ_s , between the planes in which the headgroups of the adsorbed surfactant and the bound counterions are located; see eq 3.16 and Figure 2. δ_s is sometimes termed the “thickness of the Stern layer”. To determine β_e (and δ_s), we fitted the surface tension isotherms of SDS, measured by Tajima et al.^{51–53} for 11 different concentrations of NaCl (supposedly, without dodecanol, $\Gamma_4 = 0$). The same set of experimental data was fitted by us in ref 9 (see Figure 1 therein) assuming $\delta_s = 0$. The parameter values obtained there are listed in the first row of Table 4.

The second row of Table 4 shows the values of the respective parameters obtained in the present study by using the full set of equations described in section 3.5 with $\delta_s \neq 0$. For both fits we have substituted $E_2 = 1.64$, $\delta_1 = 2$ nm, and $\delta_2 = 0.7$ nm, the same as in ref 7. In the case with $\delta_s \neq 0$, we varied four adjustable parameters:

(63) Israelachvili, J. N.; Wennerström, H. *J. Phys. Chem.* **1992**, *96*, 520.

(64) Mulqueen, M.; Blankschtein, D. *Langmuir* **1999**, *15*, 8832.

(65) Nikas, Y. J.; Puvvada, S.; Blankschtein, D. *Langmuir* **1992**, *8*, 2680.

Table 4. Parameters of the Best Fit Obtained Using $\delta_s = 0$ (ref 9) and $\delta_s \neq 0$ (this study)

model	E_1	α (\AA^2)	$\hat{\beta}$	$\hat{\beta}_e$	std dev (mN/m)
$\delta_s = 0$	12.53	29.76	2.73	0	0.81
$\delta_s \neq 0$	13.52	29.76	2.47	1.45	0.62

the dimensionless adsorption energy per DS^- ion, E_1 ; the excluded area per DS^- ion, $\alpha \equiv \alpha_{11}$; the dimensionless interaction parameter $\hat{\beta} = 2\beta_{11}/(kT\alpha_{11})$, see eq 2.6, and the dimensionless parameter β_e

$$\hat{\beta}_e \equiv \frac{\beta_e}{kT\alpha} = \frac{4\pi e^2 \delta_s}{\epsilon_s kT\alpha} \quad (4.1)$$

see eq 3.16. The standard deviation of the theoretical curve from the data points, shown in the last column of Table 4, is smaller for the fit with $\delta_s \neq 0$, which is not surprising, because the latter fit is drawn with the help of four (instead of three) adjustable parameters. Nevertheless, the relatively small standard deviations imply that both fits are very good. Concerning the values of the other parameters, the major consequence of the assumption $\delta_s \neq 0$ is the obtained somewhat greater value of E_1 (the second row of Table 4). On the other hand, the two fits give exactly the same α (Table 4). Substituting the values of α and $\hat{\beta}_e$ in eq 4.1, we obtain

$$\delta_s = \frac{\epsilon_s kT\alpha}{4\pi e^2} \hat{\beta}_e < \frac{\epsilon_s kT\alpha}{4\pi e^2} \hat{\beta}_e = 0.048 \text{ nm} \quad (4.2)$$

where, as an upper estimate, we have replaced the dielectric constant of the Stern layer, ϵ_s , with that of the bulk water, $\epsilon = 78.2$. Equation 4.2 shows that the value of δ_s is much smaller than the diameter of the water molecule, which means that from a physical viewpoint our result is $\delta_s = 0$, that is, the planes of the surfactant headgroups and of the bound counterions coincide. Different interpretations could be given to the latter result: (i) the counterions are intercalated among the headgroups, or (ii) 50% of the counterions are situated below and 50% above the plane of the headgroups, or (iii) the surfactant adsorption monolayer is corrugated due to fluctuation capillary waves and individual molecular protrusions,⁶³ which smear out the difference between the two planes. Whatever the reason could be, hereinafter we will substitute $\delta_s = 0$ and, consequently, $\beta_e = 0$. Thus the number of the adjustable parameters decreases by one.

4.2. Relations between the α Values and β Values.

Here we will follow the approach by Gurkov et al.⁶² who obtained relationships between the parameters α_{11} , α_{14} , α_{44} , β_{11} , β_{14} , and β_{44} , on the basis of physical considerations. First of all, α_{ij} is proportional to the square of the distance, r_{ij} , between the centers of two neighboring molecules, which yields the following expression for α_{14} ⁶²

$$\alpha_{14} = \left(\frac{\alpha_{11}^{1/2} + \alpha_{44}^{1/2}}{2} \right)^2 \quad (4.3)$$

Furthermore, the β values can be estimated by means of the expression⁶²

$$\beta_{ij} \approx -\pi \int_{r_{ij}}^{\infty} u_{ij}(r) r dr \quad (4.4)$$

where $u_{ij}(r)$ is the energy of interaction between two adsorbed molecules separated at a center-to-center distance r . As discussed in section 2, the β values have been found to account for the van der Waals interaction between

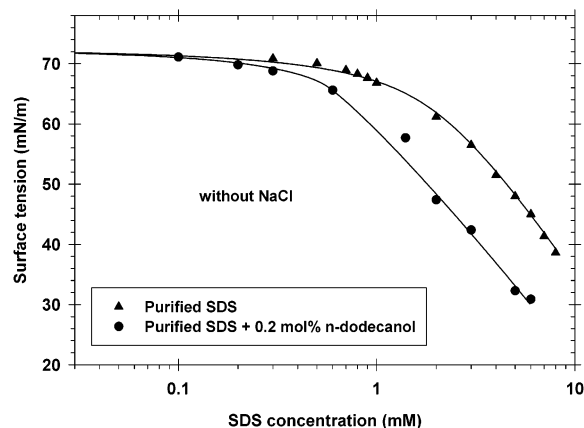


Figure 3. Comparison of data by Tajima et al.⁵¹ for purified SDS and with data by Vollhardt and Emrich²² for purified SDS + 0.2 mol % *n*-dodecanol. The theoretical curves are the best fits by the models in ref 9 for SDS and in section 3 of this paper for SDS + dodecanol.

the hydrocarbon tails of the adsorbed surfactant molecules. Then, we can employ the expression for the energy of van der Waals interaction between two identical parallel hydrocarbon chains³⁶

$$u_{ij} = -a/r^5 \quad (4.5)$$

where a is an interaction parameter, which is assumed to be the same for SDS and dodecanol, insofar as their hydrocarbon chains are identical. The substitution of eq 4.5 into eq 4.4 yields

$$\beta_{ij} = \pi a/3r_{ij}^3 \quad (4.6)$$

Using again the relationship $\alpha_{ij} \propto r_{ij}^2$, from eq 4.6 we deduce the useful expressions

$$\beta_{14} = (\alpha_{11}/\alpha_{14})^{3/2} \beta_{11}, \quad \beta_{44} = (\alpha_{11}/\alpha_{44})^{3/2} \beta_{11} \quad (4.7)$$

We can substitute $\alpha_{11} = \alpha$ and $\beta_{11} = \alpha_{11} kT \hat{\beta} / 2$, where the values of α and $\hat{\beta}$ can be taken from the first row of Table 4 (for $\delta_s = 0$), that is we know α_{11} and β_{11} from the fit of data for pure SDS (without dodecanol). Next, α_{14} is calculated from eq 4.3. Finally, for a given α_{44} we can calculate β_{14} and β_{44} from eq 4.7. Thus, in a final reckoning, from all six α and β values only one, α_{44} , remains unknown. In the next section, α_{44} is determined as an adjustable parameter from the best fit of surface-tension data for SDS + dodecanol.

4.3. Test of the Model against Data for SDS + Dodecanol. Everywhere in the present paper “dodecanol” means “*n*-dodecanol”. The experimental points in Figure 3 are (i) data by Tajima et al.⁵¹ for purified SDS and (ii) data by Vollhardt and Emrich²² for purified SDS + 0.2 mol % dodecanol. The latter concentration of dodecanol corresponds to the region of uniform fluidlike state of the surfactant adsorption layer.²² At higher concentrations of dodecanol a first-order phase transition, with formation of condensed phase domains, has been observed by Brewster angle microscopy.^{22,23} Vollhardt and Emrich²² have obtained also a surface-tension isotherm with their purified SDS, which is very close to the isotherm by Tajima et al.⁵¹ shown in Figure 3.

Here and hereafter we will use the results by Tajima et al.^{51–53} as a standard set of data for pure SDS, without

dodecanol. The theoretical curve drawn through the points without dodecanol (Figure 3) is calculated using the parameter values in the first row of Table 4. The best fit of the data with 0.2 mol % dodecanol is obtained as follows:

As before, we take $E_2 = 1.64$, $\delta_4 \approx \delta_1 = 2$ nm, and $\delta_2 = 0.7$ nm, the same as in ref 7. Because the SDS and dodecanol have identical hydrocarbon tails, it is reasonable to assume that their adsorption energies are equal, that is $E_4 = E_1 = 12.53$; see Table 4. From the same table, we take the values of the parameters $\alpha_{11} = \alpha = 29.76 \text{ \AA}^2$ and $\beta_{11} = \alpha_{11} k T \beta / 2 = 1.013 \times 10^{-15} \text{ J} \cdot \text{m}^2 \cdot \text{mol}^{-1}$. Then, for a given α_{44} , we calculate α_{14} , β_{14} , and β_{44} from eqs 4.3 and 4.7. Further, we calculate the theoretical dependence $\sigma(c_{1\infty}, c_{4\infty})$ with the help of the full set of equations described in section 3.5, using the excluded area per dodecanol molecule, α_{44} , as a single adjustable parameter. The best fit of the data for SDS + 0.2 mol % *n*-dodecanol (the lower curve in Figure 3) yields $\alpha_{44} = 20.19 \text{ \AA}^2$, which coincides with the cross-sectional area for normal alkanols in the framework of the experimental accuracy; see the last two columns of Table 1. The standard deviation of the curve from the data points is $\Delta\sigma = 0.63 \text{ mN/m}$ for this fit. The very reasonable value of α_{44} , the relatively small $\Delta\sigma$, and the fact that only one adjustable parameter has been used are strong arguments in favor of the quantitative adequacy of the van der Waals type model developed in section 3 above. The latter result gives us the certitude to propose this model for the determination of unknown contents of dodecanol in SDS samples; see section 5.

We tested the fit of the data for SDS + 0.2 mol % dodecanol in two additional aspects. First, we dropped the assumption $E_4 = E_1$ and varied E_4 as an adjustable parameter. The best fit gave $E_4/E_1 = 1.002$, which confirms the correctness of the assumption $E_4 = E_1$. Second, instead of using eq 4.7, we tried to fit the data substituting equal interaction parameters, $\beta_{14} = \beta_{44} = \beta_{11}$. The latter assumption led to a worse fit with a greater standard deviation $\Delta\sigma = 1.85 \text{ mN/m}$ and with a physically irrelevant value of the excluded area per dodecanol molecule, $\alpha_{44} = 13.06 \text{ \AA}^2$. In general, our examination showed that the procedure described in the previous paragraph provides the best fit of the data for SDS + dodecanol (see also section 5.2).

4.4. Numerical Results and Discussion. Let us summarize the facts which give us confidence in the reliability of the proposed model. First, the model fits excellently surface tension isotherms of SDS solutions at various salt concentrations and gives an excluded area per SDS molecule equal to the cross-sectional area of the sulfate headgroup; see ref 9 and section 2.2 above. Second, the model fits simultaneously adsorption isotherms of eight different *alkanols* with an excluded area per molecule equal to its geometrical cross section (eq 2.8) and an adsorption energy obeying Traube's rule (eq 2.9); see section 2.1 and Figure 1. Third, for a *mixed* solution of SDS + alkanol (dodecanol), we have fitted a surface tension isotherm with a single adjustable parameter, the excluded area per dodecanol molecule, which is determined to be practically equal to the cross-sectional area of this molecule; see Figure 3 and section 4.3. Thus, it turns out that the model provides a rather adequate description, and moreover, we have already determined all of its parameters. Then, the next step is to check and report the predictions of the model, which is done below in this section.

As already mentioned, having once determined the parameters of the model, we are able to calculate various properties of the surfactant adsorption layer, such as the adsorptions of SDS and dodecanol, Γ_1 and Γ_4 , the Gibbs

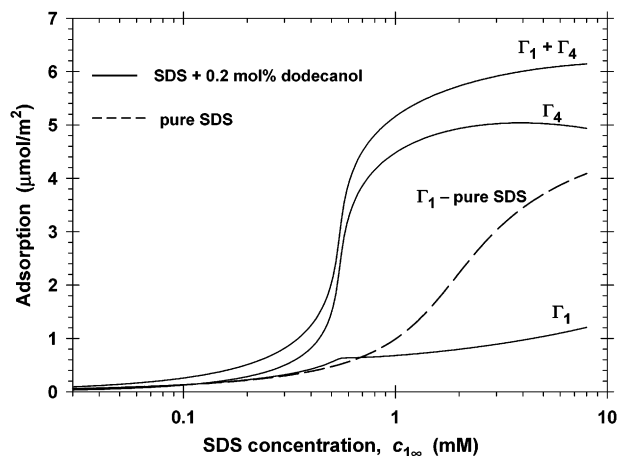


Figure 4. Theoretical curves for the adsorption of dodecyl sulfate (Γ_1) and dodecanol (Γ_4) calculated by means of the full set of equations (section 3.5) using parameter values determined from the fits in Figure 3. The solid lines are obtained for SDS + 0.2 mol % dodecanol, whereas the dashed line is for pure SDS.

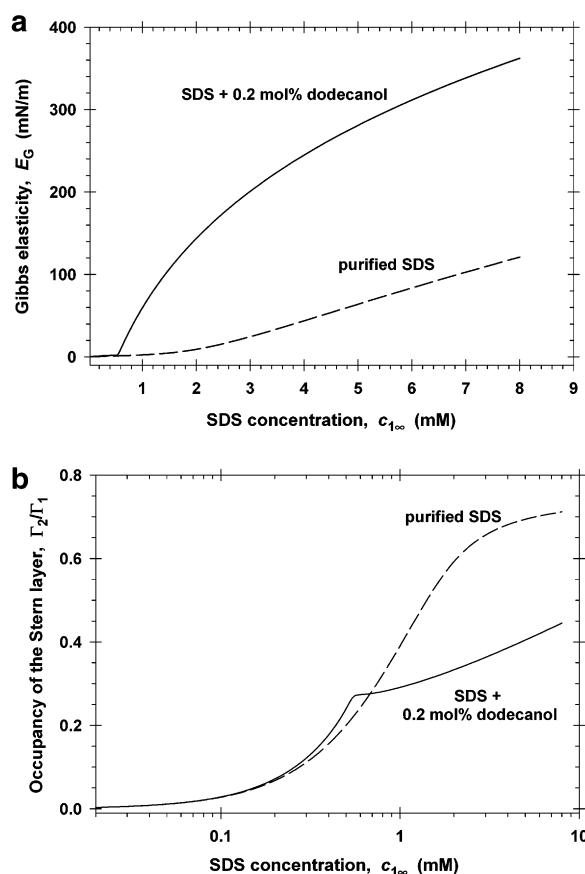


Figure 5. The Gibbs elasticity, E_G , and the occupancy of the Stern layer, Γ_2/Γ_1 , plotted vs the SDS concentration for pure SDS and for SDS + 0.2 mol % dodecanol; see the text for details.

elasticity, E_G , the occupancy of the Stern layer by adsorbed counterions, Γ_2/Γ_1 , the surface electric potential, ψ_s , etc.; see Figures 4–6. In the figures we compare results for SDS + dodecanol with those for pure SDS. In all cases, the theoretical curves are calculated by using the full set of equations, described in section 3.5, which corresponds to a van der Waals type model for a mixture of an ionic and a nonionic surfactant (see section 5.2 for the computational procedure).

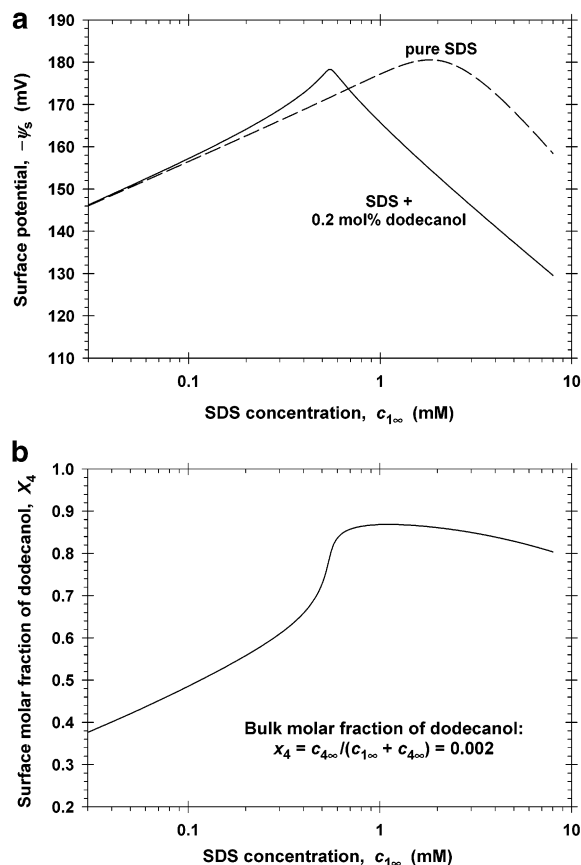


Figure 6. (a) Plot of the surface electric potential, ψ_s , vs the SDS concentration, $c_{1\infty}$, for pure SDS and for SDS + 0.2 mol % dodecanol. (b) The surface molar fraction, $X_4 = \Gamma_4 / (\Gamma_1 + \Gamma_4)$, plotted vs $c_{1\infty}$ for solutions of SDS + 0.2 mol % dodecanol.

In the computations, the bulk mole fraction of dodecanol in the surfactant blend

$$X_4 = \frac{c_{4\infty}}{c_{1\infty} + c_{4\infty}} \quad (4.8)$$

was set, respectively, 0 and 0.002 for the curves for pure SDS and SDS + dodecanol. The used parameter values are those from subsection 4.3, viz., $E_1 = E_4 = 12.53$, $E_2 = 1.64$, $\alpha_{11} = 29.76 \text{ \AA}^2$, $\alpha_{14} = 24.74 \text{ \AA}^2$, $\alpha_{44} = 20.19 \text{ \AA}^2$, $\beta_{11} = 1.013 \times 10^{-15} \text{ J}\cdot\text{m}^2\cdot\text{mol}^{-1}$, $\beta_{14} = 1.336 \times 10^{-15} \text{ J}\cdot\text{m}^2\cdot\text{mol}^{-1}$, $\beta_{44} = 1.813 \times 10^{-15} \text{ J}\cdot\text{m}^2\cdot\text{mol}^{-1}$, and $\beta_e = 0$, $\delta_1 = \delta_4 = 2 \text{ nm}$, and $\delta_2 = 0.7 \text{ nm}$.

Figure 4 shows the calculated adsorptions of dodecyl sulfate, Γ_1 , dodecanol, Γ_4 , and the total surfactant adsorption, $\Gamma_1 + \Gamma_4$, as functions of the SDS concentration. One sees that in the case of SDS + 0.2 mol % dodecanol, the adsorption Γ_4 is considerable, and even predominant in the adsorption layer ($\Gamma_4 > \Gamma_1$). The reason is that the DS^- ions are repelled by the negatively charged adsorption layer, and the subsurface concentration of DS^- , $c_{1s} = c_{1\infty} \exp(-\Phi_s)$, becomes smaller than the concentration of the nonionic dodecanol: $c_{4s} = c_{4\infty}$. With the increase of the bulk SDS concentration, $c_{1\infty}$, the adsorption Γ_1 also increases, which leads to a rise of Φ_s (Figure 6a) and strengthening of the repulsion of DS^- from the interface. It turns out that the latter effect keeps Γ_1 smaller than Γ_4 in the whole concentration range below the critical micelle concentration (cmc) (Figure 4). The dashed line in Figure 4 shows that at the same SDS bulk concentration, the adsorption of dodecyl sulfate, Γ_1 , is greater for the solution of pure SDS. This is not surprising insofar as for

$X_4 = 0.002$ a considerable part of the interface is inaccessible to the adsorption of DS^- ions, because it is occupied by dodecanol.

The above predictions of the model are consonant with the experimental observations of Vollhardt and Emrich,²² who found (by Brewster angle microscopy) that a trace amount of *n*-dodecanol in the solution produces a considerable effect on the mixed adsorption layer with SDS. It was observed that depending on the mixing ratio and the system conditions (bulk concentration, temperature), a phase transition can or cannot occur. When a phase transition happens, condensed phase domains of *n*-dodecanol are formed. They grow finally to a homogeneous condensed phase which consists of 100% dodecanol that replaces completely SDS from the interface.²²

Figure 5a compares the surface dilatational (Gibbs) elasticity, E_G , for SDS solutions with and without dodecanol. The Gibbs elasticity characterizes the Marangoni–Gibbs effect, that is the increase of the surface tension upon interfacial dilatation

$$E_G \equiv -A \left(\frac{\partial \pi_a}{\partial A} \right)_{N_1, N_4} = \Gamma_1 \left(\frac{\partial \pi_a}{\partial \Gamma_1} \right)_{\Gamma_4} + \Gamma_4 \left(\frac{\partial \pi_a}{\partial \Gamma_4} \right)_{\Gamma_1} \quad (4.9)$$

Here A denotes the interfacial area. A detailed discussion about the definition of E_G in the case of ionic surfactants can be found in refs 8 and 66. Substituting the surface pressure, π_a , from eq 3.17 (with $\beta_e = 0$) into eq 4.9, after some transformations we obtain

$$E_G = \frac{kT(\Gamma_1 + \Gamma_4)}{[1 - \alpha(\Gamma_1 + \Gamma_4)]^2} - 2\beta(\Gamma_1 + \Gamma_4)^2 \quad (4.10)$$

where α and β , both of them dependent on the composition of the adsorption layer, are defined by eqs 3.9 and 3.10. The Gibbs elasticity, calculated from eq 4.10 for pure SDS and for SDS + 0.2 mol % dodecanol, is shown in Figure 5a. One sees that for the higher SDS concentrations, $c_{1\infty} > 0.7 \text{ mM}$, E_G is much greater for the solutions with dodecanol. This result is related to the fact that in the presence of dodecanol, the total adsorption, $\Gamma_1 + \Gamma_4$, is considerably greater than that in the case of pure SDS: compare the upper curve in Figure 4 with the dashed curve in the same figure. The graphs in Figure 5a, indicating a strong increase of E_G due to addition of dodecanol to SDS, are consonant with the results of other studies,^{67–70} which report a similar effect and its stabilizing influence on foam films and foams. For example, in ref 69 it is found that the addition of 1 mol % dodecanol to pure SDS leads to foam lifetimes which are 10 times longer than those obtained in the absence of dodecanol.

Figure 5b shows the occupancy of the Stern layer by adsorbed counterions, Γ_2/Γ_1 , as a function of the SDS concentration. Qualitatively, Γ_2/Γ_1 follows the behavior of the curves Γ_1 vs $c_{1\infty}$ in Figure 4: the numerical results for solutions with and without dodecanol are close for $c_{1\infty} \leq 0.7 \text{ mM}$, but at higher SDS concentrations both Γ_1 and Γ_2/Γ_1 are greater for the solution of pure SDS. This can be attributed to the fact that when the SDS adsorption, Γ_1 , is larger, it engenders a greater surface potential, Φ_s

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(69) Brown, A. G.; Thuman, W. C.; McBain, J. W. *J. Colloid Sci.* **1953**, *8*, 491.

(70) Angarska, J. K.; Tachev, K. D.; Kralchevsky, P. A.; Mehreteab, A.; Broze, G., *J. Colloid Interface Sci.* **1998**, *200*, 31.

(see Figure 6a and eq 3.32), that implies a greater subsurface concentration of the counterions, $a_{1s} = a_{1\infty} \exp(-\Phi_s)$, which in view of the Stern isotherm, eq 3.26, leads to a greater occupancy, Γ_2/Γ_1 . Note that the occupancy of the Stern layer is significant: Γ_2/Γ_1 can be up to 0.4 and 0.7, respectively, for the solutions with and without dodecanol (Figure 5b).

Figure 6a shows a plot of the calculated surface electric potential as a function of the bulk concentration of SDS, $c_{1\infty}$, for solutions of pure SDS and of SDS + 0.2 mol % dodecanol. The curves in Figure 6a exhibit maxima at certain values of $c_{1\infty}$. Similar nonmonotonic dependence was observed in refs 3 and 7. This behavior can be attributed to the competition of two effects:⁷ (i) the increase of the surface electric charge with the rise of the surfactant adsorption, Γ_1 , and (ii) decrease of the surface potential with the increase of the ionic strength, I , due to the addition ionic surfactant, which itself is an electrolyte. At higher SDS concentrations effect ii gets the upper hand, which explains the observed maximum. Moreover, effect i is weaker for the solution containing dodecanol (Γ_1 is smaller for this solution, Figure 4), which leads to a shift of the maximum to the left (Figure 6a).

Figure 6b visualizes the dependence of the surface molar fraction of dodecanol, $X_4 = \Gamma_4/(\Gamma_1 + \Gamma_4)$, on the bulk surfactant concentration, $c_{1\infty}$, for solutions of SDS + 0.2 mol % dodecanol. The most intriguing fact is that irrespective of the low bulk molar fraction of dodecanol, $x_4 = c_{4\infty}/(c_{1\infty} + c_{4\infty}) = 0.002$, its surface molar fraction is much higher, $0.38 \leq X_4 \leq 0.86$. Moreover, at the higher surfactant concentrations, $c_{1\infty} > 0.1$ mM, the surface molar fraction of dodecanol is greater than those of the main surfactant, SDS, whose fraction in the bulk of solution is $x_1 = 0.998$. The latter fact can be utilized to detect a trace content of dodecanol in a given SDS sample by analysis of surface tension data (see section 5); such a method should be much more sensitive than any bulk analytical method.

As mentioned above, the relatively high surface molar fraction of dodecanol is due to the negative surface electric potential, which repels the DS^- ions from the close vicinity of the interface but does not affect the concentration of the nonionic dodecanol molecules. Thus, X_4 increases with the rise of $c_{1\infty}$ and $|\psi_s|$, but at the higher surfactant concentrations X_4 exhibits a maximum (Figure 6b). The latter is due to the competition of two opposite tendencies: (i) decrease of X_4 with the decrease of $|\psi_s|$ at the higher $c_{1\infty}$ (see Figure 6a), and (ii) increase of X_4 with the increase of $c_{4\infty}$ in proportion with the SDS concentration.

One way to decrease the surface fraction of dodecanol is to add electrolyte (say NaCl), which reduces $|\psi_s|$ and thus allows the major surfactant, SDS, to adsorb and displace the dodecanol; see section 5.4.

5. Determining Unknown Contents of Dodecanol

5.1. Analysis of Dodecanol in SDS Samples. Such an analysis is important, because even a trace amount of dodecanol in a given SDS sample might have a dramatic effect on the properties of the adsorption layer; see Figures 4–6. Correspondingly, the surface tension of SDS solutions may serve as the most sensitive indicator for trace contents of dodecanol.

In section 4 we determined all parameters of the two-component van der Waals model for the system SDS + dodecanol. Their values are specified after eq 4.8. Hence, if we have the surface-tension isotherm for a given SDS sample, like any of the isotherms shown in Figure 7, we are able to determine the mole fraction of dodecanol, x_4 ,

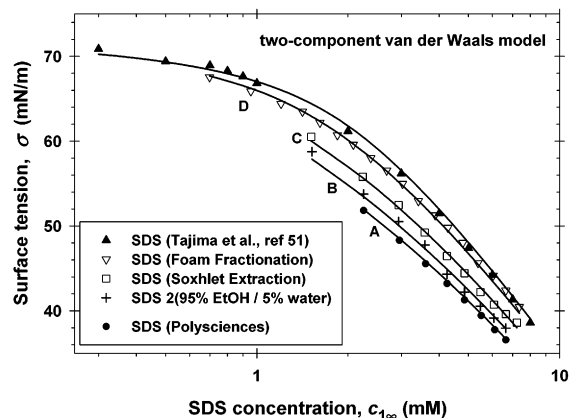


Figure 7. Plots of σ vs $c_{1\infty}$: the upper curve is obtained with data by Tajima et al.,⁵¹ whereas the lower four curves are obtained with data by Hines²¹ for SDS at various stages of purification. The curves are the best fits with the two-component van der Waals model (section 5.2); the mole fractions of dodecanol in the SDS samples, determined from the fits, are listed in Table 5.

in this sample by fitting the isotherm with the model, and using x_4 as a *single* adjustable parameter. The numerical procedure, described in the section 5.2, works very fast, so the most time-consuming steps are the obtaining of the surface tension data, $\sigma(c_{1\infty}, c_{2\infty})$, and their entering into the computer.

5.2. Principles of the Numerical Procedure. The aim of the procedure is to determine the mole fraction, x_4 , of a nonionic-surfactant admixture (like dodecanol) in a sample of an ionic surfactant (like SDS). In general, the surfactant solutions can also contain a nonamphiphilic electrolyte (like NaCl). The two-component van der Waals type model (section 3) is applied.

(1) As input data we have experimental points for the interfacial tension, $\sigma = \sigma(c_{1\infty}, c_{2\infty})$, for a given temperature, T , where, as usual, $c_{1\infty}$ and $c_{2\infty}$ are the bulk concentrations of surfactant ions (DS^-) and counterions (Na^+). The concentration of the nonamphiphilic co-ions (Cl^-) is $c_{3\infty} = c_{2\infty} - c_{1\infty}$; the ionic strength of this solution is $I = c_{2\infty}$.

(2) The constant input parameters are α_{11} , α_{44} , β_{11} , δ_1 , δ_2 , δ_4 , E_1 , E_2 , and E_4 . For the system SDS + dodecanol at the air–water interface we have (section 4.3): $\alpha_{11} = 29.76 \text{ \AA}^2$, $\alpha_{44} = 20.19 \text{ \AA}^2$, $\beta_{11}/(kT\alpha_{11}) = 1.365$, $E_1 = E_4 = 12.53 \text{ kT}$, $E_2 = 1.64 \text{ kT}$, $\delta_1 \approx \delta_4 = 2.0 \text{ nm}$, $\delta_2 = 0.7 \text{ nm}$, and $\beta_e = 0$.

(3) Next, we calculate α_{14} , β_{14} , and β_{44} from eqs 4.3 and 4.7. The activities of the ions are $a_{i\infty} = \gamma_{\pm} c_{i\infty}$ ($i = 1, 2, 3$), where⁷¹

$$\log \gamma_{\pm} = -\frac{A|Z_+Z_-|I^{1/2}}{1 + Bd_iI^{1/2}} + bI \quad (5.1)$$

$A = 0.5115 \text{ M}^{-1/2}$, $Bd_i = 1.316 \text{ M}^{-1/2}$, and $b = 0.055 \text{ M}^{-1}$; the logarithm in eq 5.1 is decimal.

(4) We assign a tentative value to the mole fraction, x_4 , of the nonionic admixture (dodecanol), which is to be determined as an adjustable parameter from the best fit of the data. Then $c_{4\infty} = x_4 c_{1\infty}$.

(5) We give tentative values to the surfactant adsorptions Γ_1 and Γ_4 in the intervals $0 \leq \Gamma_1 \leq 1/\alpha_{11}$ and $0 \leq \Gamma_4 \leq 1/\alpha_{44}$, then α and β are calculated from eqs 3.9 and 3.10.

(71) Robinson, R. A.; Stokes, R. H. *Electrolyte Solutions*; Butterworth: London, 1959.

(6) We bring eq 3.24 in the form

$$\delta_4 c_{4\infty} \exp(E_4) = \frac{\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)}$$

$$\exp\left[\frac{(2\alpha_{14} - \alpha)\Gamma_1 + (2\alpha_{44} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2\beta_{14}\Gamma_1 + 2\beta_{44}\Gamma_4}{kT}\right]$$
(5.2)

and solve it numerically to determine Γ_4 for the given value of Γ_1 . We used the bisection method (half-position iterations) to solve eq 5.2.

(7) To calculate the dimensionless surface potential, Φ_s , in eq 3.23, we substitute Γ_2 from eq 3.26 and a_{is} ($i = 1, 2$) from eqs 3.1 and 3.32. Thus, we obtain an explicit expression for Φ_s

$$\exp(-\Phi_s) =$$

$$-\delta_2 \alpha_{11} \exp(E_2) a_{2\infty} + \frac{\Gamma_1 \exp(-E_1)}{[1 - \alpha(\Gamma_1 + \Gamma_4)] \delta_1 a_{1\infty}}$$

$$\exp\left[\frac{(2\alpha_{11} - \alpha)\Gamma_1 + (2\alpha_{14} - \alpha)\Gamma_4}{1 - \alpha(\Gamma_1 + \Gamma_4)} - \frac{2\beta_{11}\Gamma_1 + 2\beta_{14}\Gamma_4}{kT}\right]$$
(5.3)

(8) The calculated $\Phi_s(\Gamma_1)$ is substituted in the equation

$$\Gamma_1 = \frac{4I}{\kappa} \sinh\left(\frac{\Phi_s}{2}\right) [1 + \delta_2 \alpha_{11} a_{2\infty} \exp(E_2 + \Phi_s)] \quad (5.4)$$

which is obtained from eq 3.31 after substituting Γ_2 and a_{2s} from eqs 3.26 and 3.1. Equation 5.4 is an implicit equation for determining Γ_1 , which is solved numerically, say, by using the bisection method.

(9) The theoretical value of the surface tension $\sigma(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}, x_4)$, corresponding to given experimental points ($c_{1\infty}^{(m)}, c_{2\infty}^{(m)}$), is then calculated from eq 3.30. Here, the superscript m numbers the experimental points.

(10) The adjustable parameter x_4 is determined by means of the least-squares method, that is, by numerical minimization of the merit function

$$\Psi(x_4) = \left\{ \sum_{m=1}^N [\sigma^{(m)} - \sigma(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}, x_4)]^2 / (N - 1) \right\}^{1/2} \quad (5.5)$$

where $\sigma^{(m)}$ is the experimental value of σ corresponding to the concentrations $c_{1\infty}^{(m)}$ and $c_{2\infty}^{(m)}$; the summation in eq 5.5 is carried out over all experimental points ($c_{1\infty}^{(m)}, c_{2\infty}^{(m)}, \sigma^{(m)}$); N is their total number. The function $\Psi(x_4)$ has a sharp minimum (see the Appendix) for some value of $x_4 \in (0, 1)$, which is the sought for molar fraction of the nonionic admixture (dodecanol) in the ionic surfactant (SDS).

(11) The surface dilatational (Gibbs) elasticity is calculated from eq 4.10.

In section 4.3 we used the same procedure to fit the lower curve in Figure 3, with the only difference that x_4 was given (0.2 mol %) and we varied α_{44} as an adjustable parameter.

5.3. Numerical Results for SDS at Various Stages of Purification. Here we apply the numerical procedure, described in the previous section, to determine the content of dodecanol in SDS samples at various stages of purification. Surface-tension isotherms obtained by Hines²¹ have been used. The starting sample was SDS (extra purified) purchased from Polysciences, Inc. (Warrington, PA), and

Table 5. Mole Fraction of Dodecanol, x_4 , in SDS Samples Determined from the Data in Figure 7

SDS sample	x_4 ($\times 10^{-4}$)	Ψ_{\min} (mN/m)
(A) Polysciences	9.59 ± 0.45	0.40
(B) 95% EtON/5% H ₂ O	7.97 ± 0.42	0.39
(C) Soxhlet extraction	5.71 ± 0.49	0.46
(D) foam fractionation	2.30 ± 0.65	0.54

described as 99.5% pure; see the lowest curve in Figure 7. First, the material was recrystallized twice from a 95% ethanol/5% water mixture; the respective data points are denoted by “+” in Figure 7. The next stage of purification was a 36 h extraction with diethyl ether in a Soxhlet apparatus,^{21,72} the squares in Figure 7. The final stage was the purification by means of a foam fractionation apparatus. The surface-tension isotherms, corresponding to all stages of purification, are compared in Figure 7 with the isotherm by Tajima et al.,⁵¹ which is chosen as a standard for pure SDS in our analysis. The theoretical curves are drawn with the help of the two-component van der Waals model (section 3) by using the numerical procedure described in section 5.2. Attributing the lowering of σ , for a given SDS concentration, to an admixture of dodecanol, from the best fits of the data we determined the molar fraction of dodecanol, x_4 , in the respective SDS sample; see Table 5.

The second column of Table 5 shows how the contents of dodecanol decrease at the consecutive stages of the purification procedure in ref 21. In particular, the first row indicates that the commercial SDS sample from Polysciences was 99.90% pure; supposedly, the data by Tajima et al.^{51–53} can serve as a standard for the surface tension of pure SDS. It should be noted that all values of x_4 in Table 5 belong to the interval $0 < x_4 < 0.2$ mol %, whose boundaries correspond to the two curves in Figure 3, which have been used to determine the parameters of the model (section 4.3). The last column in Table 5 shows the standard deviation, Ψ_{\min} , of the fits (Figure 7), corresponding to the minimum of Ψ in eq 5.5. The experimental error of x_4 , given in Table 5, has been estimated from the value of Ψ_{\min} as explained in the Appendix.

5.4. Effect of NaCl on the Contents of Dodecanol in the Adsorption Layer. In general, the two-component van der Waals model (section 3) is applicable to surfactant solutions containing a nonamphiphilic electrolyte, like NaCl. As an example, in Figure 8 we show the best fit of data measured by Todorova⁷³ for the surface tension of SDS solutions in the presence of 10 mM NaCl. The theoretical curve is drawn with the help of the procedure from section 5.2. The mole fraction of dodecanol in the used SDS sample (Acros Organics, Pittsburgh, PA), determined as an adjustable parameter from the fit in Figure 8, is $x_4 = (5.3 \pm 2.3) \times 10^{-4}$; supposedly, the data by Tajima et al.^{51–53} can serve as a standard for the surface tension of pure SDS. The standard deviation of the fit (Figure 8), corresponding to the minimum of Ψ in eq 5.5, is $\Psi_{\min} = 0.71$ mN/m; see the Appendix for the error estimates.

Figure 9 illustrates how the adding of 10 mM NaCl affects the surface electric potential, ψ_s , and the surface molar fraction of dodecanol, $X_4 = \Gamma_4 / (\Gamma_1 + \Gamma_4)$, for solutions of SDS, which contain $x_4 = 0.053$ mol % dodecanol. The curves are calculated by means of the theoretical model using the procedure and parameter values specified in section 5.2. One sees that the addition of NaCl leads to

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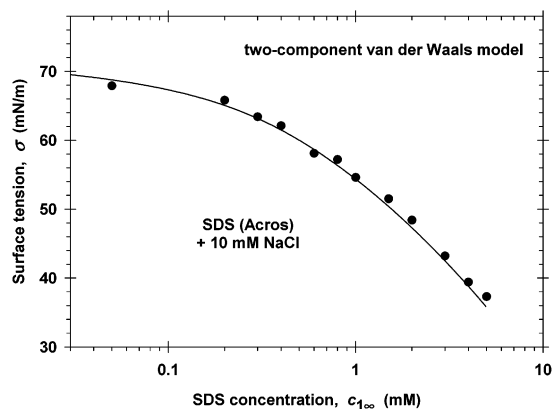


Figure 8. Plot of σ vs $c_{1\infty}$: the points are data by Todorova⁷³ for solutions of SDS + 10 mM NaCl. The curve is the best fit with the two-component van der Waals model (section 5.2), which indicates the presence of $x_4 = 0.053$ mol % dodecanol in this SDS sample.

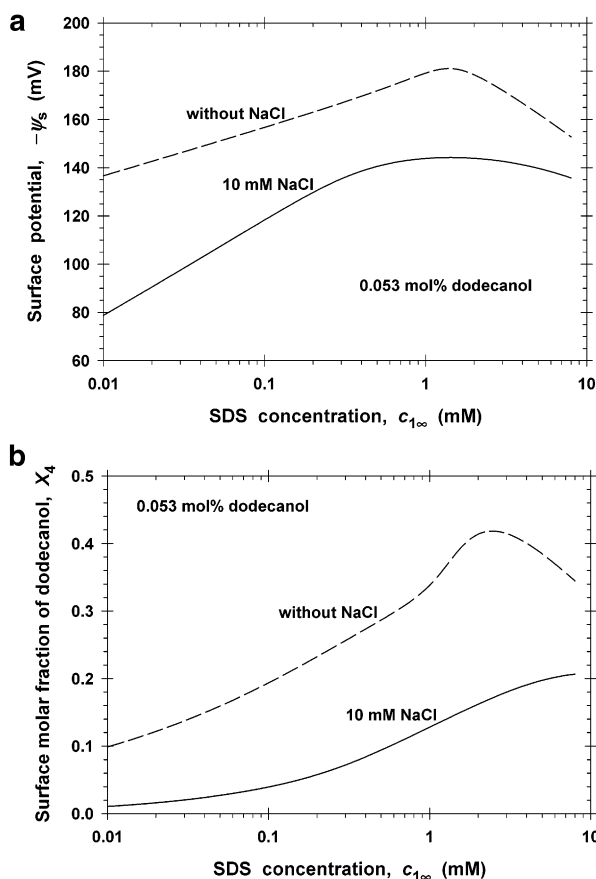


Figure 9. Plots of (a) the surface electric potential, ψ_s , and (b) the surface molar fraction of dodecanol, X_4 , as functions of the SDS concentration, $c_{1\infty}$, for solutions of SDS which contains an admixture of 0.053 mol % dodecanol.

considerably lower values of both $|\psi_s|$ and X_4 . As already mentioned, at lower $|\psi_s|$ the electrostatic repulsion of the DS^- ions by the interface is weaker, and correspondingly, their fraction in the adsorption layer, $1 - X_4$, increases. It is interesting to note that even at such trace amount, $x_4 = 0.053$ mol %, the surface molar fraction of dodecanol, X_4 , can be up to 42 and 20 mol %, respectively, for the solutions with 0 and 10 mM NaCl.

In summary, the addition of NaCl to the mixed solutions of SDS + dodecanol leads to a significant reduction of the dodecanol fraction in the surfactant adsorption layer. From

analytical viewpoint, the addition of NaCl decreases the accuracy of determining of the dodecanol content in SDS.

Finally, it should be noted that, in principle, it is possible to apply the theoretical model to the *reverse* problem, that is to calculate the surface tension isotherm from experimental data for adsorption, obtained, say, by means of radiotracers or neutron reflection; see, e.g., ref 74. Typically, the values of σ thus obtained exhibit an enormous scattering, on the order of ± 50 mN/m (!), about the expected value of σ . This extreme sensitivity of the calculated dependence $\sigma(\Gamma)$ to the experimental error of Γ is due to the following. At not-too-low surfactant concentrations, for which $\alpha\Gamma \rightarrow 1$, we have divergent terms in the surface equation of state: $\ln(1 - \alpha\Gamma) \rightarrow \infty$ in the Frumkin eq 2.2, and $(1 - \alpha\Gamma)^{-1} \rightarrow \infty$ in the van der Waals eq 2.4; similar divergent terms are present also in the equations for mixed surfactants; see eq 3.17. This leads to a rather steep dependence $\sigma(\Gamma)$, which considerably amplifies the effect of scattering of the experimental Γ . The situation is exactly the opposite for the reverse dependence, $\Gamma(\sigma)$, which has a small slope that makes it possible to determine very accurately Γ from the experimental values of σ ; supposedly, an adequate theoretical expression is used. The latter fact lies at the root of the determination of surfactant purity from the experimental surface tension.

6. Summary and Conclusions

In the present study, we use a detailed analysis of surface tension isotherm as a quantitative method for a complete characterization of the adsorption layer, including determination of surfactant adsorption, surface electric charge and potential, surface elasticity, etc. As a tool for our theoretical analysis, we employ the van der Waals model. At the cost of using somewhat longer equations, the latter model provides a precise quantitative description. Its application to fit surface-tension data for alkanols, and two anionic surfactants, gives an excluded area per adsorbed molecule equal to the geometrical area of the molecular cross section (Tables 1 and 3), and it gives also adsorption energies consonant with Traube's rule (eqs 2.9 and 2.11).

The major target of this study is to develop a theoretical method for determining small contents of dodecanol in samples SDS. Because the dodecanol and SDS have different excluded areas per molecule, in section 3 we extend the van der Waals model for the case of a two-component adsorption layer, with account for the counterion binding in the Stern layer. We started from a general expression for the surface excess free energy, eqs 3.7–3.15, and then by differentiation we derived expressions for the two-dimensional equation of state, eq 3.17, for the surface chemical potentials, eqs 3.18–3.20, for the adsorption isotherms of the various species, eqs 3.23–3.25, and for the surface dilatational elasticity, eq 4.10. Although the two-component van der Waals model contains 10 parameters, we demonstrated that 9 of them can be determined in advance, from available experimental data and theoretical relationships (sections 4.1 and 4.2). Thus, the experimental surface-tension isotherms are fitted by varying only one adjustable parameter. The model was successfully tested against data for solutions of SDS with a known content of dodecanol (section 4.3 and Figure 3).

Knowing all parameters of the model, we computed various properties of the surfactant adsorption layer as functions of the concentrations of SDS, dodecanol, and

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nonamphiphilic electrolyte. The calculated curves show that the presence of a small amount of dodecanol, as an admixture in SDS, leads to a considerable increase of the total adsorption and surface elasticity (Figures 4 and 5a) but causes a decrease in the magnitude of the surface potential and in the occupancy of the Stern layer (Figures 5b and 6a). The most striking result is that even a relatively small (0.2 mol %) fraction of dodecanol in SDS may lead to a predominant content (up to 86 mol %) of dodecanol in the mixed adsorption layer (Figure 6b).

Finally, we applied the model for determining unknown contents of dodecanol in SDS samples at different stages of purification (Figure 7 and Table 5). We fitted also surface tension data, obtained in the presence of NaCl, and quantified the content of dodecanol (section 5.4). The results show that the addition of NaCl may lead to a significant reduction in the mole fraction of dodecanol in the adsorption layer (Figure 9b).

The developed theoretical model and computational procedure, applied to the system SDS + dodecanol at air–water interface, is also appropriate for the quantitative analysis and computer modeling of the adsorption from other mixed ionic–nonionic surfactant solutions, at both air–water and oil–water interfaces. An application to the system of sodium dodecylbenzene sulfonate + unsulfonated dodecylbenzene is presented in the second part of this study.²⁵

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Appendix: Estimate of the Experimental Error of x_4

Figure 10 shows the dependencies $\Psi(x_4)$ calculated by means of eq 5.5 for the lower four curves in Figure 7. The minima of the curves determine the best fits, and the respective values of $x_4 = x_{4,\min}$ are listed in Table 5. One sees that the minima in Figure 10 are very well pronounced, and correspondingly, the position of $x_{4,\min}$ can be

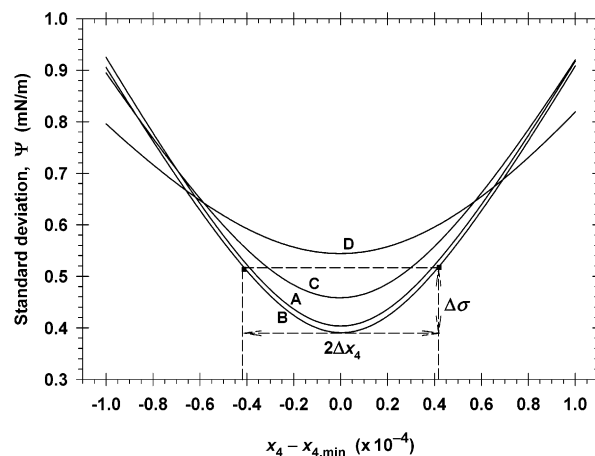


Figure 10. Dependence $\Psi(x_4)$, calculated by means of eq 5.5 for the experimental curves A, B, C, and D in Table 5 and Figure 7. The determination of Δx_4 for the lowest curve B is illustrated; see the text for details.

accurately determined. The values of $\Psi_{\min} = \Psi(x_{4,\min})$ are also given in Table 5.

There is no generally accepted procedure how to determine the error of $x_{4,\min}$ (denoted by Δx_4) for such a nonlinear fit. We proceeded in the following way. First we estimated the error of the surface tension values for the best theoretical curve

$$\Delta\sigma = \left\{ \sum_{m=1}^N [\sigma^{(m)} - \sigma(c_{1\infty}^{(m)}, c_{2\infty}^{(m)}, x_{4,\min})]^2 \right\}^{1/2} [N(N-1)]^{1/2} \quad (\text{A.1})$$

Comparing eqs A.1 and 5.5, we find that $\Delta\sigma = (\Psi_{\min}^2/N)^{1/2}$. Thus for the experimental curves A–D in Table 5 we obtain, respectively, $\Delta\sigma = 0.14, 0.13, 0.14,$ and 0.13 mN/m. Then we identify $2\Delta x_4$ with the “width” of the curve $\Psi(x_4)$ at a height $\Delta\sigma$ with respect to the minimum: this is illustrated in Figure 10 for the curve B. The results are presented as $x_4 \pm \Delta x_4$ in the second column of Table 5.

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