# Influence of Conformational Free Energy of Hydrocarbon Chains on Adsorption of Nonionic Surfactants at the Air/Solution Interface

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*Received: November 10, 1998*

The most frequently used theories of surfactant adsorption phenomena treat adsorbing molecules as structureless entities. However, surface active molecules consist of hydrophillic headgroups and hydrophobic chains. Therefore, surfactants have additional degrees of freedom associated with conformations of the chains. An unrestricted hydrophobic chain can assume practically any conformation at the interface. Adsorption of other surfactant molecules provides restriction to the number of possible conformations changing the conformational free energy. This change has to be reflected in the adsorption isotherm. We present a simple model of adsorption of soluble surfactants at the air/solution interface, taking explicitly into account the conformational statistics of hydrophobic surfactant chains. The model is applied to describe adsorption isotherms of homologous series of dimethyl-*n*-alkyl phosphine oxides with the alkyl chain length of 7−13 carbon atoms.

## Introduction

Surface active agents have been used in various fields of practical applications and basic research for a long time. Despite the theoretical and practical significance of the problem of surfactant adsorption at the air/solution interface, its theoretical description is far from being complete and some very important aspects are still not considered.

The most frequently used theoretical approach to the problem of adsorption of surface active agents relies on the application of the Frumkin adsorption isotherm:[1]

$$\frac{c_b}{a} = \frac{\Gamma}{\Gamma - \Gamma_\infty} \exp\left(-2H_s \frac{\Gamma}{\Gamma_\infty}\right) \tag{1}$$

where $c_b$ and $\Gamma$ are surfactant volume and surface molar concentrations, $a$ is the surface activity parameter or the bulk-surface distribution coefficient, $\Gamma_\infty$ is the saturation surface concentration corresponding to the closely packed monolayer, and $H_s$ is the surface interaction parameter assuming positive values for attractive interactions favoring adsorption. For $H_s = 0$, i.e., when the surface interactions are absent, the Frumkin adsorption equation simplifies to the Langmuir isotherm.[2] Lucassen-Reynders and van den Temple proved that eq 1 can be derived thermodynamically[3,4] with the Frumkin equation corresponding to the "regular" behavior of the solution at interface and the Langmuir adsorption equation describing the ideal mixing of solute and solvent molecules. Baret,[5] using kinetic concepts of molecular exchange at the interface, derived a set of adsorption isotherms for localized and nonlocalized adsorption. Parsons, applying scaled particle theory for the two-dimensional phase of Helfand et al.[6] and correcting for surface interactions, formulated a modified HFL isotherm for nonlocalized adsorption.[7] However, all of the isotherms are suitable for the description of adsorption of structureless molecules, and, as it has been underlined in the review of Chang and Frances,[8] they could not provide proper description of "steric and other interactions of hydrophobic chains of surfactant molecules".

To account for the structure of surfactant molecules and their influence on the adsorption process, Lunkenheimer and Hirte[9,10] introduced a two-state approach. They assumed that at low surface concentrations a surfactant molecule adsorbs at the interface in a different state than at high surface concentrations. Thus, the surface equation of state at low concentrations and consequently the adsorption isotherm, is different from the equation of state and adsorption equation for high surfactant surface concentrations. For intermediate concentrations, they assumed that the state of the interface is described by the mixture of low and high concentration states. The idea of the surfactant molecule adsorbing in the various states depending on the surfactant surface concentration at the interface was then developed by Fainerman et al.[11,12]

In our paper, we proposed another way of describing the influence of hydrophobic chains on surfactant adsorption based on the explicit formula accounting for the conformational free energy of surfactant tails adsorbed at an interface. We applied our theory for the description of experimental results for the adsorption of the homologous series of dimethyl-*n*-alkyl phosphine oxides at the air/solution interface.

## Theoretical Model

The adsorption isotherm of a nonionic surfactant at the air/solution interface can be formally written in the form:

$$\Gamma = B_x c_b \exp\left(-\frac{\Delta\mu_0}{kT}\right) \tag{2}$$

where $B_x$ is the constant accounting for the transformation from the molar fractions to the molar concentrations at the interface and in the bulk, $\Delta\mu_0$ is the standard Gibbs free energy of transferring a surfactant molecule from the infinitely dilute bulk

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10.1021/jp984382v CCC: $18.00 © 1999 American Chemical Society
Published on Web 05/12/1999

solution to the interface, $k$ is the Boltzmann constant, and $T$ is the absolute temperature. Following the procedure applied by Nagarayan and Ruckenstein[13] and Ben-Shaul et al.[14] for prediction of the thermodynamics of micellization, we assume that standard free energy consists of the following terms:

$$\Delta\mu_0 = \Delta\mu_{tran} + \Delta\mu_{hg} + \Delta\mu_{hc} + \Delta\mu_{cc} + \Delta\mu_{conf} \quad (3)$$

where $\Delta\mu_{tran}$ is the free energy change of transferring a surfactant molecule from the bulk of the solution to an empty interface; $\Delta\mu_{hg}$ is the headgroup steric interaction free energy which stems from the fact that the area occupied by a headgroup at an interface is excluded for the translational motion of the surfactant molecule and for the adsorption of other molecules; $\Delta\mu_{hc}$ is the free energy of other headgroup−headgroup or headgroup−chain interactions; $\Delta\mu_{cc}$ is the free energy of the van der Waals cohesive interaction between hydrocarbon chains; and $\Delta\mu_{conf}$ is the configurational free energy of surfactant tails involving all possible chain conformations as a result of the C−C bond rotations as well as rotations of the entire molecule.

The number of conformations of surfactant tails at the interface is partially restricted because a surfactant molecule is anchored to it by the headgroup, and penetration of the solution sublayer by the surfactant tail is energetically unfavorable. Additionally, when the surface concentration increases, some configurations are forbidden due to the volume exclusion hard core interactions with neighboring chains.

The headgroup steric interaction free energy can be calculated using the expression:[15]

$$\Delta\mu_{hg} = -kT \ln\left(1 - \frac{A_{hg}}{A}\right) \quad (4)$$

where $A_{hg}$ is the cross-sectional area of the headgroup, $A = 1/N_A\Gamma$ is the area per adsorbed molecule at the surface concentration $\Gamma$, $N_A$ is Avogadro's number, and the contribution of the other headgroup−headgroup, headgroup−tail, and tail−tail cohesive interactions to the free energy can be described in terms of the mean field approximation:[16]

$$\Delta\mu_{hc} + \Delta\mu_{cc} = -2H\Gamma \quad (5)$$

where $H$ is the mean force parameter, positive for the net attraction between the surfactant molecules at the interface. If we neglect the remaining configurational contribution to the free energy in eq 3 or if we include it in the mean field approximation represented by eq 5, we obtain the Frumkin adsorption isotherm:

$$c_b(1 - \theta) = a\theta \exp(-2H_s\theta) \quad (6)$$

where $\theta = \Gamma/\Gamma_\infty$ and the saturation surface concentration is defined as $\Gamma_\infty = 1/N_A A_{hg}$. The surface activity parameter a is given by $a = \Gamma_\infty/B_x \exp(\Delta\mu_{tran}/kT)$ and $H_s = H/RTA_{hg}$ is the Frumkin interaction parameter.

However, by neglecting the configurational contribution to the free energy or by treating it in the simplistic manner by including it in the potential of the mean force, we can neglect some important properties of behavior of surfactants that are crucial for our understanding of the adsorption thermodynamics of surfactants at fluid/air interfaces.

Following the approach suggested by Semenov[17] for the calculation of deformation free energy of block copolymer layers, Nagarajan and Ruckenstein[13] derived a simple formula for the determination of the configurational free energy of surfactant tails in micellar cores of various shapes. That formula was then applied by Li and Ruckenstein[18] to describe the configurational free energy of surfactant molecules adsorbed at a solid surface:

$$\frac{\Delta\mu_{conf}}{kT} \sim \frac{1}{A^2} \sim \Gamma^2 \quad (7)$$

However, because of the assumptions used to derive it, i.e., long chains and uniform chain segment density in the hydrocarbon layer, this formula seems to be only a qualitative approximation of the configurational free energy of a surfactant at the air/solution interface.

The configurational free energy per surfactant tail can be defined as:[14]

$$\Delta\mu_{conf} = -kT \ln z_{conf} \quad (8)$$

where $z_{conf}$ is the effective partition function (configurational sum) of the surfactant tail at the interface. In general, the configurational partition function can be found according to the formula:

$$z_{conf} = \sum_{\{a_i\}} \exp\left(-\frac{\epsilon(a_i)}{kT}\right) \quad (9)$$

where $\{a_i\}$ denotes the set of all possible tail configurations, i.e., all possible sequences of trans and gauche conformations of dihedral angles of a hydrocarbon chain and all possible orientations of the entire chain at the interface. The internal energy $\epsilon(a_i)$ of the chain in the conformation $a_i$ consists of the bond bending energies, torsional energies of C−C bond rotations, and the van der Waals and hard core interactions between distant (separated by more than three C−C bonds) $CH_2$ and/or $CH_3$ groups of the same chain. The van der Waals interactions between the chain at the interface and the solvent subphase as well as the hard core volume exclusion interactions with neighboring chains are also included in the internal energy $\epsilon(a_i)$.

The configurational partition function as defined by eq 9 should be strongly dependent on the surfactant surface concentration, as the presence of the other surfactant chains imposes strong restrictions on the possible chain conformation because of the volume excluded effects.

The exact calculation of the configurational free energy requires time-consuming Monte Carlo or molecular dynamic simulations of surfactant adsorption at the interface. These types of simulations have been carried out extensively for surfactants of various chain lengths, in particular for high surface coverages.[19−25] Szleifer et al.[24] using the method of exhaustive enumeration obtained direct information on the dependence of the configurational free energy of a surfactant at the air/solution interface on its surface concentration. However, the closed form analytical formula which can be directly applied for the practical purposes of fitting of experimental isotherms to a theoretical model is still unavailable.

Here we propose a simplified approach based on the results of calculations of the distribution of hydrocarbon chain conformations obtained by Vold.[26] She used the method of exhaustive enumeration of all conformations of the hydrocarbon chain anchored at the solution/air interface for the chain lengths from seven to twelve carbon atoms. In her work she did not calculate explicitly the conformational free energy because

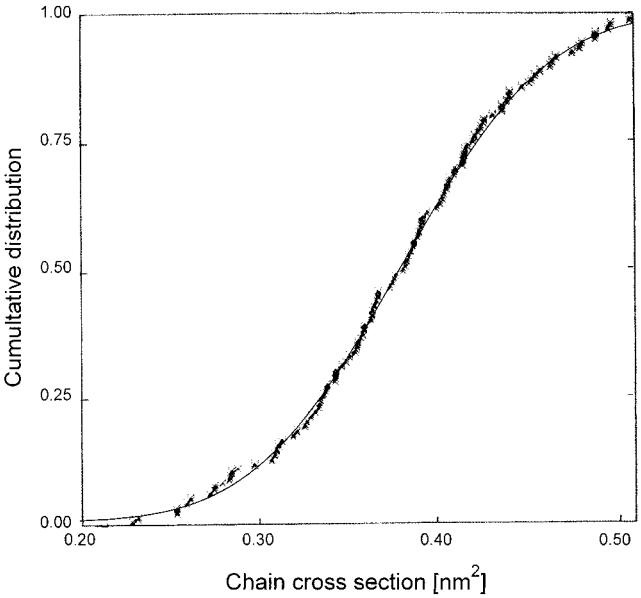


**Figure 1.** Cumultative chain conformation distribution expressed in terms of the effective chain cross-section obtained by exhaustive enumeration for the chain length of eight carbon atoms.[26] Solid line: approximation by eq 10.

the main aim of the computations was to find the length of the hydrocarbon conformers and cross-sectional area distribution. However, from the results presented in ref 26, it is possible to estimate the shape of the dependence of the chain conformation distribution function on its effective cross-sectional area as:

$$f_{\mathrm{conf}}(A_{\mathrm{c}}(a_{\mathrm{i}})) \simeq \exp\left(-\frac{(A_{\mathrm{c}}(a_{\mathrm{i}}) - A_{\mathrm{tr}})^2}{2\sigma_{\mathrm{tr}}^2}\right) \tag{10}$$

where $A_{\mathrm{c}}$ is the effective area of the chain defined as an area of the projection of a chain on the interface at given conformation $a_{\mathrm{i}}$, and $A_{\mathrm{tr}}$ and $\sigma_{\mathrm{tr}}$ are the parameters of the distribution. Figure 1 presents the cumultative distribution of the chain conformations as a function of the chain effective cross-sectional area in a given conformation. The results were obtained by Vold[26] for the chain with eight carbon atoms. The solid line represents the cumultative normal distribution given by eq 10 with $A_{\mathrm{tr}} = 0.38$ nm$^2$ and $\sigma_{\mathrm{tr}} = 6.5$ nm$^2$.

The configurational partition function can be found from:

$$z_{\mathrm{conf}} \simeq \sum_{\{a_{\mathrm{i}}\}} f_{\mathrm{conf}}(A_{\mathrm{c}}(a_{\mathrm{i}})) \exp\left(-\frac{\epsilon(a_{\mathrm{i}})}{kT}\right) \tag{11}$$

Because of the low energy difference between trans and gauche dihedral angle conformations (2.9 kJ/mol $\sim$ 1.2 kT[19]), chains are rather flexible. It suggests that as far as the torsional energy is concerned we can approximately assume that it does not considerably alter the chain conformation distribution. This approximation is supported by results presented in ref 26. The van der Waals interaction of the chain with the solution subphase should favor more flat configurations tilted toward the solution surface.[25] This can be taken into account by adopting a more flat conformation distribution function instead of one described by eq 10. Because the intrachain hard core repulsion was included in the calculations performed by Vold leading to the chain conformation distribution function approximated by eq 10, the remaining contribution to $\epsilon(a_{\mathrm{i}})$ in eq 11, which has to be considered, comes from the chain segment conformation constraints imposed by the neighboring chains adsorbed at the interface. This is in agreement with the results of the model calculations of Szleifer et al.[24,27] They showed that "the internal energy of the chain played only a secondary role, compared to that of the packing constraints in determining chain conformational statistics in micellar aggregates". It seems to be reasonable to assume the same behavior in the tail region of adsorbed surfactant at air/solution interface.

To determine the dependence of the single chain conformational partition function on surfactant surface concentration, we propose a very simple model as follows. At the low coverage of the interface by the surfactant, chains do not contact each other and the energy of the hard core steric interchain interactions is zero at any conformation of the chain. Thus, replacing the sum over conformations by integration over the distribution of effective areas of a chain in eq 11 we obtain:

$$z_{\mathrm{conf}}(\infty) = \int_{A_{\mathrm{CH2}}}^{\infty} f_{\mathrm{conf}}(A_{\mathrm{c}}) dA_{\mathrm{c}} = \int_{A_{\mathrm{CH2}}}^{\infty} \exp\left(-\frac{(A_{\mathrm{c}} - A_{\mathrm{tr}})^2}{2\sigma_{\mathrm{tr}}^2}\right) dA_{\mathrm{c}} \tag{12}$$

where $A_{\mathrm{CH2}}$ is the minimal possible effective area of the chain. It seems to be reasonable to assume this area to be equal to the cross-section of the chain being in all trans conformation and directed normally to the interface. In this case, $A_{\mathrm{CH2}} \simeq 0.21$ nm$^2$ (see Figure 1).

When the interface is partially covered with a surfactant at the surface concentration equal to $\Gamma$, we assume that all conformations with the effective area less than $A = 1/N_{\mathrm{A}}\Gamma$ are equally possible, whereas conformations with the effective area higher than $A$ are prohibited by the excluded volume interactions with the neighboring chains. Thus,

$$z_{\mathrm{conf}}(A) = \int_{A_{\mathrm{CH_2}}}^{A} \exp\left(-\frac{(A_{\mathrm{c}} - A_{\mathrm{tr}})^2}{2\sigma_{\mathrm{tr}}^2}\right) dA_{\mathrm{c}} \tag{13}$$

The difference of the configurational free energy per one molecule adsorbed at partially covered and empty interface is then given by:

$$\Delta\mu_{\mathrm{conf}} = -kT \ln \frac{z_{\mathrm{conf}}(A)}{z_{\mathrm{conf}}(\infty)} = -kT \ln \left[\frac{\int_{A_{\mathrm{CH_2}}}^{A} \exp\left(-\frac{(A_{\mathrm{c}} - A_{\mathrm{tr}})^2}{2\sigma_{\mathrm{tr}}^2}\right) dA_{\mathrm{c}}}{\int_{A_{\mathrm{CH_2}}}^{\infty} \exp\left(-\frac{(A_{\mathrm{c}} - A_{\mathrm{tr}})^2}{2\sigma_{\mathrm{tr}}^2}\right) dA_{\mathrm{c}}}\right] \tag{14}$$

The expression in bracket is in the form of Gaussian distribution function, and thus eq 14 can be easily transformed to:

$$\Delta\mu_{\mathrm{conf}} = -kT \ln \left[\frac{\mathrm{erf}\left(\frac{A - A_{\mathrm{tr}}}{\sqrt{2}\sigma_{\mathrm{tr}}}\right) - \mathrm{erf}\left(\frac{A_{\mathrm{CH2}} - A_{\mathrm{tr}}}{\sqrt{2}\sigma_{\mathrm{tr}}}\right)}{1 - \mathrm{erf}\left(\frac{A_{\mathrm{CH2}} - A_{\mathrm{tr}}}{\sqrt{2}\sigma_{\mathrm{tr}}}\right)}\right] \tag{15}$$

Introducing eqs 4, 5, and 15 into eq 2, we obtain the modified Frumkin adsorption equation with the contribution of the chain

conformation statistics explicitly taken into account:

$$c_b(1-\theta)\left[\frac{\mathrm{erf}\left(\frac{A-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)-\mathrm{erf}\left(\frac{A_{CH2}-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)}{1-\mathrm{erf}\left(\frac{A_{CH2}-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)}\right]= a\theta\exp(-2H_s\theta) \quad (16)$$

To formulate an alternative model which explicitly includes the effect of tails conformation statistics on adsorption, we use, instead of eq 16, the formula proposed by Li and Ruckenstein, i.e., eq 7. In this case, we obtain another modification of the Frumkin-type adsorption equation:

$$c_b(1-\theta) = a\theta\exp\left(-2H_s\theta + \frac{3}{2}K_s\theta^2\right) \quad (17)$$

where $K_s$ is the phenomenological parameter describing the contribution of the chain conformation statistics to the adsorption behavior of a surfactant. Taking into account the relationship between conformational free energy and relative surface coverage, we can think of $K_s$ as of the spring constant of the elastic layer of adsorbed hydrocarbon chains.

To compare our models with the experimental data for the dependence of surface tension of a surfactant solution on its concentration, we integrate the Gibbs adsorption equation:

$$\sigma = \sigma_0 - RT\int_0^{c_b}\Gamma d\ln c = \sigma_0 - RT\Gamma_\infty\int_0^{\theta(c_b)}\frac{\theta}{c}\frac{dc}{d\theta}d\theta \quad (18)$$

using adsorption isotherms given by eqs 16 and 17. Thus, the first model results in the surface equation of state:

$$\sigma = \sigma_0 + RT\Gamma_\infty[\ln(1-\theta) + H_s\theta^2 + \theta\ln E(\theta) - \int_0^\theta \ln E(\theta)d\theta] \quad (19)$$

where $\sigma_0$ is the surface tension of the pure solvent and

$$E(\theta(A)) = \frac{\mathrm{erf}\left(\frac{A-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)-\mathrm{erf}\left(\frac{A_{CH2}-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)}{1-\mathrm{erf}\left(\frac{A_{CH2}-A_{tr}}{\sqrt{2}\sigma_{tr}}\right)}$$

while integration of eq 17 leads to a simple expression:

$$\sigma = \sigma_0 + RT\Gamma_\infty[\ln(1-\theta) + H_s\theta^2 - K_s\theta^3] \quad (20)$$

In other words, the elastic contribution of adsorbed chains can be described approximately in terms of a second viral coefficient in the surface equation of state.

The applicability of our simplified approach has to be tested by the detailed calculation of the conformational distribution function for the single chain at the interface, taking into account all of the contributions we have neglected in this work. This will be done in our subsequent work. However, as the first step for the evaluation of the significance of the chain conformation contribution to surfactant adsorption at the air/solution interface, we use our approximate isotherms to describe experimental data concerning the adsorption of the homologous series of dimethyl-*n*-alkyl phosphine oxides with various lengths of the hydrocarbon chain. This is done in the subsequent section.

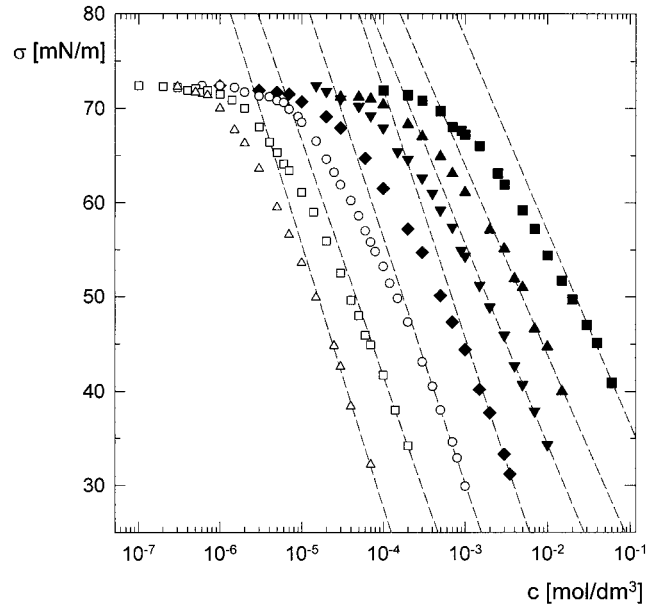


**Figure 2.** Surface tension of the homologous series of dimethyl-*n*-alkyl phosphine oxides with number of carbon atoms in the alkyl chain ranging from 7 (solid squares) to 13 (hollow triangles) as a function of surfactant volume concentration. Dashed lines represent slopes of experimental surface tension vs concentration dependence at the highest concentration studied for a given surfactant. Surface tension measured with Du Nuoy ring technique.

## Results and Discussion

In Figure 2, the experimentally measured dependence of the surface tension of dimethyl-*n*-alkyl phosphine oxide solution on its bulk concentration is illustrated. The hydrocarbon chain length ranges from 7 (solid squares) to 13 (hollow triangles) carbons. The details of the experiment are given elsewhere.[28] The dashed lines show the slope of the surface tension vs logarithm of the concentration dependence, i.e., the value of surface concentration, Γ, at or very close to CMC (critical micelle concentration). The slopes were obtained by the polynomial fit to the surface tension − log c dependence. As Figure 1 suggests, the slope, i.e., the surface concentration close to CMC, increases as the hydrocarbon chain becomes longer. It is better illustrated in Figure 3 where the surface concentration (solid circles, left axis) and area per molecule (hollow squares, right axis) at volume concentration approaching CMC, obtained from the slopes shown in Figure 2, are presented as a function of the number of carbon atoms in the chain. The error bars reflect the error of calculating surface concentration according to the Gibbs adsorption equation using the polynomial fit to the experimental points. The clear tendency of increasing surface concentration and decreasing area per molecule at the interface at CMC with increasing length of the hydrocarbon chain can be observed. It may be interpreted as a result of the balance of two interactions, the attractive van der Waals interactions between hydrocarbon chains and some repulsive interactions. The van der Waals cohesive forces, increasing with the chain length, would like to keep the chains together, minimizing the area per molecule and, thus, increasing the limiting adsorption at CMC. As a possible reason for the repulsion, we propose the elastic-like interactions due to the loss of the conformational freedom of hydrocarbon chains when the interface

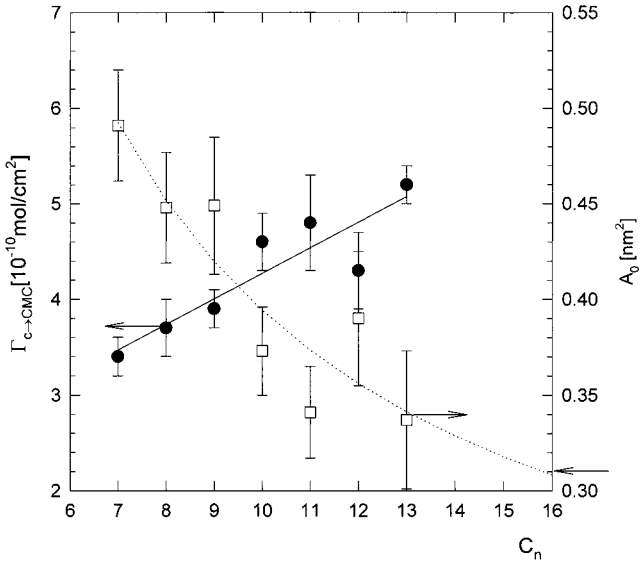


**Figure 3.** Surfactant surface concentration (solid circles, left axis) and area per molecule (hollow squares, right axis) at the surfactant volume concentration close to CMC as a function of the number of carbons in the alkyl chain. The arrow on the right axis marks the extrapolation of the area per molecule for the alkyl chain with 16 carbon atoms which can be assumed as insoluble.

**TABLE 1. Parameters for the Fit of the Experimental Data for the Dependence of Surface Tension of Dimethyl-*n*-alkyl Phosphine Oxide on the Surfactant Concentration in Solution to the Frumkin Isotherm**

| $n_c$ | $a$ (mol/dm$^3$) | $\Gamma_\infty$ ($10^{-10}$ mol/cm$^2$) | $RTH_s$ (kJ/mol) | $s$ |
|---|---|---|---|---|
| 7 | $1.05 \times 10^{-3} \pm 5 \cdot 10^{-5}$ | $3.09 \pm 0.06$ | $-0.1 \pm 0.2$ | 0.31 |
| 8 | $3.4 \times 10^{-4} \pm 2 \times 10^{-5}$ | $4.8 \pm 0.5$ | $-3.2 \pm 0.8$ | 0.45 |
| 9 | $1.45 \times 10^{-4} \pm 5 \times 10^{-6}$ | $3.7 \pm 0.1$ | $-0.3 \pm 0.2$ | 0.37 |
| 10 | $4.5 \times 10^{-5} \pm 6 \times 10^{-7}$ | $4.2 \pm 0.1$ | $-1.2 \pm 0.2$ | 0.33 |
| 11 | $2.2 \times 10^{-5} \pm 3 \times 10^{-7}$ | $4.0 \pm 0.1$ | $0.9 \pm 0.1$ | 0.44 |
| 12 | $7.1 \times 10^{-6} \pm 5 \times 10^{-6}$ | $3.8 \pm 0.1$ | $1.6 \pm 0.2$ | 0.42 |
| 13 | $3.9 \times 10^{-6} \pm 3 \times 10^{-6}$ | $4.7 \pm 0.3$ | $1.0 \pm 0.2$ | 0.48 |

becomes crowded, which we have described in the previous section. The hydrophillic repulsion of headgroups or dipole−dipole repulsive interactions may also contribute to the repulsive forces between adsorbed molecules of dimethyl-*n*-alkyl phosphine oxide, but in this study we neglect them. It is worthy to note that the similar trend of an increase of limiting surface concentration at CMC with increasing the length of the hydrocarbon chain in the homologous series has been observed for other surfactants.[29,30]

The interplay between the attractive and repulsive interactions is also evident from the data contained in Table 1. Here, we report the results for fitting parameters of the fit of experimental data for the homologous series of dimethyl-*n*-alkyl phosphine oxides shown in Figure 2 to the Frumkin isotherm (eq 6) together with the goodness of fit expressed as standard deviation of the fit:

$$s = \sqrt{\sum_{i=1}^{m} \frac{(\sigma_{ex}(c_i) - \sigma_{ev}(c_i))^2}{f_g}} \tag{21}$$

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

$$f_g = m - n - 1 \tag{22}$$

and $n$ is the number of fitted parameters.

From the values reported in Table 1 for the Frumkin interaction parameter, which is a measure of the interaction between the adsorbed molecules at the interface, one can indeed conclude that for the short chain length of the dimethyl-*n*-alkyl phosphine oxide molecule the repulsion prevails (the negative values of the Frumkin interaction parameter), while at long chain lengths ($n_c > 10$) attraction dominates. This is in agreement with our earlier hypothesis about the origin of the increasing limiting adsorption (close to CMC) with the chain length of dimethyl-*n*-alkyl phosphine oxide molecule.

To verify the hypothesis that one component of the repulsive interactions may be due to the packing constraints imposed on the possible conformations of surfactant tails in the adsorbed layer, we applied the models developed in the previous section to describe the experimental data shown in Figure 1. Table 2 illustrates the fitting parameters of the fit of experimental data to the model of adsorption according to eqs 16 and 19, while Table 3 shows the fitting parameters of the model of adsorption described by eqs 17 and 20. In the case of both models, we set constant the value of the maximum adsorption at $\Gamma_\infty = 5.4 \times 10^{-10}$ mol/cm$^2$. That value, according to the data presented in Figure 2, corresponds to a dimethyl-*n*-alkyl phosphine oxide molecule with the chain of 16 carbon atoms. One can expect that a nonionic surfactant with this length of the hydrocarbon chain is insoluble. In this case, $\Gamma_\infty = 5.4 \times 10^{-10}$ mol/cm$^2$ should roughly correspond to the minimal area per molecule attainable upon compression of the monolayer of such surfactant of 0.31 nm$^2$. The latter values correspond to the size of the dimethyl-*n*-alkyl phosphine oxide headgroup when calculated from bond lengths and sizes of atoms in the headgroup.[31] It is important to stress that unlike for the Frumkin isotherm, $\Gamma_\infty$ is no longer the fitting parameter but is a constant for a given homologous series of surfactants and is strictly connected with the size of headgroup $A_{hg}$, common for all members of the series.

Data presented in Tables 2 and 3 show that the fit of the experimental data of the dependence of surface tension of the homologous series of dimethyl-*n*-alkyl phosphine oxide on concentration of surfactant in solution to our theoretical models is much better than fit to the Frumkin isotherm (compare the last columns in Tables 1, 2, and 3). In particular, for dimethyl-*n*-alkyl phosphine oxide molecules with long hydrocarbon chains, the improvement is quite pronounced. This may lead to the conclusion that the adsorption of dimethyl-*n*-alkyl phosphine oxide is much better described by the model that explicitly treats the conformational statistics of the surfactant tails in the adsorbed layer.

The goodness of fit for two adsorption models proposed is comparable for all lengths of hydrocarbon chain of a dimethyl-*n*-alkyl phosphine oxide molecule. The fit to the model described by eqs 16 and 19 slightly better describes the experimental data but at the expense of an additional parameter. So at this stage it is very hard to tell which model describes more adequately the influence of the conformational statistics of hydrocarbon chains of surfactant molecules adsorbed at the air/solution interface.

Figure 4 illustrates the dependence of the conformational Gibbs free energy per molecule on the average area per molecule adsorbed. The results presented in Figure 4 were obtained by computation of the conformational free energy calculated

**TABLE 2. The Same as in Table 1 but the Experimental Data Fitted to the Adsorption Model According to Equations 16 and 19. $\Gamma_\infty = 5.4 \times 10^{-10}$ mol/cm$^2$ Kept Constant**

| $n_c$ | $a$ (mol/dm$^3$) | $RTH_s$ (kJ/mol) | $A_{tr}$ (nm$^2$) | $\sigma_{tr}$ (nm$^2$) | $s$ |
|---|---|---|---|---|---|
| 7 | $2.2 \times 10^{-3} \pm 2 \times 10^{-4}$ | $0.3 \pm 1.0$ | $0.79 \pm 0.05$ | $0.19 \pm 0.03$ | 0.29 |
| 8 | $5.4 \times 10^{-4} \pm 3 \times 10^{-5}$ | $0.2 \pm 0.2$ | $0.8 \pm 0.07$ | $0.31 \pm 0.1$ | 0.43 |
| 9 | $3.0 \times 10^{-4} \pm 3 \times 10^{-5}$ | $1.9 \pm 0.9$ | $0.77 \pm 0.05$ | $0.20 \pm 0.02$ | 0.30 |
| 10 | $9.5 \times 10^{-5} \pm 2 \times 10^{-6}$ | $2.4 \pm 0.3$ | $0.81 \pm 0.06$ | $0.23 \pm 0.02$ | 0.19 |
| 11 | $4.5 \times 10^{-5} \pm 8 \times 10^{-7}$ | $3.9 \pm 0.3$ | $0.79 \pm 0.03$ | $0.17 \pm 0.02$ | 0.18 |
| 12 | $1.5 \times 10^{-5} \pm 2 \times 10^{-6}$ | $4.6 \pm 0.4$ | $0.72 \pm 0.03$ | $0.16 \pm 0.02$ | 0.23 |
| 13 | $7.6 \times 10^{-6} \pm 3 \times 10^{-6}$ | $5.2 \pm 0.5$ | $0.75 \pm 0.03$ | $0.20 \pm 0.03$ | 0.33 |

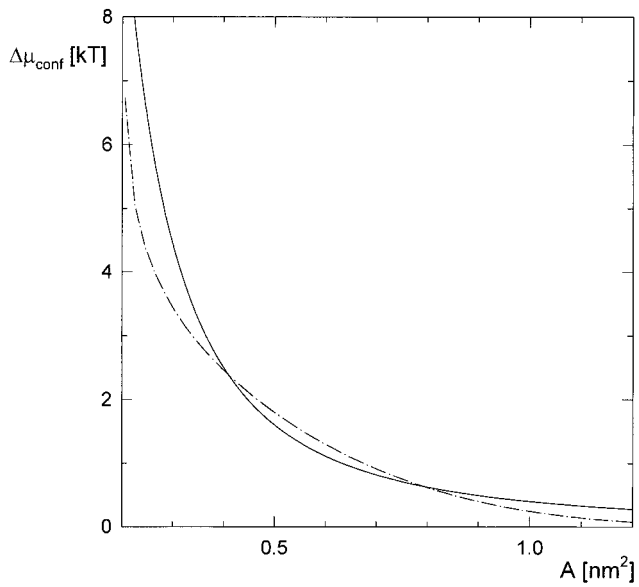


**Figure 4.** The dependence of chain conformational free energy on the area per molecule adsorbed at the interface. Solid line calculated according to eq 7, dash−dotted line computed according to eq 14 for dimethyl decyl phosphine oxide calculated using best fit parameters given in Tables 2 and 3.

**TABLE 3. The Same as in Table 1 but the Experimental Data Fitted to the Adsorption Model According to Equations 17 and 20. $\Gamma_\infty = 5.4 \times 10^{-10}$ mol/cm$^2$ Kept Constant**

| $n_c$ | $a$ (mol/dm$^3$) | $RTH_s$ (kJ/mol) | $RTK_s$ (kJ/mol) | $s$ |
|---|---|---|---|---|
| 7 | $1.8 \times 10^{-3} \pm 3 \times 10^{-4}$ | $-0.8 \pm 0.3$ | $2.4 \pm 0.2$ | 0.30 |
| 8 | $5.4 \times 10^{-4} \pm 1 \times 10^{-5}$ | $0.0 \pm 0.5$ | $3.3 \pm 0.2$ | 0.45 |
| 9 | $1.5 \times 10^{-4} \pm 1 \times 10^{-5}$ | $0.1 \pm 0.7$ | $3.6 \pm 0.5$ | 0.26 |
| 10 | $9.3 \times 10^{-5} \pm 5 \times 10^{-6}$ | $3.3 \pm 0.2$ | $4.9 \pm 0.3$ | 0.24 |
| 11 | $5.0 \times 10^{-5} \pm 1 \times 10^{-6}$ | $7.2 \pm 0.3$ | $6.3 \pm 0.3$ | 0.24 |
| 12 | $1.6 \times 10^{-5} \pm 2 \times 10^{-6}$ | $8.4 \pm 0.6$ | $7.2 \pm 0.4$ | 0.22 |
| 13 | $9.0 \times 10^{-6} \pm 3 \times 10^{-6}$ | $8.5 \pm 0.7$ | $6.2 \pm 0.4$ | 0.38 |

according to eqs 7 and 15 for dimethyl-decyl phosphine oxide using best fit parameters given in Tables 2 and 3. As it is shown in Figure 4, both models give very similar dependence for the conformational free energy. However, for high values of adsorption, i.e., for low average area per molecule, eq 7 predicts higher values for the configurational free energies than does eq 15. This has to be compensated for by higher values of the Frumkin interaction parameter as can be seen in Table 3.

Analyzing the values of the parameters in Table 2, it may be concluded that the distribution of the chain conformations defined by eq 10 and obtained from the fit of the experimental data for the surface tension of dimethyl-*n*-alkyl phosphine oxide does not depend on the chain length. This is in agreement with the similar conclusion obtained by Vold,[26] but more work has to be done to elaborate on this result. The mean of the chain effective area distribution $A_{tr}$ obtained from the fitting procedure is shifted to higher values than reported in ref 26. The most likely reason for this discrepancy is an oversimplification of our treatment of the excluded volume interactions of neighboring chains at the interface. Chains start to feel each other at surface concentrations much lower than those corresponding to the average area per molecule given by $A = 1/N_A\Gamma$. Similarly, as in the case of the hard sphere fluid at the interface (i.e., for hard disks), one molecule blocks an area four times bigger than its geometrical size.[32] Neglecting this phenomenon in the derivation of eq 19 leads to the overestimation of the mean of the chain effective area distribution. More detailed considerations are needed to find a more suitable approximate formula which takes into account the correct area blocking effect by adsorbed chain molecules. Another possible explanation of the shift of the chain conformation distribution is that the real distribution is more skewed toward larger effective areas per molecule than one assumed by eq 10. This tilt is the result of the van der Waals interaction between the chain and aqueous subphase. As it was shown in ref 25 by molecular dynamics calculations, the free hydrocarbon chain likes to assume predominantly flat conformations at the air/solution interface.

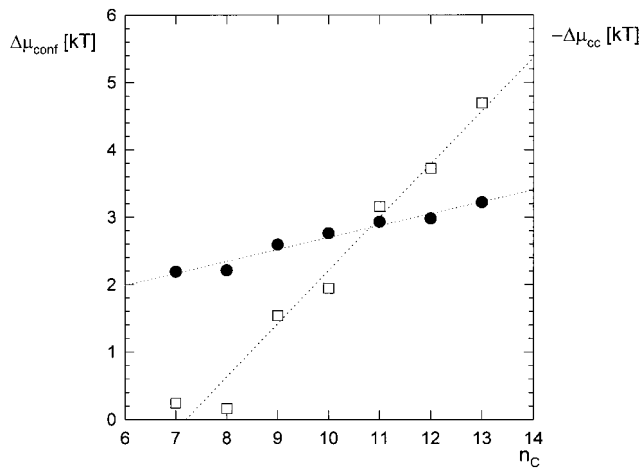


**Figure 5.** Dependence of conformational free energy obtained from eq 15 (solid dots) and cohesive interchain van der Waals free energy from eq 5 (hollow squares) on the number of carbon atoms in the chain, calculated at the same surface tension $\sigma = 35$ mN/m using best fit parameters from Table 2.

Figure 5 illustrates the balance between the conformational free energy calculated according to eq 15 and the van der Waals cohesive free energy obtained from eq 5. The calculations have been performed using best fit parameters given in Table 2 for the same value of surface tension equal to 35 mN/m. For the short hydrocarbon chains, the negative cohesive free energy needed to pack hydrocarbon chains more tightly in the adsorbed layer is to small to overcome the configurational energy, and the overall interactions are repulsive. For long chains, the opposite is true and the attraction between hydrocarbon chains prevails. This is the plausible explanation of the data presented in Table 1 for the values of the Frumkin interaction parameter

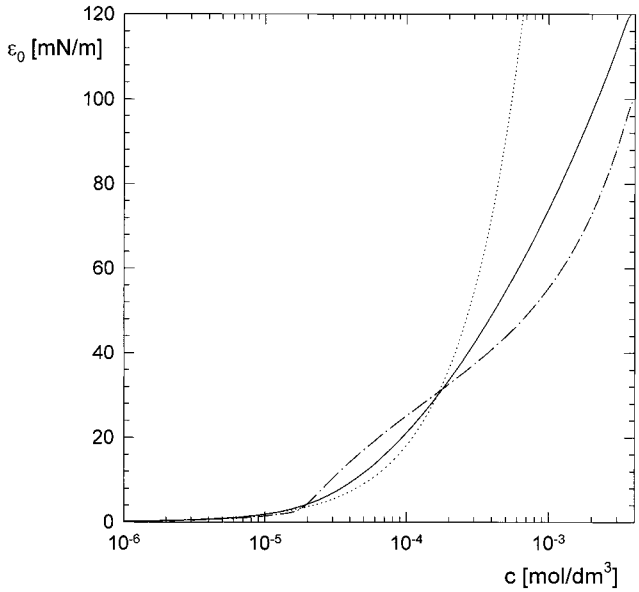


**Figure 6.** Dependence of the surface elasticity modulus for dimethyl decyl phosphine oxide on its concentration in solution, calculated using best fit parameters given in Tables 1−3. Dotted line, according to Frumkin isotherm; dash−dotted line, according to eq 19; and solid line, according to eq 20.

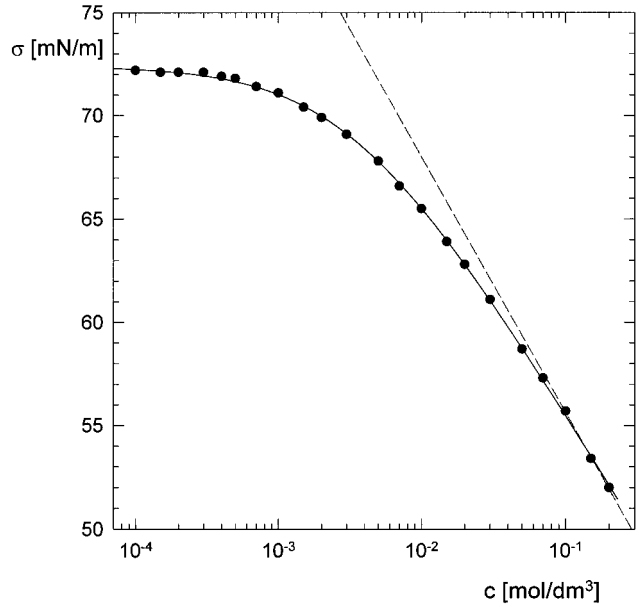


**Figure 7.** Surface tension of tri-isopropyl phosphine oxide as a function of its volume concentration. Dashed lines represent slopes of experimental surface tension vs concentration dependence at the highest concentration studied. Solid line, fit of the Langmuir isotherm with $a = 3.1 \times 10^{-3}$ mol/dm$^3$; $\Gamma_\infty = 2.0 \times 10^{-10}$ mol/cm$^2$. Standard deviation of the fit $s = 0.11$ mN/m.

$H_s$ when the Frumkin model of an adsorption uncorrected for the tails conformational effects is used to describe experimental data.

The conformation statistics of surfactant tails in the adsorbed layer not only influence the equilibrium adsorption properties but can also affect the dynamic properties of soluble surfactant adsorption layers. To demonstrate the influence of conformational effects on the surface elasticity, we calculated the Gibbs elasticity modulus:

$$\epsilon_0 = -\Gamma \frac{d\sigma}{d\Gamma} \tag{23}$$

for dimethyl-decyl phosphine oxide according to the Frumkin model of adsorption and two models proposed in this paper including explicitly the effect of the tails conformational statistics. The results are compared in Figure 6. For high concentrations of the surfactant in solution, our models taking into account conformational effects predict much lower Gibbs elasticity than one estimated from the Frumkin adsorption isotherm (compare solid and dash−dot line with the dotted line in Figure 6). This is in agreement with many experimental results, because high values of the Gibbs elasticity predicted by Frumkin model of an adsorption have been practically never observed in experiment.[33,34] The reason for this effect is that the hard core interactions between molecules of the bigger effective size (lower $\Gamma_\infty$) are replaced by soft quasielastic repulsion due to the restricted conformational freedom of surfactant tails. For intermediate surfactant concentrations, the shape of the relationship between the Gibbs elasticity modulus and surfactant concentration calculated according to the adsorption model described by eqs 16 and 19 closely resembles the dependence for *n*-decanoic acid experimentally observed by J. Earnshow et al.[35] Thus, the influence of the surfactant chain statistic can be a plausible reason for the peculiar behavior of the Gibbs elasticity modulus with increasing concentration of surfactant.

To perform the "blank test" for our hypothesis concerning the influence of the hydrocarbon tails statistics on adsorption, we have also tried to describe in terms of the proposed models the adsorption results for tri-isopropyl phosphine oxide. The shape of this molecule is almost perfectly disklike, and thus the effect of the hydrocarbon chain conformations should be absent. Indeed, the dependence of the surface tension of tri-isopropyl phosphine oxide solution on its concentration, shown in Figure 6, is perfectly described by the Frumkin adsorption isotherm with the interaction parameter $H_s = 0$ (i.e., Langmuir isotherm). The value of limiting adsorption at the highest concentration studied corresponds well to the size of tri-isopropyl phosphine oxide molecule.

## Conclusions

The experimental data for the dependence of surface tension of a homologous series of nonionic surfactants on concentration in solution indicate the presence of some repulsive interactions in the adsorbed layer. We demonstrated that this interaction can be a consequence of the decrease of conformational free energy as hydrocarbon chains become more crowded at the interface. We introduced the simple model taking explicitly into account the conformational free energy in the adsorption isotherm. The resulting isotherm provides a better description of experimental data for the dependence of surface tension of the homologous series of dimethyl-*n*-alkyl phosphine oxides on their concentration in solution than does traditional description in terms of the Frumkin isotherm. It was shown that the conformational free energy at a fixed surface pressure increases linearly with the hydrocarbon chain length. This is in agreement with the results of numerical calculations of the behavior of hydrocarbon chains at the interface. Although our model is certainly oversimplified, it helps to explain also some experimental findings concerning the dynamic behavior of surfactants at interfaces.

**Acknowledgment.** The authors thank Max-Planck-Gesellschaft and Prof. Helmut Möhwald for the support of this work and Prof. A. Pomianowski for helpful discussions.

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