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Particular Behavior of Surface Tension at the Interface between Aqueous Solution of Surfactant and Alkane

Valentin B. Fainerman,[†] Eugene V. Aksenenko,[‡] Alexander V. Makievski,[†] Mykola V. Nikolenko,[§] Aliyar Javadi,[∥,⊥] Emanuel Schneck,[⊥,¶] and Reinhard Miller*[,⊥]

[†]SINTERFACE Technologies, Berlin 12489, Germany

[‡]Institute of Colloid Chemistry and Chemistry of Water, Kyiv (Kiev) 03680, Ukraine

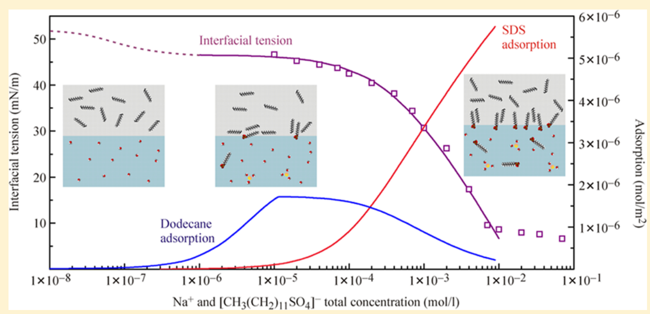
[§]Ukrainian State University of Chemical Technology, Dnipro 49000, Ukraine

[∥]Chemical Engineering Department, University of Tehran, Tehran 1417466191, Iran

[¶]Technische Universität Darmstadt, Darmstadt 64289, Germany

[⊥]Max Planck Institute of Colloids and Interfaces, Potsdam 14476, Germany

ABSTRACT: A two-component interfacial layer model was employed to describe the experimental results obtained for various surfactants. In contrast to the previous works, here it is shown that the adsorption activity of alkane depends on its interaction with the adsorbed surfactant and is proportional to the surface coverage by this surfactant. Also, it is assumed that this increase of the adsorption activity parameter is limited by some maximum value. This model provides a good description of the influence of hexane and dodecane, which results in the decrease of surface tension by 2−5 mN/m at very low surfactant concentrations. The adsorbed amounts of the surfactant and alkane molecules in this low surfactant concentration range have been calculated. The reorientation model of surfactant adsorption predicts a smaller number of alkane molecules per one surfactant molecule than that which follows from the Frumkin model.



■ INTRODUCTION

The adsorption of surfactants at fluid interfaces has been widely investigated for all types of surfactants and their mixtures with polymers or particles. The fundamental as well as practical aspects of surfactant adsorption at liquid/liquid interfaces are already summarized in books.[1−4] During the last 20 years, however, many papers were published in which the adsorption behavior and the dilational visco-elasticity of surfactant solutions at the interface in contact with different oils were discussed. In several works, surfactant adsorption layer properties at the solution/air surface were compared with those of various solution/oil interfaces using classical tensiometry,[5−7] flow-tensiometry,[8] microtensiometry,[9] or neutron reflectivity.[10] In ref 11, for example, ethoxylated alcohols at the water/heptane interface were studied, while different trimethyl alkyl ammonium bromides were investigated at the water/decane interface in ref 12, and at different water/alkane interfaces in ref 5. Also ionic liquids were characterized on oil/water interfaces.[13] Mixtures of surfactants[14−17] and mixtures of particles with surfactants were studied at water/oil interfaces.[18,19] One of the most challenging investigations was the measurement of the mass transfer across water/oil interfaces[20,21] to determine the partitioning coefficient of surfactants between water and the oil phase.[22−24] Based on the theory derived by Lucassen and Van Den Tempel,[25] the dilational rheology of proteins[26] and surfactants,[27] respectively, was determined at the solution/oil interface. The number of papers dedicated to this subject is enormous and, therefore, this can only be a subjective selection. We can only mention here few publications dedicated to practical applications, such as to the interrelations between interfacial tension and emulsion stability,[28] to the preparation of double emulsions,[29] or in the formulation of drug delivery systems.[30]

In many of the mentioned papers, it was clearly shown that the properties of surfactant adsorption layers at the water/air surface are quite different from those measured at water/oil interfaces. This has been commonly interpreted in terms of a penetration of oil molecules into the layer of the alkyl chains of the adsorbed surfactant layers, resulting in a strongly increased adsorption at this interface when compared with the amount of surfactant adsorbed at the water/air surface.

One of the most important problems discussed in our own recent work was the determination of the surfactant's distribution coefficient between the water and oil phases. Different methods can be applied to determine this

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distribution or partitioning coefficient. In ref 31, we used two series of measurements to determine the adsorption isotherm of a surfactant. For this purpose, we studied hexane drops formed in the aqueous surfactant solution and water drops formed in surfactant solutions in hexane. From these two isotherms, it was possible to calculate the distribution coefficient via the ratio of concentrations in water and oil, respectively, at which the interfacial tension was the same. The interfacial tension of alkyl trimethyl ammonium bromides at the water/air and water/oil interfaces was measured in ref 32 and it was found that the adsorption activity at the water/oil interface is essentially higher than that at the water/air interface, in agreement with findings, for example, in refs 5, 22, 26, 27. Moreover, at a very low surfactant concentration, the interfacial tension decreases by several mN/m, which cannot simply be explained by the mentioned increased adsorption activity. This phenomenon was treated in ref 32 in the framework of a theoretical model that assumed the formation of a mixed adsorption layer comprised of surfactant and oil molecules. The contribution of alkane molecules is responsible for the interfacial tension decrease from 51−52 mN/m (which is expected at very low surfactant concentrations) to values of 45−49 mN/m actually observed at these very low concentrations.

In the present work, we use again a thermodynamic model for a two-component interfacial monolayer. In this model, the presence of alkane molecules in the interfacial layer is caused by the interaction with the adsorbed surfactant. The model predicts the influence of alkanes on the decrease of the surface tension from 51−52 mN/m (pure water at the interface with alkane) to 49−45 mN/m at very low surfactant concentration, which is by 2−6 mN/m lower than that of pure water. The adsorbed amounts of alkane and surfactant molecules are also calculated from the model.

■ EXPERIMENTAL SECTION

The interfacial tension measurements were performed with the bubble/drop profile analysis tensiometers PAT-1 and PAT-2P (SINTERFACE Technologies, Germany), as described in detail elsewhere.[33] The dynamic interfacial tension values were measured in the time range from seconds up to the equilibrium of the system at 5 h for higher and 25 h for lower surfactant concentrations. The experimental error of measured values did not exceed ±0.1 mN/m. Although some of the experiments were performed at very low surfactant concentrations, the adsorbed amounts were very small so that a depletion of the surfactant due to adsorption (cf. ref 34) could be neglected.

Tridecyl (C_{13}DMPO) and dodecyl (C_{12}DMPO) dimethyl phosphine oxide were synthesized and purified as described in ref 35. Both samples had a purity of better than 99%. The measurement temperature was kept constant at 25 °C. The hexane for the oil phase was of spectroscopic grade (Labscan, Thailand) with a purity of better than 99% and used as received. All aqueous surfactant solutions were prepared using Milli-Q water having a surface tension of 72.0 ± 0.2 mN/m at 25 °C. This value was constant for up to 20 000 s. Any change of the water/hexane interfacial tension was less than 1 mN/m during a time interval of 70 000 s.

The experiments were performed with the buoyant (sessile) drop mode of PAT. The aqueous C_nDMPO solutions were filled into the measuring cell having a volume of 30 mL. The slightly oblate hexane drops were then formed at the bottom tip of a vertical steel capillary. The internal profile was conical with an inner diameter of 3.0 mm at the tip. The used drops had a surface area between 31 and 34 mm^2, which was kept constant by the PAT software. The initial size of drops was kept at about 21−23 mm^3 in all measurements. The distribution coefficient of C_{13}DMPO in hexane is 30,[31] and therefore the decrease of its concentration in aqueous solution was not more than 2%, which was taken into account when the isotherms were calculated. For C_{12}DMPO, the distribution coefficient is roughly by a factor of 4 lower. Therefore, the reduction of its concentration in aqueous solution did not exceed 0.5%.

■ THEORY

The effect of alkanes on the interfacial tension can be described either by their co-adsorption with surfactants in a mixed adsorption layer or only by adapting the surface layer properties of the surfactant molecules but without considering a co-adsorption of alkane molecules, as it is the case in the classical Frumkin adsorption model. Here, we consider the co-adsorption of alkanes as a mixed interfacial layer with the surfactant molecules, with alkane as component 1 adsorbed from the oil drop and the surfactant as component 2 adsorbed from the aqueous solution in the cuvette. To describe the adsorption process of this system, the approach based on Butler's equation was used following the lines discussed in detail, e.g., in ref 36 (see the Experimental Section therein), as applied to the mixed surface layer model developed in ref 32. It assumes a nonideality of enthalpy and ideality of entropy of the mixed surface layer, which leads to the equation of state

$$-\frac{\Pi\omega_0^*}{RT} = \ln(1 - \theta_1 - \theta_2) + a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2 \tag{1}$$

with

$$\omega_0^* = \frac{\omega_{10}\theta_1 + \omega_{20}\theta_2}{\theta_1 + \theta_2} \tag{2}$$

where the subscript $i = 1$ or 2 refers to the component, the surface pressure $\Pi = \gamma_0 - \gamma$ is the difference between γ and γ_0 being the surface tension of the solution/oil and pure water/oil interfaces, respectively, R and T are the gas law constant and absolute temperature, respectively, the parameter ω_i is the molar area and $\theta_i = \omega_i\Gamma_i$ the surface coverage by the ith component, Γ_i is the adsorption of component i, and ω_{i0} is the corresponding molar area occupied by the adsorbed molecules at zero coverage. The interaction coefficients a_1 and a_2 refer to the molecules of the same component and a_{12} to molecules of different components. In the model, the approximation $\omega_{10} \cong \omega_{20}$ is assumed. For the molar area of component 2, we can assume[32]

$$\omega_2 = \omega_{20}(1 - \varepsilon_2\Pi\theta_2) \tag{3}$$

where ε_2 is the two-dimensional relative surface layer compressibility of surfactant molecules in the surface layer. Equations 1 and 3 are applicable to determine the adsorption of the surfactant and alkane molecules. For the alkane molecules, we used $\varepsilon_1 = 0$, hence $\omega_{10} = \omega_1$.

For alkanes as the oil phase, we obtain the adsorption isotherm as

$$b_1c_1 = \frac{\theta_1}{(1 - \theta_1 - \theta_2)}\exp[-2a_1\theta_1 - 2a_{12}\theta_2] \tag{4}$$

and for the aqueous surfactant solution, the adsorption isotherm has the following form

$$b_2c_2 = \frac{\theta_2}{(1 - \theta_1 - \theta_2)}\exp[-2a_2\theta_2 - 2a_{12}\theta_1] \tag{5}$$

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Here b_1 and b_2 are the surface activity parameters of the two adsorbing components. In this study, in contrast to ref 37, the surface activity of component 1 depends on the adsorption of the surfactant, which is taken into account by the dependence $b_1 = b_{10}\theta_2$. However, this increase of b_1 is limited by a certain maximum value $b_{1,max}$.

Note, the equation of state also proposed in ref 32

$$-\frac{\Pi\omega_0^*}{RT} = \ln(1 - \theta_1 - \theta_2) + \ln(1 - \theta_{01} + \theta_1) + a_1\theta_1^2 + a_2\theta_2^2 + 2a_{12}\theta_1\theta_2 \quad (6)$$

is different from eq 1 and assumes the formation of a secondary layer of alkane molecules. This contributes additively to the surface pressure, as expressed by the second logarithmic term. The total interfacial coverage by the two layers is constant and equal to the maximum monolayer coverage θ_{01} for the case that only alkane molecules form the interfacial layer, i.e., the θ_1 value calculated from eq 4 for θ_2 = 0. However, this approach, similar to the originally proposed model, does not take into account the influence of the surfactant molecules on the interfacial activity of the alkane molecules. This effect, however, is the main issue of the present study.

For some systems, the reorientation model[31] was also used to analyze the data. This model assumes two possible orientations of adsorbed molecules. The corresponding molar areas are marked by the subscripts "min" and "max", with $\omega_{max} > \omega_{min}$. The model accounts for a surface pressure increase at very low surfactant concentrations, irrespective of the adsorption of alkane molecules, leading to the following equation of state

$$-\frac{\Pi\omega_0}{RT} = \ln(1 - \Gamma\omega) + \Gamma(\omega - \omega_0) + a(\Gamma\omega)^2 \quad (7)$$

where $\omega = (\omega_{min}\Gamma_{min} + \omega_{max}\Gamma_{max})/\Gamma$ is the average molar area, the dependence $\omega_{min} = \omega_0(1 - \varepsilon\Pi\theta)$ is assumed to account for the intrinsic compressibility similar to eq 3, $\theta = \omega\Gamma = \omega_{min}\Gamma_{min} + \omega_{max}\Gamma_{max}$ is the surface coverage, and $\Gamma = \Gamma_{min} + \Gamma_{max}$ is the total adsorption. The corresponding adsorption isotherms for components with a minimum and maximum molar area, respectively, read

$$bc = \frac{\Gamma_{min}\omega_0}{(1 - \Gamma\omega)^{\omega_{min}/\omega_0}}\exp\left(-2a\Gamma\omega\frac{\omega_{min}}{\omega_0}\right) \quad (8)$$

$$bc = \frac{\Gamma_{max}\omega_0}{(\omega_{max}/\omega_{min})^{\alpha}(1 - \Gamma\omega)^{\omega_{max}/\omega_0}}\exp\left(-2a\Gamma\omega\frac{\omega_{max}}{\omega_0}\right) \quad (9)$$

The parameter α accounts for the different adsorption activities of molecules in different adsorption states.[31]

■ RESULTS AND DISCUSSION

In Figure 1, the dynamic interfacial tension at the interface between a hexane drop and the surrounding aqueous solution of C_{12}DMPO at several low concentrations is shown. For the solutions with surfactant concentrations of 10^{-9}, 10^{-8}, and 10^{-7} mol/L the interfacial tension is significantly lower than that for the pure water/hexane interface. It can also be noted that for these three concentrations in the range 10^{-9}—10^{-7} mol/L, the interfacial tensions differ only by about 1.5 mN/m.

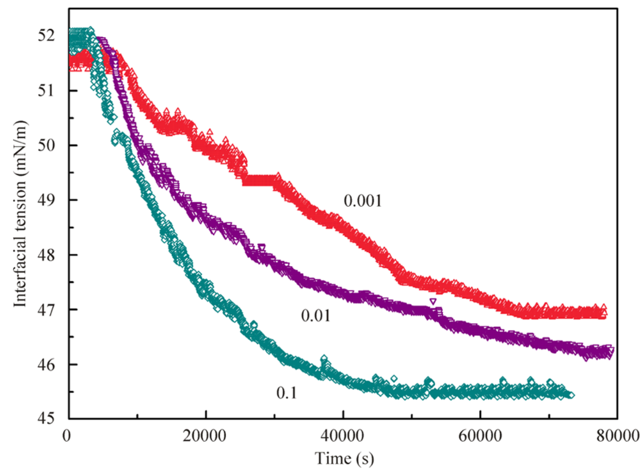

Figure 1. Dynamic interfacial tension for a hexane drop immersed in solutions of C_{12}DMPO in water at different surfactant concentrations; labels are concentrations in μmol/L.

The initial plateaus in this figure (and also in Figure 2) at short times look similar to the so-called dead time observed for protein solutions. During this period of time, the surface tension does not change, although the adsorption of protein molecules proceeds. Only when a critical amount of adsorbed proteins is reached, the tension starts to decrease. In the present study, however, the observed phenomenon is probably related to the high solubility of the investigated surfactants in the oil phase. This leads to an initial depletion of the space close to the interface, and hence to a constant interfacial tension. The lower the surfactant concentration, the longer is this period of time of almost constant interfacial tension.

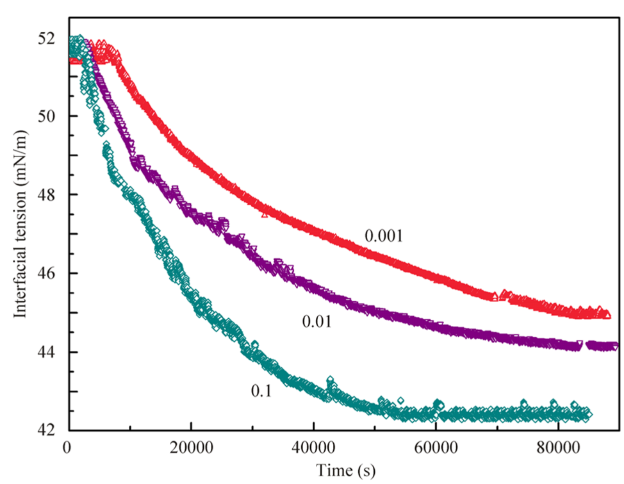

Figure 2. Dynamic interfacial tension for a hexane drop immersed in solutions of C_{13}DMPO in water at different surfactant concentrations; labels are concentrations in μmol/L.

Figure 2 illustrates the results obtained for low concentrations of C_{13}DMPO. While the solubility of C_{13}DMPO in hexane is four times higher than that of C_{12}DMPO (the distribution coefficients are 30 and 7.5, respectively), the kinetic curves shown in Figures 1 and 2 are similar. Due to the higher solubility of C_{13}DMPO in hexane, its adsorption should be much slower. Therefore, we can conclude that the interfacial tension decrease is caused by hexane molecules, rather than by the adsorbing surfactants. Note that for the

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surfactant concentrations above 10^{-6} mol/L, the equilibration rate for C_{13}DMPO solutions is 3−5 times higher than that for C_{12}DMPO solutions, which can be explained by the much higher solubility of C_{13}DMPO in hexane and its desorption into the hexane drop. This situation can be compared with the equilibration process at the surfactant concentration of 10^{-5} mol/L, which requires 10 000 and 3000 s, respectively. The results for various C_{13}DMPO concentrations were reported in ref 31

The equilibrium interfacial tension isotherms of C_{12}DMPO and C_{13}DMPO solutions in water at the interface with hexane are shown in Figure 3. The theoretical curves were calculated

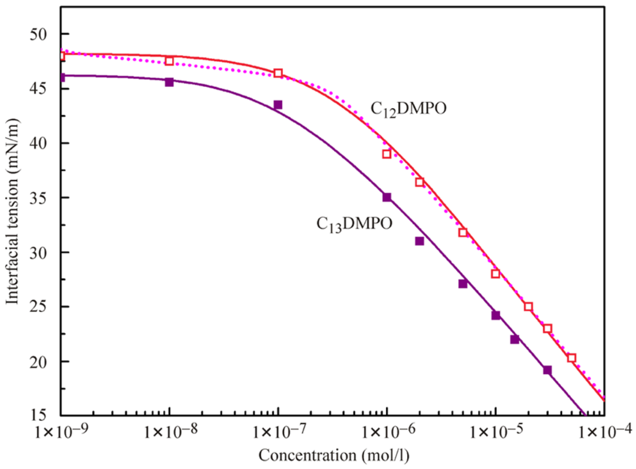

Figure 3. Equilibrium interfacial tensions between a hexane drop formed in solutions of C_{12}DMPO and C_{13}DMPO, respectively, in water at different concentrations; points are experimental data; solid curves are calculations using eqs 1−5; dotted curve-calculation using the reorientation model for the individual C_{12}DMPO solution without considering the hexane adsorption.

for the surfactant/alkane mixtures (solid lines in Figure 3) via the Frumkin adsorption model eqs 1−5 using the parameters summarized in Table 1 and for the individual C_{12}DMPO solutions using the reorientation model eqs 7−9, with the following parameter values: $\omega_{min} = 5 \times 10^5$ m^2/mol, $\omega_{max} = 6 \times 10^6$ m^2/mol, and $\alpha = 4.3$, $b = 9 \times 10^3$ m^3/mol. Although this fitting for the individual C_{12}DMPO solutions appears reasonable, an unrealistically large molar area ω_{max} had to be assumed.

The equilibrium interfacial tension values were estimated from the data shown in Figures 1 and 2 with the consideration of some additional impurity effects (the tensions at the three lowest concentrations were increased by 1 mN/m). The theory is in good agreement with the experimental data. Note, the experimental isotherms can be thus fitted only if the co-adsorption of hexane is involved; the attempts to account for the surfactant adsorption only did not lead to acceptable results for any theoretical model. Although the reorientation model provides a good fitting, the maximum area values thus estimated were unrealistically high (6×10^6 m^2/mol) and by a factor of 5 higher than the physically realistic value. Using the $b_{1,max}$ and b_0 values, it becomes possible to determine the surface coverage by surfactant molecules and the corresponding adsorbed amount. For example, the surface coverage by C_{13}DMPO which corresponds to the point where b becomes equal to $b_{1,max}$ amounts to 0.02.

Figure 4 shows the adsorption of hexane and surfactant as a function of the C_{13}DMPO concentration. At low surfactant

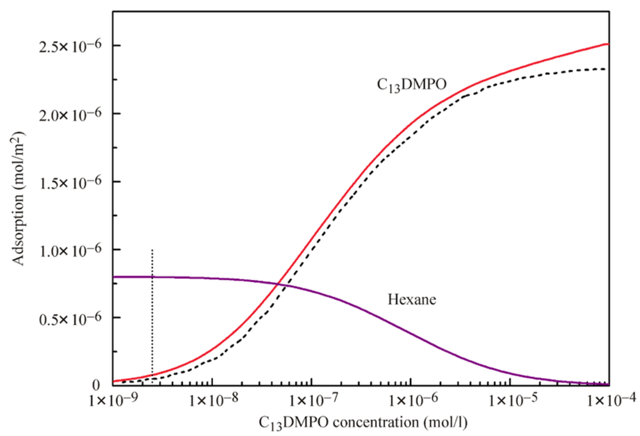

Figure 4. Dependencies of the adsorptions of hexane and surfactant on C_{13}DMPO concentration; the dotted line indicates the concentration at which the hexane adsorption exceeds that of the surfactant by a factor of 10; the dashed line corresponds to the calculated adsorbed amount of C_{13}DMPO using the Gibbs eq 10.

concentrations, hexane adsorption dominates, while at higher surfactant concentrations, the adsorption of the surfactant prevails. The dotted line indicates the concentration at which the hexane adsorption exceeds that of the surfactant by a factor of 10. With increasing C_{13}DMPO concentrations, this ratio becomes lower. The estimations using the reorientation model for the C_{13}DMPO/hexane mixed layers with realistic value for the maximum area per molecule (1.4×10^6 m^2/mol) would yield a much lower value of the adsorption ratio. For C_{13}DMPO molecules orienting the hydrocarbon tail along the interface, this value is more realistic. This problem will be discussed in a subsequent article in more detail.

Table 1. Parameters in Equations 1−5 for the Systems Studied Here

parameters	C_{12}DMPO	C_{13}DMPO	C_{12}TAB	C_{16}TAB	SDS
ω_1, 10^5 m^2/mol	3.3	3.3	3.5	3.5	3.5
$b_{1,max}$, m^3/mol	8×10^{-5}	1.2×10^{-4}	8.0×10^{-5}	5.0×10^{-5}	3.5×10^{-4}
b_{10}, m^3/mol	1.5×10^{-2}	6×10^{-3}	6.5×10^{-3}	5×10^{-3}	1.5×10^{-2}
c_1, mol/m^3	6.8×10^3	6.8×10^3	6.8×10^3	6.8×10^3	4.4×10^3
$\omega_{20,}$ 10^{5m2}/mol	4.3	4.9	4.1	4.3	2.0
b_2, m^3/mol	4.5×10^3	1.9×10^4	5.9×10^1	1.0×10^4	1.8×10^3
a_2	0	0	0	0.7	0.9
ε_2, m/mN	5.0×10^{-3}	5.0×10^{-3}	5.0×10^{-3}	3.0×10^{-3}	5.0×10^{-3}
a_{12}	0.5	0.5	1.0	0.8	0.9

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Similar results can be obtained by considering only the effect of alkanes on the surface activity of the adsorbing surfactants. It can be assumed that the adsorption equilibrium constant of the surfactant is expressed as follows: $b = b_0 + K/c$, where b_0 is the adsorption equilibrium constant of the individual surfactant, c is its bulk concentration, and K is a coefficient which expresses the effect of hexane on the surfactant's surface activity. For example, for C_{13}DMPO, the coefficient K amounts to 1.3. In this case, the theoretical curve in Figure 3 coincides with the experimental data, and the adsorption of C_{13}DMPO is approximately equal to the sum of the adsorptions of the two species (hexane and the surfactant), as shown in Figure 4. For the sake of comparison, we also show the adsorbed amounts of the surfactant calculated from the slope of the interfacial tension curve, using the fundamental adsorption equation of Gibbs

$$\Gamma_2 = -(1/RT)(\mathrm{d}\gamma/\mathrm{d}\ln c_2) \tag{10}$$

This is allowed when we assume that the oil molecules are insoluble in the aqueous phase.[38] The calculated adsorbed amounts agree quite well with those of our model.

Note the essential difference between the interfacial tensions of C_{12}DMPO solutions at the solution/air and solution/hexane interfaces, as illustrated by Figure 5. We can see that the adsorption activity at the interface with liquid hexane is essentially higher.

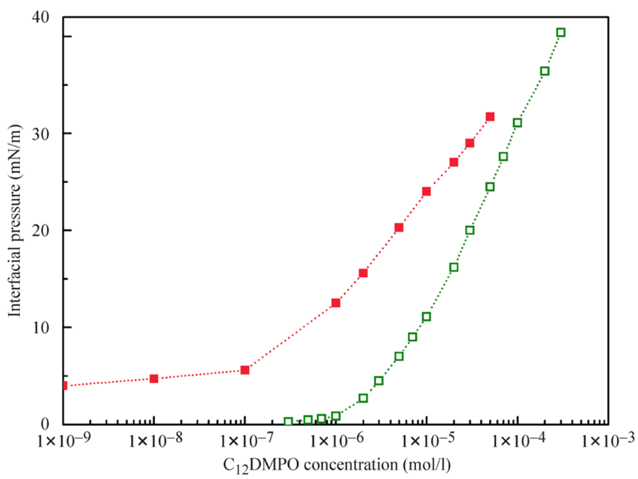

Figure 5. Surface pressure of C_{12}DMPO solutions: □ data for the water/air surface taken from ref 37 and ■ new data for the water/hexane interface; dotted lines are only guides for the eye.

The equilibrium interfacial tension isotherms of dodecyl trimethyl ammonium bromide (C_{12}TAB) and hexadecyl trimethyl ammonium bromide (C_{16}TAB) in 10 mmol/L phosphate buffer at the interface with hexane are shown in Figure 6 (reproduced from ref 32). Note that the Frumkin isotherm with parameters listed in Table 1 can be used by considering properly the presence of electrolyte.[36] A good correspondence between the experimental and calculated values is evident; similar to what was noted previously with regard to Figure 3, this good agreement could be achieved only because the hexane adsorption is taken into account.

Figure 7 illustrates the calculated dependencies of the adsorbed amounts of hexane and the surfactant on the C_{16}TAB concentration. Similar to Figure 4, at low surfactant concentrations, the hexane adsorption exceeds that of the

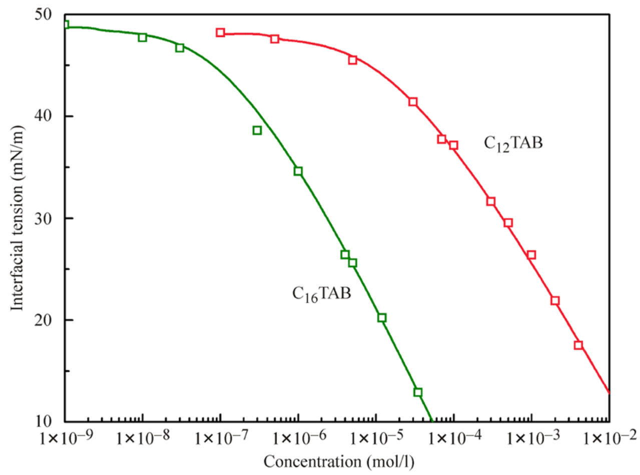

Figure 6. Equilibrium interfacial tension isotherms between a hexane drop and aqueous solutions of C_{12}TAB and C_{16}TAB, respectively, in water at various concentrations; data taken from ref 32; curves are calculated via eqs 1−5 using the parameters listed in Table 1.

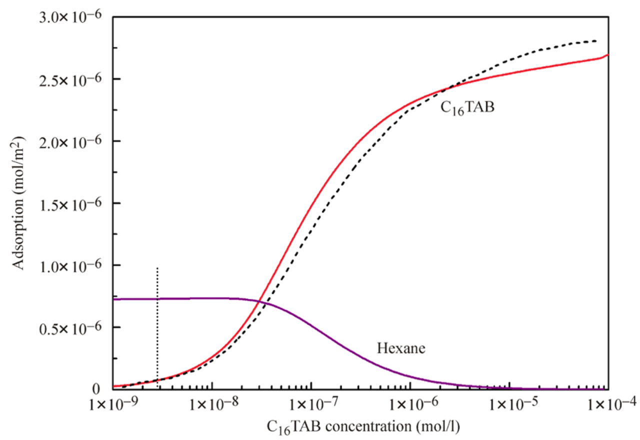

Figure 7. Adsorptions of hexane and the surfactant as a function of the C_{16}TAB concentration; dotted line indicates the concentration at which the hexane adsorption exceeds that of the surfactant by a factor of 10; the dashed line corresponds to the calculated adsorbed amount of C_{16}TAB using the Gibbs eq 10.

surfactant. Also, similar to what was obtained for C_{13}DMPO above, the estimates using the reorientation model result in lower values of the adsorption ratio. The values calculated from the Gibbs equation are again similar to those obtained from our model.

The equilibrium interfacial tension of sodium dodecyl sulfate (SDS) solutions in pure water at the interface with dodecane is shown in Figure 8. The experimental results are similar to those obtained in ref 39 for SDS at the water/hexane interface. In the absence of an electrolyte, the Frumkin adsorption model with the parameters listed in Table 1 is applicable. However, in this case, the Na^+ counter-ion is also adsorbed at the interface from the aqueous SDS solution; it was shown in ref 36 that this could be taken into account by introducing the coefficient 2 into the equation of state. This virtually results in the decrease of the ω_{20} value (which describes both the surfactant ion and counter-ion) by a factor of 2. Note that this does not apply to the solutions of nonionic surfactants because of the presence of large concentrations of inorganic electrolytes; this explains why the SDS solutions exhibit a qualitatively different behavior as

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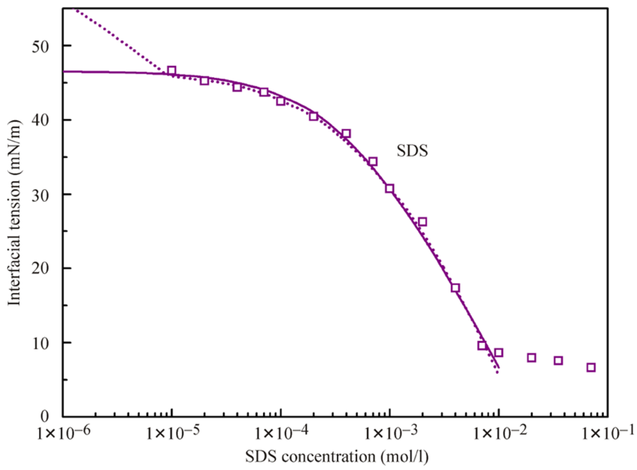

Figure 8. Equilibrium interfacial tension between dodecane and aqueous SDS solutions for different concentrations; the curves are calculated via eqs 1−5 using the parameters given in Table 1; the dotted curve was calculated via eqs 2−6.

compared to other surfactants studied here. It is seen that the calculated values agree very well with the experimental data. The experimental isotherm in Figure 8 can be described either via eqs 1−5 or eqs 2−6 (i. e., using the equation of state (6) instead of eq 1). The results obtained for this case with eqs 2−6 are shown in Figure 8 by the dotted curve.

Figure 9 illustrates the adsorption of dodecane and surfactant ions as a function of the SDS concentration, as

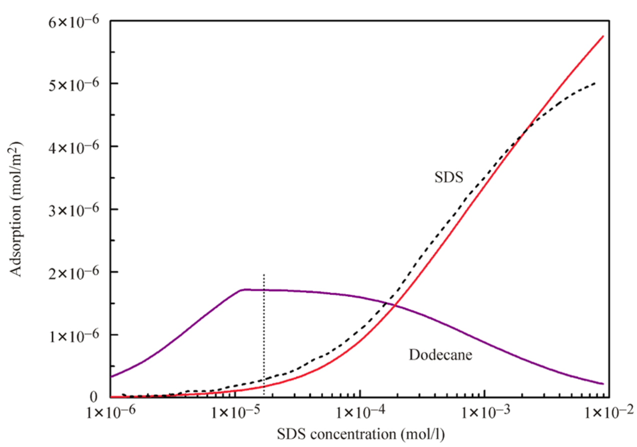

Figure 9. Adsorption of dodecane and SDS ions as a function of the SDS concentration; dotted line indicates the concentration at which the dodecane adsorption exceeds that of SDS by a factor of 10; the dashed line corresponds to the calculated adsorbed amount of SDS using Gibbs eq 10.

calculated using eqs 1−5. Note that the adsorption value, if calculated per SDS molecule, should be by a factor of 2 lower than that plotted in Figure 9, see ref 36. At very low concentrations, the dodecane adsorption exceeds that of the surfactant. In this case also, the values calculated from the Gibbs eq 10 are similar to those obtained from our model.

■ CONCLUSIONS

In many studies on surfactants adsorption at their aqueous solution interface with oil, an unexpected phenomenon was reported—a decreased interfacial tension at very low surfactant concentrations, i.e., 49−45 mN/m instead of 52−51 mN/m. These decreased tensions could not be attributed to the adsorption activity of the surfactant. Previously, this phenomenon was described by the model proposed in ref 32, which takes the co-adsorption of alkane molecules into account.

In the present study, the model of two-component interfacial layers is also employed to describe these experimental results obtained for various surfactants. However, in contrast to previous works, here it is shown that the adsorption activity of alkane molecules (governed by the model parameter b_1) depends on their interaction with the adsorbed surfactant molecules, i.e., is proportional to the surface coverage by these surfactant molecules θ_2, ($b_1 = b_{10} \times \theta_2$). Also, it is assumed that this increase of the adsorption activity parameter is limited by some maximum value $b_{1,max}$. This model is capable of describing much better the influence of hexane and dodecane on the surfactant adsorption, which results in the decrease of the interfacial tension by 2−5 mN/m at very low surfactant concentrations. The adsorbed amounts of the surfactant and alkane in this low surfactant concentration range are determined. The reorientation model for adsorbed surfactant molecules predicts a smaller number of alkane molecules per surfactant molecule than that which follows from the Frumkin model. To determine this number more accurately, the present model will have to be refined and extended by including quantum chemical calculations and other types of molecular simulations.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: miller@mpikg.mpg.de.

ORCID

Emanuel Schneck: 0000-0001-9769-2194

Reinhard Miller: 0000-0001-8943-7521

Notes

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