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ORIGINAL CONTRIBUTION

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Adsorption of sodium octylbenzenesulfonate at the liquid/air interface

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Abstract The surface tensions of aqueous solutions containing sodium octylbenzenesulfonate were measured by means of a processor tensiometer at 20°, 25°, 30° and 35 °C. A test for the layer model and thickness of the adsorbed phase is proposed. By means of a linear regression the surfactant area at liquid/air interface was calculated. Finally, the molar- and surface-related thermodynamic functions were discussed.

Key words Thermodynamics of adsorption – surface tension – surface excess – layer model

Introduction

A number of papers, e.g., [1–4] has dealt with the thermodynamics of adsorption from aqueous surfactant solutions between the bulk phase and the liquid/air interface to characterize the adsorption phase. Usually, the CMC or surface excess values are determined from the surface tensions in dependence on the concentration of surfactant. Beyond it, the aim of this paper is to discuss the different thermodynamic functions which are related to area, molar number of preferentially adsorbed component or of both components, respectively. However, to obtain the molar quantities, we need the absolute values of the adsorbed amount. In order to calculate the mole fraction of the adsorbed phase assumptions must be made about the thickness of the interface. For this purpose a test of monolayer model is proposed. The present results are based on our own measured surface tensions of sodium octylbenzenesulfonate from aqueous solutions.

Theory

The surface concentration excess of component 2 of a binary system between the solid phase, the adsorbed phase and the bulk phase

$$n_2^\sigma = n^0(x_2^0 - x_2) \equiv n_2^{e(n)} , \tag{1}$$

is easily measurable.

n^0 is the total number of moles of the solution, x_2^0 is the initial mole fraction of the preferentially adsorbed component 2 and x_2 is the mole fraction of the bulk phase at equilibrium.

The surface excess of the component two with respect to the area A is given by

$$\Gamma_2^\sigma = n_2^\sigma / A . \tag{2}$$

Using the area related amounts, which are defined by

$$y_A^\sigma = Y^\sigma / A; \quad y = s, h, g, v \tag{3}$$

the total differential of surface tension can be written

$$d\sigma = - s_A^\sigma \, dT + v_A^\sigma \, dp - \Gamma_1^\sigma d\mu_1 - \Gamma_2^\sigma \, d\mu_2 . \tag{4}$$

With $\Gamma_1^\sigma = -\Gamma_2^\sigma$ and the Duhem–Margules expression $d\mu_1 = -\frac{x_2}{x_1} d\mu_2$ at constant pressure and temperature the following expression is obtained

$$\Gamma_2^\sigma = - \frac{x_1}{R\,T} \left(\frac{\partial \sigma}{\partial \ln a_2} \right)_{T,\,p} . \tag{5}$$

Equation (5) is known as the differential kind of the Gibbs adsorption isotherm. For dilute solution the activity can be substituted by the mole fraction. Moreover, by using the approximation $x_1 = 1 - x_2 \simeq 1$ from Eq. (5) the following equation

$$\Gamma_2^\sigma = -\frac{1}{RT}\left(\frac{\partial \sigma}{\partial \ln x_2}\right)_{T,p} \tag{6}$$

is derived (see also [5]). Assumptions must be made about the structure of surface layer at the solution/air interface to calculate the surface composition x_2^s. Frequently, the mole fraction x_2^s is estimated by means of the layer model from the surface excess Γ_2^σ using the expression

$$x_2^s = \frac{\beta \Gamma x_2 + \Gamma_2^\sigma}{\beta \Gamma + (1-\beta)\Gamma_2^\sigma}; \quad \beta = A_2/A_1; \quad \Gamma = t/A_2 \tag{7}$$

in dependence on the number of layers t and the molar areas A_i of both components (see e.g. [6]). Rewriting Eq. (7) by multiplying with A_1, one can obtain

$$x_2^s = \frac{t\,x_2 + \Gamma_2^\sigma A_1}{t + (A_1 - A_2)\Gamma_2^\sigma}. \tag{8}$$

While in the case of water A_1 can be approximately estimated, the value A_2 for the surfactant is dependent on the concentration of solution and connected with the orientation of the molecules near the surface. Therefore, to calculate the mole fraction of the adsorbed phase Eq. (8) was not used, but the following way was chosen using only the molar area of water:

Starting from the equilibrium conditions of the chemical potential of water between the bulk phase and the surface phase

$$d\mu_1 = d\mu_1^s \tag{9}$$

the mole fraction of mixtures x_1^s yields

$$x_1^s = x_1 \exp\left[\frac{A_1(\sigma - \sigma_{01})}{RT}\right]. \tag{10}$$

This equation is only correct for a two-dimensional interface layer, ideal behavior of the bulk and the adsorbed phase. It is obtained from the IAS-theory (ideal adsorption solution theory) given by Myers and Prausnitz [7] and Radtke and Prausnitz [8]. Using osmometric method to measure the mixture of water/Na-*p*-octylbenzenesulfonate Fleig [9] has shown that the activity coefficients of the components in the bulk phase are nearly one within the premicellar concentration range. The activity coefficients in Eq. (9) were taken into consideration, for example, by Butler [10], Everett [11] and Rusanov [12]. One can also formulate Eq. (10) for the component two and obtain (compare [13]) from both equations the following expression

$$\sigma_{01} - \sigma_{02} = \frac{RT}{A_1}\ln\frac{x_2^s}{x_2} - \frac{RT}{A_2}\ln\frac{x_1^s}{x_1}. \tag{11}$$

Equation (11) is usually used with the simple assumption $A_1 = A_2 = \bar{A}$ [14]. But in our case we have to take into consideration the different surface areas of both components. Furthermore, the surface tension σ_{02} of the surfactant is unknown.

As a result, if the mole fraction of the adsorbed phase was determined, the surface capacities Γ_1^s, Γ_2^s and $\Gamma^s = \Gamma_1^s + \Gamma_2^s$ can be calculated from

$$\Gamma_2^\sigma = \Gamma_2^s x_1 - \Gamma_1^s x_2 = \Gamma^s (x_2^s - x_2), \tag{12}$$

using only the mole fractions of bulk phase, adsorbed phase and the surface excess.

Area of surfactant

Linearization of Eq. (8) leads to

$$\begin{aligned} t\,\frac{x_2^s - x_2}{\Gamma_2^\sigma} &= A_1 - x_2^s(A_1 - A_2) \\ &= A_2 + x_1^s(A_1 - A_2) = \bar{A}. \end{aligned} \tag{13}$$

At first it is possible to calculate the mole fraction x_1^s from Eq. (10). Secondly the surface excess can be determined from the following equation

$$\Gamma_2^\sigma = -\frac{x_1}{\nu RT}\left(\frac{\partial \sigma}{\partial \ln x_2}\right)_{T,p} \tag{14}$$

for ionic surfactants with $\nu = 2$. Then it is possible to calculate the left side of Eq. (13), if the thickness of the adsorbed phase t is given. It is taken that $t = 1$. Thus the linearity of Eq. (13) can be proved. From the slope and the intercept A_2 can be determined using linear regression method. If the linearity of Eq. (13) is not valid, then the molar area of the surfactant A_2 can be calculated in dependence on the concentration of the adsorption phase.

Figure 1 shows the monolayer test for further water/surfactant systems [15, 16]. As it is seen from Fig. 1, in the case of Na-cumolsulfonate we cannot observe a straight line for the plot of $\Gamma^{-1} = \bar{A}$ in dependence of x_2^s, therefore we cannot assume a monolayer. The physical properties of Na-cumolsulfonate are not typical for a surfactant. For example, it possesses, in comparison to other alkylarylsulfonates [17] with longer alkyl chains, a high critical micelle concentration of $x_2 = 1.64\ 10^{-3}$ [15].

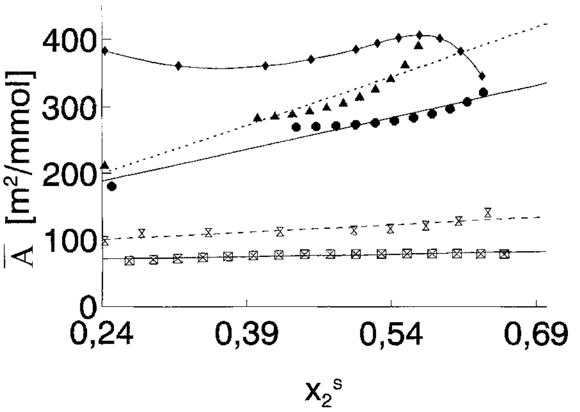

Fig. 1 Test of monolayer in premicellar concentration range for binary aqueous solutions with: ●: sodium dodecylsulfate at 25 °C, ▲: sodium dodecylsulfate at 20 °C, ⧖: dodecyldimethylamineoxide, ⊠: ammonium pentadecyle-l-sulfonate, ◆: sodium cumolsulfonate

Thermodynamic functions with respect to area and molar numbers

At constant pressure and constant mole fraction of the bulk phase the temperature dependence of surface tension (see Eq. (4)) is given by

$$\left(\frac{\partial\sigma}{\partial T}\right)_{p,x_2} = -s_A^\sigma - \Gamma_1^\sigma s_1 - \Gamma_2^\sigma s_2 = -s_A^\sigma - \Gamma_2^\sigma(s_2 - s_1) \equiv -\Delta s_A^\sigma\,, \tag{15}$$

where s_1 and s_2 are the partial molar entropies of the components of the bulk phase, respectively, and s_A^σ is the entropy of adsorption phase with respect to the area of the interface (compare with Eq. (3)). Δs_A^σ is the change of excess entropy caused by the adsorption process. The corresponding enthalpy Δh_A^σ is obtained by means of the Gibbs–Helmholtz equation

$$\Delta h_A^\sigma = \Delta g_A^\sigma + T\Delta s_A^\sigma = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_{p,x_2}\,, \tag{16}$$

with the change of the Gibbs free excess energy

$$\Delta g_A^\sigma \equiv \sigma\,. \tag{17}$$

If the whole heterogeneous system is divided into two phases: the bulk and the sorption phase, respectively, then quantities for the sorption phase with respect to the area of the solution can be introduced. Instead of Eqs. (3), (16) and (17) the following expressions are obtained

$$y_A^s = Y^s/A; \quad y = s, h, g, v\,, \tag{18}$$

$$\left(\frac{\partial\sigma}{\partial T}\right)_{p,x_2} = -s_A^s - \Gamma_1^s s_1 - \Gamma_2^s s_2 \equiv -\Delta s_A^s\,, \tag{19}$$

$$\Delta h_A^s = \Delta g_A^s + T\,\Delta s_A^s = \sigma - T\left(\frac{\partial\sigma}{\partial T}\right)_{p,x_2}\,. \tag{20}$$

Using the well known relation between extensive thermodynamic excess and absolute values

$$Y^s = Y^\sigma - n_2^\sigma(y_2 - y_1) + n_1^s y_1 + n_2^s y_2\,, \tag{21}$$

it is easy to show the validity of the following relation

$$\Delta y_A^\sigma \equiv \Delta y_A^s; \quad y = s, h, g, v\,, \tag{22}$$

where n_2^σ is the excess mole number of the second component, n_1^s, n_2^s and y_1, y_2 are the absolute mole numbers of both components in the adsorption phase and the partial molar quantities of the two components in the bulk phase, respectively.

In [18] the calculated heats of sodium dodecylsulfate from aqueous solutions at the interface liquid/air

$$\Delta h_A^\pi = \pi - T\left(\frac{\partial\pi}{\partial T}\right)_{p,x_2}; \quad \pi = \sigma - \sigma_{01}\,, \tag{23}$$

were compared with those obtained from temperature dependence of adsorption isotherms onto an activated carbon and directly measured heats of displacement by means of a flow calorimeter. σ_{01} in Eq. (23) is the surface tension of the pure first component. In this paper we are interested not only in the physical meaning of the thermodynamic functions with respect to the area, but also with respect to the mole numbers of the adsorption phase. The last values can be defined on one hand by

$$\begin{aligned}\Delta y_{\mathrm{mol}}^s &= \Delta y_A^\sigma/\Gamma^s \equiv y_A^\sigma/\Gamma^s - \Gamma_2^\sigma(y_2 - y_1)/\Gamma^s\\ &= Y^\sigma/n^s - n_2^\sigma(y_2 - y_1)/n^s; \quad y = s, h, g, v\,,\end{aligned} \tag{24}$$

where $n^s = n_1^s + n_2^s$ is the total absolute mole number of both components in the adsorption phase, and on the other hand by

$$\begin{aligned}\Delta y_{\mathrm{mol},2}^s &\equiv \Delta y_A^\sigma/\Gamma_2^s \equiv y_A^\sigma/\Gamma_2^s - \Gamma_2^\sigma(y_2 - y_1)/\Gamma_2^s\\ &= Y^\sigma/n_2^s - n_2^\sigma(y_2 - y_1)/n_2^s; \quad y = s, h, g, v\,.\end{aligned} \tag{25}$$

The previous expression is equal to the thermodynamic amounts of an integral value like the integral enthalpy of solution.

As a result of using the relations (21) and (22) the following expressions are obtained instead of (24) and (25)

$$\begin{aligned}\Delta y_{\mathrm{mol}}^s &\equiv \Delta y_A^s/\Gamma^s \equiv y_A^s/\Gamma^s - (\Gamma_1^s y_1 + \Gamma_2^s y_2)/\Gamma^s\\ &= Y^s/n^s - x_1^s y_1 - x_2^s y_2; \quad y = s, h, g, v\,,\end{aligned} \tag{26}$$

$$\begin{aligned}\Delta y_{\mathrm{mol},2}^s &\equiv \Delta y_A^s/\Gamma_2^s \equiv y_A^s/\Gamma_2^s - \Gamma_1^s y_2/\Gamma_2^s - y_2\\ &= Y^s/n_2^s - x_1^s y_1/x_2^s - y_2; \quad y = s, h, g, v\,.\end{aligned} \tag{27}$$

From (21), (22) and (24), (25) the relation

$$\Delta y^{s}_{\mathrm{mol}} \equiv x^{s}_{2} \Delta y^{s}_{\mathrm{mol},2} \tag{28}$$

is obtained.

Furthermore, it will be shown that by using the Gibbs–Helmholtz equation new thermodynamic quantities are derived, because Γ^{s} and Γ^{s}_{2} are dependent on temperature. These new quantities are defined as

$$\Delta s^{s*}_{\mathrm{mol}} = -[\partial(\sigma/\Gamma^{s})/\partial T]_{p,x_2} \tag{29}$$

$$\Delta s^{s*}_{\mathrm{mol},2} = -[\partial(\sigma/\Gamma^{s}_{2})/\partial T]_{p,x_2} \tag{30}$$

$$\Delta h^{s*}_{\mathrm{mol}} = [\partial(\sigma/\Gamma^{s}/T)/\partial(1/T)]_{p,x_2} \tag{31}$$

$$\Delta h^{s*}_{\mathrm{mol},2} = [\partial(\sigma/\Gamma^{s}_{2}/T)/\partial(1/T)]_{p,x_2} \,. \tag{32}$$

Therefore, the following expressions

$$\begin{aligned}\Delta s^{s*}_{\mathrm{mol}} &= -[\partial\sigma/\partial T]_{p,x_2}/\Gamma^{s} + (\partial \ln \Gamma^{s}/\partial T)_{p,x_2}\,\sigma/\Gamma^{s}\\ &= \Delta s^{s}_{\mathrm{mol}} + \Delta g^{s}_{\mathrm{mol}}(\partial \ln \Gamma^{s}/\partial T)_{p,x_2}\end{aligned} \tag{33}$$

$$\begin{aligned}\Delta h^{s*}_{\mathrm{mol}} &= -T[\partial\sigma/\partial T]_{p,x_2}/\Gamma^{s} + \sigma/\Gamma^{s} + T(\partial \ln \Gamma^{s}/\partial T)_{p,x_2}\,\sigma/\Gamma^{s}\\ &= T\,\Delta s^{s}_{\mathrm{mol}} + \Delta g^{s}_{\mathrm{mol}} + T\,\Delta g^{s}_{\mathrm{mol}}(\partial \ln \Gamma^{s}/\partial T)_{p,x_2}\\ &= \Delta h^{s}_{\mathrm{mol}} + T\,\Delta g^{s}_{\mathrm{mol}}(\partial \ln \Gamma^{s}/\partial T)_{p,x_2}\end{aligned} \tag{34}$$

are valid. From the last relations the next two equations can be derived

$$\Delta g^{s*}_{\mathrm{mol}} \equiv \Delta g^{s}_{\mathrm{mol}} \tag{35}$$

$$\Delta h^{s*}_{\mathrm{mol}} - T\,\Delta s^{s*}_{\mathrm{mol}} \equiv \Delta h^{s}_{\mathrm{mol}} - T\,\Delta s^{s}_{\mathrm{mol}} \,, \tag{36}$$

and also

$$\Delta s^{s*}_{\mathrm{mol}} - \Delta s^{s}_{\mathrm{mol}} = \Delta g^{s}_{\mathrm{mol}}(\partial \ln \Gamma^{s}/\partial T)_{p,x_2} \tag{37}$$

$$\Delta h^{s*}_{\mathrm{mol}} - \Delta h^{s}_{\mathrm{mol}} = T\,\Delta g^{s}_{\mathrm{mol}}(\partial \ln \Gamma^{s}/\partial T)_{p,x_2} \,. \tag{38}$$

Analogous equations can be obtained in the case of the quantities $\Delta s^{s*}_{\mathrm{mol},2}$ and $\Delta h^{s*}_{\mathrm{mol},2}$.

As a consequence the differences $(\Delta y^{s*}_{\mathrm{mol}} - x_2 \Delta s^{s}_{\mathrm{mol},2})$ with the exception of $y \equiv g$ are no longer zero (compare Eq. (28)), however the following two equations

$$\Delta s^{s*}_{\mathrm{mol}} - x^{s}_{2}\,\Delta s^{s*}_{\mathrm{mol},2} = -\Delta g^{s}_{\mathrm{mol}}\left(\frac{\partial \ln x^{s}_{2}}{\partial T}\right)_{p,x_2} \tag{39}$$

$$\Delta h^{s*}_{\mathrm{mol}} - x^{s}_{2}\,\Delta h^{s}_{\mathrm{mol},2} = T(\Delta s^{s*}_{\mathrm{mol}} - x^{s}_{2}\Delta s^{s*}_{\mathrm{mol},2}) \tag{40}$$

are valid.

Experimental

The surface tensions of the aqueous surfactant solution were determined using a Krüss K12 processor tensiometer. The measurements of mixtures containing surfactant required especially very clean experimental conditions. Starting with a concentrated solution, we repeatedly diluted the initial mixtures up to very small mole fractions of the surfactant. The surface tension was given by the simple relation

$$\sigma \cos\theta = \frac{F_w}{1} \,, \tag{41}$$

whereby θ is zero using the roughened plation plate. F_w is the so-called Wilhelmy force and 1 is the round of wetted plate. (A paper is in preparation in which we want to report about measured contact angle of the surfactant solutions onto Teflon and glass, where θ is not equal to zero.)

A mathematical–statistical approach about the errors of measurements for this method was given in [19].

Results and Discussion

In Fig. 2a the surface tensions of aqueous solutions containing sodium octylbenzenesulfonate are plotted in dependence on the mole fraction of the bulk phase x_2 at different temperatures. At 25 °C we obtained a CMC value of $x_2 = 1.34\ 10^{-4}$. From literature values for CMC of $x_2 = 1.13\ 10^{-4}$/20/, $2.65\ 10^{-4}$ [21] and $1.87\ 10^{-4}$ [9] are reported. At 30 °C a minimum can be observed within the temperature dependence of surface tensions.

Some polynomes were proposed in the literature to approximate the surface tensions as a function of mole fraction of the bulk phase. Kiraly and Dekany [22] suggest the following expression

$$\sigma - \sigma_{01} = a \ln[1 + b x_2] + \sum_{i} c_i x^{i} \,. \tag{42}$$

This equation is not useful for our problem, because it has the wrong property to oscillate. Therefore, the first derivation of the surface tension according to Eq. (14) can contain large random errors.

The equation

$$\sigma - \sigma_{01} = RT\Gamma_{\infty} \ln\left[1 - \frac{\Gamma}{\Gamma_{\infty}} - a\left(\frac{\Gamma^{2}}{\Gamma_{\infty}}\right)\right] , \tag{43}$$

presented by Frumkin [23] contains the total amount of adsorption Γ, but we need a function in dependence of mole fraction of the bulk phase.

Therefore the following expression is used

$$\sigma = a + x_2[b \ln x_2 + c \ln(2x_2) + d \ln(3x_2)] + e x_2^{1/2} \,. \tag{44}$$

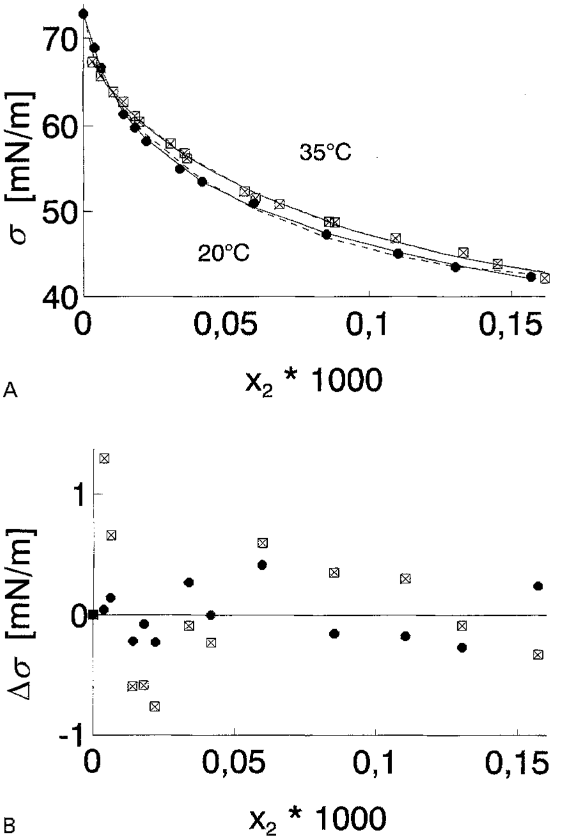

Fig. 2A Surface tensions of aqueous solutions of sodium octylbenzenesulfonate in dependence on the mole fraction x_2 at the temperatures 20 °C (●) and 35 °C (⊠) and calculated surface tensions using Eq. (44) (lines); **B** Residuals $\sigma - \sigma_{\mathrm{calc}}$ with the fitted parameter a (●) and with $a = \sigma_{01}$ (⊠)

Then the surface excess values were calculated from the slope of the surface tensions according to Eq. (14). That leads to the relation

$$\Gamma_2^\sigma = -\frac{x_1 x_2}{v_2 R T}\left\{[b \ln x_2 + c \ln(2x_2) + d \ln(3x_2) + b + c + d] + \frac{1}{2} e x_2^{-1/2}\right\}, \qquad (45)$$

with the assumption that the activity coefficient $f_2 = 1$ [9].

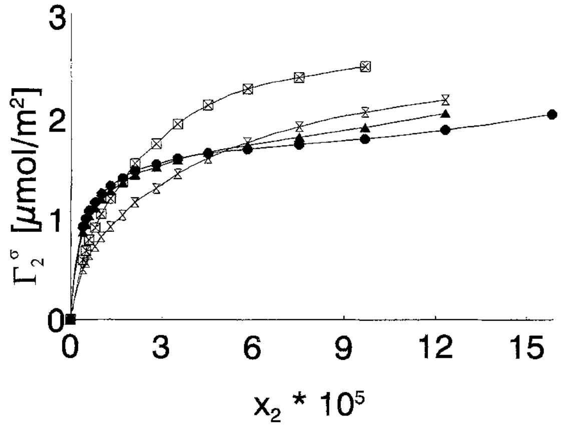

Fig. 3 Surface excess values of sodium octylbenzenesulfonate from aqueous solution at liquid/air interface at the temperatures ● : 20 °C, ▲: 25 °C, ⊠: 30 °C, ⧗: 35 °C

From Eqs. (44) and (45) for $x_2 \Rightarrow 0$ follows $\sigma = a$ and $\Gamma_2^\sigma = 0$. According to the phase separation model for micelle formation of ionic surfactants the value 2 is assumed to the correction factor v_2. The parameters of Eq. (44) are summarized in Table 1. To test Eq. (44) the approximated surface tensions are shown in Fig. 2a. In case of the interrupted line the parameter a of Eq. (44) is fixed by the experimental value of water surface tension ($a = \sigma_{01}$). In case of the dotted line the parameter a is fitted (see Table 1). For further calculations the last variant is preferred, because the residuals within the concentration range are smaller (see Fig. 2b).

Figure 3 shows the surface excess values in dependence on concentration and temperature. The deviation of the constant a in Table 1 from the surface tension of pure water can be due to numerical problems by fitting the surface tensions of solutions. In this paper it is postulated that the molar area of water A_1 is the same in the bulk as well as in the adsorption phase assuming a spherical form of water molecule according to $A_1 = \pi r^2 N_{\mathrm{A}}$. Substituting r^2 by the volume of the molecule results in

$$A_1 = (3/4)^{2/3} \pi^{1/3} V_1^{2/3} N_{\mathrm{A}}^{1/3} = 1.208\ 10^8\ V_1^{2/3}\ . \qquad (46)$$

Table 1 Parameter of Eqs. (44) and (45) for water (1)/sodium octylbenzenesulfonate (2)

T	a	b	c	d	e
20 °C	80.6758	7.6291E6	− 1.9003E7	1.1238E7	− 7721.0
25 °C	78.1781	− 4.6956E5	2.3087E6	− 1.9306E6	− 6548.7
30 °C	72.1378	− 9.8790E5	1.1568E6	− 7.7888E4	− 1833.6
35 °C	72.2856	− 2.1636E5	2.3395E5	1.8983	− 2519.4

Further expressions to calculate the molar surface area of pure component 1 are given in the literature, e.g.,

– for spherical-shaped molecules [24]

$$A_1 = V_1^{2/3} N_A^{1/3} \tag{47}$$

– for rhombic molecules [25]

$$A_1 = 2^{1/3} V_1^{2/3} N_A^{1/3} = 1.64\,10^8\,V_1^{2/3} \tag{48}$$

– for spherical molecules, where the effective surface area is represented by the cross-sectional area [26]

$$A_1 = 1.021\,10^8\,V_c^{6/15}\,V^{4/15}\,, \tag{49}$$

whereby the critical molar volume V_c and the bulk liquid molar volume V are required.

Using only the surface area of water by means of Eqs. (46) and (10) the mole fractions x_1^s and x_2^s were determined. It must be mentioned that all calculated values are represented up to the CMC. In order to use Eq. (8) the area of surfactant A_2 is needed, too. The previous expressions (46) to (49) are not suitable to calculate the surfactant area. It is known that the hydrophilic group of the surfactant, as a statistical average, is oriented to the aqueous phase and the hydrophobic tail is opposite to it. In dependence on decreasing surfactant concentration, it is possible that the orientation is a stepwise process. Near the CMC the effective surfactant area is the smallest. But in many cases for surfactants with long chains the assumption of a monolayer model is correct. Figure 4 shows a plot of $(x_2^s - x_2)/\Gamma_2^\sigma$ against the mole fraction of adsorption phase x_1^s. This plot shows that the assumption of a monolayer ($t = 1$) is meaningful. The surfactant area was also calculated from the slope as well as from the ordinate intercept (see Table 2). Moreover, the dependence of surfactant area on concentration was computed using Eq. (13) (see Fig. 5). In the case of surfactants, which do not form a monolayer at interface, for example, some alkylsulfon-

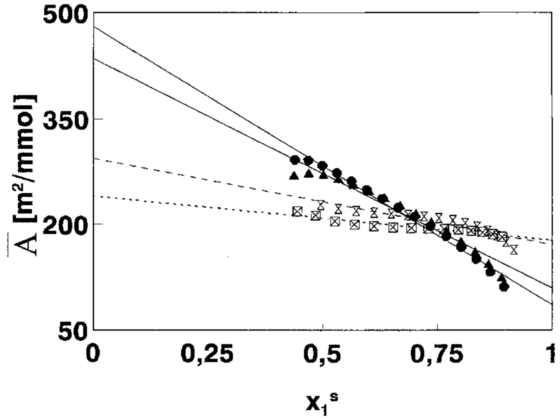

Fig. 4 Test of monolayer model according to Eq. (12) for sodium octylbenzenesulfonate at 20 °C: ●, 25 °C: ▲, 30 °C: ⊠ and 35 °C: x The function $\bar{A} = t(x_2^s - x_2)/\Gamma_2^\sigma$ is presented on the ordinate for $t = 1$

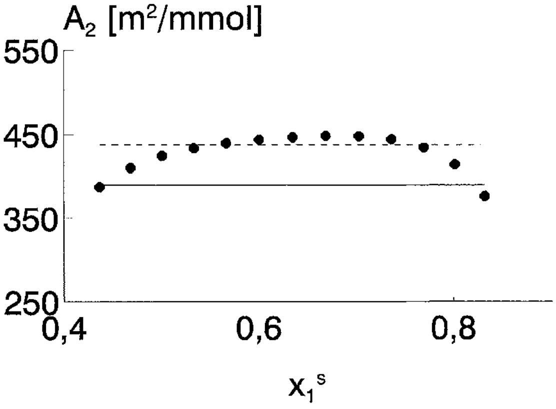

Fig. 5 Surface area of sodium octylbenzenesulfonate in dependence on the mole fraction in the surface phase x_1^s at 25 °C. Calculated values of A_2: ● from Eq. (12), ---- from the ordinate intercept, —— from the slope

Table 2 Surface area of sodium octylbenzenesulfonate molecule in aqueous solution (nm²) at various assumptions for the area of surface water molecules: 1: from ordinate intercept, 2: from slope, 3: average

Assumption for water molecule		20 °C	25 °C	30 °C	35 °C
this paper	1	0.7697	0.7211	0.3994	0.4865
	2	0.7329	0.6537	0.2210	0.3183
	3	0.7513	0.6874	0.3102	0.4024
[25]	1	0.7726	0.7247	0.4038	0.4913
	2	0.7343	0.6544	0.2176	0.3159
	3	0.7535	0.6894	0.3107	0.4036
[24]	1	0.7526	0.7066	0.3805	0.4664
	2	0.7266	0.6504	0.2340	0.3275
	3	0.7421	0.6785	0.3073	0.3969
[26]	1	0.8050	0.7634	0.4554	0.5476
	2	0.7489	0.6591	0.1683	0.2804
	3	0.7770	0.7113	0.3118	0.4136

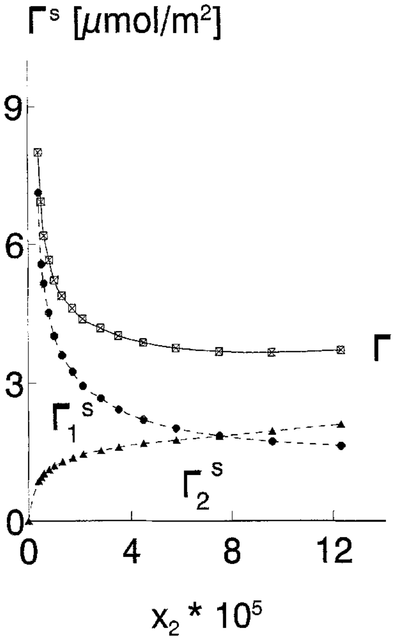

Fig. 6 The absolute surface capacities Γ_1^s, Γ_2^s of water and sodium octylbenzenesulfonate and total amount Γ^s of adsorption at liquid/air interface at 25 °C

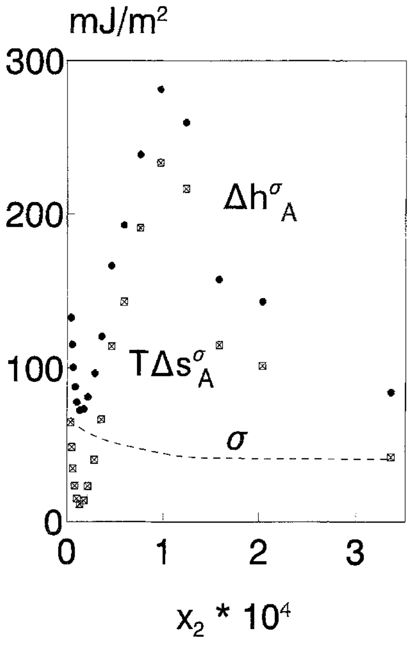

Fig. 7 Thermodynamic functions σ (– – –), Δh_A^σ (●) and $T\,\Delta s_A^\sigma$ (⊠) of sodium octylbenzenesulfonate at 25 °C with respect to the area in dependence on the mole fraction of the bulk phase

ates [16], it is necessary to vary t in Eq. (8) or to introduce expressions for A_1 and A_2 in dependence on concentration. In Fig. 6 the individual absolute values Γ_1^s and Γ_2^s together with the total amounts Γ^s are represented.

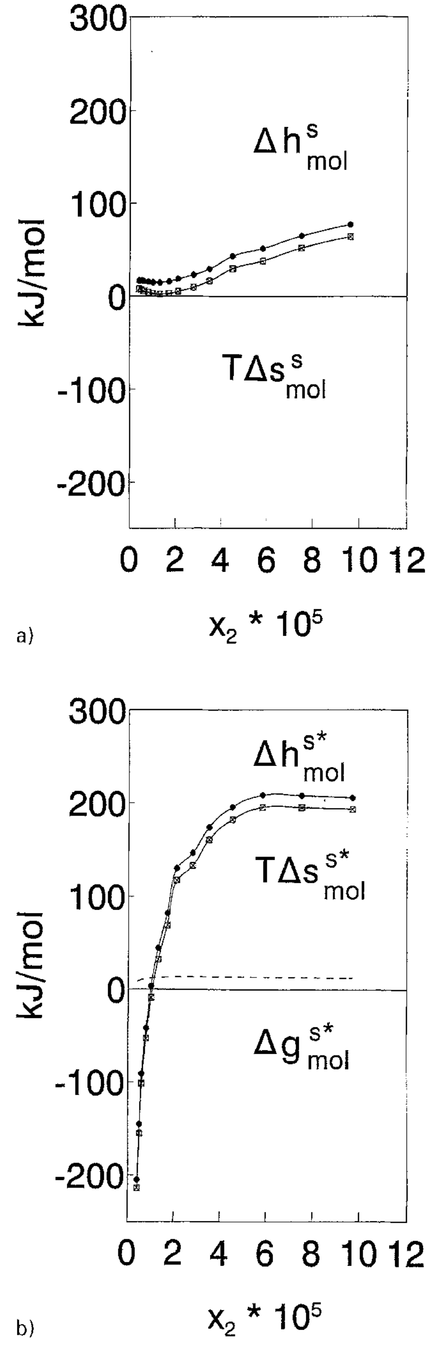

Fig. 8 Thermodynamic functions Δg_{mol}^s, Δh_{mol}^s (●), $T\,\Delta s_{mol}^s$ (⊠) (8a) and Δg_{mol}^{s*} (– – –), Δh_{mol}^{s*} (●), $T\,\Delta s_{mol}^{s*}$ (⊠) (8b) of sodium octylbenzenesulfonate at liquid/air interface vs. x_2 with respect to the total molar number at 25 °C

In Figs. 7 to 9 the thermodynamic functions with respect to the area and the mole numbers are plotted. In each case the small amounts of Gibbs free energy are remarkable in comparison to the enthalpy and the entropy. Thus the preferential adsorption of sodium

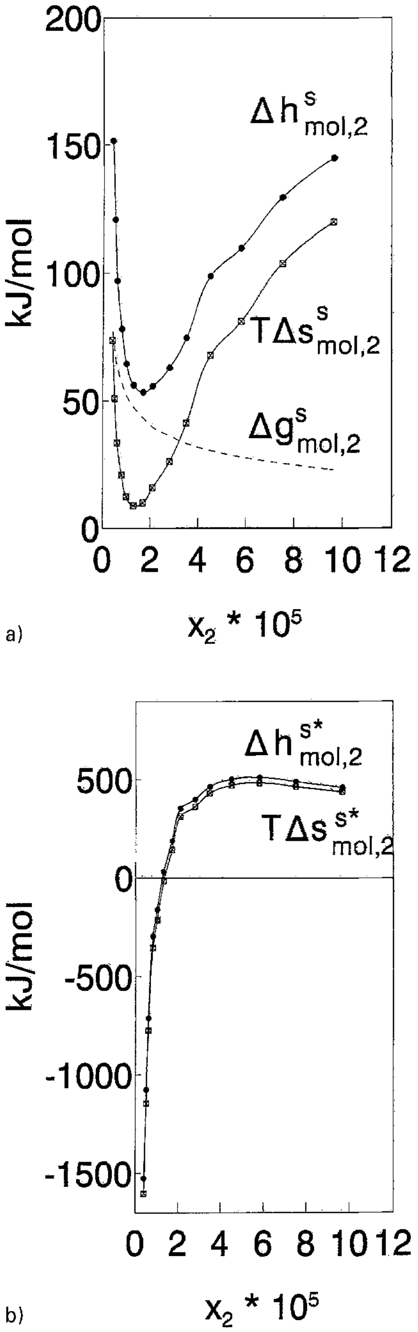

Fig. 9 Thermodynamic functions $\Delta g^{s}_{mol,2}$ (---), $\Delta h^{s}_{mol,2}$ (●), $T\,\Delta s^{s}_{mol,2}$ (⊠) (9a) and $\Delta g^{s*}_{mol,2}$, $\Delta h^{s*}_{mol,2}$ (●), $T\,\Delta s^{s*}_{mol,2}$ (⊠) (9b) of sodium octylbenzenesulfonate vs x_2 with respect to the mole number of the second component at 25 °C

octylbenzenesulfonate at liquid/air interface is determined by the enthalpic as well as by the entropic effect.

Similar results were already obtained by calculating the thermodynamic functions of binary liquid mixtures adsorbed on solids [6, 9]. It must be mentioned that the reason for the proportional behavior between the enthalpy and entropy functions is based on the estimation of the adsorption equilibrium constant K using only enthalpy data of immersion, as will be shown in the following. For a uniform adsorbent surface, when adsorption is taking place from an ideal solution and the surface solution is also ideal [7, 8], the equilibrium constant K can be expressed by [27]

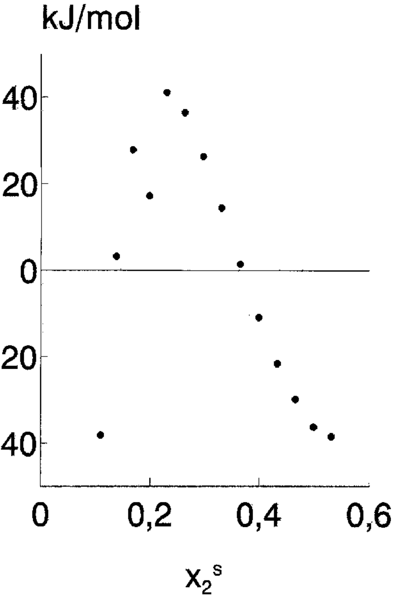

Fig. 10 Plot of $(\Delta h^{s*}_{mol} - x^{s}_{2}\Delta h^{s*}_{mol2})$ vs. x^{s}_{2} at 25 °C according to Eq. (38), respectively

$$K = \frac{x^{s}_{1} x_2}{x_1 x^{s}_{2}} . \tag{50}$$

This equation can be transformed to

$$x^{s}_{2} - x_2 = \frac{x_1 x_2}{x_2 - K/(K-1)} . \tag{51}$$

For the same ideal conditions, Everett [14] obtained the following relationship

$$\Delta_I h = x^{s}_{1} \Delta_I h^{0}_{1} + x^{s}_{2} \Delta_I h^{0}_{2} \tag{52}$$

between the specific enthalpy of the immersion of the solid $\Delta_I h$ by the two-component liquid mixture with the mole fraction x_2 and the specific enthalpies of immersion $\Delta_I h_i$ for the pure components $i = 1, 2$. This equation can be easily transformed into

$$\Delta_I h = (x^{s}_{2} - x_2)(\Delta_I h^{0}_{2} - \Delta_I h^{0}_{1}) + x_1 \Delta_I h^{0}_{1} + x_2 \Delta_I h^{0}_{2} . \tag{53}$$

Substituting in the last expression $x^{s}_{2} - x_2$ by Eq. (51) it is obvious that the ideal equilibrium constant K is only a function of enthalpy data of immersion.

The maximum within the areal related functions of Fig. 7 is nearly the CMC of $x_{2,\mathrm{CMC}} = 1.34\ 10^{-4}$. The molar-related functions were only described at concentrations of pure water up to CMC. The following micelle formation within the micelle concentration range leads to additional conditions and complicates the formalism to calculate x_2^s. Therefore, the thermodynamic functions in Figs. 8 and 9 are plotted only within the submicellar range. Due to the different temperature behavior of σ, Γ_2^s and Γ^s and by using the differentiation quotient rule in Eqs. (31)–(34) positive and negative values are observed in opposition to the area-related functions. The term T^*s can be understood as a composed effect of orientation-, solvation- or desolvation effects, interactions with other molecules and destruction of water structure. If the last mentioned effect is dominant, then the entropy is positive. Finally, Fig. 10 shows the difference between the different molar related enthalpies according to Eq. (40). The deviation between the enthalpy values related by total amount and amount of surfactant component on the one side and the molar and area related (see Eqs. (37) to (40)) on the other side can be explained by the different temperature dependences of the quantities x_2^s, Γ^s and Γ_2^s, respectively.

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