Adsorption Isotherm and Surface Tension Equation for a Surfactant with Changing Partial Molar Area. 2. Nonideal Surface Layer

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An adsorption model is proposed that assumes different partial molar surface areas ω for adsorbed molecules depending on the degree of saturation of the adsorption layer. Equations for an adsorption isotherm and a surface tension isotherm are derived for the adsorption of one single surfactant or of a mixture of surfactants. The model assumes that the molecules may adsorb in two different states, i.e., large at smaller surface pressures Π, and smaller at large surface pressures Π. Adsorption data of *N-n*-hexadecyl-*N,N*-dimethylammonio acetic acid bromide at the solution/air interface are used to demonstrate the application of the theory. Experimental results are in very good agreement with the model.

Introduction

The asymmetry of a surfactant molecule can be the reason that it may occupy a different area in the adsorption layers at liquid−gas or liquid−liquid interfaces. The portion of molecules in an adsorbed state characterized by a certain partial molar area depends on the surface pressure and is controlled by the well-known principle of Braun−Le-Chatelier for adsorption layers.[1−3] In part 1 of this work equations for the adsorption and surface tension isotherms were derived for surfactant solutions forming ideal surface layers.[4] It was shown in particular that this new model not only is an alternative to known isotherm equations based on the intermolecular interaction concept but also can predict completely new effects. At the same time, when a reorientation of surfactant molecules at the surface is considered, interaction between different molecular species in the surface layer has also to be taken into account. Thus both these effects have to be considered in a rigorous theory simultaneously.

Another important point closely related with molecular reorientation is the nonideality of the surface layer entropy, which is to be accounted for when the components with different partial molar areas are mixed together. Frumkin[5] was the first to consider intermolecular interaction. Equations that describe the adsorption layers of the solutions of a single surfactant or two surfactants with intermolecular interaction were proposed in refs 6−16. The nonideality of mixing entropy of molecules possessing different sizes was discussed in refs 16−21. In refs 22 and 23 the intermolecular interaction at the electrode−solution interface was taken into consideration; here it was also assumed that the molecules can be adsorbed in two different orientations.

In the present paper equations are derived that describe nonideal adsorption layers of surfactants having a partial molar area varying with the surface pressure. These equations are compare with relationships from literature. Using a suitable fitting procedure, the theory is compared with experimental data.

Theory

The relationship between the molar fractions of the *i*th component of the system (or the *i*th state of the same component) in the bulk (α) and at the surface (s) can be written[4,21,24] as

$$\ln\frac{f_i^s x_i^s}{K_i f_i^\alpha x_i^\alpha} = -\frac{\gamma\omega_i}{RT} \qquad (1)$$

where f is the activity coefficient, x is the molar ratio, γ is the surface tension, R is the gas constant, T the temperature, ω the partial molar area demand, $K_0 = 1$ (subscript $i = 0$ refers to the solvent), and $K_i = (x_i^s/x_i^\alpha)|_{x_i^\alpha \to 0}$ $(i \geq 1)$ are the respective distribution coefficients at infinite dilution. Assuming the bulk solution to be ideal, the equation of state for a nonideal surface layer can be obtained from eq 1 (cf ref 4):

$$\Pi = -\frac{RT}{\omega_0}(\ln x_0^s + \ln f_0^s) \qquad (2)$$

and the equation of adsorption isotherm:

$$\ln\frac{f_i^s x_i^s}{K_i x_i^\alpha} = \frac{\omega_i}{\omega_0}(\ln x_0^s + \ln f_0^s) \qquad (3)$$

where $\Pi = \gamma_0 - \gamma$ is the surface pressure, and γ_0 is the surface tension of the solvent.

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Introducing the surface coverage θ_i instead of the mole fractions in the form $x_i^s \approx \theta_i = \Gamma_i \omega_i$ or $\theta_i = \Gamma_i \omega_\Sigma$, eqs 2 and 3 transform into

$$\Pi = -\frac{RT}{\omega_0}\left[\ln\left(1 - \sum_{i \geq 1}\theta_i\right) + \ln f_0^s\right] \tag{4}$$

$$K_i c_i = \frac{\theta_i f_i^s}{\left(1 - \sum_{i \geq 1}\theta_i\right)^{n_i}(f_0^s)^{n_i}} \tag{5}$$

where c is the bulk concentration, $n_i = \omega_i/\omega_0$, and ω_Σ is the average partial molar area.

The activity coefficients, which are given by the intermolecular interaction (enthalpic nonideality, f_i^{sH}) can be calculated using the regular solution theory:[25−28]

$$RT \ln f_k^{sH} = \sum_i \sum_j (A_{ik}^s - {}^1/_2 A_{ij}^s)\theta_i\theta_j \tag{6}$$

where $A_{ij}^s = U_{ii}^s + U_{jj}^s - 2U_{ij}^s$, U_{ii}^s, and U_{ij}^s are the energies of interaction between the species in the surface layer.

Lucassen-Reynders[21] gave the following expression for the activity coefficient of any surface layer component for nonideal entropy of mixing:

$$\ln f_k^{sE} = 1 - n_k \sum_i (\theta_i/n_i) \tag{7}$$

Additivity leads to

$$f_i^s = f_i^{sH} f_i^{sE} \quad \text{or} \quad \ln f_i^s = \ln f_i^{sH} + \ln f_i^{sE} \tag{8}$$

For the solution of two surfactants (1 and 2), or for two states of the same surfactant in the surface layer, the substitution of eqs 6−8 into eqs 4 and 5 leads to

$$\Pi = -\frac{RT}{\omega_0}\left[\ln(1 - \theta_1 - \theta_2) + \theta_1\left(1 - \frac{1}{n_1}\right) + \theta_2\left(1 - \frac{1}{n_2}\right) + a_1\theta_1^2 + a_2\theta_2^2 + a_{12}\theta_1\theta_2\right] \tag{9}$$

$$b_i c_i = -\frac{\theta_i}{(1 - \theta_1 - \theta_2)^{n_i}}\exp(-2a_i\theta_i - 2a_{12}\theta_j) \times$$
$$\exp[(1 - n_i)(a_1\theta_1^2 + a_2\theta_2^2 + a_{12}\theta_1\theta_2)] \tag{10}$$

where $a_1 = A_{01}$; $a_2 = A_{02}$; $a_{12} = (A_{01} + A_{02} - A_{12})/2$; $b_i = K_i \exp(n_i - a_i - 1)$; $i = 1, 2$; $j = 1, 2$ ($j \neq i$). If eqs 10 describe two states of the same surfactant in the surface, then $c_1 = c_2 = c$. The equation of state for the surface layer (9) is similar to that proposed in ref 23 for the same system, while the equations of the adsorption isotherm (10) differ from those presented in ref 23 by an extra exponential term on the right-hand side. This term, however, can be neglected if n_i does not differ significantly from unity. The results presented here are not exactly the same as obtained in ref 23, because another theoretical approach was used here. In ref 23 the model equation for the adsorption isotherm was solved simultaneously with the Gibbs' fundamental equation, and the differential d(ln c) was not defined rigorously enough. Another problem discussed earlier[4] is that the dividing surface for the model equation and Gibbs equation was defined in different ways.

In our opinion, the use of eq 1 following from an equation proposed by Butler[24] enables one to develop straightforward theoretical models for the description of surfactants adsorption layers at the liquid−fluid interface. One can easily verify that all known equations describing the interfacial state of solutions of one or two surfactants involving both intermolecular interaction and nonideal entropy (cf. ref 16) are limiting cases of eqs 9 and 10.

Equations 9 and 10 comprise seven parameters (n_1, n_2, b_1, b_2, a_1, a_2, and a_{12}) for two components or for two states of one surfactant. It is clear that in this form these equations are not readily applicable. One can derive simpler equations for describing the adsorption of one surfactant possessing i different states (ω_i) of molecules in surface layer, using the same definitions of the dividing surface (Lucassen-Reynders' dividing surface[9]), ω_0 and θ_i as in our previous paper:[4] $\theta_i = \Gamma_i \omega_\Sigma$, $\omega_0 = \omega_\Sigma$, and $\Sigma\Gamma_{i \geq 0} = 1/\omega_\Sigma$. Then the value of average molar area for all states is defined by

$$\omega_\Sigma = \left(\sum_{i \geq 0}\Gamma_i \omega_i\right)\bigg/\left(\sum_{i \geq 0}\Gamma_i\right) \tag{11}$$

The reasons for this choice have been discussed in ref 4. We can add here that only for this particular choice of the dividing surface ($\omega_0 = \omega_\Sigma$), the portion of the surface occupied by the surfactant molecules of the ith state ($\theta_i = \Gamma_i \omega_\Sigma$) is equal to the molar portion of a given state at the surface ($x_i^s = \Gamma_i/\Sigma_{i \geq 1}\Gamma_j \equiv \Gamma_i \omega_\Sigma$). This justifies the transformation of eqs 2 and 3 into eqs 4 and 5.

If we assume that the solvent−surfactant and surfactant−surfactant intermolecular interactions do not depend on the state of surfactant molecules in the surface (ω_i), it follows from the regular solution theory (cf., refs 25−28 and eq 6) that

$$\ln f_0^{sH} = a\Gamma_\Sigma^2 \omega_\Sigma^2 \tag{12}$$

$$f_i^{sH} = a(1 - \Gamma_\Sigma \omega_\Sigma)^2, \quad i \geq 1 \tag{13}$$

where a is the intermolecular interaction constant, and $\Gamma_\Sigma = \Sigma_{i \geq 1}\Gamma_i$ is the total adsorption of surfactant in all states. For our choice of the dividing surface position, eqs 7 can be transformed into

$$\ln f_i^{sE} = 1 - \omega_i \sum_{j \geq 0}\Gamma_j = 1 - n_i, \quad i \geq 1 \tag{14}$$

$$\ln f_0^{sE} = 1 - \omega_0 \sum_{j \geq 0}\Gamma_j = 0 \tag{15}$$

It is seen that the condition $\omega_0 = \omega_\Sigma$ means that the activity coefficient of the solvent molecules in the surface layer depends on the intermolecular interaction and is independent of the size of mixed molecules.

Using relations 8 and 12−15, from eqs 4 and 5 and assuming that $K_i = K = $ constant, one obtains

$$\Pi = -\frac{RT}{\omega_\Sigma}[\ln(1 - \Gamma_\Sigma \omega_\Sigma) + a(\Gamma_\Sigma \omega_\Sigma)^2] \tag{16}$$

$$bc = \frac{\Gamma_i \omega_\Sigma}{(1 - \Gamma_\Sigma \omega_\Sigma)^{n_i}}\exp(-n_i) \times$$
$$\exp[-2a\Gamma_\Sigma \omega_\Sigma + a(1 - n_i)(\Gamma_\Sigma \omega_\Sigma)^2] \tag{17}$$

where $b = K \exp(-a - 1)$; $n_i = \omega_i/\omega_\Sigma$.

It is seen, in contrast to eqs 9 and 10, that in the case of solutions of a single surfactant in two adsorption states (1 and 2), expressions 16 and 17 depend on four parameters only: ω_1, ω_2, b, and a. An important relation (adsorption principle of Braun−Le Chatelier[1]) follows from the eq 17 for any two states i and j:

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$$\frac{\Gamma_i}{\Gamma_j} = \exp\left(\frac{\omega_i - \omega_j}{\omega_\Sigma}\right)\exp\left(\frac{(\omega_i - \omega_j)\Pi}{RT}\right) \qquad (18)$$

As compared to the relation derived earlier (cf. eq 28 in ref 4), the consideration of the entropy of mixing gives rise to an additional exponential factor in eq 18. This means that the portion of molecules in states with $\omega_i > \omega_j$ in the surface layer increases as compared with the ideal model. In ref 4 an empirical constant $\alpha = \ln(b_i/b_j)$ had to be introduced in order to account for states with greater values of ω_i possessing higher adsorption activity. Now this constant has not to be used in eqs 17 and 18, as the factor $\exp[(\omega_i - \omega_j)/\omega_\Sigma]$ had entered into the calculations. Thus with the consideration of nonideality in this study, the number of parameters in the equations of state and adsorption isotherms had not increased as compared to the ideal model considered earlier.[4]

Using eq 18, the total adsorption can be expressed via the adsorption in any particular state. For state 1 the equation reads

$$\Gamma_\Sigma = \Gamma_1 \sum_{i \geq 1}\exp\left(-\frac{\omega_1 - \omega_i}{\omega_\Sigma}\right)\exp\left[\frac{(\omega_1 - \omega_i)\Pi}{RT}\right] \qquad (19)$$

The mean partial molar surface of all states is given by

$$\omega_\Sigma = \frac{\displaystyle\sum_{i \geq 1}\omega_i\exp\left(-\frac{\omega_1 - \omega_i}{\omega_\Sigma}\right)\exp\left[\frac{(\omega_1 - \omega_i)\Pi}{RT}\right]}{\displaystyle\sum_{i \geq 1}\exp\left(-\frac{\omega_1 - \omega_i}{\omega_\Sigma}\right)\exp\left[\frac{(\omega_1 - \omega_i)\Pi}{RT}\right]} \qquad (20)$$

If there are only two possible orientations of surfactant molecules at the surface (states 1 and 2, with $\omega_1 > \omega_2$), eq 17 can be simplified. Expressing the adsorption in the ith state via the total adsorption, one can transform eq 17 into

$$bc =$$

$$\frac{\Gamma_\Sigma\omega_\Sigma\exp\left(-\dfrac{\omega_2}{\omega_1}\right)\exp\left[-2a\Gamma_\Sigma\omega_\Sigma + a\left(1 - \dfrac{\omega_2}{\omega_\Sigma}\right)(\Gamma_\Sigma\omega_\Sigma)^2\right]}{(1 - \Gamma_\Sigma\omega_\Sigma)^{\omega_2/\omega_\Sigma}\left\{1 + \exp\left(\dfrac{\omega_1 - \omega_2}{\omega_\Sigma}\right)\exp\left[-\dfrac{(\omega_1 - \omega_2)\Pi}{RT}\right]\right\}} \qquad (21)$$

Equations 16, 20, and 21 have to be used in a computer-fitting program to find the optimal set of parameters ω_1, ω_2, b, and a. Some results of experimental data processing are presented in the following section. Here only some remarks will be made concerning the applicability of the model considered to describe ionic surfactant adsorption.

Equations of state and adsorption isotherms for ionics can be derived rigorously, both in presence and absence of interfacial reorientation of the molecules, starting from Butler's eq 24 including the electrochemical potential instead of the chemical potential. If the electrical potential of the surface is relatively high, due to the adsorption of surfactant ions, an additional term proportional to Γ_Σ will enter the right-hand side of eq 16, cf. refs 29–32. This addition is, however, rather small as compared to the logarithmic term in eq 16. On the other hand, if the electrical surface potential is small, then its effect on Π is negligible.[31]

To summarize, eqs 16, 20, and 21 can be used to describe the ionic surfactant solutions without any significant error, if the combined adsorption of surfactant ions and counterions is taken into consideration.[30,31] Clearly the value of the constant

a calculated for such systems by a fitting program will be affected also by interion interactions in the surface layer.

Results and Discussion

The surface tension isotherms $\gamma(\log c)$ for aqueous solutions of (*N-n*-alkyl-*N,N*-dimethylammonio)acetic acid bromides presented in refs 33–35 were used to verify the two-state model of the surfactant in a nonideal surface monolayer. For pH $= 7$ (*N-n*-alkyl-*N,N*-dimethylammonio)acetic acid bromides are transformed into betaines (BHBR) with the structure (cf. ref 33):

$$\begin{array}{c} CH_3 \\ | \\ R - N^+ - CH_2 - COO^- \\ | \\ CH_3 \end{array}$$
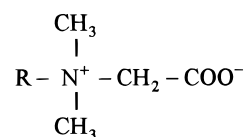
The betaines studied are water soluble up to alkyl chains R of 16 C atoms. That is why the BHBR homological series from C_8 to C_{16} was chosen to verify the applicability of the new adsorption isotherm. The isotherms presented in refs 33–35 span over a rather wide range of Π: from 0 to 35–40 mN/m. Another important reason for this consideration is that a nonideal (non-Langmuirian) adsorption behavior was found in refs 34 and 35 for the higher molecular BHBR homologues. It was emphasized in part 1[4] that this effect can possibly result from a reorientation of BHBR molecules within the surface, which was not taken into account.

To calculate the adsorption characteristics of BHBR from the experimental surface tension isotherms $\Pi = \Pi(c)$, a computer-fitting program was implemented based on eqs 16, 20, and 21. In these equations $a = 0$ was assumed, i.e., only the nonideality of entropy of the surface layer was considered. Therefore, similar to the Frumkin isotherm for solutions of single surfactants,[30] only three free parameters are used to describe the BHBR adsorption behavior: ω_1, ω_2, and b. The fitting procedure proceeds as follows: While the values of ω_1 and ω_2 are varied, for each chosen pair the values of b_i for each of the n experimental points $\Pi_i = \Pi_i(c_i)$, $i = 1, 2, ..., n$ were calculated. A mean value of b was calculated as the weighted average over all n values:

$$b = \sum_{i=1}^{n}b_i\frac{\Delta\Pi_i}{\Pi_n - \Pi_1} \qquad (22)$$

where $\Delta\Pi_i = (\Pi_{i+1} - \Pi_{i-1})/2$ is the Π range corresponding to the ith point. The set of the parameters ω_1 and ω_2 was considered to be optimal when the difference ΔS was minimal:

$$\Delta S = \sum_{i=1}^{n}|\log c_{ex,i} - \log c_{cal,i}|\Delta\Pi_i = \min \qquad (23)$$

The subscripts ex and cal refer to the experimental and calculated (for the same Π_i) surfactant concentrations, respectively. As the values $\Delta c_i = |c_{ex,i} - c_{cal,i}|$ are small as compared to $c_{ex,i}$, one can transform the minimization condition eq 23 into a dimensionless form:

$$\epsilon = \sum_{i-1}^{n}\frac{\Delta c_i}{c_{ex,i}}\frac{\Delta\Pi_i}{\Pi_n - \Pi_1} = \min \qquad (24)$$

ϵ is the weighted average (over Π) of the relative deviations between the experimental and calculated c_i values.

TABLE 1: Parameters of Adsorption Isotherms for (*N-n*-Alkyl-*N,N*-dimethylammonio) Acetic Acid Bromides at pH = 7

| surfactant	reorientational isotherm				Langmuir isotherm		
	ω_1 (10^9 cm^2/mol)	ω_2 (10^9 cm^2/mol)	b (cm^3/mol)	ϵ (%)	ω (10^9 cm^2/mol)	b_L (cm^3/mol)	ϵ_L (%)
BHB8	2.6	2.72	1.02×10^4	3.0	2.72	5.55×10^4	3.1
BHB9	2.94	2.90	3.57×10^5	3.5	2.90	1.94×10^6	3.6
BHB10	2.92	2.92	1.21×10^6	5.4	2.92	6.58×10^6	5.4
BHB11	3.60	2.24	2.80×10^6	4.2	2.68	1.09×10^7	4.5
BHB12	7.60	2.54	1.80×10^7	2.1	2.80	3.41×10^7	4.0
BHB13	10.8	2.74	6.12×10^7	2.7	2.80	8.21×10^7	3.3
BHB14	14.2	2.54	2.46×10^8	2.4	2.34	2.52×10^8	3.5
BHB15	15.4	2.64	6.48×10^8	4.1	2.45	6.42×10^8	6.2
BHB16	19.8	2.52	1.70×10^9	2.0	2.40	1.59×10^9	8.1
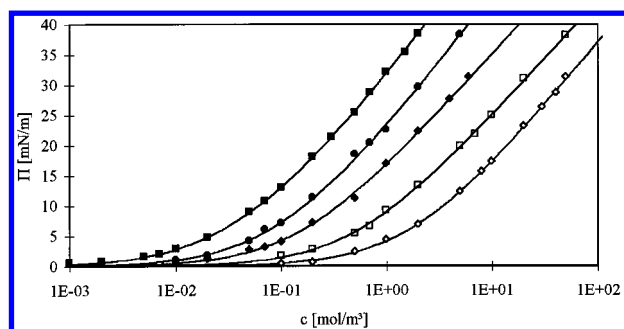
Figure 1. Surface pressure isotherms for the solutions of BHBR with R = 8 ($\diamond$), 9 ($\square$), 10 ($\blacklozenge$), 11 ($\bullet$), and 12 ($\blacksquare$); the experimental points are taken from refs 33−35; the curves are calculated from eqs 16, 20, and 21 for the parameters presented in Table 1.
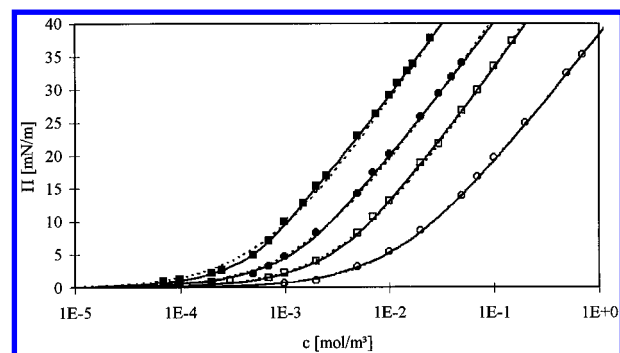
Figure 2. As in Figure 1 for the BHBR with R = 13 ($\circ$), 14 ($\square$), 15 ($\bullet$), and 16 ($\blacksquare$); the dotted lines are calculated from the Szyszkowski−Langmuir eq 25.

The Szyszkowski−Langmuir surface tension isotherm

$$\Pi = \frac{RT}{\omega} \ln(1 + b_L c) \qquad (25)$$

was also used to interpret the experimental isotherm data for the BHBRs. In this case only the ω value was varied. To calculate the constant b_L and to optimize the value of ω, eqs 22 and 24 were employed.

The experimental and theoretic surface tension isotherms for BHBR solutions are presented in Figures 1 and 2. In Table 1 the values of optimal parameters calculated using the fitting program for the reorientation isotherm and the Langmuir isotherm are summarized. It has to be mentioned first that a close correspondence exists between the experiment and the theory for all BHBRs studied: the value of ϵ varies between 2 and 5%. The values of ω_1 and ω_2 for low-molecular-homologues ($R \leq 11$) are close to each other; therefore the results calculated from the "reorientation" fitting procedure coincide with those obtained for the Langmuir isotherm. However, for the homologues C$_{12}$ and higher, the reorientation isotherm leads to values ω_1 which exceed ω_2 significantly. The values of ϵ which results from the "reorientation" fitting procedure are 1.5−2 times lower than those obtained from the
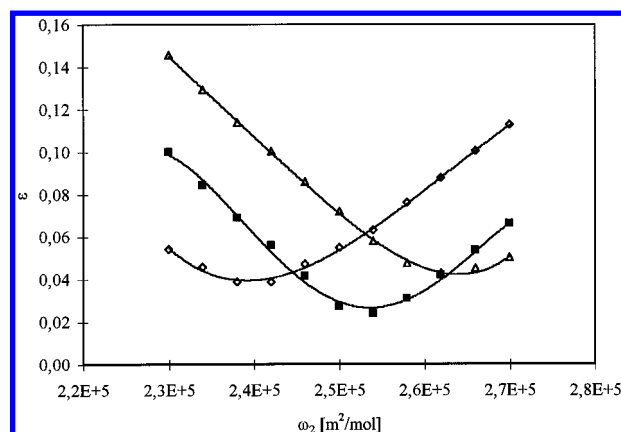
Figure 3. Dependence of relative deviation ϵ on ω_2 for BHB14 calculated for $\omega_1 = 10^{10}$ ($\diamond$), 1.4×10^{10} ($\blacksquare$, optimal value) and 1.8×10^{10} /cm^2/mol (Δ).
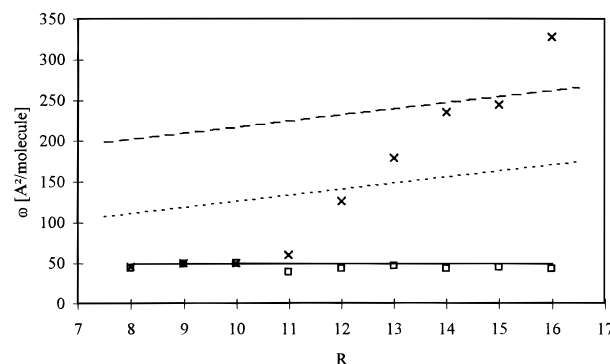
Figure 4. Dependence of ω_1 and ω_2 on R for BHBR molecules calculated from the isotherms $\Pi = \Pi(c)$ ($\times$ and $\square$, respectively), and estimated from the geometry of BHBR molecule in the two states: vertical (dotted line) and horizontal (dashed line) orientation of the alkyl chain. In the calculations of maximum surface area various mutual positions of the groups in the BHBR molecule were allowed.

"Langmuir" fitting. The two theoretical isotherms are shown in Figure 2. The difference is rather significant, especially in the low surface pressure region where, according to eq 18, the surfactant molecules are more likely to be adsorbed in a state of maximum partial molar area ω_1. This effect cannot be reproduced by a Langmuir isotherm.

The dependencies $\epsilon = \epsilon(\omega_2)$ corresponding to the optimal value of $\omega_1 = 1.4 \times 10^{10}$ cm^2/mol and two nonoptimal values of ω_1 for BHB14 are presented in Figure 3. It is seen that a rather deep and sharp minimum in the ω_2 dependence exists. The minimum with respect to ω_1 is less pronounced but also exists, which indicates that the optimal value of ω_1 can be determined. The error of the determination of optimal ω_2 values is of the order of 2−5%, while for ω_1 this error is significantly higher, up to 20%.

The values of ω_1 and ω_2 estimated from the surface tension isotherms for BHBR solutions are compared in Figure 4 with calculated molecular geometries of BHBR molecules existing

in two states. The range of possible theoretical values of ω_1 in Figure 4 extends over possible configurations of BHBR molecule lying flat on the water surface. The ω_1 dependence on the number of C atoms in the alkyl chain was determined from molecular dynamics calculations of all possible ω_1 values for the BHB16 molecule.[4] For $R < 16$ approximate theoretical values for ω_1 were estimated from these calculations for BHB16 and the area per one flat methylene group (which was taken to be 7.5 Å^2). The value of ω_2 for trans configurations of the polar groups of vertically oriented BHBR molecule is 49 Å^2, cf. ref 4. As the value of ω_2 is determined mainly by the size and configuration of the polar group, the estimated theoretical value of $\omega_2 = 49$ Å^2 for all BHBR homologues was used. The thermal motion of alkyl chains and their mutual interaction can affect the ω_2 dependence on R. This fact is confirmed experimentally; in the homologeous series of sodium alkyl sulfates the ω_2 dependence on R shows a minimum between $R = 10$ and 11.[36]

Satisfactory agreement between experiment and theory for ω_2 was obtained. No significant dependence of ω_2 on R (within the limits of the error in the calculation of ω_2) can be observed. The experimental values of ω_1 obtained from the fitting programmme for low-molecular homologues ($R < 11$) coincide with the ω_2 values. At the same time, the theoretical ω_1 values for the same homologues are 2−3 times larger than ω_2. Thus one can conclude that the theoretical prediction of the capability of BHBR molecules to occupy larger interfacial area is invalid for $R \leq 11$. A possible explanation for this nontrivial result is that the hydrophilic/hydrophobic balance for these low-molecular-weight BHBR homologues is shifted toward the hydrophilicity. As the result, some methylene groups of the BHBR molecule adjacent to the polar group are drawn into the water phase due to strong interaction of the polar group with water, while the limited flexibility of C−C bonds prevents the remaining portion of the alkyl chain from laying flat at the solution/water interface. For long alkyl chains, however, the situation is rather different. Figure 4 demonstrates a satisfactory agreement between the theoretical and experimental values of ω_1 for $R \geq 13$. Note that the experimental value of ω_1 for BHB16 exceeds that reported earlier[4] by about 30%. The reason for this discrepancy is that in the present study the experimental dependence $\Pi = \Pi(c)$ was extended into the region $c < 2 \times 10^{-7}$ mol/L. In contrast to ref 4, the nonideality of surface entropy has been considered here, and the error has been minimized with respect to ϵ and not to $\Delta\gamma$. However, comparing the two experimental ω_1 values and calculated value from the BHB16 molecular geometry a satisfactory agreement is attained.

Conclusions

The equations of the adsorption isotherm and of the surface layer state are derived for the surfactant molecules with variable partial molar surface area for the case of nonideal surface layers. Both components of the surfactant activity coefficient of the surface were taken into account: nonideality of enthalpy and entropy of mixing. The nonideality of entropy can be related to the fact that the partial surface area of the surfactant depends on the molecular state of the surfactant at the surface. General equations are derived, from which well-known adsorption isotherms for one surfactant or mixtures or for varying states of surfactant molecules within the surface layer follow as particular cases. Choosing the dividing surface according to Lucassen-Reynders and using a number of simplifications, a reduced number of independent parameters of only four for the case of single surfactants possessing two interfacial states, and three free parameters (equivalent to the Frumkin isotherm) when only the nonideality of entropy was taken into account.

The fitting program developed enables one to calculate the partial molar surface area of surfactant molecules in the states of maximum (ω_1) and minimum (ω_2) surface area from the experimental surface tension isotherms.

Experimental data for aqueous solutions of betaines with various alkyl chain lengths (8 to 16 C atoms) were used to calculate ω_1 and ω_2 and to compare to their molecular geometry. It was shown that despite a quite strong asymmetry of the betaine molecules studied (the ratio of ω_1 to ω_2 varies from 2.5 to 5), only one interfacial state exists for the low-molecular-weight homologues ($R \leq 11$), while the molecules with longer alkyl chain ($R \geq 13$) are capable for adsorption in two states. In this case the ω_1 values determined from the $\gamma(c)$ dependence using a fitting program agree well with the theoretical calculations of the molecular geometry.

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