On the Interaction of Insoluble Alkyl Alcohol Monolayers with Aqueous Solutions of Ionic Surfactants

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The interaction between so-called alkyl alcohol (C_5-C_8) monolayers and aqueous solutions of ionic surfactants with different hydrophilic properties, i.e. calcium di-2-ethylhexyl sulfosuccinate and sodium dodecyl sulfate, has been studied with the help of a Langmuir-Adam film balance. A decrease or increase in surface pressure of the alkyl alcohol monolayers with the addition of surfactants is observed. The shift of the critical concentration (cmc) to increasing surfactant concentration occurs at intermediate surface pressures. This is interpreted as due to the formation of mixed alcohol-surfactant aggregates. The maximum of the cmc as a function of the pressure can be explained by a thermodynamic treatment assuming competition between a pressure dependent solubility of alcohol molecules and the formation of mixed alcohol surfactant complexes. The amount of alkyl alcohol required to react with the surfactant has been evaluated at different surface pressures, which shows values similar to those known from cosurfactant studies in the bulk phase. Critical micelle concentrations of the surfactants were verified by conductivity measurements.

Introduction

Water/air interfaces offer the considerable experimental advantage, as compared with oil/water interfaces, of manipulating easily a two-phase equilibrium; for example, between an insoluble alcohol monolayer and a homogeneous aqueous surfactant solution. "Insoluble" is not considered to be an exact notion but depends on the method of detection. However, it is generally agreed that alcohols with increasing apolar chains are expected to show decreasing solubilities in water. In other words, due to their increasing amphiphilic properties with the hydrocarbon chain lengths, the alcohols tend to be accumulated in the interface. From these considerations it is to be expected a priori that a certain group of alcohols with a relatively short chain length should show surface pressure dependent solubilities in the aqueous bulk phase.

It should be mentioned that also another case is possible in the frame of this experiment: the pressure dependent solubility of surfactant molecules from the bulk in the surface phase (e.g. SDS and 1-octanol).

Such experiments can be carried out with the help of the well-known Langmuir-Adam film balance, which has shown in the past to be a very versatile instrument in surface science [1–12]. In this way it is possible to vary quite sensitively the concentration of one of the components in the aqueous bulk phase and thus to follow the aggregational behaviour of the system by simultaneous surface pressure and conductivity measurements. The motivation of the present investigation was our general interest in the cosurfactant principle [13], [14], and in particular to find out whether this technique is sensitive enough to detect different kinds of association structures between the monomeric and micellar states. It could be shown that mixed alcohol surfactant aggregates are formed and that a very idealized thermodynamic treatment is suitable to describe the essential features of the experimental results in the ternary bulk phase. The SDS/1-octanol system may also be described with an essentially similar approach. However in this case, to a first approximation, a binary surface phase has to be considered.

Experimental

a) Materials. All film forming substances, i.e. 1-octanol, 1-heptanol, and 1-pentanol were supplied by Fluka, Buchs, Switzerland. These were high grade purity samples (>99%) and used without further treatment. The calcium di-2-ethylhexyl-sulfosuccinate and the corresponding potassium salt were prepared from the sodium di-2-ethylhexyl-

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sulfosuccinate (= AOT) by ion exchange using Amberlite IR-120 columns. Ether and benzene were applied as volatile solvents for spreading the film forming compounds. Both these products were also obtained from Fluka. Bi-distilled water was used throughout the measurements.

b) *Measurements.* The surface pressure-area measurements were carried out with the help of a Langmuir-Adam film balance. This balance consisted of a long shallow solid teflon trough, reinforced teflon barriers, and a sensitive torsion wire system. The entire apparatus was mounted on a heavy iron plate which could be adjusted horizontally and vertically and damped considerably disturbing vibrations. The readings were taken with the help of an optical arrangement. The trough was filled with distilled and deionized water and then the assembly was allowed to reach equilibrium in a thermostated room. The water surface was swept many times with the help of a movable barrier. The film was spread at high surface areas. This area was then reduced by small decrements. The film was finally compressed to collapse as observed by a sudden decrease in pressure.

The alcohol surfactant interaction was investigated by spreading initially an alcohol monolayer and then compressing it to a definite surface pressure. After attenuation of the equilibrium pressure a known amount of a concentrated surfactant solution was injected into the trough. A suitable time interval was again provided to attain the equilibrium pressure. The change in surface pressure at constant area due to the penetration of surfactant molecules or to the loss of alcohol molecules to the aqueous bulk phase was recorded at each addition of surfactant solution.

Extreme care was taken to prevent contamination. Before each experiment, all parts of the film balance that stay in contact with water were thoroughly cleaned by successive washing and soaking in reagent grade methyl alcohol, carbon tetrachloride and finally with acetone.

The experiments were carried out at 18 ± 0.1 °C. It was found, however, that small variations in temperature had no detectable effect on the surface pressure determination.

Conductivity measurements were accomplished using a standard conductivity cell and a Wayne-Kerr RC-bridge 221 operating at 1591.5 Hz. Also a specially constructed conductivity cell with gold-plated electrodes was used in order to determine conductivity changes in the aqueous bulk phase of the trough as a function of the surface pressure of the alcohol monolayer.

Results and Discussion

The first figure (Fig. 1) shows a diagram typical with respect to the surface pressure dependence on the surfactant concentration. The various plots correspond to different initial surface pressure values. It is clearly seen from Fig. 1 that all the curves have pronounced breaks which correspond at the lowest and the two highest surface pressures to the critical micelle concentration of calcium di-2-ethylhexyl sulfosuccinate. The latter was determined by conductivity measurements (see Figure 2). Figure 3 exhibits the functional relationship between an apparent CMC of Ca(di-2-ethylhexyl sulfosuccinate)$_2$ and the alcohol surface pressures for 1-pentanol, 1-heptanol and 1-octanol. The same diagram also shows the situation for potassium di-2-ethylhexyl sulfosuccinate as a function of the surface pressure of 1-octanol. The Fig. 3 shows that the amplitudes and the positions of the maximum shifts of the CMC are clearly dependent on the particular alcohol, also the property of the counterion of the di-2-ethylhexyl sulfosuccinate changes the maximum shift of the cmc. In Fig. 4 a linear relationship between the calcium di-2-ethylhexyl sulfosuccinate-concentration and that of the different alcohols within the aqueous bulk phase is shown. Finally, Fig. 5 presents the results regarding the sodium dodecylsulfate/1-octanol/water system. An analogous shift of the CMC as a function of the SDS-concentration (Fig. 5) and of the surface pressure (π) (Fig. 6) is observed.

The following model is suggested to interpret the main features of the experimental results regarding the dependence of the surface pressure on the surfactant concentration, in particular the initial processes of micellization and alcohol-surfactant interactions. It will be assumed that a complex is formed between the surfactant and the alcohols which is responsible for the shift of the critical micelle concentration of the respective surfactant in the aqueous bulk surfactant solution. Hence, two equilibria

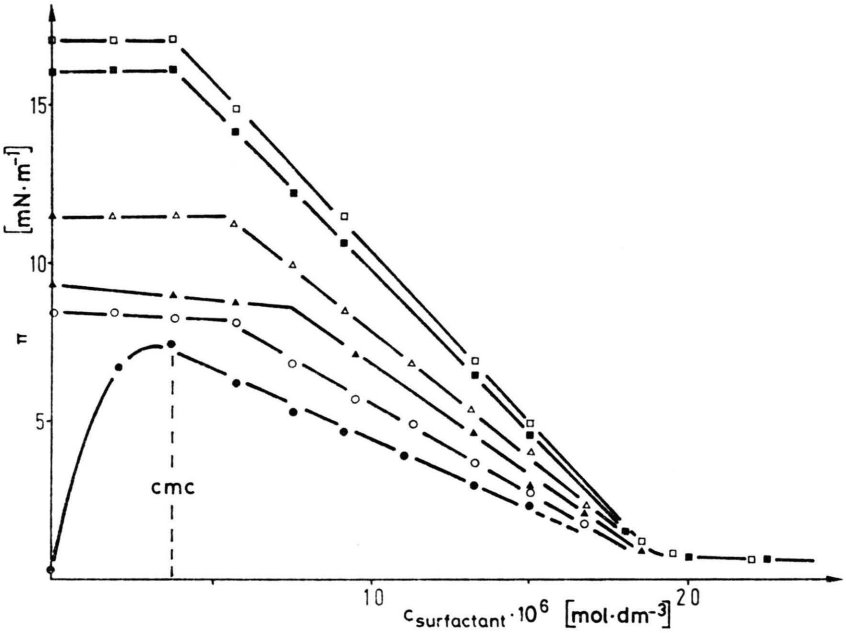

Fig. 1. Variation of the surface pressure (π) of an 1-octanol monolayer in equilibrium with aqueous solutions of calcium di-2-ethylhexyl sulfosuccinate at different initial pressures.

are to be considered, i.e.

$$nS + mA \overset{K}{=} S_nA_m \quad \text{and} \quad rS \overset{K_s}{=} S_r\,. \tag{1}$$

Application of the mass action law to the complex formation and the micellization process yields

$$[S_nA_m] = K[S]^n[A]^m\,, \tag{1a}$$

$$[S_r] = K_s[S]^r\,, \tag{1b}$$

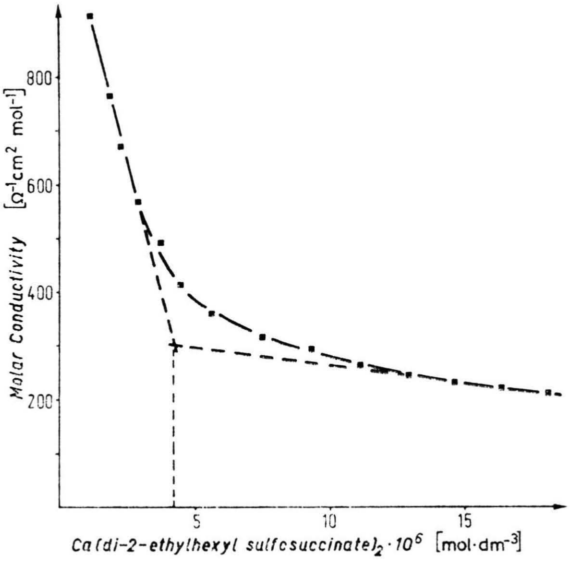

Fig. 2. Molar conductivity (Ω^{-1} cm^2 mol^{-1}) vs concentration of calcium di-2-ethylhexyl sulfosuccinate.

where n, m, and r are equilibrium association numbers of the surfactant S and alcohol molecules A in bulk solution. According to the mass conservation, the surfactant concentration in solution can be related to the weighed-in concentration of surfactant, i.e.

$$\begin{aligned}[S_0] &= [S] + r[S_r] + n[S_nA_m] \\ &= [S](1 + rK_s[S]^{r-1} + nK[S]^{n-1}[A]^m)\,.\end{aligned} \tag{2}$$

In agreement with the experiments we are interested in the concentration region close to the cmc where the concentrations of the complexes and the micelles can be neglected with respect to the surfactant monomer amount, i.e.

$$1 \gg rK_s[S]^{r-1} + nK[S]^{n-1}[A]^m\,.$$

K_s denotes the association constant of the surfactant relating micelles and monomers in the frame of the pseudo-phase model and K the stability constant of the complex.

Thus, combining Eqs. (1a) and (2) yields

$$[S_nA_m] = K[S_0]^n[A]^m\,. \tag{3}$$

To proceed further we need information regarding the equilibrium concentration of alcohol in the bulk phase. Accordingly, the surface phase, i.e. the alcohol monolayer, has to be considered in some de-

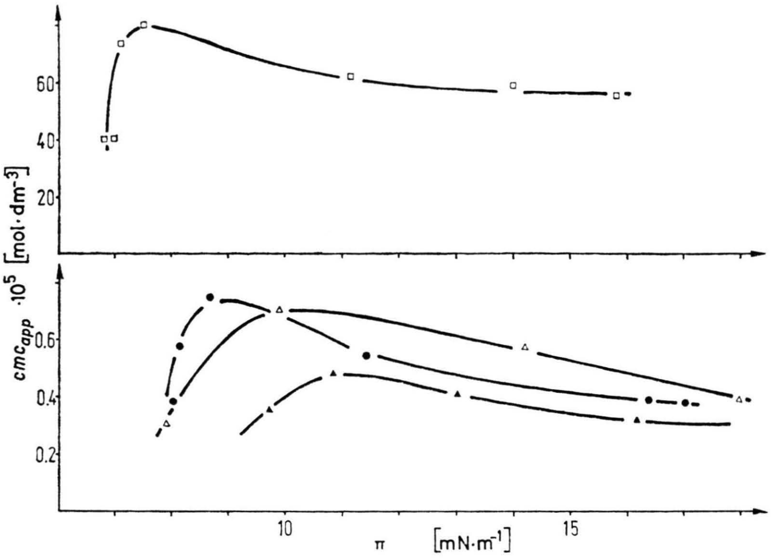

Fig. 3. Variation of the apparent critical micelle concentration of potassium (upper part of figure) and calcium di-2-ethylhexyl sulfosuccinate with the surface pressure (π): ●, □: 1-octanol, △: 1-heptanol, ▲: 1-pentanol monolayers in equilibrium with aqueous surfactant solutions.

tail. With regard to the results (Fig. 3) a maximum value of the apparent cmc versus the surface pressure is observed.

In order to explain this fact it will be assumed that two processes are competing, i.e. a pressure dependent interaction of the alcohol molecules in the surface phase* and the above mentioned alco-

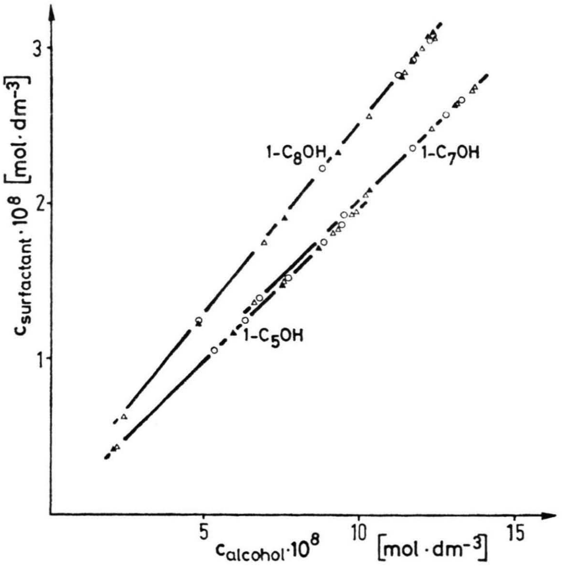

Fig. 4. Correlation between alkyl alcohol and Ca(di-2-ethylhexyl sulfosuccinate)$_2$ concentrations in the aqueous bulk phase. The data are obtained by the following procedure: $A(\pi_0 - \pi) = RT \ln(\Gamma_0/\Gamma)$, where Γ_0 is the alcohol concentration in the monolayer in equilibrium with the pure aqueous bulk phase. Γ is the corresponding concentration in equilibrium with an aqueous surfactant solution. $\Gamma_0 - \Gamma$ is the amount of dissolved alcohol in the presence of surfactant, assuming that the solubility of alcohol in the pure aqueous phase is negligible. △, ▲, ○, correspond to different surface pressures of the alcohol monolayers.

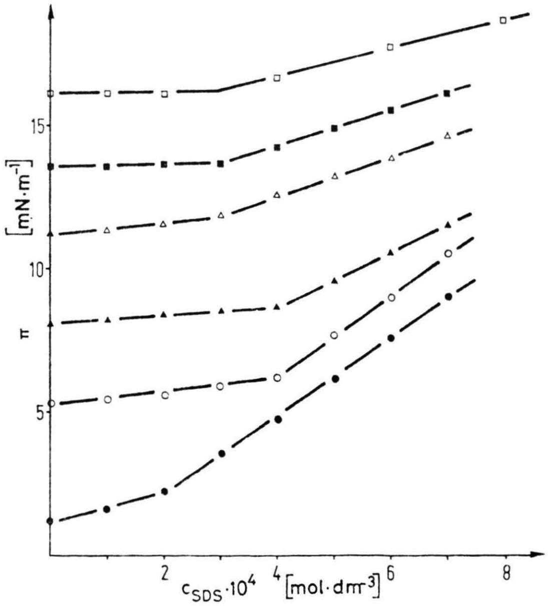

Fig. 5. Variation of surface pressure (π) of 1-octanol monolayer in equilibrium with aqueous solutions of sodium dodecyl-sulfate (SDS) at different initial pressures.

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* Adsorption behaviour of alcohols with association in the adsorbed layer has recently been discussed by G. H. Findenegg et al., Progr. Colloid Polymer Sci. **67**, 131 (1980).

hol/surfactant complex formation in the bulk phase. It appears that an essential effect of increasing the surface pressure is a squeezing out of water molecules from the water layer which stays in immediate contact with the polar head groups of the alcohol molecules. This process is described by

$$A(\mathrm{H_2O})_\nu = \frac{\nu}{a} A_{(a/\nu)}(\mathrm{H_2O})_{a-\varrho} + \frac{\nu\varrho}{a}(\mathrm{H_2O}), \qquad (4)$$

where ν in the frame of this model is not the water of hydration but the "water-half-sphere" which could be formally attached to one alcohol molecule in the surface phase.

The water set free by the "compression" of the surface layer, i.e. $(\nu\varrho/a)(\mathrm{H_2O})$ (see Eq. (4)), is added to the bulk phase. The surface pressure dependent equilibrium constant K^σ of the process depicted in Eq. (4) is given by Eq. (5) where a, is the association number of the respective alcohol molecules.

$$K^\sigma(\pi) = \left(\frac{\pi}{\pi^0}\right)^{(\nu-a)/a}. \qquad (5)$$

Equation (5) permits one to derive the pressure dependent chemical potential of the alcohol monomers in the surface phase, i.e.

$$\mu_\mathrm{A}^\sigma - \mu_\mathrm{A}^{\sigma_0} = RT\ln\left(\frac{\pi}{\pi^0}\right)^{(\nu-a)/a}, \qquad (6)$$

where μ_A^σ and $\mu_\mathrm{A}^{\sigma_0}$ denote the chemical potentials of alcohol monomers in the surface monolayer with respect to the surface pressures π and π^0. The latter is a reference pressure at high dilution were the molecules have just sufficient area to rotate freely in two dimensions, i.e. π^0 is a function of the chain length, $\mu_\mathrm{A}^{\sigma_0}$ then refers to the condition $\pi = \pi^0$.

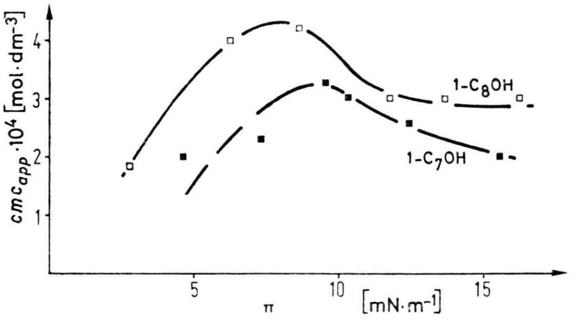

Fig. 6. Variation of critical micelle concentration of sodium dodecyl sulfate with surface pressure (π). □: 1-octanol-, ■: 1-heptanol-monolayers in equilibrium with aqueous surfactant solutions.

In order to relate the alcohol molecules in the surface and bulk phases we have to consider the phase equilibrium with respect to the monomers, thus

$$\mu_\mathrm{A}^\sigma = \mu_\mathrm{A}^\mathrm{b}. \qquad (7)$$

The superscript b refers to the bulk phase.

Combining Eqs. (6) and (7) and introducing the concentration dependence of the chemical potential of the alcohol molecules in the bulk phase, we obtain

$$\mu_\mathrm{A}^{\sigma_0} + \left(\frac{\nu-a}{a}\right) RT\ln\left(\frac{\pi}{\pi^0}\right) = \mu_\mathrm{A}^{\mathrm{b},\ominus} + RT\ln[A]/[A^0]. \qquad (8)$$

$\mu_\mathrm{A}^{\mathrm{b},\ominus}$ is the standard chemical potential of the alcohol molecules in the bulk phase under the condition $[A] = [A^0]$. The latter concentration denotes a reference state which is defined by the condition that $\pi = \pi^0$ and $\mu_\mathrm{A}^{\sigma_0} = \mu_\mathrm{A}^{\mathrm{b},\ominus}$. Equation (8) yields the equilibrium concentration of alcohol molecules in the bulk phase, i.e.

$$[A] = [A^0]\left(\frac{\pi}{\pi^0}\right)^{(\nu-a)/a} \cdot \exp\{(\mu_\mathrm{A}^{\sigma_0} - \mu_\mathrm{A}^{\mathrm{b},\ominus})/RT\}. \qquad (9)$$

Equations (3) and (9) can be combined in such a way as to demonstrate the experimentally observed pressure and concentration dependent behaviour of the apparent critical micelle concentration of the surfactant due to the alcohol-surfactant complex formation, hence

$$\frac{[S_nA_m]}{[A]} = K[S_0]^n\left\{[A^0]\left(\frac{\pi}{\pi^0}\right)^{(\nu-a)/a} \cdot \exp\{(\mu_\mathrm{A}^{\sigma_0} - \mu_\mathrm{A}^{\mathrm{b},\ominus})/RT\}\right\}^{m-1}. \qquad (10)$$

To elucidate the physical significance of Eq. (10) it may be rewritten in a slightly different form, i.e.

$$\frac{[S_nA_m]}{[A]} = \left\{\left(\frac{\pi}{\pi^0}\right)^{(\nu-a)/a} / \text{“ccc”}\right\}^{m-1} \qquad (11)$$

since at constant temperature the exponential term in Eq. (10) is constant and can be combined with $[A^0]$. This constant can be included in the critical complex concentration, "ccc", which is represented analytically by

$$\text{“ccc”} = \left(\frac{1}{K[S_0]^n\,\mathrm{const}}\right)^{1/(m-1)}. \qquad (12)$$

Equation (11) tells us that we should expect a strong increase in complex formation as soon as the ratio on the right hand side of Eq. (11) becomes greater than 1. In the present case the situation appears to be a little bit more complicated since the exponent of the surface pressure ratio also depends upon the surface pressure via ν and (eventually) a, the association number of the alcohol molecules. The "dehydrating" process depicted in Eq. (4) which could easily be visualized to be pressure dependent, could be interpreted as a decrease in the solubility of alcohol molecules in the bulk solution. Hence a reciprocal pressure dependence of ν is to be expected. Naturally, also a could be pressure dependent. However this would introduce another adjustable parameter which usually decreases the evidence of a model. Principally, both parameters could be surface pressure dependent.

Equation (11) also contains π^0, hence it is to expected and actually seen that the onset, $[S_n A_m]/[A]$, of complex formation depends on the chain lengths of the alcohol molecules. It is easily seen that $\pi^0_{\mathrm{C}_i\mathrm{OH}} > \pi^0_{\mathrm{C}_{i+1}\mathrm{OH}}$ if the same reference state at constant number of alcohol molecules is assumed. From Eq. (11) one has to conclude that with increasing values of π^0 the onset of the complex formation should be shifted to higher surface pressure values. This is actually seen from Fig. 3 and confirmed by conductivity measurements. A more detailed discussion does not appear reasonable in view of the above made assumptions. However, from the above reasoning some kind of maximum value regarding the cmc shift could be expected: two competing reactions are assumed to proceed according to our model. These are the formation of the alcohol/surfactant complex in the bulk phase and the interaction of the alcohol molecules and/or a dehydrating process in the surface layer. At low surface pressure values there are not sufficient alcohol molecules in the bulk phase available in order to promote the complex formation. With increasing pressure this complex formation is detected by a shift of the apparent cmc to larger surfactant concentrations. In relation to Eq. (2), the mass balance, it is to be expected that the apparent cmc can actually serve as an indicator for the alcohol/surfactant complex formation. At higher surface pressures processes in the surface layer must come into play, i.e. a dehydrating phenomenon as sketched above or an induced association of alcohol molecules which again decrease the chemical potential of the alcohol molecules in the surface layer and hence their concentration in the bulk phase.

In order to evaluate the maximum shift of the apparent cmc with the applied surface pressure, one has to differentiate Eq. (11) with respect to π/π^0, i.e.

$$\frac{\mathrm{d}\ln[S_n A_m]}{\mathrm{d}(\pi/\pi^0)} = -\frac{\mathrm{const}}{a(\pi/\pi^0)^2}\ln\left(\frac{\pi}{\pi^0}\right) + \frac{\mathrm{const}}{a(\pi/\pi^0)^2} - \frac{a\cdot\mathrm{const}}{(\pi/\pi^0)} = 0\,. \tag{13}$$

In order to derive this equation it has been assumed that ν is proportional to $1/(\pi/\pi^0)$. It follows from Eq. (15) that

$$\ln(\pi/\pi^0)_{\max} = 1 - a^2(\pi/\pi^0)_{\max}\,. \tag{13a}$$

Equation (13a) predicts the maximum value of $[S_n A_m]/[A]$ at $\pi/\pi^0 = 1$ if the parameter a is taken to be 1. This value of π/π^0 almost coincides with the theoretical plot (Fig. 7) of Equation (11). However, Fig. 7 has been plotted with $\nu = 1.1/(\pi/\pi^0)$ instead taking $\nu = 1/(\pi/\pi^0)$ as has been assumed in deriving Eq. (13a) from Equation (13). Generally, Eq. (13a) would contain an additional factor relating ν and $1/(\pi/\pi^0)$.

Finally, it should be pointed out that Eq. (11) had to be plotted with a constant parameter a to yield a reasonable coincidence with Fig. 3 indicating, apparently, a negligible pressure dependent association for short chain alcohols as compared to long chain alcohol molecules.

Having discussed the situation in the bulk phase, the apparent opposite case using SDS and 1-octanol (or 1-heptanol) should shortly be considered. Quite analogous relations to those developed for the first

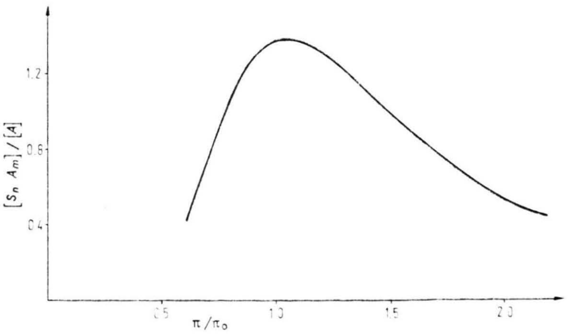

Fig. 7. Theoretical plot calculated according to Eq. (11), choosing the parameters: $\nu = 1.1/(\pi/\pi^0)$, $a = 1$, "ccc" $= 0.9$, and $m = 4$ (experimental parameter).

case can be applied. One has to keep in mind, however, that now the aggregation formation proceeds in the alcohol surface phase, i.e. one has to consider approximately a binary system. This can already be concluded from the purely phenomenologic observation that the conductivity does not depend on the concentration of the SDS and is strongly fluctuating (high resistance of the aqueous solution). Contrary to a "normal" solvent, the alcohol component can be "diluted" by decreasing the surface pressure. With the same model assumption as in the first case, one starts with an analogous Eq. (3), i.e. the formation of an alcohol-surfactant complex at low surface pressures. The phase equilibrium between the bulk and surface phases has now to be considered with respect to the surfactant, hence an equation similar to Eq. (4) has to be derived. The next step will be analogous to Eq. (10), however by considering instead the ratio $\Gamma_{S_i A_j}/\Gamma_S$. Then one has to introduce the mass conservation with regard to the surfactant in the surface phase at a particular pressure (π):

$$n^\sigma_{S,\pi} = n^\sigma_S \left\{1 + i K^\sigma(\pi) \left(\frac{\Gamma_{A_a}}{K_{\mathrm{a}}{}^\sigma(\pi)}\right)^{j/a} \cdot \Gamma_S^{i-1} + s K_{\mathrm{s}}{}^\sigma \Gamma_S^{s-1}\right\}, \tag{14}$$

where in the second term on the right hand side, which corresponds to $\Gamma_{S_i A_j} = K^\sigma(\pi) \Gamma_S^i \Gamma_A^j$, the mass action law with respect to a change in the property of the alcohol has been introduced. By this means a competition between the complex formation and changes of the alcohol property is simulated. If it is assumed that at increasing surface pressures a demixing process exceeds the alcohol-surfactant complex formation, the micellization in two dimensions (surfactant "islands") starts to control $n_S{}^\sigma$, if the third term is large compared with one. The onset of the steepness of the $\pi(c)$-plots may be due to the fact that the chemical potential of the surfactant monomers in the presence of "micelles" within the surface phase is smaller than that of the SDS monomers in the bulk phase. The cmc of SDS in the aqueous bulk phase is about one order of magnitude larger (15) than the "cmc" values corresponding to the aggregation process in the surface phase. Moreover, $K_{\mathrm{s}}{}^\sigma$ is taken to be independent of the surface pressure to a first approximation which appears to be confirmed by Figs. 5 and 6. Also the maximum (Fig. 6) of the "cmc"(π)-plot can be inferred from these considerations if initially the alcohol-surfactant complex formation is favoured.

It appears remarkable that relatively elementary thermodynamic considerations describe qualitatively rather satisfactory the experimental results by applying in both examples the same assumptions regarding the two components, alcohol and surfactant.

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