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SURFACTANT ADSORPTION PARAMETERS DETERMINED FROM SURFACE TENSION DATA AS MEASURED BY DROP AND BUBBLE PROFILE ANALYSIS TENSIOMETRY

Abstract: Drop and bubble profile analysis tensiometry is the most frequently used methodology for studies of surfactant adsorption at liquid interfaces. However, there is depletion of surfactant molecules caused by adsorption when drop profile analysis tensiometry is applied for surface tension measurements at low surfactant bulk concentration. This depletion can lead to wrong characteristic adsorption parameters when not quantitatively corrected in the data analysis. We show for the two surfactants CTAB and Tween 20, that particularly the values for the adsorption activity coefficient and the molar area of adsorbed molecules are largely overestimated when using drop profile analysis data. It is shown that bubble profile analysis data provide correct values of the adsorption characteristics. The data analysis presented here is based on the Frumkin adsorption model.

Keywords: Adsorption of surfactant, bubble and drop profile analysis tensiometry, depletion effects due to adsorption, Frumkin adsorption model.

1. Introduction

Surface active molecules – surfactants – are omnipresent in our daily life and applied in many modern technologies. The optimum use of surfactants requires good knowledge of their surface properties. The surface tension isotherms measured for aqueous solutions of surfactants as a function of bulk concentration give access to the most important fundamental information about the properties of the surfactant adsorption layers, such as surface activity, molar area at the surface and critical micelle concentration [[1]].

Among the various surface tension methods, the bubble and drop profile analysis tensiometry is the most frequently used one to day. The pioneer for this methodology was A.W. Neumannwho published a number of fundamental papers about this method which he called ADSA (Axisymmetric Drop Shape Analysis) [1,2,3,4].Recently, the state of the art of this methodology was described with details referring to the Profile Analysis Tensiometer PAT1 (SINTERFACE Technologies, Berlin, Germany) [[1]].

It was discussed in [**Ошибка! Закладка не определена.**] that in studies with protein solutionsa depletion happens due to the adsorption of part of the protein molecules at the drop surface. In contrast, when using an air bubble immersed in the protein solution, the depletion due to protein adsorption at the bubble surface is negligible. From the difference between the obtained data the adsorbed amount of protein can be estimated [[1]].

The mentioned depletion effects in protein adsorption experiments appear as the used bulk concentrations are very low. However, also studies of solutions of strongly surface-active moleculescan be affected by this phenomenon. Thus, it is important to know from what surface activity and surfactant bulk concentration on the mentioned depletion effects become important and have to be quantitatively considered.

In a recent work, we presented experimental data for the surface tension isotherms of three different surfactants: sodium dodecyl sulphate (SDS), hexadecyl trimethyl ammonium bromide (CTAB) and the non-ionic surfactant Polyoxyethylene(20)sorbitanmonolaurate (Tween20) [1]. In this work a protocol was proposed thattakes into account the mass balance of the amount of surfactant adsorbed at the drop surface and remaining in the drop bulk. It is the purpose of this short communication to show how the erroneous use of surface tension isotherm data can lead to large errors in the determination of characteristic adsorption data for the studied surfactants.

2. Adsorption model for describing the experimental isotherm data

The Frumkin adsorption model is one of the most frequently used one for many surfactant systems although it had been proposed already almost 100 years ago [1]. The equation of state for this model reads

$$-\frac{\Pi\omega_0}{RT} = \ln(1-\theta) + a\theta^2 \qquad (1)$$

while the adsorption isotherm has the form

$$bc = \frac{\theta}{1-\theta}\exp(-2a\theta) \qquad (2)$$

Here$\theta = \Gamma\omega$ *is* the surface coverage, $\Gamma$is the adsorption, $\omega$is the molar area, $\Pi = \gamma_0 - \gamma$is the surface pressure withγ_0 and γbeing the surface tension of the solvent and solution, respectively, $a$is the interaction parameter, $R$is the gas law constant, $T$is the temperature, and $b$is the adsorption activity coefficient. In [8] it was assumed that the intrinsic compressibility coefficient εdepends on the surface coverage, however, for the discussion here, we will assume that this coefficient is negligible in order to simplify the discussion of the adsorption parameters.

To quantify the depletion effects appearing during the adsorption of surfactants at the surface of a single drop, we have to make a quantitatively mass balance. In [**Ошибка! Закладка не определена.**] it was shown that the final concentration inside a drop is given by

$$c = c_0 - (A/V)\Gamma \qquad (3)$$

While c_0 is the initial surfactant concentration in the drop having the volume V and the surface area A. Introducing this final bulk concentration c into the adsorption isotherm given by Eq. (2) we obtain:

$$b\left(c_0 - \frac{A}{V}\Gamma\right) = \frac{\theta}{1-\theta}\exp(-2a\theta) \qquad (4)$$

The set of Eqs. (1) and (2) can be used for the analysis of data obtained from experiments without any depletion effects, as it is the case for bubble profile analysis tensiometry. In contrast, using isotherm data measured with drop profile analysis tensiometry, a depletion appears and Eqs. (1) and (4) have to be used to correct the evident loss of molecules in the drop volume caused by adsorption at the drop surface.

The question we want to answer here is now, what happens when we apply the original Frumkin model, as given by Eqs. (1) and (2), to data measured by drop profile analysis without considering depletion effects. Note, this was the well accepted procedure done before we discussed the depletion effects due to adsorption.

The amount of lost surfactant molecules due to adsorption can be estimated by Eq. (3) and is mainly given by the ratio of drop area over drop volume A/V. In routine experiments, the drop surface area is about 0.35 cm^2 while the volume is about 0.02 cm^3, so that the ratio is A/V=17.5 cm^{-1}, i.e. A/V » 1 cm. For bubbles of the same size like the drop, immersed into a surfactant solution of say 20 cm^3 volume, the ratio is A/V=0.0175 cm^{-1}, i.e. three orders of magnitude less. Note, for smaller drops the ration A/V is even larger, which is less favourable and the loss of surfactant determined via Eq. (3).

3. Materials and experimental methods

The experimental data we want to reinterpret here were obtained in [**Ошибка! Закладка не определена.**]by using the drop and bubble profile analysis tensiometer PAT-1 (SINTERFACE Technologies, Germany) [1].The surfactants studiedin [**Ошибка! Закладка не определена.**] were SDS, decanol, CTAB and Tween20.As the data obtained for SDS did not show any measurable depletion effects, and for decanol only very little effects, we will not discuss them here. Note, for all surfactants having a surface activity less than that of decanol or SDS any depletion effects can be neglected. We do not want to present an extensive discussion on how the surface activity of a surfactant is defined, but we just use the value of the adsorption activity coefficient b in Eq. (2) as a useful parameter. The larger the value of b is, the higher is the surface activity of the corresponding surfactant.

4. Results and Discussion

The experimental results presented in Figs. 1 and 2 are replotted from [8]. There are two sets of data in the given isotherms, one measured with drop profile (black squares) and one measured with bubble profile analysis tensiometry (red circles). As expected for the two rather strong surface-active surfactants, the data points obtained from bubble experiments are further left at lower concentrations than those measured with single drops. This was expected because to reach the same surface tension with a single drop, we need a higher initial bulk concentration. During the experiment, the concentration inside the single drops decreases due to the loss of surfactant molecules adsorbed at the drop surface.

Following the target of this work, the experimental data were fitted by the Frumkin adsorption model given by Eqs. (1) and (2). As mentioned already further above, we used the Frumkin adsorption model in its classical form as derived in [**Ошибка! Закладка не определена.**] and did not add the dependence of the molar area of adsorbed surfactant molecules as function of the surface coverage θ, as it was made in [**Ошибка! Закладка не определена.**], i.e. assuming a so-called intrinsic compressibility coefficient which allows a qualitatively better reflection of the experimental findings by the model. In the data analysis performed here, we also did not consider the obviously happening depletion due to adsorption. This "wrong" approach on purpose was made in order to demonstrate the impact of depletion effects on the adsorption parameter values. The results of fitting are summarized in Table 1.

Table1 - Model parameters used for fitting of experimental data
by the classical Frumkin adsorption model given by Eqs. (1) and (2)

Surfactant	Experimental mode	ω, 10^5 m^2/mol	b, m^3/mol	a	Line in the figure
CTAB,					Fig. 1
	Drop	2.36	40	0.95	dashed line
	Bubble	2.1	14.7	1.8	solid line
Tween 20					Fig. 2
	Drop	2.27	300	0.7	dashed line
	Bubble	1.6	170	0.6	solid line

As we can see, in particular the value of the adsorption activity coefficient obtained for the drop data as much larger than that for the bubble data. For CTAB this value for the coefficient b is almost three times larger, which means the isotherm is shifted to larger concentrations by a factor of almost 3, a shift of half an order of magnitude. The molar area obtained from the drop data is also larger (by more than 10%) as compared to the bubble data. This would mean that the molecules require more area at the interface, or in other words are less close packed, as we would conclude from the data obtained from bubble experiments.

For the second surfactant discussed here, the non-ionic surfactant Tween 20, the situation is quite similar. The surface activity coefficient is decreased by a factor of about 2 (larger value of b for the drop data), while the area per adsorbed molecule is larger by even 30%. These changes can be evaluated as dramatic and reflect a strongly different adsorption behaviour.

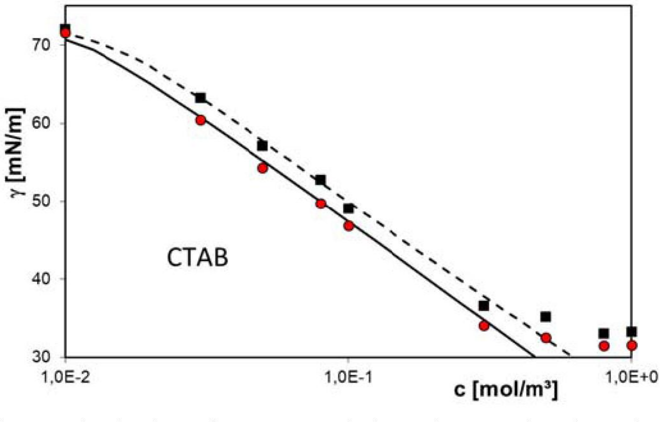

Figure 1 - Equilibrium surface tension isotherm for aqueous solutions of CTAB plotted as a function of the initial solution concentration, as measured by bubble profile (●) and drop profile analysis tensiometry (■); lines represent the results of fitting the adsorption model to the experimental data

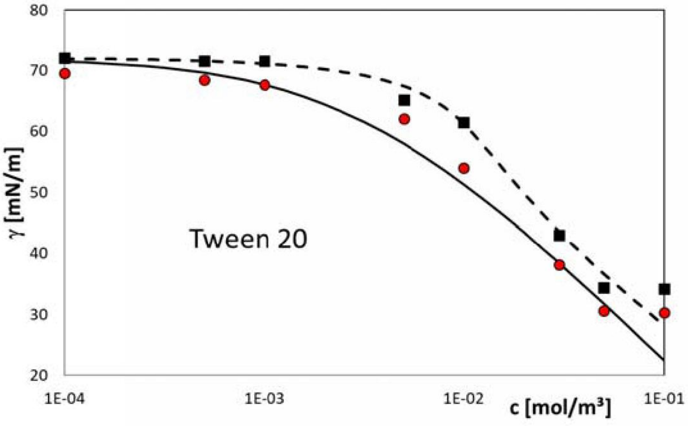

Figure 2 - Equilibrium surface tension isotherm for aqueous solutions of Tween 20 plotted as a function of the initial solution concentration, as measured by bubble profile (●) and drop profile analysis tensiometry (■); lines represent the results of fitting the adsorption model to the experimental data

Let us somehow generalize the findings so that we can apply them to other surfactant systems. It was shown that for the given experimental conditions the ratio of A/V for drops (17.5 cm^{-1}) is much larger than 1 cm^{-1}, while it is much smaller than 1 cm^{-1} for bubble data. Assuming that typical values of the adsorbed amount Γ are between 10^{-11}mol/cm² and 10^{-9}mol/cm², we obtain for the second term $(A/V)\Gamma$ on the right-hand side of Eq. (3) values of roughly 10^{-10} to 10^{-8}mol/cm³, i.e. 10^{-4} to 10^{-2}mol/m³. This is exactly the concentration range in which the two studied surfactants adsorb (see Figs. 1 and 2). Their surface activity, expressed by the adsorption activity coefficient b, let us expect this. We know that at a bulk concentration of $c \approx 1/b$ the surface layer is covered by approximately 50%, i.e. the parameter 1/b refers to a concentration which tells us where we must expect serious depletion effects. For all concentrations below 1/b, these depletion effects must be essential. For CTAB this means for concentrations below about 10^{-1}mol/m³ and for Tween 20 below 10^{-2}mol/m³ the depletion effects are remarkable. Comparing this finding with experiments for the various surfactants studied and applied in surface science and technology (cf. the isotherms given in [**Ошибка! Закладка не определена.**] for many surfactants), we can conclude that for example for Triton X100 or the oxyethylated alcohols like $C_{12}EO_5$ or $C_{14}EO_5$ the depletion effects are substantial, while for SDS and shorter chain alkyl sulphates, DeTAB (decyl trimethyl ammonium bromide) or $C_{10}EO_8$the depletion effects are negligible and errors will not appear when drop profile data are analysed and interpreted with the classical version of the Frumkin or any other adsorption model.

Finally, we should compare the parameter values in Table 1 with those published in [**Ошибка! Закладка не определена.**] using a more refined adsorption model. The absolute values deviate from those presented in the table. This is clear as the parameters are not completely independent of each other. During the fitting process, any change in one parameter value causes changes in the optimum values of any other parameter. This is particularly true for the technical surfactant Tween 20, which is obviously a large mixture of many surface-active compounds. Thus, only the complete set of parameter values describes the adsorption behaviour of a surfactant sufficiently well. Note, however, the parameter values given in Table 1 are based on fitting drop and bubble data by exactly the same adsorption model and all discussed differences originate from the depletion effects, which were neglected on purpose when fitting the drop data (although these effects are essential).

5. Conclusions

As discussed recently in [8], a specialcorrection and fitting algorithm has to be applied to determine the characteristic adsorption parameters from experimental data obtained from drop profile analysis tensiometry. This algorithm is based on the balance between the surfactant mass in the drop bulk and the amount adsorbed at the drop surface. Exact knowledge about the surface area and volume of the drop is required for these corrections as shown above.When ignoring the mentioned effects, the error made by this erroneous procedure is significant and can lead to wrong conclusions.

Similar mistakes are sometimes made in studies on emulsions. When supporting emulsion properties, often interfacial tension studies are performed in order to determine the number of surfactants adsorbed at drop surfaces. In the case, however, when the emulsion drops are rather small (much smaller than the drops used in tensiometry so that the ratio A/V becomes even much larger than here), the amount of adsorbed surfactant is enormous and data measured at macroscopic interfaces are not relevant. As shown here, errors in the determined coefficient b used to estimate the order of magnitude for the required concentration $c>1/b$ for covering the emulsion drop surfaces sufficiently by surfactant molecules, can lead to wrong values, too loweven by several orders of magnitude.

It could be recommended to use only bubble profile tensiometry in order to avoid errors in the determination of adsorption characteristics for surfactants. Experimentalists know, however, that experiments with single drops are much easier performed than with bubbles immersed in a solution container. In addition, some specific samples can be provided only in extremely small quantities so that drop profile analysis with single drops (typically with volumes of 20 μl) is the method of choice while for bubble experiments a much larger amount of solution (typically 10-25 ml) would be required required.

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ТАМШЫЛАР МЕН КӨПІРШІКТЕР СҰЛБАСЫН ТАЛДАУ АРҚЫЛЫ БЕТТІК КЕРІЛУДІ ӨЛШЕУ ӘДІСІМЕН БЕТТІК-АКТИВТІ ЗАТТАРДЫҢ АДСОРБЦИЯЛЫҚ ПАРАМЕТРЛЕРІН АНЫҚТАУ

Аннотация: Тамшылар мен көпіршіктер сұлбасын талдау тензиометриясы беттік-активті заттардың сұйық беттердегі адсорбциясын зерттеуде жиі қолданылады. Алайда, бұл әдісті беттік-активті заттардың (БАЗ) төмен концентрациясында қолдану БАЗ-дардың көлемдегі мөлшерінің азаюына апарады. Бұл өзгеріс беттік-активті заттардың адсорбциялық параметрлерін анықтау барысында ауытқулар беруі мүмкін, сол себепті алынған сандық нәтижелерге түзетпелер енгізу қажет. Осыған орай адсорбциялық белсендігі мен мольдік ауданы жоғары болған CTAB және Tween 20 сияқты екі БАЗ үшін адсорбциялық мәліметтер берілген. Көпіршіктер сұлбасын талдау арқылы алынған мәліметтер адсорбцияны дұрыс сипаттайтындығы көрсетілген. Талдау Фрумкиннің адсорбция моделінде жасалған.

Тірек сөздер: Беттік-активті заттардың адсорбциясы, тамшылар мен көпіршіктер сұлбасын талдау тензиометриясы, адсорбция барысында зат мөлшерінің азаюы, Фрумкиннің адсорбция моделі.

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АДСОРБЦИОННЫЕ ПАРАМЕТРЫ ПАВ (ПОВЕРХНОСТНО-АКТИВНОГО ВЕЩЕСТВА), УСТАНОВЛЕННЫЕ ИЗМЕРЕНИЕМ ДАННЫХ ПОВЕРХНОСТНОГО НАТЯЖЕНИЯ МЕТОДОМ АНАЛИЗА ПРОФИЛЯ КАПЕЛЬ И ПУЗЫРЬКОВ

Аннотация. Тензиометрия анализа профиля капель и пузырьков является наиболее часто используемой методикой для исследования адсорбции поверхностно-активного вещества на жидких межфазных границах. Однако, происходит уменьшение поверхностно-активных молекул в объемной концентрации в связи с их адсорбцией при использовании тензиометрического метода анализа, применяемого при измерении поверхностного натяжения ПАВ при малых концентрациях. Это уменьшение в объеме может привести к неправильным характеристикам параметров адсорбции, если не ввести количественные поправки при анализе данных. Представлены данные для двух поверхностно-активных веществ: CTAB и Tween 20, в частности, для которых значительно завышены данные коэффициента адсорбционной активности и молярной площади адсорбированных молекул при анализе данных профиля капли. Показано, что данные анализа профиля пузырьков представляют правильные значения адсорбционных характеристик. Анализ данных основан на модели адсорбции Фрумкина.

Ключевые слова: Адсорбция ПАВ, тензиометрия анализа профиля капель и пузырьков, эффект обеднения раствора при адсорбции, модель адсорбции Фрумкина.