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A Criterion for judging the purity of surfactant solutions based on diffusion controlled adsorption kinetics

R. Miller and K. Lunkenheimer

Central Institute of Organic Chemistry of the Academy of Sciences of the GDR, Berlin-Adlershof, G.D.R.

Abstract: Based on the theory of diffusion controlled adsorption, simple relations are derived for judging the grade of purity of surfactant solutions. The difference of surface tension values between adsorption and desorption under well-defined conditions is used as the experimental measure. Experimental data on surface-chemically pure *n*-alkyl dimethyl phosphine oxides demonstrate the application of the relations derived. It could be demonstrated that it is also possible to use the criterion to evaluate the concentration and surface activity of present impurities in surfactant solutions.

Key words: Purity of surfactant solutions, criterion of purity, diffusion controlled adsorption model.

Notations

a_i – surface activity parameter
β – ratio of the initial to the final area in the case of compression of the adsorption layer (desorption experiments)
c_i – bulk concentration
D_i – diffusion coefficient
Γ_∞ – maximum surface concentration
Γ_i – surface concentration
σ – surface tension
t – time
indices:
i – number of the component ($i = 2$ main component, $i = 3, \ldots$ contaminations)
A – adsorption
D – desorption

1. Introduction

Investigations of adsorption layers aim at the determination of specific static and dynamic properties of the surfactant used. However, the literature shows that very contradictory results are obtained for the same surfactant by different authors.

It could be proved that besides methodological problems the presence of surface active impurities is the main reason for these discrepancies [1–3]. To obtain specific data of surfactant adsorption layers a criterion is necessary with the help of which the grade of purity of the solution can be judged. Only a small number of attempts to formulate such a criterion have been published [4, 5]. Recently we derived a general criterion which can detect traces of surface active impurities [6]. It is related to any purification procedure and defines the conditions for surface-chemically pure surfactant solutions. The criterion need not assume any adsorption kinetics model but can only be applied in connection with a purification procedure.

In the present paper a simple criterion for judging the purity of surfactant solutions will be formulated based on the theory of diffusion controlled adsorption kinetics. Moreover, the criterion enables one to identify surface active impurities by their surface activity and concentration.

2. Theoretical basis

The model of diffusion controlled adsorption and desorption was applied as the basis of all calculations presented here. It was formulated and solved for the case of adsorption of a surfactant at fluid interfaces by Ward and Tordai [7] and Hansen [8] and generalized to the case of desorption processes by Cini et al. [9].

The generalization to surfactant mixtures [10] leads to the following system of integral Equations

$$\Gamma_i = \Gamma_{i,b} + 2\sqrt{\frac{D_i}{\pi}}\ \Big(C_{i,c}\sqrt{t} - \int_0^{\sqrt{t}} C_i(0, t-\tau)\, d\sqrt{\tau}\Big),\ i = 2, 3, \ldots, n, \qquad (1)$$

where subscripts i denote the substances ($i = 2$ main component, $i = 3, 4, \ldots$ impurities), $\Gamma_i\,(t)$ is the surface concentration as a function on time t, $c_{i,o}$ and $c_i\,(0, t)$ are the concentrations in the bulk and subsurface, respectively, and D_i are the diffusion coefficients of the components, while $\Gamma_{i,b}$ represents the surface concentration at time $t = 0$. To solve the integral Equation system relations between $\Gamma_i\,(t)$ and $c_i\,(0, t)$ have to be added to complete the mathematical problem. In the following calculations we will use a generalized Langmuir absorption isotherm [11]

$$\Gamma_i = \Gamma_\infty \frac{C_i / a_i}{1 + \sum\limits_{k\,zz}^{n} C_k\, l\, a_k}\ ,\ i = 2, 3, \ldots, n \qquad (2)$$

which is a sufficient approximation for surfactant mixtures in the concentration range applied in the present study. The numerical solution of the nonlinear integral Equation system was performed following the algorithm proposed in [10].

3. The adsorption time as a simple criterion

The first attempt to define a quantitative condition for the purity of a surfactant solution on the basis of adsorption kinetics data was presented by Mysels and Florence [4]. The relations derived presume a knowledge of the surface chemical data of the impurity and suppose a real establishment of the adsorption equilibrium. According to the findings analysed in [12] it is more reasonable to take into account not only the establishment of the adsorption equilibrium but also that of a succeeding desorption process. In [2, 3] it was demonstrated that the difference between surface tension values of an adsorption layer in adsorption and desorption is an experimentally useful measure to evaluate the purity of surfactant solutions. Originating from these findings a criterion based on a diffusion controlled adsorption mechanism will be derived.

Therefore the times $t^A = t^D$ were calculated which are necessary for the process of adsorption and a succeeding desorption (after compression of the adsorption layer with a ratio $\beta = 2$) to obtain surface tension values $\sigma_A\,(t^A)$ and $\sigma_D\,(t^D)$ which fulfil the relation

$$\Delta\sigma(t^A, t^D) = \sigma_A(t^A) - \sigma_D(t^D) \leq 0.2\ \text{mN/m}. \qquad (3)$$

In other words we determined the time necessary to obtain a surface tension difference $\Delta\sigma$ of Equation (3) which is equal to or smaller than the accuracy of the measuring procedure. Figure 1 represents the function $t^A = t^D$ (the same times for both the adsorption and desorption process were chosen for simplicity) on the parameter a_2 calculated for the following standard conditions

$$D_2 = 5 \cdot 10^{-6}\ \text{cm}^2/\text{s},\ \Gamma_\infty = 5 \cdot 10^{-10}\ \text{mol/cm}^2,$$
$$c_2 = a_2,\ \beta = 2. \qquad (4)$$

The function can be approximated by the relation

$$t^A = t^D = t_o \cdot \exp\left[-18 - \frac{3}{2}\ln\frac{a_2}{a_o}\right] \qquad (5)$$

with $t_o = 1$ s and $a_o = 1$ mol/cm³.

The only datum necessary to apply the criterion Equations (3), (5) is the parameter a_2 of the surfactant to be investigated. It can be approximated by the concentration at which the equilibrium surface tension approaches a value of about 64 mN/m

$$a_2 \approx c_2\,(\sigma = 64\ \text{mN/m}). \qquad (6)$$

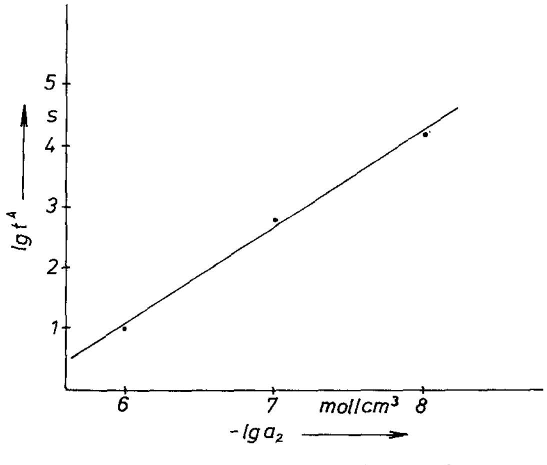

Fig. 1. Calculated time t^A necessary to obtain surface tension differences $\Delta\sigma = 0.2$ mN/m in function of the surface activity parameter a_2

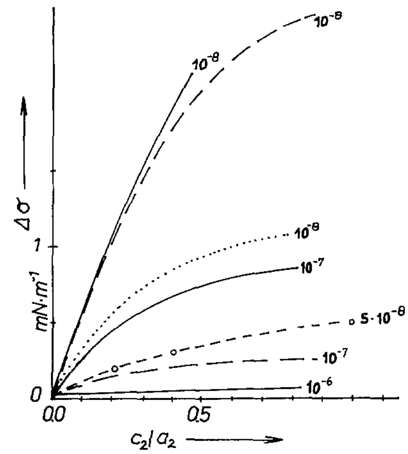

Fig. 2. Calculated surface tension difference $\Delta\sigma$ in function of the relative concentration c_2/a_2 at different times $t^A = 60$ s (——), 600 s (– – –), 3600 s (····); the figures at the curves reflect the a_2-values used; experimental points (○○○) are obtained for decyl dimethyl phosphine oxide solutions ($a_2 = 5 \cdot 10^{-8}$ mol/cm³)

To decide whether a surfactant is surface-chemically pure or not, first the characteristic time t^A of Equation (5) must be calculated and then the surface tension difference of Equation (3) at the concentration $c_2 = a_2$ can be measured. If the condition of Equation (3) is fulfilled the solution is surface-chemically pure.

The range of application of the criterion given by Equations (3) and (5) covers the following intervals

$$3 \cdot 10^{-8}\ \text{mol/cm}^3 \leq a_2 \leq 10^{-6}\ \text{mol/cm}^3,$$
$$10 \leq a_2/a_3 \leq 100,$$
$$c_3/a_3 \leq 0.1,\ t \leq 10 \cdot t^A. \qquad (7)$$

Most of the surfactants used in practice can be characterized by the criterion of Equations (3), (5) according to the restrictions (7) but for some surfactants, especially those of very high surface activity, a larger application range is of interest.

4. Criterion for a larger application range

Instead of Equation (3) it is possible to use the function

$$\Delta\sigma = \sigma_A\,(t^A) - \sigma_D\,(t^D)$$
$$= \Delta\sigma\,(t^A, t^D, c_2/a_2, c_3/a_3, \beta) \qquad (8)$$

as the criterion of purity. At first we assume that the relative concentration of impurities is negligibly small $c_3/a_3 \approx 0$. On the basis of a diffusion controlled adsorption and desorption the curves of Figure 2 were calculated. These theoretically found values $\Delta\sigma_{\text{theo}}$ can be compared with experimentally determined ones $\Delta\sigma_{\text{exp}}$ and the criterion now reads

$$|\Delta\sigma_{\text{exp}} - \Delta\sigma_{\text{theo}}| \leq 0.2\ \text{mN/m}. \qquad (9)$$

If Equation (9) is fulfilled the surfactant solution investigated is surface-chemically pure. The experimental points in Figure 2 represent some data obtained for aqueous solutions of *n*-decyl dimethyl phosphine oxide. They are in good agreement with the theoretically predicted values. The application range of criterion (9) is much larger then that of Equations (3), (5) but the sensitivity concerning the relative activity of the impurities a_2/a_3 and the relative concentration c_3/a_3 depends on the time $t^A = t^D$ used.

To find out optimal times t^A to detect contaminations characterized by the parameters c_3/a_3 and a_2/a_3 model calculations were performed based on the integral Equation system Equations (1), (2) for the following values of the parameters

$$t^A = t^D = 10,\ 60,\ 600,\ 3600\ \text{s};$$
$$a_2 = 10^{-8},\ 10^{-7},\ 10^{-6}\ \text{mol/cm}^3;$$
$$a_2/a_3 = 10,\ 100,\ 1000;$$
$$c_2/a_2 \in [0.1, 1.0];\ c_3/a_3 \in [0, 1.0]. \qquad (10)$$

For all combinations of these parameters $\Delta\sigma$-values were tabulated, an example of which is presented in Table 1. All values are calculated on the basis of the following standard conditions

$$D_2 = D_3 = 5 \cdot 10^{-6}\ \text{cm}^2/\text{s};$$
$$\Gamma_\infty = 5 \cdot 10^{-10}\ \text{mol/cm}^3;$$
$$\beta = 2. \qquad (11)$$

Table 1. Surface tension differences $\Delta\sigma$ calculated for the following conditions: $a_2 = 10^{-7}$ mol/cm³, $t^A = 60$ s, $a_2/a_3 = 100$

$c_2/a_2 =$ $c_3/a_3 =$	0.1	0.2	0.4	0.8
0.0	0.26	0.45	0.69	0.86
0.1	0.36	0.54	0.77	0.94
0.3	0.54	0.73	0.96	1.11
0.9	1.12	1.30	1.52	1.65

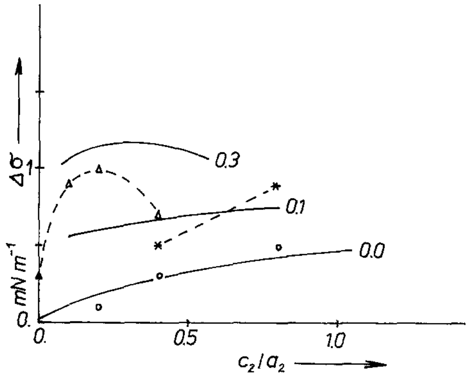

Fig. 3. Comparison of theoretical (solid lines) and experimental results (dashed lines) for a system consisting of decyl dimethyl phosphinoxide as main component and dodecyl dimethyl phosphine oxide as simulated impurity at different values of $c_3/a_3 = 0.0$ (○), 0.1 (∗), 0.3 (△); parameter used: $a_2 = 5 \cdot 10^{-8}$ mol/cm³, $a_3 = 5 \cdot 10^{-9}$ mol/cm³ and conditions (11)

(The complete tables are available from the authors.) We can learn from these tables that with increasing surface activity a_2 of the main component and increasing relative surface activity of the impurity a_2/a_3 the optimal time to detect contaminations becomes greater and greater. As pointed out earlier [6] the grade of surface-chemical purity is strongly connected with the experimental time t^A and the criterion holds in time interval $t \leq 10 \cdot t^A$ only. For longer times $t \geq 10 \cdot t^A$ the purity has to be checked again under the special circumstances.

The application of the tables enables one not only to evaluate the absolute grade of a surfactant solution concerning potential impurities but also gives the possibility to evaluate present surface active impurities by their relative concentration c_3/a_3 and relative surface activity a_2/a_3. To demonstrate this a surfactant mixture consisting of differently composed surface-chemically pure solutions of decyl and dodecyl dimethyl phosphine oxide was investigated as a simulation of a contaminated surfactant solution. The result of this simulation is presented in Figure 3. A rather good agreement between experimental and theoretically predicted values is found. A full agreement could not be expected because of the use of standard conditions (11), which do not reflect the real values, the use of a generalized Langmuir isotherm (i. e. a constant Γ_∞-value), and because of the use of an idealized diffusion model without taking into account lateral transports during compression etc.

When identifying impurities in real surfactant solutions one has to bear in mind that in the theory only one impurity component was supposed. Thus it is not possible to define the impurity exactly but to evaluate the main surface active contaminant.

5. Conclusions

Based on a diffusion controlled kinetics of adsorption and desorption of surfactants and surfactant mixtures relations are presented which allow to judge the grade of purity of surfactant solutions. The surface tension difference between adsorption and desorption under well defined conditions is used as the experimental measure to apply the derived criterion. The following results can be formulated:

1. For most of the surfactants the fulfilment of Equation (3) under condition (5) is a sufficient criterion to judge the grade of purity of their solutions.
2. For strong surface active components the times t^A calculated by Equation (5) become very large and one has to use Equation (9) as the criterion, where the theoretical values are calculated by using the diffusion controlled adsorption model (Fig. 2).
3. Applying the theory of adsorption kinetics of surfactant mixtures it is also possible to evaluate the relative activity a_2/a_3 and relative concentration c_3/a_3 of present impurities by measuring $\Delta\sigma$-values under appropriate conditions.

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Authors' address:

R. Miller
Central Institute of Organic Chemistry of the
Academy of Sciences of the GDR
Rudower Chaussee 5
DDR-1199 Berlin-Adlershof, G.D.R.