

The analysis of dynamic surface tension of sodium alkyl sulphate solutions, based on asymptotic equations of adsorption kinetic theory

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Abstract

We analysed existing and newly derived asymptotic solutions of the adsorption kinetic equations for the liquid phase interface in the regions of infinitely small and infinitely great surface lifetimes (t) for the cases of one and of a few surfactants, on non-deforming and deforming surfaces, under non-stationary, stationary and quasi-stationary conditions, assuming either the diffusion adsorption mechanism or mixed adsorption mechanism.

It was proved that in the region $t \rightarrow \infty$, the adsorption barrier does not influence the dynamic surface tension σ , but the role of surface-active contaminants is significant. In contrast, in the region $t \rightarrow 0$, the role of contaminants is small, but the adsorption barrier influences the dynamic surface tension substantially.

The dynamic surface tension of sodium alkyl sulphate solutions was measured by the maximum bubble pressure method, in the t range 0.001–10 s. In the region $t \rightarrow \infty$ we obtained good agreement of experimental results with asymptotic formulae. The diffusion adsorption mechanism of the surfactant solutions studied was confirmed and we also estimated the concentration values of the surfactant admixtures. Small additions of the more active surfactant sodium tetradecyl sulphate to sodium dodecyl sulphate substantially influences the shape of the σ – t curve in the region $t \rightarrow \infty$, increasing (in full accordance with theoretical considerations) the tangent value of the curve inclination of the dependence of σ on $t^{-1/2}$. In the regions $t \rightarrow 0$, long-chained high molecular weight sodium alkyl sulphates adsorb according to the diffusion mechanism, whereas for sodium decyl and dodecyl sulphates the existence of the adsorption barrier was confirmed. We corroborated experimentally the absence of any influence of surfactant admixtures on the values of dynamic surface tension at $t \rightarrow 0$.

Key words: Adsorption kinetic theory; Dynamic surface tension; Surface-active contaminants; Surfactants

Introduction

During the last two decades considerable success in the theoretical and experimental study of the phenomena of surfactant adsorption kinetics on liquid phase interfaces has been achieved [1–3]. The main theoretical method for analysing non-stationary processes on freshly formed surfaces (on both deforming and non-deforming surfaces) is the

classic equation of Ward and Tordai [4], which allows only numerical solutions for the general case. Joos and co-workers [5,6] were the first to make systematic use of the asymptotic analytical solution, derived by Hansen [7], of the Ward–Tordai equation for the region of long lifetimes.

The asymptotic equation of Joos and Hansen gives a good description of the results obtained for many surfactants by different methods [8–16].

At the same time, the results, which have been obtained up to now, do not fully exploit all the

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possibilities of asymptotic solutions. Particularly, the complex use of such solutions for $t \rightarrow \infty$ and $t \rightarrow 0$ (here t is the surface lifetime) shows good prospects for the theoretical analysis of experimental results.

In the present paper we shall analyse the above-mentioned solutions and obtain new asymptotic solutions for the case of non-stationary adsorption of one surfactant on a freshly formed non-deforming surface and on a deforming one for both the diffusion mechanism and mixed mechanism of adsorption. Then we shall consider the case of two-surfactant adsorption and then the stationary and quasi-stationary adsorption processes on the deforming surface. Also we shall obtain asymptotic equations for a system subject to instantaneous deformation of the expansion–compression type.

For the experimental test of the asymptotic equations we shall use new results, and also those published earlier, from studies of dynamic surface tension of water solutions of sodium alkyl sulphates (from decyl up to hexadecyl) and of normal low molecular weight alcohols.

Theory

Asymptotic solutions at $t \rightarrow \infty$

The adsorption value, as a function of time for the case of a non-deforming freshly formed surface, can be expressed by the widely known equation of Ward and Tordai [41]:

$$\Gamma = 2c_0 \left(\frac{Dt}{\pi} \right)^{1/2} - 2 \left(\frac{D}{\pi} \right)^{1/2} \int_0^t c_s(t-\tau) d\tau^{1/2} \quad (1)$$

where c_0 is the volume concentration, c_s is the subsurface concentration, which is a function of time, D the diffusion coefficient, Γ the adsorption and t the time. As $t \rightarrow \infty$ the value c_s (in this case $c_s \rightarrow c_0$) can be factored outside the integral sign. Thus, we have

$$\Delta c_{t \rightarrow \infty} = c_0 - c_s = \Gamma \left(\frac{\pi}{4Dt} \right)^{1/2} \quad (2)$$

It is necessary to note that as Eq. (1) presents the most general form of the solution of the diffusion–kinetic problem, it follows that Eq. (2) at $t \rightarrow \infty$ must be applicable both to purely diffusion adsorption kinetics and for mixed adsorption kinetics. As $\Delta c \rightarrow 0$, then using Gibbs' equation,

$$d\sigma = -RT\Gamma d \ln c \quad (3)$$

we can derive a Joos equation [5,6] from Eq. (2):

$$\Delta \sigma_{t \rightarrow \infty} = \sigma - \sigma_\infty = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4Dt} \right)^{1/2} \quad (4)$$

where σ is the dynamic surface tension, σ_∞ the equilibrium surface tension, R the gas constant and T the temperature. Equation (4) can be written in the form of a derivative of σ with respect to $t^{-1/2}$:

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4D} \right)^{1/2} \quad (5)$$

Thus in coordinates $\sigma-t^{-1/2}$ under the condition $t \rightarrow \infty$ it follows that theoretical and experimental results for the dynamic surface tension of one non-ionic surfactant solution must be described by the linear dependence with the angular coefficient, determined by the right-hand side of Eq. (5). In the case of an ionic 1:1 charged surfactant, Eq. (5) transforms to the following equation [10]:

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{2RT\Gamma^2}{c_0} \left(\frac{\pi}{4D} \right)^{1/2} \quad (6)$$

Many papers have been published on the numerical solution of Eq. (1) for the diffusion and mixed adsorption kinetic mechanisms [17–22]. As regards this, independently of the form of the adsorption barrier introduced (Langmuir kinetics [17–19,21], Langmuir kinetics and electric double layer [20], the structural barrier is present in a thin superficial layer [22]), on all graphs of the dependences σ on t or Γ on t , presented in the cited papers, curves for the mixed and diffusion mechanisms of adsorption at $t \rightarrow \infty$ merge into one common curve.

As an example, Fig. 1, expressed in the coordi-

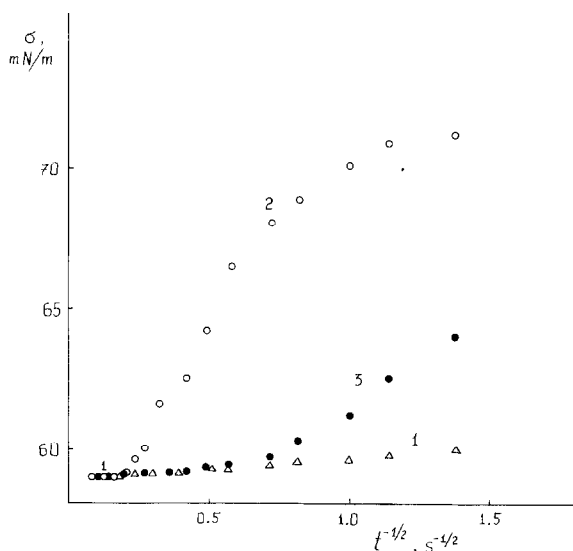


Fig. 1. Calculation results [18] from Eq. (1) in the coordinates of Eq. (5): Δ , diffusion kinetics; \circ , mixed mechanism at $\beta = 10^{-6} \text{ m s}^{-1}$; \bullet , mixed mechanism at $\beta = 10^{-5} \text{ m s}^{-1}$.

nates of Eq. (5), presents results calculated in Ref. 18 for the following system: maximum adsorption value $\Gamma_{\infty} = 5 \times 10^{-6} \text{ mol m}^{-2}$, equilibrium adsorption $\Gamma_0 = 3.33 \times 10^{-6} \text{ mol m}^{-2}$, $D = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $c_0 = 1 \text{ mol m}^{-3}$. As one can see, the dependence of σ on $t^{-1/2}$ as $t \rightarrow \infty$ ($t^{-1/2} \rightarrow 0$) is a linear one, and the value $d\sigma/dt^{-1/2}$, obtained from the graph, coincides with the value calculated according to the asymptotic Eq. (5), that is, $d\sigma/dt^{-1/2} = 1.1 \text{ mN m}^{-1} \text{ s}^{1/2}$. The length of the linear section depends on the value of the adsorption barrier. The higher the adsorption barrier, that is, the smaller is the constant β in the kinetic equation of Langmuir [17],

$$\frac{d\Gamma}{dt} = \beta c_s \left(1 - \frac{\Gamma}{\Gamma_{\infty}} \right) - \alpha \Gamma \quad (7)$$

(where β and α are constants of adsorption rate and desorption rate respectively), then the smaller is the linear section of the dependence of σ on $t^{-1/2}$ described by Eq. (5). The region of this linear dependence is estimated approximately at $t^{-1/2} \leq \beta(\pi/D)^{1/2}$.

If in the solution studied we have two or more

surfactants, then the solution of the diffusion kinetics problem can be represented by the system of Eq. (1) for all surfactants [23]. Calculations carried out in Refs. 23 and 24 have shown that, depending on the correlations of concentrations and adsorption activities of surfactants in the surface layer, at large t values there can be either adsorption of both surfactants, or adsorption of the more active surfactant and desorption of the other. The asymptotic solutions at $t \rightarrow \infty$ for the case of mixed solutions represent the system of Eq. (2) for every surfactant.

Making use of Gibbs' equation for a multi-component solution

$$d\sigma = - \sum_i RT \Gamma_i d \ln c_i \quad (8)$$

and assuming that subsurface concentration values are independent variable quantities, we obtain

$$\Delta\sigma_{t \rightarrow \infty} = \sum_i \frac{RT \Gamma_i^2}{c_{0i}} \left(\frac{\pi}{4D_i t} \right)^{1/2} \quad (9)$$

Thus, comparing Eq. (9) and Eq. (4) one can see that the condition of subsurface concentration independence leads us to the addition of $\Delta\sigma$ for all solution components. This takes place only at small adsorption values Γ_i .

If $\Gamma_j^2/c_{0j} \gg (\Gamma_i^2/c_{0i})_{i \neq j}$, then all terms on the right-hand side of Eq. (9), excluding Γ_j^2/c_{0j} , can be ignored. Such a case must be described by Eq. (5), where Γ and c_0 are related to the more surface active component.

On Fig. 2 we present, in the same coordinates as for Eq. (5), the results of calculations [18] for the following system (mixture of sodium dodecyl sulphate (1) and dodecyl alcohol (2)): $\Gamma_{\infty} = 5 \times 10^{-6} \text{ mol m}^{-2}$, $\Gamma_{01} = \Gamma_{02} = 1.66 \times 10^{-6} \text{ mol m}^{-2}$, $D_1 = D_2 = 5 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $c_{02} = 0.01 \text{ mol m}^{-3}$ and $c_{01} = 1 \text{ mol m}^{-3}$. Whether the summand for sodium alkyl sulphate in the right-hand side of Eq. (9) ($\Gamma_1^2/c_{01} = 0.01 \Gamma_2^2/c_{02}$) is accounted for or not, we obtain from Eq. (5) $d\sigma/dt^{-1/2} = 26 \text{ mN m}^{-1} \text{ s}^{1/2}$, and that fully coincides with the inclination angle of the tangent to the curve, presented on Fig. 2 at $t \rightarrow \infty$.

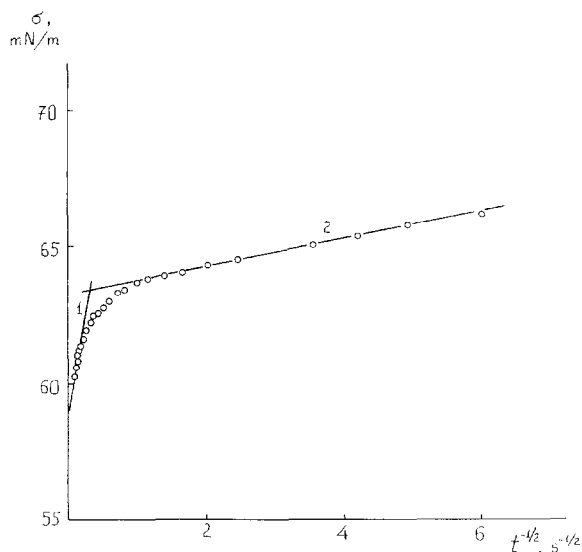


Fig. 2. Calculation results [18] for the solution of two surfactants for the diffusion mechanism of adsorption.

We could indicate one more feature of the dependence presented in Fig. 2. In the region of large t values (but not infinite ones), the curve has one more linear section (2). The component, whose concentration is bigger, absorbs mainly in this region. Assuming $\Gamma_2 = 0$ (in this case $\Gamma_1 = 2.5 \times 10^{-6} \text{ mol m}^{-2}$), we can obtain from Eq. (5) the following expression: $d\sigma/dt^{-1/2} = 0.6 \text{ mN m}^{-1} \text{ s}^{1/2}$, that approximately corresponds to the tangent of the inclination angle of the curve in Fig. 2 (section 2).

The liquid phase interface in the adsorption process can deform. The most important and often occurring case (in experiments) is where the relative surface deformation rate θ is inversely proportional to its lifetime

$$\theta = \frac{d \ln A}{dt} = \xi t^{-1}$$

The modified equation of Ward and Tordai for the case where $\xi = 2/3$ (droplet or bubble growing at a constant volume rate) was obtained in Refs. 25 and 26. The asymptotic solution at $t \rightarrow \infty$, following from the above-mentioned equation and obtained in Ref. 27, can be represented in the

following form for a non-ionic surfactant:

$$\Delta\sigma_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{7\pi}{12Dt} \right)^{1/2} \quad (10)$$

or in the form

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{7\pi}{12D} \right)^{1/2} \quad (11)$$

For an ionic surfactant the right-hand terms of Eqs. (10) and (11) contain a multiplier equal to two.

The general asymptotic equation for the case of random ξ values follows from the solution obtained in Ref. 26. For non-ionic surfactants one can write the following:

$$\Delta\sigma_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left[\frac{\pi(2\xi + 1)}{4Dt} \right]^{1/2} \quad (12)$$

or

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left[\frac{(2\xi + 1)\pi}{4D} \right]^{1/2} \quad (13)$$

For the bubble growing at constant pressure, we have $\xi \approx 0.5$ [14,15], i.e.

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{2D} \right)^{1/2} \quad (14)$$

The Eqs. (12) and (13) can be presented in the form of Eqs. (4) and (5) by introducing the value of effective time:

$$t_{\text{ef}} = \frac{t}{2\xi + 1} \quad (15)$$

For a 1:1 charged ionic surfactant the right-hand terms of Eqs. (12)–(14) are multiplied by 2.

There is a certain analogy between the asymptotic solutions considered above for the non-stationary adsorption process and solutions for the stationary or quasi-stationary processes on the deforming surface. In Ref. 28, from the solution of the convective diffusion equation for the stationary (independent of time) process, and at the condition

$\theta \Rightarrow$ constant, the following equation was obtained:

$$\Delta c = c_0 - c_s = \Gamma \left(\frac{\pi \theta}{2D} \right)^{1/2} \quad (16)$$

With due account of Gibbs' equation (Eq. (3)), at small deviations from equilibrium it follows from Eq. (16) that [6]

$$\Delta \sigma_{t \rightarrow \infty} = \sigma - \sigma_\infty = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi \theta}{2D} \right)^{1/2} \quad (17)$$

In Ref. 6 the similarity of Eqs. (4) and (17) was shown. If we assume in Eq. (17) that $\theta = 0.5t^{-1}$, then it can be transformed to Eq. (4). Evidently, it is physically more reasonable to search for the analogy between Eqs. (17) and (12) (non-stationary adsorption process on the deforming surface). Let us note that using $\theta = f(t)$ in Eq. (17) is a rough enough approximation, as it changes the stationary problem, whose solution is Eq. (16), to the quasi-stationary one. Nevertheless, at $\xi = 0.5$, i.e. at $\theta = 0.5t^{-1}$, from Eq. (17) it follows that

$$\Delta \sigma_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4Dt} \right)^{1/2} \quad (18)$$

and this value is only $\sqrt{2}$ smaller than that predicted by Eqs. (12) or (14).

The simplicity of the analytic solution of the stationary diffusion problem and subsequent transition to the non-stationary problem, and also the stationary coincidence of the results obtained with those following from the non-stationary problem solution, substantiate this approach [28] for more complex non-stationary problems. Specifically, for the solution of the two surfactants [29,30] the quasi-stationary approach at $\xi = 0.5$ also leads to Eq. (9).

The stationary and quasi-stationary models for the case of the barrier adsorption mechanism were used in Refs. 8, 9, 14, 15, 31 and 32. For a non-ionic surfactant at $\xi = 0.5$ the following equation for the mixed adsorption mechanism was obtained [15]:

$$\Delta \sigma = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4Dt} \right)^{1/2} + \frac{RT\Gamma^2}{2c_0\beta t} \quad (19)$$

where β is the absorption rate constant. As for the non-stationary model, at $t \rightarrow \infty$ the influence of the adsorption barrier is negligible. Taking the derivative of σ with respect to $t^{-1/2}$ we obtain from Eq. (19)

$$\frac{d\sigma}{dt^{-1/2}} = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4D} \right)^{1/2} + \frac{RT\Gamma^2}{c_0\beta t^{1/2}} \quad (20)$$

As $t \rightarrow \infty$ ($t^{-1/2} \rightarrow 0$), the second term in the right-hand part of Eq. (20) vanishes. Thus we have

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{RT\Gamma^2}{c_0} \left(\frac{\pi}{4D} \right)^{1/2} \quad (21)$$

which coincides exactly with Eq. (5) for non-stationary adsorption.

For ionic surfactants the stationary model leads to a somewhat different result from the non-stationary one. As in the stationary problem the condition of electric neutrality follows from the equality of ion streams which have different diffusion coefficients, then instead of Eq. (6) in this case, at $\xi = 0.5$, we obtain [15]

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{kRT\Gamma^2}{c_0} \left(\frac{\pi}{4D_1} \right)^{1/2} \quad (22)$$

where $k = 1 + (D_1/D_2)^{1/2}$ and D_1 and D_2 are diffusion coefficients of the surface-active ion and counterion respectively. As one can see $1 < k < 2$.

The equation which coincides in form with Eq. (5), follows also from the general solution of the diffusion problem for the case of instantaneous expansion or compression of the surface [33]:

$$\Delta \sigma = \epsilon_0 \frac{\Delta A}{A_0} \exp(2\omega_0 t) \operatorname{erfc}(2\omega_0 t)^{1/2} \quad (23)$$

where A_0 and ΔA are the initial surface and the value of surface change: $\epsilon = -d\sigma/d \ln \Gamma$ and $\omega_0 = (dc_0/d\Gamma)^2 D/2$. At $t \rightarrow \infty$ we can derive approximately from Eq. (23):

$$\Delta \sigma_{t \rightarrow \infty} = \epsilon_0 \frac{\Delta A}{A_0} [1 - (2\pi\omega_0 t)^{-1/2}] \quad (24)$$

For the non-ionic surfactant, using Gibbs equation

(Eq. (3)), we obtain from Eq. (24)

$$\left(\frac{d\sigma}{dt^{-1/2}}\right)_{t \rightarrow \infty} = -\frac{\Delta A}{A_0} \frac{RT\Gamma^2}{c_0} \left(\frac{1}{\pi D}\right)^{1/2} \quad (25)$$

For a 1:1 charged ionic surfactant, the multiplier 2 can be added in the right-hand part of Eq. (25). For the mixture of surfactants, from the equation derived in Ref. 33, it follows that

$$\left(\frac{d\sigma}{dt^{-1/2}}\right)_{t \rightarrow \infty} = -\frac{\Delta A}{A_0} \sum_i \frac{\Gamma_i}{\Gamma_T} \frac{RT\Gamma_i^2}{c_{i0}} \left(\frac{1}{\pi D_i}\right)^{1/2} \quad (26)$$

where $\Gamma_T = \sum_i \Gamma_i$, i.e. contributions of different surfactants to the $\Delta\sigma$ value are added just as in the case of the quasi-stationary process. The inclusion of the adsorption barrier in the problem [33] leads at $t \rightarrow \infty$ to results that agree well with those obtained for the non-stationary and quasi-stationary models.

From the performed analysis it follows that at $t \rightarrow \infty$ the surface tension value of the non-deforming surface, of the deforming one according to the specified law, or of a surface subjected to instantaneous deformation, is described by the equation

$$\left(\frac{d\sigma}{dt^{-1/2}}\right)_{t \rightarrow \infty} = \frac{\gamma RT\Gamma^2}{c_0} \left(\frac{\pi}{4D}\right)^{1/2} \quad (27)$$

where the constant γ depends only on the conditions that characterize the surface deformation and surfactant type (non-ionic or ionic). Here the existence of an adsorption barrier does not influence the form of the dependence of σ on t , which in this case is subordinated to Eq. (27). This conclusion, which is correct purely mathematically, cannot be extended in practice to the case of adsorption kinetics when the range of linear dependence of σ on t becomes vanishingly small. Where the surfactant is a mixture in which a highly active surfactant is present, then the dependence of σ on t is described by Eq. (27), which will include parameters specifying this surfactant.

Thus the coincidence of the experimental dependence of σ on $t^{-1/2}$ at $t \rightarrow \infty$ with the theoretical one from Eq. (27) cannot be proof of a diffusion mechanism of surfactant adsorption, as is evident

from the above-mentioned analysis, but simultaneously it is a good criterion for the purity of the tested surfactant.

The asymptotic solutions at $t \rightarrow 0$

In the right-hand part of Eq. (1) at $t \rightarrow 0$, it is possible in the case of the diffusion mechanism to neglect the second summand. Thus we have

$$\Gamma = 2c_0 \left(\frac{Dt}{\pi}\right)^{1/2} \quad (28)$$

The surface tension of the solution of $\sigma \rightarrow \sigma_0$ (σ_0 is the surface tension of solvent) is described, in the case of an ideal surface layer, by the following equation:

$$\sigma = \sigma_0 - nRT\Gamma \quad (29)$$

where $n=1$ for non-ionic and $n=2$ for ionic surfactants. Substituting Eq. (28) in Eq. (29), we obtain

$$\sigma_{t \rightarrow \infty} = \sigma_0 - 2nRTc_0 \left(\frac{Dt}{\pi}\right)^{1/2} \quad (30)$$

Taking the derivative of Eq. (30) with respect to $t^{1/2}$, we transform Eq. (30) to the form

$$\left(\frac{d\sigma}{dt^{1/2}}\right)_{t \rightarrow 0} = -2nRTc_0 \left(\frac{D}{\pi}\right)^{1/2} \quad (31)$$

Thus, for the diffusion mechanism of adsorption on the non-deforming surface, the experimental values of σ must have a linear dependence on $t^{1/2}$ with the angular coefficient determined by the right-hand part of Eq. (31).

For the multicomponent surfactant solution we obtain, at $t \rightarrow 0$, for the diffusion mechanism of adsorption

$$\Gamma = \sum_i \Gamma_i = \sum_i 2c_{0i} \left(\frac{D_i t}{\pi}\right)^{1/2} \quad (32)$$

and

$$\left(\frac{d\sigma}{dt^{1/2}}\right)_{t \rightarrow 0} = -\sum_i 2n_i RTc_{0i} \left(\frac{D_i}{\pi}\right)^{1/2} \quad (33)$$

From Eqs. (32) and (33) it follows that a surface-active contaminant, which is present in the solution of the main surfactant, does not influence the dependence of σ on t , at $t \rightarrow 0$, i.e. in contrast to the region where $t \rightarrow \infty$, this dependence is not sensitive to the influence of such contaminants.

If the adsorption kinetics do not represent a diffusive process, then with the condition of a significant barrier, it is possible to obtain the simple asymptotic equation at $t \rightarrow 0$. In this case the value of subsurface concentration c_s in Eq. (1) can be factored outside the integral sign. The kinetic equation of Langmuir (Eq. (7)) at small t values (i.e. $t \rightarrow 0$) can be presented in the form

$$\Gamma = \beta t c_s \quad (34)$$

Substituting the value c_s from Eq. (34) into Eq. (2), we obtain after some algebraic manipulation

$$\Gamma = 2c_0 \left(\frac{Dt}{\pi} \right)^{1/2} \left[1 + \frac{2}{\beta} \left(\frac{D}{\pi t} \right)^{1/2} \right]^{-1} \quad (35)$$

Finally instead of Eq. (31), in the presence of an adsorption barrier, we obtain

$$\left(\frac{d\sigma}{dt^{1/2}} \right)_{t \rightarrow 0} = -2nRTc_0 \left(\frac{D_{\text{ef}}}{\pi} \right)^{1/2} \quad (36)$$

where the value of the effective diffusion coefficient D_{ef} is determined according to the equation

$$D_{\text{ef}} = D \left[1 + \frac{2}{\beta} \left(\frac{D}{\pi t} \right)^{1/2} \right]^{-2} \quad (37)$$

Thus, for the barrier adsorption mechanism or for the mixed mechanism, i.e. when $(2/\beta)(D/\pi t)^{1/2} > 0$, the value D_{ef} can become less than D . Therefore the asymptotic solutions in the region of $t \rightarrow 0$ can be used for the analysis of the adsorption process mechanism. If we calculate D_{ef} in accordance with experimental data, we can calculate the adsorption rate constant β .

Equation (35) follows also from the approximate equation for the mixed adsorption kinetics [21]:

$$\frac{d\Gamma}{dt} = \frac{(d\Gamma/dt)_k (d\Gamma/dt)_d}{(d\Gamma/dt)_k + (d\Gamma/dt)_d} \quad (38)$$

where subscripts d and k designate adsorption rates for the diffusion and kinetic mechanisms respectively. At $\Gamma \rightarrow 0$ and $t \rightarrow 0$, we have from Eqs. (1) and (7)

$$(d\Gamma/dt)_k = \beta c_0 \quad (39)$$

and

$$(d\Gamma/dt)_d = c_0 (D/\pi t)^{1/2} \quad (40)$$

After substitution of Eqs. (39) and (40) into Eq. (38) we obtain

$$\frac{d\Gamma}{dt} = c_0 \left(\frac{D}{\pi} \right)^{1/2} \frac{1}{t^{1/2} + \frac{1}{\beta} \left(\frac{D}{\pi} \right)^{1/2}} \quad (41)$$

After integration of Eq. (41) we obtain

$$\Gamma = 2c_0 \left(\frac{D}{\pi} \right)^{1/2} \left\{ t^{1/2} - \frac{1}{\beta} \ln \left[1 + \beta \left(\frac{\pi t}{D} \right)^{1/2} \right] \right\} \quad (42)$$

Equation (42) is more rigorously defined than Eq. (35), since the assumption $c_s = \text{constant}$ is not used. Equation (35) follows from Eq. (42), if one uses the first term of the expansion (into a series):

$$\ln x = 2 \left[\frac{x-1}{x+1} + \frac{(x-1)^3}{3(x+1)^3} \dots \right] \quad (43)$$

i.e. when $(1/\beta)(D/\pi t)^{1/2} \gg 1$, which is the criterion of the barrier mechanism of adsorption.

All the above-mentioned asymptotic solutions for $t \rightarrow 0$ can easily be generalized for the case where the surface is deformed according to the law defined by Eq. (9). In this case the value t in Eqs. (28), (30), (33), (36) and (37) represents the effective time, determined by Eq. (15).

In the case of instantaneous surface expansion or compression it follows from Eq. (23) at $t \rightarrow 0$ that

$$\Delta\sigma = \epsilon_0 \frac{\Delta A}{A_0} \left[1 - 2 \left(\frac{2\omega_0 t}{\pi} \right)^{1/2} \right] \quad (44)$$

For a non-ionic surfactant, using Gibbs' equation

(Eq. (3)) and Langmuir's isotherm

$$\frac{\Gamma}{\Gamma_{\infty}} = \frac{bc_0}{1 + bc_0} \quad (45)$$

and from Eq. (44), we obtain

$$\left(\frac{d\sigma}{dt^{1/2}} \right)_{t \rightarrow \infty} = -2n \frac{AA_0}{A_0} RTc_0(1 + bc_0)^2 \left(\frac{D}{2\pi} \right)^{1/2} \quad (46)$$

In the case of the mixed adsorption mechanism, Eq. (38) leads to Eq. (46) with the coefficient D that represents the effective value of D_{ef} , determined according to Eq. (37).

Materials and methods

Sodium alkyl sulphates (from decyl up to hexadecyl) were purified by extraction in hexane for 20 h with subsequent repeated recrystallization from ethanol. The impurity content did not exceed 1%, and we detected in the purified specimens only lower homologues of sodium alkyl sulphates. All solutions were prepared with bidistilled water. The propyl alcohol was purified by vacuum distillation.

The study of dynamic surface tension was done by the maximum bubble pressure method. The block scheme and detailed description of the instrument MPT-1 (Lauda, Germany) has been given in Refs. 14 and 34. This instrument was provided with an electric and acoustic frequency registering meter for registration of the bubble formation frequency. The division of the time interval between consecutive bubbles into surface lifetime and so-called "dead time" is based on the existence of the critical point on the dependence graph of pressure against air flow rate. At this point a transition occurs from the bubble mode to jet mode. The procedures for measurements and calculations in this instrument are fully automated. The range of surface lifetime measurement is from 0.001 up to 10 s. The error in the surface tension measurement does not exceed 0.5 mN m^{-1} . The results which we obtained with the help of the instrument MPT-1 coincide with the data from the oscillating jet method and

from the inclined plate method [34]. It is necessary to note that in spite of the general use of the maximum bubble pressure method for the study of dynamic surface tension, new instruments, described in the scientific literature [35–38], have substantial disadvantages in comparison with the MPT-1 instrument.

The bubble surface lifetime t is determined from the equation [14,34]

$$t = \tau_b - \tau_d = \tau_b \left(1 - \frac{Lp_c}{L_cp} \right) \quad (47)$$

where τ_b is the time interval between bubbles, τ_d the dead time, L the air flow rate through the capillary, and p the air pressure in the measuring system which is connected to the capillary. The values of L and p with the subscripts "c" refer to the critical point.

The effective lifetime can be calculated according to Eq. (15):

$$t_{\text{ef}} = \frac{t}{2\xi + 1}$$

where $\xi = \sin \varphi / (1 + \sin \varphi)$ is the relative deformation rate of the bubble surface during the first stage of its growth; $\varphi = \arccos(\sigma/\sigma_0)$ and σ_0 is the surface tension of the solvent.

The value of dynamic surface tension can be calculated according to the Laplace equation:

$$p = \frac{2\sigma}{r} + \rho gh \quad (48)$$

where r is the capillary radius (about 0.08 mm), ρ the density of the liquid, h the depth of capillary immersion in the liquid and g the acceleration due to gravity. The error in the determination of h is not more than 0.1 mm.

It is necessary to emphasize that the applicability of the above-mentioned equations to the instrument MPT-1 is determined by the special features of the instrument design, particularly by the large volume of the measuring system in comparison with the bubble volume, as a consequence of which the pressure value in the growing bubble coincides

with the pressure value in the measuring system, and besides that, $p = \text{constant}$ (at given τ_b) at any given moment.

Results and discussion

Region of long t

The dependences of dynamic surface tension for sodium tetradecyl sulphate (TDSNa) and sodium hexadecyl sulphate (HDSNa) on $t^{-1/2}$, presented in the figures of Ref. 15, agree well with the calculations according to Eq. (6).

In Figs. 3 and 4 we present some experimental results for solutions of sodium decyl sulphate (DeSNa). Figure 4 includes information on the reproducibility of the results. In this experiment solutions of DeSNa with given concentration levels were prepared independently, using different weighed samples, different chemical bottles and measuring cells of the instrument. As one can see, the absolute error values of two parallel experiments is no more than 0.5 mN m^{-1} , and the slopes of the dependence of σ on $t^{-1/2}$ coincide, i.e. the dynamic effects are fully reproduced. In the region of $t^{-1/2} < 1 \text{ s}^{-1/2}$ we observe some “dumping” of experimental points; this corresponds to the theoretical results, presented in Fig. 2, and provides

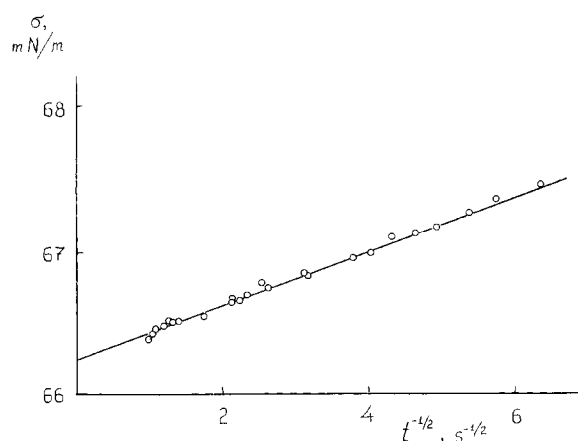


Fig. 3. Dependence of dynamic surface tension for DeSNa solution ($c_0 = 4 \text{ mol m}^{-3}$) on $t^{-1/2}$.

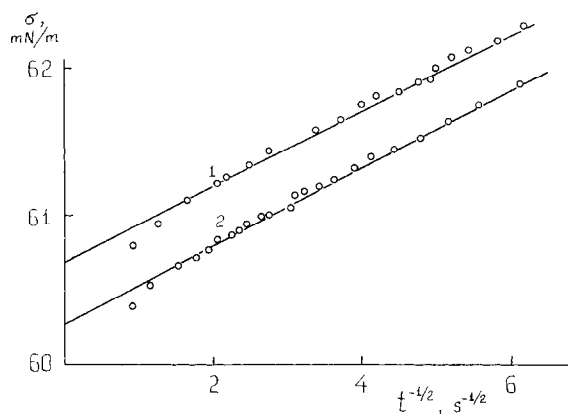


Fig. 4. Dependence of dynamic surface tension, as in Fig. 3, at $c_0 = 8 \text{ mol m}^{-3}$ for two different experiments (curves 1 and 2).

evidence for the presence of surface-active contaminants.

In Figs. 5 and 6 we present analogous dependences for sodium dodecyl sulphate (DDSNa). Here we can see the good correspondence of the experimental results to the theoretical laws. In the region of $t^{-1/2} < 1 \text{ s}^{-1/2}$, just as in the case of DeSNa solution, the slope is somewhat bigger. The experimental proofs of the influence of surface-active contaminants on the σ - $t^{-1/2}$ dependence behaviour for DDSNa solution are presented in

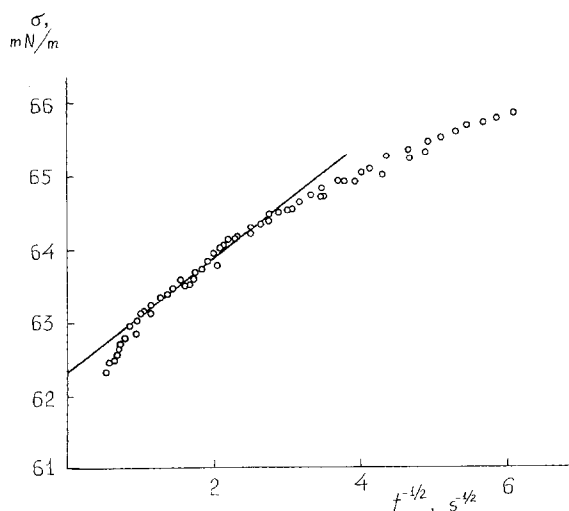


Fig. 5. Dependence of dynamic surface tension for DDSNa solution ($c_0 = 2 \text{ mol m}^{-3}$) on $t^{-1/2}$.

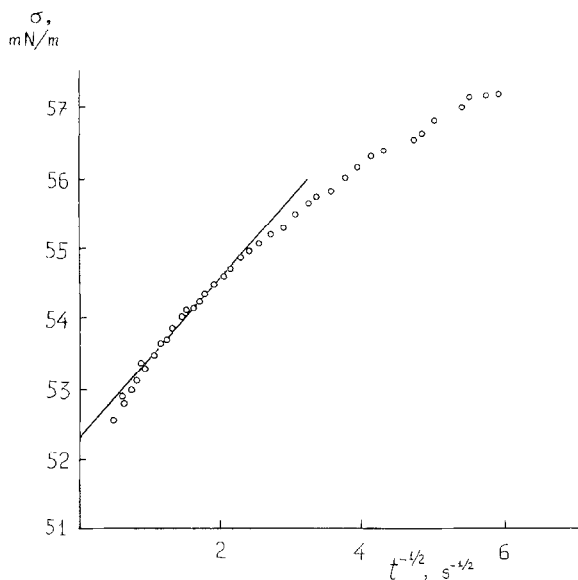


Fig. 6. Dependence of dynamic surface tension, as in Fig. 5, at $c_0 = 4 \text{ mol m}^{-3}$.

Figs. 7 and 8. On Fig. 7 we present data for the “contaminated” DDSNa solution. The “contaminated” DDSNa solution is an industrial specimen, purified from alcohols and inorganic impurities;

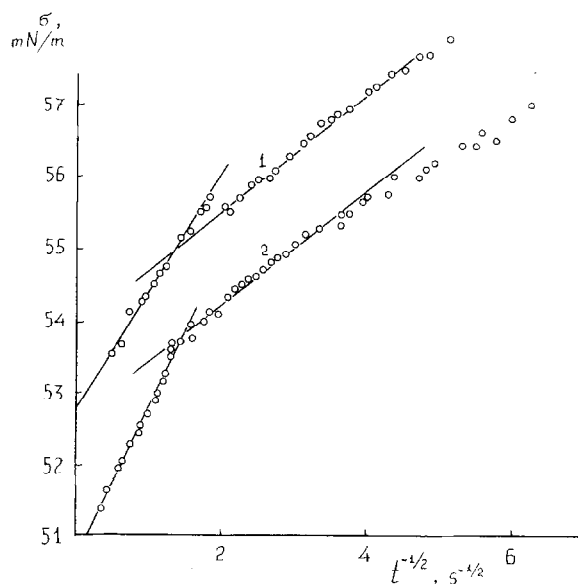


Fig. 7. Dependence of dynamic surface tension for the solution of “contaminated” DDSNa at $c_0 = 1.04 \text{ g l}^{-1}$ (curve 1) and $c_0 = 1.152 \text{ g l}^{-1}$ (curve 2) on $t^{-1/2}$.

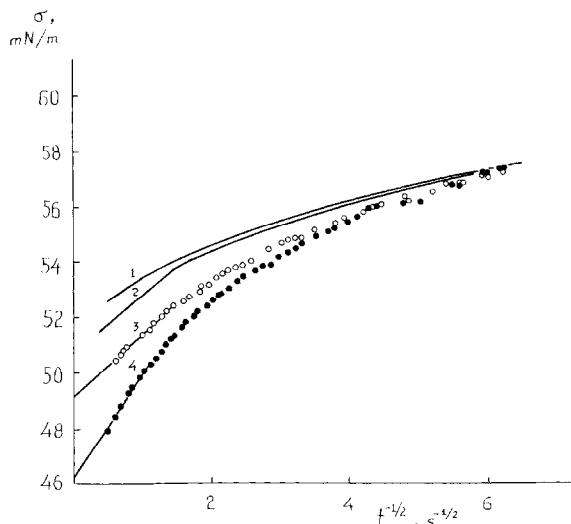


Fig. 8. Dependence of dynamic surface tension for the DDSNa solution at $c_0 = 1.152 \text{ g l}^{-1}$ on $t^{-1/2}$: curve 1, pure DDSNa (Fig. 6); curve 2, “contaminated” DDSNa (Fig. 7); curve 3, DDSNa with the admixture of 5% TDSNa; curve 4, DDSNa with the admixture of 10% TDSNa.

however, in contrast to the pure DDSNa, it contains (according to the results of chromatographic analysis) up to 5% of homologues, including TDSNa. For this specimen of DDSNa the slope of the straight line section at $t^{-1/2} \rightarrow 0$ is substantially higher than for the pure specimen, and transition to the steeper dependence of σ on $t^{-1/2}$ is observed at lower t values. In Fig. 8 we present the dependences of σ on $t^{-1/2}$ for the pure DDSNa with 5% and 10% additions of TDSNa. As one can see, the bigger the TDSNa addition, the bigger is the slope of the σ – $t^{-1/2}$ plot at $t \rightarrow \infty$. However, at small t (smaller than 50 ms), the results for all specimens of DDSNa solution coincide, as in this t region the adsorption of DDSNa generally occurs.

Equation (8) allows us to analyse the results obtained. Thus for a solution of two ionic surfactants it follows that

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{2RT\Gamma_1^2}{c_{01}} \left(\frac{\pi}{4D_1} \right)^{1/2} + \frac{2RT\Gamma_2^2}{c_{02}} \left(\frac{\pi}{4D_2} \right)^{1/2} \quad (49)$$

where parameters with subscripts 1 and 2 are related correspondingly to DDSNa and TDSNa solutions. During the calculation with Eq. (49) we assumed $\Gamma_{\infty 1} = \Gamma_{\infty 2} = 5 \times 10^{-6} \text{ mol m}^{-2}$, $D_1 = D_2 = 3 \times 10^{-10} \text{ m}^2 \text{ s}^{-1}$, $b_1 = 0.5 \text{ m}^3 \text{ mol}^{-1}$ and $b_2 = 2.0 \text{ m}^3 \text{ mol}^{-1}$; these last two values are constants of Langmuir's equation of adsorption:

$$\Gamma_i = \Gamma_{\infty i} \frac{b_i c_{0i}}{1 + b_1 c_{01} + b_2 c_{02}} \quad (50)$$

where $\Gamma_{\infty i}$ is the value of maximum adsorption.

Experimental results and calculations are presented in Table 1. As one can see, the experimental and theoretical values of $d\sigma/dt^{-1/2}$ increase with the growth of partial TDSNa concentration in the mixture; however, they agree with one another only to within an order of magnitude. As in the solutions of pure DeSNa and DDSNa, we are possibly seeing here the important role of surface-active impurities. Let us try to estimate their concentration levels.

Assuming in Eqs. (49) and (50) that $\Gamma_{\infty 1} = \Gamma_{\infty 2}$, $D_1 = D_2$ and $c_{02} \ll c_{01}$, i.e. $c_0 \approx c_{01}$ (here subscripts 1 and 2 refer to the main surfactant and to the impurity respectively), and taking into account that $\Gamma = \Gamma_1 + \Gamma_2$, we transform Eq. (49) to the form

$$\left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} = \frac{2RT\Gamma^2}{c_0} \left(\frac{\pi}{4D_{\text{ef}}} \right)^{1/2} \quad (51)$$

where

$$D_{\text{ef}} = D \frac{(1 + b_2 c_{02}/b_1 c_{01})^4}{(1 + b_2^2 c_{02}/b_1^2 c_{01})^2} \quad (52)$$

Assuming in Eq. (52) that $b_2 c_{02} \ll b_1 c_{01}$, we obtain

approximately

$$c_{02} = c_{01} \frac{b_1^2}{b_2^2} \left[\left(\frac{D}{D_{\text{ef}}} \right)^{1/2} - 1 \right] \quad (53)$$

If the surface-active contaminant is the corresponding alcohol, then $b_2/b_1 \approx 100$ [18]. From the experimental data presented in Figs. 3–8, it follows that $D/D_{\text{ef}} = 3$ in the region of $t \rightarrow \infty$, and thus we have $c_{02} \approx 10^{-4} c_{01}$. In other words, the alcohol concentration value is about 0.01% of the concentration level of the main surfactant. Such a quantity of alcohol can be generated as a result of hydrolysis in the course of the experiment. We must note also that the conditions used during derivation of Eq. (53) are fulfilled at the values of c_{02} found.

In Table 2 we collect together the results of experiments and calculations for all the sodium alkyl sulphates studied. Experimental values of $(d\sigma/dt^{-1/2})_{t \rightarrow \infty}$ and the values of diffusion coefficients presented in the table were used for the calculation of the adsorption value using Eq. (6). These results are shown in the last column of the table. In the preceding column we present Γ values that were obtained from the isotherm of the surface tension or taken from the published data. As one can see, the adsorption values obtained from the static and dynamic experiments agree well. If one tries to use values of $d\sigma/dt^{-1/2}$ at $t^{-1/2} < 1 \text{ s}^{-1/2}$ for calculations (these are represented by the “dumped” curve sections in Figs. 3–8), then we shall obtain “dynamic” values of Γ which are approximately 1.3–1.5 times higher than those presented in Table 2.

Thus we believe that in full agreement with the theoretical results, at large t values the surface barrier is absent from the sodium alkyl sulphate solutions. Small deviations of $d\sigma/dt^{-1/2}$ in the region of largest t are connected probably with the small quantity of highly active contaminants. Alcohols, formed in the sodium alkyl sulphate solutions as a result of hydrolysis, could be such contaminants.

It is necessary to note that results of these studies agree well with experimental results obtained

Table 1
Comparison of the theoretical and experimental results for the mixture of DDSNa and TDSNa at $c_0 = 1.152 \text{ g l}^{-1}$ and at $t \rightarrow \infty$

Proportion of TDSNa in the mixture (%)	$(d\sigma/dt^{-1/2})_{t \rightarrow \infty}$ (mN m ⁻¹ s ^{1/2})		$10^{-6} \Gamma_1$ (mol m ⁻²)	$10^{-6} \Gamma_2$ (mol m ⁻²)
	Exp.	Theory		
5	2.4	1.1	2.9	0.6
10	3.8	1.4	2.4	1.1

Table 2
Data for sodium alkyl sulphates at $t \rightarrow \infty$

Surfactant, temp.	c_0 (mol m ⁻³)	$(d\sigma/dt^{-1/2})_{t \rightarrow \infty}$ (mN m ⁻¹ s ^{1/2})	$10^{-10}D$ (m ² s ⁻¹)	$10^{-6}\Gamma$ (mol m ⁻²)	
				From isotherm	From Eq. (6)
DeSNa 24°C	4	0.19	3.2	1.16	1.48
	8	0.22	3.2	1.95	2.25
	16	0.25	3.2	3.00	3.40
DDSNa 24°C	1	0.40	3.0	0.88	1.27
	2	0.70	3.0	2.30	2.36
	4	1.10	3.0	3.53	4.20
TDSNa 30°C	2	3.00	2.5	3.50	3.90
HDSNa 40°C	0.6	12.7	2.3	3.50	4.20

earlier [39]. However, in Ref. 39 the region of $t \rightarrow \infty$ was not analysed in detail and therefore the conclusion about non-diffusion adsorption kinetics of sodium alkyl sulphate solutions was applied over the entire t region without any limitations. The same disadvantage occurs in Refs. 20 and 40 where the results of earlier published studies for DDSNa were analysed.

In Ref. 41 the dynamic surface tension of DDSNa and TDSNa solutions were determined according to the droplet form at the sharp change-over of its volume and surface area. The application of Eq. (25) (with coefficient 2) to the results [41] allows us to draw the following conclusions.

(i) At $t \rightarrow \infty$ the results of calculations made using Eq. (25) and experimental data of Ref. 41 for the purified specimens DDSNa and TDSNa have a good correlation between them.

(ii) For the non-purified DDSNa the experimental value of $(d\sigma/dt^{-1/2})_{t \rightarrow \infty}$ is an order of magnitude greater than the value obtained with Eq. (25), which in accordance with the theoretical results, provides evidence of highly active contaminants in the specimen.

Although the main objects of the present studies are sodium alkyl sulphates, similar results at $t \rightarrow \infty$ were obtained for other systems too. By way of example in Fig. 9, in the coordinates of Eq. (5), we present the experimental data for the propyl

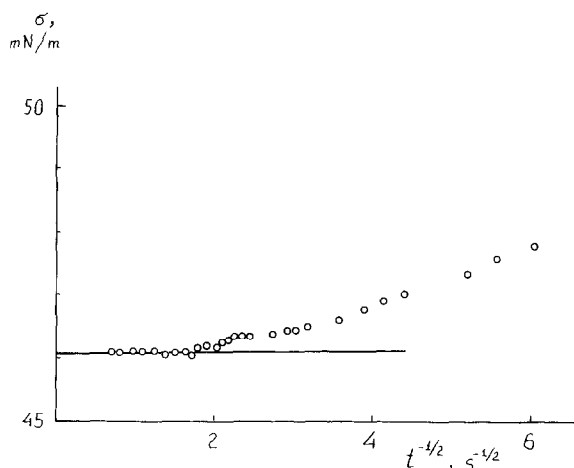


Fig. 9. Dependence of dynamic surface tension of propyl alcohol solution ($c_0 = 500$ mol m⁻³) on $t^{-1/2}$.

alcohol solution. The straight line plotted through the experimental points at $t \rightarrow \infty$ coincides with the one calculated using Eq. (5) with the following parameters: $\Gamma = 6 \times 10^{-6}$ mol m⁻² and $D = 5 \times 10^{-10}$ m² s⁻¹. These parameters coincide with those already published in the literature [42]. No surface-active contaminants were present in the specimen studied.

In Ref. 42 and in the set of earlier published papers (see Ref. 3) it was proved that low molecular alcohols are examples of systems that adsorb according to the non-diffusion mechanism.

However, in the region of $t \rightarrow \infty$, in full accordance with the results of the theoretical analysis, the adsorption barrier is absent.

The sharp rise of the curve in Fig. 9 at $t^{-1/2} > 1.5 \text{ s}^{-1/2}$ provides evidence for the change in adsorption mechanism. This conclusion follows from comparison with the calculation results presented in Fig. 1. Let us estimate the value of the adsorption barrier. Proceeding from Eq. (19) and taking the derivative with respect to t^{-1} , we obtain with due account of Eq. (21)

$$\frac{d\sigma}{dt^{-1}} = \left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} \left(\frac{t^{1/2}}{2} \right) + \frac{RT\Gamma^2}{2c\beta} \quad (54)$$

In Fig. 10 we present the same data as in Fig. 9, but in coordinates of Eq. (54).

With the condition

$$\frac{d\sigma}{dt^{-1}} \gg \left(\frac{d\sigma}{dt^{-1/2}} \right)_{t \rightarrow \infty} \left(\frac{t^{1/2}}{2} \right) \quad (55)$$

which is true for both linear sections of the curve presented in Fig. 10, it follows from Eq. (54) that

$$\frac{d\sigma}{dt^{-1}} = \frac{RT\Gamma^2}{2c\beta} \quad (56)$$

This correlation (Eq. (56)) represents the experimental condition of the adsorption barrier at large t values and $\Delta\sigma \rightarrow 0$.

For section 1 in Fig. 10 we found from Eq. (56)

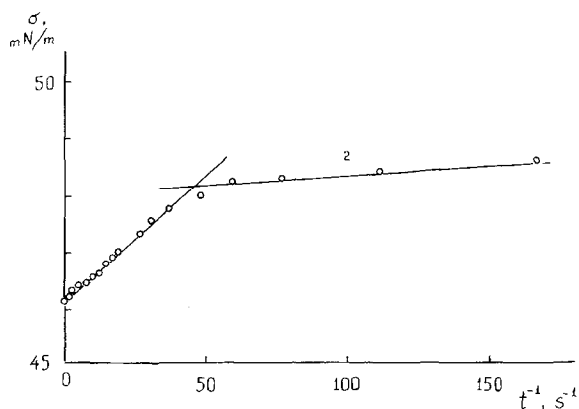


Fig. 10. Dependence of dynamic surface tension for the propyl alcohol solution ($c_0 = 500 \text{ mol m}^{-3}$) on t^{-1} .

that $\beta = 2 \times 10^{-6} \text{ m s}^{-1}$, and for section 2 $\beta = 3 \times 10^{-5} \text{ m s}^{-1}$. These results for the order of magnitude and also for the dependence of β on t agree with those obtained by other more complex methods [3,42].

Region of short t

In Fig. 11 the experimental data for TDSNa solution and HDSNa in the region of small t are presented in coordinates of Eq. (31). The diffusion coefficient values calculated with this equation are equal to $(1.5\text{--}2.0) \times 10^{-10} \text{ m s}^{-1}$, in good agreement with the D values in the region of $t \rightarrow \infty$ (Table 2). Thus in the region of $t \rightarrow 0$ the adsorption mechanism of TDSNa and HDSNa has a diffusion nature. These results correlate with ones obtained earlier for TDSNa by the maximum bubble pressure method [39]. However, in the region of intermediate t values the data [39] provide evidence for the existence of an adsorption barrier in the TDSNa solution. This follows also from the results of Ref. 41 (instantaneous deformation of the expansion and compression type) for the region of small t . As in the experiments [41] at $t \rightarrow 0$, the adsorption value of TDSNa is different from zero,

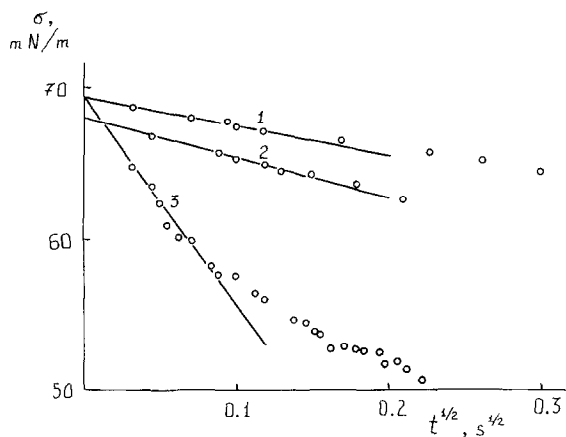


Fig. 11. Dependence of dynamic surface tension of HDSNa solutions at $c_0 = 0.6 \text{ mol m}^{-3}$ at 40°C (curve 1) and 50°C (curve 2) and of TDSNa solution at $c_0 = 2 \text{ mol m}^{-3}$ and 30°C (curve 3) on $t^{1/2}$.

then the data of the present paper and the data of Refs. 39 and 41 agree well.

The results for DeSNa and DDSNa solutions of different concentrations plotted in coordinates of Eq. (31) are presented in Figs. 12 and 13. Theoretical straight lines were calculated according to Eq. (31) at the D value presented in Table 2. As

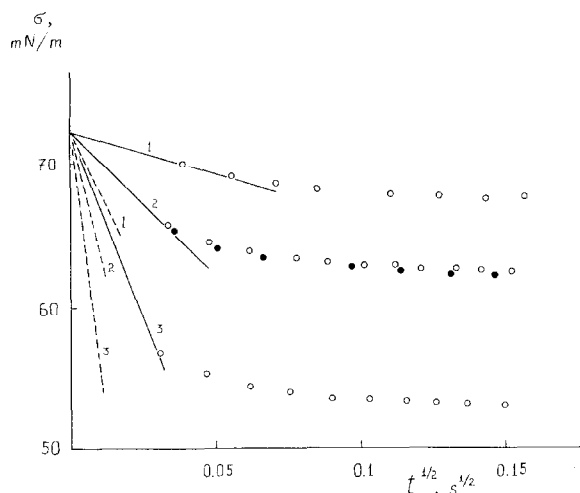


Fig. 12. Dependence of dynamic surface tension of DeSNa solutions at $c_0 = 4 \text{ mol m}^{-3}$ (curves 1), $c_0 = 8 \text{ mol m}^{-3}$ (curves 2) and $c_0 = 16 \text{ mol m}^{-3}$ (curves 3) on $t^{1/2}$. The broken lines represent calculations using Eq. (31).

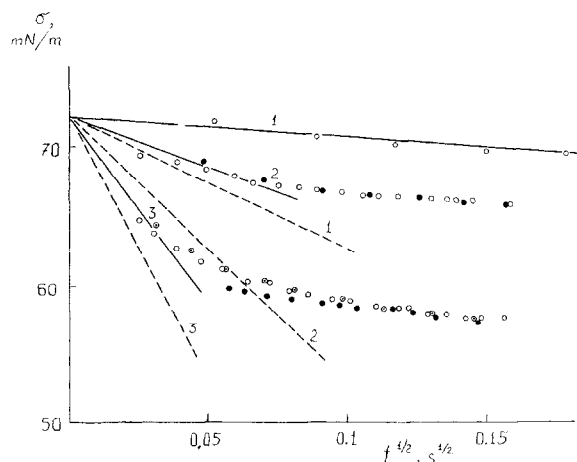


Fig. 13. Dependence of dynamic surface tension of DDSNa solutions at $c_0 = 0.288$ (curves 1), 0.576 (curves 2) and 1.152 g l^{-1} (curves 3) on $t^{1/2}$: \circ , pure DDSNa; \odot , DDSNa with admixture of 5% TDSNa; \bullet , "contaminated" DDSNa. The broken lines represent calculations using Eq. (31).

one can see from the comparison of experimental and theoretical dependences, for DDSNa solution $D_{\text{ef}} < D$, and for DeSNa solution $D_{\text{ef}} \ll D$. Equation (37) allows us to estimate the value of the constant β for DeSNa and DDSNa solutions.

The values of β thus obtained agree well as regards the order of magnitude and the dependence behaviour with the data from Refs. 3 and 39. Values of $D_{\text{ef}} \ll D$ for DDSNa at $t \rightarrow 0$ and $\Gamma \neq 0$ also follow from the data of Ref. 41.

As one could expect, the presence of the surface-active impurities does not influence the dependence of σ on $t^{1/2}$ at $t \rightarrow 0$. The data obtained for the solution of DDSNa which contains TDSNa were described by the same curve as pure DDSNa.

Thus we conclude that the dependence of σ on $t^{1/2}$ at $t \rightarrow 0$ is a good indicator of the adsorption process mechanism.

Conclusion

The simple analytic form of the solutions for adsorption kinetics equations in the region of maximum and minimum values of surface lifetimes allows us to analyse various systems of different complexity, without resorting to the use of approximate or numerical solutions in the range of intermediate lifetimes. It is very evident that asymptotic solutions at $t \rightarrow \infty$ in all of the adsorption mechanisms do not include the adsorption barrier. The experiments in this t region are good criteria for the presence or absence of surface-active impurities. In contrast, the region of $t \rightarrow 0$ is less sensitive to the presence of contaminants; however, the slower kinetics (in comparison with the diffusion theory) of the surface tension decrease in this region definitely indicates the existence of an adsorption barrier.

In the present work we obtained the asymptotic solutions at $t \rightarrow \infty$ and $t \rightarrow 0$ for the solutions of a single surfactant, and also for surfactant mixtures at different conditions: a non-stationary adsorption process on non-deforming and deforming surfaces, stationary and quasi-stationary processes for a

dilatationally deforming surface, and also the diffusive and mixed kinetics of adsorption.

The experimental studies, performed with the help of the highly sensitive automatic computerized instrument MPT-1 (maximum bubble pressure method) for sodium alkyl sulphates, fully confirmed the results of theoretical studies. Specifically, for all surfactants at $t \rightarrow \infty$ we proved the diffusion mechanism of adsorption. The presence of surface-active impurities and their concentration levels were estimated according to the dependence of σ on $t^{-1/2}$. For the low molecular weight sodium alkyl sulphates in the region of $t \rightarrow 0$, the results obtained indicate the presence of the surface adsorption barrier.

References

- 1 J. Kretzschmar and R. Miller, *Adv. Colloid Interface Sci.*, 36 (1991) 65.
- 2 R. Miller and G. Kretzschmar, *Adv. Colloid Interface Sci.*, 37 (1991) 97.
- 3 V.B. Fainerman, *Usp. Khim.*, 54 (1985) 1613.
- 4 A.F. Ward and L. Tordai, *J. Chem. Phys.*, 14 (1946) 453.
- 5 R. Van den Bogaert and P. Joos, *J. Phys. Chem.*, 83 (1979) 2244.
- 6 E. Rillaerts and P. Joos, *J. Phys. Chem.*, 96 (1982) 3471.
- 7 R.S. Hansen, *J. Phys. Chem.*, 60 (1964) 637.
- 8 J. Van Hansel and P. Joos, *Colloids Surfaces*, 24 (1987) 139.
- 9 J. Van Hansel and P. Joos, *Colloid Polym. Sci.*, 267 (1989) 1026.
- 10 G. Serrien and P. Joos, *J. Colloid Interface Sci.*, 139 (1990) 149.
- 11 P. Joos and J. Van Hansel, *Colloids Surfaces*, 33 (1988) 99.
- 12 K. Lunkenheimer, G. Serrien and P. Joos, *J. Colloid Interface Sci.*, 134 (1990) 407.
- 13 J.P. Fang and P. Joos, *Colloids Surfaces*, 65 (1992) 113.
- 14 V.B. Fainerman, *Colloids Surfaces*, 62 (1992) 333.
- 15 V.B. Fainerman and A.V. Makievski, *Colloids Surfaces*, 69 (1993) 249.
- 16 J.P. Fang and P. Joos, *Colloids Surfaces*, 65 (1992) 121.
- 17 R. Miller and G. Kretzschmar, *Colloid Polym. Sci.*, 258 (1980) 85.
- 18 R. Miller and K. Lunkenheimer, *Colloid Polym. Sci.*, 260 (1982) 1148.
- 19 R.P. Borwankar and D.T. Wasan, *Chem. Eng. Sci.*, 38 (1983) 1637.
- 20 R.P. Borwankar and D.T. Wasan, *Chem. Eng. Sci.*, 41 (1986) 199.
- 21 V.B. Fainerman, Yu.M. Rakita and V.M. Zadara, *Kolloidn. Zh.*, 49 (1987) 80.
- 22 Yu.M. Rakita and V.B. Fainerman, *Kolloidn. Zh.*, 51 (1989) 714.
- 23 R. Van den Bogaert and P. Joos, *J. Phys. Chem.*, 84 (1980) 190.
- 24 V.B. Fainerman, Yu.M. Rakita, S.V. Lylyk and V.M. Zadara, *Zh. Phys. Khim.*, 61 (1987) 131.
- 25 R. Miller, *Colloid Polym. Sci.*, 258 (1980) 179.
- 26 P. Joos and E. Rillaerts, *J. Colloid Interface Sci.*, 79 (1981) 96.
- 27 P. Joos, J.P. Fang and G. Serrien, *J. Colloid Interface Sci.*, 151 (1992) 144.
- 28 F. Van voorst Vader, Th.F. Erkelens and M. Van den Tempel, *Trans. Faraday Soc.*, 60 (1964) 1170.
- 29 E. Rillaerts and P. Joos, *J. Colloid Interface Sci.*, 88 (1982) 1.
- 30 V.B. Fainerman, S.V. Lylyk and V.D. Yamilova, *Kolloidn. Zh.*, 49 (1987) 509.
- 31 V.B. Fainerman, *Kolloidn. Zh.*, 48 (1986) 758.
- 32 V.B. Fainerman, *Zh. Phys. Khim.*, 62 (1988) 393.
- 33 R. Miller, J. Loglio, U. Tesei and K.-H. Schano, *Adv. Colloid Interface Sci.*, 37 (1991) 73.
- 34 V.B. Fainerman, R. Miller and P. Joos, *Colloid Polym. Sci.*, 271 (1993).
- 35 X.Y. Hua and M.J. Rozen, *J. Colloid Interface Sci.*, 124 (1988) 652.
- 36 K.J. Mysels, *Langmuir*, 5 (1989) 442.
- 37 L.L. Schramm and W.H.F. Green, *Colloid Polym. Sci.*, 270 (1992) 694.
- 38 Tz.H. Iliev and C.D. Dushkin, *Colloid Polym. Sci.*, 270 (1992) 370.
- 39 V.B. Fainerman, *Colloids Surfaces*, 57 (1991) 249.
- 40 Ch.H. Chang and E.I. Franses, *Colloids Surfaces*, 69 (1992) 189.
- 41 R. Miller, R. Sedev, K.-H. Schano, C. Ng and A.W. Neumann, *Colloids Surfaces*, 69 (1993) 209.
- 42 V.B. Fainerman and S.V. Lylyk, *Kolloidn. Zh.*, 44 (1982) 598.