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Kinetics of the Formation of Adsorption Layers at a Solution–Air Interface

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Studies of the kinetics of the adsorption of surface-active substances (SAS) from solutions have been reviewed. The influence of the chemical structure of the SAS (the length and degree of branching of the hydrocarbon chains and the nature of the polar group) on the mechanism of the adsorption process and the adsorption-kinetic characteristics of the SAS has been analysed. The correlation between the values of the adsorption and desorption rate coefficients and the adsorption equilibrium coefficient has been discussed.
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I. INTRODUCTION

There has recently been a significant increase in the number of papers dealing with the study of the kinetics of the adsorption of surface-active substances (SAS) at the interfaces between solutions and air or a liquid. The interest in this problem is due to the fact that many processes associated with the adsorption of SAS at these interfaces (the surface separation of substnaces, dispersion, including emulsification, and also foaming, wetting, spreading, etc.) and many surface phenomena in biological systems take place under conditions in which equilibrium between the surface layer and the bulk of the solution is not established. The study of the kinetics of adsorption gives important information on the nature of surface phenomena. It is needed, in particular, for an understanding of the mechanism of the action of SAS in technological processes and the control of their action.

It is known that a considerable time is required to establish the equilibrium surface tension at the freshly formed surface of SAS solutions. Three main mechanisms are considered to be responsible for the delay in establishing equilibrium. Milner[1] suggested that the delay is due to the diffusion of the solute from the volume of the solution to the surface layer (in present-day terms diffusion to the pre-surface layer directly adjoining the surface layer). The concept of a surface barrier decreasing the rate of the transfer of a substance from the pre-surface layer to the surface layer was proposed by Doss.[2] It is considered that another possible factor decreasing the rate of establishment of the equilibrium surface tension is related to processes of reorientation of the adsorbed SAS molecules in the surface layer. Hansen,[3] who first pointed out this possibility on the basis of published data,[4] however concluded that reorientation processes have only a slight influence on the surface tension of solutions of SAS with low molecular weight. A recent review[5] gave bulk diffusion and processes of rearrangement in the surface layer as the main factors determining the rate of decrease of the surface tension.

There are very few monographs or reviews on the kinetics of adsorption at liquid phase interfaces. In addition to the review[5] already mentioned, which deals chiefly with processes of adsorption on a surface undergoing periodic deformation, the only published summaries are in an out-of-date review[6] and a section in a monograph.[7] These reviews make practically no reference to the results of studied published in the Soviet literature.

The aim of the present work is to examine briefly the results of theoretical studies of the kinetics of adsorption from solutions containing one SAS in non-micellar form (mainly at freshly formed non-deformed liquid phase interfaces), to summarise experimental data on the kinetics of the adsorption of SAS at a solution–air interface, and to analyse the principal regular features of this process. Most attention has been paid to the adsorption of SAS of low molecular weight.

II. THE THEORETICAL STUDY OF THE KINETICS OF ADSORPTION FROM SOLUTIONS

A most important stage in the development of the theory of the kinetics of adsorption at liquid phase interfaces was a study[8] which solved in general form the problem of the diffusion of SAS from the bulk of a solution with adsorption at a phase boundary, first formulated in Ref. 9.

The physical picture of the adsorption process can be represented as follows. The initial moment of time corresponds to the formation of a fresh surface (flow of liquid from a nozzle, bubbling, etc.) or the instantaneous removal of SAS from the surface of a solution (for example by means of a moving barrier). At this moment, the concentration of the SAS in the surface layer is equal to its concentration in the bulk. Estimates show[10] that only 10^{-9} s after the moment of formation of the phase boundary, the concentration of SAS in the pre-surface layer decreases practically to zero (with the condition that there is no barrier to adsorption). This produces a concentration gradient, leading to the directed diffusion of the SAS from the bulk to the surface layer. When a surface barrier is present, and also as equilibrium is approached, the difference between the concentrations of the SAS in the pre-surface layer and in the bulk decreases, with a corresponding decrease in the diffusion flux and the rate of adsorption. Thus the kinetics of adsorption at any

moment of time can be determined by solving the diffusion equation if the concentration in the pre-surface layer is known.

For a planer surface, the problem can be written as follows:[8,9,11,12]

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2}\ ;\quad x>0,\ t>0\ , \tag{1}$$

$$c = c_0;\quad x>0,\quad t=0\ , \tag{2}$$

$$c = c_0;\quad x\to\infty,\quad t>0\ , \tag{3}$$

$$AD\frac{\partial c}{\partial x} = \frac{\mathrm{d}(\Gamma A)}{\mathrm{d}t}\ ;\quad x=0,\ t>0\ . \tag{4}$$

Here, c is the concentration of the SAS; c_0 the concentration of the SAS in the bulk of the solution at the initial moment and under equilibrium conditions; t the time elapsed from the moment of formation of the surface; x the coordinate ($x = 0$ corresponds to the solution–air interface); D the diffusion coefficinet; Γ the dynamic adsorption; and A the area of the surface. Eqn.(4) is the condition for preservation of the quantity of SAS.

A more general formulation of the problem contains instead of Eqn.(1) a convective diffusion equation, and instead of Eqn.(4) equations for the balance of the SAS in the surface layer with allowance for the diffusion and convective fluxes.[11,13]

For a non-deformed surface (A = conts), the boundary condition (4) reduces to the form[8,9]

$$D\frac{\partial c}{\partial x} = \frac{d\Gamma}{\mathrm{d}t}\ ;\quad x=0,\ t>0 \tag{5}$$

and for a deformed surface it can be written in the form[11,12]

$$D\frac{\partial c}{\partial x} = \frac{\mathrm{d}\Gamma}{\mathrm{d}t} + \Gamma\nu(t);\ x=0,\ t>0 \tag{6}$$

where $\nu(t) = d\ln A/dt$ is the rate of deformation of the surface.

The solution of the problem (1)–(3) and (5) is written in the form[8,14,15]

$$\Gamma = 2c_0\left(\frac{Dt}{\pi}\right)^{1/2} - \left(\frac{D}{\pi}\right)^{1/2}\int_0^t \frac{c(0,\tau)}{(t-\tau)^{1/2}}\,\mathrm{d}\tau \tag{7}$$

where τ is the integration variable.

It can be seen that the most general formulation of the boundary condition for $x = 0$ (Eqns.(4)–(6)) leads to an integral equation relating the values of the adsorption and the concentration of the SAS in the pre-surface layer. The subsequent course of the solution of the problem involves the introduction of additional equations which make it possible to eliminate $c(0, t)$ from Eqn.(7).

Two different approaches have been used. In the first, it is assumed that equilibrium between the pre-surface layer and the surface layer is established very rapidly, and that the rate of the adsorption process is determined exclusively by the rate of diffusion (diffusion mechanism of adsorption). In this case the relationship between the quantities Γ and $c(0, t)$ is given by the adsorption isotherm equation. The second, more general approach takes account of both the rate of diffusion and the rate of establishment of equilibrium between the surface layer and the pre-surface layer (mixed adsorption mechanism). This approach uses adsorption kinetic equations relating Γ and $c(0, t)$ under non-equilibrium conditions. Finally, there is a particular case when the rate of diffusion is high compared with the rate of establishment of equilibrium between the surface layer and the pre-surface layer (kinetic or adsorption mechanism of adsorption). In this case the concentration of the SAS in all parts of the solution (including the pre-surface layer) at any moment of time is equal to c_0. In this case the rate of adsorption is described by adsorption kinetic equations containing c_0 instead of $c(0, t)$.

An expression for the dynamic adsorption Γ for the diffusion mechanism of adsorption can be obtained using, for example, the Frumkin adsorption isotherm[16]

$$bc_0 = \frac{\theta_0}{1-\theta_0}\exp(-2a\theta_0) \tag{8}$$

which effectively describes the equilibrium adsorption of SAS at liquid phase interfaces.[17,18] When it is used for dynamic conditions (that is when $c(0, t)$ and θ are used instead of c_0 and θ_0 respectively), Eqn.(7) gives:[19,20]

$$\theta = \frac{2c_0}{\Gamma_\infty}\left(\frac{Dt}{\pi}\right)^{1/2} - \frac{1}{\Gamma_\infty b}\left(\frac{D}{\pi}\right)^{1/2}\int_0^t \frac{\theta\exp(-2a\theta)}{(1-\theta)(t-\tau)^{1/2}}\,\mathrm{d}\tau\ . \tag{9}$$

In Eqns.(8) and (9), b is the adsorption equilibrium constant; a the interaction coefficient of the SAS molecules in the surface layer; $\theta_0 = \Gamma_0/\Gamma_\infty$ the equilibrium degree of covering of the surface layer; Γ_0 the equilibrium value of the adsorption corresponding to the concentration c_0; Γ_∞ the maximum value of the adsorption (saturated monolayer); and $\theta = \Gamma/\Gamma_\infty$ the degree of covering of the surface layer under dynamic conditions.

Eqn.(9) does not have an analytical solution. It has been obtained only for a linear isotherm.[21] Numerical solutions of Eqn.(9) were obtained in Refs. 22–24 for the Langmuir isotherm ($a = 0$), and in Refs. 19 and 20 for the Frumkin isotherm. In these cases, dimensionless parameters are used, decreasing the number of solutions to be calculated. The problem of the kinetics of adsorption at a growing spherical surface was examined in Refs. 12, 13, 22, 23, 25–27.

The process of the exchange of SAS molecules between the pre-surface layer and the surface layer is described by the Langmuir equation,[28] which gives the total flux of SAS to the surface as the difference between the forward (adsorption) and back (desorption) fluxes. The magnitude of the forward flux is assumed to be proportional to the concentration of the SAS in the pre-surface layer and the fraction of unoccupied surface, and the magnitude of the back flux is assumed to be proportional to the adsorption:

$$I = \beta c(0, t)(1-\theta) - \alpha\Gamma \tag{10}$$

where I is the resultant flux, and β and α the rate constants of adsorption and desorption respectively.

Eqn.(10) provides an additional boundary condition to Eqn.(4) in the solution of Eqn.(1). When there is no deformation of the surface, the magnitude of the flux I is obviously equal to the rate of adsorption:

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0, t)(1-\theta) - \alpha\Gamma\ . \tag{11}$$

For a deformed surface, the rate of adsorption is given by the expression:[11]

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0,t)(1-\theta) - \alpha\Gamma - \Gamma\nu(t)\ . \tag{12}$$

The kinetic equation (11) is applicable only for an ideal surface layer, since for $d\Gamma/dt = 0$ it becomes the Langmuir isotherm. The kinetic equation for the surface layer described by the Frumkin isotherm (8) has the form:[29]

$$\frac{\mathrm{d}\Gamma}{\mathrm{d}t} = \beta c(0, t)(1-\theta) - \alpha\Gamma\exp(-2a\theta)\ . \tag{13}$$

A different form of kinetic equation of this type is given in Ref. 30; other versions of the kinetic treatment of Eqn. (8) are also possible.[31] Eqn. (13) with allowance for isotherm (8) can be rewritten as follows:

$$\frac{d\theta}{dt} = \frac{\beta}{\Gamma_\infty}\left[c(0,t)(1-\theta) - \frac{\theta}{b}\exp(-2a\theta)\right] \qquad (14)$$

where $b = \beta/\alpha\Gamma_\infty$.

Substitution of the magnitude of the concentration in the pre-surface layer, obtained from the solution of the diffusion-kinetic problem (1)–(3) and (5) in Eqn. (11) gives the expression:[14,15,32]

$$\frac{d\Gamma}{dt} = \beta\left[c_0 - \frac{1}{(\pi D)^{1/2}}\int_0^t \frac{d\Gamma/d\tau}{(t-\tau)^{1/2}}\,d\tau\right](1-\theta) - \alpha\Gamma \ . \qquad (15)$$

The same problem can be solved by another method, by the simultaneous solution of Eqn. (7) and the corresponding kinetic equation. Use of Eqn. (14) gives[29]

$$\theta = \frac{2c_0}{\Gamma_\infty}\left(\frac{D}{\pi}\right)^{1/2}\left\{t^{1/2} - \frac{1}{2}\int_0^t \left[\frac{d\theta/d\tau}{L(1-\theta)} + \frac{\theta\exp(-2a\theta)}{bc_0(1-\theta)}\right]\frac{d\tau}{(t-\tau)^{1/2}}\right\} \qquad (16)$$

where $L = \beta c_0/\Gamma_\infty$.

Eqns. (15) and (16) give exact solutions of the diffusion-kinetic problem for the mixed adsorption mechanism. Some results of calculations using Eqn. (16) are given in Refs. 29 and 33.

The adsorption and desorption rate constants appearing in Eqns. (10)–(16) can be specified using the molecular-kinetic approach[14,34] or expressed in terms of transition state theory.[35,36] The constants β and α cannot yet be calculated theoretically, so that the expressions given in the works cited are used only to interpret experimental data.

If the surface barrier is sufficiently high, the rate of adsorption will be determined by the rate at which this barrier is overcome, that is by the actual kinetics of adsorption. In this case, instead of Eqn. (14), it is possible to write:

$$\frac{d\theta}{dt} = \frac{\beta c_0}{\Gamma_\infty}\left[(1-\theta) - \frac{\theta}{bc_0}\exp(-2a\theta)\right] . \qquad (17)$$

From Eqn. (17), for $a = 0$, $\beta = \text{const}$, $\alpha = \text{const}$, and $\Gamma|_{t=0} = 0$ it follows that[37,38]

$$\theta = \frac{bc_0}{1+bc_0}\left[1 - \exp(-t/\tau_0)\right] \qquad (18)$$

where $\tau_a = [\alpha + \beta c_0/\Gamma_\infty]^{-1}$ is the purely adsorption relaxation time. The kinetics of adsorption for the kinetic mechanism on a deformed surface were examined in Ref. 11.

The results of studies of the non-equilibrium properties of freshly formed surface layers are most frequently represented in the form of the dependence of the dynamic surface tension of the SAS solutions on the lifetime of the surface layer. In the case of the diffusion mechanism of adsorption, it is fairly simple to go from the dynamic adsorption to the dynamic surface tension. In this case, it is usually assumed that the relationship between the surface tension and the adsorption under dynamic conditions is described by the same expression as under equilibrium conditions.[3,39] For example, for non-ideal surface layers of SAS, described by the Frumkin isotherm (8), the relationship between the equilibrium decrease in the surface tension π_0 and the adsorption is given by the Frumkin equation of state:[16–18]

$$\Pi_0 = -\Gamma_\infty RT\left[\ln(1-\theta_0) + a\theta_0^2\right] . \qquad (19)$$

Similarly, for dynamic conditions, it is possible to write:

$$\Pi = -\Gamma_\infty RT\left[\ln(1-\theta) + a\theta^2\right] . \qquad (20)$$

The applicability of this assumption is based on the observation of the principle of local equilibrium, which is used in the theory of the diffusion-controlled kinetics of adsorption.[40] The simplest equation for Π for the diffusion mechanism of adsorption is obtained for $\theta \ll 1$:

$$\Pi = 2RTc_0\left(\frac{Dt}{\pi}\right)^{1/2} . \qquad (21)$$

For the kinetic mechanism of the adsorption process, the surface tension is usually also assumed to depend only on the magnitude of the adsorption. In contrast to the case of the diffusion mechanism, however, this approach is approximate, since the secondary chemical potentials are not introduced into the calculation.[40] A difference in the relationships between Π and Γ under equilibrium conditions and under dynamic conditions may be due, for example, to processes of orientation and structure formation in the surface layer, where for identical adsorption the non-oriented layer may have higher values of the surface tension. For solutions of SAS with low molecular weights, this difference apparently does not exceed the uncertainty of the measurements. This can be seen not only from the works already cited[3,4] but also from a comparison of the results of studies[41,42] in which the kinetics of adsorption of sodium dodecyl sulphate were measured using radioactive tracers, and studies[43–45] of the same SAS using the methods of Wilhelmy and the maximum pressure in a bubble. As shown in Ref. 46, the values of the adsorption rate constants calculated form the data in Refs. 41–45, in spite of the introduction of Eqn. (20) for the treatment of the results from Refs. 43–45.

Where the kinetics of adsorption are described by Eqn. (18), Eqn. (20) gives:[38]

$$\Pi = \Gamma_\infty RT\ln\frac{1+bc_0}{1+bc_0\exp(-t/\tau_a)} . \qquad (22)$$

The possibility of calculating dynamic adsorption from the known diffusion and adsorption-kinetic characteristics of SAS (Eqns. (15) and (16)) is a significant achievement of the theory of the kinetics of adsorption. The fact that methods for the theoretical calculation of the constants β and α are imperfect, however, restricts the applicability of the theory described, and raises to prominance the problem of the experimental study of the adsorption-kinetic characteristics of SAS and their dependence on the nature of the substance, the composition of the solution and the surface layer, etc. The use of Eqns. (15) and (16) to calculate the values of the constants β and α from experimental data on the dynamic surface tension of solutions encounters difficulties which are practically impossible to overcome, because of the complex dependence of the constant β on θ and t.

The present author proposed and justified[29,33,47] an approximate model of the mixed adsorption process. According to this model, the rate of adsorption for a fixed degree of covering of the surface layer can be represented as the sum:

$$\frac{1}{d\theta/dt} = \frac{1}{(d\theta/dt)_k} + \frac{1}{(d\theta/dt)_d} . \qquad (23)$$

The subscripts "d" and "k" refer to the diffusion and kinetic mechanisms respectively, and $(d\theta/dt)_d$ and $(d\theta/dt)_k$ are determined from Eqns. (9) and (17).

If the values of the back rates of adsorption appearing in Eqn. (23) are interpreted as the corresponding resistances, the complete resistance to the motion of the molecules of the SAS from the bulk of the solution into the surface layer can be represented as the sum of the diffusion and kinetic resistances. The mixed kinetics of a first-order chemical reaction at a phase boundary are treated similarly.[48]

An advantage of Eqn.(23) is that it can be used to calculate the adsorption-kinetic characteristics of SAS. It makes it possible to use the experimental values of $d\theta/dt$ and the values of $(d\theta/dt)_d$ calculated from Eqn.(9) to determine the rate of adsorption for the kinetic mechanism

$$\left(\frac{d\theta}{dt}\right)_k = \frac{(d\theta/dt)\cdot(d\theta/dt)_d}{(d\theta/dt)_d - d\theta/dt} \qquad (24)$$

and hence the constant β (using Eqn.(17)). The experimental values of the constants β and α obtained by this method are discussed below.

In addition to the two-stage model of the adsorption process (diffusion–adsorption) described above, approaches not involving the introduction of a kinetic equation are also being developed: the surface potential method,[41] equalisation of the chemical potential,[31] and a diffusion method similar to that proposed in Ref.31, in which the surface layer is assigned a lower diffusion coefficient (compared with the bulk).[49]

On the other hand, in an approach proposed by Rebinder,[50] diffusion is ignored, and the decrease in the surface tension is described as a first-order reaction. The resulting expression has the form

$$\sigma = \sigma_0 + B_0 \exp(-kt) \qquad (25)$$

where σ_0 and σ represent respectively the equilibrium and dynamic surface tension of the solution, and k the rate constant. Eqn.(25) is widely used for the treatment of experimental results, and, as shown in Ref.51, is a particular case of Eqn.(22), describing purely adsorption kinetics.

The above discussion cannot claim to cover completely all the problems of the theory of the kinetics of adsorption at liquid phase interfaces. Without departing from the main theme of the review, reference can be made to studies of such important problems as the kinetics of adsorption from multicomponent solutions,[52–55] the kinetics of adsorption accompanied by mass transfer through the phase boundary,[56–58] the kinetics of adsorption and the dynamic surface elasticity for a surface undergoing periodic deformation,[5,59–64] and the kinetics of adsorption from micellar solutions with allowance for the breakdown of the micelles.[65–68]

III. EXPERIMENTAL METHODS

The dynamic surface tension of SAS solutions is studied by methods using oscillating and tapering jets, the shape and weight of a drop, the maximum bubble pressure, propagation of a capillary wave, by Wilhelmy's method, etc. The jet method is also used to measure the dynamic surface electric potential. Direct measurements of dynamic adsorption are made using radioactive tracers. The methods most frequently used can be examined briefly from the viewpoint of their correspondence to the theoretical models described in the previous section.

The theory of the oscillations of a liquid jet, developed by Rayleigh and Bohr,[69] formed the basis of one of the most widely encountered methods, namely the oscillating liquid jet method. The theory developed in Ref.69 took no account of the non-uniformity of the initial rate profile along the cross-section of the jet, or the surface elasticity. Approximate account was taken of these factors comparatively recently.[70–72] Direct experimental studies of the surface velocity of jets of water and SAS solutions,[73,74] and other published data,[71,72] indicate that the calculated values of the surface tension and the lifetime of the surface are insufficiently reliable in direct proximity to the nozzle (the first few oscillations). This explains the large discrepancies in the results obtained for the same systems by different authors.

The method based on the surface electric potential of a liquid jet[4,75] is free from a number of disadvantages of the oscillating jet method; in the determination of the lifetime of the surface and its rate of deformation by this method, however, difficulties arise as a result of the uncertainty of the calculation of the velocity of the surface of the jet, and also because of the Marangoni effect.[73,74] One modification of the jet method is the trough method with measurement of either the surface tension of a flowing film of liquid[76] or its surface electric potential.[4]

In the drop volume method, the correct interpretation of the results of the measurements requires allowance on the one hand for the existence of convective currents in the volume of the drop and on the other hand for the deformation (expansion) of the surface of the drop during its growth. The models of radial[12,23,25–27] and circulating[77] flow of liquid in a growing drop give significantly different expressions for the dynamic adsorption. Since the actual picture of the flow of liquid in a drop is fairly complex, the determination of the mechanism of adsorption and the calculation of the kinetic parameters of adsorption from the experimental values of the dynamic surface tension, obtained by the drop volume method, are associated with appreciable uncertainty, particularly for the diffusion mechanism of adsorption or mechanisms close to it.

The maximum bubble pressure method provides unique possibilities with respect to the time range of the measurements—from 1 ms to 1000 ms and more, which is much greater than for all other methods. The determination of the lifetime of the surface in the range of high frequencies of bubble formation and the nned to take account of the deformation of the surface of the bubble during the measurements are the main problems associated with this method; they were successfully resolved in Refs.78–82. For low values of the time, the uncertainty of the determination σ is ~1 mN m^{-1}, and the uncertainty of the determination of the lifetime is 1 ms.[81] With a comparatively simple method for taking account of the deformation of the surface,[83] it is possible to calculate the adsorption-kinetic characteristics of SAS from the results of measurements of the dynamic surface tension of their solutions.

Slow changes in surface tension are studied by Wilhelmy's method. A fresh surface is created by removing the surface layer of the solution by suction.[84]

A method involving the measurement of the surface tension of a surface expanding at a given rate has been proposed.[85]

The capillary wave method[86,87] and the method of small periodic deformations[63,64] raise the question of whether the mechanisms of adsorption are the same and whether the values of the rate constants of adsorption and desorption, calculated from the results of measurements of the dynamic surface tension by the usual methods, are equal to the values obtained from data on the propagation of a capillary wave or with periodic deformations of the surface. The answer apparently is that they are not. Thus the rate constant for the adsorption of a given SAS in the general case (see section IV) depends on different parameters, including the lifetime of the surface layer with a definite degree of covering. The periodic deformations involving elongation and contraction during the passage of capillary waves or the movement of a barrier influence the structure of the surface layer and hence the values of the constants β and α.

The radioactive tracer method[41,42] gives reliable values of the dynamic adsorption if the correction for the radioactivity of the bulk of the solution is small. This condition is

satisfied to the greatest extent by tritium, which has recently been used to study equilibrium adsorption. In Refs. 41, and 42, however, the range of reliable values of Γ was restricted to $t > 100$ s.

IV. THE KINETICS OF THE ADSORPTION OF SAS WITH DIFFERENT STRUCTURES

Experimental studies of the kinetics of the adsorption of SAS are carried out to investigate the mechanism of the process (diffusion, kinetic, or mixed) and the conditions under which a given mechanism is realised, and also to determine the rate constants of adsorption and desorption (for the kinetic or mixed mechanisms) and their dependence on the chemical structure of the SAS, its concentration, the presence of added substances in the solution, the degree of covering of the adsorption layer, and its lifetime.

In Refs. 46, and 47 an attempt was made to analyse some of these relationships on the basis of an approximate theory of the mixed adsorption process using a comparatively small amount of experimental data published by different authors on the dynamic surface tension of SAS solutions. Recent detailed studies of the kinetics of the adsorption of normal alcohols[81] and sodium alkyl sulphates[88] from aqueous solutions at their interface with air, and other recently published data, not only make it possible to analyse in much more detail the problem of the relationship between the properties of an SAS and its adsorption-kinetic characteristics but also to obtain a number of important results not discussed earlier.

To analyse the adsorption-kinetic characteristics of SAS, only those experimental studies which satisfy the following requirements have been selected from the large number studied: careful preparation and purification of the specimens; detailed information on the equilibrium surface tension of the solutions; and the use of reliable methods to study the dynamic surface tension. The preceding section shows that the last requirement is not satisfied, in particular, by the oscillating jet method, and some of the data obtained by this method were used only for qualitative estimates.

The results of studies of the kinetics of adsorption from solutions of non-ionogenic SAS can be examined first. A large number of papers (see Ref. 81) have been devoted to the study of the dynamic surface tension of aqueous solutions of normal alcohols. The results of studies by the present author using the maximum bubble pressure method,[81] covering a wide range of surface lifetimes (from 0.001 s to 100 s) for aqueous solutions of alcohols with different hydrocarbon chain lengths (from propanol to decanol), can be summarised as follows: in the homologous series of alcohols, with increase in the length of the molecule by one methylene group, the adsorption rate constant increases by a factor of 3–3.5†, that is to the same extent as the adsorption equilibrium constant. The increase in the adsorption rate constant (for 6 or 7 carbon atoms in the alcohol molecule) leads to a change in the adsorption mechanism: the low-molecular-weight alcohols are adsorbed by a kinetic mechanism, and the high-molecular-weight alcohols by a diffusion mechanism. These results for high-molecular-weight alcohols (heptanol and above) for the most part agree with the data in Ref. 89, where the surface electric potential of a liquid jet was used.

The authors of Ref. 90 (maximum bubble pressure method) and Ref. 91 (breaking meniscus method) studied comparatively dilute decanol solutions. Under these conditions, a slower (compared with Ref. 81) decrease in the surface tension with time was observed. Analysis of these results indicates that decanol is adsorbed by a diffusion mechanism at $t < 10$ s, and by a mixed mechanism, with approximately equal diffusion and kinetic resistances, for longer times. The values of the constants β for $t > 10$ s, calculated from the data in Refs. 90 and 91, were found to be much lower than those obtained by extrapolating the values of β for low-molecular-weight alcohols into the range of low values of t.[81] The decrease in the constant β with increase in t, previously observed in Refs. 46 and 47, is a common property of most SAS, and indicates appreciable structural changes in the adsorption layer, as a result of which the disordered orientation of the molecules for short lifetimes of the surface layer is gradually replaced by a more organised structure, which exerts appreciable resistance to the movement of the SAS molecules into the surface layer.

Another explanation for the dependence of the constant β on the lifetime of the surface layer is possible. It is known (see section III) that in all the methods used to study the dynamic surface tension of solutions in the range of short times (jet, drop, and bubble methods), the surface of the solution increases during the measurements, the increase being revealed to a greater extent at low values of t and to a smaller extent at large values of t. Thus the dependence of β on t can also be represented as the dependence of β on the rate of deformation of the surface $\nu(t)$. Since it is known from rheology that the structure of an object depends on the rate of its deformation, the decrease in the constant β with increase in t (decrease in $\nu(t)$) can apparently be attributed not only to a delay in the production of the equilibrium structure of the surface layer but also to a difference in the extent of its greakdown with increase in the surface area.

A mixed mechanism was also detected in a study of the kinetics of desorption from decanol monolayers at a constant surface pressure.[92]

The position of the polar group in the alcohol molecule has some influence on the rate of adsorption. Thus the rate of the decrease in the surface tension is slightly lower in s-octyl and t-hexyl alcohol solutions than in solutions of the corresponding normal alcohols.[93–95]

The kinetics of adsorption of normal acids are similar to those of the corresponding alcohols.[90,96] In particular, for decanoic acid (as for decanol), the published data[90,91,97] indicate a diffusion mechanism of adsorption at $t < 10$ s. The kinetics of the adsorption of undecanoic acid, calculated from the data of Ref. 98 (Wilhelmy's method), are close to purely diffusion kinetics throughout the entire range of lifetimes of the surface layer (from 200 s to 3000 s).

The results of measurements of the modulus of the dynamic surface elasticity of solutions of decanoic acid in the range of angular frequencies 10^{-2}–10^{2} s^{-1} also indicate a diffusion mechanism of adsorption.[64]

The maximum bubble pressure method (t = 1–100 s) has been used[99] to measure the dynamic surface tension of aqueous solutions of decyldimethylphosphine oxide ($C_{10}H_{21}PO(CH_3)_2$), dodecyldimethylphosphine oxide ($C_{12}H_{25}PO(CH_3)_2$), and dodecyldimethylamine oxide ($C_{12}H_{25}NO(CH_3)_2$). Comparison of the experimental data with the results of calculations using the diffusion equations showed that in the region of the lowest values of t studied (less than 1–2 s), these substances are adsorbed by a diffusion mechanism, but mixed adsorption kinetics are observed at longer times. This agrees with the results of a study[26] in which the initial slope of the curves on coordinates σ–t, given in Ref. 99, were used to determine the diffusion coefficients; the results showed good agreement with the

†For C_3–C_7 alcohols.

actual values. A detailed treatment of the data of Ref. 99 with a determination of the values of the constants β was carried out in Ref. 46. All the SAS indicated show a decrease in the constant β with increase in the degree of covering by the adsorption layer and increase in its lifetime. As in the case of the normal alcohols, the adsorption rate constants for the alkyldimethylphosphine oxides icnrease with increased length of the hydrocarbon chain.

The kinetics of the adsorption of non-ionogenic SAS with polyethylene oxide hydrophilic groups have been studied.[38,99,100–105] The results of measurements of the dynamic surface tension of aqueous solutions of the dodecyl ethers of heptaethylene glycol and nonaethylene glycol, and the hexadecyl ether of decaethylene glycol, by Wilhelmy's method at $t > 50$ s indicate that these SAS are adsorbed by a diffusion mechanism.[103,104] The same adsorption mechanism is observed for the hexadecyl ether of octaethylene glycol (ring separation method, $t > 600$ s).[105]

In Ref. 100, the kinetics of the adsorption of the dodecyl ethers of hexa-, hepta-, and octaethylene glycols in the range of surface lifetimes 0.05–0.9 s were studied using the dynamic surface electric potential at the surface of a flowing film of solution (the trough method). Assuming that the relationship between the surface electric potential of the solution and the magnitude of the adsorption is the same under dynamic and under equilibrium conditions, the authors cited used the results obtained for the dodecyl ether of hexaethylene glycol to calculate the magnitude of the adsorption.[100] The values of θ which they obtained were found to be lower than those calculated using diffusion theory.

The dynamic surface tension of aqueous solutions of the dodecyl ether of hexaethylene glycol was also measured in Ref. 99 (maximum bubble pressure method, $t = 1–100$ s). Treatment of the results[99] showed that the diffusion mechanism of adsorption is observed at low concentrations of the SAS (less than 0.02 mole m^{-3}) throughout the entire range of lifetimes t. With increase in the SAS concentration, the range corresponding to the diffusion mechanism of adsorption decreases to 5–10 s, and at longer times a mixed adsorption mechanism is observed. To reconcile the results of Refs. 100 and 99, it must be assumed that the slow change in the surface electric potential is related not to the kinetics of adsorption but to the slow relaxation of the structure of the surface layer, which does not influence the surface tension. This relaxation process may be determined by the orientation of the polyethylene glycol fragment of the SAS molecule.

Measurements of the modulus of dynamic elasticity of the surface of aqueous solutions of the dodecyl ethers of hexaethylene glycol and triethylene glycol in the range of angular frequencies $10^{-2}–10^{-1}$ s^{-1} also indicate a diffusion mechanism for the adsorption of these SAS, as in the case of the dodecyl ether of pentaethylene glycol at a very low angular frequency ($10^{-3}–10^{-2}$ s^{-1}).[63]

The degree of branching of the hydrocarbon chain of the molecule of a non-ionogenic SAS has a considerable influence on the adsorption mechanism and on the magnitude of the adsorption rate constant. The results of studies of the dynamic surface tension of aqueous solutions of di-isobutylphenoxyheptaethylene glycol ($[(CH_3)_3C]_2C_6H_3O(C_2H_4O)_7H$) by the maximum bubble pressure method ($t = 2–30$ s)[38] and by the drop weight method ($t = 0.05–2$ s)[101] indicate a kinetic adsorption mechanism. Thus molecules with highly branched hydrocarbon chains are adsorbed much more slowly than those with linear chains. Their adsorption rate constants also decrease more rapidly with increase in the degree of covering of the adsorption layer (in addition to the above SAS, this is also observed for alkyldimethylphosphine oxides and dodecyldimethylamine oxide[99]).

Among anionic SAS, the kinetics of adsorption from solutions have been studied in most detail for sodium alkyl sulphate solutions (see Ref. 88). Detailed studies of the dynamic surface tension of aqueous solutions have been carried out for sodium decyl, dodecyl, and tetradecyl sulphates in the range of surface lifetime 0.001–500 s (maximum bubble pressure method).[88] The mechanism of the adsorption of sodium decyl sulphate is kinetic throughout the entire range of values of t studied, that of sodium dodecyl sulphate is kinetic at $t > 0.005$ s, and that of sodium tetradecyl sulphate is diffusion at $t < 0.005$ s and kinetic at $t > 0.02$ s.

The magnitude of the rate constant of the adsorption of sodium alkyl sulphates decreases as equilibrium is approached, but the dependence of b on t for different SAS concentrations and degrees of covering of the surface layer is given by a single curve. For a more detailed study of the nature of the surface barrier to adsorption, the kinetics of the decrease in the surface tension when various electrolytes and non-electrolytes were added to the solution were studied.[88] The addition of inorganic electrolytes generally leads to an increase in the range of surface lifetimes in which the diffusion mechanism of adsorption is observed, and to an increase in the adsorption rate constant β. Exceptions are also observed, however. Thus the addition of multiply-charged counter-ions at low lifetimes (low degrees of covering of the surface layer) decreases the rate of adsorption, probably because of their structure-forming action on the surface layer of water.

The results of measurements of the constant β in aqueous solutions of sodium alkyl sulphates with and without the addition of inorganic electrolytes are summarised in Fig. 1 in the form of the dependence of β on the adsorption equilibrium constant b. This dependence was given for the first time for a comparatively small number of SAS in Refs. 46 and 47. The adsorption rate constant for a given lifetime of the surface layer in the range $b < 10$ m^3 $mole^{-1}$ increases rapidly with increase in the adsorption equilibrium constant. Further increase in the constant b as a result of an increase in the quantity of added inorganic electrolytes does not lead to an increase in β, because of the specific action of these electrolytes on the structure and properties of the surface layer of water.[88]

The relationship between the kinetics of the decrease in the surface tension of SAS solutions and the structure of the surface layer of water was observed particularly clearly in a study of aqueous solutions of sodium alkyl sulphates containing added normal alcohols with different chain lengths.[88] It was established that for approximately equal (low) concentrations of the added alcohols in the surface layer, low-molecular-weight alcohols (methanol, ethanol, and propanol), which apparently stabilise the water structure, decrease the rate of adsorption, whereas high-molecular-weight alcohols (pentanol, hexanol, heptanol, and octanol), which apparently break down the water structure, increase the rate of adsorption of the sodium alkyl sulphates.

Thus the results of Ref. 88 indicate that the surface barrier to the adsorption of the sodium alkyl sulphates at the solution–air interface is due both to electrostatic repulsion between the adsorbed and adsorbing ions (since it is suppressed by the addition of inorganic electrolytes) and by effects which are probably related to the need to break hydrogen bonds between the water molecules in the surface layer (suppressed by the addition of electrolytes and non-electrolytes which break down the water structure).

In Refs. 53 and 76, Wilhelmy's method on a flowing film of solution (the trough method) was used to study the kinetics of the adsorption of sodium decanoate, dodecanoate, the tetradecanoate in the presence of 0.1 M NaOH in the surface lifetime range 0.01–1.0 s. The use of more accurate values of

the diffusion coefficients of these substances (5.0×10^{-10}, 4.7×10^{-10}, and 4.4×10^{-10} $m^2 s^{-1}$ respectively)[106] instead of the value 2.8×10^{-10} $m^2 s^{-1}$ used in Ref. 53 indicates that sodium tetradecanoate is adsorbed by a diffusion mechanism, and sodium dodecanoate by a mixed mechanism. It is impossible to say anything definite about the mechanism of the adsorption of sodium decanoate, since its adsorption is close to equilibrium in the surface lifetime range studied.

The dynamic surface tension of aqueous solutions of sodium hexadecanoate was studied by the maximum bubble pressure method in Ref. 107. The pH of the medium and the addition of an inorganic electrolyte (0.2 M KNO_3) had a significant influence on the rate of decrease in σ. At pH 8.2, at which the rate of the decrease is a maximum, the kinetics of adsorption in the presence of the inorganic electrolyte are purely diffusion. At other pH values, and also in solutions without an added inorganic electrolyte, adsorption takes place by a mixed mechanism.

The kinetics of the adsorption of sodium di-iso-octyl succinate-1-sulphonate ($C_{20}H_{37}O_4SO_3Na$) were studied in Refs. 78 and 108. In Ref. 78, the maximum bubble pressure method was used (t = 0.01–0.2 s). Analysis of the experimental results shows that sodium di-iso-octyl succinate-1-sulphonate is adsorbed from aqueous solutions by a mixed mechanism throughout practically the entire range of surface layer lifetimes studied. The adsorption rate constant decreases with increase in t and increases when small quantities of sodium chloride are added.

The kinetics of the adsorption of cationic SAS were studied in Refs. 86, 87, 109–112. Analysis of the observed dependence of σ on t for dodecyltrimethylammonium chloride (fluctuating jet method, t = 0.005–0.05 s)[109] leads to the following conclusions: for $t < 0.01$ s, the mechanism of the adsorption of this SAS is diffusion, but at $t > 0.01$ s a mixed mechanism is observed, and the adsorption rate constant decreases with increase in t.

The maximum bubble pressure has been used[110] to study the influence of change in pH (from 7 to 12.5) on the dynamic and equilibrium surrace tension of an aqueous solution of dodecylammonium acetate ($C_{12}H_{25}NH_3COOCH_3$) and of dodecylammonium chloride with and without the addition of sodium acetate. The lowest value of the equilibrium surface tension and the highest rate of decrease in σ were observed at pH 9.85, at which dodecylammonium acetate is hydrolysed (to dodecylamine). In this case, a diffusion mechanism of adsorption is observed at t < 2–3 s, and a mixed mechanism with increase in the lifetime (to t = 100–200 s). The constant β decreases with increase in t. As expected, the addition of small quantities of sodium acetate has no influence on the kinetics of the adsorption of dodecylammonium acetate at pH 9.85, since there is no electrostatic surface barrier in this case.

The dynamic surface tension of aqueous solutions of hexadecyltrimethylammonium bromide has been measured (maximum bubble pressure method, t = 200–3000 s) in the range of values of σ close to equilibrium.[111] Treatment of these

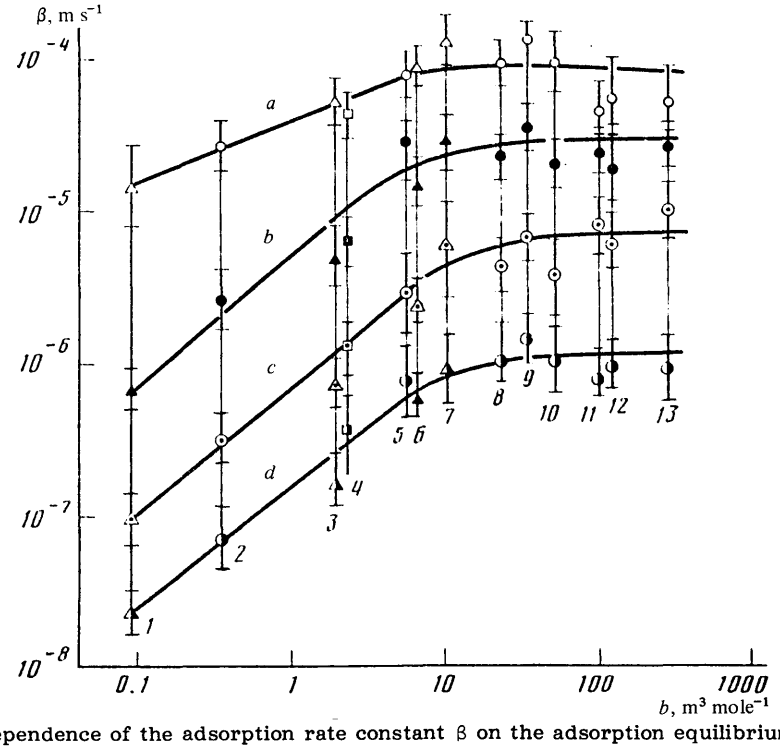


Figure 1. Dependence of the adsorption rate constant β on the adsorption equilibrium constant b for surface lifetimes of 0.01 s (*a*), 0.1 s (*b*), 1 s (*c*), and 10 s (*d*) for sodium alkyl sulphates: *1*) NaDeS in water; *2*) NaDS in water; *3*) NaDeS in 0.1 M NaCl; *4*) NaTS in water; *5*) NaDS in 0.1 M $LiNO_3$; *6*) NaDeS in 0.5 M NaCl; *7*) NaDeS in 0.1 M NaCl; *8*) NaDS in 0.1 M $NaNO_3$; *9*) NaDS in 0.01 M $MgCl_2$; *10*) NaDS in 0.1 M NaCl; *11*) NaDS in 0.3 M NaCl; *12*) NaDS in 0.05 M $MgCl_2$; *13*) NaDS in 0.5 M NaCl; temperature 25°; NaDeS = $C_{10}H_{21}OSO_3Na$, NaDS = $C_{12}H_{25}OSO_3Na$, NaTS = $C_{14}H_{29}OSO_3Na$.[88]

results showed[112] that the mechanism of the adsorption of this SAS is close to kinetic. The adsorption rate constant of hexadecyltrimethylammonium bromide decreases with increase in the lifetime and degree of covering of the surface layer, and is almost independent of the temperature of the solution; this feature, and the decrease in β with increase in temperature for sodium alkyl sulphate solutions,[36,88] indicates that the surface barrier to adsorption has an appreciable entropy component.

The rate constants for the adsorption and desorption of octyl-, decyl-, and dodecylammonium chlorides have also been determined by the capillary wave method.[86,87] The values of β for the cationic SAS, like the value obtained in these studies for the constant β for sodium dodecyl sulphate, are probably too high, because of the destructive action of the capillary waves on the structure of the surface layer, which is thus as it were continuously renewed. The material examined above, however, shows that the values of the constant β are higher for surfaces with a short lifetime than for long-lived surfaces.

Finally, brief mention may be made of the principal results of studies of the kinetics of formation of adsorption layers of polymers. Published data[113–118] indicate that the mechanism of this process is complex and depends on many factors. As a rule, at low concentrations of the polymers in solution at low degrees of covering of the surface layer, the adsorption mechanism is close to diffusion, but with increase in the concentration the role of the surface barrier increases. This last feature is associated with an increasing contribution from electrostatic repulsion forces[113,117] and with structural changes in the surface layer.[116–118] The rate of adsorption of polymers is influenced considerably by the pH of the solution, the presence of inorganic electrolytes, the sign and number of electric charges on the molecule, the hydrophobic character of the SAS, etc. The dependence of the surface tension of polymer solutions on the lifetime of the surface is described satisfactorily by Eqn.(25).

V. GENERAL REGULAR FEATURES AND CORRELATIONS

Comparison of the values of the adsorption rate constants obtained experimentally for different SAS reveals a number of regular features. If the values of β are compared for low or medium degrees of covering of the surface layer and fixed values of t for SAS with alkyl chains R of equal length, it is possible to write the following order of increase in the constant β: $R-OSO_3Na < R-N(CH_3)_3Cl < R-NO(CH_3)_2 < R-NH_2 < R-COOH < R-OH < R-PO(CH_3)_2 < R-O(C_2H_4O)_6H$.

It should be noted that the surface activity of the substances increases in this order, that is in this case, as in the case of sodium alkyl sulphates (see Fig.1), a correlation is observed between the adsorption rate constant and the adsorption equilibrium constant. It may therefore be expected that the relationship between β and b will not be sensitive to the characteristic features of the chemical structure of the SAS, and for fixed values of θ and t the same relationship will describe all the results obtained. This

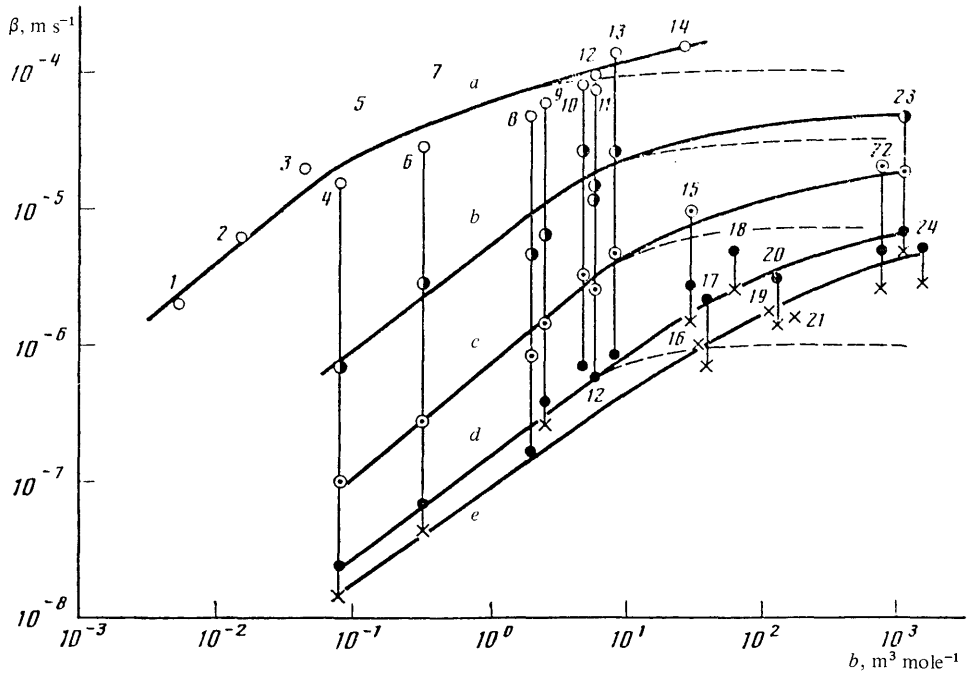


Figure 2. Dependence of the adsorption rate constant β on the adsorption equilibrium constant for surface lifetimes of 0.01 s (*a*), 0.1 s (*b*), 1 s (*c*), 10 s (*d*) and 50 s (*e*) and solution temperatures of 20–25 °C for the following surface-active substances: *1*) C_3H_7OH; *2*) C_4H_9OH; *3*) $C_5H_{11}OH$; *4*) $C_{10}H_{21}OSO_3Na$; *5*) $C_6H_{13}OH$; *6*) $C_{12}H_{25}OSO_3Na$; *7*) $C_7H_{15}OH$; *8*) $C_{10}H_{21}OSO_3Na$ in 0.1 M NaCl; *9*) $C_{14}H_{29}OSO_3Na$; *10*) $C_{12}H_{25}OSO_3Na$ in 0.1 M $LiNO_3$; *11*) $C_{20}H_{37}O_4SO_3Na$; *12*) $C_{10}H_{21}OSO_3Na$ in 0.5 M NaCl; *13*) $C_{10}H_{21}OSO_3Na$ in 1.0 M NaCl; *14*) $C_{12}H_{25}N(CH_3)_3Cl$ in 0.1 M NaCl; *15*) $C_{10}H_{21}PO(CH_3)_2$; *16*) $C_9H_{19}COOH$; *17*) $C_{12}H_{25}NO(CH_3)_2$; *18*) $C_{10}H_{21}OH$; *19*) $C_{10}H_{21}COOH$; *20*) $C_{12}H_{25}NH_2$; *21*) $C_{16}H_{33}OSO_3Na$; *22*) $C_{12}H_{25}PO(CH_3)_2$; *23*) $[(CH_3)_3C]_2C_6H_3O(C_2H_4O)_7H$; *24*) $C_{12}H_{25}O(C_2H_4O)_6H$ (from data in Refs.38, 78, 81, 88, 90, 91, 97–99, 101, 107–110).

relationship for $\beta < 0.5-0.8$ is shown in Fig. 2, which also gives the results obtained for sodium alkyl sulphates with the addition of inorganic electrolytes at $b < 10$ m^3 mole^{-1}; the graphs for $b > 10$ m^3 mole^{-1} in these systems are given by broken lines.

The results given in Fig. 2 show that there is a correlation between the dynamic and equilibrium adsorption characteristics of SAS. For high values of t, the dependence of $\lg\beta$ on $\lg b$ is practically linear throughout the entire range of values of b, whereas for short lifetimes the slope of the curve decreases with increase in b. This is apparently related to the fact that β has a limiting value of $\sim 10^{-2}-10^{-3}$ m s^{-1} (in the complete absence of a surface barrier).[36] In the range in which $\lg\beta$ is linearly dependent on $\lg b$, the following equation is applicable[46,47]

$$\lg\beta = k_1 + k_2 \lg b \qquad (26)$$

where k_1 depends on t, and $k_2 \cong 0.7$.

An interesting feature is that, as noted earlier,[46,47] a similar relationship between the rate constant and the equilibrium constant is observed for a number of chemical reactions, for example reactions involving radicals.[119] There is thus a definite analogy between the kinetics of the adsorption of SAS at a solution–air interface and the kinetics of certain chemical reactions. This analogy provides an additional basis for a chemical approach to the process of adsorption at this boundary, leading, in particular, to the possibility of treating adsorption as an exchange reaction with the formation of an intermediate complex from SAS and water molecules.[81]

It also follows from Fig. 2 that the addition of appreciable quantities of inorganic electrolytes leads to a decrease in the constant β, related to the influence of inorganic electrolytes on the exchange processes in the surface layer.

The results obtained up to the present show that there is a definite relationship between the surface activity of an SAS and the mechanism of its adsorption. Fig. 3 shows the relationship between the adsorption equilibrium constant and the lifetime ranges of the surface layers of different SAS during which these substances are adsorbed by a diffusion mechanism or by a kinetic mechanism. For substances with a low surface activity ($b < 0.1$ m^3 mole^{-1}), the adsorption takes place by a kinetic mechanism throughout the entire range of values of t accessible for measurement. With increase in the surface activity, a certain range of lifetimes appears in which adsorption takes place by a diffusion mechanism, and for substances with a very high surface activity ($b > 1000$ m^3 mole^{-1}), adsorption takes place by a diffusion mechanism throughout the entire range of values of t. For di-isobutylphenoxyheptaethylene glycol (point No. 23 in Fig. 3), the range of the kinetic mechanism of adsorption is anomalously large, and this, as discussed above, is related to the branched nature of its molecule.

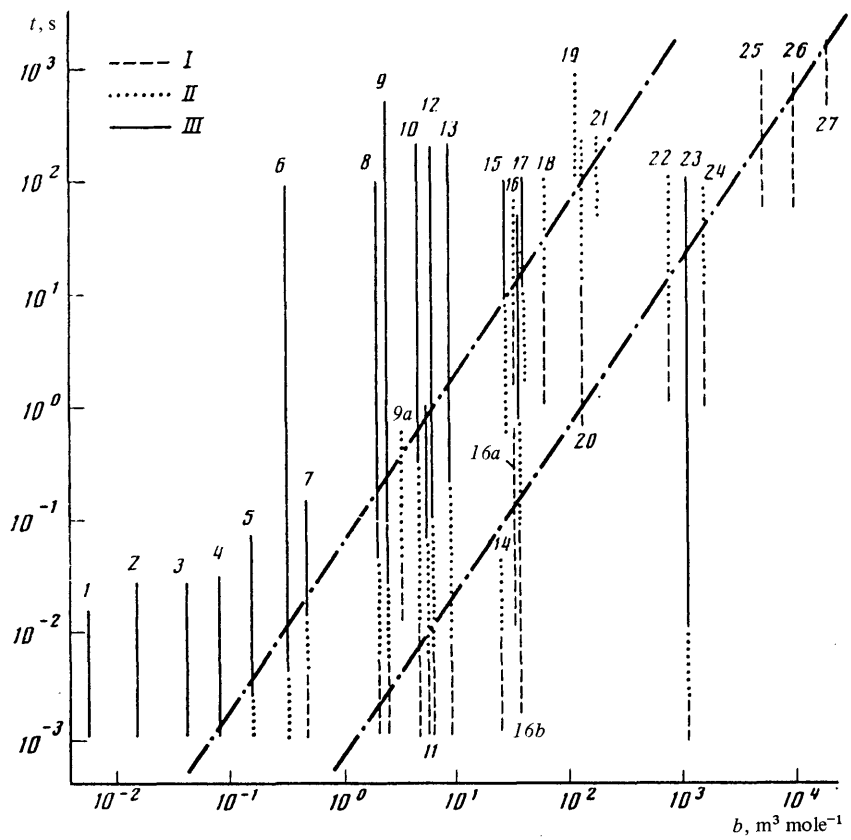


Figure 3. Ranges of different surface-active substance surface layer lifetimes in which diffusion (*I*), mixed (*II*), and kinetic (*III*) adsorption mechanisms are observed. Numbering: *1–24*) same as in Fig. 2; *9a*) $C_{11}H_{23}COONa$ in 0.1 M NaOH; *16a*) $C_{13}H_{25}COONa$ in 0.1 M NaOH; *16b*) $C_{12}H_{25}OSO_3Na$ in 0.01 M $MgCl_2$; *25*) $C_{12}H_{25}O(C_2H_4O)_7H$; *26*) $C_{16}H_{33}O(C_2H_4O)_{10}H$; *27*) $C_{16}H_{33}O(C_2H_4O)_8H$ (from data in Refs. 38, 53, 76, 78, 81, 88, 90, 91, 97–99, 101, 103–105, 107–110).

Fig. 3 contains straight lines which divide the entire field of values of $b-t$ into three regions. To the left of the straight line a the kinetics of adsorption are generally controlled by the surface barrier. The field of values of $b-t$ lying to the right of the straight line b corresponds chiefly to the diffusion mechanism of adsorption, whereas for values of b and t lying between these straight lines, the mixed mechanism predominates. This result is very important, since it makes it possible to predict the mechanism of an adsorption process on the basis of data on the equilibrium adsorption characteristics of SAS.

Since the lifetime of the surface layer determines its degree of covering by SAS molecules, a correlation between the value of the adsorption equilibrium constant and the degree of covering of the surface layer at which a given mechanism of adsorption is realised can be expected. Thus for substances with a low surface activity ($b < 0.1\ m^3\ mole^{-1}$), at least for $\theta > 0.1$, adsorption takes place by a kinetic mechanism, whereas for substances with a high surface activity ($b > 1000\ m^3\ mole^{-1}$), at least for $\theta < 0.9$, adsorption takes place by a diffusion mechanism.

Finally, the correlation between the desorption rate constant α and the adsorption equilibrium constant can be considered. The dependence of α on b can readily be obtained using the data in Fig. 2 and the relationship $b = \beta/\alpha\Gamma_\infty$. The results are given in Fig. 4, and show that the nature of the dependence of α on b is the opposite of the corresponding dependence of β on b. For comparatively weakly surface-active substances ($b < 0.1\ m^3\ mole^{-1}$), the constant α is independent of b. The constant α decreases with increase in b. The decrease in the desorption rate constant is particularly marked for sodium dodecyl sulphate solutions containing large quantities of added inorganic electrolytes (shown by the broken line in Fig. 4), since for these systems, for $b > 10\ m^3\ mole^{-1}$, the constant β does not increase with increase in the surface activity.

The physical significance of the constant α is that it is the probability that the SAS molecule penetrates the surface layer in unit time. Thus the quantity α^{-1} is the time for which the molecule is in the adsorbed state (adsorption time). According to Fig. 4, the adsorption time increases with increase in t, and for a given lifetime and high values of b it increases with increase in the surface activity of the substance.

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To summarise the discussion of studies of the kinetics of the adsorption of SAS at a solution–air interface, it can be concluded that at the present time the main regular features of this process have been outlined, and a number of regular features established, making it possible to advance to reach various conclusions about the characteristic features of the kinetics of the adsorption of a given SAS.

At the same time, a number of problems have not been completely clarified or have not been clarified at all: the influence of the sign and magnitude of the charge and the positions of the polar groups in the SAS molecule on the value of β and on the adsorption mechanism; the relationship between the rate of deformation of the surface and the adsorption-kinetic characteristics of the SAS; the mechanism of processes of structure formation in the surface layer, including processes involving a change in its structure with time; the influence of temperature on the kinetics of the adsorption of different SAS; and the analysis of the energy

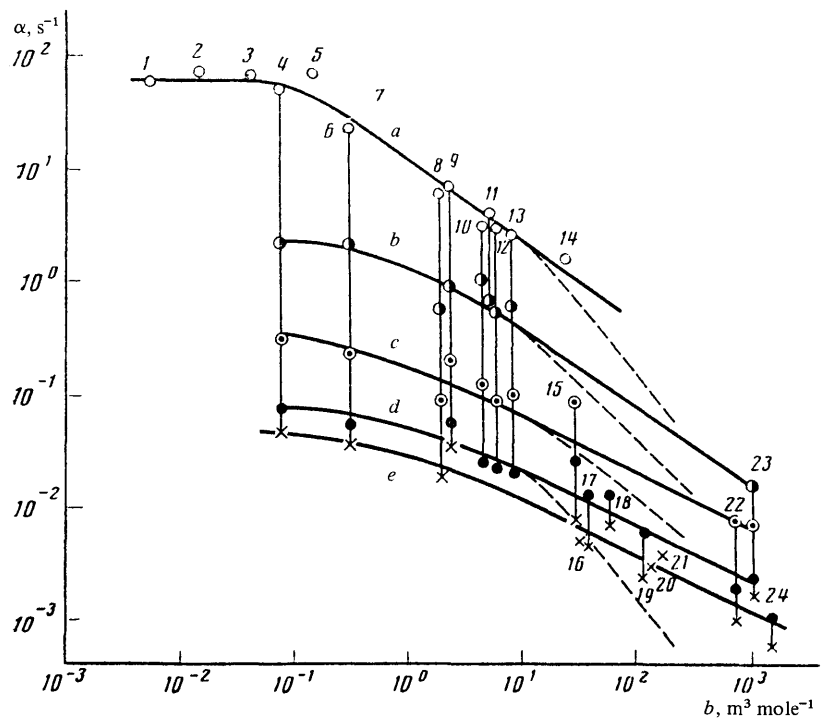


Figure 4. Dependence of the desorption rate constant α on the adsorption equilibrium constant for different surface-active substances. The numbering is the same as in Fig. 2 (from data in Refs. 38, 78, 81, 88, 90, 91, 97–99, 101, 107–110).

characteristics of the transition state. The kinetics of adsorption from multicomponent solutions, and adsorption at a liquid–liquid interface, have been very little studied. The solution of these problems will facilitate the development of the general theory of surface phenomena, will give information on the surface forces, structure, rheology, and intermolecular interactions in adsorption layers, and will provide a basis for the development of new criteria for the synthesis and selection of highly effective SAS and compositions acting under non-equilibrium conditions.

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