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Effect of Convection on Formation of Adsorbed Surfactant Film under Dynamic Change of Solution Surface Area

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Abstract—The dynamics of the formation of a surface phase in aqueous solutions of surfactants in a tray with the Langmuir barrier system during one compression–expansion cycle of the interface boundary is investigated both experimentally and theoretically. Organic salts of fatty acids such as potassium laurate, caprylate, and acetate, which are members of the same homologous series, were used as surfactants. It is experimentally determined that the dependence of the surface pressure increment measured under the maximum compression of the surface on the volume concentration has a maximum, the position of which is different for all the studied surfactant solutions. It is shown that the position of the maximum corresponds to the concentration value at which a saturated monolayer of surfactant molecules is formed at the interface boundary. A theoretical model that considers the effect of the forced convection arisen in the bulk of the solution upon changing the surface area is proposed for the interpretation of the experimental results. The model allows one to render the main kinetic characteristics of the adsorption/desorption processes involving the compounds under study. A good agreement between the theoretical and experimental results is observed, but there is a discrepancy between them when diffusion is considered to be the only way surfactant molecules are transferred into the bulk phase. Based on the data, a new method for determination of the Langmuir–Shishkovsky constant is proposed.

Keywords: dynamic adsorption, interface, forced convection, mass transfer, surfactants.

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INTRODUCTION

As is known, surfactants are capable of substantially changing the properties of interfaces in heterogeneous media through the adsorption/desorption processes. This feature of surfactants is used both by nature, for example, in cell membranes or for the operation of an alveolus in lungs, and by humans in a number of technological processes in the power engineering, chemical and petrochemical industries, medicine, etc. [1, 2]. It is important to note that these processes are carried out, as a rule, under dynamically changing conditions. In the majority of technological processes, two effects are observed. First, a surface is maintained clean enough from impurities for an extremely short time period (to several milliseconds), after that a film of adsorbed substances starts to form. Second, the surface moves, and this gives rise to an inevitable disturbance of the equilibrium of adsorption/desorption processes. Moreover, a surface gradient of the surfactant concentration can be generated immediately after the formation of an adsorption layer, which gives rise to an additional motion of the liquid because of the Marangoni effect [3–8]. Hence, the knowledge on the dynamic adsorption rather than the relationships obtained under the condition of static equilibrium is required for the effective use of surfactants and their mixtures [9].

In contrast to the equilibrium state, the dynamic adsorption is a transitory process and characterized by nonuniform distribution of a surfactant over the surface and in the bulk of a liquid. It is unavoidably accompanied by the convection and diffusion processes delivering surfactant molecules from a bulk phase to an adsorption layer and back [1, 2].

A difference between the adsorption kinetics and dynamics should be noted here. The term "kinetics" usually implies the adsorption process depending on time, which is carried out under artificial static conditions. On the contrary, the "dynamic adsorption" is such a nonstationary process that includes the consideration of both phenomena (diffusion and convection) taking place in a continuous medium adjacent to the surface and changes occurring in the surface itself under the influence of a contiguous medium. Consequently, the solution of each new problem for a dynamic adsorption layer always requires an individual approach. If a significant number of works starting from the classic works of Gibbs [10] and Langmuir [11] are devoted to the adsorption kinetics, then the second direction, for which an interdisciplinary approach and additional knowledge in the area of hydrodynamics and convection theory are required, has started just from the works of Levich [12]. Among more recent publications, the theoretical and experimental study of dynamic properties of the formation of a surface phase in the series of works by Joss is worthy of note, the results of which are compiled in the monograph [2]. The studies of the group of authors, which are compiled in the monograph [1] focused also on the dynamics of the adsorption/desorption processes, can be mentioned in addition.

We more thoroughly examine the works devoted to the effect of forced convection on the adsorption/desorption processes occurring under the dynamic change of the surface area. Thus, the analytical solution of the problem of nonstationary adsorption in the common form has been built in the earlier work [13] for the system, in which only diffusion mechanisms operate but the surface area remains constant. In [14], the solution from [13] is generalized to the case of a dynamic change in the surface. Since the solution found in several problems did not agree with experiment, it was proposed to consider a term describing the convection that arises because of the movement of the barrier in the equation for the surfactant concentration in the bulk of a liquid [15]. It turned out that the surface dilatation rate is conserved constant with the barriers diverging by some (nonlinear) law, while the entire system quickly yields to a stationary regime. An analytical solution that agrees well with the experiment carried out by the same authors was obtained for this regime. In the series of studies performed by Joss with a coauthor [16–20], an analytical solution obtained under an arbitrary law of motion for barriers was shown for the cases when the barriers diverge [16–19] and converge [20]. Furthermore, it was shown that the problem with a convective component that strongly complicates the construction of a solution can be brought to the problem with a complex diffusion law but without convection by using the Levich expansion [12]. The demonstration of the fact that the problems with a contracting surface substantially differ from the problem with an expanding surface is an important achievement of the above works, since the convective adjustment introduced in [15] requires a correction in the first case. In [17], this point is discussed in detail.

It should be noted that the interest of researchers was mainly focused on the expanding surface, since the methods for the experimental determination of the dynamic surface tension, such as the method of a growing bubble, and the method of a hanging drop or the capillary method, were developed particularly with this circumstance [1]. In this context, Langmuir's barrier setup [1, 21, 22] created about a hundred years ago is usually considered as a simpler and inert system designed, primarily, for the study of simple and relatively long dynamic processes in the condition of a flat surface. At present, the method is applied, as a rule, for the verification of results obtained on more modern equipment. Moreover, an example of the expanding surface is more convenient for the theoretical analysis, since it allows one to avoid the appearance of a singularity in the computations. There is only one publication in the series of works [2, 16–20], which is devoted to the surface contraction changing by a special law, according to which the specific surface area (the ratio of the area covered by the barrier to the surface still remaining free) changes at a constant rate [20], appreciably simplifying calculations. The calculations were also supplemented by the experimental data for solutions of caprylic acid and surfactant Triton X-45, which agree well with the computational results. The authors of the present work have been carrying out studies on the topic given above for some time [23–26], but the results presented here are most consequential and comprehensive.

This work offers for the reader's attention contains several new points in the problem formulation. It is devoted to the study of the dynamic adsorption in monocomponent solutions of the homologous series of potassium salts of fatty acids which have not yet been analyzed in such a way. The Langmuir barrier system has been repeatedly employed in recent decades for studying the systems containing soluble surfactants. At first glance, the simplest and most natural linear motion law was chosen as a main regime of the motion of barriers, which gives rise to a nonstationary rate of change of the specific surface area. In addition, the case of converging barriers is considered. In general, the approach proposed by Levich [12] and Joss [2, 16–20] is used in the theoretical analysis, though the adsorption problem formulation itself for the dynamically contracting surface and the analytical solution are novel. The latter made it possible to detect a phenomenon that has remained unnoticed [20] and to propose an earlier unknown method for determination of the Langmuir–Shishkovsky constant.

EXPERIMENTAL

The most developed methods for the study of surface properties of different fluids today are physicochemical methods based on tensiometry, i.e., the study of the surface properties of interface boundaries by measuring the surface tension. The determination of the surface tension value usually is the first step in working with surfactants, since it serves as a basis for the calculation of other interface characteristics. There are two types of surface tension measurement methods, namely, the static and dynamic methods. The first type of method is intended for determining the surface characteristics in the equilibrium state, that is, at a completely shaped surface layer. The dynamic methods are applicable to systems in which the surface phase is forming when a surfactant layer is created on the newly formed surface as a result of the adsorption/desorption processes [21].

The experimental studies described below in this article were performed on the Langmuir barrier system (KSV Ltd., Finland) [22]. It proved itself well suited for measuring the properties of surfaces containing an insoluble surfactant [27–29]. However, this method can also be successfully used for the study of dynamic properties in the formation of surfaces in liquid systems containing a water-soluble surfactant [1, 2]. The barrier system makes it possible to analyze the dynamic surface properties of solutions in a wide range of lifetimes of the surface phase and is characterized by a higher sensitivity at low concentrations.

Solutions of potassium salts of fatty (organic) acids belonging to the same homologous series, namely, potassium acetate (CH_3COOK), caprylate ($C_7H_{15}COOK$), and laurate ($C_{11}H_{23}COOK$), were chosen as objects of studies in the present work. These substances differ from each other by the chain lengths of the hydrocarbon radical in the molecule, which consists of 2, 8, and 12 carbon atoms, respectively. The difference in the structure gives rise to a change in the work required to transfer molecules from the bulk to the surface, and as a result, in the surface properties of solutions upon transition from one homologue to another. It causes the differences in the surface activity and in the characteristic time of the transition of molecules to the interface. The experiments were carried out with solutions of the salts in a one-molar (one mole of a substance per 1 L of water) solution of potassium hydroxide. An alkaline medium prevents the hydrolysis reactions, which lead to the formation of an insoluble precipitate and, thereby, to the impossibility of reproducing the results [30, 31]. Bidistilled water preliminarily filtered through a deionizing filter was used for the preparation of solutions. The multistage water purification was carried out with the purpose of removing random impurities of both organic and inorganic origin, which serve, generally, as surfactants with respect to the water–air interface.

Before beginning each experiment, the barrier system consisting of a shallow rectangular tray made of hydrophobic fluroplastic and two mobile barriers made of hydrophilic polyacetal was thoroughly cleaned. The tray was thermally equilibrated by the circulation of water through the channels located underneath. The temperature was controlled by a thermocouple immersed in a solution and was not allowed to exceed $23 \pm 0.1°C$. After all the preliminary manipulations, the tray was filled with a working solution, which was maintained motionless for 20 min before each measurement to achieve a partial distribution of the surfactant between the surface and bulk phases. During each experiment, the rate of movement of the barriers was maintained constant and varied from one experiment to another in the range from 10 to 100 mm/min. The barriers located on the surface of the tray filled with a solution first approached each other at some fixed rate and then, after reaching the preset position, stopped and immediately began to move at the same rate in the opposite direction. The balance indications and the position of the barriers were transmitted to the computer in real time. The disc of the Wilhelmy scale, which was constantly immersed into a solution, registered the magnitude of capillary forces acting from the interface side. The balance indications were reset at the beginning of each experiment. Thus, the balance recorded a deviation of the surface tension from the initial equilibrium value (surface pressure), which is caused by variations in the surfactant density at the interface due to an increase or decrease in the surface area.

RESULTS AND DISCUSSION

The dependences of the surface tension change on the surface area over one contraction–expansion cycle of the free surface enclosed between the barriers for different volume concentrations of the studied solutions are given in Fig. 1. The curves correspond to different rates of movement of the barriers. As seen from the diagrams, convergence of the barriers gives rise to an increase in the surface pressure; this is caused by an increase in the surface concentration of the surfactant upon reducing the surface area. However, the curves corresponding to the contraction and expansion are not the same, since a fraction of the surfactant molecules has time to be desorbed into the bulk phase during the surface contraction, and the contribution that is made by the particles remaining at the interface to the pressure change becomes significantly less than it was before. It should also be noted that the surface pressure is sensitive to an increase

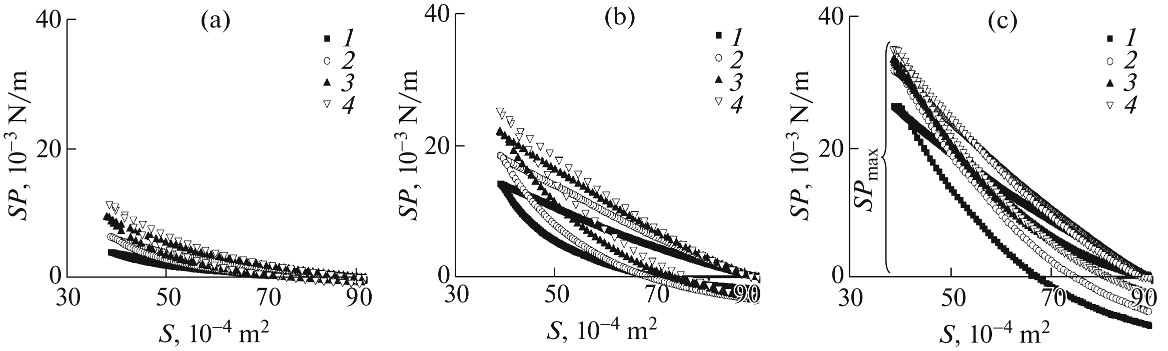

Fig. 1. Dependences of the surface pressure on the surface area for solutions of potassium (a) laurate and (b) caprylate with a concentration of C_0 = 0.0036 mol/L, and for a solution of (c) potassium acetate with a concentration of C = 1.5 mol/L at different rates (v) of the motion of barriers, specifically, at (curve *1*) 10, (curve *2*) 25, (curve *3*) 50, and (curve *4*) 100 mm/min.

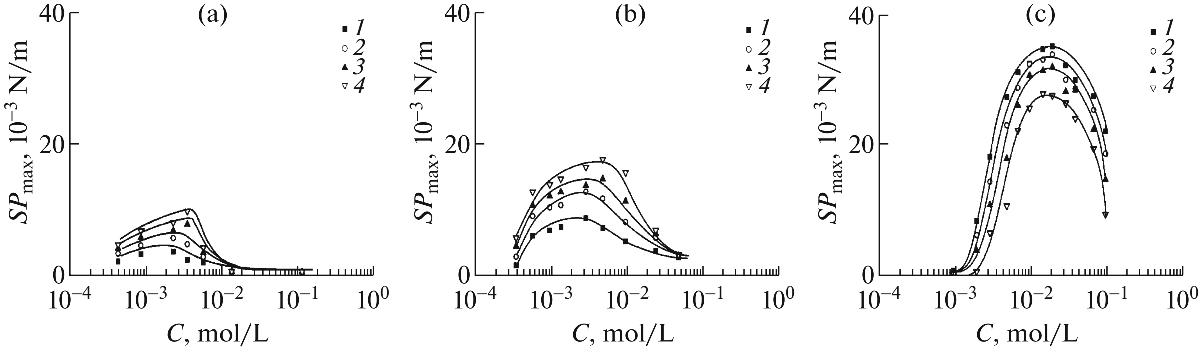

Fig. 2. Dependences of the maximum value of the surface pressure increment on the volume concentration of potassium (a) laurate, (b) caprylate, and (c) acetate at different rates (v) of the motion of barriers, specifically, at (curve *1*) 10, (curve *2*) 25, (curve *3*) 50, and (curve *4*) 100 mm/min.

in the contraction rate. As a result, each subsequent curve lies higher than the previous one, which can be explained as follows: the higher is the rate of movement of the barriers, the fewer the number of surfactant molecules having time to move from the surface into the bulk phase in consequence of the desorption process. This gives rise to a larger value of the maximum surface pressure increment (SP_{max}) registered at the moment of the maximum contraction.

The SP_{max} value depends on the surfactant type and its concentration, as well as on the motion rate of the barriers. Taking into account the last circumstance, the maximum surface pressure increment–volume concentration diagrams for different rates of movement of the barriers are plotted (Fig. 2) based on the data obtained by the authors of the present study. There is a clearly expressed maximum in each of the curves, the position of which is determined by the rates of movement of the barriers and by the nature of the studied surfactant. Upon increasing the length of the surfactant molecule, the position of the maximum is shifted towards the region of lower concentrations. On the contrary, the amplitude at the point of the maximum is decreased upon transition to longer homologues.

The presence of the extrema on the curves can be explained by the competition between two effects differently connected with the volumetric concentration. On one hand, an increase in the latter value gives rise to an increase in the surface concentration of the surfactant and, consequently, to a greater surface pressure increment when the surface contracts. Therefore, an increase in the SP_{max} value is observed at low concentrations. When the surface concentration reaches the limiting value corresponding to different volumetric concentration values for different substances, a further increase in the surface pressure when the convergence of the barriers ceases, and the curves yield to saturation. On the other hand, the rate of mass transfer processes between the bulk and surface phases increases with an increase in the volumetric concentration, which should lead to a decrease in the surface pressure increment in high concentrations.

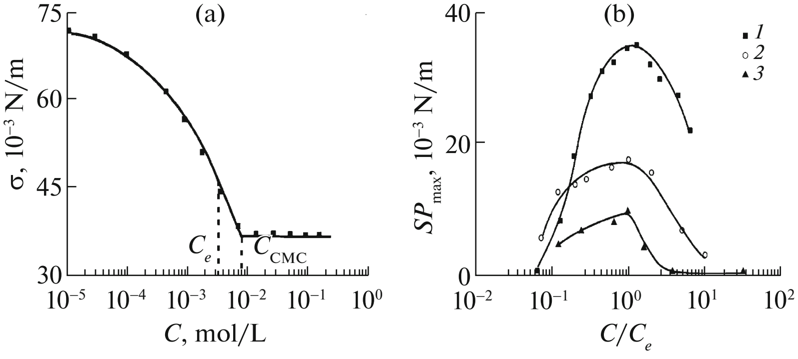

Fig. 3. (a) Surface tension isotherm for a solution of potassium laurate; (b) dependences of the maximum value of the pressure change on the relative volume concentration of potassium (curve *1*) acetate, (curve *2*) caprylate, and (curve *3*) laurate at a barrier motion rate of $v = 100$ mm/min.

Because of the combination of these effects, a nonmonotonic dependence is observed in the experiments. Based on the above, it can be assumed that the maxima of the curves should be observed in the concentration region close to the saturation concentration, at which the surface phase is filled up as much as possible.

The saturation concentrations for all the studied solutions were measured in additional experiments. The so-called "surface tension isotherms," i.e., the dependences of the surface tension of a solution being in equilibrium with the surface phase on the volume concentration of the surfactant at a constant temperature, were plotted with this purpose. The isotherm for a potassium laurate solution is shown in Fig. 3a. According to the Gibbs equation, the volume concentration, at which the initial nonlinear section transforms into a linear dependence (the C_e point in the diagram), corresponds to the formation of a saturated monolayer of surfactant molecules in the surface phase. The second special point on the graph is C_{CMC}, i.e., the critical micelle concentration, above which the surface tension does not change further. A second-order phase transition corresponding to the formation of stable conglomerates, micelles, takes place in the solution near this value. Further addition of the substance into the solution causes the surfactant molecules to adhere to the already existing micelles. The volume concentration of free molecules remains constant in this case, and hence the surface tension does not change.

The dependences of the $SP_{\max}$ value on the amount of a surfactant per unit of volume for all three substances, which are obtained at the same rate of movement of the barriers, are shown in Fig. 3b. The volume concentration is related to the saturation concentration C_e for each of the substances. One can see that the maxima of the curves for all the solutions are positioned near the unity value, which confirms the assumptions made above. The physical meaning of the displayed nonmonotonic function will be clarified more precisely in the theoretical analysis.

MATHEMATICAL MODEL

Let us construct a theoretical model describing the processes of nonstationary diffusion and adsorption/desorption of a surfactant at the interface boundary and its vicinity under the conditions of a dynamically changing surface area of a solution. Let us arrange the coordinate system of the plot as follows: the x axis is directed along the interface and the z axis is perpendicular to it in such a way that the condition $z = 0$ would assign a surface and the axis itself would be aligned inside the liquid phase. Let us limit ourselves to the two-dimensional problem formulation. The volume and surface concentrations of a surfactant can be designated as $C(t, x, z)$ and $\Gamma(t, x)$, respectively.

The following mass transfer equation in the bulk of a solution is the main relation determining the dynamics of a dissolved surfactant:

$$\frac{\partial C}{\partial t} + \mathbf{v} \cdot \nabla C = D \Delta C, \tag{1}$$

where $\mathbf{v}(t, x, z)$ is the liquid flow velocity and D the diffusion coefficient of the surfactant in the liquid phase.

Diffusion Solution

First, let us find a solution that does not take into account the contribution of forced convection. Only diffusion operates in this case, so the problem becomes one-dimensional and Eq. (1) takes the following form:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial z^2}, \tag{2}$$

where $C = C(t, z)$. The diffusion equation of a surfactant in the solution bulk should be supplemented by two equations for the surface concentration $\Gamma(t)$, which will serve as boundary conditions for Eq. (2). One of them, reckoning the geometry of the discussed system, has the following form:

$$\frac{d\Gamma}{dt} + \Gamma\frac{d\ln S(t)}{dt} = D\frac{\partial C}{\partial z}\bigg|_{z=0}, \tag{3}$$

where $S(t)$ denotes the dynamically changing surface area. The equation (3) was obtained for the first time in [14]. Nevertheless, the boundary condition given by Eq. (3) for Eq. (2) is not sufficient for the correct description of the mass transfer processes, since it introduces the new function $\Gamma(t)$, and it is therefore necessary to have one more ratio that would connect the surface concentration of a surfactant with its concentration in the solution bulk. The following procedures are usually implemented when this ratio is selected. First, the characteristic times of the diffusion and adsorption/desorption processes are compared. If the characteristic time of diffusion turns out to be much longer than the time of establishing the mass equilibrium between the surface and near-surface layers owing to the adsorption/desorption processes, then we talk of the diffusion-controlled adsorption kinetics [1, 2, 32]. In this case, the surfactant molecules are delivered to the surface almost immediately upon any changes in the solution bulk and the system is in the state of thermodynamic equilibrium. A particular form of relationship between the Γ and C values depends on the choice of the isotherm. Within the analyzed problem, it is convenient to choose the Langmuir isotherm [11]

$$\Gamma = \Gamma_\infty\frac{C_0}{C_0 + K_2/K_1}, \tag{4}$$

where Γ_∞ is the limiting surface concentration of the monolayer of a particular surfactant, C_0 is the initial value of the molar concentration of a surfactant in the liquid bulk, and K_1 and K_2 are the adsorption and desorption coefficients, respectively. In the literature, the K_2/K_1 ratio is called the Langmuir–Shishkovsky constant. The ratio given by Eq. (4) indicates that the concentrations of a surfactant in the near-surface layer and on the surface are in exact proportion to each other, which does not change in time.

If the ratio between the characteristic times in the system is inverse, i.e., the diffusion processes are much faster than the adsorption/desorption processes, then there is no equilibrium in the system and the dynamic relationship between the concentrations should be introduced [1, 2, 32]. The following Langmuir dynamic equation is most commonly used [11]:

$$\frac{d\Gamma}{dt} = K_1C_0(1 - \Gamma/\Gamma_\infty) - K_2\,\Gamma/\Gamma_\infty. \tag{5}$$

Within the adsorption-controlled kinetics described by Eq. (5), diffusion proceeds so rapidly that the concentration of a surfactant in the near-surface layer is a constant equal to the C_0 value, since diffusion manages all the time to remove redundant molecules from the surface in the case of desorption or to bring back new molecules in the case of adsorption. It is easy to notice that Eq. (4) is just a stationary solution of Eq. (5).

Finally, if either process cannot be preferred, then we talk of the mixed kinetics [1, 2, 32]. This is the most complicated case for theoretical analysis, since the Langmuir equation takes the following nonlinear form:

$$\frac{d\Gamma}{dt} = K_1C(t,0)(1 - \Gamma/\Gamma_\infty) - K_2\,\Gamma/\Gamma_\infty. \tag{6}$$

One can see that the solution of Eq. (6) depends on Eq. (2), since the concentration of a surfactant in the near-surface layer takes a nonstationary value here and Eq. (6) cannot be solved without it.

Let us assume that the processes in the system follow a scenario of the diffusion-limited kinetics. To find the evolution of the system in this case, it is necessary to solve Eq. (2) with the boundary conditions given by Eqs. (3) and (4), and with the following initial conditions:

$$t = 0: \ \Gamma = \Gamma_e, \quad C = C_0. \tag{7}$$

Herein, Γ_e corresponds to the equilibrium value of the surface concentration of a surfactant at the very beginning of the motion of the barriers.

In general terms, the formal solution of Eqs. (2)–(4) and (7) can be written as follows (see [14]):

$$\Gamma(t) = \Gamma_e - \int_0^t \Gamma(t)\frac{d\ln(S(t))}{dt}dt + 2\sqrt{\frac{D}{\pi}}\int_0^{\sqrt{t}} (C_0 - C(t-\lambda,0))d\sqrt{\lambda}. \tag{8}$$

Although the solution of Eq. (8) is poorly suited to further analysis, since the $\Gamma(t)$ function is given implicitly. One can carry on as follows: if the deviations from the equilibrium are insignificant, then the integrand in the second integral can be written as follows:

$$C_0 - C(t-\lambda,0) \approx \frac{dC}{d\Gamma}(\Gamma_0 - \Gamma(t-\lambda)). \tag{9}$$

Generally speaking, the substitution of Eq. (9) is a nontrivial task and requires additional argumentation. Rather detailed studies in this direction were carried out in a series of works by Joss et al. [16–20], which showed that this assumption is correct in most cases. To get an explicit expression relative to $\Gamma(t)$, the first integral in Eq. (8) can be approximated according to the mean-value theorem, as follows:

$$\int_0^t \Gamma(t)\frac{d\ln(S(t))}{dt}dt \approx \langle\Gamma(t)\rangle(\ln S(t) - \ln S(0)), \tag{10}$$

where $\langle\Gamma(t)\rangle$ is the mean adsorption value that can be approximately considered as $\langle\Gamma(t)\rangle \approx \Gamma_e$.

Like in the experiment, let us further analyze the specific case of the dynamically changing surface. Let the initial spot of the surface phase be rectangular and be $S_0 = HL$, where H and L are the width and the length of the surface area, respectively. Considering that the problem is symmetric, we assume that only one barrier is movable in the mathematical model. If we suppose that this barrier starts to move to the right with a constant velocity V in such a way that the length of the rectangle is reduced and its width remains fixed, then the area of the spot contracts by the law $S(t) = HL - HVt$, where the velocity V is measured in mm/min. Let us write down this expression in dimensionless form after dividing it by the S_0 value:

$$S(t) = 1 - vt, \tag{11}$$

where $v = V/L$.

Taking into account Eqs. (9)–(11), an analytical expression can be obtained from Eq. (8) after a series of transformations in the following final form:

$$\Delta\Pi(S) = -\frac{RTC_0\Gamma_\infty^2}{(C_0 + K_2/K_1)^2}\frac{G\ln S}{(G + \sqrt{1-S})}, \tag{12}$$

where $\Delta\Pi$ is the excess surface pressure that appears owing to the adsorption process, and T is the temperature. The expressions for the Langmuir isotherm given by Eq. (4) and for the Gibbs isotherm $d\Pi/dC = \Gamma_e RT/C_0$ were used in the derivation of Eq. (12). In addition, it was assumed that the deviations from equilibrium are so small that $\Delta\Pi = \Pi - \Pi_e \approx (\Gamma - \Gamma_e)\,d\Pi/d\Gamma$. As a result of the transformations, the dimensionless G parameter representing the ratio of the characteristic diffusion time τ_D to the characteristic barrier motion time τ_v was produced in Eq. (12), which can be expressed as follows:

$$G = \frac{\sqrt{\pi}}{2}\sqrt{\frac{\tau_D}{\tau_v}} = \frac{\sqrt{\pi}}{2}\frac{d\Gamma}{dC}\sqrt{\frac{v}{D}}.$$

Assuming that the studied system evolves in accordance with the diffusion kinetics scenario, it is possible to evaluate the G value from the experimental data given above. In the experiments with potassium caprylate, this parameter was $G \approx 0.19\sqrt{V}$, where V is the dimensional velocity of the barriers in mm/min.

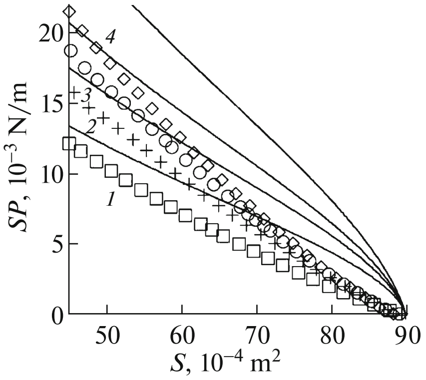

Fig. 4. Dependences of the surface pressure on the surface area for a solution of potassium laurate at different rates (v) of the motion of barriers, specifically, at (curve *1* and □) 10, (curve *2* and +) 25, (curve *3* and ○) 50, and (curve *4* and ◇) 100 mm/min; the experimental data are shown by the markers and the theoretical curves calculated by Eq. (12) at a fixed molar solution concentration of $C_0 = 0.0036$ mol/L without taking into account the convective summand are shown by the lines.

Taking into consideration these comments, the theoretical curves calculated from Eq. (12) were compared with the experimental curves shown in Fig. 1b (only the opposing motion of the barriers, which gives rise to the contraction of the surface, is considered). The results obtained for different velocities of the barriers are given in Fig. 4, where the surface area is expressed in dimensional units for the comparison with the experimental results. As seen from Fig. 4, the theoretical results are poorly correlated with the experimental data. From the very beginning of the system evolution (the diagram should be viewed from right to left), the theory predicts a more rapid increase in the surface pressure caused by the approaching barriers.

Solution with Allowance for Forced Convection

As found above, the theoretical relationships without considering the convective term poorly describe the processes in the studied system. To correct this, we introduce the following magnitude of the surface deformation rate:

$$\Theta(t) = \frac{1}{S}\frac{dS}{dt} = -\frac{v}{1 - vt} = \pm\frac{\partial v_x}{\partial x}, \tag{13}$$

where the + sign corresponds to the expansion of the surface and the – sign to the contraction. As shown in works by Joss et al. [16–20], the convective transfer of a surfactant arises inevitably along the interface boundary and in the viscous skin-layer adjacent to it because of the deformation of the interface. The necessity of introducing the term describing the convective transfer into the equations when studying the dynamics of formation of a surface phase is also determined by the experimental results given in Fig. 4. The characteristic time of the surface change due to the motion of the barriers turns out to be much less than the relaxation time for any of the investigated surfactants, which is of the order of 10^2 and 10^4 s for potassium laurate and caprylate, respectively. Nevertheless, the surface concentration for all the solutions has time to adapt to the surface area change, which implies the presence of a mass transfer mechanism between the bulk and surface phases that is faster than the adsorption and desorption processes. Convective transfer appears to do this. If the convective term is discarded, then the calculated results have a significant discrepancy with the experiment.

We also note that researchers, as a rule, consider a special law of motion for the barriers, which leaves the deformation rate Θ invariant. As seen from Eq. (13), the deformation rate varies in time according to the linear law of motion of the barriers, which is adopted in the present work (Eq. (11), thereby substantially complicating the problem.

Using Eq. (13) and the equation of continuity, one can evaluate the velocity field, which is formed during motion of the converging barriers:

$$v_x = \Theta(t)x, \quad v_z = -\Theta(t)z. \tag{14}$$

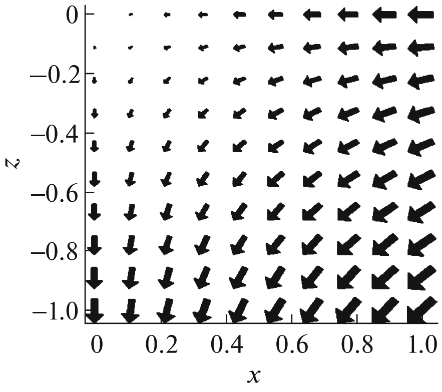

Fig. 5. Qualitative pattern of the liquid flow rate field at the start of barrier motion.

The velocity field calculated according to Eq. (14) for the time $t = 0$ when the barriers start to move is given in Fig. 5. Since the velocity tends to infinity on moving away from the interface, the approximation given by Eq. (14) is valid only in the thin near-surface layer of a liquid.

Taking into consideration Eq. (14) and reckoning the mass transfer processes only along the z axis, the mass transfer equation for a surfactant given by Eq. (1) can be rewritten as follows:

$$\frac{\partial C}{\partial t} + \Theta(t) z \frac{\partial C}{\partial z} = D \frac{\partial^2 C}{\partial z^2}. \tag{15}$$

We supplement Eq. (15) by the following boundary condition depending on the adsorption value $\Gamma(t)$:

$$\frac{d\Gamma}{dt} + \Theta(t)\Gamma = D \left.\frac{\partial C}{\partial z}\right|_{z=0}. \tag{16}$$

Herein, the term on the right side of the equation describes the incoming flow of a surfactant from the solution bulk to the surface owing to the diffusion process. Taking into consideration that the relaxation process on the surface of this system proceeds rather fast, the term responsible for the diffusion of a surfactant along the surface in Eq. (16) can be omitted. The second boundary condition connecting the surface and volume concentration of a surfactant, i.e., the Langmuir isotherm given by Eq. (4), is left the same. The initial condition given by Eq. (7) will be also the same.

Taking into account the explicit form of the surface deformation upon the linear contraction of the surface (Eq. (13)), we write Eqs. (15) and (16) in the following form:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial z^2} + \frac{zv}{1 - vt} \frac{\partial C}{\partial z}, \tag{17}$$

$$\frac{d\Gamma}{dt} = D \left.\frac{\partial C}{\partial z}\right|_{z=0} + \frac{v}{1 - vt}\Gamma. \tag{18}$$

One can see from this that the problem becomes more complicated as compared to Eqs. (2) and (3), and no longer comes to the simple diffusion equation with its well-known formal solution.

To integrate Eqs. (17) and (18) with the boundary and initial conditions given by Eqs. (4) and (7), we apply the transformation proposed by Levich [12]. To accomplish this, we make the following substitution of variables:

$$\tau = \frac{t}{1 - vt}, \quad Z = \frac{z}{1 - vt}, \tag{19}$$

which allows one to confine Eqs. (17) and (18) to the following expressions:

$$\frac{\partial C}{\partial \tau} = D \frac{\partial^2 C}{\partial Z^2}, \tag{20}$$

$$\frac{d}{d\tau}\left(\frac{\Gamma}{1 - vt}\right) = D \left.\frac{\partial C}{\partial Z}\right|_{Z=0}. \tag{21}$$

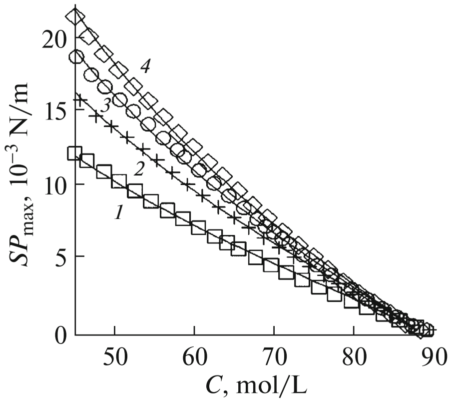

Fig. 6. Dependences of the surface pressure on the surface area for a solution of potassium caprylate at different rates (v) of the motion of barriers, specifically, at (curve *1* and □) 10, (curve *2* and +) 25, (curve *3* and ○) 50, and (curve *4* and ◊) 100 mm/min; the experimental data are shown by the markers and the theoretical curves calculated by Eq. (12) at a fixed molar solution concentration of $C_0 = 0.0036$ mol/L with taking into account the convective summand are shown by the lines.

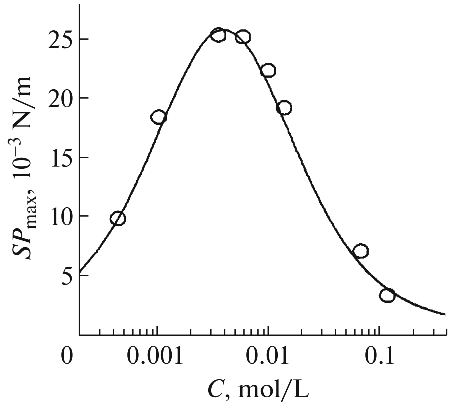

Fig. 7. Dependences of the maximum value of the pressure change on the volume concentration of potassium caprylate at a barrier velocity $v = 100$ mm/min, where the experimental data are marked by the "○" sign and the theoretical curve calculated by Eq. (23) is shown by the solid line.

It is clearly seen that the equation for the volumetric concentration took the form of the classical diffusion equation after the substitution of variables in accordance with Eq. (19).

The nonstationary boundary value problem given by Eqs. (20) and (21) can be solved exactly using the Laplace transforms [33]. As a result, the formally represented solution can be obtained, which implicitly contains the sought adsorption function $\Gamma(\tau)$,

$$\Gamma(\tau) = (1 - vt)\left(\Gamma_e + 2\sqrt{\frac{D}{\pi}}\int\limits_0^{\sqrt{\tau}} (C_0 - C(\tau - \lambda, 0))\,d\sqrt{\lambda} + 2v\int\limits_0^{\tau} \Gamma(\tau)\,d\frac{1}{1 - vt}\right). \tag{22}$$

To resolve Eq. (22) with respect to the $\Gamma(\tau)$ function, one can use the procedures discussed above. Let us rewrite the integrand in the first integral in accordance with Eq. (9), considering that the adsorption/desorption processes quickly enough restore the equilibrium in the surface phase on changing the surface area (the diffusion-limited kinetics is implemented). The second integral can be replaced by the approximate value in accordance with the mean value theorem, as follows:

$$\int\limits_0^{\tau} \Gamma(\tau)\,d\frac{1}{1 - vt} \approx \langle \Gamma(\tau) \rangle \left(\frac{1}{1 - vt} - 1\right). \tag{23}$$

The approximation of the integrals in Eq. (22) makes it possible to express the $\Gamma(\tau)$ function explicitly. Assuming further that the deviations from the equilibrium are small, i.e., $\Pi - \Pi_e \approx (\Gamma - \Gamma_e)\, d\Pi/d\Gamma$, we come to the following final expression for the surface pressure evolution:

$$\Delta\Pi(S) = \sqrt{\frac{\pi v}{4D}} \frac{RTC_0\Gamma_\infty^2}{\left(C_0 + K_2/K_1\right)^2} \frac{(1-S)}{\sqrt{S}\left(G\sqrt{S} + \sqrt{1-S}\right)}, \tag{24}$$

where $S(t)$ is still the dimensionless area of the interface, which varies in the range from 1 to 0. Taking into account Eq. (11), the final formula given by Eq. (24) can be expressed through time; however, it is easier to write it through the interface area for the purpose of comparison with the experimental data.

If the surface contracts quickly enough and $G \gg 1$, then Eq. (24) at the beginning of evolution becomes close to the linear relationship $\Delta\Pi(S) \approx (1-S)/S$. In another extreme case, when the motion of the barriers is so slow that the diffusion processes have time to equalize the concentration ($G \ll 1$), then $\Delta\Pi(S) \approx \sqrt{(1-S)/S}$. In the both cases, the curve has no extrema and the surface pressure changes monotonically. Assuming that the studied system develops in accordance with the diffusion kinetics scenario, the G parameter value for potassium caprylate can be estimated as $G \approx 0.19\sqrt{V}$, where V is the dimensional motion rate of the barriers in mm/min and the dimension of the factor 0.19 is $(\text{min/mm})^{1/2}$. Considering this remark, the theoretical curves calculated by Eq. (24) were compared to the experimental curves (see Fig. 1b). The overall results are given in Fig. 6, where the dependences of the surface pressure change on the surface area for different motion rates of the barriers are shown (the surface area is expressed in dimensional units for the comparison with the experiment).

As seen from Fig. 6, there is an excellent agreement between the experimental and theoretical data for potassium caprylate for all the barrier motion rates used in the experiment (the results can be compared with Fig. 4, in which a diffusion solution is given). The same as in the experiment, the surface pressure value for a fixed concentration (mol/L) of potassium caprylate increases with an increase in the velocity of the barriers (Fig. 6). However, this tendency manifests itself differently for different volume concentrations of the surfactant in a solution. The experiment shows that there is such a C_0 value, for which the surface pressure growth upon the motion of the barriers is maximum (see Fig. 2b). Using Eq. (24), we try to find the physical meaning of the appearance of extrema in the dependency graphs of the surface pressure maximum values on the volumetric concentration of a surfactant, which are shown in Fig. 2b. To accomplish this, we fix the value $S = 0.5$ that corresponds to half the path traveled by each of the barriers (the surface area in dimensional units is about 45 cm^2) and see how the experimental points fit the theoretical curve, for example, in the case of the barrier velocity of $v = 100$ mm/min (Fig. 7).

Differentiating Eq. (24) with respect to the C_0 value, the following value for the concentration maximum C_e is obtained:

$$C_e = \frac{K_2}{K_1} \approx 4.0 \times 10^{-3} \quad \text{mol/L}. \tag{25}$$

Thus, the curve maximum corresponds to the case when the concentration of a surfactant in the bulk phase equals the Langmuir–Shishkovsky constant, i.e., $a = K_2/K_1$. As seen from the Langmuir isotherm expressed by Eq. (4), the physical meaning of the C_e constant is the initial concentration of a surfactant in the mixture volume, at which the monolayer is half-filled with surfactant molecules after establishing equilibrium. Equation (25) allows one to evaluate from the experiment the ratio between the adsorption and desorption coefficients, $K_2 = K_1C_0 \approx 4.0 \times 10^{-3} K_1$. The adsorption and desorption coefficients cannot be determined separately within the diffusion-limited kinetics law, since it is believed a priori that the diffusion time is certainly longer than the adsorption time. Equation (24) was derived with exactly this assumption.

CONCLUSIONS

A good agreement between the experimental and theoretical results confirms the need to consider convection in the transfer of surfactant molecules between the bulk and surface phases. The approach described here allows one to propose a simpler and faster method for determination of the kinetic constants of adsorption/desorption processes. This is particularly important for surfactants with very long relaxation times when the construction of the equilibrium surface tension isotherm may take up to several weeks of operation time.

The results obtained in the present work make it possible to determine the type of sorption kinetics of a surfactant and the ratio between the most important characteristics of this process, namely, the adsorption and desorption coefficients. However, the kinetic scenario can be approximately determined without carrying out a complex mathematical analysis. The following dimensionless parameter can be used for this purpose:

$$R = \frac{\Gamma_\infty^2 \hat{K}_2}{a^2 D}, \tag{26}$$

which is a ratio of the characteristic diffusion time to the characteristic adsorption/desorption time. If the R parameter is large, then the kinetics of the system is diffusion; if it is small, then adsorption. As for the values included in Eq. (26), it can be stated that the reduced desorption coefficient $\hat{K}_2 = K_2/\Gamma_\infty$ at times of up to 20 ms depends very little on the compound type and is 100 s^{-1} [2]. The monolayer saturation value also very weakly depends on the nature of the compound and is approximately 5×10^{-10} mol/cm^2. The Langmuir–Shishkovsky constant is determined from the experiment by Eq. (25). The diffusion coefficient of potassium caprylate can be taken as 10^{-6} cm^2/s. The following estimation can be obtained as a result: $R \approx 2$. This means that potassium caprylate can be related, with some reservations, to the substances following diffusion kinetics. Such an analysis carried out for potassium laurate, gives rise to a larger value of $R \approx 20$. As a matter of fact, the maximum of the curve for potassium laurate is shifted towards lower concentrations (Fig. 3). Overall, the results are quite consistent with the Joss's observation [2] asserting that a surfactant comprised of heavier molecules of the same homologous series demonstrates more pronounced diffusion kinetics.

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