

Adsorption kinetics under the influence of barriers at the subsurface layer

Theodor D. Gurkov

Received: 12 February 2011 / Revised: 22 June 2011 / Accepted: 5 September 2011 / Published online: 27 September 2011
© Springer-Verlag 2011

Abstract At the initial stage of surfactant adsorption (when the layer is relatively diluted), the kinetics may be dominated by factors related to the transfer of molecules through the subsurface region and onto the interface. We consider two independent physical effects: (1) diffusion through a subsurface layer with nanometer thickness, where structuring or molecular interactions can impose substantial changes on the transfer rate, as compared with the bulk diffusion and (2) hindrance to the act of adsorption itself, when the molecules hit the interface from a place directly adjacent to it. These two effects are taken into account by formulating a model which includes the balance of fluxes in the subsurface layer. This model allows one to find analytical solution for the adsorption as a function of time. Application of the theory is illustrated by analyzing experimental data for two proteins which adsorb on air/water interface. Attention is paid to the particular case when the resistance to adsorption is relatively small but is still significant as compared with the bulk diffusion. Then, the theoretical fit of the adsorption vs. time can be implemented in a specific linear scale. The overall resistance of the interfacial zone comprises additive contributions from the hindrance to the act of adsorption and from the (retarded) diffusion through the subsurface layer. They are incorporated into one physical parameter (or characteristic time), which influences the kinetics.

Keywords Mass transport resistance · Kinetic barriers · Adsorption of proteins · Barrier-diffusion control · Subsurface layer

T. D. Gurkov (✉)
Department of Chemical Engineering, Faculty of Chemistry,
University of Sofia,
James Bourchier Avenue 1,
Sofia 1164, Bulgaria
e-mail: tg@lcepe.uni-sofia.bg

Introduction

The adsorption of surface-active species plays an important role in stabilizing various fluid dispersions. Sufficiently fast adsorption kinetics has to ensure that newly created particles (e.g., emulsion drops and foam bubbles) will survive during dispersion formulation. For this reason, the initial stages of the adsorption process bear practical significance. In many applications, proteins are used as stabilizing agents. Their adsorption can be influenced by the complexity of the molecules, which are large and prone to undergo configurational changes at the interface, get involved in various interactions, etc. Such features lead to complications of the adsorption process that need to be adequately described.

A key question in studying the adsorption kinetics has been whether it is diffusion or barrier controlled. In some cases with proteins, the initial stage after starting from a clean interface is believed to be diffusion controlled [1, 2]. Then, the slow rate-determining process is the transfer of molecules by diffusion from the bulk to the subsurface (the latter is defined as a place in the bulk which is immediately adjacent to the physical interface). The adsorption from the subsurface onto the interface supposedly happens swiftly, if the barriers are absent or small. The theoretical description of this process can be accomplished by accepting that the subsurface concentration (c_{sub}) remains practically zero, because of the instantaneous adsorption of all molecules which arrive by diffusion [3, 4]. This assumption is plausible for diluted layers at short times and leads to the following result:

$$\Gamma(t) = 2c_0 \sqrt{\frac{D}{\pi}} \sqrt{t} \quad (1)$$

where Γ is the adsorbed amount, t denotes time, c_0 is the bulk concentration, and D is the diffusion coefficient of the

surfactant molecules in the bulk solution. For the diffusion-controlled adsorption, an alternative approach is to accept that the interface and the subsurface rest in local equilibrium (and $c_{\text{sub}} > 0$), which is a consequence from the assumed fast exchange of surfactant between them. Thus, an adsorption isotherm is written [5, 6], to connect Γ with the subsurface concentration, c_{sub} . The mathematical problem to find $\Gamma(t)$ can be solved analytically either when the isotherm is linear, or when it can be linearized under the restriction of small perturbations. In the first case, application of the Henry isotherm, $\Gamma \propto c_{\text{sub}}$, gives the Sutherland's equation [5], whose series expansion at short times coincides with Eq. 1. The particular dependence $\Gamma \propto \sqrt{t}$, Eq. 1, has been considered as a characteristic feature of the diffusion-controlled adsorption [7] (see also the discussion below). Its manifestation as such, with the correct D in Eq. 1, has been observed experimentally with certain surfactants (Ref. [8] provides an example).

Barriers to adsorption decrease the rate of transfer of molecules from the subsurface region onto the interface. These barriers may originate from different physical sources. One effect, operative at higher surface coverage, is due to the steric hindrance from already adsorbed molecules which occupy part of the area, thus hampering the accommodation of new incoming molecules. This can be taken into account in different ways [4, 9], depending on whether the layer is tangentially mobile or immobile. At low surface coverage (negligible steric hindrance), barriers may be engendered by the necessity for the molecules to acquire certain specific configuration in order to settle on the interface properly, or by long-range repulsive forces such as electrostatic ones, or by structuring of the subsurface zone.

In the limiting case of pure barrier control, the diffusion is much faster than the rate-determining step of subsurface to interface transfer. So, the subsurface concentration, c_{sub} , will approximately be equal to the bulk concentration, c_0 , then, the predicted $\Gamma(t)$ dependence is exponential or linear [2].

A mathematically rigorous treatment of the adsorption process under mixed barrier-diffusion control, when the rates of diffusion and the subsurface-to-interface transfer are comparable, is presented in [6] (for arbitrary coverage). The exchange between the subsurface and the interface is represented as a sum of adsorption and desorption fluxes, with linearized rate expressions for small initial deviations from equilibrium. The prediction of the theory [6] is that at short times the process should always be barrier controlled, with $\Gamma \propto t$; the long-time asymptotic is always dominated by diffusion.

In experiments with proteins, one often encounters a situation when $\Gamma \propto \sqrt{t}$ at relatively short times, but the diffusion coefficient calculated from the slope in Eq. 1 does not correspond to the independently determined bulk value D . Then, the diffusivity derived from the $\Gamma \propto \sqrt{t}$ dependence is

called “apparent,” D_{app} . As far as $D_{\text{app}} < D$, the effect is usually attributed to the influence of adsorption barriers (envisaging those relevant to low coverage at the initial stage of adsorption).

In order to cope with the case of $\Gamma \propto \sqrt{t}$ with $D_{\text{app}} < D$, Liggieri et al. and Ravera et al. [10, 11] proposed a model in which the adsorption barriers (of all kinds) were included when considering the flux from the subsurface to the interface (at $x=0$ in their notation). The following boundary condition was adopted [10]:

$$\frac{d\Gamma}{dt} = D^* \left(\frac{\partial c}{\partial x} \right)_{x=0}$$

with D^* being a renormalized diffusion coefficient. Its purpose is to take into account the existence of an energy barrier, E_a , which manifests itself in overall retardation of the transfer of molecules from the subsurface to the interface [10, 11]:

$$D^* = D \exp(-E_a/(k_B T)) \quad D_{\text{app}} = D^{*2}/D \quad (2)$$

Here, k_B represents the Boltzmann constant, and T is the temperature. In Refs. [10, 11], the formulation of the mathematical problem was completed by assuming a certain relationship between Γ and c_{sub} .

The approach of using Eq. 1 with D_{app} instead of D , and determining the activation barrier E_a from D_{app}/D according to Eq. 2, has been chosen by some authors to interpret experimental adsorption kinetics data [12–14]. Values of E_a of the order of several times $k_B T$ were reported. An unexplained feature of the results was that D_{app} (and hence, E_a) often depended on the surfactant concentration, c_0 [14, 15]. In the frames of a more detailed study, the interactions between the arriving molecules and the air/water or oil/water interfaces were modeled to calculate the energy barriers, as they would contribute to D_{app} [16].

On the other hand, Moorkanikkara and Blankshtein [17, 18] have recently developed a theory for the adsorption kinetics in diluted surfactant layers under mixed barrier-diffusion control. The subsurface-to-interface transfer was described by the simple kinetic equation

$$\frac{d\Gamma}{dt} = k c_{\text{sub}} \quad (3)$$

where the adsorption rate constant, k , contains information for the activation barriers. A naturally occurring characteristic time was defined [17] as $\tau_s = D/k^2$. A complicated $\Gamma(t)$ function was approximated as $\sim \sqrt{t}$ at times much longer than τ_s , and k could be obtained from the intercept [17]. A rate equation similar to Eq. 3 was used by Middelberg et al. [2] for interpretation of protein adsorp-

tion (under barrier control) and estimation of the activation energy from the value of k .

In fact, there are two approaches to incorporate the barriers which retard the adsorption (at low surface coverage): (1) by means of an apparent diffusivity near the interface and (2) through the kinetic constant k , Eq. 3. In the literature, these approaches have been used separately; their specific domains of relevance were not discussed. This may leave the impression that only one of them is preferable or correct. Actually, as will be shown below, both of them may be needed for a realistic description of the surfactant adsorption kinetics. Indeed, the diffusivity and the rate constant are associated with different underlying physical phenomena, each of them depending on its own specific factors, and this has to be recognized. Therefore, it will be instructive to sort out how the two aforementioned approaches can be combined to appropriately characterize particular systems.

Our purpose in this work is to formulate a model description of surfactant adsorption, taking into account two different physical mechanisms for existence of barriers that affect the rate at which molecules enter the interface:

1. The rate of diffusion transfer (Brownian migration) across a thin subsurface layer contiguous to the interface may be different from that in the bulk. This effect may be engendered, e.g., by interactions between the arriving surfactant molecules and the interface (or the outer phase). Specifically, interactions of relatively longer range are expected to be of influence here, like van der Waals or electrostatic ones. So, the diffusion will occur in an external force field. Such a case was considered by MacLeod and Radke [19], who solved numerically the electrodiffusion problem. The energy of van der Waals interactions can also affect the diffusion; for a sphere (with radius R) approaching an interface this energy is $W = -AR/(6d)$ [20], where d is the gap width. As an example, the Hamaker constant A for a protein molecule near air/water boundary can be estimated as $A = -5.7k_B T$ (from data in Ref. [21]); it corresponds to repulsion. Hence, at $d \sim R$, which is of the order of nanometers for proteins, the interaction energy is about $k_B T$.

Another important factor to affect the diffusion through the subsurface layer is the possible structuring of the solvent molecules near the interface, such as that of water near a hydrophobic phase [22]. This case was addressed by Yousef and Mc Coy [23] and Rakita and Fainerman [24], who considered the diffusion in two regions: through the volume phase, and in a thin subsurface layer where the diffusion coefficient was much smaller than the bulk value. That retarded diffusion was attributed to surface layers of oriented water

molecules [23, 24]. Analytical solutions of the mathematical problem were obtained in Refs. [23, 24] (using different boundary conditions).

2. The act of adsorption itself, when the molecules get on the interface from a position directly adjacent to it, may have its rate depending on the collision efficiency. The latter can be influenced by such factors as proper orientation of the molecule, suitable conformation in the case of proteins and polymers, steric forces, etc. Those factors lead to inability of some molecules to adsorb upon hitting the interface, so only a fraction of collisions will be efficient. This mechanism is usually described with a rate equation written by analogy with the chemical kinetics (such is Eq. 3); the underlying phenomena are indeed similar.

The above two mechanisms are physically different and need to be considered as separate components in the complete picture of the adsorption. Of course, they may be operative simultaneously. Both of them influence the overall (macroscopically observed) kinetics of molecules entering the interface. We include diffusion through a subsurface layer of thickness L (~ 10 nm), with effective diffusion coefficient D_{eff} different from that in the bulk. Instead of seeking a detailed solution for the concentration profile within this very thin layer, we offer a model description using the mass balances. The kinetics of adsorption onto the interface from the adjoining liquid is characterized by a rate constant; no assumption is made about barrier or diffusion control. The treatment is confined to relatively low surface coverages (to the extent that the lateral hindrance to adsorption remains weak), and when the desorption flux is insignificant. Under these conditions, analytical solution is derived, which is generally applicable for different types of surfaces and adsorbates. For the sake of concreteness, we use the theory to interpret experimental data for the adsorption kinetics of proteins.

Description of the adsorption kinetics

We consider adsorption of surfactant from a bulk solution to a planar phase boundary. The model is sketched in Fig. 1. Let x be the coordinate perpendicular to the interface. A zone of immediate vicinity to the interface is designated as the “subsurface layer,” with thickness L . In the latter layer, the diffusion is influenced by structuring or interactions. The place $x=0$ is the boundary between the subsurface layer and the bulk (Fig. 1). The diffusion in the bulk is unrestricted, and is characterized by the diffusion coefficient D . The interface to which the molecules ultimately adsorb is located at $x=-L$.

The bulk concentration, $c(t, x)$, obeys the one-dimensional diffusion equation in its usual form:

$$\frac{\partial c}{\partial t} = D \frac{\partial^2 c}{\partial x^2} \quad x > 0 \quad (4)$$

An appropriate initial condition refers to a uniform surfactant solution at $t=0$:

$$c(t = 0, x \geq 0) = c_0 \quad (5)$$

Here, c_0 stands for the concentration in the bulk, which is also the limiting value of $c(t, x)$ far away from the interface at later times:

$$c(t > 0, x \rightarrow \infty) = c_0 \quad (6)$$

Equation 6 is a boundary condition to Eq. 4. At $x=0$, we will use the notation $c(t, x = 0) \equiv c_s(t)$.

The adsorption, Γ (amount of surfactant per unit area) increases with time, due to mass transfer from the place in the volume phase which is in immediate vicinity to the interface; this is $x=-L$ in Fig. 1. We will use the notation $c(t, x = -L) \equiv c_i(t)$. In general, the rate $d\Gamma/dt$ is often set to be equal to the difference between the rates of adsorption and desorption [6, 19]:

$$\frac{d\Gamma}{dt} = kc_i \left(1 - \frac{\Gamma}{\Gamma_\infty}\right) - k_d \Phi(\Gamma) \quad (7)$$

Here, k and k_d are the kinetic constants of adsorption and desorption, respectively; Γ_∞ is the maximum attainable value

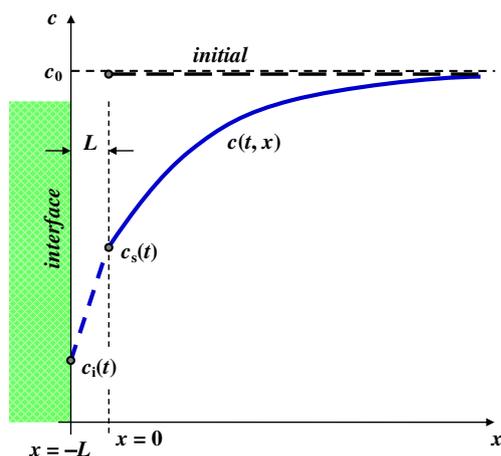


Fig. 1 Sketch of the concentration distribution of surfactant near the interface, in the frames of the adopted model. The subsurface layer of thickness L is not drawn to scale (actually, L is very small in comparison with the characteristic diffusion length)

of Γ , and the function $\Phi(\Gamma)$ is related to the equilibrium isotherm—in equilibrium $d\Gamma/dt=0$ and

$$\frac{k}{k_d} c_i = \frac{\Phi(\Gamma)}{1 - \Gamma/\Gamma_\infty} \quad (7a)$$

For instance, the Langmuir isotherm corresponds to $\Phi(\Gamma) = \Gamma/\Gamma_\infty$; the adsorption takes place on localized sites. Eq. 7 (with $\Phi \propto \Gamma$) was combined with the bulk diffusion equation in a problem formulated by Baret [25], who pointed out that numerical solution was only possible; the parameter k takes into account the hindrance to the act of adsorption due to barriers [25]. Miller and Kretzschmar [26] solved numerically this diffusion-kinetic problem, with Eq. 7 as boundary condition, keeping the desorption term $\propto k_d\Gamma$; the ranges of parameter values relevant to mixed diffusion-kinetic control of the adsorption process were analyzed [26].

In the present work, we will consider the rate of adsorption to be much greater than the rate of desorption; correspondingly, the term with k_d in Eq. 7 will be discarded. This case corresponds to initial (faster) stages of adsorption, before the equilibrium is approached. Close to equilibrium, the adsorption and desorption rates become approximately equal, but they both can be very low (as the driving force vanishes). Especially with proteins, the desorption rate is well known to be extremely low [27], whenever the adsorption is in monolayer form. This is most probably due to free energy contribution from reconfiguration of the molecules at the surface.

The multiplier $(1 - \Gamma/\Gamma_\infty)$ in the adsorption term, Eq. 7, pertains exclusively to the case of localized adsorption. This factor takes into account the hindrance, experienced by the incoming molecules at the interface, which is due to already adsorbed molecules. It is often said that $(1 - \Gamma/\Gamma_\infty)$ is the probability to have a free space to accommodate an incoming molecule. When the layer is tangentially mobile (non-localized adsorption), then the effect of lateral hindrance is quite small, which has been demonstrated quantitatively by MacRitchie and Alexander [9]. From the experimental data in Ref. [9], it follows that the factor multiplying c_i in Eq. 7 is much closer to unity than $(1 - \Gamma/\Gamma_\infty)$, up to moderate Γ . This factor of “saturation” has exponential form, $\exp(-\Gamma\Delta A)$, with $\Delta A \ll 1/\Gamma_\infty$ for many proteins [9]. Thus, in order that the hindrance effect should be significant in decelerating the adsorption in mobile layers, Γ has to be higher as compared with the localized case. Baret [28] considered statistical models where the multiplier $(1 - \Gamma/\Gamma_\infty)$ in Eq. 7 is absent (i.e., it is replaced by 1), for non-localized adsorption. Ref. [28] contains a discussion of several surface equations of state, which take into account the lateral molecular interactions and different degrees of mobility, in the context of the adsorption kinetics.

Here, we will assume that $(1 - \Gamma/\Gamma_\infty)$ in Eq. 7 can be substituted with unity, which is permissible when the layer

is tangentially mobile and Γ is not too high. Such is often the case of adsorption on *liquid* interfaces, if the surface coverage is incomplete (in other words, Γ is lower than Γ_∞ , but not necessarily much lower; it is sufficient that the molecules should have translational degree of freedom). Therefore, Eq. 7 acquires the form:

$$\frac{d\Gamma}{dt} = k c_i(t) \quad (8)$$

where $c_i(t)$ is an unknown function which has to be determined. For the purpose of developing a model, the advantage of Eq. 8 is that it is linear. The range of validity of the aforementioned assumptions may be checked when the theory is compared with experimental data (see below).

The kinetic constant k (Eq. 8) includes the frequency, ν , of collisions of the molecules at $x=-L$ with the interface, and the probability for success of these collisions. The latter probability depends on the activation energy barrier, E_a , through the factor $\exp(-E_a/(k_B T))$ and also on the orientation and steric factor, p , which takes into account other contingent requirements for success of a collision, besides the energy [29]. In the frames of the theory of active collisions in the chemical kinetics [29], the mechanism of adsorption with barrier at $x=-L$ may be represented as a first-order chemical reaction, Eq. 8; $k = \nu p \exp[-E_a/(k_B T)]$. The collision frequency, ν , can be deduced from the kinetic theory of thermal motion. The energy barrier, E_a , is relevant to cases when the successful act of adsorption (subsurface-to-interface jump) is possible only for those molecules that possess sufficient energy, above a certain threshold [29]. With proteins, other factors can also be relevant to the outcome of an attempt for adsorption. For example, finding a proper conformation at the interface (upon hitting it) may be a prerequisite for a molecule to attach. Factors of this type are incorporated into the parameter p ; physically, they are not bound to the energy of the molecule and E_a . Along this line of reasoning, it has to be kept in mind that often the interpretation of experimental data furnishes a single “effective” kinetic constant, that is, k . If one wishes to quantify the separate contributions in k , like ν , p , E_a , additional effort has to be spent. For instance, the analysis of the temperature dependence of k would provide an estimate for E_a . Another choice for construing k could be to arbitrarily set $p=1$ and assign all effects (of eventually different physical origin) to the Boltzmann term, $\exp[-E_a/(k_B T)]$. Then, the activation barrier, E_a , will necessarily have the meaning of an effective quantity. Such an approach was adopted in Ref. [2]. We will use the constant k without going into details about its constituents; further discussion on this matter can be found in Ref. [2].

The boundary condition to Eq. 4 at $x=0$ can be specified with the fluxes from the bulk and through the subsurface layer:

$$D \left(\frac{\partial c}{\partial x} \right)_{x=0^+} = D_{\text{eff}} \frac{c_s - c_i}{L} \quad (9)$$

The right-hand side of Eq. 9 represents the flux from $x=0$ toward $x=-L$ (Fig. 1); we have adopted an approximation for it. Physically, the transfer across the subsurface layer is via diffusion (Brownian migration). Hence, an “engineering approach” may be used to express the flux in terms of the overall concentration gradient in the thin layer (Eq. 9). The constant of proportionality, D_{eff} , is necessarily an effective quantity. We will not attempt to analyze the detailed spatial distribution of the concentration within the subsurface layer. In the proposed model, this is not needed. All effects influencing the molecular transfer there (van der Waals or electrostatic interactions, structuring, etc.) will be incorporated into the macroscopic parameter D_{eff} . Formally, it may be written that $D_{\text{eff}} \equiv D \exp(-\phi/(k_B T))$, with ϕ playing the role of a “barrier” to diffusion.

Now, it remains to define the mass balance in the subsurface layer:

$$\frac{d}{dt} \int_{x=-L}^0 c(t, x) dx = D \left(\frac{\partial c}{\partial x} \right)_{x=0^+} - \frac{d\Gamma}{dt} \quad (10)$$

The integral in the left-hand side of Eq. 10 may be approximated according to the trapezium rule:

$$\frac{L}{2} \frac{d}{dt} [c_i(t) + c_s(t)] = D \left(\frac{\partial c}{\partial x} \right)_{x=0^+} - \frac{d\Gamma}{dt} \quad (11)$$

A similar approach of considering the material balance in layers of finite thickness was implemented by Diamant et al. [30, 31]. In Ref. [30], the liquid in the vicinity of the interface was divided into several discrete layers. At the boundaries between them, the corresponding fluxes were specified, which allowed writing the equations of mass conservation.

The system of Eq. 4–6, 8, 9, and 11 represents a complete set that can be solved analytically, with the goal to obtain the functions $\Gamma(t)$, $c_s(t)$, $c_i(t)$. The mathematical problem can be simplified without significant inaccuracy, using a particular feature of the solution: the ratio between the time-dependent concentrations $c_s(t)$, $c_i(t)$ remains practically constant

$$\frac{c_s(t)}{c_i(t)} \approx \text{Const.} \quad (12)$$

This is due to the following reasons: Since the interface is enriched with surfactant during the adsorption, it is

natural to expect that shortly after the start of the process there will be $\Gamma > Lc_0 > Lc_s > Lc_i$. (The thickness of the subsurface layer is supposedly very small, and molecules come to the interface from distances much longer than L .) Consequently, the left-hand side of Eq. 11 will be smaller in comparison with the two terms on the right. We may introduce a zero-order approximation by accepting Eq. 11 in the form

$$\frac{d\Gamma}{dt} = D \left(\frac{\partial c}{\partial x} \right)_{x=0^+} \quad (\text{zero order}) \quad (11a)$$

Now, Eqs. 8 and 9 immediately yield a relation between $c_s(t)$ and $c_i(t)$, at arbitrary time t :

$$\frac{c_s(t)}{c_i(t)} = 1 + \frac{kL}{D_{\text{eff}}} \quad (\text{zero order}) \quad (12a)$$

In reality, since the full Eq. 11 differs from Eq. 11a, the constancy of the ratio c_s/c_i will not be maintained exactly, as in Eq. 12a, but will hold only approximately, Eq. 12. One can nevertheless identify the constant in Eq. 12:

$$\frac{c_s(t)}{c_i(t)} \approx 1 + \frac{kL}{D_{\text{eff}}} \quad (12b)$$

With the help of the latter relation, we can define a first-order approximation of Eq. 11. The function $c_i(t)$ in the left-hand side of Eq. 11 is expressed through $c_s(t)$ by substituting with the zero-order approximation, Eq. 12b. In this way, c_i is excluded and Eq. 11 is simplified to read

$$\beta L \frac{dc_s}{dt} = D \left(\frac{\partial c}{\partial x} \right)_{x=0^+} - \frac{d\Gamma}{dt} \quad (13)$$

where the dimensionless parameter β is

$$\beta \equiv \frac{1}{2} \left(\frac{2 + kL/D_{\text{eff}}}{1 + kL/D_{\text{eff}}} \right) \quad (14)$$

The possible values of β lie between 0.5 and 1. We can say in advance that the numerical results presented below confirm the applicability of Eq. 13. It is verified a posteriori that the obtained ratio of $c_s(t)$ to $c_i(t)$ from the final solutions does not differ appreciably from the zero-order approximation, Eq. 12a. As the adsorption progresses, the full solution departs significantly from the zero-order values of c_s and c_i (which are given by $c_s=c_0$ and Eq. 12a); still, the ratio $c_s(t)/c_i(t)$ continues to satisfy Eq. 12b.

To find the analytical solution of the set of Eq. 4–6, 8, 9, and 13, we use the method of Laplace transformations. From Eqs. 4–6:

$$\tilde{c}(s, x) = \frac{c_0}{s} + \left[\tilde{c}_s(s) - \frac{c_0}{s} \right] \exp \left(-x \sqrt{\frac{s}{D}} \right) \quad (15)$$

where the tilde denotes the respective transform, e.g., $\tilde{c}(s, x) \equiv \mathbf{L}[c(t, x)]$, $\tilde{c}_s(s) \equiv \mathbf{L}[c(t, x=0)] = \mathbf{L}[c_s(t)]$, and s

is the Laplace variable. The kinetic Eq. 8 and the boundary condition, Eq. 9, can be transformed to yield

$$\tilde{c}_i = \tilde{c}_s + \left(\tilde{c}_s - \frac{c_0}{s} \right) \frac{L\sqrt{D}}{D_{\text{eff}}} \sqrt{s} \quad (16)$$

Here, Eq. 15 has been used for the required derivative $[\partial \tilde{c}(s, x)/\partial x]_{x=0^+}$. The material balance, Eq. 13, is also transformed; from the result, we eliminate $\tilde{\Gamma}$ and \tilde{c}_i and obtain an explicit expression for \tilde{c}_s :

$$\tilde{c}_s(s) = \frac{c_0}{s} - \frac{k_1 c_0}{s(k_1 + \lambda\sqrt{s} + s)} \quad (17)$$

In Eq. 17, two auxiliary constants are introduced, $k_1 [s^{-1}]$, and $\lambda [s^{-1/2}]$:

$$k_1 \equiv \frac{k}{\beta L}; \quad \lambda \equiv \frac{\sqrt{D}}{\beta L} \left(1 + \frac{kL}{D_{\text{eff}}} \right) \quad (18)$$

In order to invert the Laplace transform in Eq. 17, we need to factorize the denominator and cast the ratio into the form of a sum of two terms. Let us set

$$k_1 + \lambda\sqrt{s} + s = (\sqrt{s} + \alpha_1) (\sqrt{s} + \alpha_2) \quad (19)$$

$$\text{where } \alpha_1 = \frac{1}{2} \left(\lambda + \sqrt{\lambda^2 - 4k_1} \right), \quad \alpha_2 = \frac{1}{2} \left(\lambda - \sqrt{\lambda^2 - 4k_1} \right) \quad (20)$$

$$k_1 = \alpha_1 \alpha_2, \quad \lambda = \alpha_1 + \alpha_2 \quad (21)$$

The Laplace inversion of Eq. 17 is now straightforward, with the help of the formulae listed in the Appendix. The final result for $c_s(t)$ reads:

$$c_s(t) = -\frac{k_1 c_0}{\alpha_1 - \alpha_2} \left[\frac{1}{\alpha_1} F(\alpha_1^2 t) - \frac{1}{\alpha_2} F(\alpha_2^2 t) \right] \quad (22)$$

For the sake of brevity, we use the auxiliary function $F(p) \equiv e^p \text{erfc}(\sqrt{p})$, Eq. 34, as suggested in the Appendix. At $t \rightarrow 0$, Eq. 22 satisfies the initial condition $c_s(0) = c_0$; at $t \rightarrow \infty$ $c_s \rightarrow 0$.

In this work, we will confine ourselves to real values of α_1 and α_2 (that is, to $\lambda^2 \geq 4k_1$, Eq. 20), which corresponds to the physical situation practically always, as will become evident from the discussion below. If for some reason complex α_1 and α_2 are needed, Eq. 22 retains its validity; however, then the practical computation of F encounters difficulties. To overcome those, it is advisable to represent F in terms of the so-called “plasma function”, as described in Ref. [6].

Equations 16 and 17, after inversion using the Appendix, lead to an expression for c_i :

$$c_i(t) = c_s(t) - c_0 \frac{k\sqrt{D}}{\beta D_{\text{eff}}} \frac{1}{\alpha_1 - \alpha_2} [F(\alpha_2^2 t) - F(\alpha_1^2 t)] \quad (23)$$

The solution for the time dependence of the adsorption, $\Gamma(t)$, follows from the transformed Eq. 13, in which $\tilde{c}_s(s)$ is substituted from Eq. 17, and the result is inverted utilizing the relations in the Appendix. Finally,

$$\Gamma(t) = \Gamma_0 - c_0 \frac{\lambda\sqrt{D}}{k_1} + \frac{2c_0}{\sqrt{\pi}} \sqrt{Dt} - \beta L [c_s(t) - c_0] + \frac{k_1 c_0 \sqrt{D}}{\alpha_1 - \alpha_2} \left[\frac{1}{\alpha_2^2} F(\alpha_2^2 t) - \frac{1}{\alpha_1^2} F(\alpha_1^2 t) \right] \quad (24)$$

Here, $\Gamma_0 = \Gamma(t = 0)$. Examples of application of Eq. 24 will be discussed below, focusing on the case of protein adsorption at air/water interface, where $\Gamma(t)$ is liable to experimental measurement.

Let us estimate the typical order of magnitude of the parameters λ and α_1 . From the definition of λ , Eq. 18, we see that $\lambda > \sqrt{D}/L$. For the characteristic thickness of the subsurface layer, L , we choose the value 10 nm. This roughly corresponds to the distance at which an arriving molecule (of protein) is anticipated to start experiencing the influence of the interface (and $D_{\text{eff}} \neq D$); 10 nm represents several molecular diameters for proteins. As far as D is larger than about $5 \times 10^{-7} \text{ cm}^2/\text{s}$ [16], we have $\lambda > 700 \text{ s}^{-1/2}$, so $\alpha_1 > 350 \text{ s}^{-1/2}$ (Eq. 20). Therefore, the dimensionless time $\alpha_1^2 t$ in Eqs. 22–24 greatly exceeds unity for all experimentally accessible timescales. Hence, $F(\alpha_1^2 t)$ can be replaced by the respective asymptote:

$$F(p) \rightarrow \frac{1}{\sqrt{\pi p}} \text{ at } p \gg 1 \quad (25)$$

It is worthwhile to mention that Eq. 24 has the specific form of $\Gamma = c_0 f(t)$, which stems from the accepted approximations of the linear theory. Here the function $f(t)$ contains material constants of the system, but not the bulk concentration. Therefore, the dynamic values of Γ follow a modified Henry’s law ($\Gamma \propto c_0$ at fixed time). Such type of dependence is expressed by Eq. 1 for diffusion-controlled adsorption at short times; it was confirmed experimentally for nonionic surfactants [8], where $\Delta\sigma = 2RTc_0\sqrt{Dt/\pi}$ was found to hold for the surface tension change at different c_0 (with $\Delta\sigma = RT\Gamma$). In the case of mixed barrier-diffusion-controlled adsorption (with k only), the $\Gamma(t)$ dependence obtained in Ref. [17] was again of the type $\Gamma = c_0 f(t)$.

Examples for application of the theory

Let us first consider the asymptotic behavior of the subsurface concentration, $c_s(t)$, and the adsorption, $\Gamma(t)$, at long times—this requires both $\alpha_1^2 t$ and $\alpha_2^2 t$ to be much larger than unity. As explained above, the condition $\alpha_1^2 t \gg 1$ always holds. Hence, we will be interested in the case when $\alpha_2^2 t \gg 1$, in such a way that $F(\alpha_2^2 t)$ in Eqs. 22–24 can be represented by the asymptote (25). Physically, this will hold if

$$\frac{k}{\sqrt{D}} \left(\frac{1}{2} \sqrt{t} - \frac{L\sqrt{D}}{D_{\text{eff}}} \right) \gg 1, \quad (26)$$

meaning relatively small resistance to adsorption (relatively large values of k , D_{eff}). Then, by substitution of $F(\alpha_i^2 t) \approx 1/(\alpha_i \sqrt{\pi t})$, $i = 1, 2$, Eq. 22 acquires the form

$$c_s(t) = c_0 \frac{\lambda}{k_1} \frac{1}{\sqrt{\pi t}} \quad (27)$$

which is actually the long-time asymptote at $\alpha_1^2 t \gg 1$, $\alpha_2^2 t \gg 1$ sought for. The equation for $\Gamma(t)$, Eq. 24, can now also be converted to an expansion for long times in the same way; the result reads

$$\Gamma(t) = \Gamma_0 + c_0 \left(\beta L - \frac{\lambda\sqrt{D}}{k_1} \right) + \frac{2c_0}{\sqrt{\pi}} \sqrt{Dt} + \frac{c_0}{k_1} \times \left(\frac{\sqrt{D}}{k_1} \lambda^2 - \sqrt{D} - \beta\lambda L \right) \frac{1}{\sqrt{\pi t}} \quad (28)$$

Equation 28 suggests a useful scale for data analysis—it can be cast into the following shape:

$$\frac{\Gamma(t)}{c_0} - \frac{2}{\sqrt{\pi}} \sqrt{Dt} = \text{const.} + \frac{1}{k_1} \times \left(\frac{\sqrt{D}}{k_1} \lambda^2 - \sqrt{D} - \beta\lambda L \right) \frac{1}{\sqrt{\pi t}} \quad (29)$$

Interestingly, the RHS of Eq. 29 gives exactly the deviation of the real adsorption from a hypothetical purely diffusion-controlled process (for the latter, RHS=0, cf. Eq. 1). Hence, Eq. 29 provides direct information for the influence of barriers. The left-hand side, when plotted vs. $t^{-1/2}$, should give a straight line. We illustrate the expected dependence with data taken from the literature. Figure 2 shows the results for $\Gamma(t)$ of histone I (from calf thymus), on air/water interface, Ref. [16], presented according to Eq. 29. The bulk diffusion coefficient, D , is assumed to be $5.13 \times 10^{-7} \text{ cm}^2/\text{s}$, as provided in [16]; $c_0 = 1.5 \times 10^{-4} \text{ wt.}\%$.

In Fig. 2, a satisfactory straight line is observed in a certain finite interval of $t^{-1/2}$. When discussing the predictions of Eq. 29, one has to bear in mind the limitations of its validity. First, Eq. 29 represents an expansion for long times, or small $t^{-1/2}$ (cf. Eqs. 27 and 28). So, if $t^{-1/2}$ is big enough,

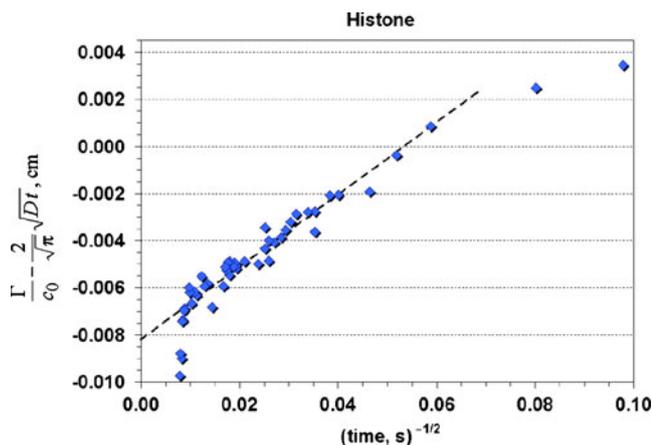


Fig. 2 Measured $\Gamma(t)$ for a protein, presented in the scale of Eq. 29. At times longer than ~ 236 min, the data start deviating from the theory

Eq. 29 will cease to hold. In addition, at short times it may be difficult to accurately measure Γ . Note the presence of some points that deviate from the straight line in Fig. 2 at large $t^{-1/2}$ (small t). On the other hand, there are also points which lie below the line at the smallest values of $t^{-1/2}$ (large t). This behavior should be attributed to the fact that the theory cannot be applied if Γ increases too much at very long times. The approximations of our model include disregarding the lateral repulsion in the interfacial layer at high Γ —see the comments to Eq. 7 and the captions to Figs. 2 and 4.

The slope of the line in Fig. 2 is $0.1539 \text{ cm s}^{1/2}$. The latter value can be interpreted in view of the coefficient multiplying $t^{-1/2}$ in the right-hand side of Eq. 29. First, we may compare the terms in the parentheses. For the rate constant k , an order of magnitude evaluation may be based on what was reported by Middelberg et al. [2] for a certain polypeptide, $k \sim 10^{-5} \text{ cm/s}$. Values for other proteins fall in the same range, as will be discussed below. Given the fact that λ is large (see the end of “Description of the adsorption kinetics”), we conclude that \sqrt{D} and $\beta\lambda L$ are insignificant and negligible in comparison with the first term in the parentheses, Eq. 29. Hence,

$$\frac{\Gamma(t)}{c_0} - \frac{2}{\sqrt{\pi}} \sqrt{Dt} = \text{const.} + \frac{\sqrt{D}}{\sqrt{\pi}} \left(\frac{\lambda}{k_1}\right)^2 \frac{1}{\sqrt{t}} \quad (30)$$

Next, we deduce from Eq. 18 that

$$\frac{\lambda}{k_1} = \frac{L\sqrt{D}}{D_{\text{eff}}} + \frac{\sqrt{D}}{k} \quad (31)$$

The quantity λ/k_1 may be regarded as a total “resistance” of the interfacial region (when it is larger, $d\Gamma/dt$ is smaller—cf. Eq. 30). λ/k_1 comprises two contributions: the first one, $L\sqrt{D}/D_{\text{eff}}$, is associated with the diffusion through the subsurface layer, while the second one, \sqrt{D}/k , comes from hindrance to the act of adsorption when the molecules hit the

interface. In effect, Eq. 31 resembles the formula for two (electric) resistances connected in series.

From the slope in Fig. 2 and from Eq. 30 one finds $\lambda/k_1 = 19.52 \text{ s}^{1/2}$ for histone. This sets a relation between the two physical parameters k , D_{eff} , insofar as they should comply with the experimental results, and therefore, should satisfy Eq. 31 with the fixed λ/k_1 quoted above. Figure 3 displays a plot of the corresponding values of k and D_{eff} . It turns out to be impossible to determine k and D_{eff} separately; the data for Γ at relatively short times in the adsorption process (until Eq. 8 remains valid) do not contain sufficient information for that. There is only one parameter which can be extracted from the $\Gamma(t)$ curve, Fig. 2, and it is λ/k_1 . (The intercept in Fig. 2 depends again on λ/k_1 .) This parameter incorporates the effects of both k and D_{eff} on the adsorption.

Figure 3 demonstrates that different regimes are possible. In the region of large D_{eff} and small k , the kinetic constant k is mainly responsible for retardation of the adsorption. In this particular case, $k = 3.67 \times 10^{-5} \text{ cm/s}$ is obtained for histone I. The latter value is of the same order of magnitude as the reported $k = 1.75 \times 10^{-5} \text{ cm/s}$ for Lac28 helical peptide [2]. Alternatively, in the region of small D_{eff} and large k (Fig. 3), the effective diffusion coefficient in the subsurface layer is the predominant rate-determining factor. If so, then $D_{\text{eff}} = 4.5 \times 10^{-11} \text{ cm}^2/\text{s}$ is obtained for histone I. This is equivalent to a “barrier” of $\phi \sim 9.3 k_B T$, if one accepts the qualitative representation $D_{\text{eff}} = D \exp(-\phi/(k_B T))$. Of course, a range of values of k , D_{eff} exists where both the hindrance to the act of adsorption and the (retarded) diffusion through the subsurface layer exert a significant influence on the overall kinetics. This range corresponds to the middle part of the curves in Fig. 3.

Calculation according to Eq. 24 can be implemented to fit Γ for histone; the result is shown in Fig. 4. The kinetic behavior of Γ is sensitive only to the value of α_2 . Theoretical curves for different pairs of k , D_{eff} (from Fig. 3), associated

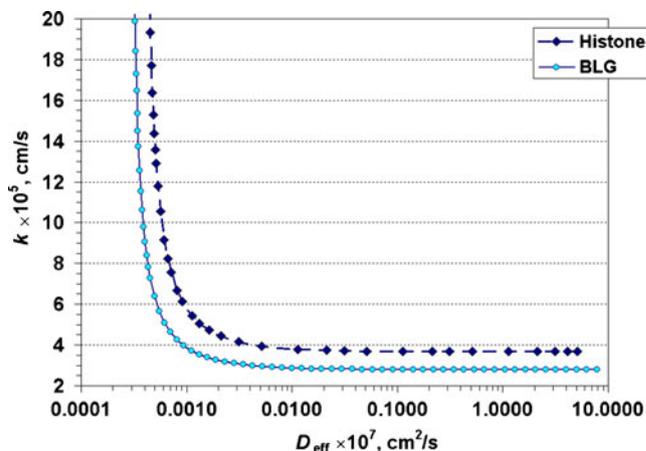


Fig. 3 Pairs of k , D_{eff} which agree with the experimental $\Gamma(t)$ dependence: see Eq. 31 for histone and Eq. 33 for BLG

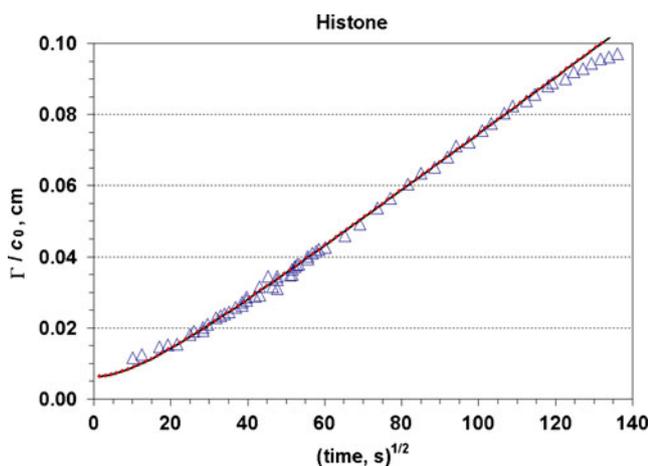


Fig. 4 Fit of Γ for histone, according to Eq. 24; $k=5.07 \times 10^{-5}$ cm/s, $D_{\text{eff}}=1.33 \times 10^{-10}$ cm²/s, $\beta=0.8621$, $k_1=58.795$ s⁻¹, $\lambda=1,147.4$ s^{-1/2}, $\alpha_1=1,147.3$ s^{-1/2}, and $\alpha_2=0.05124$ s^{-1/2}. At times longer than ~ 236 min, the data start deviating from the theory

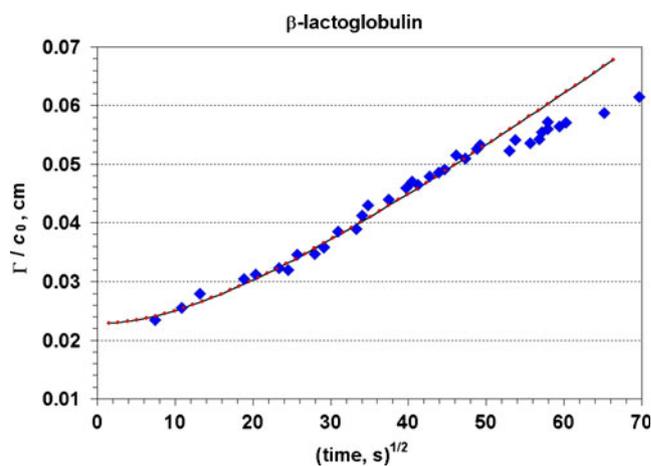


Fig. 5 Fit of Γ for BLG, according to Eq. 24; $k=4.26 \times 10^{-5}$ cm/s, $D_{\text{eff}}=8.10 \times 10^{-11}$ cm²/s, $\beta=0.8277$, $k_1=51.443$ s⁻¹, $\lambda=1,628.0$ s^{-1/2}, $\alpha_1=1,627.9$ s^{-1/2}, and $\alpha_2=0.03160$ s^{-1/2}. (The value of α_2 indicates slower kinetics in comparison to that in Fig. 4.) At times longer than ~ 46.8 min, the data start deviating from the theory

with different α_1 , are essentially identical. This observation confirms that one physical parameter is relevant to the kinetics. (Γ_0 is also adjusted in Fig. 4, but it is not related to the adsorption mechanism.) To draw the fit in Fig. 4, we have chosen a pair of k , D_{eff} in the middle of the respective curve in Fig. 3.

Series expansion of α_2 from Eq. 20 gives:

$$\alpha_2 = \frac{k_1}{\lambda} + \frac{k_1^2}{\lambda^3} + \frac{2k_1^3}{\lambda^5} + \dots \approx \frac{k_1}{\lambda} \quad (32)$$

This is a consequence from the fact that k_1/λ^2 is a small dimensionless parameter (varying between 7.2×10^{-6} and 7.2×10^{-5} with the data for histone in Fig. 3). So, Eq. 32 furnishes a simple relation between the slope in Eq. 30 and α_2 .

The characteristic time $\alpha_2^{-2} = 380.9$ s defines a scale for the adsorption process. If the time and/or α_2 are such that $\alpha_2^2 t \gg 1$ (and the model assumptions still hold, especially Eq. 8), then the terms $F(\alpha_2^2 t)$, $F(\alpha_2^2 t)$ vanish and the kinetics becomes entirely diffusion controlled—from Eq. 24, it follows that $\Gamma(t) = \text{const.} + 2c_0 \sqrt{Dt/\pi}$, as predicted by the classical theory of Ward and Tordai [3]. Indeed, large α_2 corresponds to small resistance of the interfacial region, cf. Eqs. 31 and 32.

Let us consider the case when $\alpha_2^2 t$ is not very large (specifically, below ~ 10), so that $F(\alpha_2^2 t)$ in Eqs. 22–24 cannot be represented by the asymptote (25). Consequently, the expansion (28) will cease to be valid and the scale in Fig. 2 will not be applicable. One has to use Eq. 24 for data fitting. As an example of such a case, we take $\Gamma(t)$ for β -lactoglobulin (BLG) on air/water interface, reported in Ref. [16]. Figure 5 demonstrates that the data are in good agreement with the theory, Eq. 24. The fitting curve depends on one adjustable parameter, α_2 (besides the unimportant

Γ_0); it is insensitive to α_1 . Hence, reasonable pairs of values of k and D_{eff} will be those which refer to $\alpha_2 = \text{const.}$, fixed by the best fit. From Eqs. 18 and 20, one derives:

$$\frac{1}{\alpha_2} + \frac{\alpha_2}{k_1} = \frac{\lambda}{k_1} = \frac{L\sqrt{D}}{D_{\text{eff}}} + \frac{\sqrt{D}}{k} \quad (33)$$

This is another form of Eq. 31, written in terms of α_2 . The “resistance”, represented by the right-hand side of Eq. 33, is approximately equal to $1/\alpha_2$ since the series expansion (32) remains valid in the case of BLG as well.

The characteristic time for BLG, $\alpha_2^{-2} = 1,001.4$ s (Fig. 5), turns out to be longer than that of histone (380.9 s). Therefore, the adsorption of BLG is slower. Figure 3 displays the pairs of k and D_{eff} which are consistent with Eq. 33, where $\alpha_2=0.0316$ s^{-1/2}. As can be expected, k and D_{eff} are seen to be lower for BLG. From the limiting values of k and D_{eff} (that correspond to the regions where they are rate determining), we estimate the difference between the energy barriers to adsorption for the two proteins. This difference amounts to $\sim 0.3 k_B T$ (both from k and from D_{eff}).

An interesting feature of the kinetic equation for Γ , Eq. 24, is observed when the dependence $\Gamma(t)$ is considered in a relatively short time interval. The functions $F(p)$, Eq. 34, which are present in Eq. 24, deviate rather slowly from a linear dependence $\propto \sqrt{p}$. Consequently, Eq. 24 may yield a plot that looks approximately linear in a scale of Γ vs. \sqrt{t} . It is easy to misinterpret this apparent trend as a manifestation of diffusion-controlled adsorption, Eq. 1. An indication for a problem may come from the fact that the obtained slope $d\Gamma/d\sqrt{t}$ would not give realistic values for D as predicted by Eq. 1. We illustrate this situation with the data from Fig. 5. One can draw quite satisfactory straight line, $\Gamma/c_0 \propto \sqrt{t}$, for times between 9.1 and 40.3 min. The

slope of this line, if interpreted by Eq. 1, gives $D=5.4 \times 10^{-7}$ cm²/s while the correct bulk diffusion coefficient, measured independently, is $D=7.8 \times 10^{-7}$ cm²/s [16]. The discrepancy is obviously due to the fact that Eq. 24 should be applied, in order to describe the influence of barriers; Eq. 1 can provide only an apparent value for D , D_{app} . The latter depends on the time domain accessible for experimental measurements. At longer times in the evolution of the adsorption process, the slope $c_0^{-1}d\Gamma/d\sqrt{t}$ would be greater; that trend was discussed also in Ref. [17] (section 3.1.2). The corresponding D_{app} would be larger. In addition, D_{app} may also depend on the surfactant concentration in the bulk [4]. At higher concentrations, D_{app} is expected to decrease, because of the steric hindrance for adsorption in the crowded layer of higher surface coverage [4]. This physical effect is not considered in the present paper; it is connected with the term $(1 - \Gamma/\Gamma_\infty)$ in Eq. 7. Our main equation, Eq. 24, has the specific form of $\Gamma/c_0=f(t)$, which does not predict dependence of D_{app} on c_0 since $f(t)$ in the right-hand side does not contain c_0 .

Short-time asymptote of Eq. 24 can be derived by expanding at $\alpha_1^2 t \ll 1$, $\alpha_2^2 t \ll 1$; this yields $[\Gamma(t) - \Gamma_0]/c_0 = \text{const.} + kt + O(t^{3/2})$. However, the limit $\alpha_1^2 t \ll 1$ is experimentally inaccessible, even for milliseconds (see the end of “Description of the adsorption kinetics”). Therefore, a more realistic time domain of $\alpha_1^2 t \gg 1$ and $\alpha_2^2 t \ll 1$ may be explored—it corresponds to seconds or minutes for proteins. Then, Eq. 24 acquires the form $[\Gamma(t) - \Gamma_0]/c_0 = \text{const.} + b_1 t^{-1/2} + b_2 \sqrt{t} + O(t)$, where $b_1 \approx \alpha_2(\alpha_1 \beta L - \sqrt{D})/\alpha_1^3 \sqrt{\pi}$; $b_2 \approx 2\alpha_2 \beta L/\sqrt{\pi}$.

The above results are obtained by analysis of data for the time dependence of the adsorbed amount, $\Gamma(t)$. Direct measurement of the latter requires special techniques, so it is often preferred to use the simpler classical dynamic surface tension, $\sigma(t)$, in order to gain information about the adsorption kinetics. Then, the interpretation encounters the necessity to consider the relation between σ and Γ , because the theoretical balances are written in terms of Γ . This may lead to additional complications, specifically pertaining to σ . An important physical effect which influences the surface tension, σ , was examined by Miller et al. [32], who took into account the possible existence of the adsorbed molecules in two states (configurations), with different occupied areas per molecule, and respective Γ_1 and Γ_2 . In the frames of a diffusion-controlled adsorption theory, isotherms were used in Ref. [32] to describe the local equilibrium between the subsurface concentrations and Γ_1 and Γ_2 . Then, a kinetic process of transition from one state of the molecules to the other was found to lead to agreement of the theory with the experimental surface tension, σ , for proteins [32]. In a more general perspective, if one has to interpret dynamic data for σ , it could be appropriate to consider both effects: on one hand,

adsorption barriers can impede the subsurface-to-interface transfer and affect $\Gamma(t)$, while on the other hand, processes within the interface, such as molecular reorientation, reconfiguration, etc., may additionally influence σ .

The ramifications related to σ can be avoided if the surface excess itself, Γ , is measured directly. This task can be implemented by a number of well established methods [33], [34], such as ellipsometry, neutron reflection, infrared spectroscopy. The kinetic aspects, however, require careful consideration—when the adsorption is fast, and at short times, static liquid surfaces are unsuitable for experimental work (due to problems with their creation, and because of the requirement for fast data acquisition). One has to apply special dynamic techniques which involve surface area expansion and liquid flow, engendering convective transfer of surfactant [34], [35]. As an example, we can mention here the overflowing cylinder method [34]. In these cases, it is important to take into account the hydrodynamics of the particular processes [35]; comparison with experiment is only possible via comprehensive models. In view of such models, the approach proposed in the present work may be useful—it can help to incorporate the kinetics of surfactant adsorption into the whole picture.

Conclusions

The initial stage of surfactant adsorption (when the layer is relatively diluted, so that the lateral confinement and the desorption can be neglected) carries information for the influence of factors related to the transfer of molecules through the subsurface region and onto the interface. Physically, two separate effects may exist: (1) diffusion through a subsurface layer with nanometer thickness, where structuring or molecular interactions can impose considerable changes on the transfer rate, as compared with the bulk diffusion and (2) hindrance to the act of adsorption itself, when the molecules hit the interface from a place directly adjacent to it. The former phenomenon is quantified by an effective diffusion coefficient, and the latter—by a kinetic constant (in a widely accepted analogy with the chemical kinetics). In the present work, a simple model is formulated by considering the balance of fluxes in the subsurface layer. This model allows one to find analytical solution for the adsorption as a function of time. Such an approach seems advantageous (in the sense of easier usage, clearer picture, etc.), over a possible more sophisticated model that would require numerical solution. The theory is applied for analysis of experimental data for $\Gamma(t)$ of two proteins on air/water interface. Attention is paid to the particular case when the resistance to adsorption is relatively small but is still significant as compared with the bulk diffusion. Then, the theoretical fit of $\Gamma(t)$ can be implemented in a specific linear scale.

The overall resistance of the interfacial zone comprises additive contributions from the hindrance to the act of adsorption (represented by k), and from the (retarded) diffusion through the subsurface layer, represented by D_{eff} . They are incorporated into one physical parameter (or characteristic time), which influences the kinetics of $\Gamma(t)$. One possible route to separate the two components of resistance is to analyze sets of data in which the relative importance of k and D_{eff} is different. For example, non-surface-active additives can be used in an aqueous solution to change its viscosity. In such a way the value of D_{eff} for the adsorbing surfactant (as well as D) will be affected, while the kinetic constant k should be independent from the viscosity of the medium. Then, fitting of adsorption data with the theory will show variations in the full resistance of the interfacial zone which will be due solely to D_{eff} , so the physical contribution of k can be distinguished.

Acknowledgments This work was partially supported by the EU program COST, Action D43—“Colloid and Interface Chemistry for Nanotechnology.” The author also wishes to thank the National Science Fund of Bulgaria (grants no. DO-02-82/2008 and DCVP-02/2-2009, National Centre for New Materials, “UNION”), for the partial financing.

Appendix

Several inverse Laplace transformations, used for the derivations in the text, are listed below. With the auxiliary function

$$F(p) \equiv e^p \operatorname{erfc}(\sqrt{p}) \quad (34)$$

where $\operatorname{erfc}(y) \equiv 1 - \frac{2}{\sqrt{\pi}} \int_0^y e^{-z^2} dz$ is the complementary error function, one writes:

$$L^{-1} \left[\frac{1}{\sqrt{s} + \alpha} \right] = \frac{1}{\sqrt{\pi t}} - \alpha F(\alpha^2 t) \quad (35)$$

$$L^{-1} \left[\frac{1}{\sqrt{s}(\sqrt{s} + \alpha)} \right] = F(\alpha^2 t) \quad (36)$$

$$L^{-1} \left[\frac{1}{s(\sqrt{s} + \alpha)} \right] = \frac{1}{\alpha} [1 - F(\alpha^2 t)] \quad (37)$$

$$L^{-1} \left[\frac{1}{s\sqrt{s}(\sqrt{s} + \alpha)} \right] = \frac{2}{\sqrt{\pi}} \frac{\sqrt{t}}{\alpha} - \frac{1}{\alpha^2} [1 - F(\alpha^2 t)] \quad (38)$$

Here, L^{-1} denotes the inverse Laplace transform, α is an arbitrary constant (may be complex), t is time, and s is the Laplace variable.

Besides, from Eq. (34) it follows that $F(0)=1$; $F(\infty)=0$.

References

- Graham DE, Phillips MC (1979) *J Colloid Interface Sci* 70:403–414
- Middelberg APJ, Radke CJ, Blanch HW (2000) *Proc Natl Acad Sci USA* 97:5054–5059
- Ward AFH, Tordai L (1946) *J Chem Phys* 14:453–461
- Eastoe J, Dalton JS (2000) *Adv Colloid Interface Sci* 85:103–144
- Miller R, Makievski AV, Fainerman VB (2001) Dynamics of adsorption from solutions. In: Fainerman VB, Moebius D, Miller R (eds) *Surfactants: chemistry, interfacial properties, applications*. Elsevier, Amsterdam, p 287
- Danov KD, Valkovska DS, Kralchevsky PA (2002) *J Colloid Interface Sci* 251:18–25
- Lyklema J (1991) *Fundamentals of interfacial and colloid science*. Fundamentals, vol 1. Academic, London
- Eastoe J, Dalton JS, Rogueda PGA, Crooks ER, Pitt AR, Simister EA (1997) *J Colloid Interface Sci* 188:423–430
- MacRitchie F, Alexander AE (1963) *J Colloid Sci* 18:458–463
- Ravera F, Liggieri L, Steinchen A (1993) *J Colloid Interface Sci* 156:109–116
- Liggieri L, Ravera F, Passerone A (1996) *Colloids Surfaces A* 114:351–359
- Wierenga PA, Meinders MJB, Egmond MR, Voragen AGJ, de Jongh HHJ (2003) *Langmuir* 19:8964–8970
- Pogorzelski SJ, Kogut AD (2001) *Oceanologia* 43:389–404
- Song KB, Damodaran S (1991) *Langmuir* 7:2737–2742
- Liu F, Wang Zh, Sun D, Wei X, Zhou W, Li G, Zhang G (2006) *J Dispersion Sci Technol* 27:657–663
- Sengupta T, Razumovsky L, Damodaran S (1999) *Langmuir* 15:6991–7001
- Moorkanikkara SN, Blankschtein D (2006) *J Colloid Interface Sci* 296:442–457
- Moorkanikkara SN, Blankschtein D (2006) *J Colloid Interface Sci* 302:1–19
- MacLeod CA, Radke CJ (1994) *Langmuir* 10:3555–3566
- Israelachvili JN (1992) *Intermolecular and surface forces*. Academic, London
- Basheva ES, Gurkov TD, Christov NC, Campbell B (2006) *Colloids Surfaces A* 282–283:99–108
- Eriksson JC, Henriksson U (2007) *Langmuir* 23:10026–10033
- Yousef A, Mc Coy BJ (1983) *J Colloid Interface Sci* 94:497–501
- Rakita Yu M, Fainerman VB (1989) *Colloid J (USSR)* 51:714–720
- Baret JF (1968) *J Phys Chem* 72:2755–2758
- Miller R, Kretschmar G (1980) *Colloid & Polymer Sci* 258:85–87
- Guzman RZ, Carbonell RG, Kilpatrick PK (1986) *J Colloid Interface Sci* 114:536–547
- Baret JF (1969) *J Colloid Interface Sci* 30:1–12
- Missen RW, Mims CA, Saville BA (1999) *Introduction to chemical reaction engineering and kinetics*. Wiley, New York
- Diamant H, Andelman D (1996) *J Phys Chem* 100:13732–13742
- Diamant H, Ariel G, Andelman D (2001) *Colloids Surfaces A* 183–185:259–276
- Miller R, Aksenenko EV, Fainerman VB, Pison U (2001) *Colloids Surfaces A* 183–185:381–390
- Zhmdud B, Tiberg F (2005) *Adv Colloid Interface Sci* 113:21–42
- Bain CD (2008) *Adv Colloid Interface Sci* 144:4–12
- Noskov BA (1996) *Adv Colloid Interface Sci* 69:63–129