A diffusion-based approach to mixed adsorption kinetics

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Abstract

A new theoretical approach has been developed which allows mixed kinetics of non-ionic surfactants to be studied in the unitary framework of an extended diffusion-controlled problem. This treatment not only allows one to consider a large class of surface models, but also provides a better understanding of the relation existing between the presence of a potential barrier and the diffusion-controlled adsorption. In particular it is shown that the assumption of the presence of adsorption barriers does not depend on the local equilibrium hypothesis. In fact the theoretical treatment takes into account the possibility that mixed kinetics also occur in the absence of potential barriers. By this treatment a general equation is obtained which allows the adsorption as a function of time to be evaluated by numerical or analyical procedures for a given particular surface model.

Keywords: Adsorption kinetics; Diffusion-controlled adsorption; Freundlich model; Langmuir model; Liquid surfaces; Local equilibrium; Mixed kinetics; Non-ionic surfactants

1. Introduction

Several processes of great scientific and technological impact are governed by dynamic mass exchange in liquid mixtures: the adsorption kinetics of some specific constituents at fluid–fluid interfaces often play a major role in determining the final results. Thus modelling the adsorption kinetics represents a necessary step to fully understand and improve such processes as oil recovery, lubrication, stabilisation of emulsions and interfaces [1], and production of pharmaceuticals [2] and cosmetics. Moreover, concerning basic research, adsorption kinetics are also a powerful tool for studying the structure and interactions of the surfactants at fluid–fluid interfaces.

The first quantitative model for adsorption kinetics was established by Ward and Tordai [3] who considered adsorption kintics to be controlled only by diffusion. In this model the exchange of mass at the interface is considered at equilibrium compared with the bulk diffusion (local equilibrium).

Under these hypotheses, the increase of the adsorption equals the diffusion flux at the surface. Thus, by considering the interface as a geometric plane surface and by choosing a system of coordinates with the x axis normal to the surface and directed towards the solution, this balance reads

$$\frac{d\Gamma}{dt} = D\frac{\partial C}{\partial x}\bigg|_{x=0^+} \tag{1}$$

where Γ is the adsorption (surface excess concentration), $C \equiv C(x, t)$ is the concentration profile at time t, and D is the surfactant diffusion coefficient. Within these assumptions the problem is described

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by the Fick equation:

$$\frac{\partial C}{\partial t} = D\frac{\partial^2 C}{\partial x^2} \qquad (2)$$

Eq. (2) with the boundary condition (1) and the adsorption isotherm gives a relation between the sub-surface concentration, $C_s(t)$, and the adsorption $\Gamma(t)$. This classical approach provides an expression for $\Gamma(t)$ in the integral form:

$$\Gamma(t) = \sqrt{\frac{D}{\pi}}\left[2C^\infty\sqrt{t} - \int_0^t \frac{C_s(\tau)}{\sqrt{t-\tau}}\,d\tau\right] \qquad (3)$$

This approach, which has been improved further by Hansen [4] and Sutherland [5], is frequently used by many authors and seems to be applicable to the description of most experimental observations [6–9]. However, especially with surfactant molecules of a particular size and structure, diffusion is not the only mechanism controlling adsorption kinetics, as observed experimentally [10–12]: the exchange kinetics of surfactant between the surface and the buk adjacent to it also have to be taken in consideration. This latter mechanism manifests itself as an apparent lowering of the diffusion coefficient calculated from adsorption kinetics experiments [13,14]. Moreover, this effect has been generally identified with the presence of an adsorption activation energy [2,15] and/or with the need for orientation and re-organisation of the adsorbing molecules [10]. The presence of an adsorption barrier means that of the molecules close to the surface, only those that can overcome the energy barrier can adsorb. If one considers for example that the rotational energy also contributes to the total energy of the molecule, the need for orientation can act as an energetic barrier to adsorption, which can also be caused for example by molecular configuration changes or by interfacial restructuring.

The most general way to study adsorption kinetics consists of considering two time-dependent processes. The first one is the exchange of matter between that portion of solution close to the surface and the surface phase: this process may occur by crossing an adsorption potential barrier. This first effect induces a second one: diffusion in the bulk phase. The whole process is called "mixed kinetics" when neither of these two individual mechanisms can be neglected with respect to the other or, more precisely, when the characteristic times of these two mechanisms are comparable.

Baret [16] was the first to approach the problem of mixed kinetics by solving the diffusion problem with an appropriate boundary condition taking into account the kinetics of the exchange of matter at the surface. Since then, this approach has been improved and widely used by some authors [17–21].

In two recent papers [22,23] an approach has been presented in which the mixed adsorption kinetics of non-ionic surfactants are treated as an extended diffusion process when linear adsorption is considered. Such a description is based on the definition of a particular renormalised diffusion coefficient, deduced by the analysis of the kinetic equation of adsorption, which describes the exchange of surfactant between the bulk and the surface.

In the present study, this approach is improved and generalised so as to cover a wide range of surface models. Indeed, hereafter it is shown that by defining a suitable physical model, mixed kinetics can be treated, in the most general case, as an extended diffusion-controlled problem, in which a particular boundary condition, derived from the kinetics equation, accounts for the exchange of molecules at the interface. Moreover, Eq. (3) will be derived as a particular case.

The main advantage of this approach is that the problem of the mixed adsorption kinetics can be solved in a unitary mathematical framework, whatever the mechanisms governing the dynamic process are. Moreover, it allows the consequences to the assumptions made about the exchange mechanism of surfactant at the interface (equilibrium of adsoption, presence of potential barriers, surfactant re-organisation, etc.) to be carefully evaluated. In particular, the theory takes into account the possibility of adsorption kinetics which differ from diffusion-controlled kinetics even in the absence of adsorption potential barriers.

2. Theory

The physical model adopted for the description of the adsorption kinetics can be summarised in the following points:

(1) the kinetic exchange of matter due to adsorption occurs only in a layer of thickness d close to the surface;

(2) the value of d is of the order of a few mean free paths of the adsorbing molecules in the solution, so it can be considered negligible from a macroscopic point of view;

(3) the transport mechanism at $x > d$ is the diffusion proper with the actual diffusion coefficient D;

(4) the concentration at a distance d is $C(d, t) \equiv C_1(t)$;

(5) the concentration at the surface, $C(0, t) \equiv C_0(t)$, is a function of the adsorption Γ to be defined on the basis of the adsorption kinetic equation.

From points (1)–(3) is follows from a macroscopic point of view that the transport mechanism varies at the surface: for $x > 0$ the transport process is diffusion with diffusion coefficient D, while at $x = 0$ the adsorption proper occurs.

It is important to point out that, in the framework of this model, $C_1(t)$ corresponds to the subsurface concentration, as defined in the Ward and Tordai description. $C_1(t)$ is the actual physical concentration at distance d from the surface. However, $C_0(t)$ has no real physical meaning, but represents the link which makes the model equivalent to the actual system: its expression is found by consideration of the kinetic adsorption equation.

2.1. Mixed kinetics

In most models used, the adsorption flux has a linear dependence on the concentration C_1 and the desorption flux depends only on the adsorption, so that the kinetic adsorption equation takes on the general form [20]:

$$\frac{d\Gamma}{dt} = k_a g(\Gamma) C_1 - k_d f(\Gamma) \tag{4}$$

where the rates of adsorption, k_a, and desorption, k_d, depend on the model considered for the surface phase [15,24] and can be written in terms of microscopic quantities related to molecular kinetics. $f(\Gamma)$ and $g(\Gamma)$ are, also, functions specific to the

surface model. In particular, if a potential adsorption barrier ϵ_a exists, the rate of adsorption can be written as [15,22]

$$k_a = \frac{\bar{v}}{4} \exp\left(-\frac{\epsilon_a}{kT}\right) \tag{5}$$

where k is the Boltzmann constant, T is the absolute temperature and $\bar{v}$ is the mean velocity of the surfactant molecules. Thus Eq. (4), after dividing and multiplying the right-hand side by d, reads:

$$\frac{d\Gamma}{dt} = D^* g(\Gamma) \left(\frac{C_1 - C_0}{d}\right) \tag{6}$$

where

$$C_0 \equiv \frac{k_d}{k_a} \frac{f(\Gamma)}{g(\Gamma)} \tag{7}$$

and

$$D^* \equiv \frac{\bar{v}d}{4} \exp\left(-\frac{\epsilon_a}{kT}\right) \tag{8}$$

The definition given in Eq. (7) is the relationship between $C_0(t)$ and Γ that, as discussed above, links the model to the actual physical system. It is worth noting that, by definition, C_0 coincides with the particular C_1 value which can be found by solving Eq. (4) for $d\Gamma/dt = 0$, i.e. the adsorption isotherm. Moreover, by using the expression of the actual diffusion coefficient found in Appendix 1, the renormalised diffusion coefficient D^* reads:

$$D^* = D \exp\left(-\frac{\epsilon_a}{kT}\right) \tag{9}$$

(D^* reduces to the actual diffusion coefficient in the case of zero adsorption potential barrier.) By considering the macroscopic limit of Eq. (6) one obtains

$$\frac{d\Gamma}{dt} = g(\Gamma) D^* \left.\frac{\partial C}{\partial x}\right|_{x=0^+} \tag{10}$$

In this way, the kinetic equation has been written in terms of the concentration gradient at the surface, which is a macroscopic quantity. Eq. (10) can be used as a boundary condition for the diffusion problem. Note that Eq. (10) also shows that in the present model the transport process in the whole

system (bulk plus surface) is equivalent to a diffusive one with a discontinuity of the diffusion coefficient which is constant in the bulk and dependent on the adsorption at the surface: $D(x) = D$ for $x > 0$ and $D(0) = g(\Gamma)D^*$. Thus, mixed kinetics can be treated as an extended diffusion problem and the expression for $\Gamma(t)$ is found through the solution of this problem.

By solving the Fick equation by Laplace transform techniques for $x > 0$, with the boundary condition

$$C(0, t) = C_0(t) \tag{11}$$

and the initial condition

$$C(x, 0) = C^\infty \tag{12}$$

and by substituting $C(x, t)$ into Eq. (10), one obtains an integro-differential equation for $\Gamma(t)$:

$$\frac{1}{g(\Gamma)} \frac{d\Gamma}{dt} = \sqrt{\frac{D_a}{\pi}} \left[\frac{C^\infty}{\sqrt{t}} + \frac{1}{2} \int_0^t \frac{C_0(\tau)}{\sqrt{(t - \tau)^3}} \, d\tau \right] \tag{13}$$

where C_0 is given by Eq. (7) and the apparent diffusion coefficient D_a [22] has been introduced:

$$D_a = \frac{D^{*2}}{D} = D \exp\left(-2 \frac{\epsilon_a}{kT} \right) \tag{14}$$

Eq. (13) can be integrated to obtain the more useful form:

$$\int_0^\Gamma \frac{1}{g(\Gamma)} \, d\mu = \sqrt{\frac{D_a}{\pi}} \left[2C^\infty \sqrt{t} - \int_0^t \frac{C_0(\tau)}{\sqrt{t - \tau}} \, d\tau \right] \tag{15}$$

Eq. (15) represents the master equation for the present treatment and it will be applied to the different kinds of surface model.

2.2. Diffusion-controlled adsorption

As already explained by many authors [4,10,18] adsorption is diffusion-controlled if the exchange of matter between the surface phase and the layer of solution adjacent to it has a characteristic time much smaller than the time of diffusion. For this reason, this exchange can be considered, at any time, to be at equilibrium (local equilibrium). Thus,

the dynamics of the process are due to the diffusion process, and the relationship between the adsorption and the concentration close to the surface is expressed by the adsorption isotherm. In the framework of the present model, "local equilibrium" implies that, in Eq. (6), the time derivative of the adsorption is zero, leading to

$$C_0(t) = C_1(t) \tag{16}$$

In contrast, the global diffusion process is not at equilibrium and an incident diffusion flux is present at $x = d$, i.e.

$$\Phi_{\text{diff}} = D \frac{\partial C}{\partial x} \bigg|_{x = d} \tag{17}$$

When the macroscopic limit has been reached, i.e. when d approaches zero, this diffusion flux can be considered to be directly incident on the surface and to be responsible for the increase in adsorption. Thus, in this case, the condition (10) must be replaced by Eq. (1). As a consequence, the physical picture of the Ward and Tordai description is obtained, where the sub-surface concentration C_s is $C_1 = C_0$. Therefore:

$$\Gamma(t) = \sqrt{\frac{D}{\pi}} \left[2C^\infty \sqrt{t} - \int_0^t \frac{C_0(\tau)}{\sqrt{t - \tau}} \, d\tau \right] \tag{18}$$

3. Results and discussion

It is interesting to note that in the framework of this model, the presence of the adsorption barrier does not depend on the characteristic times of the two principal time-dependent phenomena, i.e. adsorption kinetics and diffusion. In fact the process can be characterised by a "local equilibrium" of adsorption even in the presence of an important adsorption barrier. In some cases, it is possible to have $\epsilon_a = 0$ without a local equilibrium of adsorption, because this theoretical approach provides mixed adsorption kinetics with $\epsilon_a = 0$. Indeed, Eq. (15) has been derived by using the kinetic equation (6) without any restriction on the value of the adsorption barrier, so that it still describes the system when $\epsilon_a = 0$ ($D_a = D$). Moreover, regardless of what value ϵ_a is, we have demonstrated that

under the hypothesis of local equilibrium, the Ward and Tordai equation still holds and does not depend on ϵ_a. This means that for diffusion-controlled adsorption the presence of an adsorption barrier is somewhat masked. These last considerations clearly show that the widely used equivalence between absence of adsorption barrier and local equilibrium should not be accepted without question.

Table 1 summarises the quantities to be substituted in Eq. (15) for some of the surface models compatible with Eq. (4). These models refer to two classes: one with $g(\Gamma) = (1 - \Gamma/\Gamma^\infty)$ and the other with $g(\Gamma) = 1$, corresponding respectively to models in which the adsorption flux is dependent or independent of surface coverage [15]. Γ^∞ is the saturation adsorption.

In the case of Henry adsorption, an analytic solution exists for Eq. (15):

$$\Gamma(t) = C^\infty L^* \left[1 - \exp\left(\frac{D_a t}{L^{*2}}\right) \operatorname{erfc} \sqrt{\frac{D_a t}{L^{*2}}} \right] \qquad (19)$$

where $L^* = k_d/k_a$. This equation, which was derived and discussed in Ref. [22], reduces to the Sutherland equation (5) in the absence of potential barriers ($D_a = D$).

In general, when non-linear models are under consideration, only numerical solutions of Eq. (15) can be found. For this purpose the numerical schema described in Appendix 2 can be used.

Table 1 summarises the quantities to be used in the application of Eq. (15) to some of the most used surface models. Essentially, there are two classes of models depending on whether $g(\Gamma)$ is or is not really a function of Γ.

For the adsorption models with $g(\Gamma) = 1$ (e.g. linear adsorption), Eq. (15) reads:

$$\Gamma(t) = \sqrt{\frac{D_a}{\pi}} \left[2C^\infty \sqrt{t} - \int_0^t \frac{C_0(\tau)}{\sqrt{(t-\tau)}} d\tau \right] \qquad (20)$$

This equation becomes identical to the Ward and Tordai equation in the case of a zero adsorption potential barrier. Thus, in this case, it is not possible to determine if the adsorption is at local equilibrium or not. In practice, for $g(\Gamma) = 1$, the cases of zero adsorption potential barrier and diffusion-controlled adsorption give the same expression for $\Gamma(t)$. In contrast, when models with $g(\Gamma) \neq 1$ (e.g. Langmuir) are under consideration, the conditions of local equilibrium and no adsorption barriers lead to two different behaviours of $\Gamma(t)$.

For the sake of clarity we examine the Freundlich model and Langmuir model, as representatives of these two principal classes of surface models.

Fig. 1 shows the adsorption vs. time curve for

Table 1
Summary of the quantities to be used in Eq. (15) for the principal surface models compatible with Eq. (4). Γ^∞ is the saturation adsorption, m and K are the Freundlich empirical constants, b is the co-area, a is the Langmuir–Szyskowsky coefficient and H is linked to the interaction molecular energy

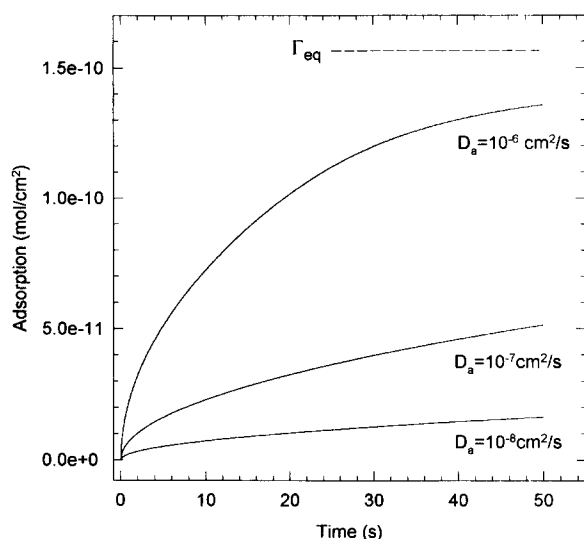| Model	C_0	$\int_0^\Gamma \frac{du}{g(u)}$
Henry	$\dfrac{k_d}{k_a}\Gamma$	Γ
Freundlich	$\left(\dfrac{\Gamma}{K}\right)^{1/m}$; $K = (k_a/k_d)^m$	Γ
Van der Waals	$\dfrac{k_d}{k_a}\dfrac{\Gamma}{1-b\Gamma}\exp\left(\dfrac{b\Gamma}{1-b\Gamma} - \dfrac{2H\Gamma}{kT}\right)$	Γ
Langmuir	$a\dfrac{\Gamma}{\Gamma^\infty - \Gamma}$; $a = \Gamma^\infty\dfrac{k_d}{k_a}$	$\Gamma^\infty \ln\left(\dfrac{\Gamma^\infty}{\Gamma^\infty - \Gamma}\right)$
Frumkin	$a\dfrac{\Gamma}{\Gamma^\infty - \Gamma}\exp\left(\dfrac{2H\Gamma}{kT}\right)$; $a = \Gamma^\infty\dfrac{k_d}{k_a}$	$\Gamma^\infty \ln\left(\dfrac{\Gamma^\infty}{\Gamma^\infty - \Gamma}\right)$

Fig. 1. Theoretical adsorption vs. time for Freundlich kinetics. The values of the apparent diffusion coefficients correspond to different values of the adsorption potential barrier. $D_a = 10^{-6}$ cm^2 s^{-1} is of the order of magnitude of the ordinary diffusion coefficient ($\epsilon_a = 0$). The empirical Freundlich constants used in the calculation are [25]: $m = 0.12$, $K = 1.31 \times 10^{-9}$ mol $^{(1-m)}$ cm$^{-(2-3m)}$. The equilibrium value is $\Gamma_{eq} = 1.56 \times 10^{-10}$ mol cm^{-2}.

Fig. 2. Theoretical adsorption vs. time for Langmuir kinetics, with $\Gamma^\infty = 1.5 \times 10^{-10}$ mol cm^{-2}, $a = 10^{-8}$ mol cm^{-3} and $C^\infty = 10^{-7}$ mol cm^{-3}: (1) diffusion-controlled adsorption ($D = 10^{-6}$ cm^{2}s^{-1}); (2) mixed kinetics in the absence of potential barrier ($D_a = 10^{-6}$ cm^2 s^{-1}); (3) mixed kinetics with potential barrier ($D_a = 10^{-8}$ cm^2 s^{-1}). The equilibrium value is $\Gamma_{eq} = 1.36 \times 10^{-10}$ mol cm^{-2}.

the Freundlich model, for some values of D_a corresponding to different values of the adsorption barrier ϵ_a. The values of the empirical constants m and K are the experimental ones obtained for Triton X-100 at a hexane/water interface reported in Ref. [25]. As expected, the characteristic time of adsorption increases on increasing the energy barrier. This is in agreement with the expression of the characteristic time of adsorption which in the context of the present theory can be written in analogy with that of the diffusion-controlled adsorption (Ref. 10), i.e.

$$\tau_D = \frac{1}{D_a}\left(\frac{\partial \Gamma_{eq}}{\partial C^\infty}\right)^2 \qquad (21)$$

Fig. 2 shows the theoretical curves of $\Gamma(t)$ for diffusion-controlled adsorption, mixed kinetics with $\epsilon_a = 0$ and mixed kinetics with $\epsilon_a \neq 0$, when the Langmuir model is assumed with the values of the empirical parameters, a and Γ^∞, being compatible with the experimental ones found in the literature [10]. By using this theoretical analysis it is always
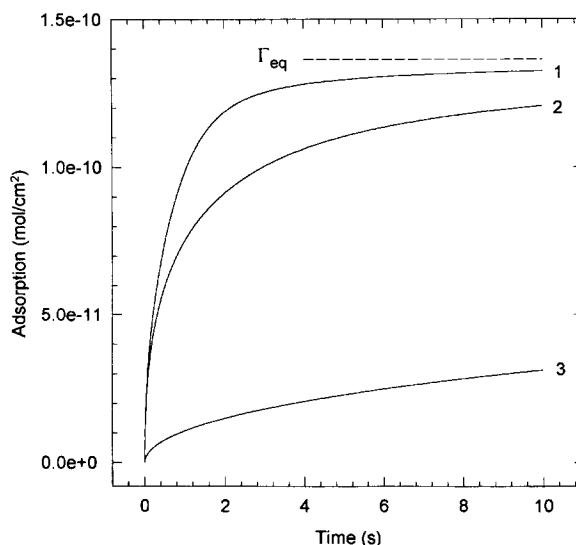
possible to establish if an experimental system follows diffusion-controlled kinetics or mixed kinetics and, in this latter case, to evaluate the adsorption potential barrier. In particular the possibility of mixed kinetics with $\epsilon_a = 0$ can be assessed.

Moreover, as one can expect, diffusion-controlled adsorption is always faster than mixed kinetics.

For the Langmuir model, the relative adsorption Γ/Γ_{eq} as a function of t/τ_D is independent of D_a and Γ^∞, for both diffusion-controlled and mixed adsorption: their behaviour being characterised only by C^∞/a. These plots are shown in Figs. 3a–3c, in order to compare these two types of kinetics as a function of C^∞/a.

The split between the two curves decreases according to the value of C^∞/a and the two processes become practically coincident when $C^\infty/a < 10^{-1}$. Thus, for this model, mixed kinetics in the absence of an adsorption barrier are effectively different from diffusion-controlled kinetics only for $C^\infty/a > 10^{-1}$.

As shown by Figs. 2 and 3, the behaviour of $\Gamma(t)$ at short times is the same for both diffusion-
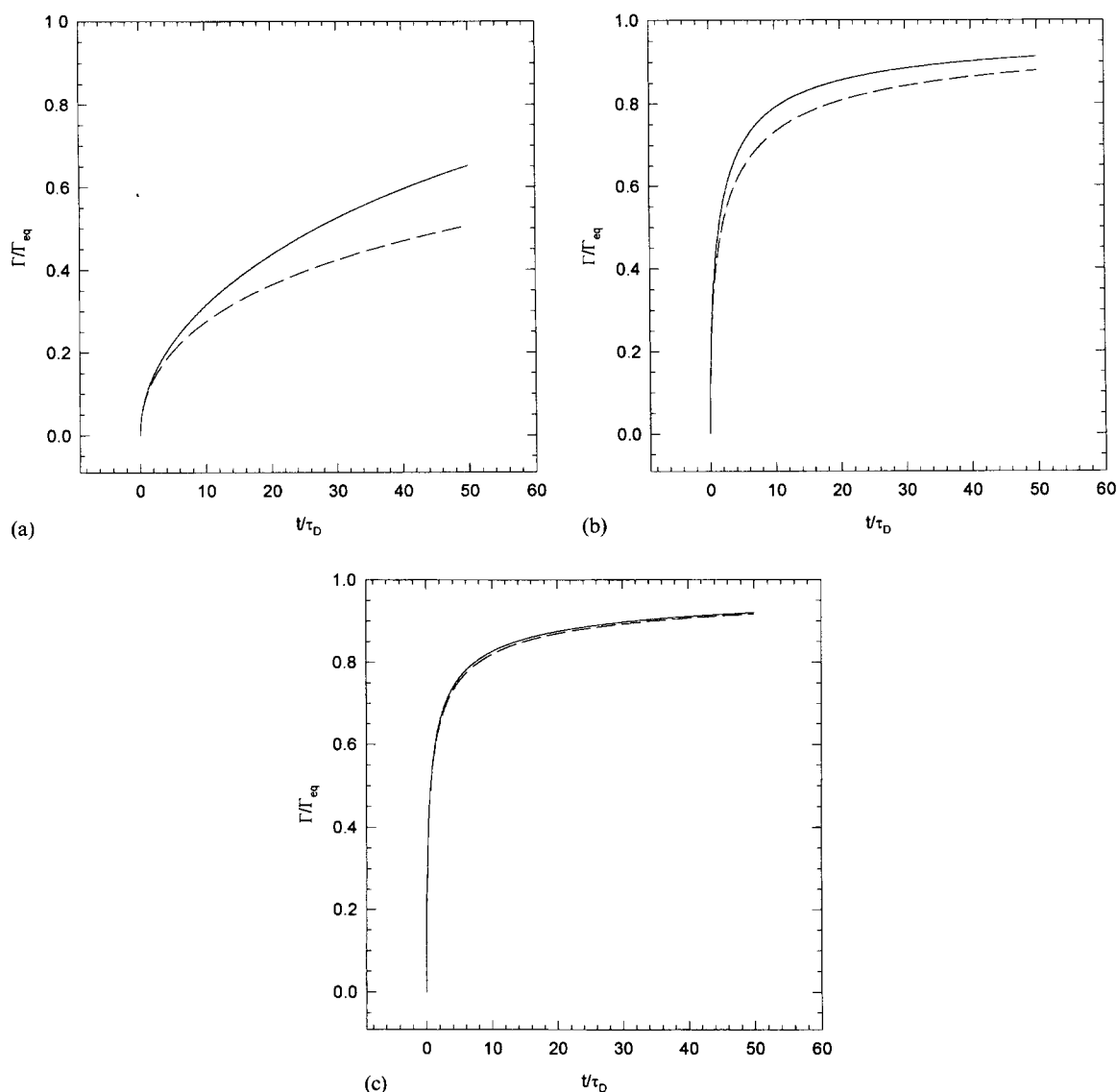
Fig. 3. Predicted influence of C^∞/a on the dimensionless adsorption vs. dimensionless time for Langmuir kinetics under the hypotheses of diffusion-controlled kinetics (solid line) and mixed kinetics (broken line): (a) $C^\infty/a = 10$; (b) $C^\infty/a = 1$; (c) $C^\infty/a = 10^{-1}$.

controlled and mixed kinetics without a barrier; in fact for short times both Eqs. (15) and (18) give:

$$\Gamma(t) = 2C^\infty \sqrt{\frac{D}{\pi}} \sqrt{t} \tag{22}$$

Thus from an experimental point of view, the analysis of the short time data does not help in assessing the difference in the two behaviours. It is then necessary to use a procedure which takes into account the whole experimental kinetics. For this, procedures based on the fitting of Eq. (15) to experimental data seem to be suitable. Moreover, experimental methodologies able to collect large amounts of data during a single adsorption kinetics process are required.

4. Conclusions

In the present paper it has been shown that mixed adsorption kinetics can be described as an extended diffusion problem, for a wide range of surface models by assuming a suitable model. The effect of adsorption barriers is introduced as an apparent diffusion coefficient defined on the basis of the microscopic transport of matter between the bulk and the surface.

One of the interesting consequences of this approach is that the assumptions of local equilibrium and absence of adsorption barriers are independent, so that the theory allows for mixed kinetics even in the absence of an adsorption barrier. In the current literature these two assumptions are generally identical. Although this is correct in some cases, the results of the present work show that justification for this is required. However, on the basis of the present theory, one can deduce that the two assumptions are not equivalent for models taking into account surface saturation, as the case when the Langmuir or Frumkin isotherm is used. Indeed, if surface saturation plays a role in the exchange kinetics, the number of molecules which approach the surface and adsorb decreases with increasing surface coverage. Thus the characteristic time for the kinetic exchange may become comparable with that for diffusion, also without adsorption barriers.

Because in some cases the differences between diffusion-controlled kinetics and mixed kinetics in the absence of adsorption barriers can be visualised experimentally, such studies should be used to verify whether or not surfactant systems exist that follow this type of adsorption kinetics. For this, however, accurate experimental methodologies are needed for the evaluation of Γ over a large temporal range. At present new methodologies are under development, most of them based on the direct measurement of the capillary pressure [26–28] which seems to be sufficiently reliable for this problem.

Appendix 1

Microscopic expression for the diffusion coefficient

Let us consider a geometrical surface $x = x_0$ in the solution. The incident diffusion flux, from the right-hand of the surface, is given by the Fick equation:

$$\Phi_{\text{diff}} = D \left. \frac{\partial C}{\partial x} \right|_{x = x_0} \tag{A1}$$

The same flux can also be written as the difference between the number of molecules crossing the surface $x = x_0$ from the right-hand side and the number of molecules coming from the same surface, from left to right, that is:

$$\Phi_{\text{diff}} = \frac{1}{4} \bar{v} C_{(x_0+d)} - \frac{1}{4} \bar{v} C_{(x_0)} = \frac{1}{4} \bar{v} d \left[\frac{C_{(x_0+d)} - C_{(x_0)}}{d} \right] \tag{A2}$$

where d is the minimum thickness over which a volume concentration can be defined. Thus d is the length scale used for the differentiation of C. As a consequence the macroscopic limit of Eq. (A2) is

$$\Phi_{\text{diff}} = \frac{1}{4} \bar{v} d \left. \frac{\partial C}{\partial x} \right|_{x = x_0} \tag{A3}$$

By comparing Eqs. (A1) and (A3), one obtains:

$$D = \frac{\bar{v} d}{4} \tag{A4}$$

The length d is the same defined in point (2) of Section 2 concerning the model adopted for the theoretical treatment of adsorption kinetics and it is of the order of a few mean free paths. A more precise definition of d is not needed because the solutions of the adsorption problem do not explicitly depend on it. In Refs. [29,30] similar arguments are used to find a relation between the diffusion coefficient and the mean free path of the molecules.

Appendix 2

Numerical solution of Eq. (15)

Eq. (15) can be put into the form:

$$\Psi[\Gamma(t)] = \sqrt{\frac{D_a}{\pi}} \left[2C^\infty \sqrt{t} - 2 \int_0^{\sqrt{t}} C_0(t - \tau) \, \mathrm{d}\sqrt{\tau} \right] \tag{B1}$$

where

$$\Psi = \int_0^\Gamma \frac{1}{g(\mu)}\, d\mu \tag{B2}$$

For the models adopted here, $\psi(\Gamma)$ has the explicit forms listed in Table 1. The numerical solution of Eq. (B1) with the initial condition $\Gamma(0) = 0$ has been obtained as an adaptation of the schema suggested in Refs. [31] and [32]. $\Gamma(t)$ is evaluated at the times $t_{n+1} = n\Delta t$. The sampling interval Δt is constant and it has been chosen to be of the order of 1% of the characteristic time τ_D. The integrals are approximated by the trapezoid rule.

After some rearrangement, the discretization of Eq. (B1) gives:

$$\Psi(t_{n+1}) = \begin{cases} 0 & \text{for } n = 0 \\[2mm] \sqrt{\dfrac{D_a \Delta t}{\pi}}\,[2C^\infty - C_0(t_2)] & \text{for } n = 1 \\[2mm] A_n - \sqrt{\dfrac{D_a \Delta t}{\pi}}\,C_0(t_{n+1}) & \text{for } n \geq 2 \end{cases}$$

$$\tag{B3}$$

where

$$A_n = \sqrt{\frac{D_a \Delta t}{\pi}}\left\{ 2\sqrt{n}\,C^\infty - C_0(t_n) \right.$$

$$\left. - \sum_{j=1}^{n-1} [C_0(t_{n-j}) - C_0(t_{n-j+1})](\sqrt{j+1} - \sqrt{j}) \right\}$$

Note that A_n contains only terms with index $\leq n$. It is then known at each nth calculation step. Eq. (B3) at each n is coupled with the isotherm

$$C_0(t_{n+1}) = \frac{k_d f[\Gamma(t_{n+1})]}{k_a g[\Gamma(t_{n+1})]}$$

and with the expression of $\Psi(t_{n+1})$ calculated by Eq. (B2). Thus, for each $n \geq 1$ one can iteratively solve this system of three equations to obtain $\Gamma(t_{n+1})$ and $C_0(t_{n+1})$.

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