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Historical perspective

Adsorption–desorption kinetics of surfactants at liquid surfaces

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ABSTRACT

The paper discusses adsorption and desorption energy barriers for macroscopic interfaces of surfactant solutions. Literature data suggest that adsorption and desorption are not always fully diffusion controlled. Apart from electrostatic barriers that lead to strong deviations, other types of barriers are less easy to identify, because smaller deviations from diffusion controlled mechanisms are evidenced.

Complete models involving both diffusion and sorption barriers are very complex and involve many adjustable parameters, making the data analysis frequently unreliable. Empirical equations of state are used in most cases, although they are inaccurate, especially close to the *cmc*. The variation of sorption energies with surface concentration is not accurately described in the models. Finally, convection can mask the effect of sorption energy barriers. Experiments are presented to illustrate the main difficulties encountered.

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Contents

1. Introduction

Dynamic phenomena at liquid interfaces are usually modeled using interfacial tension only (see for instance references in [1]). This is in general acceptable for pure fluids, but when surfactants

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are present a number of complications arise: surface tension gradients can be created during the motion of surfactant molecules at the interface (Marangoni effects), and time-dependent adsorption–desorption processes play a role when the interfaces are expanded or compressed. All these phenomena have important consequences in dynamic phenomena involving surfactant solutions, such as wetting/coating, multiphase flow, time evolution of emulsions and foams, among others [1].

In order to understand better adsorption/desorption processes, many studies have been performed [2]. Convection can frequently be neglected in these studies and most literature data were analyzed assuming that the transport toward and away from the interface is controlled by diffusion. However, already in the 1930s, deviations from diffusion controlled adsorption mechanisms were reported, and the existence of adsorption energy barriers was postulated [3]. It was recognized later that some of the deviations were due to surface active contaminants, present either in the liquids or in surfactant batches or produced in situ, for instance by surfactant hydrolysis [4]. The case of desorption energy barriers has received much less attention, although they were clearly evidenced during the exchange of surfactant molecules between micelles and water: in this case, the adsorption is diffusion-controlled, but the desorption time depends on surfactant hydrophobic chain length [5]. One therefore expects that desorption energy barriers will be also present at macroscopic interfaces. During the 1990s commercial instruments became available, which allowed more accurate investigations of adsorption/desorption kinetics at macroscopic interfaces to be performed [2] and many new studies were carried out [6–8].

Adsorption–desorption models involving both diffusion and energy barriers have been proposed in the literature, but they involve a large number of adjustable parameters. Hence, data analysis is difficult even with the more complete data sets obtained with the new accurate methods. In the following, we will review and discuss the recent literature, which deals mainly with surfaces of aqueous solutions containing a single surfactant species. We will therefore limit the discussion to this type of interfaces unless stated otherwise. We will also present experiments done in our laboratory to support the discussion. We will summarize at the end of the review the issues that need further investigations in order to fully clarify which theories can be used to model safely the dynamic behavior of interfaces in practical situations.

2. Theoretical models

Surfactants, being surface active molecules, adsorb at the surface of aqueous solutions. They form a surface monolayer and the surface tension γ is decreased with respect to the surface tension of pure water γ_w. The kinetics of adsorption and desorption is described by diffusive and barrier controlled models.

2.1. Diffusion controlled adsorption

When convection is absent and adsorption and desorption are diffusion limited, Ward and Tordai derived a model for the prediction of the time variation of the surface concentration Γ for the surface of a surfactant solution initially free of surfactant [9]:

$$\Gamma = 2C \sqrt{\frac{D\,t}{\pi}} - 2\sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} C_s(t-\tau)d\sqrt{\tau} \tag{1}$$

where C is the bulk concentration of the surfactant far from the surface, Cs its bulk concentration near the surface (sub-surface region) and D its diffusion coefficient. The second term accounts for the desorption events occurring at long times, preventing the increase of surface concentration above its equilibrium value. At short

times, this term can be neglected and Γ varies linearly with $\sqrt{t}$:

$$\Gamma \sim 2C \sqrt{\frac{D\,t}{\pi}} \tag{2}$$

The equilibrium value of the surface concentration can be calculated from the variation of the surface tension γ with bulk surfactant concentration C, using the Gibbs equation:

$$\Gamma = -\frac{1}{k_B T} \frac{d\gamma}{d\ln C} \tag{3}$$

with k_B the Boltzmann constant, and T the absolute temperature. This equation is valid for dilute solutions and nonionic surfactants. Expressions for ionic surfactants differ by a numerical factor, generally difficult to estimate [10]. Note that Eq. (3) can only be used below the critical micellar concentration (cmc), because above this concentration, micelles form and the surface tension remains constant [11]. In general, the equilibrium surface concentration Γ saturates close to the cmc.

The surface concentration is in general not experimentally accessible and the surface tension is used instead. When there are no energy barriers for adsorption or desorption, one can assume that when surfactant molecules arrive or depart from the surface, the bulk concentration changes instantaneously in such a way that the equilibrium between the amount of surfactant in the bulk and at the surface is maintained. The bulk concentration can then be related to the surface tension using the relations between Γ, γ and C valid at equilibrium: Γ_{eq} (C_{eq}) and γ_{eq} (C_{eq}).

At short times, Γ is small and the surface tension can be written as: $\gamma \sim \gamma_w - k_B T \Gamma$, which using Eq. (2) leads to:

$$\gamma \sim \gamma_w - 2k_B TC \sqrt{\frac{Dt}{\pi}} \tag{4}$$

When the system is close to equilibrium, another approximation is frequently used:

$$\gamma - \gamma_{eq} \sim \frac{k_B T\, \Gamma_{eq}^2}{C} \sqrt{\frac{\pi}{4Dt}} \tag{5}$$

As observed experimentally, the surface tension varies first as $\sqrt{t}$ and at the end of the adsorption process as $1/\sqrt{t}$. Eqs. (4) and (5) were extensively used in the past. Nowadays, Eq. (1) can be integrated numerically, and the whole surface tension versus time curve can be used for data fitting [12]. In general, the surface tension variation with surface concentration is approximated by expressions derived from the Langmuir or Frumkin equations of state. However, the equations of state are generally incompatible with the Gibbs equation [13]. Procedures to avoid the use of these equations and to determine the relation γ_{eq} (Γ_{eq}) directly will be described in §4.

2.2. Role of adsorption and desorption barriers

When there is no instantaneous equilibrium between the bulk and surface concentrations, for instance if there are large adsorption or desorption energy barriers, the surface concentration Γ is no longer linked to the bulk concentration by the Gibbs relation and a more detailed description of the kinetic processes in the vicinity of the adsorbed layer is required. The simplest description of adsorption and desorption kinetics is given by the Langmuir Eq. (10):

$$\frac{d\Gamma}{dt} = k_a C_s(\Gamma_\infty - \Gamma) - k_d \Gamma \tag{6}$$

denoting the surface concentration at saturation by Γ_∞; k_a and k_d are respectively the adsorption and desorption constants, related to the adsorption and desorption energies E_a and E_d by: $k_{a,d} = k^0_{a,d} \exp(E_{a,d}/k_B T)$. When the energies $E_{a,d}$ are small compared to $k_B T$, k_a and k_d are constant. At equilibrium $d\Gamma/dt = 0$ and Eq. (6) leads then to the *Langmuir equation* for $\Gamma(C)$:

$$\frac{C}{a} = \frac{\Gamma/\Gamma_\infty}{1 - \Gamma/\Gamma_\infty} \tag{7}$$

where $a = k_d/k_a$ is the *Szyszkowski* concentration. This equation represents qualitatively well the equilibrium curves $\Gamma(C)$ obtained from the experimental curve $\gamma(C)$ using the Gibbs equation (Eq. (3)). In general, however, adsorption and desorption are activated processes that depend on the surfactant concentration. The popular *Frumkin's* Eq. (10) corresponds to linear variations of E_a and E_d with surface concentration: $E_{a,d} = k_B T \nu_{a,d} (\Gamma/\Gamma_\infty)$. This leads to:

$$\frac{\Gamma/\Gamma_\infty}{1 - \Gamma/\Gamma_\infty} = \frac{C}{a} \exp\left(-\frac{2H}{k_B T}\frac{\Gamma}{\Gamma_\infty}\right) \tag{8}$$

where $H = k_B T (\nu_a - \nu_d)/2$ is an interaction energy related to the concentration dependence of the sorption energies (H is negative when interactions between surfactant molecules in the monolayers are attractive, positive if they are repulsive).

When the surfactant is ionic, the electrostatic energy associated to the charged monolayer also contributes to the adsorption energy. An electrostatic repulsion barrier builds up during the adsorption process and increases with increasing surface concentration, slowing down the adsorption of further surfactant molecules. When there are no other energy barriers than those due to the electrostatic surface potential and when Γ is sufficiently close to Γ_∞ [14]:

$$\frac{(\Gamma/\Gamma_\infty)^3}{1 - \Gamma/\Gamma_\infty} = \left(\frac{C}{b}\right)^2 \tag{9}$$

where $b = (a \lambda \Gamma_\infty^2/2)^{1/2}$, $\lambda = e^2/(\varepsilon k_B T)$ is 4π times the Bjerrum length, e being the elementary electrical charge and ε the dielectric constant.

When diffusion is fast compared to the adsorption/desorption steps, the limiting process is controlled by the sorption barriers. The kinetics are no longer described by the Ward and Tordai equation; Eq. (6) should be used instead. This situation occurs for instance when the surfactant concentration is large. Then diffusion is fast, C_s is constant and equal to the bulk concentration C so Eq. (6) simplifies to:

$$\frac{d\Gamma}{dt} = k_{eff}\left(\Gamma_{eq} - \Gamma(t)\right) \tag{10}$$

with the effective desorption rate $k_{eff} = k_a C + k_d$

The surface concentration then varies exponentially with time:

$$\Gamma = \Gamma_{eq} + \left(\Gamma_0 - \Gamma_{eq}\right) e^{-k_{eff} t} \tag{11}$$

3. Experimental results

Surfactants are able to form micelles and the adsorption/desorption process considered in the present paper should bear resemblance to the exchange of surfactant molecules between micelles and bulk. Let us therefore recall briefly the main features of these exchanges. It is nowadays well established that the adsorption rate to micelles is roughly constant (of the order of $10^{12} \, \text{m}^{-3} \, \text{mol}^{-1} \, \text{s}^{-1}$), whereas the desorption rate varies considerably with chain length, from values of about $10^9 \, \text{s}^{-1}$ for six carbons chains to $10^5 \, \text{s}^{-1}$ for sixteen carbon chains: this rate decreases by a factor of order 10 when two carbons are added to the chain, as the *cmc*, and for the same reasons [5]. This result is currently explained by saying that when a CH_2 group is translated from water to a

hydrophobic environment, the free energy penalty is about $k_B T$ [15]. This results in an energy barrier for desorption, but not for adsorption, which is simply diffusion controlled.

We will now discuss exchanges between surface and bulk for the surfactant solutions

3.1. Barrier-controlled adsorption

3.1.1. Concentrated surfactant solutions

In order to evidence more easily sorption barriers, concentrated solutions were used: in this case, diffusion is fast and adsorption could become fully controlled by the barriers. Note that this applies only to non-electrostatic barriers, because self-screening of the electrostatic interactions occurs in concentrated solutions of ionic surfactants.

A fast technique for the measurement of surface tension is the oscillating jet method, allowing to access times of the order of milliseconds [16]. Other fast techniques include the maximum bubble pressure [17] and the overflowing cylinder [18]. Below 0.1 s, it was shown that convection is important, making the precise data analysis difficult in the case of the maximum bubble pressure method [17]. With the overflowing cylinder, it is possible to measure the velocities using laser Doppler velocimetry. The method was implemented with in situ infrared spectroscopy or ellipsometry: in this way, it became possible to measure directly the surface concentration [18]. Indirect methods such as studies of surface wave propagation allow the determination of the surface elastic modulus, which is affected by the adsorption/desorption kinetics. Unfortunately, an anomalous dissipation is frequently observed, in which case the classical description of the coupling of surface waves (capillary and compression) does not hold, preventing a satisfactory data analysis. To date, the anomalous dissipation remains unexplained although it likely originates from sorption barriers [19].

The first investigations of the existence of sorption barriers were made with fatty alcohols using the jet method and go back to the 1930s. The results were contradictory, many authors claiming that barriers were present in the case of short chain alcohols. The issue was clarified later by Noskov, who identified the possible sources of error in the previous measurements and presented new well controlled experiments, including oscillating jets, maximum bubble pressure and capillary wave propagation studies. These studies clearly demonstrated that adsorption was purely diffusion controlled whatever the alcohol chain length [16].

Joos et al., besides alcohol solutions, also investigated concentrated surfactant solutions: fatty acids, bolaforms (surfactants with two polar heads), an ionic surfactant (SDS, sodium dodecylsulfate) and a series of cationic surfactants with different chain lengths (C_nTAB, alkyl trimethyl ammonium bromides), with or without small amounts of added salt. They found that for aqueous solutions of these surfactants, k depended linearly on the surfactant bulk concentration, k_d was nearly independent of chain length with k_d/Γ_∞ of the order of $100 \, \text{s}^{-1}$ for all systems, while k_a increased significantly with chain length roughly as the inverse of the critical micellar concentration (*cmc*)[20–22]. These results are quite puzzling, because they are exactly the opposite of what is found for the exchange of surfactant molecules between micelles and bulk. However, the data should be re-analyzed because these authors also evidenced barriers in the case of fatty alcohols and it is now known that they cannot be observed with the techniques used. In their data analysis, Joos et al. considered that the bulk concentration was homogeneous up to the sub-surface region throughout the experiments while convection should be important and needs to be taken into account [23].

There is another relaxation process in concentrated surfactant solutions containing micelles, in which the micelles break as a whole, with a rate much lower than the rate of expulsion of a single surfactant from the micelles. These rates are however still too fast to be detected for surfactants with small chain lengths [5]. It is thus generally admitted that micelles do not adsorb as a whole at liquid surfaces; they are rather

depleted, but they dissociate fast and serve as reservoirs of monomers [6,24]. When the surfactant chain length is large however, the micelle lifetime can be longer than the diffusion time, as recently observed in overflowing cylinder experiments [25,26]. Micelles then break directly at the surface as in the case of lipid vesicles which have still longer lifetimes [27].

3.1.2. Dilute solutions of ionic surfactants. Electrostatic adsorption barriers

Exponential time variations of the surface tension, as predicted by Eq. (11), have been seen in the case of adsorption of ionic surfactants once diffusion has brought sufficient surfactant at the surface to create a repulsive electrostatic barrier [14,28]. A theoretical analysis allows evaluating the electrostatic contribution to the energy barrier [29]. Fig. 1 shows measurements made on aqueous solutions of dodecyl trimethyl ammonium bromide (DTAB) done with a maximum bubble pressure instrument. The prediction for diffusion limited adsorption is shown in Fig. 1 left, and a clear deviation is seen at long times. The inset shows a semi-log plot of $\gamma - \gamma_{eq}$, evidencing an exponential final decay. Fig. 1 right shows the same curve together with that measured with a solution containing salt, in order to screen the electrostatic potential: the adsorption is purely diffusion controlled in this case.

These results may seem contradictory with the behavior observed with micelles. However, the electrostatic barriers are observed not only in the absence of salt but also at small surfactant concentrations, smaller than the *cmc*, in order to keep the ionic strength of the solutions small. This could be why electrostatic barriers were not observed in micellar systems.

3.2. Mixed diffusion-kinetic transport

Other methods such as the expanding [30] or pendant drop [31] and similar experiments in Langmuir troughs were also used to address the issue of surfactant transfer between bulk solution and interface. Because the times accessible with these methods are longer, more dilute solutions were used and the surface tension evolves both due to diffusion and exchanges between sub-surface and surface. Although there is a relative consensus on the adsorption behavior from dilute solutions, fitting adsorption and desorption data with diffusion-controlled transport frequently provides diffusion coefficients smaller than expected. The fitted coefficients can differ by as much as a factor of three between adsorption and desorption experiments, even when performing experiments with the same solutions [32]. Mixed diffusion-kinetic transport models were therefore proposed [12,33]. It was found that assuming constant values for k_a and k_d in Eq. (6) (i.e. constant energy barriers), was not sufficient to fit the data, but that a linear dependence of adsorption and desorption energies on Γ was necessary. This is consistent with

the fact that Eq. (6) leads to the Langmuir equation of state at equilibrium (dΓ/dt = 0), while with the corrections adopted, a Frumkin equation of state is obtained, which usually better fits equilibrium surface tension data. The desorption rates k_d, although scattered, have been found much smaller for long chain alcohols such as decanol ($\sim$10 s^{-1} [34], 2.7 s^{-1} [35], 0.1 s^{-1} [36]) than for shorter chained ones, from propanol to heptanol ($\sim$100 s^{-1}) [21]. However, the concentrations studied were smaller roughly by a factor 1000 (in the range 10 to 100 μM in ref [34–36] instead of 10 to 100 mM in [21]), and one could argue that the differences in k_d are possibly due to the influence of the surface concentration (which also increases with chain length) on the energy barriers. Note however that experiments with faster techniques did not evidence any energy barrier at all for alcohols.

Experiments with nonionic surfactants, of the alkyl polyoxyethylene glycol ethers series (C_iE_j, i.e. a chain with i carbon atoms and j oxyethylene groups) were also performed. For $C_{12}E_6$, Pan et al. [33] found $k_d \sim 1.4 \times 10^{-4}$ s^{-1}, whereas Lucassen and Giles [37] found that the surfactant transport was diffusion controlled. Pan et al. claim that the difference is due to the fact that Lucassen and Giles use too many parameters for data fitting. Lee et al. [32] studied the series C_iE_8 and, at the difference of alcohols [21], they found that the desorption rate varies considerably with hydrocarbon chain length (a factor 15 when i changes by a factor 2), whereas the adsorption rate is relatively constant: $k_a \sim 6$ m^{3}mol^{-1} s^{-1}. More complete studies on both alcohol and nonionic surfactants showed that k_a increased linearly with bulk concentration, remaining in the range (0.1–10^3) m^{3}mol^{-1} s^{-1} [38]. This result is compatible with the findings for surfactant exchanges with micelles, although the rates are lower by many orders of magnitude [5].

It should be noted that the noise in standard dynamic surface tension curves makes the exact determination of the sorption rates difficult especially when diffusion is the major contribution to the transport process. Furthermore, in the investigations described above, the surface tension needs to be related to the surface concentration and the equation used is usually an empirical equation of state $\gamma_{eq}(\Gamma_{eq})$.

Recent experiments were performed with extremely dilute solutions of nonionic surfactants $C_{12}E_6$, $C_{12}E_5$, $C_{12}E_3$ and of an ionic surfactant, CTAB (in the presence of large amounts of salt, 0.1 M) [30,39]. This allowed to slow down diffusion and to determine the exact function $\Gamma_{eq}(C_{eq})$, using a bubble technique. It was also found that for both $C_{12}E_6$ and CTAB, the transport to the surface was diffusion controlled [30].

3.3. Use of convection

Methods using rinsing and stirring procedures were introduced some years ago to speed up diffusion and to evidence possible sorption
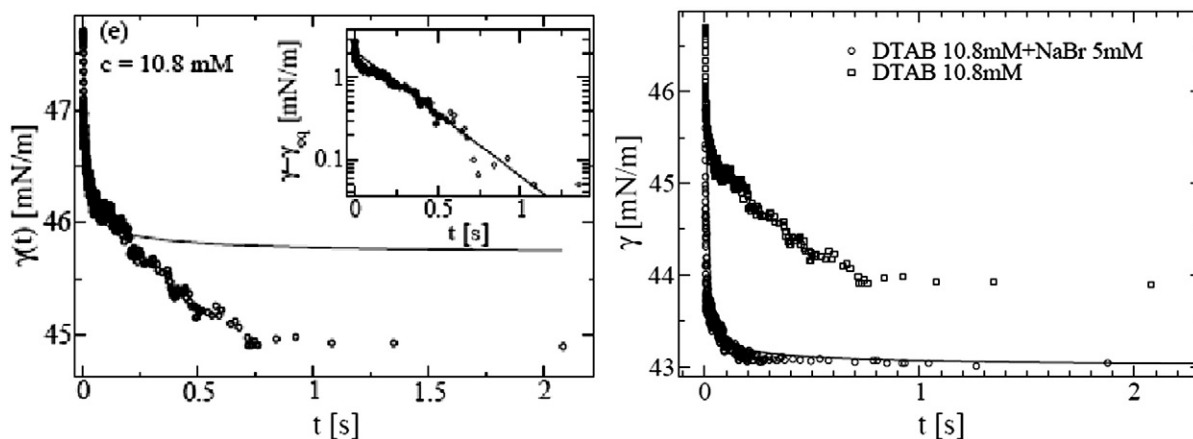

Fig. 1. Surface tension versus time for solutions containing 10.8 mM DTAB. Left: the line is the prediction for diffusion-limited adsorption; inset: the line is an exponential fit. Right: comparison of data in the presence and absence of salt. Data from [28].

barriers. Desorption barriers were reported for a series of alkyl dimethyl phosphine oxides [40]. The measured desorption coefficients k$_d$ were found to be 4.1×10^{-3} s^{-1} (C8, eight carbon chain), 2.8×10^{-3} s^{-1} (C10), 2.1×10^{-3} s^{-1} (C12), and 5.5×10^{-4} s^{-1} (C14). These coefficients are much smaller than those measured with micelles and decrease with chain length instead of increasing. In other experiments, sorption barriers were found absent in solutions of anionic surfactants [41,42]. Exceptions are CTAB with no salt added, where an electrostatic adsorption barrier was evidenced (as in the experiments quoted in §3.1) and pluronics, which are polymeric surfactants that adsorb quasi-irreversibly [41].

The rinsing mechanism was investigated further recently using neutron reflectometry to directly measure the surface concentration Γ [43]. The authors investigated sodium dodecylbenzene sulfonate solutions and showed that desorption was purely diffusion controlled.

Alvarez et al. introduced a microtensiometer that measures dynamic surface tension at microscale surfaces. Since the diffusion time decreases with decreasing radius of curvature, the microtensiometer increases the range of measurable kinetic processes. Dynamic surface tension measurements for C$_{12}$E$_8$ were shown to follow diffusion-limited dynamics [44]. In a later study, these authors used a low Reynolds number flow in the bulk solution to further increase the rate of diffusion. The transition from diffusion to kinetic-limited transport was still not observed for the surfactants considered C$_{12}$E$_8$ and C$_{14}$E$_8$, but lower bounds on the adsorption and desorption rate constants were determined that are much larger than previously reported rate constants [45].

It should be noted that convection is expected to not only speed up diffusion but also to facilitate adsorption when barriers are present. In experiments with SDS at oil–water interfaces [14], the equilibrium was reached after many hours when measurements were made with a pendant drop and in a few minutes when they were made using a Wilhelmy plate, in which case, withdrawal of the plate may create convection at the level of the interface. This effect has been quantified in the case of nanoparticle surface layers: in this case, the adsorption energy barrier E$_a$ is huge, and the particles only come at the surface if vigorous stirring is used, so that the hydrodynamic energy exceeds E$_a$ [46]. The adsorption kinetics of nanoparticles at the air–water surface strongly accelerates when interfacial compression/expansion cycles are used [47].

In summary, despite the large number of studies since the 1930s, the question of adsorption and desorption barriers is still surprisingly far from clear, except perhaps for the case of electrostatic barriers. We will illustrate in the following the difficulties encountered in the analysis of such measurements using two model surfactant systems: C$_{12}$E$_6$, a non-ionic surfactant, and CTAB with 100 mM of added NaBr, a cationic one with sufficient added electrolyte that no electrostatic barriers should be present. We will also discuss how to model the desorption of these surfactants from air–water interfaces.

4. Illustrations of difficulties

4.1. Equations of state

In most reported studies, the surface tension is measured and an equation of state (Langmuir, Frumkin etc.) is used to link γ and Γ. It was shown [32] that the kinetic data are better described when the sorption energies are written as:

$$E_{a,d} = k_B T \, \nu_{a,d} (\Gamma/\Gamma_\infty)^n \qquad (12)$$

leading to:

$$\frac{\Gamma/\Gamma_\infty}{1-\Gamma/\Gamma_\infty} = \frac{C}{a} \exp\left[-\frac{2H}{k_B T}\left(\frac{\Gamma}{\Gamma_\infty}\right)^n\right] \qquad (13)$$

The case $n = 1$ corresponds to the Frumkin Eq. (8). The relation $\gamma(\Gamma)$ then writes:

$$\gamma-\gamma_w = \Gamma_\infty k_B T \, \ln \, (1-\Gamma/\Gamma_\infty) - 2n \, H\Gamma_\infty(\Gamma/\Gamma_\infty)^{n+1}/(n+1) \qquad (14)$$

It has been shown long ago that such an empirical equation of state introduces large errors in the calculations of equilibrium monolayer properties, especially close to the *cmc* and that relating the surface tension to surface concentration with the Gibbs equation was a better option provided one needs to transform surface tension data into surface concentration data [48]. It was also shown recently that the empirical equations of state are not valid from a thermodynamic point of view [13]. Procedures to avoid the use of these equations and to determine $\gamma(\Gamma)$ directly were devised as described in §3. These procedures involve ellipsometry, vibrational spectroscopy or neutron reflectivity [18,43]. Bubble methods can also give access to the equation of state when extremely dilute surfactant solutions are used [30,39].

We will illustrate below the difference between empirical and experimental equations of state. In the experiment, a bubble is rapidly compressed, so the surface concentration is increased by the ratio of initial to final area to a value Γ. The surface concentration becomes rapidly homogeneous as surface tension gradients result in fast surface
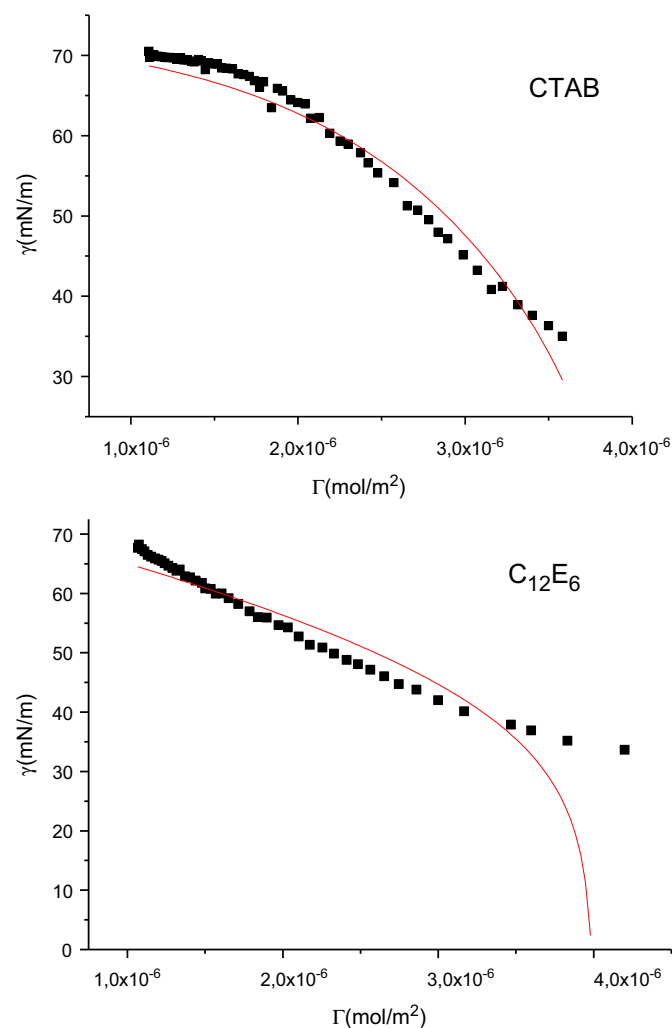

Fig. 2. Equilibrium equation of state for CTAB (+0.1 M salt) and C$_{12}$E$_6$. Points are experimentally determined and the curve is the fit with the equation of state 14. We fixed $\gamma_w = 72.2$ mN/m and $\Gamma_\infty = 4 \times 10^{-6}$ mol/m^2, as determined independently [30]. The best fits were obtained with $n = 2.48$ and $2H/k_B T = 4.35$ for CTAB and $n = 0.06$ and $2H/k_B T = 34.9$ for C$_{12}$E$_6$.

convection. The surface tension decreases just after the expansion, but diffusion toward the bulk is slow in view of the extremely small surfactant concentration and desorption has no time to proceed. This then gives the value of the equilibrium surface tension γ for an equilibrium surface concentration Γ [30]. The experimental equations of state for the two surfactants are shown in Fig. 2.

One sees that the empirical equation of state 14 fits poorly the experimental data, especially close to Γ_∞, i.e. for solutions close to the *cmc*. When these empirical equations are used to fit of dynamic surface tension data, it is therefore likely that wrong values for the sorption barriers will be obtained.

4.2. Desorption experiments

Experiments on these extremely dilute solutions were also used to investigate the adsorption kinetics which was found purely diffusion-controlled in both cases [30]. We will describe below desorption experiments. The surface tension has been measured, and converted to a surface concentration, the relaxation of which after a compression is shown in Fig. 3.

4.2.1. Diffusion-limited desorption

Diffusion limited desorption can be described by an approach similar to that of Ward and Tordai, modified to describe diffusion away from a curved interface, in order to predict the time variation of the surface concentration. Details can be found in the appendix.
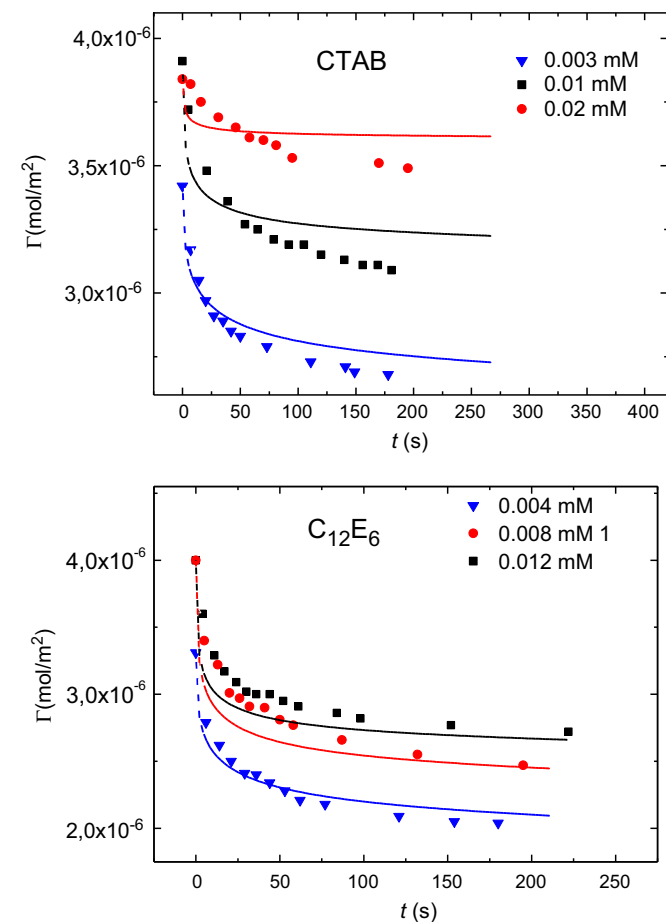
Fig. 3. Time variation of the surface concentration as a function of time after rapid compression, for different bulk concentrations. The lines are simulations with a diffusion model, with no adjustable parameters, using the diffusion constants measured for the adsorption process with the same solutions: 3.8×10^{-10} m^2/s for C$_{12}$E$_6$ and 3.0×10^{-10} m^2/s for CTAB.

Fig. 3 shows that desorption is slower than what is expected in a diffusion limited case. For both systems, the difference between calculations and experiments becomes more important at high surfactant concentrations. This suggests that the relaxation may not be purely diffusion limited, and that a desorption energy barrier influences the desorption process, this energy barrier increasing when the equilibrium surface concentration increases.

One could of course argue that better fits could be obtained leaving the diffusion coefficient adjustable. This has been remarked by other authors who could fit desorption data nicely with the diffusion equation but found different diffusion coefficients for the different concentrations of the same surfactant, which of course is unphysical [32] and also leads the authors to conclude the presence of a barrier.

4.2.2. Kinetically controlled desorption

Having seen that the desorption is not purely diffusion controlled, let us show the results using a kinetically controlled desorption model. In the case of kinetically limited desorption there is no equilibrium between the interface and the bulk solution, and it is assumed that the diffusion of the molecules out of the interfacial layer is faster than the molecular transfer between interface and sub-surface: the concentration in the subsurface layer and in the bulk are then equal and constant in time. Note that here, Γ was deduced from γ using the equation of state. This is however not in contradiction with the fact that surface and bulk are not equilibrated; it just assumes that the monolayer reaches equilibrium much more quickly.

Eq. (10) predicts that $\Gamma(t)$ is exponential $\Gamma = \Gamma_{eq} + (\Gamma_0 - \Gamma_{eq}) \exp(-k_{eff} t)$, where Γ_0 is the initial surface concentration. Fig. 4 shows the results of the fits for the data of Fig. 3 with the two surfactants.
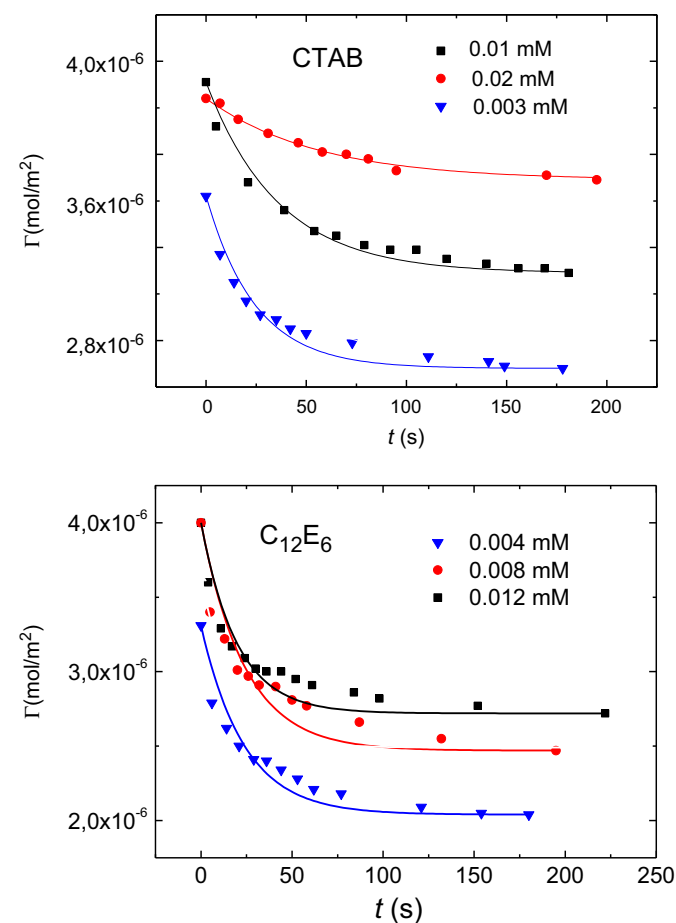
Fig. 4. Exponential fits for the surface concentration time evolution after a rapid compression for the two surfactant solutions CTAB/100 mM NaBr and C$_{12}$E$_6$.

As seen in Fig. 4, these data can also be described by an exponential decay. The fits are far from perfect but (especially for CTAB) the quality is better than that obtained using the diffusion limited desorption model (Fig. 3). The desorption rate constants k_{eff} are found constant for both surfactants, at 0.04–0.05 s^{-1} for $C_{12}E_6$ and 0.02–0.04 s^{-1} for CTAB.

4.2.3. Mixed diffusion-kinetic desorption

Because no satisfactory fits were obtained with either diffusion-controlled or barrier-controlled models, we tried the mixed model of ref [32]. We used a 10^{-5} M CTAB solution with 100 mM NaBr. The different curves shown in Fig. 5 are for different initial compressions. The value of Γ_0 is thus different for the three curves.

As in ref 26, we solved simultaneously Eq. (1) (to which the curvature term was added, see Appendix) and Eq. (6). We assumed that k_a and k_d were the same as those used to fit the equation of state (Fig. 2). As in ref 26, we assumed that k_a was constant, the only adjustable parameter being k_d^0.

One can see in Fig. 5 that the quality of the data fitting is good, but the values obtained for k_d^0 depend on Γ_0. From bottom to top: for $\Gamma_0 = 3.4$ mol/m^2, $k_d^0 = 2 \ 10^{-3} \ s^{-1}$, for $\Gamma_0 = 3.6$ mol/m^2, $k_d^0 = 8 \ 10^{-4} \ s^{-1}$ and for $\Gamma_0 = 3.9$ mol/m^2, $k_d^0 = 4 \ 10^{-4} \ s^{-1}$. It is therefore not possible to fit the data with a constant k_d^0, meaning that the chosen surface concentration variation for the sorption energies is not appropriate. This result in itself is not suprising, in view of the poor fits obtained for the equation of state, but it demonstrates that the data fitting should involve supplementary parameters. Since the deviations to diffusion-controlled adsorption mechanisms are small, it seems difficult to extract many more parameters from data fitting.

5. Conclusions

The existence of adsorption and desorption barriers for macroscopic interfaces in surfactant solutions has been postulated already in the 1930s. Since then, a considerable amount of work has been devoted to the question. In contrast to the surfactant exchanges between micelles and the solution, which are now well described, surfactant exchanges between the surface monolayer and the solution still remain poorly understood. A large number of contradictory data are reported in the literature. The origin of the discrepancies lies in the inaccuracies of the different models used. Complete models involving both diffusion and sorption barriers are however very complex and involve many adjustable parameters.

Experiments converge to indicate that in some cases, adsorption and desorption are not fully diffusion controlled. The case of electrostatic barriers is the clearest, because the observed kinetics are very different from diffusive kinetics. The case of other types of barriers is less obvious, because experiments only evidence small deviations from diffusion controlled mechanisms.

The use of empirical equations of state is frequent. We have illustrated here how different the surface concentrations predicted by these equations are from the actual concentrations, especially close to the *cmc*. These differences make the data analysis difficult, because it is not practical to handle an equation of state which has no explicit form.

Models frequently assume that the sorption energies are simple functions of surface concentrations, i.e. power laws. Experiments suggest that these dependencies are not appropriate and that more parameters are needed for the data analysis.

Finally, experiments show that electrostatic adsorption barriers are lowered and even suppressed when convection is present. This questions the validity of sorption barrier determinations, especially in experiments where convection is used to speed up the diffusion process

In summary, much work remains to be done to fully clarify the adsorption–desorption kinetics at liquid interfaces.

Appendix A. Materials and methods

A.1. Materials

Two surfactant systems were studied, a nonionic surfactant, hexaethylene glycol monododecyl ether ($C_{12}E_6$) and an ionic one, hexadecyl trimethyl ammonium bromide (CTAB) with 100 mM sodium bromide NaBr in order to screen the electrostatic interactions. All chemicals are from Sigma Aldrich.

A.2. Experimental methods

All the experiments were carried out using a rising bubble tensiometer Tracker (Teclis, France). During the experiments, a bubble was created and then after some time (aging of the interface) it was compressed quickly so as to increase the surface concentration rapidly above its equilibrium value. As soon as the compression was stopped, the surface tension (γ) as a function of the time (t) was recorded as it increased due to the re-equilibration of the surface concentration. The relation between sub-surface concentration and surface concentration Cs (Γ) has been obtained by linking the experimental equilibrium surface tension data γ (C) and the equation of state γ (Γ), the diffusion coefficient is taken as found in adsorption experiments, which means that there are no adjustable parameters in the calculations.

A.3. Simulations. Diffusion limited desorption

Matlab simulations have been performed to study the variations of surface concentration with time during the desorption process. Because the experiments were performed with drops, we have used the generalized Ward and Tordai equation in which the term $D/b \ [Ct - \int_0^t C_s(t)d\tau]$ is added to Eq. (1), b being the bubble radius [32]. The concentration profile from the sub-surface to the bulk infinitive can thus be obtained. The input parameters include the initial sub-surface concentration, the relation of the surface concentration with the sub-surface concentration and also the diffusion constant values. The initial sub-surface concentration can be obtained from the equilibrium relation of the surface concentration with the sub-surface concentration and the known initial surface concentration. At each step of the simulation, a concentration profile from the sub-surface to the bulk can be obtained. By increasing
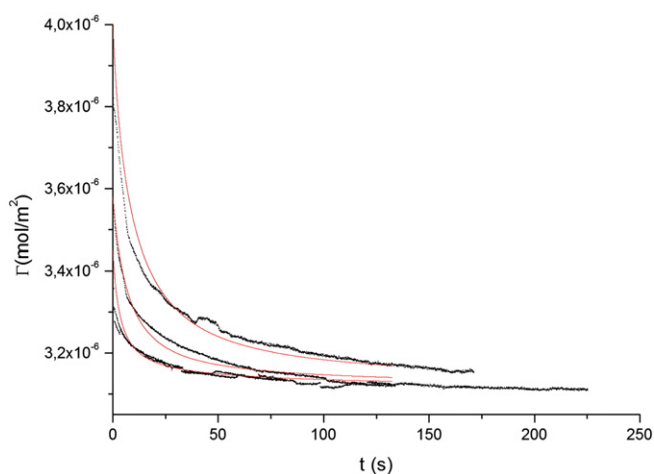
Fig. 5. Time variation of the surface concentration for a solution containing 10^{-5} M CTAB + 0.1 M NaBr after a rapid compression with different amplitudes. Fits with a mixed diffusion-barrier controlled model.

the simulation steps, the concentration profile from the sub-surface to the bulk becomes flatter, meaning that the convergence is gradually reached. At the end of the process, the time variation of the surface concentration is obtained.

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