

Kinetics of surfactant adsorption at fluid/fluid interfaces: non-ionic surfactants

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Abstract. – We present a model treating the kinetics of adsorption of soluble surface-active molecules at the interface between an aqueous solution and another fluid phase. The model accounts for both the diffusive transport inside the solution and the kinetics taking place at the interface using a free-energy formulation. In addition, it offers a general method of calculating dynamic surface tensions. Non-ionic surfactants are shown, in general, to undergo a diffusion-limited adsorption, in accord with experimental findings.

Surface-active agents (*surfactants*) play a major role in various fields, including petrochemical technologies, detergents, biological systems, etc. In some important cases, equilibrium properties of the surfactant adsorption are not sufficient, and knowledge of kinetic processes is required. In particular, we mention processes of fast wetting, foaming and the stability of liquid films. The kinetics of surfactant adsorption have been addressed by numerous experimental and theoretical studies, and various experimental techniques have been devised, primarily aimed at the measurement of dynamic interfacial tensions [1].

The pioneering theoretical work of Ward and Tordai [2] formulated a time-dependent relation between the surface density of surfactants adsorbed at an interface and their concentration at the sub-surface layer of solution, assuming a diffusive transport from the bulk solution. Consequent theoretical works have focused on providing a second closure relation between these two variables. Various relations have been suggested, resembling equilibrium isotherms [3], [4], or having a kinetic differential form [5], [6]. Such theories have been quite successful in describing the experimentally observed adsorption of common non-ionic surfactants. Yet, they suffer from several drawbacks: i) The closure relation between the surface density and sub-surface concentration, which expresses the kinetics taking place just at the interface, is introduced as an *external* boundary condition, and does not uniquely arise from the model itself; ii) the calculated dynamic surface tension relies on an *equilibrium* equation of state, and assumes that it also holds out of equilibrium [7]; iii) similar theories cannot be successfully extended to describe more complicated, *ionic* surfactant solutions [8]. In the current paper we would like to briefly present an alternative approach, overcoming these three drawbacks.

Consider an interface between an aqueous solution of non-ionic surfactants and an air or oil phase at $x = 0$. At $x \rightarrow \infty$, the solution is in contact with a bulk reservoir of surfactants, where the chemical potential and surfactant volume fraction are fixed to be μ_b and ϕ_b , respectively. We consider a dilute solution, *i.e.* the surfactant volume fraction is much smaller than unity throughout the solution. The concentration is also smaller than the critical micelle concentration (cmc), so the surfactants are dissolved only as monomers. At the interface itself, however, the volume fraction may become large.

We write the excess in free energy per unit area due to the interface (*i.e.* the change in interfacial tension) as a functional of the surfactant volume fraction in the bulk solution, $\phi(x > 0)$, and its value at the interface, ϕ_0 , $\Delta\gamma[\phi] = \int_0^\infty \Delta f[\phi(x)]dx + f_0(\phi_0)$. The first term is the contribution from the bulk solution, whereas the second is the contribution from the interface itself. The sharp, “step-like” profile considered has led us to treat the bulk solution and the interface as two coupled sub-systems, rather than a single one [9]. The bulk sub-system is considered as an ideal, dilute solution, including only ideal entropy of mixing and the contact with the reservoir, and neglecting gradient terms,

$$\Delta f(\phi) = \{T[\phi \ln \phi - \phi - (\phi_b \ln \phi_b - \phi_b)] - \mu_b(\phi - \phi_b)\}/a^3, \quad (1)$$

where a denotes the surfactant molecular dimension and T the temperature (we set the Boltzmann constant to unity). However, since ϕ_0 may become much larger than $\phi(x > 0)$, we must take into account at the interface the finite molecular size and interactions between surfactant molecules,

$$f_0(\phi_0) = \{T[\phi_0 \ln \phi_0 + (1 - \phi_0) \ln(1 - \phi_0)] - \alpha\phi_0 - (\beta/2)\phi_0^2 - \mu_1\phi_0\}/a^2. \quad (2)$$

The first term is due to the entropy of mixing, recalling that ϕ_0 is not necessarily small; the second accounts for the energetic preference of the surfactants to lie at the interface; the third is the energy of lateral attraction between neighbouring surfactants at the interface; and the last term accounts for the contact with the solution adjacent to the interface, where the chemical potential is μ_1 .

Variation of $\Delta\gamma$ with respect to $\phi(x)$ yields the excess in chemical potential at a distance x from the interface, $\Delta\mu(x) = a^2\delta\Delta\gamma/\delta\phi(x) = T \ln \phi(x) - \mu_b$ for $x > 0$, and $\Delta\mu_0 = a^2\delta\Delta\gamma/\delta\phi_0 = T \ln[\phi_0/(1 - \phi_0)] - \alpha - \beta\phi_0 - \mu_1$. From these equations we can deduce, as expected, $\mu_b = T \ln \phi_b$ and $\mu_1 = T \ln \phi_1$, where ϕ_1 denotes the sub-surface volume fraction.

Thermodynamic equilibrium. – In equilibrium the chemical potential is equal to μ_b throughout the entire system (the variations of $\Delta\gamma$ vanish). From the variation with respect to $\phi(x)$ we obtain the equilibrium profile, $\phi(x) \equiv \phi_b$ for $x > 0$, and from the variation with respect to ϕ_0 the equilibrium adsorption isotherm,

$$\phi_0 = \phi_b / [\phi_b + \exp[-(\alpha + \beta\phi_0)/T]]. \quad (3)$$

We have recovered the *Frumkin adsorption isotherm*, which reduces to the well-known *Langmuir adsorption isotherm* [10] when the interaction term is neglected ($\beta = 0$). From eq. (2) and the above variations one also obtains the equilibrium equation of state, $\Delta\gamma = [T \ln(1 - \phi_0) + (\beta/2)\phi_0^2]/a^2$, expressing the equilibrium dependence of the surface pressure, $\Pi = -\Delta\gamma$, on the surface coverage, ϕ_0 , according to a lattice-gas model.

Out of Equilibrium. – We assume proportionality between velocities and the chemical-potential gradient [11], and take the surfactant mobility to be D/T , according to the Einstein relation (D being the surfactant diffusivity). At positions not adjacent to the interface we obtain for the surfactant current density $j(x) = -\phi(D/T)\partial\mu/\partial x = -D\partial\phi/\partial x$, and

applying the continuity condition, $\partial\phi/\partial t = -\partial j/\partial x$, get the ordinary *diffusion equation*, $\partial\phi/\partial t = D\partial^2\phi/\partial x^2$.

The proximity of the interface requires a more careful treatment. First, we discretize the expression for $\Delta\gamma$ on a lattice with cells of length a , $\Delta\gamma[\phi] = a\sum_{i=1}^{\infty}\Delta f(\phi_i) + f_0(\phi_0)$, where $\phi_i \equiv \phi(x = ia)$. Discretized current densities, j_i , can be similarly defined. Since we do not allow molecules to leave the interface towards the other phase ($j_0 = 0$), we have from continuity $\partial\phi_0/\partial t = -j_1/a$, and can therefore write $\partial\phi_1/\partial t = -(j_2 - j_1)/a = (D/a)\partial\phi/\partial x|_{x=a} - \partial\phi_0/\partial t$. Applying the Laplace transform to the equations for $\partial\phi/\partial t$ and $\partial\phi_1/\partial t$ while assuming an initial uniform state, $\phi(x, t = 0) \equiv \phi_b$, a relation is obtained between the surface coverage and sub-surface volume fraction,

$$\phi_0(t) = (1/a)\sqrt{D/\pi} \left[2\phi_b\sqrt{t} - \int_0^t \phi_1(\tau)(t - \tau)^{-1/2}d\tau \right] + 2\phi_b - \phi_1. \quad (4)$$

This relation is similar to the classical result of Ward and Tordai [2], except for the term $2\phi_b - \phi_1$. The difference is due to fine details we have considered near the interface and our initial condition, and it vanishes when a goes to zero. Finally, we find the equation determining the kinetics at the interface itself,

$$\partial\phi_0/\partial t = \phi_1 D(\mu_1 - \mu_0)/a^2 T = (D/a^2)\phi_1 \{ \ln[\phi_1(1 - \phi_0)/\phi_0] + \alpha/T + \beta\phi_0/T \}. \quad (5)$$

Note that the conditions at the interface are very different from those inside the aqueous solution, and the diffusivities, D , appearing in the equations above, cannot be expected to have strictly the same value. Solution of eqs. (4) and (5) allows one to find the time-dependent surface coverage, $\phi_0(t)$.

By writing the above equations, we have separated the kinetics of the system into two coupled kinetic processes. The first takes place inside the bulk solution and is described by eq. (4), whereas the second takes place at the interface and is described by eq. (5). Two limiting cases correspond to the relative speed of these two processes. i) *Diffusion-limited adsorption* applies when the process inside the solution is much slower than the one at the interface. One can then assume that the interface is in constant equilibrium with the adjacent solution, *i.e.* the variation with respect to ϕ_0 vanishes, so ϕ_0 immediately responds to changes in ϕ_1 via the equilibrium isotherm. ii) *Kinetically limited adsorption* takes place when the kinetic process at the interface is the slower one. In this case, the solution is assumed to be in constant equilibrium with the bulk reservoir, *i.e.* the variation with respect to $\phi(x)$ vanishes [$\phi(x > 0) = \phi_b$], and ϕ_0 changes with time according to eq. (5).

Looking at eq. (4) we can identify the *time scale of diffusion* for attaining the equilibrium coverage, $\phi_{0,\text{eq}}$,

$$\tau_d = (\phi_{0,\text{eq}}/\phi_b)^2 a^2 / D. \quad (6)$$

Characteristic values of a^2/D correspond to very short times (on the order of nanoseconds), but the prefactor of $(\phi_{0,\text{eq}}/\phi_b)^2$ is typically very large (on the order of, say, 10^{11}). Thus, the diffusion time scales may reach minutes, as indeed observed in practice. In order to estimate the *time scale of kinetic adsorption* at the interface, we examine the asymptotic behaviour of eq. (5) close to equilibrium and find ⁽¹⁾ $\phi_{0,\text{eq}} - \phi_0(t) \sim \exp[-t/\tau_k]$, with

$$\tau_k \simeq (\phi_{0,\text{eq}}/\phi_b)^2 (a^2/D) \exp[-(\alpha + \beta\phi_{0,\text{eq}})/T]. \quad (7)$$

(1) Close to equilibrium we can also write eq. (5) as

$$\partial\phi_0/\partial t \simeq (D\phi_b/a^2\phi_{0,\text{eq}})[\exp[(\alpha + \beta\phi_0)/T]\phi_1(1 - \phi_0) - \phi_0],$$

which coincides with the adsorption-desorption form of the Frumkin (or Langmuir, when $\beta = 0$) kinetic equation used by previous authors [5], [6].

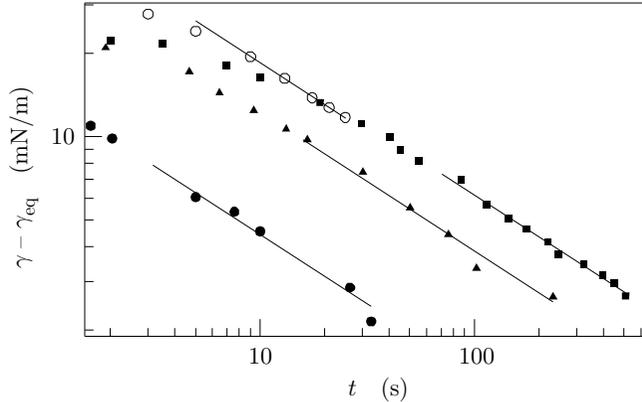


Fig. 1. – A variety of non-ionic surfactants were experimentally found to exhibit diffusion-limited adsorption. Four examples of dynamic surface tension measurements are given: 9.49×10^{-5} M of decyl alcohol (open circles), from ref. [12]; 2.32×10^{-5} M of Triton X-100 (squares), from ref. [6]; 6×10^{-5} M of $C_{12}EO_8$ (triangles) and 4.35×10^{-4} M of C_{10} PY (solid circles), both from ref. [13]. Note the asymptotic $t^{-1/2}$ behaviour, characteristic of a diffusion-limited adsorption, and shown by the solid fitting lines.

Since the value of D at the interface is not expected to be drastically smaller than that inside the solution, comparison of eq. (6) and (7) leads to the conclusion that $\tau_d > \tau_k$. This result is somewhat expected, since we did not include any potential barrier in f_0 . Adding such a barrier, $+\epsilon\phi_0$, to eq. (2) will result in a factor of $\exp[\epsilon/T]$ in τ_k , describing a kinetic limitation. We thus expect, in general, that *non-ionic surfactants should exhibit diffusion-limited adsorption*. This, indeed, has been observed for quite a large number of non-ionic surfactants [1] ⁽²⁾. The “footprint” of diffusion-limited adsorption is the asymptotic time dependence [4] $\phi_{0,eq} - \phi_0(t) \sim \sqrt{\tau_d/t}$. Any dependence between the surface tension and surface coverage will lead to a similar asymptotic time dependence of the dynamic surface tension as well. Four examples of experimental results are given in fig. 1, all exhibiting the expected asymptotic $t^{-1/2}$ behaviour.

We return now to the interfacial tension during the process of diffusion-limited adsorption. As stated above, in this limit the interfacial contribution, $f_0(\phi_0)$, is at its minimum all the time, and $\Delta\gamma$ is given therefore by $\int_0^\infty \Delta f[\phi(x)]dx + [T \ln(1-\phi_0) + (\beta/2)\phi_0^2]/a^2$. If, in addition, we neglect the bulk contribution (recalling that it completely vanishes at equilibrium) we are left with the equilibrium equation of state. Therefore, *relating the surface tension to surface coverage via the equilibrium equation of state approximately holds also out of equilibrium*. Note that this statement is valid only in the case of *diffusion-limited adsorption*, where f_0 is at its minimum during the whole process. The dependence of $\Delta\gamma$ on ϕ_0 , as defined by the equation of state, is shown in fig. 2 a). Since ϕ_0 constantly increases with time, we expect the *time* dependence of $\Delta\gamma$ to qualitatively resemble the curve depicted in fig. 2 b). This, indeed, resembles the curves found in experiments (*e.g.* [6]). Note the almost constant slope in the beginning of the process; the surface coverage significantly changes without a corresponding change in the surface tension. It is a result of the competition between the entropy and interaction terms appearing in the equation of state. The surface tension will start falling roughly when the second derivative of $\Delta\gamma$ with respect to ϕ_0 changes sign (see

⁽²⁾ Note that in the discussion above we have completely neglected a third time scale — that needed for lateral diffusion and molecular re-orientation at the interface. If, however, due to certain molecular constraints, this time scale is no longer negligible, exceptions to the above conclusions are to be expected [14].

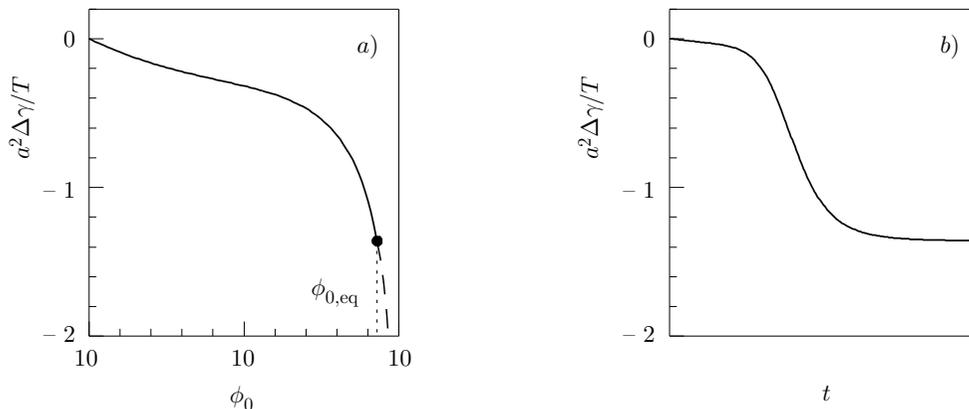


Fig. 2. – a) The relation between surface tension and surface coverage in a diffusion-limited adsorption. The energy constants are set to the (realistic) values $\alpha = 12 T$ and $\beta = 3 T$. b) Schematic time dependence of the surface tension, as expected from a dependence $\Delta\gamma(\phi_0)$ such as in a).

fig. 2a)), *i.e.* when $1 - \phi_0 \sim (\beta/T)^{-1/2}$. As one examines surfactant solutions of increasing bulk concentrations, this surface coverage will be attained earlier along the process, and the initial plateau will shrink, until finally vanishing behind the finite experimental resolution. This trend is indeed observed experimentally [15].

We have presented above an alternative model for the kinetics of non-ionic surfactant adsorption at fluid/fluid interfaces. It is a more complete model, in the sense that the kinetics in the *entire* system, in the bulk solution as well as at the interface, are described without the need for an additional, externally inserted boundary condition. We have shown that relating the dynamic surface tension to surface coverage via the equilibrium equation of state, a procedure employed by practically all previous authors, is justified only in the case of diffusion-limited adsorption. Since the adsorption of non-ionic surfactants is generally limited by diffusion, this assumption did not affect the validity of previous theories. We do not expect similar theories to be applicable to *kinetically limited* systems, such as salt-free ionic surfactant solutions [8]. In contrast, our model allows, using the definition of $\Delta\gamma$ given above, for the calculation of dynamic surface tensions regardless of such limitations. Like any other free-energy formulation, the model can be easily extended to include additional interactions. A natural candidate should be the electrostatic interaction, *i.e.* extension of the model to *ionic* surfactants. This problem will be addressed in a future paper [16].

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