

Dynamics of Surfactant Adsorption at Air/Water interface

Introduction:

The equilibrium surface tension γ_{eq} of a surfactant solution is not reached instantaneously. Surfactant molecules must first diffuse from the bulk solution to the interface, then adsorb and reorganize at the surface. This note discusses the processes governing the dynamics of surfactant exchange between the bulk and the interface.

1. Surface Tension Dynamics

When a new interface is created in a surfactant solution, the initial surface tension γ is nearly equal to that of the pure solvent γ_0 . Over time, γ decreases to its equilibrium value γ_{eq} . The duration of this process can vary widely, from milliseconds to several days, depending on the surfactant type, concentration, and molecular properties. The interfacial (surface excess) concentration of surfactants depends on the adsorption–desorption kinetics. At equilibrium, the flux of monomers absorbing to the interface j_{ads} balances the desorption flux j_{des} .

If the interface is perturbed (e.g., stretched), the surface excess concentration Γ immediately after the perturbation becomes lower than the equilibrium value Γ_{eq} . To restore equilibrium, j_{ads} temporarily exceeds j_{des} , driving monomers from the bulk to the interface. Conversely, when the surface is compressed, $\Gamma > \Gamma_{eq}$, and desorption dominates until balance is re-established.

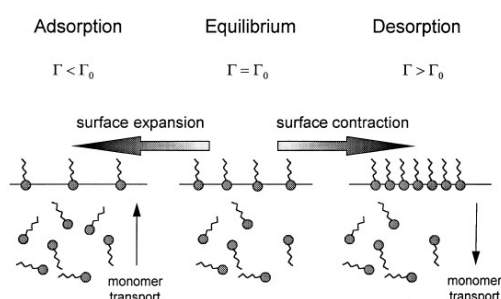


Figure 1: Surface expansion and contraction may drive the flux of monomer to the interface.

The kinetic mechanism of surfactant adsorption at interfaces can be described by the differential equation:

$$\frac{d\Gamma}{dt} = j_{ads} - j_{des}$$

where Γ is the surface excess concentration, j_{ads} the adsorption flux, and j_{des} the desorption flux.

When a fresh interface is formed, $\Gamma < \Gamma_{eq}$. Consequently, a net flux of monomers occurs from the bulk solution to the interface. This adsorption process reduces the surface tension from its initial value γ_0 (that of the pure solvent) to the equilibrium value γ_{eq} , corresponding to $\Gamma = \Gamma_{eq}$.

There are two main models of Monomer Transport and Adsorption (Fig. 2):

- **Diffusion-Controlled Model**

Assumes that monomers diffuse from the bulk to the subsurface region adjacent to the interface. Once in the subsurface, monomers adsorb instantaneously at the interface. Here, the diffusion process is the rate-determining step, while adsorption at the surface is considered very fast.

- **Mixed Kinetics–Diffusion Model**

Monomers still diffuse from the bulk to the subsurface, but the **rate-controlling step** is their transfer from the subsurface to the interface. Once the monomers have diffused to the subsurface, there may be an adsorption barrier present preventing the monomers from adsorbing. Adsorption can be hindered by increased surface pressure, limited number of vacant adsorption sites, steric effects or unfavorable orientation of the molecule near the interface. These constraints can prevent adsorption, leading some molecules to “back-diffuse” into the bulk. As a result, the timescale of surface tension relaxation is longer than in the purely diffusion-controlled case.

Dynamic surface tension (DST) plays a critical role in many industrial and biological processes [1]. For example:

- **Photographic industry:** During thin gelatin film formation, high flow velocities require precise DST control to avoid defects and irregularities.
- **Agrochemicals:** Fast wettability improves the spreading of pesticides on plant leaves.
- **Metallurgy, paper, and textiles:** DST influences coating, wetting, and spreading processes essential to product quality.

Dynamics of Surfactant Adsorption at Air/Water interface

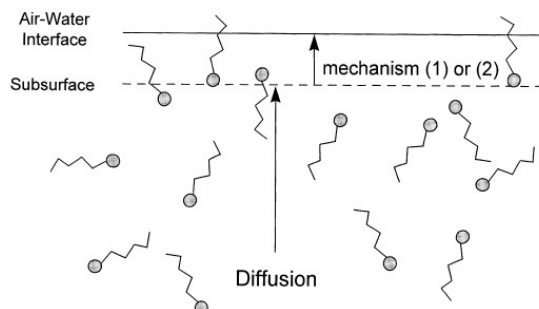


Figure 2: Transport of monomers to the interface. Once the monomers have diffused to the subsurface, they will either instantaneously adsorb at the interface in accordance with the diffusion-controlled model (1) or will have to pass through a potential barrier to adsorb (2).

One biological system where control of **dynamic surface tension (DST)** is crucial is the lung, where proper regulation of DST ensures the efficient functioning of alveoli. In this context, phospholipids serve as the primary surface-active agents. Beyond biology, DST plays a vital role in a wide range of applications involving emulsifiers, wetting agents, and foaming agents. In fact, wherever surfactants are employed, DST represents a key property that governs performance. Recent advances in both experimental techniques and theoretical modeling have renewed interest in this field, stimulating significant progress in understanding and application.

2. Thermodynamics of adsorption

2.1 Gibbs Equation

The surface excess of surfactants at interface is given by the Gibbs equation:

$$\Gamma = -\frac{1}{nRT} \frac{d\gamma}{d\ln C}$$

Here Γ is the equilibrium surface excess, R the gas constant, T the Kelvin temperature and C the bulk surfactant concentration, n = number of species into which the surfactant dissociates:

- $n=1$ for non-ionic surfactants, neutral molecules or ionic surfactants in the presence of excess electrolyte
- $n=2$ for 1:1 ionic surfactant, assuming electrical neutrality of the interface.

The adsorption isotherm, Γ vs. C , can therefore be obtained by measuring the surface tension γ at different bulk surfactant concentrations.

2.2 Diffusion mechanism

The **Ward and Tordai equation** describes the kinetics of surfactant adsorption by accounting for both the diffusion of monomers from the bulk to the interface and the **back-diffusion** of monomers from the subsurface into the bulk as the interface becomes increasingly occupied.

At the beginning of the process, adsorption is dominated by monomers from the subsurface layer, under the reasonable assumption that each molecule arriving at the interface is likely to encounter an empty site. However, as adsorption progresses and the interface becomes more crowded, the probability increases that an arriving monomer will encounter an already occupied site. In this case, adsorption is hindered, and back-diffusion into the bulk must be considered.

If the subsurface concentration is known, the diffusion of molecules between the subsurface and the bulk can be described using **Fick's laws of diffusion**. Incorporating these considerations, the **classical Ward and Tordai equation** is expressed in its standard form as:

$$\Gamma(t) = 2C_0 \sqrt{\frac{Dt}{\pi}} - \sqrt{\frac{D}{\pi}} \int_0^{\sqrt{t}} C_s d(\sqrt{t-\tau})$$

where C_0 is the bulk surfactant concentration, D the monomer diffusion coefficient, C_s the concentration in the subsurface, and τ is a dummy variable of integration.

Limiting laws can be used to account for the DST when γ is close to that of the solvent γ_0 , and for when it is close to the equilibrium value γ_{eq} . These asymptotic equations are:

- Short time approximation $t \rightarrow 0$:

At the start of the adsorption process there will be no back diffusion so neglecting this term:

$$\Gamma(t) = 2C_0 \sqrt{\frac{Dt}{\pi}}$$

At the start of adsorption, the surfactant solution can be treated as dilute so:

Dynamics of Surfactant Adsorption at Air/Water interface

$$\gamma(t \rightarrow 0) = \gamma_0 - 2nRTC_0 \sqrt{\frac{Dt}{\pi}}$$

- Long time approximation $t \rightarrow \infty$:

The subsurface concentration will get closer to the bulk concentration, and C_s can be factored outside the back diffusion integral and with Gibbs equation the long-time approximation is:

$$\gamma(t \rightarrow \infty) = \gamma_{eq} + \frac{nRT\Gamma_{eq}^2}{C} \sqrt{\frac{\pi}{4Dt}}$$

2.3 Mixed diffusion-kinetics controlled adsorption

In this mechanism, monomers diffuse from the bulk solution to the subsurface, following the same diffusion equations as in a diffusion-only process. However, unlike purely diffusion-controlled adsorption, monomers in the subsurface are not instantaneously adsorbed at the interface.

For a monomer to penetrate the surface film, it may need to adopt a specific configuration. This is particularly relevant for long-chain surfactants, polymers, or proteins, where adsorption may be hindered if the chain is closely entangled. Instead of immediately reaching the adsorbed state, the monomer may back-diffuse into the bulk solution.

Once the surfactant solution is above its CMC, the micelles present in the solution have a certain lifetime for break-up. If the micelles are stable and long-lived, the molecules in the micelles may not be available for adsorption. In effect, the concentration of molecules diffusing to the interface will be equal to the CMC, regardless of the bulk concentration of surfactant, implying that the DST will not increase significantly above the CMC.

The concept of an **adsorption barrier** can encompass all factors that hinder surfactant adsorption, including steric constraints, chain entanglement, and micelle stability. This barrier slows down the adsorption rate, making the transfer of monomers from the subsurface to the interface the rate-determining step. If none of these factors are significant during adsorption, the adsorption barrier is effectively zero, and the process is controlled purely by diffusion.

Baret [1] made the first significant attempt to account for the adsorption barrier and summarized the process as: *"the number of solute molecules that adsorb at the interface is equal to the number of solute molecules which, having diffused from the bulk to the subsurface, cross the adsorption barrier."* He further concluded that diffusion dominates at the initial stage of adsorption, but as the interface approaches maximum coverage, the process transitions to mixed kinetics.

An important contribution to understanding interfacial kinetic barriers was provided by Liggieri and Ravera [2,3]. Their model builds on the Ward and Tordai framework but introduces a **renormalized diffusion coefficient**, which accounts for both diffusion to the subsurface and the crossing of the adsorption barrier. In this approach, only subsurface molecules with energy exceeding ϵ_a can adsorb, while only adsorbed molecules with energy exceeding ϵ_d can desorb. Here, ϵ_a and ϵ_d are the activation energies for adsorption and desorption, respectively.

The renormalized diffusion coefficient D^* incorporates the effect of these activation barriers and is related to the physical diffusion coefficient D through an Arrhenius-type relationship, defined as:

$$D^* = D \cdot \exp\left(-\frac{\epsilon_a}{RT}\right)$$

As $\epsilon_a \rightarrow 0$, $D^* \rightarrow D$ and the process tends towards the diffusion-only controlled mechanism. Using D^* , this process can now be considered as a diffusion problem, which can be solved using Fick's equation with the new boundary condition:

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

giving the Ward and Tordai equation considering the potential adsorption barrier:

$$\Gamma(t) = 2C_0 \sqrt{\frac{D_a t}{\pi}} - 2 \sqrt{\frac{D_a}{\pi}} \int_0^{\sqrt{t}} C_s d(\sqrt{t-\tau})$$

$$\text{with } D_a = \frac{D^{*2}}{D} = D \cdot \exp\left(-\frac{2\epsilon}{RT}\right)$$

Dynamics of Surfactant Adsorption at Air/Water interface

3. Discussion on different cases

3.1 Dynamic surface tension of monomeric non-ionic surfactant solution

Lin et al. [4] investigated decanol solutions and concluded that cohesive forces between adsorbed molecules significantly influence adsorption kinetics. These long-chain alcohols, with small polar head groups, experience strong attractive van der Waals interactions as the interface becomes saturated. It was suggested that these cohesive forces contribute to the observed energy barrier to adsorption. Lin et al. [5] examined two non-ionic polyoxyethylene alcohols, $C_{12}E_8$ and $C_{10}E_8$ and analyzed the dynamic surface tension (DST) data in a similar manner. For both surfactants, they concluded that the controlling mechanism for mass transfer can shift with bulk concentration—from being diffusion-controlled at low concentrations to mixed kinetic–diffusion controlled at higher concentrations. Figure 3 illustrates how the apparent or effective diffusion coefficient D_{eff} , decreases as the surfactant concentration increases. This indicates that the adsorption of $C_{10}E_8$ molecules onto a clean air/water interface is not purely diffusion controlled but is increasingly influenced by kinetic barriers at higher concentrations.

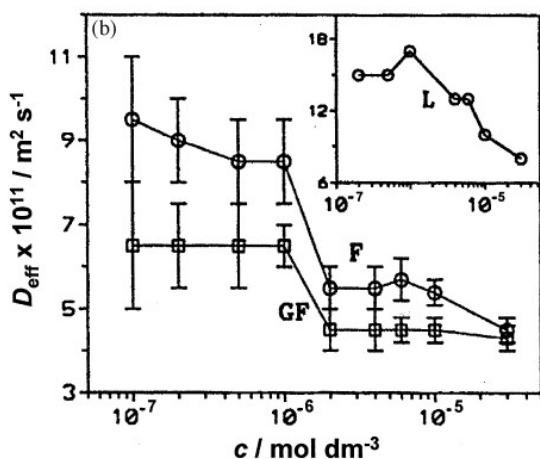


Figure 3: Values of the effective diffusion coefficient D_{eff} from the dynamic surface tension data of $C_{10}E_8$ and the model predictions from the Frumkin (F), generalized Frumkin (GF) and Langmuir (L) isotherms as a function of concentration.[4]

They concluded that the adsorption/desorption process varies significantly with surface coverage rather than

purely bulk concentration and the adsorption becomes more difficult as the surface becomes more crowded.

3.2 Dynamic surface tension of micellar non-ionic surfactant solution

If the overall micellar lifetime exceeds the time required for the surface tension γ to reach equilibrium γ_{eq} , the micellized surfactant may not be immediately available for adsorption, and hence the DST will decay more slowly. The adsorption of monomers creates a concentration gradient in the subsurface region. This gradient is restored toward equilibrium both through the usual diffusion of monomers from the bulk and via the breakup of micelles in the subsurface.

3.3 Dynamic surface tension of anionic surfactants

A major challenge in studying anionic surfactants is ensuring purity. In addition to surface-active impurities from unreacted intermediates and hydrolysis of unreacted reagents, trace amounts of divalent ions can significantly influence the equilibrium surface tension γ vs $\ln C$ curve. For most anionic surfactants studied, the initial stages of dynamic surface tension (DST) measurements were consistent with diffusion-controlled adsorption. Although, especially with the short chain surfactants, there was some evidence for an adsorption barrier, although this may have been due to impurities. Analysis of DST curves at long and short times gave similar behavior as for the non-ionic described previously. At short times the process appears to be essentially diffusion-controlled, and at the end the DSTs are consistent with an adsorption barrier, similar in magnitude to that of the nonionic. This suggests that the DST mechanism is not strongly affected by the chemical nature of the surfactant. However, it remains difficult to determine from these studies whether the charged nature of the interface significantly affects adsorption dynamics, and further work is required to clarify this issue. Charge effects have also been considered from a theoretical viewpoint by MacLeod and Radke [6], who concluded that, under similar conditions, the adsorption rates of anionic surfactants are approximately an order of magnitude lower than those of comparable non-ionic. This can be interpreted as anionic surfactants exhibiting a larger effective adsorption barrier than non-ionic, although such pronounced differences were not directly evident from experimental observations.

Dynamics of Surfactant Adsorption at Air/Water interface

4. Measurement of the efficiency of surfactant adsorption [7]

4.1 pC_{20} parameter

A simple measure of surfactant adsorption efficiency is the negative logarithm of the bulk surfactant concentration required to achieve a 20 mN/m reduction in surface tension (Fig. 4):

$$pC_{20} = -\log C_{(-\Delta\gamma=20)}$$

When the surface tension of the pure solvent has been decreased about 20 mN/m by adsorption of the surfactant, the surface (excess) concentration Γ of the surfactant is close to its saturation value. The Frumkin isotherm confirm that this decrease indicates a saturation of 84-99.9% of the surface. The determination of this parameter requires a complete γ vs $\log C$ plot for each surfactant under investigation. The pC_{20} , rather than the concentration C_{20} itself, is used because the negative logarithm can be related to standard free energy change ΔG° involved in the transfer of the surfactant molecule from the interior of the bulk liquid phase to the interface.

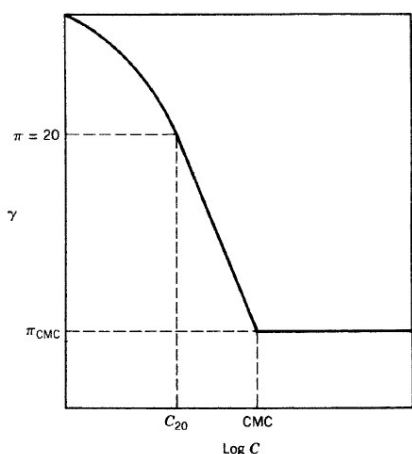


Figure 4: Surface tension vs $\log C$ plot illustrating pC_{20} and effectiveness of surface tension reduction.

The efficiency of adsorption of a surfactant at the aqueous solution–air interface, as measured by the pC_{20} value, is enhanced by the following factors:

1. Increasing the number of carbon atoms in the hydrophobic chain.
2. A straight (linear) alkyl chain rather than a branched chain with the same number of carbon atoms.

3. A single hydrophilic group at the end of the hydrophobic chain, rather than at a central location or having multiple hydrophilic groups.

4. A nonionic or zwitterionic hydrophilic group, rather than an ionic one.

5. For ionic surfactants, decreasing the effective charge of the hydrophilic group by (a) using of a more tightly bound (less hydrated) counterion, (b) increasing the ionic strength of the aqueous phase.

4.2 Surface tension reduction

Surface tension reduction occurs when surfactant molecules replace solvent molecules at the interface. The efficiency of a surfactant in lowering surface tension should therefore reflect its concentration at the interface relative to that in the bulk liquid. A suitable measure of this efficiency is the ratio of the surface concentration of surfactant C^s to its bulk concentration C at equilibrium C^s/C .

The surface concentration of surfactant is related to its surface excess concentration Γ by the relation:

$$C^s = 10^3 \frac{\Gamma}{d} + C$$

Where d is the thickness of the interfacial region. For surfactants, Γ is in the range 1 to $5 \cdot 10^{-10}$ mol/L, while $d = 50 \cdot 10^{-8}$ cm or less and $C = 0.001$ or less. Thus, the approximation gives:

$$\frac{C^s}{C} \sim 10^3 \frac{\Gamma}{Cd}$$

When the tension has been reduced by 20 mN/m the value of Γ approaches its maximum, and most surfactant molecules are slightly tilted at the interface. Assuming that the thickness of the interfacial region d is determined by the height of the surfactant normal to the interface, d is inversely proportional to the minimal surface area per adsorbed molecule a^s . A larger value of a^s generally indicates a smaller angle of the surfactant with respect to the interface, a smaller value of a^s indicates an orientation of the surfactant more perpendicular to the interface. Since:

$$a^s = \frac{K}{\Gamma} \propto \frac{1}{d}$$

The ratio Γ/d may be treated as a constant, and the surface-to-bulk concentration ratio can be expressed as

Dynamics of Surfactant Adsorption at Air/Water interface

$\frac{C^S}{C} \propto \frac{K'}{C} \pi = 20$, where K and K' are constants. This relationship indicates that the bulk surfactant concentration required to achieve a 20 mN/m reduction in surface tension C_{20} serves not only as a measure of the efficiency of adsorption at the liquid–gas interface, but also as an indicator of the surfactant's efficiency in reducing surface tension.

4.3 CMC/ C_{20} parameter

A convenient way of measuring the relative effects of some structural or micro-environmental factor on micellization and on adsorption is to determine its effect on the CMC/ C_{20} ratio, where C_{20} is the concentration of surfactant in the bulk phase that produces a reduction of 20 mN/m in the surface tension of the solvent.

An increase in the CMC/ C_{20} ratio indicates that micellization is inhibited more than adsorption, or that adsorption is promoted more than micellization. A decrease in the CMC/ C_{20} ratio indicates that adsorption is inhibited more than micellization or micellization is favored more than adsorption. The CMC/ C_{20} ratio, therefore, affords insights into the adsorption and micellization processes.

The CMC/ C_{20} ratio is also an important factor in determining the value to which the surface tension of the solvent can be reduced by the presence in its solution of the surfactant. The data show that for single-chain compounds of all types listed, the CMC/ C_{20} ratio:

1. Is not increased substantially by increasing the length of the alkyl chain of the hydrophobic group (from C_{10} to C_{16}) in ionic surfactants.
2. Is increased by the introduction of branching in the hydrophobic group or positioning of the hydrophilic group in a central position in the molecule.
3. Is increased by the introduction of a larger hydrophilic group.
4. Is increased greatly for ionic surfactants by increasing the ionic strength of the solution or using a more tightly bound counterion, especially one containing an alkyl chain of six or more carbon atoms. For a nonionic surfactant, the effect of the addition of electrolyte is more complex, depending upon the nature of the electrolyte added, its salting-in or salting-out effect, and its possible complex formation with the nonionic. In some cases, the CMC/ C_{20}

ratio is increased, in other cases it is decreased by the addition of electrolyte, and in still others there is little effect.

5. Is decreased by an increase in temperature in the range 10–40°C.
6. Is increased considerably by the replacement of a hydrocarbon chain by a fluorocarbon- or silicone-based chain.
7. Is increased considerably by the replacement of air as the second phase at the interface by a saturated aliphatic hydrocarbon and decreased slightly when the second liquid phase is a short-chain aromatic or unsaturated hydrocarbon.

The greater steric effect on micellization than on adsorption at the aqueous solution–air interface is illustrated by (2), (3), (5), and (6); the greater effect of the electrical factor on adsorption than on micellization is illustrated by (4). The greater difficulty of accommodating a bulky hydrophobic group in the interior of a spherical or cylindrical micelle rather than at a planar interface (e.g., air–water) is presumably the reason for observations (2) and (6) above. The increase in the CMC/ C_{20} ratio with replacement of air by a saturated aliphatic hydrocarbon is due to an increased tendency to adsorb at the latter interface, while the micellization tendency is not changed significantly. The small decrease in the ratio when the second phase is an aromatic or unsaturated hydrocarbon is due to the increased tendency to form micelles, which is almost equaled by the increased tendency to adsorb.

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Dynamics of Surfactant Adsorption at Air/Water interface

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