

Chapter 1 in the book:

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CHAPTER 1

PLANAR FLUID INTERFACES

An interface or membrane is one of the main “actors” in the process of particle-interface and particle-particle interaction at a fluid phase boundary. The latter process is influenced by mechanical properties, such as the interfacial (membrane) tension and the surface (Gibbs) elasticity. For interfaces and membranes of low tension and high curvature the interfacial bending moment and the curvature elastic moduli can also become important. As a rule, there are surfactant adsorption layers at fluid interfaces and very frequently the interfaces bear some electric charge. For these reasons in the present chapter we pay a special attention to surfactant adsorption and to electrically charged interfaces.

Our purpose is to introduce the basic quantities and relationships in mechanics, thermodynamics and kinetics of fluid interfaces and surfactant adsorption, which will be further currently used throughout the book. Definitions of surface tension, interfacial bending moment, adsorptions of the species, surface of tension and equimolecular dividing surface, surface elasticity and adsorption relaxation time are given. The most important equations relating these quantities are derived, their physical meaning is interpreted, and appropriate references are provided. In addition to known facts and concepts, the chapter presents also some recent results on thermodynamics and kinetics of adsorption of ionic surfactants. Four tables summarize theoretical expressions, which are related to various adsorption isotherms and types of electrolyte in the solution. We hope this introductory chapter will be useful for both researchers and students, who approach for a first time the field of interfacial science, as well as for experts and lecturers who could find here a somewhat different viewpoint and new information about the factors and processes in this field and their interconnection.

1.1. MECHANICAL PROPERTIES OF PLANAR FLUID INTERFACES

1.1.1. THE BAKKER EQUATION FOR SURFACE TENSION

The balance of the linear momentum in fluid dynamics relates the local acceleration in the fluid to the divergence of the pressure tensor, \mathbf{P} , see e.g. Ref. [1]:

$$\rho \frac{d\mathbf{v}}{dt} = -\nabla \cdot \mathbf{P} \quad (1.1)$$

Here ρ is the mass density of the fluid, \mathbf{v} is velocity and t is time; in fact the pressure tensor \mathbf{P} equals the stress tensor \mathbf{T} with the opposite sign: $\mathbf{P} = -\mathbf{T}$. In a fluid at rest $\mathbf{v} \equiv 0$ and Eq. (1.1) reduces to

$$\nabla \cdot \mathbf{P} = 0 \quad (1.2)$$

which expresses a necessary condition for hydrostatic equilibrium. In the bulk of a liquid the pressure tensor is isotropic,

$$\mathbf{P} = P_B \mathbf{U} \quad (1.3)$$

as stated by the known Pascal law (\mathbf{U} is the spatial unit tensor; P_B is a scalar pressure). Indeed, all directions in the bulk of a uniform liquid phase are equivalent. The latter is not valid in a vicinity of the surface of the fluid phase, where the normal to the interface determines a special direction. In other words, in a vicinity of the interface the force acting across unit area is not the same in all directions. Correspondingly, in this region the pressure tensor can be expressed in the form [2,3]:

$$\mathbf{P} = P_T (\mathbf{e}_x \mathbf{e}_x + \mathbf{e}_y \mathbf{e}_y) + P_N \mathbf{e}_z \mathbf{e}_z \quad (1.4)$$

Here \mathbf{e}_x , \mathbf{e}_y and \mathbf{e}_z are the unit vectors along the Cartesian coordinate axes, with \mathbf{e}_z being oriented normally to the interface; P_N and P_T are, respectively, the normal and the tangential components of the pressure tensor. Due to the symmetry of the system P_N and P_T can depend on z , but they should be independent of x and y . Thus a substitution of Eq. (1.4) into Eq. (1.3) yields one non-trivial equation:

$$\frac{\partial P_N}{\partial z} = 0 \quad (1.5)$$

In other words, the condition for hydrostatic equilibrium, Eq. (1.3), implies that P_N must be constant along the normal to the interface; therefore, P_N is to be equal to the bulk isotropic pressure, $P_N = P_B = \text{const}$.

Let us take a vertical strip of unit width, which is oriented normally to the interface, see Fig. 1.1. The ends of the stripe, at $z = a$ and $z = b$, are supposed to be located in the bulk of phases 1 and 2, respectively. The real force exerted to the strip is

$$F_T^{(\text{real})} = \int_a^b P_T(z) dz \quad (1.6)$$

On the other hand, following Gibbs [4] one can construct an *idealized* system consisting of two uniform phases, which preserve their bulk properties up to a mathematical dividing surface modeling the transition zone between the two phases (Fig. 1.1). The pressure everywhere in the idealized system is equal to the bulk isotropic pressure, $P_B = P_N$. In addition, a surface tension σ

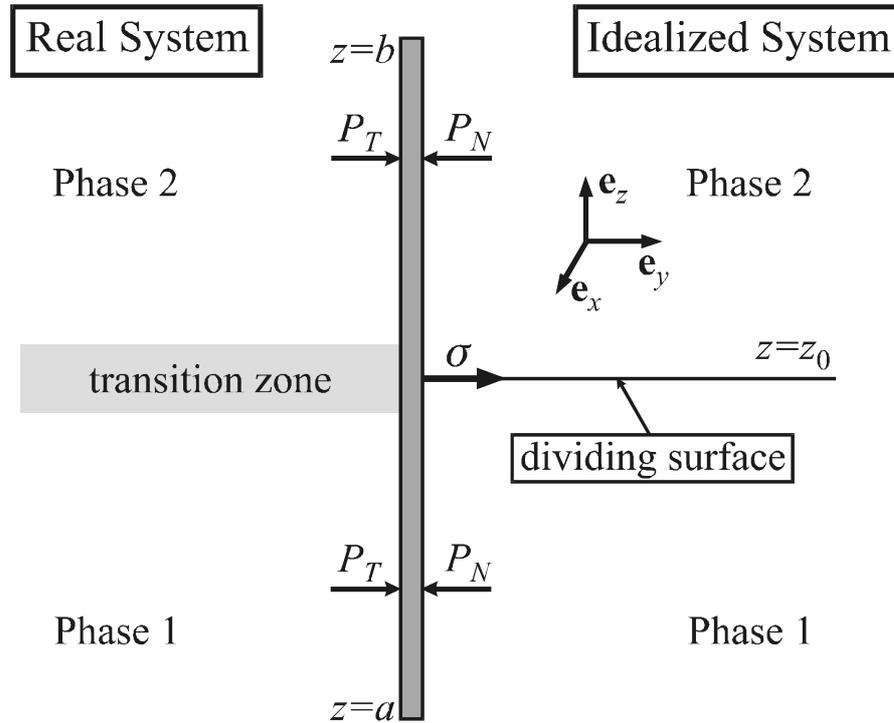


Fig. 1.1. Sketch of a vertical strip, which is normal to the boundary between phases 1 and 2.

is ascribed to the dividing surface in the idealized system. Thus the force exerted to the strip in the idealized system (Fig. 1.1) is

$$F_T^{(\text{idealized})} = \int_a^b P_N dz - \sigma \quad (1.7)$$

The role of σ is to make up for the differences between the real and the idealized system. Setting $F_T^{(\text{idealized})} = F_T^{(\text{real})}$ from Eqs. (1.6) and (1.7) one obtains the Bakker [5] equation for the surface tension:

$$\sigma = \int_{-\infty}^{+\infty} (P_N - P_T) dz \quad (1.8)$$

Since the boundaries of integration $z = a$ and $z = b$ are located in the bulk of phases 1 and 2, where the pressure is isotropic ($P_T = P_N$), we have set the boundaries in Eq. (1.8) equal to $\pm\infty$. Equation (1.8) means that the real system with a planar interface can be considered as if it were composed of two homogeneous phases separated by a planar membrane of zero thickness with

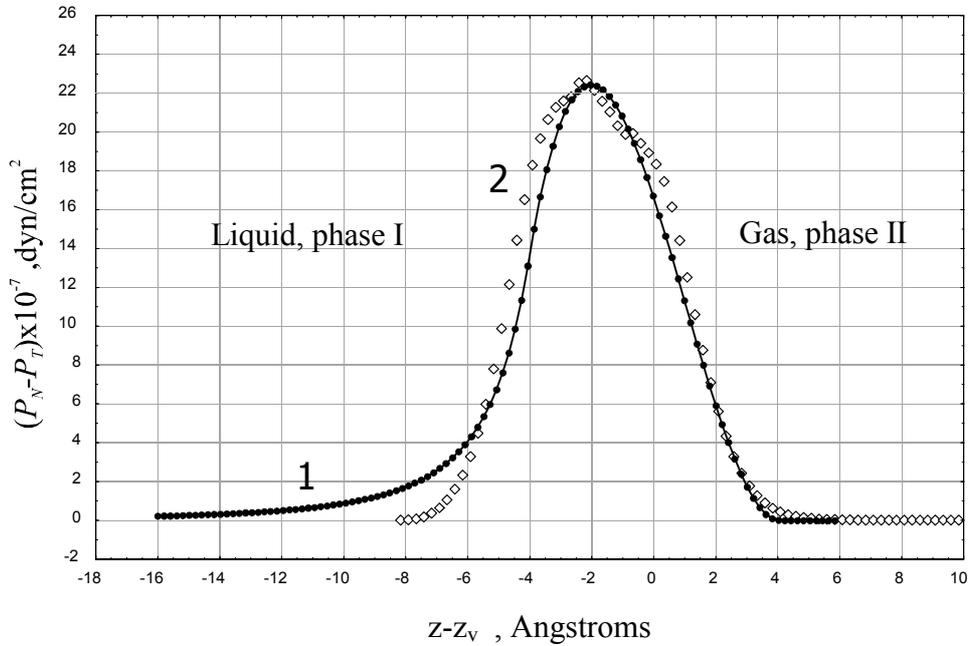


Fig. 1.2. Anisotropy of the pressure tensor, ΔP , plotted vs. the distance to the equimolecular dividing surface, $z - z_v$, for interface liquid argon-gas at 84.3 K; Curves 1 and 2 are calculated by the theories in Refs. [8] and [10].

tension σ given by Eq. (1.8). The latter equation gives a hydrostatic definition of surface tension. Note that this definition does not depend on the exact location of the dividing surface. The quantity

$$\Delta P \equiv P_N - P_T \quad (1.9)$$

expresses the anisotropy of the pressure tensor. The function $\Delta P(z)$ can be obtained theoretically by means of the methods of the statistical mechanics [6-9]. As an illustration in Figure 1.2 we present data for ΔP vs. $z-z_v$ for the interface liquid argon–gas at temperature $T = 84.3$ K; z_v is the position of the so called “equimolecular” dividing surface (see Section 1.2.2 below for definition). The empty and full points in Fig. 1.2 are calculated by means of the theories from Refs. [8] and [10], respectively. As seen in Fig. 1.2, the width of the transition

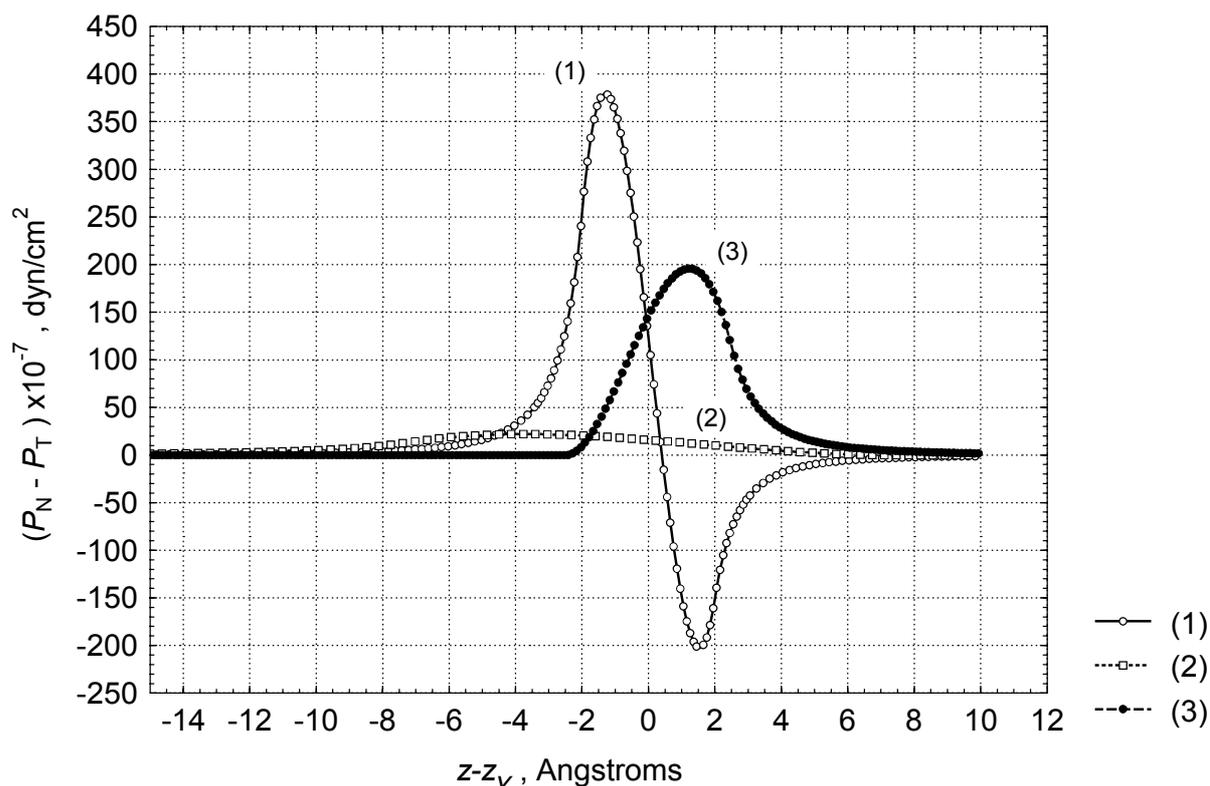


Fig. 1.3. Anisotropy of the pressure tensor, ΔP , plotted vs. the distance to the equimolecular dividing surface, $z-z_v$, calculated by the theory in Ref. [10] for the phase boundaries n-decane–gas (curve 1), gas–water (curve 2) and n-decane–water (curve 3).

zone between the liquid and gas phases (in which $\Delta P \neq 0$) is of the order of 10 \AA . On the other hand, the maximum value of the anisotropy $\Delta P(z)$ is about $2 \times 10^8 \text{ dyn/cm}$, i.e. about 200 atmospheres, which is an impressive value. The area below the full line in Fig. 1.2 gives the surface tension of argon at that temperature, $\sigma = 13.45 \text{ mN/m}$, in accordance with Eq. (1.8).

Curves 1, 2 and 3 in Fig. 1.3 present $\Delta P(z)$ calculated in Ref. [10] for the interfaces n-decane/gas, gas/water and n-decane/water, respectively. One see that $\Delta P(z)$ typically exhibits a single maximum for a liquid-gas interface, whereas $\Delta P(z)$ exhibits a loop (maximum and minimum) for a liquid-liquid interface. For all curves in Fig. 1.3 the width of the interfacial transition zone is of the order of 10 \AA .

1.1.2 INTERFACIAL BENDING MOMENT AND SURFACE OF TENSION

To make the idealized system in Fig. 1.1 hydrostatically equivalent to the real system we have to impose also a requirement for equivalence with respect to the acting force moments (in addition to the analogous requirement for the acting forces, see above). The moment exerted on the strip in the real system (Fig. 1.1) is

$$M^{(\text{real})} = \int_a^b P_T(z) z dz \quad (1.10)$$

Likewise, the moment exerted on the stripe in the idealized system is [11]:

$$M^{(\text{idealized})} = \int_a^b P_N z dz - \sigma z_0 + \frac{1}{2} B_0 \quad (1.11)$$

Here $z = z_0$ is the position of the dividing surface and B_0 is an interfacial bending moment (couple of forces), which is to be attributed to the dividing surface in order to make the idealized system equivalent to the real one with respect to the force moments. Setting $M^{(\text{idealized})} = M^{(\text{real})}$ from Eqs. (1.8), (1.10) and (1.11) one obtains an expression for the interfacial bending moment:

$$B_0 = 2 \int_{-\infty}^{+\infty} (P_N - P_T)(z_0 - z) dz \quad (1.12)$$

As in Eq. (1.8) we have extended the boundaries of integration to $\pm\infty$. From the viewpoint of mechanics *positive* B_0 represents a force moment (a couple of forces), which tends to bend the dividing surface around the phase, for which \mathbf{e}_z is an *outer* normal (in Fig. 1.1 this is phase 1). The comparison of Eqs. (1.8) and (1.12) shows that unlike σ , the interfacial bending moment B_0 depends on the choice of position of the dividing surface z_0 . The latter can be defined by imposing some additional physical condition; in such a way the “equimolecular” dividing surface is defined (see Section 1.2.2 below). If once the position of the dividing surface is determined, then the interfacial bending moment B_0 becomes a physically well defined quantity. For example, the values of the bending moment, corresponding to the equimolecular dividing surface, for curves No. 1, 2 and 3 in Fig. 1.3 are, respectively [10]: $B_0 = 2.2, 2.3$ and 5.2×10^{-11} N.

One possible way to define the position, z_0 , of the dividing surface is to set the bending moment to be identically zero:

$$B_0 \Big|_{z_0=z_s} \equiv 0 \quad (1.13)$$

Combining Eqs (1.8), (1.12) and (1.13) one obtains [2]

$$z_s = \frac{1}{\sigma} \int_{-\infty}^{+\infty} (P_N - P_T) z dz \quad (1.14)$$

Equation (1.14) defines the so called *surface of tension*. It has been first introduced by Gibbs [4], and it is currently used in the conventional theory of capillarity (see Chapter 2 below). At the surface of tension the interface is characterized by a single dynamic parameter, the interfacial tension σ , this considerably simplifies the mathematical treatment of capillary problems. However, the physical situation becomes more complicated when the interfacial tension is low; such is the case of some emulsion and microemulsion systems, lipid bilayers and biomembranes. In the latter case, the *surface of tension* can be located far from the actual transition region between the two phases and its usage becomes physically meaningless.

Indeed, for $\sigma \rightarrow 0$ Eq. (1.14) yields $z_s \rightarrow \infty$. Therefore, a mechanical description of an interface of *low* surface tension needs the usage of (at least) two dynamic quantities: interfacial (surface) tension and bending moment. In fact, B_0 is related to the so called *spontaneous curvature* of the interface. In Chapter 3 we will come to this point again.

1.1.3. ELECTRICALLY CHARGED INTERFACES

As a rule, the boundaries between two phases (and the biomembranes, as well) bear some electric charge. Often it is due to the dissociation of surface ionizable groups or to adsorption of charged amphiphilic molecules (surfactants). It should be noted that even the boundaries water-air and water-oil (oil here means any liquid hydrocarbon immiscible with water) are electrically charged in the absence of any surfactant, see e.g. refs. [12] and [13]. If the surface of an aqueous phase is charged, it repels the *coions*, i.e. the ions of the same charge, but it attracts the *counterions*, which are the ions of the opposite charge, see Fig. 1.4. Thus a non-uniform distribution of the ionic species in the vicinity of the charged interface appears, which is known as *electric double layer* (EDL), see e.g. Ref. [14].

The conventional model of the EDL stems from the works of Gouy [15], Chapman [16] and Stern [17]. The EDL is considered to consist of two parts: (I) *interfacial (adsorption) layer* and (II) *diffuse layer*. The interfacial (adsorption) layer includes charges, which are immobilized (adsorbed) at the phase boundary; this includes also adsorbed (bound) counterions, which form the so called *Stern layer*, see Fig. 1.4. The diffuse layer consists of free ions in the aqueous phase, which are involved in Brownian motion in the electrical field created by the charged interface. The boundary, which separates the adsorption from the diffuse layer, is usually called the *Gouy plane*.

The conventional theory of the electric double layer is briefly presented in Section 1.2.4 below. For our purposes here it is sufficient to take into account that the electric potential varies across the EDL: $\psi = \psi(z)$. The thickness of the diffuse EDL could be of the order of hundred (and even thousand) nm, i.e. it is much greater than the thickness of the interfacial transition zone (cf. Figs. 1.2 and 1.3). This fact requires a special approach to the theoretical description of the

charged interfaces, which can be based on the expression for the Maxwell electric stress tensor [18]:

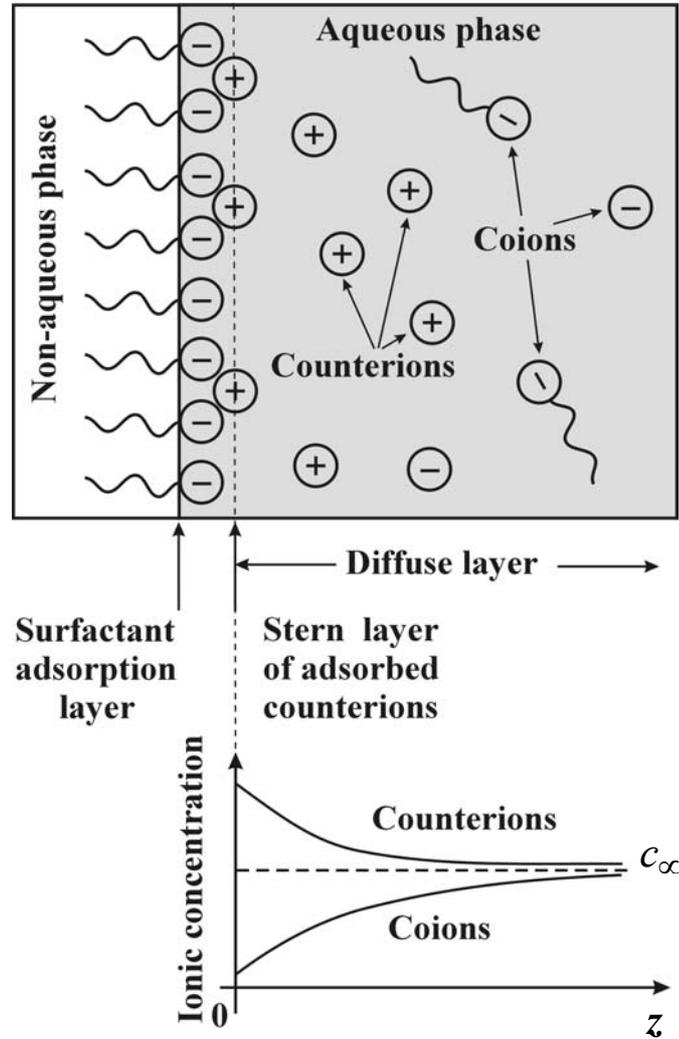


Fig. 1.4. Sketch of the electric double layer in a vicinity of an adsorption monolayer of ionic surfactant. (a) The diffuse layer contains free ions involved in Brownian motion, while the Stern layer consists of adsorbed (bound) counterions. (b) Near the charged surface there is an accumulation of counterions and a depletion of coions, whose bulk concentrations are both equal to c_∞ .

$$P_{ik} = (P_0 + \frac{\epsilon}{8\pi} E^2) \delta_{ik} - \frac{\epsilon}{4\pi} E_i E_k \quad (i, k = 1, 2, 3) \quad (1.15)$$

Here δ_{ik} is the Kronecker symbol (the unit matrix), ϵ is the dielectric permittivity of the medium (usually water), E_i is the i -th component of the electric field,

$$E_i = -\frac{\partial\psi}{\partial x_i}, \quad E^2 = \sum_{i=1}^3 E_i^2, \quad (1.16)$$

$x = x_1$, $y = x_2$ and $z = x_3$ are Cartesian coordinates, and P_0 is an isotropic pressure, which can vary across the EDL due to the osmotic effect of the dissolved ionic species.

As already mentioned, in the case of plane interface we have $\psi = \psi(z)$, and then Eq. (1.15) reduces to the following two expressions:

$$P_N \equiv P_{zz} = P_0 - \frac{\varepsilon}{8\pi} \left(\frac{d\psi}{dz} \right)^2 \quad (1.17)$$

$$P_T \equiv P_{xx} = P_{yy} = P_0 + \frac{\varepsilon}{8\pi} \left(\frac{d\psi}{dz} \right)^2 \quad (1.18)$$

Eqs. (1.17) and (1.18) can be applied to describe the pressure tensor within the diffuse part of the electric double layer.

Now, let us locate the plane $z = 0$ in the Gouy plane separating the diffuse (at $z > 0$) from the adsorption layer. Then by means of the Bakker equation (1.8) one can represent the surface tension σ as a sum of contributions from the adsorption and diffuse layers:

$$\sigma = \sigma_a + \sigma_d \quad (1.19)$$

where

$$\sigma_a = \int_{-\infty}^0 (P_N - P_T) dz, \quad \sigma_d = \int_0^{+\infty} (P_N - P_T) dz \quad (1.20)$$

Substituting Eqs. (1.17) and (1.18) into the above equation for σ_d , one obtains a general expression for the contribution of the *diffuse* layer to the interfacial tension [19,20]:

$$\sigma_d = -\frac{\varepsilon}{4\pi} \int_0^{\infty} \left(\frac{d\psi}{dz} \right)^2 dz \quad (1.21)$$

Equation (1.21) shows that the contribution of the diffuse electric double layer to the interfacial tension, σ_d , is always negative, i.e. the interactions in the diffuse layer tend to decrease the total

interfacial tension σ . Explicit expressions for σ_d , obtained by means of the double layer theory for various types of electrolytes, can be found in Table 1.3 below.

1.1.4. WORK OF INTERFACIAL DILATATION

Let us consider an imaginary rectangular box containing portions of phases 1 and 2, and of the interface between them. As before, we will assume that the interface is parallel to the coordinate plane xy , and the sides of the rectangular box are also parallel to the respective coordinate planes. Moving the sides of the box one can create a small change of the volume of the box, δV , with a corresponding small change of the interfacial area, δA . The work δW carried out by the external forces to create this deformation can be calculated by means of a known equation of fluid mechanics [1]:

$$\delta W = - \int_V (\mathbf{P} : \delta \mathbf{D}) dV \quad (1.22)$$

Here $\delta \mathbf{D}$ is the strain tensor (tensor of deformation) and “:” denotes double scalar product of two tensors (dyadics):

$$(\mathbf{AB}) : (\mathbf{CD}) \equiv (\mathbf{A} \cdot \mathbf{D})(\mathbf{B} \cdot \mathbf{C}) \quad (1.23)$$

Since we consider displacements of the sides of our rectangular box along the normals to the respective sides, the strain tensor has diagonal form in the Cartesian basis [21,22]:

$$\delta \mathbf{D} = \mathbf{e}_x \mathbf{e}_x \frac{\delta(dx)}{dx} + \mathbf{e}_y \mathbf{e}_y \frac{\delta(dy)}{dy} + \mathbf{e}_z \mathbf{e}_z \frac{\delta(dz)}{dz} \quad (1.24)$$

Here $\delta(dx)$ denotes the extension of a linear element dx of the continuous medium in the course of deformation. Equation (1.24) shows that the eigenvalues of the strain tensor are the relative extensions of linear elements along the three axes of the Cartesian coordinate system. Substituting Eqs. (1.4) and (1.24) into Eq. (1.22) one can derive [22]:

$$\delta W = -P_N \int_V \left(\frac{\delta(dx)}{dx} + \frac{\delta(dy)}{dy} + \frac{\delta(dz)}{dz} \right) dx dy dz + \int_V (P_N - P_T) \left(\frac{\delta(dx)}{dx} + \frac{\delta(dy)}{dy} \right) dx dy dz \quad (1.25)$$

The increments of the elementary volume and area in the process of deformation are

$$\delta(dV) = dydz \delta(dx) + dx dz \delta(dy) + dx dy \delta(dz), \quad \delta(dA) = dy \delta(dx) + dx \delta(dy) \quad (1.26)$$

Combining Eqs. (1.8), (1.25) and (1.26) one finally obtains

$$\delta W = -P_N \delta V + \sigma \delta A \quad (1.27)$$

Here $-P_N \delta V$ expresses the work of changing the volume and $\sigma \delta A$ is the *work of interfacial dilatation*. Equation (1.27) gives a connection between the mechanics and thermodynamics of the fluid interfaces.

1.2. THERMODYNAMICAL PROPERTIES OF PLANAR FLUID INTERFACES

1.2.1. THE GIBBS ADSORPTION EQUATION

Let us consider the same system as in section 1.1.4 above. The Gibbs fundamental equation, combining the first and the second law of thermodynamics, is [2,4]

$$dU = TdS - P_N dV + \sigma dA + \sum_i \mu_i dN_i, \quad (1.28)$$

where T is the temperature; U and S are the internal energy and entropy of the system, respectively; μ_i and N_i are the chemical potential and the number of molecules of the i -th component (species); the summation in Eq. (1.28) is carried out over all components in the system. Equation (1.28) states that the internal energy of the system can vary because of the transfer of heat (TdS) and/or matter ($\sum_i \mu_i dN_i$), and/or due to the mechanical work, δW , carried out by external forces, see Eq. (1.27).

Following Gibbs [4], we construct an idealized system consisting of two bulk phases, which are uniform up to a mathematical dividing surface modeling the boundary between the two phases. Since the dividing surface has a zero thickness, the volumes of the two phases in the idealized system are additive:

$$V = V^{(1)} + V^{(2)} \quad (1.29)$$

We assume that the bulk densities of entropy, $s^{(k)}$, internal energy, $u^{(k)}$, and number of molecules, $n_i^{(k)}$, are known for the two neighboring phases ($k = 1,2$). Then the entropy, internal energy and number of molecules for phase “ k ” of the idealized system are:

$$S^{(k)} \equiv s^{(k)}V^{(k)}; \quad U^{(k)} \equiv u^{(k)}V^{(k)}; \quad N_i^{(k)} \equiv n_i^{(k)}V^{(k)} \quad (k = 1,2) \quad (1.30)$$

Each of the two uniform bulk phases has its own fundamental equation [2,4]:

$$\begin{aligned} dU^{(1)} &= TdS^{(1)} - P_B dV^{(1)} + \sum_i \mu_i dN_i^{(1)} \\ dU^{(2)} &= TdS^{(2)} - P_B dV^{(2)} + \sum_i \mu_i dN_i^{(2)} \end{aligned} \quad (1.31)$$

It is presumed that we deal with a state of thermodynamic equilibrium, and hence the temperature T and the chemical potentials μ_i are uniform throughout the system [23]; in addition, $P_N = P_B = \text{const.}$, see Eq. (1.5) above. Next, we sum up the two equations (1.31) and subtract the result from Eq. (1.28); thus we obtain:

$$dU^{(s)} = T dS^{(s)} + \sigma dA + \sum_i \mu_i dN_i^{(s)}, \quad (1.32)$$

where

$$U^{(s)} \equiv U - U^{(1)} - U^{(2)}, \quad S^{(s)} \equiv S - S^{(1)} - S^{(2)}, \quad N_i^{(s)} \equiv N_i - N_i^{(1)} - N_i^{(2)} \quad (1.33)$$

are, respectively, surface excesses of internal energy, entropy and number of molecules of the i -th species; these excesses are considered as being attributed to the dividing surface. Equation (1.32) can be interpreted as the fundamental equation of the interface [4,24]. Since the interface is uniform, then $dU^{(s)}$, $dS^{(s)}$ and $dN_i^{(s)}$ can be considered as amounts of the respective extensive thermodynamic parameters corresponding to a small portion, dA , of the interface; then Eq. (1.32) can be integrated to yield [2,4]:

$$U^{(s)} = TS^{(s)} + \sigma A + \sum_i \mu_i N_i^{(s)}, \quad (1.34)$$

Finally, we differentiate Eq. (1.34) and compare the result with Eq. (1.32); thus we arrive at the Gibbs [4] adsorption equation:

$$d\sigma = -\frac{S^{(s)}}{A}dT - \sum_i \Gamma_i d\mu_i \quad (1.35)$$

where

$$\Gamma_i \equiv \frac{N_i^{(s)}}{A} = \int_{-\infty}^{z_0} (n_i(z) - n_i^{(1)})dz + \int_{z_0}^{+\infty} (n_i(z) - n_i^{(2)})dz \quad (1.36)$$

is the adsorption of the i -th species at the interface; $n_i(z)$ is the actual concentration of component “ i ” as a function of the distance to the interface, z , cf. Eq. (1.33); z_0 denotes the position of the dividing surface. Figure 1.5a shows qualitatively the dependence $n_i(z)$ for a *non-amphiphilic* component, i.e. a component, which does not exhibit a tendency to accumulate at the interface; if phase 1 is an aqueous solution, then the water can serve as an example for a non-amphiphilic component. On the other hand, Figure 1.5b shows qualitatively the dependence $n_i(z)$ for an *amphiphilic* component (*surfactant*), which accumulates (adsorbs) at the interface, see the maximum of $n_i(z)$ in Fig. 1.5b.

1.2.2. EQUIMOLECULAR DIVIDING SURFACE

As discussed in section 1.1.2 above, the definition of the dividing surface is a matter of choice. In other words, one has the freedom to impose one physical condition in order to determine the position of the dividing surface. This can be the condition the adsorption of the i -th component to be equal to zero [4]:

$$\Gamma_i \Big|_{z_0=z_v} \equiv 0 \quad (\text{equimolecular dividing surface}) \quad (1.37)$$

The surface thus defined is called equimolecular dividing surface with respect to component “ i ”. In order to have $\Gamma_i \equiv 0$ the sum of the integrals in Eq. (1.36) must be equal to zero. This means that the positive and negative areas, which are comprised between the continuous and dashed lines in Fig. 1.5a,b and denoted by (+) and (–), must be equal.

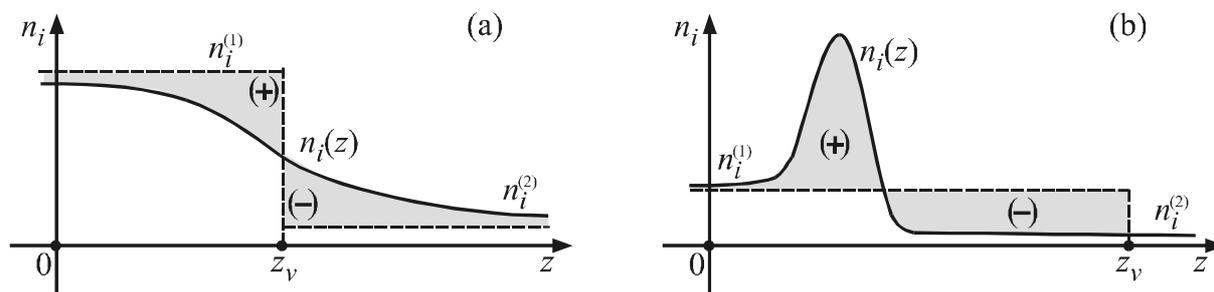


Fig. 1.5. Illustrative dependence of the density n_i of the i -th component on the distance z to the interface for (a) non-amphiphilic component and (b) amphiphilic component; z_v denotes the position of the equimolecular dividing surface; $n_i^{(1)}$ and $n_i^{(2)}$ are the values of n_i in the bulk of phases 1 and 2.

As seen in Fig. 1.5a, if component “ i ” is non-amphiphilic (say the water as a solvent in an aqueous solution), the equimolecular dividing surface, $z = z_v$, is really situated in the transition zone between the two phases. In contrast, if component “ i ” is an amphiphilic one, then the equimolecular dividing surface, $z = z_v$, is located far from the actual interfacial transition zone (Fig. 1.5b). Therefore, to achieve a physically adequate description of the system, the equimolecular dividing surface is usually introduced with respect to the solvent; it should never be introduced with respect to an amphiphilic component (surfactant).

1.2.3. THERMODYNAMICS OF ADSORPTION OF NONIONIC SURFACTANTS

A molecule of a nonionic surfactant (like all amphiphilic molecules) consists of a hydrophilic and a hydrophobic moiety. The hydrophilic moiety (the “headgroup”) can be a water soluble polymer, like polyoxiethylene, or some polysaccharide [25]; it can be also a dipolar headgroup, like those of many phospholipids. The hydrophobic moiety (the “tail”) usually consists of one or two hydrocarbon chain(s). The adsorption of such a molecule at a fluid interface is accompanied with a gain of free energy, because the hydrophilic part of an adsorbed molecule is exposed to the aqueous phase, whereas its hydrophobic part contacts with the non-aqueous (hydrophobic) phase.

Let us consider the boundary between an aqueous solution of a nonionic surfactant and a hydrophobic phase, air or oil. We choose the dividing surface to be the equimolecular dividing

surface with respect to water, that is $\Gamma_w = 0$. Then the Gibbs adsorption equation (1.35) reduces to

$$d\sigma = -\Gamma_1 d\mu_1 \quad (T = \text{const.}) \quad (1.38)$$

where the subscript “1” denotes the nonionic surfactant. Since the bulk surfactant concentration is usually relatively low, one can use the expression for the chemical potential of a solute in an ideal solution [23]:

$$\mu_1 = \mu_1^{(0)} + kT \ln c_1 \quad (1.39)$$

where c_1 is the concentration of the nonionic surfactant and $\mu_1^{(0)}$ is a standard chemical potential, which is independent of c_1 , and k is the Boltzmann constant. Combining Eqs. (1.38) and (1.39) one obtains

$$d\sigma = -kT \Gamma_1 d \ln c_1 \quad (1.40)$$

The surfactant adsorption isotherms, expressing the connection between Γ_1 and c_1 are usually obtained by means of some molecular model of the adsorption. The most popular is the Langmuir [26] adsorption isotherm,

$$\frac{\Gamma_1}{\Gamma_\infty} = \frac{Kc_1}{1 + Kc_1} \quad (1.41)$$

which stems from a lattice model of localized adsorption of *non-interacting* molecules [27]. In Eq. (1.41) Γ_∞ is the maximum possible value of the adsorption ($\Gamma_1 \rightarrow \Gamma_\infty$ for $c_1 \rightarrow \infty$). On the other hand, for $c_1 \rightarrow 0$ one has $\Gamma_1 \approx Kc_1$; the adsorption parameter K characterizes the surface activity of the surfactant: the greater K the higher the surface activity.

Table 1.1 contains the 6 most popular surfactant adsorption isotherms, those of Henry, Freundlich, Langmuir, Volmer [28], Frumkin [29], and van der Waals [27]. For $c_1 \rightarrow 0$ all other isotherms (except that of Freundlich) reduce to the Henry isotherm. The physical difference between the Langmuir and Volmer isotherms is that the former corresponds to a physical model of localized adsorption, whereas the latter – to non-localized adsorption. The Frumkin and van der Waals isotherms generalize, respectively, the Langmuir and Volmer isotherms for the case, when there is interaction between the adsorbed molecules; β is the parameter,

Table 1.1. The most popular surfactant adsorption isotherms and the respective surface tension isotherms.

	<ul style="list-style-type: none"> Surfactant adsorption isotherms (for nonionic surfactants: $a_{1s} \equiv c_1$)
Henry	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty}$
Freundlich	$Ka_{1s} = \left(\frac{\Gamma_1}{\Gamma_F} \right)^{1/m}$
Langmuir	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}$
Volmer	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \right)$
Frumkin	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(-\frac{2\beta\Gamma_1}{kT} \right)$
van der Waals	$Ka_{1s} = \frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT} \right)$
	<ul style="list-style-type: none"> Surface tension isotherm $\sigma = \sigma_0 - kTJ + \sigma_d$ (for nonionic surfactants: $\sigma_d \equiv 0$)
Henry	$J = \Gamma_1$
Freundlich	$J = \frac{\Gamma_1}{m}$
Langmuir	$J = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty} \right)$
Volmer	$J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1}$
Frumkin	$J = -\Gamma_\infty \ln\left(1 - \frac{\Gamma_1}{\Gamma_\infty} \right) - \frac{\beta\Gamma_1^2}{kT}$
van der Waals	$J = \frac{\Gamma_\infty \Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{\beta\Gamma_1^2}{kT}$

which accounts for the interaction. In the case of van der Waals interaction β can be expressed in the form [30,31]:

$$\beta = -\pi kT \int_{r_0}^{\infty} \left[1 - \exp\left(-\frac{u(r)}{kT}\right) \right] \approx -\pi \int_{r_0}^{\infty} u(r) r dr$$

where $u(r)$ is the interaction energy between two adsorbed molecules and r_0 is the distance between the centers of the molecules at close contact. The comparison between theory and experiment shows that the interaction parameter β is important for air-water interfaces, whereas for oil-water interfaces one can set $\beta = 0$ [32,33]. The latter fact, and the finding that $\beta > 0$ for air-water interfaces, leads to the conclusion that β takes into account the van der Waals attraction between the hydrocarbon tails of the adsorbed surfactant molecules across air (such attraction is missing when the hydrophobic phase is oil).

What concerns the parameter K in Table 1.1, it is related to the standard free energy of adsorption, $\Delta f = \mu_1^{(0)} - \mu_{1s}^{(0)}$, which is the energy gain for bringing a molecule from the bulk of the water phase to a diluted adsorption layer [34,35]:

$$K = \frac{\delta_1}{\Gamma_{\infty}} \exp\left(\frac{\mu_1^{(0)} - \mu_{1s}^{(0)}}{kT}\right) \quad (1.42)$$

Here δ_1 is a parameter, characterizing the thickness of the adsorption layer, which can be set (approximately) equal to the length of the amphiphilic molecule.

Let us consider the integral

$$J \equiv \int_0^{c_1} \frac{dc_1}{c_1} = \int_0^{\Gamma_1} \frac{d \ln c_1}{d \Gamma_1} d \Gamma_1 \quad (1.43)$$

The derivative $d \ln c_1 / d \Gamma_1$ can be calculated for each adsorption isotherm in Table 1.1, and then the integration in Eq. (1.43) can be carried out analytically. The expressions for J , obtained in this way, are also listed in Table 1.1. The integration of the Gibbs adsorption isotherm, Eq. (1.40), along with Eq. (1.43) yields

$$\sigma = \sigma_0 - kTJ, \quad (1.44)$$

which in view of the expressions for J in Table 1.1 presents the surfactant adsorption isotherm, or the two-dimensional (surface) equation of state.

Table 1.2. Expressions for the Gibbs elasticity of adsorption monolayers (valid for both nonionic and ionic surfactants), which correspond to the various types of isotherms in Table 1.1.

Type of surface tension isotherm	Gibbs elasticity E_G
Henry	$E_G = kT\Gamma_1$
Freundlich	$E_G = kT\frac{\Gamma_1}{m}$
Langmuir	$E_G = kT\Gamma_1\frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1}$
Volmer	$E_G = kT\Gamma_1\frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2}$
Frumkin	$E_G = kT\Gamma_1\left(\frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} - \frac{2\beta\Gamma_1}{kT}\right)$
van der Waals	$E_G = kT\Gamma_1\left[\frac{\Gamma_\infty^2}{(\Gamma_\infty - \Gamma_1)^2} - \frac{2\beta\Gamma_1}{kT}\right]$

An important thermodynamic parameter of a surfactant adsorption monolayer is its Gibbs (surface) elasticity:

$$E_G \equiv -\Gamma_1\left(\frac{\partial\sigma}{\partial\Gamma_1}\right)_T \quad (1.45)$$

Expressions for E_G , corresponding to various adsorption isotherms, are shown in Table 1.2. As an example, let us consider the expression for E_G , corresponding to the Langmuir isotherm; combining results from Tables 1.1 and 1.2 one obtains

$$E_G = \Gamma_\infty kTKc_1 \quad (\text{for Langmuir isotherm}) \quad (1.45a)$$

One sees that for Langmuirian adsorption the Gibbs elasticity grows linearly with the surfactant concentration c_1 . Since the concentration of the monomeric surfactant cannot exceed the critical micellization concentration, $c_1 \leq c_{\text{CMC}}$, then from Eq. (1.45a) one obtains

$$E_G \leq (E_G)_{\max} = \Gamma_{\infty} kT K c_{\text{CMC}} \quad (\text{for Langmuir isotherm}) \quad (1.45b)$$

Hence one could expect higher elasticity E_G for surfactants with higher c_{CMC} ; this conclusion is consonant with the experimental results [36].

The Gibbs elasticity characterizes the lateral fluidity of the surfactant adsorption monolayer. For high values of the Gibbs elasticity the adsorption monolayer at a fluid interface behaves as tangentially immobile. Then, if a particle approaches such an interface, the hydrodynamic flow pattern, and the hydrodynamic interaction as well, is approximately the same as if the particle were approaching a solid surface. For lower values of the Gibbs elasticity the so called “Marangoni effect” appears, which can considerably affect the approach of a particle to a fluid interface. These aspects of the hydrodynamic interactions between particles and interfaces are considered in Chapter 6 below.

The thermodynamics of adsorption of *ionic* surfactants (see Section 1.2.5 below) is more complicated because of the presence of long-range electrostatic interactions in the system. As an introduction, in the next section we briefly present the theory of the electric double layer.

1.2.4. THEORY OF THE ELECTRIC DOUBLE LAYER.

Boltzmann equation and activity coefficients. When ions are present in the solution, the (electro)chemical potential of the ionic species can be expressed in the form [23]

$$\mu_i = \mu_i^{(0)} + kT \ln a_i + Z_i e \psi \quad (1.46)$$

which is more general than Eq. (1.39) above; here e is the elementary electric charge, ψ is the electric potential, Z_i is the valency of the ionic component “ i ”, and a_i is its activity. When an electric double layer is formed in a vicinity a charged interface, see Fig. 1.4, the electric potential and the activities of the ionic species become dependent on the distance z from the interface: $\psi = \psi(z)$, $a_i = a_i(z)$. On the other hand, at equilibrium the electrochemical potential, μ_i , is uniform throughout the whole solution, including the electric double layer (otherwise diffusion fluxes would appear) [23]. In the bulk of solution ($z \rightarrow \infty$) the electric potential tends to a constant value, which is usually set equal to zero; then one can write

$$\lim_{z \rightarrow \infty} \psi(z) = 0 \quad (1.47)$$

$$\lim_{z \rightarrow \infty} \left(\frac{d\psi}{dz} \right) = 0 \quad (1.48)$$

Setting equal the expression for μ_i at $z \rightarrow \infty$ and that for μ_i at some finite z , and using Eqs. (1.46) and (1.47), one obtains [23]:

$$a_i(z) = a_{i\infty} \exp \left[- \frac{Z_i e \psi(z)}{kT} \right] \quad (1.49)$$

where $a_{i\infty}$ denotes the value of the activity of ion “ i ” in the bulk of solution. Equation (1.49) shows that the activity obeys a Boltzmann type distribution across the electric double layer (EDL). If the activity in the bulk, $a_{i\infty}$, is known, then Eq. (1.49) determines the activity $a_i(z)$ in each point of the EDL. The studies on adsorption of ionic surfactants [32,33,20] show that a good agreement between theory and experiment can be achieved using the following expression for $a_{i\infty}$:

$$a_{i\infty} = \gamma_{\pm} c_{i\infty} \quad (1.50)$$

where $c_{i\infty}$ is the bulk concentration of the respective ion, and the activity coefficient γ_{\pm} is to be calculated from the known semiempirical formula [37]

$$\log \gamma_{\pm} = - \frac{A |Z_+ Z_-| \sqrt{I}}{1 + B d_i \sqrt{I}} + bI \quad (1.51)$$

which originates from the Debye-Hückel theory; I denotes the ionic strength of the solution:

$$I \equiv \frac{1}{2} \sum_i Z_i^2 c_{i\infty} \quad (1.52)$$

where the summation is carried out over all ionic species in the solution. When the solution contains a mixture of several electrolytes, then Eq. (1.51) defines γ_{\pm} for each separate electrolyte, with Z_+ and Z_- being the valences of the cations and anions for *this* electrolyte, but with I being the *total* ionic strength of the solution, accounting for all dissolved ionic species [37]. The log in Eq. (1.51) is decimal, d_i is the diameter of the ion, A , B , and b are parameters,

whose values can be found in the book by Robinson and Stokes [37]. For example, if the ionic strength I is given in moles per liter (M), then for solutions of NaCl at 25°C the parameters values are $A = 0.5115 \text{ M}^{-1/2}$, $Bd_i = 1.316 \text{ M}^{-1/2}$ and $b = 0.055 \text{ M}^{-1}$.

Integration of Poisson-Boltzmann equation. The Poisson equation relating the distribution of the electric potential $\psi(z)$ and electric charge density, $\rho_e(z)$, across the diffuse double layer can be presented in the form [14]

$$\frac{d^2\psi}{dz^2} = -\frac{4\pi}{\varepsilon}\rho_e, \quad (1.53)$$

Let us choose component 1 to be a coion, that is an ion having electric charge of the same sign as the interface. It is convenient to introduce the variables

$$\Phi(z) \equiv \frac{Z_1 e \psi(z)}{kT}, \quad \tilde{\rho}_e \equiv \frac{\rho_e}{Z_1 e}, \quad z_k \equiv \frac{Z_k}{Z_1} \quad (k = 1, 2, \dots, N) \quad (1.54)$$

For symmetric electrolytes Φ and $\tilde{\rho}_e$ thus defined are always positive irrespective of whether the interface is positively or negatively charged. Combining Eqs. (1.49), (1.53) and (1.54) one obtains

$$\frac{d^2\Phi}{dz^2} = -\frac{1}{2}\kappa_c^2 \tilde{\rho}_e = -\frac{1}{2}\kappa_c^2 \sum_{i=1}^N z_i a_{i\infty} \exp(-z_i \Phi) \quad (1.55)$$

where

$$\kappa_c^2 \equiv \frac{8\pi Z_1^2 e^2}{\varepsilon kT} \quad (1.56)$$

As usual, the z -axis is directed along the normal to the interface, the latter corresponding to $z = 0$. To obtain Eq. (1.55) we have expressed the bulk charge density in terms of effective concentrations, i.e. activities, $\rho_e(z) = \sum_i Z_i e a_i(z)$, rather than in terms of the net concentrations, $\rho_e(z) = \sum_i Z_i e c_i(z)$. For not-too-high ionic strengths there is no significant quantitative difference between these two expressions for $\rho_e(z)$, but the former one considerably simplifies the mathematical derivations; moreover, the former expression has been combined with

Eq. (1.49), which is rigorous in terms of activities (rather than in terms of concentrations). Integrating Eq. (1.55) one can derive

$$\left(\frac{d\Phi}{dz}\right)^2 = \kappa_c^2 \sum_{i=1}^N a_{i\infty} [\exp(-z_i \Phi) - 1] \quad (1.57)$$

where the boundary conditions $\Phi|_{z \rightarrow \infty} = 0$ and $(d\Phi/dz)|_{z \rightarrow \infty} = 0$ have been used, cf. Eqs. (1.47), (1.48) and (1.54). Note that Eq. (1.57) is a nonlinear ordinary differential equation of the first order, which determines the variation of the electric potential $\Phi(z)$ across the EDL. In general, Eq. (1.57) has no analytical solution, but it can be solved relatively easily by numerical integration. Analytical solution can be obtained in the case of symmetric electrolyte, see Eq. (1.65) below.

Further, let ρ_s be the surface electric charge density, i.e. the electric charge per unit area of the interface. Since the solution, as a whole, is electroneutral, the following relationship holds [14]:

$$\rho_s = - \int_0^{\infty} \rho_e(z) dz \quad (1.58)$$

Substituting $\rho_e(z)$ from Eq. (1.55) into Eq. (1.58) and integrating the second derivative, $d^2\Phi/dz^2$, one derives

$$\left(\frac{d\Phi}{dz}\right)_{z=0} = -\frac{1}{2}\kappa_c^2 \tilde{\rho}_s, \quad \tilde{\rho}_s \equiv \frac{\rho_s}{Z_1 e} \quad (1.59)$$

The combination of Eqs. (1.57) and (1.59) yields a connection between the surface charge density, ρ_s , and the surface potential, $\Phi_s \equiv \Phi(z=0)$, which is known as the Gouy equation [15,38]:

$$\tilde{\rho}_s = \frac{2}{\kappa_c} \left\{ \sum_{i=1}^N a_{i\infty} [\exp(-z_i \Phi_s) - 1] \right\}^{1/2}, \quad \Phi_s \equiv \frac{Z_1 e \psi_s}{kT} \quad (1.60)$$

Note that because of the choice component 1 to be a coion, the sign of Φ_s and $\tilde{\rho}_s$ is always positive and that is the reason why in Eq. (1.60) we have taken sign “+” before the square root.

To obtain an expression for calculating the diffuse layer contribution to the surface tension, σ_d , we first combine Eqs. (1.21) and (1.54):

$$\sigma_d = -\frac{2kT}{\kappa_c^2} \int_0^\infty \left(\frac{d\Phi}{dz} \right)^2 dz = \frac{2kT}{\kappa_c^2} \int_0^{\Phi_s} \left(\frac{d\Phi}{dz} \right) d\Phi \quad (1.61)$$

A substitution of Eq. (1.57) into Eq. (1.61) yields

$$\sigma_d = -\frac{2kT}{\kappa_c} \int_0^{\Phi_s} \left\{ \sum_{i=1}^N a_{i\infty} [\exp(-z_i \Phi) - 1] \right\}^{1/2} d\Phi \quad (1.62)$$

Expressions for σ_d , obtained by means of Eq. (1.62) for solutions of surfactant and various electrolytes, can be found in Table 1.3 below, as well as in Ref. [20].

Analytical expressions for $Z_1:Z_1$ electrolyte. Analytical expression for $\Phi(z)$ can be obtained in the simpler case, when the solution contains only symmetric, $Z_1:Z_1$ electrolyte, that is $Z_2 = -Z_1$ ($Z_i = 0$ for $i > 2$). In this case Eq. (1.57) can be represented in the form

$$\frac{d\Phi}{dz} = -2\kappa \sinh\left(\frac{\Phi}{2}\right) \quad (Z_1:Z_1 \text{ electrolyte}) \quad (1.63)$$

where

$$\kappa \equiv \frac{1}{2} \kappa_c \sum_{i=1}^N z_i^2 a_{i\infty} \quad (1.64)$$

is known as the Debye screening parameter. The integration of Eq. (1.63) yields an analytical expression for the variation of the electric potential $\Phi(z)$ across the EDL [14]:

$$\Phi(z) = 4 \operatorname{arctanh} \left[\tanh\left(\frac{\Phi_s}{4}\right) \exp(-\kappa z) \right] \quad (Z_1:Z_1 \text{ electrolyte}) \quad (1.65)$$

Equation (1.65) shows that the electric potential, created by the charged interface, decays exponentially in the depth of solution, that is $\Phi(z) \propto \exp(-\kappa z)$ for $z \rightarrow \infty$. The inverse Debye parameter, κ^{-1} , represents a decay length, which characterizes the thickness of the EDL. The Gouy equation (1.60), giving the connection between surface charge and surface potential, also simplifies for $Z_1:Z_1$ electrolyte:

$$\tilde{\rho}_s = \Gamma_1 - \Gamma_2 = \frac{4}{\kappa_c} \sqrt{a_{2\infty}} \sinh\left(\frac{\Phi_s}{2}\right) \quad (Z_1:Z_1 \text{ electrolyte}) \quad (1.66)$$

where Γ_1 and Γ_2 are the adsorptions of the ionic components 1 and 2, respectively. For the same case the integration in Eq. (1.62) can be carried out analytically and the following simpler expression for the diffuse layer contribution to the surface tension can be derived [19,38,39]:

$$\sigma_d = -\frac{8kT}{\kappa_c} \sqrt{a_{2\infty}} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right] \quad (Z_1:Z_1 \text{ electrolyte}) \quad (1.67)$$

The above equations serve as a basis of the thermodynamics of adsorption of ionic surfactants.

1.2.5. THERMODYNAMICS OF ADSORPTION OF IONIC SURFACTANTS

Basic equations. Combining Eqs. (1.46), (1.47) and (1.49) one obtains a known expression for the chemical potential: $\mu_i = \mu_i^{(0)} + kT \ln a_{i\infty}$. The substitution of the latter expression into the Gibbs adsorption equation (1.35) yields [19,33,40,41]:

$$d\sigma = -kT \sum_{i=1}^N \tilde{\Gamma}_i d \ln a_{i\infty} \quad (T = \text{const}) \quad (1.68)$$

Here with $\tilde{\Gamma}_i$ we denote the adsorption of the i -th component; $\tilde{\Gamma}_i$ represents a surface excess of component “ i ” with respect to the *uniform* bulk solution. For an ionic species this means that $\tilde{\Gamma}_i$ is a total adsorption, which include contributions from *both* the adsorption layer (surfactant adsorption layer + adsorbed counterions in the Stern layer, see Fig. 1.4) and the diffuse layer.

Let us define the quantities

$$\Lambda_i \equiv \int_0^\infty [a_i(z) - a_{i\infty}] dz, \quad \Gamma_i \equiv \tilde{\Gamma}_i - \Lambda_i \quad (1.69)$$

Λ_i and Γ_i can be interpreted as contributions of the diffusion and adsorption layers, respectively, into the total adsorption $\tilde{\Gamma}_i$. Using the theory of the electric double layer and the definitions (1.69) one can prove (see Appendix 1A) that the Gibbs adsorption equation (1.68) can be presented into the following equivalent form [20]

$$d\sigma_a = -kT \sum_{i=1}^N \Gamma_i d \ln a_{is} \quad (T = \text{const}) \quad (1.70)$$

where $\sigma_a = \sigma - \sigma_d$ is the contribution of the adsorption layer into the surface tension, σ_d is the contribution of the diffuse layer, defined by Eq. (1.21), and

$$a_{is} = a_{i\infty} \exp(-z_i \Phi_s), \quad z_i \equiv \frac{Z_i}{Z_1}, \quad (1.71)$$

is the subsurface activity of the i -th ionic species. The comparison between Eqs. (1.68) and (1.70) shows that the Gibbs adsorption equation can be expressed either in terms of σ , $\tilde{\Gamma}_i$ and $a_{i\infty}$, or in terms of σ_a , Γ_i and a_{is} . In Appendix 1A it is proven that these two forms are equivalent. To derive explicit adsorption and surface tension isotherms, below we specify the type of ionic surfactant and non-amphiphilic salt in the solution.

Surfactant and salt are 1:1 electrolytes. We consider a solution of an ionic surfactant, which is a symmetric 1:1 electrolyte, in the presence of additional common symmetric 1:1 electrolyte (salt). Here we assume that the counterions due to the surfactant and salt are identical. For example, this can be a solution of sodium dodecyl sulfate (SDS) in the presence of NaCl. We denote by $c_{1\infty}$, $c_{2\infty}$ and $c_{3\infty}$ the bulk concentrations of the surface active ions, counterions, and coions, respectively. For the special system of SDS with NaCl $c_{1\infty}$, $c_{2\infty}$ and $c_{3\infty}$ are the bulk concentration of the DS^- , Na^+ and Cl^- ions, respectively. The requirement for the bulk solution to be electroneutral implies $c_{2\infty} = c_{1\infty} + c_{3\infty}$. The multiplication of the last equation by γ_{\pm} , which according to Eq. (1.51) is the same for all monovalent ions, yields

$$a_{2\infty} = a_{1\infty} + a_{3\infty} \quad (1.72)$$

The adsorption of the coions of the non-amphiphilic salt is expected to be equal to zero, $\Gamma_3 = 0$, because they are repelled by the similarly charged interface (however, $\Lambda_3 \neq 0$: the integral in Eq. (1.69) gives a negative Λ_3 , see Fig. 1.4; hence $\tilde{\Gamma}_3 = \Lambda_3 \neq 0$). Then the Gibbs adsorption equation (1.70) can be presented in the form

$$d\sigma_a = -kT(\Gamma_1 d \ln a_{1s} + \Gamma_2 d \ln a_{2s}) \quad (1.73)$$

The differentials in the right-hand side of Eq. (1.73) are independent (one can vary independently the concentrations of surfactant and salt), and moreover, $d\sigma_a$ is an exact (total) differential. Then according to the Euler condition [23] the cross derivatives must be equal, viz.

$$\frac{\partial \Gamma_1}{\partial \ln a_{2s}} = \frac{\partial \Gamma_2}{\partial \ln a_{1s}} \quad (1.74)$$

A surfactant adsorption isotherm, $\Gamma_1 = \Gamma_1(a_{1s}, a_{2s})$, and a counterion adsorption isotherm, $\Gamma_2 = \Gamma_2(a_{1s}, a_{2s})$, are *thermodynamically compatible* if they satisfy Eq. (1.74). Integrating Eq. (1.74) one obtains

$$\Gamma_2 = \frac{\partial J}{\partial \ln a_{2s}} \quad (1.75)$$

where we have introduced the notation

$$J \equiv \int_0^{a_{1s}} \Gamma_1(\hat{a}_{1s}, a_{2s}) \frac{d\hat{a}_{1s}}{\hat{a}_{1s}} \quad (1.76)$$

To determine the integration constant in Eq. (1.75) we have used the condition that for $a_{1s} = 0$ (no surfactant in the solution) we have $\Gamma_1 = 0$ (no surfactant adsorption) and $\Gamma_2 = 0$ (no binding of counterions at the headgroups of adsorbed surfactant). The integral J in Eq. (1.76) can be taken analytically for all popular surface tension isotherms, see Table 1.1. Differentiating Eq. (1.76) one obtains $\Gamma_1 = \partial J / \partial \ln a_{1s}$. The substitution of the latter equation, together with Eq. (1.75) into Eq. (1.73), after integration yields

$$\sigma_a = \sigma_0 - kTJ, \quad (1.77)$$

where σ_0 is the value of σ for pure water. Combining Eqs. (1.19) and (1.77) one obtains the surface tension isotherm of the ionic surfactant:

$$\sigma = \sigma_0 - kTJ + \sigma_d, \quad (1.78)$$

where σ_d is given by Eq. (1.67) and expressions for J , corresponding to various adsorption isotherms, are available in Table 1.1. Note that for each of the isotherms in Table 1.1 Γ_1 depends on the product Ka_{1s} , that is $\Gamma_1 = \Gamma_1(Ka_{1s})$. Then Eq. (1.76) can be transformed to read

$$J \equiv \int_0^{Ka_{1s}} \Gamma_1(X) \frac{dX}{X} \quad (1.79)$$

Differentiating Eq. (1.79) one can bring Eq. (1.75) into the form [20]

$$\Gamma_2 = \Gamma_1 \frac{\partial \ln K}{\partial \ln a_{2s}} \quad (1.80)$$

which holds for each of the surfactant adsorption isotherms in Table 1.1. Note that Eq. (1.80) is valid for a general form of the dependence $K = K(a_{2s})$, which expresses the dependence of the equilibrium constant of surfactant adsorption on the concentration of the salt in solution.

Let us consider a linear dependence $K = K(a_{2s})$, that is

$$K = K_1 + K_2 a_{2s} \quad (1.81)$$

where K_1 and K_2 are constants. The physical meaning of the linear dependence of K on a_{2s} in Eq. (1.81) is discussed below, see Eqs. (1.118)–(1.128) and the related text. The substitution of Eq. (1.81) into Eq. (1.80) yields [20]

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_2 a_{2s}}{K_1 + K_2 a_{2s}} \quad (1.82)$$

Equation (1.82) is in fact a form of the *Stern isotherm* [17,38]. One can verify that the Euler condition (1.74) is identically satisfied if Γ_2 is substituted from Eq. (1.82) and Γ_1 is expressed by either of the adsorption isotherms in Table 1.1. In fact, Eq. (1.81) is the necessary and sufficient condition for thermodynamic compatibility of the Stern isotherm of *counterion* adsorption, Eq. (1.82), with either of the *surfactant* adsorption isotherms in Table 1.1. In other words, a given isotherm from Table 1.1, say the Langmuir isotherm, is thermodynamically compatible with the Stern isotherm, if only the adsorption parameters K , K_1 and K_2 in these isotherms are related by means of Eq. (1.81). The constants K_1 and K_2 have a straightforward physical meaning. In view of Eqs. (1.42) and (1.81)

$$K_1 = \frac{\delta_1}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_1^{(0)}}{kT}\right) \quad (1.83)$$

where $\Delta\mu_1^{(0)}$ has the meaning of standard free energy of adsorption of surfactant from ideal dilute solution to ideal adsorption monolayer in the absence of dissolved non-amphiphilic salt; the thickness of the adsorption layer δ_1 is about 2 nm for SDS. Note that the Langmuir and Stern isotherms, Eqs. (1.41) and (1.82), have a similar form, which corresponds to a statistical model considering the interface as a lattice of equivalent, distinguishable, and independent adsorption sites, without interactions between bound molecules [27]. Consequently, an expression, which is analogous to Eq. (1.83), holds for the ratio K_2/K_1 [the latter is a counterpart of K in Eq. (1.41)]:

$$\frac{K_2}{K_1} = \frac{\delta_2}{\Gamma_\infty} \exp\left(\frac{\Delta\mu_2^{(0)}}{kT}\right) \quad (1.84)$$

where δ_2 is the thickness of the Stern layer (c.a. the diameter of a hydrated counterion) and $\Delta\mu_2^{(0)}$ has the meaning of standard free energy of adsorption (binding) of a counterion from an ideal dilute solution into an ideal Stern layer. In summary, the parameters K_1 and K_2 are related to the standard free energies of surfactant and counterion adsorption.

The above equations form a full set for calculating the surface tension as a function of the bulk surfactant and salt concentrations (or activities), $\sigma = \sigma(a_{1\infty}, a_{2\infty})$. There are 6 unknown variables: σ , Φ_s , a_{1s} , Γ_1 , a_{2s} and Γ_2 . These variables are to be determined from a set of 6 equations as follows. Equation (1.49) for $i=1,2$ provides 2 equations. The remaining 4 equations are: Eqs. (1.66), (1.78), (1.82) and one surfactant adsorption isotherm from Table 1.1, say the Langmuir isotherm.

Comparison of theory and experiment. As illustration we consider an interpretation of experimental data by Tajima et al. [42,43] for the surface tension vs. surfactant concentrations at two concentrations of NaCl: $c_{3\infty} = 0$ and $c_{3\infty} = 0.115$ M, see Fig. 1.6. The ionic surfactant used in these experiments is tritiated sodium dodecyl sulfate (TSDS), which is 1:1 electrolyte (the radioactivity of the tritium nuclei have been measured by Tajima et al. to determine directly the surfactant adsorption). Processing the set of data for the interfacial tension $\sigma = \sigma(c_{1\infty}, c_{2\infty})$ as a function of the bulk concentrations of surfactant ions, $c_{1\infty}$, and counterions, $c_{2\infty}$, one can determine the surfactant adsorption, $\Gamma_1(c_{1\infty}, c_{2\infty})$, the counterion

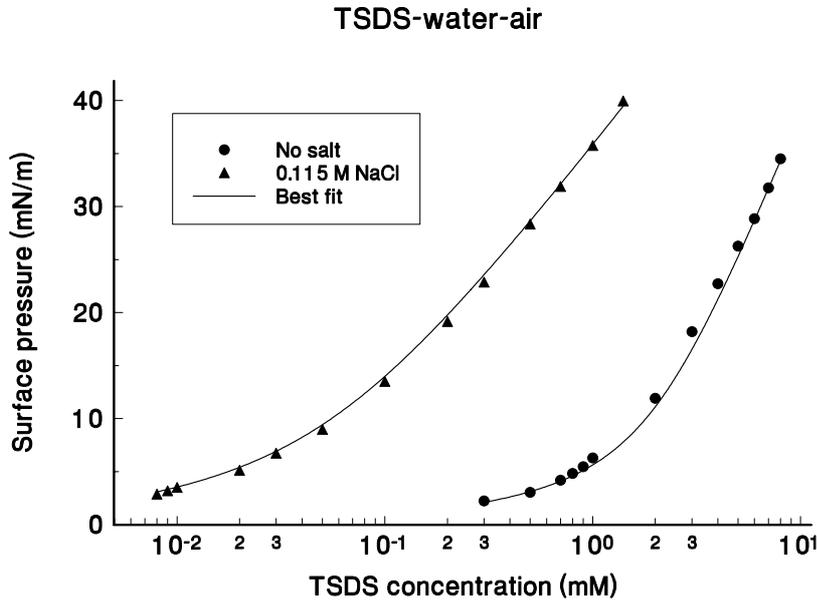


Fig. 1.6. Surface pressure at air-water interface, $\sigma_0 - \sigma$, vs. the surfactant (TSDS) concentration, $c_{1\infty}$, for two fixed NaCl concentrations: 0 and 0.115 M; the symbols are experimental data from Refs. [42] and [43]; the continuous lines represent the best fit by means of the theory from Ref. [20].

adsorption, $\Gamma_2(c_{1\infty}, c_{2\infty})$, and the surface potential, $\psi_s(c_{1\infty}, c_{2\infty})$. To fit the data in Fig. 1.6 the Frumkin isotherm is used (see Table 1.1). The theoretical model contains four parameters, β , Γ_∞ , K_1 and K_2 , whose values are to be obtained from the best fit of the experimental data. The parameters values can be reliably determined if only the set of data for $\sigma = \sigma(c_{1\infty}, c_{2\infty})$ contains experimental points for *both* high and low surfactant concentrations, and for *both* high and low salt concentrations; the data by Tajima et al. [42,43] satisfy the latter requirement. (If this requirement is not satisfied, the merit function exhibits a flat and shallow minimum, and therefore it is practically impossible to determine the best fit [20]).

The value of Γ_∞ , obtained in Ref. [20] from the best fit of the data in Fig. 1.6, corresponds to $1/\Gamma_\infty = 37.6 \text{ \AA}^2$. The respective value of K_1 is $156 \text{ m}^3/\text{mol}$, which in view of Eq. (1.83) gives a standard free energy of surfactant adsorption $\Delta\mu_1^{(0)} = 12.8 kT$ per TDS^- ion, that is 31.3 kJ/mol . The determined value of K_2/K_1 is $8.21 \times 10^{-4} \text{ m}^3/\text{mol}$, which after substitution in Eq. (1.84) yields a standard free energy of counterion binding $\Delta\mu_2^{(0)} = 1.64 kT$ per Na^+ ion, that is 4.04 kJ/mol .

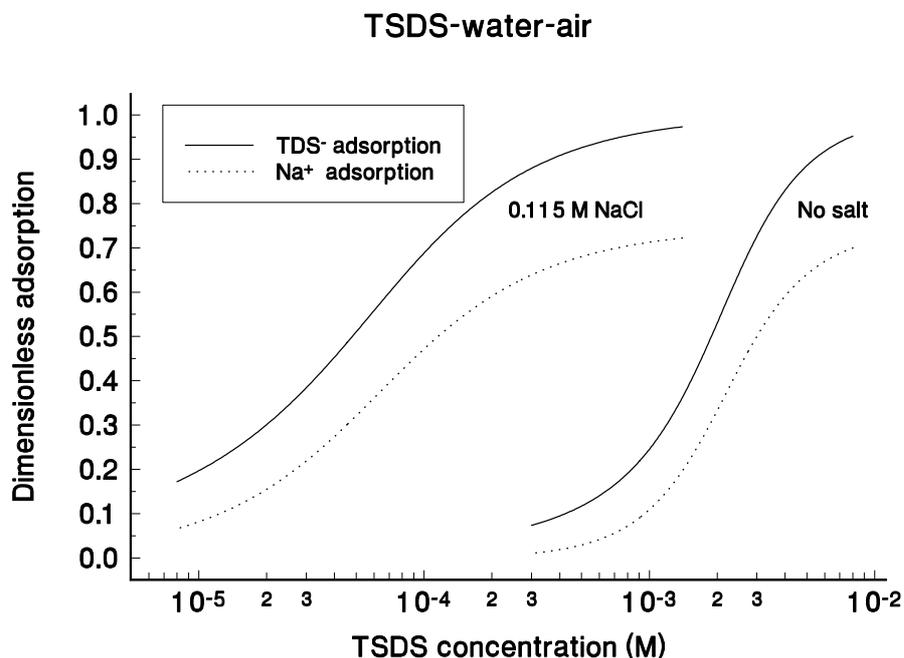


Fig. 1.7. Plots of the calculated adsorptions of surfactant Γ_1/Γ_∞ (the full lines), and counterions Γ_2/Γ_∞ (the dotted lines), vs. the surfactant (TSDS) concentration, $c_{1\infty}$. The lines correspond to the best fit of the data in Fig. 1.6 obtained in Ref. [20].

The value of the parameter β is positive ($2\beta\Gamma_\infty/kT = +0.8$), which indicates attraction between the hydrocarbon tails of the adsorbed surfactant molecules.

Figure 1.7 shows calculated curves for the adsorptions of surfactant, Γ_1 (the full lines), and counterions, Γ_2 (the dotted lines), vs. the TSDS concentration, $c_{1\infty}$. These lines represent the variation of Γ_1 and Γ_2 along the two experimental curves in Figure 1.6. One sees that both Γ_1 and Γ_2 are markedly greater when NaCl is present in the solution. The highest values of Γ_1 for the curves in Fig. 1.7 are $4.30 \times 10^{-6} \text{ mol/m}^2$ and $4.20 \times 10^{-6} \text{ mol/m}^2$ for the solutions with and without NaCl, respectively. The latter two values compare well with the saturation adsorptions measured by Tajima [42,43] for the same system by means of the radiotracer method, viz. $\Gamma_1 = 4.33 \times 10^{-6} \text{ mol/m}^2$ and $3.19 \times 10^{-6} \text{ mol/m}^2$ for the solutions with and without NaCl.

In Fig. 1.8 the occupancy of the Stern layer, $\theta = \Gamma_2/\Gamma_1$, is plotted vs. the surfactant concentration for the curves in Fig. 1.7. For the solution *without* NaCl Γ_2/Γ_1 rises from 0.15

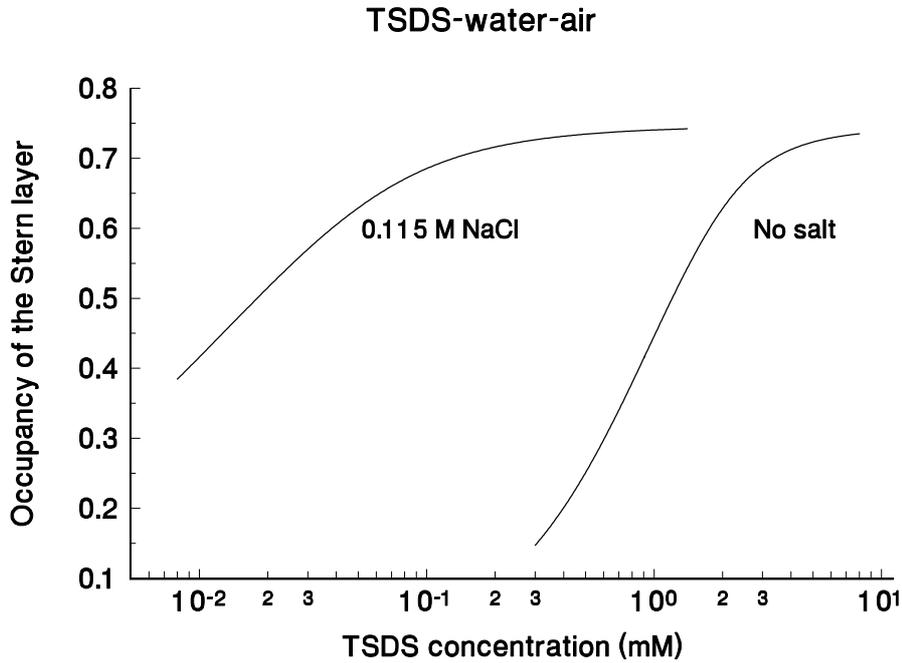


Fig. 1.8. Calculated occupancy of the Stern layer by adsorbed counterions, Γ_2/Γ_1 , vs. the surfactant (TSDS) concentration, $c_{1\infty}$, for two fixed NaCl concentrations: 0 and 0.115 M. The lines correspond to the best fit obtained in Ref. [20] for the data in Fig. 1.6.

up to 0.74 and then exhibits a tendency to level off. As it could be expected, the occupancy Γ_2 / Γ_1 is higher for the solution *with* NaCl; even at TSDS concentration 10^{-5} M the occupancy is about 0.40; for the higher surfactant concentrations θ levels off at $\Gamma_2 / \Gamma_1 = 0.74$ (Fig. 1.8). The latter value is consonant with data of other authors [44–47], who have obtained values of Γ_2 / Γ_1 up to 0.70 – 0.90 for various ionic surfactants; pronounced evidences for counterion binding have been obtained also in experiments with solutions containing surfactant micelles [48–53]. These results imply that the counterion adsorption (binding) should be always taken into account.

The fit of the data in Fig. 1.6 gives also the values of the surface electric potential, ψ_s . For the solutions with salt the model predicts surface potentials varying in the range $|\psi_s| = 55 - 95$ mV within the experimental interval of surfactant concentrations, whereas for the solution without salt the calculated surface potential is higher: $|\psi_s| = 150 - 180$ mV (note that for TSDS ψ_s has a negative sign). Thus it turns out that measurements of surface tension, interpreted by means

of an appropriate theoretical model, provide a method for determining the surface potential ψ_s in a broad range of surfactant and salt concentrations. The results of this method could be compared with other, more direct, methods for surface potential measurement, such as the electrophoretic ζ -potential measurements [12,13,54,55], or Volta (ΔV) potential measurements, see e.g. Ref. [56].

Surfactant is 1:1 electrolyte, salt is $Z_3:Z_4$ electrolyte. In this case we will number the ionic components as follows: index “1” – surfactant ion, index “2” – counterion due to the surfactant, index “3” – coion due to the salt, and index “4” – counterion due to the salt. As before, we assume that the *coions* due to the salt do not adsorb at the interface: $\Gamma_3 = 0$. The *counterions* due to the surfactant and salt are considered as separate components, which can exhibit a competitive adsorption in the Stern layer (see Fig.1.4). The analogs of Eqs. (1.81) and (1.82) for the case under consideration are [20]:

$$K = K_1 + K_2 a_{2s} + K_4 a_{4s} \quad (1.85)$$

$$\frac{\Gamma_i}{\Gamma_1} = \frac{K_i a_{is}}{K_1 + K_2 a_{2s} + K_4 a_{4s}} \quad (i = 2,4) \quad (1.86)$$

where K_1 , K_2 and K_4 are constants. All expressions for surfactant adsorption isotherms and surface tension isotherms given in Table 1.1 are valid also in the present case. Different are the forms of the Gouy equation and of the expression for σ_d , which depend on z_3 and z_4 in accordance with Eqs. (1.60) and (1.62). In particular, the integration in Eq. (1.62) can be carried out analytically for some types of electrolyte. Table 1.3 summarizes the expressions for the Gouy equation and σ_d , which have been derived in Ref. [20] for the cases, when the salt is 1:1, 2:1, 1:2 and 2:2 electrolyte. (Here 2:1 electrolyte means a salt of bivalent counterion and monovalent coion.) One may check that in the absence of salt ($a_{4\infty} = 0$) all expressions in Table 1.3 reduce either to Eq. (1.66) or to Eq. (1.67). More details can be found in Ref. [20].

Gibbs elasticity for ionic surfactants. The definition of Gibbs (surface) elasticity is not well elucidated in the literature for the case of *ionic* surfactant adsorption monolayers. That is the reason why here we devote a special discussion to this issue.

Table 1.3. Special forms of the Gouy equation (1.60) and of the expression for σ_d , Eq. (1.62), for solutions of surfactant which is 1:1 electrolyte, and salt which is 1:1, 2:1, 1:2 and 2:2 electrolyte.

Type of salt	Expressions obtained from Eqs. (1.60) and (1.62)
1:1	$\Gamma_1 - \Gamma_2 - \Gamma_4 = \frac{4}{\kappa_c} \sqrt{a_{2\infty} + a_{4\infty}} \sinh\left(\frac{\Phi_s}{2}\right)$ $\sigma_d = -\frac{8kT}{\kappa_c} \sqrt{a_{2\infty} + a_{4\infty}} \left[\cosh\left(\frac{\Phi_s}{2}\right) - 1 \right]$
2:1	$\Gamma_1 - \Gamma_2 - 2\Gamma_4 = \frac{2\sqrt{I_1}}{\kappa_c y} (y^2 - 1)g_1; \quad I_1 \equiv a_{2\infty} + 3a_{4\infty}; \quad \lambda^2 \equiv \frac{a_{4\infty}}{I_1}; \quad y \equiv \exp\frac{\Phi_s}{2}$ $\sigma_d = \frac{2kT\sqrt{I_1}}{-\kappa_c} \left[\left(y + \frac{2}{y} \right) g_1 - 3 + \frac{1 - 3\lambda^2}{\lambda} \ln \left \frac{\lambda y + g_1}{\lambda + 1} \right \right]; \quad g_1 \equiv (1 - \lambda^2 + \lambda^2 y^2)^{1/2}$
1:2	$\Gamma_1 - \Gamma_2 - \Gamma_4 = \frac{2\sqrt{I_2}}{\kappa_c u} (1 - u^2)g_2; \quad I_2 \equiv a_{2\infty} + \frac{3}{2}a_{4\infty}; \quad v^2 \equiv \frac{a_{4\infty}}{2I_2}; \quad u \equiv \exp\left(-\frac{\Phi_s}{2}\right)$ $\sigma_d = \frac{2kT\sqrt{I_2}}{-\kappa_c} \left[\left(u + \frac{2}{u} \right) g_2 - 3 + \frac{1 - 3v^2}{v} \ln \left \frac{vu + g_2}{v + 1} \right \right];$ $g_2 \equiv (1 - v^2 + v^2 u^2)^{1/2}$
2:2	$\Gamma_1 - \Gamma_2 - 2\Gamma_4 = \frac{4}{\kappa_c} \sqrt{a_{2\infty}} \sinh\left(\frac{\Phi_s}{2}\right) \sqrt{1 + \chi^2 q^2}; \quad q \equiv \cosh\left(\frac{\Phi_s}{2}\right)$ $\sigma_d = \frac{4kT\sqrt{a_{2\infty}}}{-\kappa_c} \left[q\sqrt{1 + \chi^2 q^2} - \sqrt{1 + \chi^2} + \frac{1}{\chi} \ln \left \frac{\chi q + \sqrt{1 + \chi^2 q^2}}{\chi + \sqrt{1 + \chi^2}} \right \right]; \quad \chi^2 \equiv \frac{4a_{4\infty}}{a_{2\infty}}$

The physical concept of surface elasticity is the most transparent for monolayers of *insoluble* surfactants. The changes of σ and Γ_1 in the expression $E_G = -\Gamma_1(\partial\sigma/\partial\Gamma_1)$ correspond to variations in surface tension and adsorption during a real process of interfacial dilatation.

In the case of a soluble *nonionic* surfactant the detected increase of σ in a real process of interfacial dilatation can be a pure manifestation of surface elasticity only if the period of dilatation, Δt , is much shorter than the characteristic relaxation time of surface tension, $\Delta t \ll \tau_\sigma$. Otherwise the adsorption and the surface tension would be affected by the diffusion supply of surfactant molecules from the bulk of solution toward the expanding interface. The diffusion transport tends to reduce the increase of surface tension upon dilatation, thus apparently rendering the interface less elastic and more fluid. To describe the variation of the surface tension after an initial dilatation one is to solve the diffusion equation using an appropriate initial condition (see Section 1.3.1 for details). In such a case the Gibbs elasticity, E_G , enters the theoretical expressions through this initial condition, which corresponds to an “instantaneous” dilatation of the interface (that is $\Delta t \ll \tau_\sigma$), see e.g. Ref. [57]. This “instantaneous” dilatation decreases the adsorptions Γ_i and the subsurface concentrations c_{is} of the species (the subsurface is presumed to be always in equilibrium with the surface), but the bulk concentrations $c_{i\infty}$ remain unaffected [58,59]. This initially created difference between c_{is} and $c_{i\infty}$ further triggers the diffusion process. Now, let us try to extend this approach to the case of ionic surfactants.

In the case of solution of an *ionic* surfactant, a non-uniform diffuse electric double layer (EDL) is formed in a vicinity of the interface; this is the major difference with the case of nonionic surfactant. The main question is whether or not the electric field in the EDL should be affected by the initial “instantaneous” dilatation of the interface. This problem has been examined in Ref. [60] and it has been established that a variation of the electric field during the initial dilatation leads to theoretical results devoid of sense. This is due to the following two facts:

(i) The speed of propagation of the electric signals is much greater than the characteristic rate of diffusion. (2) Even a small initial variation in the surface charge density ρ_s immediately gives rise to an electric potential, which is linearly increasing with the distance from the interface (potential of a planar wall). Thus a small initial perturbation of the interface would

immediately affect the ions in the whole solution; of course, such an initial condition is physically unacceptable. In reality, a linearly growing electric field could not appear in the ionic solution, because a variation of the surface charge density would be immediately suppressed by exchange of counterions, which are abundant in the subsurface layer of the solution (see Fig. 1.4). The theoretical equations suggest the same: to have a mathematically meaningful initial condition for the diffusion problem, the initial dilatation must be carried out at constant surface charge density ρ_s ($\rho_s = \text{const.}$ means also $\Phi_s = \text{const.}$, see Eq. 1.66). Thus we can conclude that the initial “instantaneous” interfacial dilatation, which is related to the definition of Gibbs elasticity of a soluble ionic surfactant, must be carried out at $\rho_s = \text{const.}$ From Eq. (1.19) one obtains

$$(d\sigma)_{\rho_s} = (d\sigma_a)_{\rho_s} + (d\sigma_d)_{\rho_s} \quad (1.87)$$

We recall that σ_a and σ_d are, respectively, the contributions of the adsorption and diffusion layers to the total interfacial tension, σ . An interfacial dilatation at constant ρ_s and Φ_s does not alter the diffuse part of the EDL, and consequently, $(d\sigma_d)_{\rho_s} \equiv 0$. Since, $\sigma_a = \sigma_0 - kTJ$, the expressions for J in Table 1.1 show that σ_a depends only on Γ_1 at constant temperature. Then the definition of Gibbs elasticity of nonionic adsorption layers, Eq. (1.45), can be extended to ionic adsorption layers in the following way:

$$E_G \equiv -\Gamma_1 \left(\frac{\partial \sigma}{\partial \Gamma_1} \right)_{T, \rho_s} = -\Gamma_1 \left(\frac{\partial \sigma_a}{\partial \Gamma_1} \right)_T \quad (1.88)$$

The dependence of σ on Γ_1 for nonionic surfactants is the same as the dependence of σ_a on Γ_1 for ionic surfactants, see the surface tension isotherms in Table 1.1. Then Eqs. (1.45) and (1.88) show that the expressions for E_G in Table 1.2 are valid for *both* nonionic and ionic surfactants. The effect of the surface electric potential on the Gibbs elasticity E_G of an ionic adsorption monolayer is implicit, through the equilibrium surfactant adsorption Γ_1 , which depends on the electric properties of the interface. To illustrate this let us consider the case of Langmuir isotherm; combining expressions from Tables 1.1 and 1.2 we obtain $E_G = \Gamma_\infty kTKa_{1s}$. Further, using Eqs. (1.49) and (1.81) we derive

$$E_G = \Gamma_\infty kTa_{1\infty} \left(K_1 e^{-\Phi_s} + K_2 a_{2\infty} \right) \quad (\text{for Langmuir isotherm}) \quad (1.89)$$

Equation (1.89) visualizes the effect of salt on E_G : when the salt concentration increases, $a_{2\infty}$ also increases, but the (dimensionless) surface potential Φ_s decreases; then Eq. (1.89) predicts an increase of E_G with the salt concentration. Note also that the values of E_G , calculated from the fits, like that in Fig. 1.6, depend on the type of the used adsorption isotherm; for example, the Frumkin isotherm gives values of E_G , which are systematically larger than those given by the van der Waals isotherm. The latter is preferable for fluid interfaces insofar as it corresponds to the model of non-localized adsorption.

The definition of Gibbs elasticity given by Eq. (1.88) corresponds to an “instantaneous” ($\Delta t \ll \tau_\sigma$) dilatation of the *adsorption* layer (that contributes to σ_a) without affecting the *diffuse* layer and σ_d . This will cause an initial change in the subsurface concentrations c_{is} of the species, which will further trigger a diffusion transport of components across a changing electric double layer. Thus we reach again the subject of the adsorption kinetics, which is considered in the next section.

1.3. KINETICS OF SURFACTANT ADSORPTION

When a colloidal particle approaches an interface from the bulk of solution, or when an attached particle is moving throughout the interface, the surfactant adsorption layer is locally disturbed (expanded, compressed, sheared). The surfactant solution has the property to damp the disturbances by diffusion of surfactant molecules from the bulk to the interface (or in the opposite direction). If the particle motion is slow enough (compared with the relaxation time of surface tension τ_σ) the interface will behave as a two-dimensional fluid and surface elastic effects will not arise. On the contrary, if the characteristic time of the process of particle motion is comparable with or smaller than τ_σ , the motion of the particle will be accompanied by surface elastic effects and adsorption dynamics. The criterion, showing when the latter effects would appear, is related to the relaxation time of the surface tension τ_σ .

Our attention in the present section will be focused on the theoretical results about τ_σ obtained for various types of surfactant adsorption, as follows: (i) adsorption under diffusion control, (ii) adsorption under electro-diffusion control, (iii) adsorption under barrier (kinetic) control,

(iv) adsorption from micellar solutions, (v) adsorption from protein solutions. Our purpose is to give a brief review and related references in the context of the subject of this book; detailed information about the variety of experimental methods and theoretical approaches can be found elsewhere [58-66].

1.3.1. ADSORPTION UNDER DIFFUSION CONTROL

Insofar as we are interested mainly in the relaxation time τ_σ , we will restrict our considerations to a physical situation, in which the interface is instantaneously expanded at the initial moment $t = 0$ and then (for $t > 0$) the diffusion transport of surfactant tends to saturate the adsorption layer, and eventually to restore the equilibrium in the system. In other words, the interfacial expansion happens only at the initial moment, and after that the interface is quiescent and the dynamics in the system is due only to the diffusion of surfactant.

The adsorption process is a consequence of two stages: the first one is the diffusion of surfactant from the bulk to the subsurface and the second stage is the transfer of surfactant molecules from the subsurface to the surface. When the first stage (the surfactant diffusion) is much slower than the second stage, and consequently determines the rate of adsorption, the process is termed adsorption under *diffusion* control; it is considered in the present section. The opposite case, when the second stage is slower than the first one, is called adsorption under *barrier (or kinetic)* control and it is presented in Section 1.3.3. If an electric double layer is present, the electric field to some extent plays the role of a slant barrier; this intermediate case of adsorption under *electro-diffusion* control, is presented in Section 1.3.2.

Here we consider a solution of a nonionic surfactant, whose concentration, $c_1 = c_1(z, t)$, depends on the position and time because of the diffusion process. As before, z denotes the distance to the interface, which is situated in the plane $z = 0$. The surfactant adsorption and the surface tension vary with time: $\Gamma_1 = \Gamma_1(t)$, $\sigma = \sigma(t)$. The surfactant concentration obeys the equation of diffusion:

$$\frac{\partial c_1}{\partial t} = D_1 \frac{\partial^2 c_1}{\partial z^2} \quad (z > 0, t > 0) \quad (1.90)$$

where D_1 is the diffusion coefficient of the surfactant molecules. The exchange of surfactant between the solution and its interface is described by the boundary condition

$$\frac{d\Gamma_1}{dt} = D_1 \frac{\partial c_1}{\partial z} \quad (z = 0, t > 0) \quad (1.91)$$

which states that the rate of increase of the adsorption Γ_1 is equal to the diffusion influx of surfactant per unit area of the interface. The three equations necessary to determine the three unknown functions, $c_1(z, t)$, $\Gamma_1(t)$ and $\sigma(t)$, are in fact Eqs. (1.90), (1.91) and one of the adsorption isotherms, $\Gamma_1 = \Gamma_1(c_1)$, given in Table 1.1. Except the Henry isotherm, all other isotherms in Table 1.1 give a nonlinear connection between Γ_1 and c_1 . As a consequence, an analytical solution of the problem can be obtained only if the Henry isotherm can be used, or if the deviation from equilibrium is small and the adsorption isotherm can be linearized:

$$\Gamma_1(t) - \Gamma_{1e} \approx \left(\frac{\partial \Gamma_1}{\partial c_1} \right)_e [c_{1s}(t) - c_e] \quad (1.92)$$

c_{1s} stands for the subsurface concentration; here and hereafter the subscript “ e ” means that the respective quantity refers to the equilibrium state. The set of three linear equations, Eqs. (1.90)–(1.92), have been solved by Sutherland [65]. The result, which describes the relaxation of a *small* initial interfacial dilatation, reads:

$$\frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} = \frac{\Gamma_1(t) - \Gamma_{1e}}{\Gamma_1(0) - \Gamma_{1e}} = \exp\left(\frac{t}{\tau_\sigma}\right) \operatorname{erfc}\left(\sqrt{\frac{t}{\tau_\sigma}}\right) \quad (1.93)$$

where

$$\tau_\sigma \equiv \frac{1}{D_1} \left(\frac{\partial \Gamma_1}{\partial c_1} \right)_e^2 \quad (1.94)$$

is the characteristic relaxation time of surface tension and adsorption, and

$$\operatorname{erfc}(x) \equiv \frac{2}{\sqrt{\pi}} \int_x^\infty \exp(-x^2) dx \quad (1.95)$$

is the so called complementary error function [67, 68]. The asymptotics of the latter function for small and large values of the argument are [67, 68]:

$$\operatorname{erfc}(x) = 1 - \frac{2}{\sqrt{\pi}}x + O(x^3) \text{ for } x \ll 1; \quad \operatorname{erfc}(x) = \frac{e^{-x^2}}{\sqrt{\pi}x} \left[1 + O\left(\frac{1}{x^2}\right) \right] \text{ for } x \gg 1 \quad (1.96)$$

Combining Eqs. (1.93) and (1.96) one obtains the short-time and long-time asymptotics of the surface tension relaxation:

$$\frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} = \frac{\Gamma_1(t) - \Gamma_{1e}}{\Gamma_1(0) - \Gamma_{1e}} = 1 - \frac{2}{\sqrt{\pi}} \sqrt{\frac{t}{\tau_\sigma}} + O\left[\left(\frac{t}{\tau_\sigma}\right)^{3/2}\right] \quad (t \ll \tau_\sigma) \quad (1.97)$$

$$\frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} = \frac{\Gamma_1(t) - \Gamma_{1e}}{\Gamma_1(0) - \Gamma_{1e}} = \sqrt{\frac{\tau_\sigma}{\pi t}} + O\left[\left(\frac{\tau_\sigma}{t}\right)^{3/2}\right] \quad (t \gg \tau_\sigma) \quad (1.98)$$

Equation (1.98) is often used as a test to verify whether the adsorption process is under diffusion control: data for $\Delta\sigma(t) = \sigma(t) - \sigma_e$ are plotted vs. $1/\sqrt{t}$ and it is checked if the plot complies with a straight line. We recall that Eqs. (1.97) and (1.98) are valid in the case of a *small* initial perturbation; alternative asymptotic expressions for the case of *large* initial perturbation have been derived for nonionic surfactants by Hansen [69] and for ionic surfactants by Danov et al. [70].

Using thermodynamic transformations one can relate the derivative in Eq. (1.94) to the Gibbs elasticity E_G ; thus Eq. (1.94) can be expressed in an alternative form:

$$\tau_\sigma = \frac{1}{D_1} \left(\frac{\Gamma_1^2 kT}{c_1 E_G} \right)_e^2 \quad (1.99)$$

Substituting E_G from Table 1.2 into Eq. (1.99) one could obtain expressions for τ_σ corresponding to the various adsorption isotherms. In the special case of Langmuir adsorption isotherm one can present Eq. (1.99) in the form

$$\tau_\sigma = \frac{1}{D_1} \frac{(K\Gamma_\infty)^2}{(1 + Kc_1)^4} = \frac{1}{D_1} \frac{(K\Gamma_\infty)^2}{(1 + E_G / (\Gamma_\infty kT))^4} \quad (\text{for Langmuir isotherm}) \quad (1.100)$$

Equation (1.100) visualizes the very strong dependence of the relaxation time on the surfactant concentration c_1 ; in general, τ_σ can vary with many orders of magnitude as a function of c_1 . Equation (1.100) shows also that high Gibbs elasticity corresponds to short relaxation time, and vice versa.

As a quantitative example let us take typical values of the parameters: $K_1 = 15 \text{ m}^3/\text{mol}$, $1/\Gamma_\infty = 40 \text{ \AA}^2$, $D_1 = 5.5 \times 10^{-6} \text{ cm}^2/\text{s}$ and $T=298 \text{ K}$. Then substituting $c_1 = 6.5 \times 10^{-6} \text{ M}$ in Eqs. (1.45a) and (1.100) we calculate $E_G \approx 1.0 \text{ mN/m}$ and $\tau_\sigma \approx 5 \text{ s}$. In the same way, for $c_1 = 6.5 \times 10^{-4} \text{ M}$ we calculate $E_G \approx 100 \text{ mN/m}$ and $\tau_\sigma \approx 5 \times 10^{-4} \text{ s}$.

As already mentioned, to directly measure the Gibbs elasticity E_G , or to precisely investigate the dynamics of surface tension, one needs an experimental method, whose characteristic time is smaller compared to τ_σ . Equation (1.100) and the above numerical example show that when the surfactant concentration is higher, the experimental method should be faster. Various experimental methods are available, whose operational time scales cover different time intervals. Methods with a shorter characteristic operational time are the oscillating jet method [71-73], the oscillating bubble method [74-77], the fast-formed drop technique [78, 79], the surface wave techniques [80-83] and the maximum bubble pressure method [84-88]. Methods of longer characteristic operational time are the inclined plate method [89, 90] and the drop-weight techniques [91-93]; see Ref. [64] for a detailed review.

1.3.2. ADSORPTION UNDER ELECTRO-DIFFUSION CONTROL

Let us consider a solution of an ionic surfactant and salt; for simplicity we assume that the counterions due to the surfactant and salt are the same (an example is SDS and NaCl, both of them releasing Na^+ counterions; the coions are DS^- and Cl^-). The adsorption of surfactant at the interface creates surface charge, which is increasing in the course of the adsorption process. The charged interface repels the new-coming surfactant molecules, but attracts the conversely charged counterions; some of them bind to the surfactant headgroups thus decreasing the surface charge density and favoring the adsorption of new surfactant molecules.

The transport of the i -th ionic species, with valency Z_i and diffusion coefficient D_i , under the influence of electrical potential ψ , is described by the set of electro-diffusion equations [58,59,94]:

$$\frac{\partial c_i}{\partial t} = D_i \frac{\partial}{\partial z} \left(\frac{\partial c_i}{\partial z} + \frac{Z_i e}{kT} c_i \frac{\partial \psi}{\partial z} \right) \quad (z > 0, t > 0) \quad i = 1, 2, 3 \quad (1.101)$$

The indices $i = 1, 2$ and 3 denote the surfactant ion, the counterion and the coion, respectively; c_i is the bulk concentrations of the i -th ion which depends on time t and the distance z to the interface. The second term in the parentheses in Eq. (1.101), the so called “electromigration” term, accounts for the effect of the electric field on diffusion. The electric potential ψ is related to the bulk charge density through the known Poisson equation,

$$\frac{\partial^2 \psi}{\partial z^2} = -\frac{4\pi e}{\epsilon} [Z_1 c_1 + Z_2 c_2 + Z_3 c_3], \quad (1.102)$$

Now we have two adsorbing species: the surfactant ions and the counterions; the coions are not expected to adsorb at the interface: $\Gamma_3 = 0$; on the other hand, $\tilde{\Gamma}_3 = \Lambda_3 \neq 0$, see Eq. (1.69).

Then the generalization of Eq. (1.91) is

$$\frac{d\Gamma_i}{dt} = D_i \left(\frac{\partial c_i}{\partial z} + \frac{Z_i e}{kT} c_i \frac{\partial \psi}{\partial z} \right) \quad (z=0, t>0) \quad i=1,2. \quad (1.103)$$

Note that the supply of surfactant ions to the interface is promoted by the gradient of concentration, ∇c_1 , but it is opposed by the gradient of electric field, $\nabla \psi$. The two effects compensate each other in such a way, that the effect of ∇c_1 is slightly predominant (otherwise, there would not be surfactant adsorption). For the conversely charged counterions these tendencies have the opposite direction with a predominant effect of $\nabla \psi$.

It is not an easy task to solve the electro-diffusion problem based on Eqs. (1.101)–(1.103). Dukhin *et al.* [95-98] have developed a quasi-equilibrium model assuming that the characteristic diffusion time is much greater than the time of formation of the electrical double layer, and consequently, the electro-diffusion problem is reduced to a mixed barrier-diffusion controlled problem. Bonfillon and Langevin [99] investigated the case of small periodic surface corrugations. MacLeod and Radke [94] obtained numerical solutions of the electro-diffusion problem without taking into account the effect of counterion binding, i.e. the formation of a Stern layer.

Analytical results for the long-time asymptotics of adsorption and surface tension have been obtained in Refs. [60,70,100] without making simplifications of the physical model. Assuming

small deviations from equilibrium the adsorption isotherm is linearized and a counterpart of Eq. (1.92) is obtained:

$$\Delta\Gamma_i(t) \equiv \Gamma_i(t) - \Gamma_{i,e} = \left(\frac{\partial\Gamma_i}{\partial c_{1s}} \right)_e \Delta c_{1s}(t) + \left(\frac{\partial\Gamma_i}{\partial c_{2s}} \right)_e \Delta c_{2s}(t) \quad (i=1,2) \quad (1.104)$$

where $\Delta c_{is}(t) \equiv c_{is}(t) - c_{is(e)}$, $i=1,2$, are the perturbations in the subsurface concentrations of surfactant ions and counterions. As usual, the subscript “s” denotes subsurface concentration and the subscript “e” refers to the equilibrium state. We recall that in the case of ionic surfactant two types of adsorptions can be introduced: Γ_i , which is mostly due to the surfactant ions and counterions immobilized at the interface, and $\tilde{\Gamma}_i = \Gamma_i + \Lambda_i$ which includes also a contribution from the whole diffuse EDL, see Eq. (1.69). Equation (1.104) expresses a *local* equilibrium between surface and subsurface; such an equation cannot be written for $\tilde{\Gamma}_i$, because the latter quantity has a non-local, integral character. The result for the long-time asymptotics of the adsorption relaxation, derived on the basis of Eqs. (1.101)–(1.104), is [60,70]:

$$\frac{\Delta\Gamma_i(t)}{\Delta\Gamma_i(0)} \equiv \frac{\Gamma_i(t) - \Gamma_{i,e}}{\Gamma_i(0) - \Gamma_{i,e}} = \sqrt{\frac{\tau_i}{\pi t}} \quad (t \gg \tau_i, i=1,2) \quad (1.105)$$

where the adsorption relaxation time τ_i is defined as follows [60,70]:

$$\tau_i = \frac{1}{\kappa^2} \left(g_{i1} G_1(\lambda) + \frac{2\lambda\tilde{q}}{p} g_{i2} + g G_2(\lambda) \right)^2 \quad (i=1,2) \quad (1.106)$$

where κ is the Debye screening parameter, Eq. (1.64), and the following notation is used:

$$g \equiv g_{11}g_{22} - g_{12}g_{21}, \quad g_{ji} \equiv \kappa \left(\frac{\partial\Gamma_j}{\partial c_{is}} \right)_e \quad (i,j=1,2)$$

$$p \equiv 1 + \zeta^2 + (g_{11} - g_{21})\eta\zeta^3 + (g_{22} - g_{12})/\zeta, \quad \zeta = \exp(-\Phi_{s,e}/2)$$

$$\tilde{h} \equiv \left(\frac{1-\eta}{D_1} + \frac{\eta}{D_3} \right)^{1/2}, \quad \tilde{q} \equiv \frac{1}{\sqrt{2}} \left(\frac{\eta}{D_1} + \frac{1}{D_2} + \frac{1-\eta}{D_3} \right)^{1/2}, \quad \eta \equiv \frac{c_{1\infty}}{c_{2\infty}}$$

$$G_1(\lambda) \equiv \left[2\eta\lambda\tilde{q} + (1-\eta)(1+\zeta^2)\tilde{h} \right] \frac{\zeta^2}{p}, \quad G_2(\lambda) \equiv \left[2\eta\lambda\tilde{q} + (1-\eta)\tilde{h} \right] \frac{\zeta}{p}$$

$$\lambda = 1 \quad \text{for small initial perturbation: } \Delta\Gamma_{i,e}(0) \ll \Gamma_{i,e}$$

$$\lambda = (1 + \zeta\Gamma_{2,e}/\Gamma_{1,e})(1 + \zeta)^{-1} \quad \text{for large initial perturbation: } \Gamma_{i,e}(0) = 0$$

The above algebraic equations enable one to calculate the relaxation times of surfactant and counterion adsorption, τ_1 and τ_2 , using Eq. (1.106). From Eqs. (1.74), (1.81), (1.82) and the adsorption isotherms in Table 1.1 (with $a_{is} \approx c_{is}$) one can deduce relatively simple expressions for the coefficients g_{ji} [60]:

$$g_{21} = \frac{\Gamma_2}{\Gamma_1} g_{11}, \quad g_{12} = \frac{\Gamma_2 c_{1s}}{\Gamma_1 c_{2s}} g_{11}, \quad g_{22} = \frac{\Gamma_2^2 c_{1s}}{\Gamma_1^2 c_{2s}} g_{11} + \frac{\kappa K_1 K_2 \Gamma_1}{(K_1 + K_2 c_{2s})^2} \quad (1.107)$$

$$g_{11} = \frac{\kappa \Gamma_1}{c_{1s} J_{\Gamma 1}}, \quad J_{\Gamma 1} \equiv \frac{E_G}{kT \Gamma_1} \quad (1.108)$$

Using the expressions for E_G for the various isotherms in Table 1.2, one can easily calculate $J_{\Gamma 1}$ and all coefficients g_{ji} from Eqs. (1.107)–(1.108). The result for the long-time asymptotics of the surface tension relaxation is [60,70]:

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} \equiv \frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} = \sqrt{\frac{\tau_\sigma}{\pi t}} \quad (t \gg \tau_\sigma) \quad \text{for small initial perturbation} \quad (1.109a)$$

$$\Delta\sigma(t) \equiv \sigma(t) - \sigma_e = E_G \sqrt{\frac{\tau_\sigma}{\pi t}} \quad (t \gg \tau_\sigma) \quad \text{for large initial perturbation} \quad (1.109b)$$

where the characteristic relaxation time is determined by the expression [70]

$$\sqrt{\tau_\sigma} = (1+w)\sqrt{\tau_1} - w\sqrt{\tau_2} - \frac{2\tilde{q}w\lambda}{\kappa} \tanh \frac{\Phi_{s,e}}{4}, \quad w \equiv \frac{2}{J_{\Gamma 1}} \tanh \frac{\Phi_{s,e}}{2} \quad (1.110)$$

where, as usual, $\Phi_{s,e}$ is the equilibrium value of the dimensionless surface potential, cf. Eq. (1.54) and the relaxation times τ_1 and τ_2 are given by Eq. (1.106). It should be noted that usually $\lambda \approx 1$ and, therefore, the values of τ_1 , τ_2 and τ_σ are not so sensitive to the magnitude of

the initial perturbation: small or large. In this respect τ_1 , τ_2 and τ_σ can be considered as general kinetic properties of the adsorption monolayer from an ionic surfactant [70].

Let us now discuss the similarities and dissimilarities of the adsorption relaxation under diffusion and electro-diffusion control, which correspond to the cases of nonionic and ionic surfactants, respectively. In both cases $\Delta\Gamma_1(t)$ and $\Delta\sigma(t)$ tend to zero proportionally to $1/\sqrt{t}$, cf. Eqs. (1.98), (1.105) and (1.109). Hence, from the fact that the plot of $\Delta\sigma(t)$ vs. $1/\sqrt{t}$ is linear it is impossible to determine whether the adsorption is under diffusion or electro-diffusion control. The difference is that the slope of this plot depends on the concentration of added salt in the case of electro-diffusion control. Another difference is that for nonionic surfactants the relaxation time is the same for adsorption and surface tension, see Eq. (1.105), whereas for ionic surfactants these relaxation times are different: $\tau_\sigma \neq \tau_1 \neq \tau_2$. The latter difference originates from the presence of diffuse electric double layer, whose relatively slow relaxation affects stronger τ_σ than τ_1 and τ_2 . To visualize the difference between τ_σ , τ_1 and τ_2 , and to examine their dependence on the concentration of the dissolved salt, below we consider an illustrative example.

The values of the parameters β , Γ_∞ , K_1 and K_2 , determined from the fits of the data in Fig. 1.6 (see Section 1.2.5) can be used to calculate the values of all parameters entering Eq. (1.106) and (1.110). Figure 1.9 shows the relaxation times of surface tension, surfactant adsorption and counterion adsorption, τ_σ , τ_1 , and τ_2 , respectively, calculated in this way in Ref. [70]. They are plotted as functions of the surfactant concentration, $c_{1\infty}$, for a solution, which does not contain NaCl: $c_{3\infty} = 0$. First of all, one notices the wide range of variation of the relaxation times, which is 3 - 4 orders of magnitude. In particular, the relaxation time of surface tension, τ_σ , drops from 0.1 s down to 1×10^{-5} s. Next, one sees that systematically $\tau_2 < \tau_1 < \tau_\sigma$; the difference between these three relaxation times can be greater than one order of magnitude for the lower surfactant concentrations. Thus one can conclude that the terms with $\Phi_{s,e}$ in Eq. (1.110), which lead to a difference between τ_1 and τ_σ , play an important role, especially for the lower surfactant concentrations. Figure 1.9 demonstrates that the approximation $\tau_\sigma \approx \tau_1$, which is widely used in literature, is applicable only for the higher surfactant concentrations,

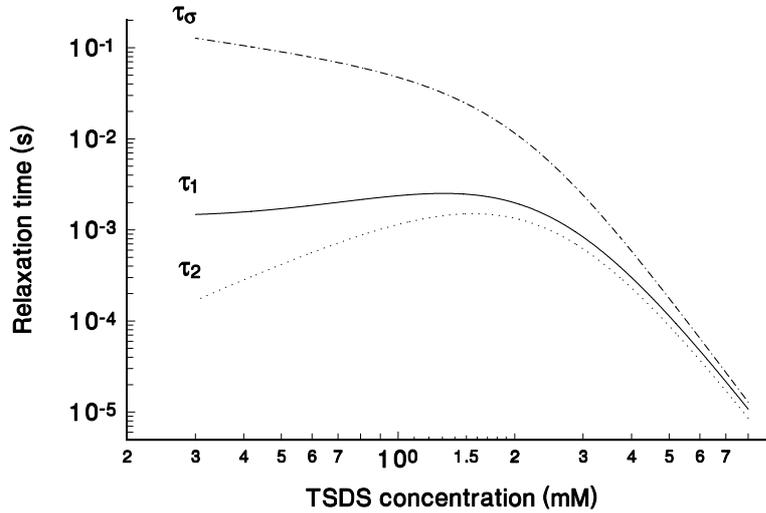


Fig. 1.9. Relaxation times of surface tension, τ_σ , of surfactant adsorption, τ_1 , and of counterion adsorption, τ_2 , calculated in Ref. [70] for surfactant solutions without added salt by means of Eqs. (1.106) and (1.110) as functions of surfactant (TSDS) concentration, $c_{1\infty}$, using parameters values determined from the best fit of the data in Fig. 1.6; a large initial perturbation is assumed.

for which $\tau_\sigma \rightarrow \tau_1$. Note also that τ_2 keeps always smaller than τ_1 and τ_σ , that is the adsorption of counterions relaxes always faster than does the adsorption of surfactant ions and the surface tension. Moreover, τ_2 exhibits a non-monotonic behavior (Figure 1.9). The initial increase in τ_2 with the rise of the TSDS concentration can be attributed to the fact that the strong increase of the occupancy of the Stern layer, Γ_2 / Γ_1 , with the rise of surfactant concentration (see Fig. 1.8, the curve without salt) leads to a decrease of the surface charge density and a proportional decrease of the driving force of counterion supply, $\nabla\psi$.

To demonstrate the effect of salt on the relaxation time of surface tension, in Fig. 1.10 τ_σ is plotted vs. $c_{1\infty}$ for a wider range of surfactant concentrations (than that in Fig. 1.9) and for 4 different salt concentrations denoted in the figure. Again, one sees that τ_σ varies with many orders of magnitude: from more than 100 s down to 10^{-5} s. As seen in Fig. 1.10, the addition of salt (NaCl) accelerates the relaxation of the surface tension for the higher surfactant

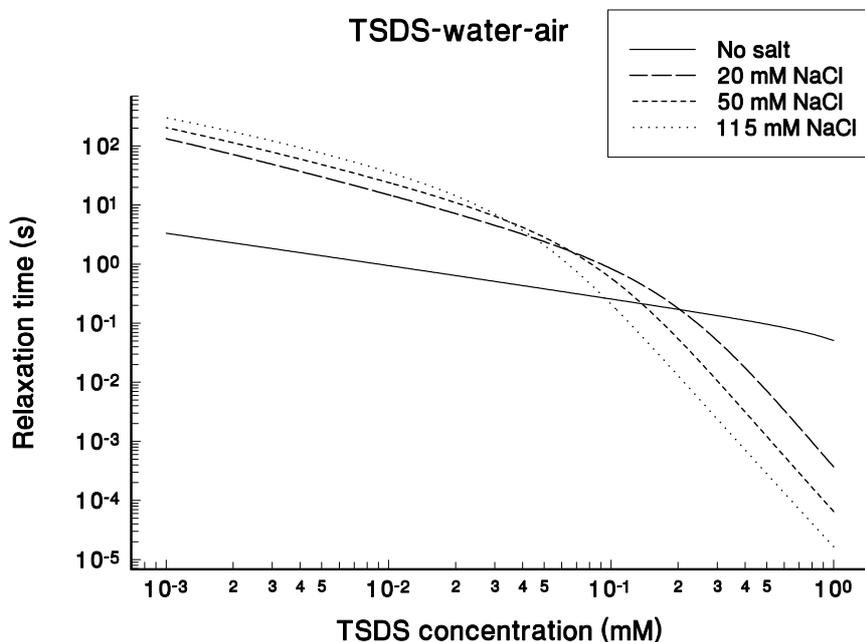


Fig. 1.10. Relaxation time of surface tension, τ_σ , vs. surfactant (TSDS) concentration, $c_{1\infty}$, calculated in Ref. [70] by means of Eq. (1.110) for four different NaCl concentrations using parameters values determined from the best fit of the data in Fig. 1.6; a large initial perturbation is assumed.

concentrations, but decelerates it for the lower surfactant concentrations. This curious inversion of the tendency can be interpreted in the following way. The accelerating effect of salt at the higher surfactant concentrations can be attributed to the suppression of the electric double layer by the added salt. For the lower surfactant concentrations (in the region of Henry) the latter effect is dominated by another effect of the opposite direction. This is the increase of $(\partial\Gamma/\partial c_{1\infty})_{c_{2\infty}}$ due to the added salt. Physically, the effect of $(\partial\Gamma/\partial c_{1\infty})_{c_{2\infty}}$ can be explained as follows [60]. At *low* surfactant concentrations the diffusion supply of surfactant is very slow and it controls the kinetics of adsorption. In the absence of salt the equilibrium surfactant adsorption monolayer is comparatively diluted, so the diffusion flux from the bulk is able to quickly equilibrate the adsorption layer. The addition of salt at low surfactant concentrations strongly increases the equilibrium surfactant adsorption (see Fig. 1.7); consequently, much longer time is needed for the slow diffusion influx to equilibrate the interface (the left-hand side branches of the curves in Fig. 1.10). More details can be found in Ref. [60,70].

1.3.3. ADSORPTION UNDER BARRIER CONTROL

The adsorption is under barrier (kinetic) control when the stage of surfactant transfer from the subsurface to the surface is much slower than the diffusion stage because of some kinetic barrier. The latter can be due to steric hindrance, spatial reorientation or conformational changes accompanying the adsorption of the molecules. The electrostatic (double-layer) interaction presents a special case, which is considered in the previous Section 1.3.2. First, we will restrict our considerations to the case of pure barrier control without double layer effects. In such a case the surfactant concentration is uniform throughout the solution, $c_1 = \text{const.}$, and the increase of the adsorption $\Gamma_1(t)$ is solely determined by the “jumps” of the surfactant molecules over the adsorption barrier, separating the subsurface from the surface:

$$\frac{d\Gamma_1}{dt} = Q \equiv r_{\text{ads}}(c_1, \Gamma_1) - r_{\text{des}}(\Gamma_1) \quad (1.111)$$

r_{ads} and r_{des} are the rates of surfactant adsorption and desorption. The concept of barrier-limited adsorption originate from the works of Bond and Puls [101], and Doss [102]. Further this theoretical model has been developed in Refs. [103-110]. Table 1.4 summarizes the most popular expressions for the total rate of adsorption under barrier control, Q , see Refs. [108-112]. The quantities K_{ads} and K_{des} in Table 1.4 are the rate constants of adsorption and desorption, respectively. Their ratio gives the equilibrium constant of adsorption

$$K_e \equiv K_{\text{ads}} / K_{\text{des}} = \Gamma_\infty K \quad , \quad (1.112)$$

The expression $K_e = \Gamma_\infty K$, is valid for the Henry, Langmuir, Frumkin, Volmer and van der Waals isotherms; likewise, for the Freundlich isotherm $K_e = \Gamma_\infty K_F$; the parameters Γ_∞ , K and K_F are the same as in Table 1.1. Setting $Q = 0$ (which corresponds to the equilibrium state of the system) each expression in Table 1.4 reduces to the respective equilibrium adsorption isotherm given in Table 1.1, as it should be expected. In addition, for $\beta = 0$ the Frumkin expression for Q reduces to the Langmuir expression. For $\Gamma_1 \ll \Gamma_\infty$ both the Frumkin and Langmuir expressions in Table 1.4 reduce to the Henry expression.

Substituting the expressions for Q from Table 1.4 into Eq. (1.111) and integrating one can derive explicit expressions for the relaxation of surfactant adsorption:

Table 1.4. Expressions for the total rate of reversible surfactant adsorption, Q , corresponding to six different kinetic models [110].

Type of adsorption isotherm	Total rate of reversible adsorption $Q = r_{\text{ads}}(c_1, \Gamma_1) - r_{\text{des}}(\Gamma_1)$
Henry	$Q = K_{\text{ads}} c_1 - K_{\text{des}} \Gamma_1$
Freundlich	$Q = K_{\text{ads}} K^{m-1} c_1^m - K_{\text{des}} \Gamma_1$
Langmuir	$Q = K_{\text{ads}} c_1 \left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) - K_{\text{des}} \Gamma_1$
Frumkin	$Q = K_{\text{ads}} c_1 \left(1 - \frac{\Gamma_1}{\Gamma_\infty}\right) - K_{\text{des}} \Gamma_1 \exp\left(-\frac{2\beta \Gamma_1}{kT}\right)$
Volmer	$Q = K_{\text{ads}} c_1 - K_{\text{des}} \Gamma_1 \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1}\right)$
van der Waals	$Q = K_{\text{ads}} c_1 - K_{\text{des}} \Gamma_1 \frac{\Gamma_\infty}{\Gamma_\infty - \Gamma_1} \exp\left(\frac{\Gamma_1}{\Gamma_\infty - \Gamma_1} - \frac{2\beta \Gamma_1}{kT}\right)$

$$\frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} \approx \frac{\Gamma_1(t) - \Gamma_{1,e}}{\Gamma_1(0) - \Gamma_{1,e}} = \exp\left(-\frac{t}{\tau_\sigma}\right) \quad (1.113)$$

Equation (1.113) holds for $\Delta\sigma(t) = \sigma(t) - \sigma_e$ only in the case of small deviations from equilibrium, whereas there is not such a restriction concerning $\Delta\Gamma_1(t) = \Gamma_1(t) - \Gamma_{1,e}$; the relaxation time in Eq. (1.113) is given by the expressions

$$\tau_\sigma = (K_{\text{des}})^{-1} \quad (\text{Henry and Freundlich}) \quad (1.114)$$

$$\tau_\sigma = \left(K_{\text{des}} + \frac{K_{\text{ads}} c_1}{\Gamma_\infty}\right)^{-1} \quad (\text{Langmuir}) \quad (1.115)$$

Equation (1.113) predicts that the perturbation of surface tension, $\Delta\sigma(t) = \sigma(t) - \sigma_e$, relaxes exponentially. This is an important difference with the cases of adsorption under diffusion and electro-diffusion control, for which $\Delta\sigma(t) \propto 1/\sqrt{t}$, cf. Eqs. (1.98), (1.105) and (1.109). Thus a

test whether or not the adsorption occurs under purely barrier control is to plot data for $\ln[\Delta\sigma(t)]$ vs. t and to check if the plot complies with a straight line.

When the rate of transfer of surfactant molecules from the subsurface to the surface is not-too-slow compared with the rate of diffusion, one deals with the more general case of mixed *barrier-diffusion* control [110]. In such a case, the “kinetic” boundary condition (1.111) is used in conjunction with the “diffusion” boundary condition (1.91). Numerical analysis of this process has been performed on the basis of the Henry and Langmuir models [113], and the Frumkin model [111]. Analytical solution of the mixed (diffusion-barrier) problem has been published in Ref. [59] for the case of the Henry isotherm:

$$\frac{\Gamma_1(t) - \Gamma_1(0)}{\Gamma_{1,e} - \Gamma_1(0)} = F(\tau, b_2) - F(\tau, b_1), \quad F(\tau, b) \equiv \frac{1 - \exp(b^2\tau) \operatorname{erfc}(b\sqrt{\tau})}{2b\sqrt{\alpha^2 - 1}} \quad (1.116)$$

where $\tau = K_{\text{des}}t$ is dimensionless time, $b_{1,2} = \alpha \pm (\alpha^2 - 1)^{1/2}$ are dimensionless parameters with $\alpha = K_{\text{ads}} / (4D_1K_{\text{des}})^{1/2}$ being a dimensionless diffusion-kinetic ratio; the complementary error function $\operatorname{erfc}(x)$ is defined by Eq. (1.95). Equation (1.116) is valid not only for $\alpha > 1$, but also in the case $\alpha < 1$ (fast diffusion). Despite the fact that in the latter case b_1 and b_2 become complex numbers, Eq. (1.116) gives real values of $\Gamma_1(t)$. In the limit $\alpha \rightarrow 0$ (complete barrier control) Eq. (1.116) reduces to Eqs. (1.113)–(1.114). In fact, Eq. (1.116) describes the transition from diffusion to adsorption control: for $\alpha > 1/\sqrt{2}$ the diffusion control is predominant and $\Delta\Gamma(t) \propto 1/\sqrt{t}$ for $t \rightarrow \infty$; on the other hand, for $\alpha < 1/\sqrt{2}$ the barrier control is predominant and $\Delta\Gamma(t)$ decays exponentially for $t \rightarrow \infty$. One can estimate the characteristic time of relaxation under mixed diffusion-barrier control by using the following combined expression:

$$\tau_\sigma \approx \frac{1}{K_{\text{des}}} \left(\alpha + |\alpha^2 - 1|^{1/2} \right)^2 \quad (1.117)$$

For $\alpha \ll 1$ Eq. (1.117) reduces to the result for barrier control, Eq. (1.114), whereas for $\alpha \gg 1$ Eq. (1.117), along with Eq. (1.112), gives the expression for diffusion control, Eq. (1.94), for the Henry isotherm. Other results for the mixed diffusion-barrier problem can be found in Refs. [114-118].

The case of mixed *barrier-electrodifffusion* control also deserves some attention insofar as it can be important for the kinetics of adsorption of some ionic surfactants. We will consider the same system as in Section 1.3.2, that is a solution of an ionic surfactant M^+S^- with added non-amphiphilic salt M^+C^- . Here S^- is the surfactant ion, M^+ is the counterion and C^- is the coion due to the salt.

First, let us consider *Langmuir*-type adsorption, i.e. let us consider the interface as a two-dimensional lattice. Further, we will use the notation θ_0 for the fraction of the free sites in the lattice, θ_1 for the fraction of the sites containing adsorbed surfactant ion S^- , and θ_2 for the fraction of the sites containing the complex of adsorbed surfactant ion with a bound counterion. Obviously, one can write

$$\theta_0 + \theta_1 + \theta_2 = 1 \quad (1.118)$$

The adsorptions of surfactant ions and counterions can be expressed in the form:

$$\Gamma_1/\Gamma_\infty = \theta_1 + \theta_2; \quad \Gamma_2/\Gamma_\infty = \theta_2 \quad (1.119)$$

Following Kalinin and Radke [119], let us consider the "reaction" of adsorption of S^- ions:



where A_0 symbolizes an empty adsorption site. In accordance with the rules of the chemical kinetics one can express the rates of adsorption and desorption in the form:

$$r_{1,ads} = K_{1,ads}\theta_0 c_{1s}, \quad r_{1,des} = K_{1,des}\theta_1 \quad (1.121)$$

where, as before, c_{1s} is the subsurface concentration of surfactant; $K_{1,ads}$ and $K_{1,des}$ are constants. In view of Eqs. (1.118)-(1.119) one can write $\theta_0 = (\Gamma_\infty - \Gamma_1)/\Gamma_\infty$ and $\theta_1 = (\Gamma_1 - \Gamma_2)/\Gamma_\infty$. Thus, with the help of Eq. (1.121) we obtain the adsorption flux of surfactant:

$$Q_1 \equiv r_{1,ads} - r_{1,des} = K_{1,ads}c_{1s}(\Gamma_\infty - \Gamma_1)/\Gamma_\infty - K_{1,des}(\Gamma_1 - \Gamma_2)/\Gamma_\infty \quad (1.122)$$

Next, let us consider the reaction of counterion binding:



The rates of the direct and the reverse reactions are, respectively,

$$r_{2,ads} = K_{2,ads}\theta_1 c_{2s}, \quad r_{2,des} = K_{2,des}\theta_2 \quad (1.124)$$

where $K_{2,ads}$ and $K_{2,des}$ are the respective rate constants, and c_{2s} is the subsurface concentration of counterions. Having in mind that $\theta_1 = (\Gamma_1 - \Gamma_2)/\Gamma_\infty$ and $\theta_2 = \Gamma_2/\Gamma_\infty$, with the help of Eq. (1.124) we deduce an expression for the adsorption flux of counterions:

$$Q_2 \equiv r_{2,ads} - r_{2,des} = K_{2,ads} c_{2s} (\Gamma_1 - \Gamma_2) / \Gamma_\infty - K_{2,des} \Gamma_2 / \Gamma_\infty \quad (1.125)$$

Up to here, we have not used simplifying assumptions. If we can assume that the reaction of counterion binding is much faster than the surfactant adsorption, then we can set $Q_2 \equiv 0$, and Eq. (1.125) reduces to the Stern isotherm:

$$\frac{\Gamma_2}{\Gamma_1} = \frac{K_{St} c_{2s}}{1 + K_{St} c_{2s}}, \quad K_{St} \equiv K_{2,ads} / K_{2,des} \quad (1.126)$$

Note that Eq. (1.126) is equivalent to Eq. (1.82) with $K_{St} \equiv K_2 / K_1$. Next, a substitution of Γ_2 from Eq. (1.126) into Eq. (1.122) yields

$$Q_1 \equiv r_{1,ads} - r_{1,des} = K_{1,ads} c_{1s} (\Gamma_\infty - \Gamma_1) / \Gamma_\infty - K_{1,des} (1 + K_{St} c_{2s})^{-1} \Gamma_1 / \Gamma_\infty \quad (1.127)$$

Equation (1.127) shows that the adsorption flux of surfactant is influenced by the subsurface concentration of counterions, c_{2s} .

If there is equilibrium between surface and subsurface, then we have to set $Q_1 \equiv 0$ in Eq. (1.127), and thus we obtain the Langmuir isotherm for an ionic surfactant:

$$K c_{1s} = \Gamma_1 / (\Gamma_\infty - \Gamma_1), \quad K \equiv (K_{1,ads} / K_{1,des}) (1 + K_{St} c_{2s}) \quad (1.128)$$

Note that the above expression for the adsorption parameter K is equivalent to Eq. (1.81), with $K_1 \equiv K_{1,ads} / K_{1,des}$. This result demonstrates that the linear dependence of K on c_{2s} can be deduced from the reactions of surfactant adsorption and counterion binding, Eqs. (1.120) and (1.123).

In the case of *Frumkin*-type adsorption isotherm an additional effect of interaction between the adsorbed surfactant molecules is taken into account. Then, instead of Eq. (1.122), one can derive

$$Q_1 \equiv r_{1,ads} - r_{1,des} = K_{1,ads} c_{1s} (\Gamma_\infty - \Gamma_1) / \Gamma_\infty - F_{1,des} (\Gamma_1 - \Gamma_2) / \Gamma_\infty \quad (1.129)$$

where $F_{1,des}$ depends on Γ_1 , because an adsorbed surfactant molecule "feels" the presence of other adsorbed molecules at the interface. The latter dependence can be expressed as follows

$$F_{1,\text{des}} = K_{1,\text{des}} \exp\left[-\frac{2\beta\Gamma_1}{kT}\right] \quad (1.130)$$

see Table 1.4 and Ref. [110].

1.3.4. ADSORPTION FROM MICELLAR SURFACTANT SOLUTIONS

As known, beyond a given critical micellization concentration (CMC) surfactant aggregates (micelles) appear in the surfactant solutions. In general, the micelles exist in equilibrium with the surfactants monomers in the solution [50,51]. If the concentration of the monomers in the solution is suddenly decreased, the micelles release monomers until the equilibrium concentration, equal to CMC, is restored at the cost of disassembly of a part of the micelles. The relaxation time of this process is usually in the millisecond range.

The dilatation of the surfactant adsorption layer leads to a transfer of monomers from the subsurface to the surface, which causes a transient decrease of the subsurface concentration of monomers. The latter is compensated by disintegration of a part of the micelles in the

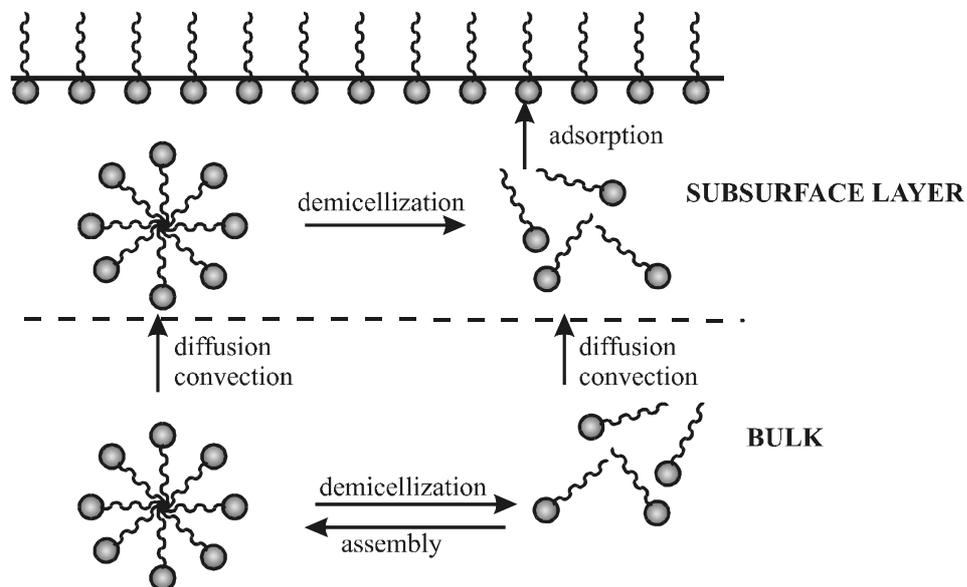


Fig. 1.11. In the neighborhood of an expanded adsorption monolayer the micelles release monomers to restore the equilibrium surfactant concentration at the surface and in the bulk. The concentration gradients give rise to diffusion of micelles and monomers.

subsurface layer, see Fig. 1.11. This process is accompanied by a diffusion transport of surfactant monomers and micelles due to the appearance of concentration gradients. In general, the micelles serve as a powerful source of monomers which is able to quickly damp any interfacial disturbance. Therefore, the presence of surfactant micelles strongly accelerates the kinetics of adsorption.

The theoretical model by Aniansson et al. [120-123] describes the micelles as polydisperse aggregates, whose growth or decay happens by exchange of single monomers:



Here j denotes the aggregation number of the micelle; K_j^+ and K_j^- are rate constants of micelle assembly and disassembly. The general theoretical description of the diffusion in such a solution of polydisperse aggregates taking part in chemical reactions of the type of Eq. (1.131) is a heavy task; nevertheless, it has been addressed in several works [124-127].

Approximate models, which however account for the major physical effects in the system, also have been developed [128-134]. The basis of these models is the experimental fact that the size distribution of the micelles has a well pronounced peak, so they can be described approximately as being monodisperse with a mean aggregation number, m , corresponding to this peak. Other simplification used is to consider small deviations from equilibrium. In this case any reaction mechanism of micelle disassembly gives a linear dependence of the reaction rate on the concentration, i.e. one deals with a reaction of “pseudo-first order”. As an example, we give an expression for the relaxation of surface tension of a micellar solution at small initial deviation from equilibrium derived in Ref. [125]:

$$\frac{\sigma(t) - \sigma_e}{\sigma(0) - \sigma_e} = \frac{\Gamma_1(t) - \Gamma_{1,e}}{\Gamma_1(0) - \Gamma_{1,e}} = \frac{1}{g_1 - g_2} [E(g_1, \tau) - E(g_2, \tau)] \exp\left(-\frac{t}{\tau_m}\right) \quad (1.132)$$

where $E(g, \tau) = g \exp(g^2 \tau) \operatorname{erfc}(g\sqrt{\tau})$, $\tau = t/\tau_d$, $g_{1,2} = [1 \pm \sqrt{1 + 4\tau_d/\tau_m}]/2$,

$$\tau_m = [K_d (1 + m^2 c_{m,e} / c_{1,e})]^{-1}, \quad \tau_d = (\partial\Gamma_1 / \partial c_1)_e^2 / D_1. \quad (1.133)$$

τ_m and τ_d are the characteristic relaxation times of micellization and monomer diffusion, see Ref. [135]; K_d is rate constant of micelle decay; as earlier, the subscript “e” refers to the equilibrium state and m is the micelle aggregation number. In the absence of micelles one is to substitute $\tau_d/\tau_m \rightarrow 0$; then $g_1 = 1$, $g_2 = 0$, and Eq. (1.132) reduces to Eq. (1.93), as it should be expected. One can estimate the characteristic time of relaxation in the presence of micelles by using the following combined expression:

$$\tau_\sigma \approx \frac{4\tau_d}{\left(1 + \sqrt{1 + 4\tau_d/\tau_m}\right)^2} \quad (1.134)$$

According to the latter expression $\tau_\sigma \approx \tau_m$ for $\tau_d \gg \tau_m$ and $\tau_\sigma \approx \tau_d$ for $\tau_d \ll \tau_m$.

Note, that Eq. (1.134) is applicable only for small perturbations. An approximate analytical approach, which is applicable for both small and large deviations from equilibrium, is developed in Ref. [134].

1.3.5. ADSORPTION FROM SOLUTIONS OF PROTEINS

The kinetics of adsorption of proteins and other macromolecules is a complex process, in which several steps, some of them occurring simultaneously, can be conceptually identified [136,137]: (i) transport of the native protein to the interface by diffusion; (ii) adsorption-desorption from the phase boundary, which can happen under barrier control, see section 1.3.3; (iii) changes in the molecular structure (denaturation) including unfolding and spreading of the molecules over the interface; (iv) rearrangement of some structural groups of the adsorbed protein molecules. Many results accumulated in this field can be found in Refs. [63,138-140].

As an example let us consider a process of protein adsorption including stages (i) and (iii). We denote by Γ_1 and Γ_2 the adsorptions of the native and the denatured protein, respectively. The changes of Γ_1 and Γ_2 due to the denaturation process are equal by magnitude but have opposite signs. Then the interfacial mass balances for the two modifications of protein at the interface take the form [141]:

$$\frac{d\Gamma_1}{dt} = D_1 \left(\frac{\partial c_1}{\partial z} \right)_{z=0} - k_p (\Gamma_1 - \Gamma_{1,e}) \quad (1.135)$$

$$\frac{d\Gamma_2}{dt} = -k_p (\Gamma_2 - \Gamma_{2,e}) \quad (1.136)$$

where k_p is a kinetic rate constant of protein denaturing. The integration of Eq. (1.136) yields

$$\Gamma_2 = \Gamma_{2,e} (1 - \exp(-k_p t)) \quad (1.137)$$

To estimate the diffusion flux at the interface one can employ the approximated formula [141]:

$$\left(\frac{\partial c_1}{\partial z} \right)_{z=0} \approx \frac{c_{1,e} - c_{1s}}{\sqrt{\pi D_1 t}} \quad (1.138)$$

Combining Eqs. (1.135) and (1.138), and integrating one obtains

$$\frac{\Delta\Gamma_1(t)}{\Delta\Gamma_1(0)} = \exp \left[- \left(\sqrt{\frac{4t}{\pi \tau_d}} + k_p t \right) \right] \quad (1.139)$$

where τ_d is the same as in Eq. (1.133) and, as usual, $\Delta\Gamma_1(t) = \Gamma_1(t) - \Gamma_{1,e}$. Further, for the relaxation of surface tension one obtains [141]:

$$\frac{\Delta\sigma(t)}{\Delta\sigma(0)} = \left\{ (1 - \varphi) \exp \left[- \left(\sqrt{\frac{4t}{\pi \tau_d}} \right) \right] + \varphi \right\} \exp(-k_p t); \quad \varphi \equiv \frac{(\partial\sigma / \partial\Gamma_2)_e}{(\partial\sigma / \partial\Gamma_1)_e + (\partial\sigma / \partial\Gamma_2)_e} \quad (1.140)$$

The relaxation of surface tension, described by Eq. (1.140), exhibits two characteristic relaxation times: that of diffusion, τ_d , and that of denaturation (conformational changes), k_p^{-1} .

1.4. SUMMARY

From a micromechanical viewpoint the interfacial tension and bending moment can be interpreted as integral effects of the anisotropy of the pressure tensor in the transition zone between two fluid phases, see Eqs. (1.8) and (1.12). Usually, the width of this transition zone is very small, of the order of several nanometers (Figs. 1.2 and 1.3). However, if the interface of an aqueous solution is electrically charged, the width of the transition zone could rise up to the

order of micrometers because of the formation of a diffuse electric double layer in a vicinity of the phase boundary. In the latter case the interfacial tension (and the bending moment as well) can be expressed as a sum of a double-layer and a non-double-layer contribution, Eq. (1.19).

The thermodynamics of fluid interfaces describes how the composition in the bulk of solution determines the composition at the phase boundary and the interfacial tension. Various surfactant adsorption isotherms can be used to process experimental data; the most popular of them are listed in Table 1.1, where the respective surface tension isotherms are also shown. In the case of solutions of ionic surfactants two types of adsorptions can be introduced: $\tilde{\Gamma}_i$, which represents a surface excesses of component “*i*” with respect to the uniform bulk solution, and Γ_i representing a surface excess with respect to the non-uniform diffuse electric double layer, see Eq. (1.69). Correspondingly, the Gibbs adsorption equation for a charged interface can be expressed in two equivalent forms, Eqs. (1.68) and (1.70). Not only surfactant ions, but also counterions, do adsorb at the interface; the counterionic adsorption can be described by the Stern isotherm, Eq. (1.82), which is thermodynamically compatible with the surfactant adsorption isotherms (Table 1.1) if only Eq. (1.81) is satisfied. The occupancy of the Stern layer by adsorbed counterions could rise up to 70 - 80 % (Fig. 1.8) and should not be neglected. The double-layer contribution to the interfacial tension depends on the valence of the electrolyte, see Table 1.3.

The value of the Gibbs elasticity, E_G , of an adsorption layer determines whether the interface behaves as a two-dimensional fluid or as an elastic body. This rheological behavior can strongly influence the attachment of a particle to an interface, as well as the capillary forces between attached particles. Definitions for Gibbs elasticity of adsorption layers from non-ionic and ionic surfactants are presented and discussed, see Eqs. (1.45), (1.88) and Table 1.2.

For soluble surfactants the effect of the Gibbs elasticity can be suppressed by the diffusive supply of surfactant to an expanding interface; the diffusion tends to render the interface more fluid. Thus one can estimate whether or not the effect of Gibbs elasticity will show up by a comparison of the characteristic adsorption relaxation time with the characteristic time of the specific process. Expressions for the relaxation time of surface tension, τ_σ , are presented for the cases of adsorption kinetics under diffusion control: Eq. (1.94); electro-diffusion control:

Eq. (1.110); barrier control: Eqs. (1.114)–(1.115), mixed diffusion-barrier control: Eq. (1.117), adsorption from micellar solutions, Eq. (1.134), and adsorption from protein solutions, see Eq. (1.140). The quantities introduced in Chapter 1, and the relationships between them, are important for the theoretical description of the particle-interface interaction and the particle-particle capillary forces, as this will be seen in the next chapters.

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