

# Chapter 4

## Thermodynamics of Interfaces in Soft-Matter Systems

Gerhard H. Findenegg

**Abstract** Thermodynamics of interfaces provides a framework to relate measurable quantities to other important yet not directly accessible equilibrium properties of interfacial systems. For liquid/gas and liquid/liquid interfaces (fluid interfaces) the interfacial tension and its dependence on temperature and composition can be measured, while the adsorbed amounts of the components are not accessible. Conversely, for solid/fluid interfaces the adsorbed amount can be measured but the interfacial tension (free energy) is not accessible. For both cases the Gibbs equation represents a bridge between the two kinds of quantities. In this chapter we explain the application of the Gibbs equation with a focus on soft matter systems. We also discuss the meaning of surface excess amounts and their relation to (absolute) surface concentrations which appear in adsorbate equations of state. Finally we briefly touch the additional features of charged interfaces and of ionic equilibria at interfaces.

### 4.1 Thermodynamic Quantities and Relations

#### 4.1.1 Introduction

Interfaces represent thin regions between macroscopic phases in which the properties gradually change from those of one adjacent phase to those of the other. Because of this inhomogeneous nature of interfaces, a thermodynamic treatment of their properties has been a challenge to generations of scientists. Different formalisms have been developed to cope with this problem. One intuitively appealing way of treating a surface is to consider it as a distinct phase of finite thickness and volume, so that adsorption and related phenomena can be treated analogous to

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G.H. Findenegg (✉)  
Stranski Laboratory of Physical and Theoretical Chemistry,  
Technical University Berlin, 10623 Berlin, Germany  
e-mail: findenegg@chem.tu-berlin.de

phase equilibria. This approach was pursued, among others, by Bakker [1] and Guggenheim [2]. However, the clarity of the surface phase formalism is deceptive, as there is no way to define unambiguously the thermodynamic properties of this surface phase. An alternative formalism for defining the thermodynamic properties was proposed by Gibbs in 1878 [3]. In this treatment the surface is regarded as a mathematical dividing plane between the two macroscopic phases, and the properties of the interface are defined as a *surface excess* relative to a hypothetical reference system in which all properties remain uniform up to the dividing plane. Surface excess quantities often have no intuitively simple interpretation, but their importance lies in the fact that they represent measurable quantities.

In this short review we focus on adsorption phenomena from liquid phases at different types of interfaces (liquid/gas, liquid/liquid and liquid/solid). The treatment is limited to interfaces at which specific curvature effects can be neglected. We show how surface excess quantities suitably defined for these types of interfaces can be determined experimentally and interpreted in terms of physical models. The examples chosen are related to soft matter at aqueous interfaces.

### 4.1.2 Surface Tension

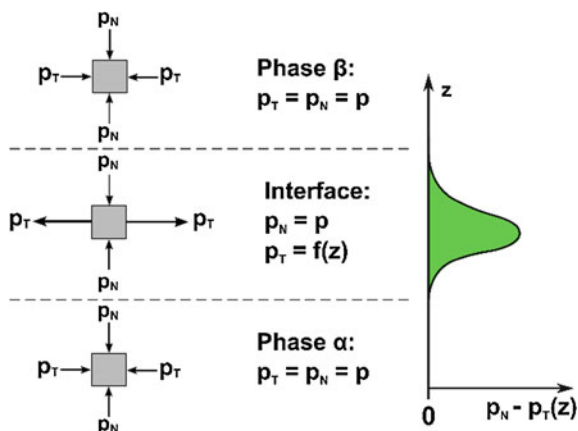
The liquid/vapour interface of fluids represents an inhomogeneous region in which the local density changes from high to low values at a length scale of a few molecular diameters. We consider a flat interface in the plane  $xy$  as sketched in Fig. 4.1. When neglecting gravity, a force balance on an infinitesimal cube centred at point  $x, y, z$  in the system gives [4]

$$\frac{\partial p_{xx}(x, y, z)}{\partial x} = \frac{\partial p_{yy}(x, y, z)}{\partial y} = \frac{\partial p_{zz}(x, y, z)}{\partial z} = 0 \quad (4.1)$$

where  $p_{xx}$ ,  $p_{yy}$ , and  $p_{zz}$ , are the pressures exerted on surfaces normal to the  $x$ ,  $y$ , and  $z$  axis, respectively. Since the local density depends only on  $z$ , the coordinate normal to the interface, but not on the position in the  $xy$  plane, the pressure components  $p_{xx}$ ,  $p_{yy}$ , and  $p_{zz}$  can be only functions of  $z$ . Also, because of the condition of isotropy in the  $xy$  plane,  $p_{xx} = p_{yy}$ . Equation 4.1 can therefore be written as

$$\begin{aligned} \frac{\partial p_{zz}(z)}{\partial z} &= 0 \text{ or } p_{zz} = \text{const} \equiv p_N \\ p_{xx} &= p_{yy} = p_T(z) \end{aligned} \quad (4.2)$$

Hence in a two-phase system with planar interface the conditions for hydrostatic equilibrium are: (i) the normal pressure  $p_N$  is constant and equal to the pressure  $p$  of the coexistent bulk phases; (ii) sufficiently far from the interface, the transverse pressure  $p_T$  is also equal to  $p$ , but in the interfacial region  $p_T(z) \neq p_N$ . It can be shown that the interfacial tension  $\gamma$  is given by [1]



**Fig. 4.1** Components of the pressure tensor across the interface of phases  $\alpha$  and  $\beta$ : The normal component  $p_N$  is independent of the position, the transverse component  $p_T$  is a function of  $z$  and assumes negative values in the interfacial region. Accordingly, the pressure difference  $p_N - p_T$  has positive values in this region but is zero elsewhere

$$\gamma = \int_{-\infty}^{\infty} [p - p_T(z)] dz \quad (4.3)$$

The integration can be taken from  $-\infty$  to  $+\infty$  because  $p_T(z)$  differs from  $p$  only near the interface. Equation 4.1 can be taken as a mechanical definition of the interfacial tension. An idea of the magnitude of the stress acting within the interface is obtained by the following elementary calculation. The width of the surface of simple liquids at their normal boiling point is about 1 nm and a typical value of the surface tension is  $30 \text{ mN m}^{-1}$ . Since  $p = 1 \text{ bar}$  this means that the average value of  $p_T(z)$  in the interface is about  $-300 \text{ bar}$ . This large value makes it plausible that the surface tension can dominate phenomena at the mesoscopic and even at a macroscopic level. The expression for  $\gamma$  in Eq. (4.3) is obtained by considering the isothermal reversible work  $\delta W$  for increasing the surface area of the interface by an increment  $\delta A$  at constant volume, i.e.,  $\gamma = \delta W / \delta A$ . Hence in the language of thermodynamics the surface tension represents the change in free energy  $F$  of the two-phase system with an infinitesimal change of the surface area at constant temperature  $T$  and volume  $V$ , viz.,  $\gamma = (\partial F / \partial A)_{T,V}$ , expressed in SI units in  $\text{J m}^{-2}$ .

### 4.1.3 Adsorption as a Surface Excess

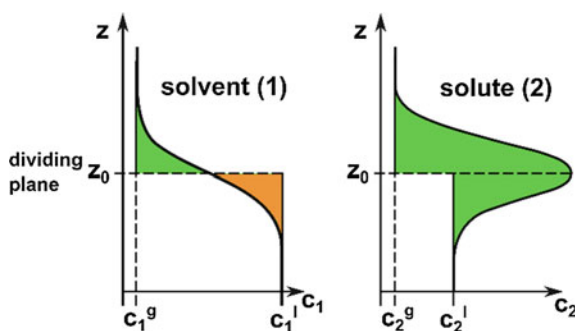
Adsorption generally stands for the enrichment of substances at an interface, but different situations prevail at different types of interface. For example, gas adsorption leads to a higher *density* of the gas near the surface. At liquid/solid

interfaces, on the other hand, enrichment of one component of a mixture goes at the expense of the other component(s), causing changes in *composition* near the surface, and adsorption may be viewed as a displacement of solvent by the solute in the surface layer of the liquid.

The solid phase often represents a more or less inert external medium. This is different in the case of fluid interfaces (liquid/gas or liquid/liquid), where all components may be present at significant concentrations in both phases. In this latter situation it is conceptually difficult to define the adsorbed amount of a component. This problem was solved by Gibbs by introducing the concept of *surface excess quantities* and *relative adsorption*. To rationalize this concept consider the concentration profiles  $c_k(z)$  of the components of a binary mixture ( $k = 1, 2$ ) across a liquid/vapour interface, where the local concentration  $c_k(z)$  changes from  $c_k^l$  to  $c_k^g$  in a monotonic or nonmonotonic manner (Fig. 4.2). The surface excess amount of component  $k$  is now defined as the difference between the known total amount  $n_k$  and the amount in a hypothetical reference system in which the two phases would extend up to a mathematical dividing plane located at some position  $z_0$ . The surface excess amount of component  $k$  is then given by

$$n_k^\sigma = n_k - (c_k^l V^l + c_k^g V^g) \quad (4.4)$$

For given values of  $n_k$  and total volume  $V = V^l + V^g$ , and known concentrations  $c_k^l$  and  $c_k^g$ , the value of the surface excess  $n_k^\sigma$  is not yet defined in a singular way but depends on precisely how the volume  $V$  is divided into the volumes  $V^l$  and  $V^g$ . For a geometric interpretation of the surface excess  $n_k^\sigma$  consider a cylindrical volume with the concentration profile  $c_k(z)$  along the cylinder axis. The overall amount  $n_k$  of component  $k$  in this cylinder is obtained by integration of  $c_k dV = c_k(z) A dz$ , where  $A$  represents the basal area of the cylinder (and thus the area of the interface).



**Fig. 4.2** Sketch of the concentration profiles  $c(z)$  of solvent (*left*) and solute (*right*) across the liquid/vapour interface. In the Gibbs convention the dividing plane (position  $z_0$ ) is chosen such that for the solvent (component 1) the two integrals on the *right-hand side* of Eq. (4.5) become equal in magnitude with opposite sign, so that  $\Gamma_1^\sigma = 0$ . With this choice of  $z_0$ , Eq. (4.5) yields a well-defined surface excess  $\Gamma_2^\sigma$  for the solute, called the relative adsorption  $\Gamma_2^{(1)}$

For the surface excess amount per unit area, i.e., the surface excess concentration  $\Gamma_k^\sigma = n_k^\sigma/A$  (units: mol/m<sup>2</sup>) of a binary mixture we thus obtain:

$$\Gamma_k^\sigma = \int_{-\infty}^{z_0} [c_k(z) - c_k^l] dz + \int_{z_0}^{\infty} [c_k(z) - c_k^g] dz \quad (4.5)$$

The superscript  $\sigma$  on  $n_k^\sigma$  and  $\Gamma_k^\sigma$  indicates ‘surface excess’ but, as explained above, these quantities need to be specified by choosing a suitable location of the dividing plane ( $z_0$ ). The following specifications are important for the different kinds of interfaces:

**Relative adsorption (Gibbs prescription):** This is mostly adopted to quantify the adsorption at the liquid/gas interface of *solutions* (solute components  $k$ ) in a solvent (component 1): In a geometric way the relative adsorption of the solutes can be rationalized by placing the dividing surface at a position  $z_0$  such that  $\Gamma_1^\sigma = 0$  (‘equimolar’ dividing surface for the solvent). Relative surface excess concentrations are denoted as  $\Gamma_k^{(1)}$ , where the superscript (1) indicates “relative to the solvent”. Depending on the concentration profiles of solvent and solute the relative surface excess of a solute can be positive or negative. Experimentally, the relative adsorption  $\Gamma_k^{(1)}$  of solutes adsorbed at the liquid/air interface can be obtained by surface tension measurements as a function of solute concentration (see Eq. (4.17)).

**Reduced adsorption:** This is used to quantify adsorption from mixtures in which no component is distinguished as the solvent. In a geometric way the reduced adsorption of the components can be imagined by placing the dividing surface at a position  $z_0$  such that  $\sum_{k=1}^n \Gamma_k^\sigma = 0$ . Reduced surface excess concentrations are denoted as  $\Gamma_k^{(n)}$ , where the superscript ( $n$ ) indicates that the sum of the surface excess amounts of all  $n$  components is zero. Hence for a binary system,  $\Gamma_2^{(n)} = -\Gamma_1^{(n)}$ . The reduced surface excess  $\Gamma_k^{(n)}$  and similar specifications are mostly used to characterize adsorption at solid/liquid interfaces, where  $\Gamma_k^{(n)}$  can be measured from the change in concentration before and after equilibration with the adsorbent (see Eq. 4.42). Relative adsorption and reduced adsorption are interrelated by  $\Gamma_2^{(1)} = \Gamma_2^{(n)} / (1 - x_2^l)$ , where  $x_2^l$  is the mole fraction of component 2 in the liquid phase.

**Two-solvent relative adsorption:** Adsorption of solutes at liquid/liquid interfaces is usually defined relative to the solvents of both phases. Denoting the two solvents as components 1 and 2, then according to this prescription  $\Gamma_1^\sigma = 0$  and  $\Gamma_2^\sigma = 0$ . The surface excess concentration of solutes ( $k = 3, 4, \dots$ ) relative to the two solvents is denoted as  $\Gamma_k^{(1,2)}$ . This definition, which goes beyond the original Gibbs formalism, implies that we are placing two ‘equimolar’ dividing surfaces, one for each solvent. Hence the volume of the system is no longer the sum of the two bulk phases  $\alpha$  and  $\beta$ , but now given by  $V = V^\alpha + V^\beta + V^\sigma$ , where the excess volume  $V^\sigma$  may be positive or negative. The surface excess concentrations  $\Gamma_k^{(1,2)}$  can be

obtained from measurements of the interfacial tension as a function of concentration (see Eq. 4.18).

As mentioned above, the surface excess concentrations  $\Gamma_k^{(1)}$ ,  $\Gamma_k^{(n)}$ , and  $\Gamma_k^{(1,2)}$  are measurable quantities based on clear operational definitions. Working with these quantities has the disadvantage, however, that they lack a simple physical interpretation. To overcome this problem, physical models of the interfacial layer have been introduced. Usually it is assumed that the surface layer has a uniform composition with concentrations  $\Gamma_k^s$  of the individual components  $k$ . Such a surface phase model will be introduced in Sect. 4.2.3, where it will be shown how the surface concentrations can be calculated from the experimentally accessible surface excess concentrations.

#### 4.1.4 Gibbs Adsorption Equation

The Gibbs formalism of surface excess quantities outlined above can be applied to all extensive thermodynamic quantities of the system (internal energy  $U$ , enthalpy  $H$ , entropy  $S$ , Helmholtz free energy  $F$ , Gibbs free energy  $G$ , etc.) except the volume  $V$ . The surface excess  $X^\sigma$  of a quantity  $X$  is defined as [5]

$$X^\sigma = X - X^\alpha - X^\beta \quad (4.6)$$

where  $X$  represents the value for the entire two-phase system, while  $X^\alpha$  and  $X^\beta$  relate to the homogeneous phases  $\alpha$  and  $\beta$ , when their volumes extend up to the dividing surface.  $V^\sigma = 0$  is implicit in the Gibbs formalism, because the bulk phases extend up to the dividing surface. Remarkably, thermodynamic relations between the excess quantities can be formulated just as if it was a separate phase. The most important relation between the surface excess quantities is the Gibbs equation, which has the general form

$$d\gamma = -s^\sigma dT - \sum_{k=1}^n \Gamma_k^\sigma d\mu_k \quad (4.7)$$

Here,  $s^\sigma = S^\sigma/A$  is the surface excess entropy per unit area,  $\Gamma_k^\sigma$  is the surface excess concentration of component  $k$  defined relative to the same convention for the Gibbs dividing surface as  $s^\sigma$ , and  $\mu_k$  is the chemical potential of component  $k$  at the given temperature  $T$  and composition of the system. According to Eq. (4.7) the Gibbs equation relates changes in surface tension to changes in temperature and the chemical potential of the solutes.

The chemical potential of component  $k$  in the surface can be defined by [5]

$$\mu_k^s = \left( \frac{\partial F}{\partial n_k^\sigma} \right)_{T, V, A, n_j^\sigma} \quad (4.8)$$

Here  $F$  is the Helmholtz free energy ( $F = U - TS$ ) of the whole system and  $A$  is the area of the interface. The condition of equilibrium with respect to diffusion of component  $k$  to the interface from the adjacent phases  $\alpha$  and  $\beta$  can be shown to be

$$\mu_k^\alpha = \mu_k^s = \mu_k^\beta = \mu_k \quad (4.9)$$

where  $\mu_k^\alpha$  and  $\mu_k^\beta$  are the chemical potentials in the adjacent bulk phases. Hence  $\mu_k$  in Eq. (4.7) is the common value of the chemical potential throughout the system. Alternatively, the chemical potential can be defined by

$$\mu_k^a = \left(\frac{\partial F}{\partial n_k^a}\right)_{T,V,\gamma,n_k^a} \quad (4.10)$$

Here the superscript  $a$  is used to differentiate this chemical potential from that defined by Eq. (4.8). Equilibrium between a liquid phase and the interface is then shown to exist when

$$\mu_k^l = \mu_k^s = \mu_k^a - \gamma \underline{a}_k \quad (4.11)$$

where  $\underline{a}_k = \left(\frac{\partial A}{\partial n_k^a}\right)_{T,V,\gamma,n_k^a}$  is the partial molar area of component  $k$  in the surface. Equation 4.11 expresses the fact that when the derivative  $\partial F/\partial n_k^a$  is taken at constant interfacial tension  $\gamma$  rather than constant surface area  $A$ , the dependence on  $\gamma$  must be added by the term  $\gamma \underline{a}_k$ .

## 4.2 Fluid Interfaces

### 4.2.1 Surface of Pure Liquids and Liquid/Liquid Interface of Partially Miscible Binary Systems

For the liquid/vapour interface of a pure fluid, when choosing the ‘equimolar’ dividing surface ( $\Gamma^\sigma = 0$ ), the Gibbs equation (Eq. 4.7) reduces to  $s^\sigma = -(d\gamma/dT)$ . For simple liquids both  $\gamma$  and  $-(d\gamma/dT)$  decrease monotonically with increasing temperature from the triple point to the critical point. Water is not a simple liquid. It has a high surface tension ( $72.0 \text{ mN m}^{-1}$  at  $25^\circ\text{C}$ ) and  $-(d\gamma/dT)$  exhibits a maximum near  $200^\circ\text{C}$ . When the critical temperature  $T_c$  of a fluid is approached along the vapour/liquid coexistence line, the densities of the liquid and vapour phase become equal and the interface vanishes at the critical point. Close to  $T_c$  the vanishing of the surface tension follows a universal law [6]

$$\gamma(T) = \gamma_0(T_c - T)^m \quad (4.12)$$

where  $\gamma_0$  is a material constant and the index  $m$  has a universal value ( $m \approx 1.25$ ). From Eqs. (4.7) and (4.12) the surface excess entropy as a function of temperature then becomes

$$s^\sigma(T) = m\gamma_0(T_c - T)^{m-1} \quad (4.13)$$

This relation tells us that pure liquids have a positive excess entropy that decreases progressively as the critical point is approached. Physically,  $s^\sigma > 0$  means that molecules in the topmost layers of the liquid phase have a higher free volume and thus a higher translational entropy than those in the interior of the liquid.

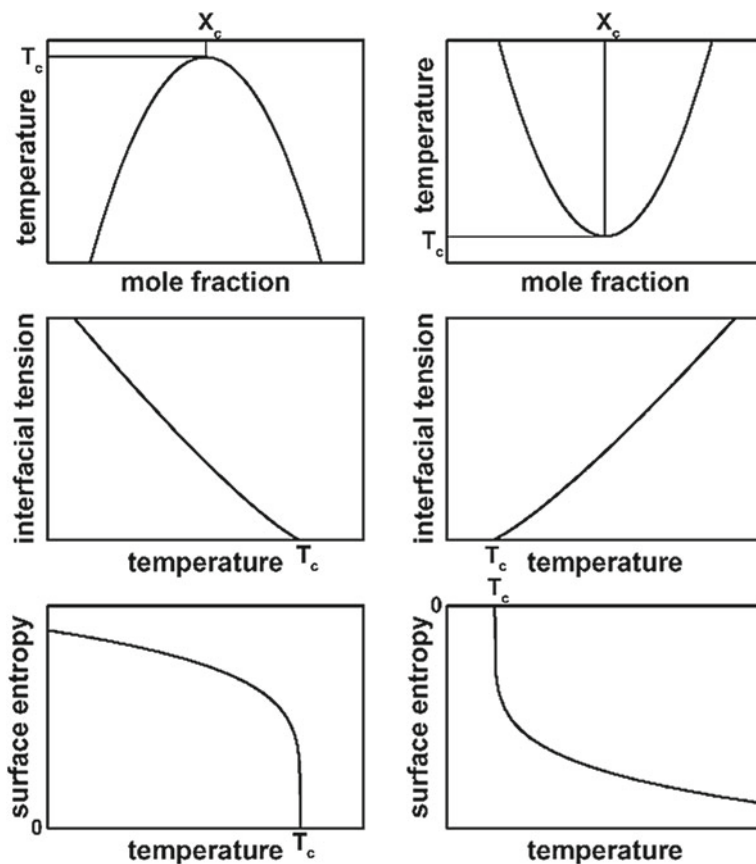
From a thermodynamic point of view, the liquid/liquid interface of binary systems with a lower miscibility gap behaves similar to the liquid/vapour interface of a pure fluid. The interfacial tension  $\gamma(T)$  again follows Eq. (4.12) as the critical temperature (consolute temperature)  $T_c$  is approached, and with  $s^{(1,2)} = -(\partial\gamma/\partial T)_p$  we find a positive surface excess entropy which falls off steeply near  $T_c$ , as shown in the graphs at the left-hand side of Fig. 4.3. Systems with an upper miscibility gap exhibit a different behaviour, as shown on the right-hand side of Fig. 4.3. In this case phase separation starts at a lower critical point and the interfacial tension increases with temperature. The temperature dependence of  $\gamma$  and  $s^{(1,2)}$  can again be described by Eqs. (4.12) and (4.13) when replacing  $(T_c - T)^m$  by  $(T - T_c)^m$  and introducing a minus sign on the r.h.s. of Eq. (4.13). Hence the liquid/liquid interface of systems with an upper miscibility gap exhibits a negative surface excess entropy  $s^{(1,2)}$ . Examples of systems with an upper miscibility gap are aqueous systems of proton acceptors (e.g., ethers or polyethers). Such systems typically have negative values of the excess enthalpy and excess entropy of mixing in the bulk liquid state ( $H^E < 0, S^E < 0$ ) [7].

Does the generic behaviour of liquid surfaces also apply to complex liquids? In the past decades interesting model systems have been studied, in which colloidal particles dispersed in a solvent replace the molecules of a simple fluid, and a non-adsorbed polymer is added to tune the interaction between the colloid particles (see Chap. 3 by R. Tuinier). In a certain range of polymer concentrations phase separation into a colloidal liquid (rich in colloid and poor in polymer) and a colloidal gas (poor in colloid and rich in polymer) occurs (Fig. 4.4) [8, 9]. Experiments and theoretical work have shown that in such systems, at states well away from the critical point, the interfacial tension scales as the thermal energy ( $k_B T$ ) divided by the square of the particle diameter  $d$ , i.e., [10]

$$\gamma \sim \frac{k_B T}{d^2} \quad (4.14)$$

For particles of diameter 25 nm this factor is of order 1  $\mu\text{N/m}$ , i.e., about 4 orders of magnitude lower than the surface tension of molecular liquids. Theoretical and experimental studies also indicate a rapid decrease of the interfacial tension with decreasing difference in the particle number density in the two phases,



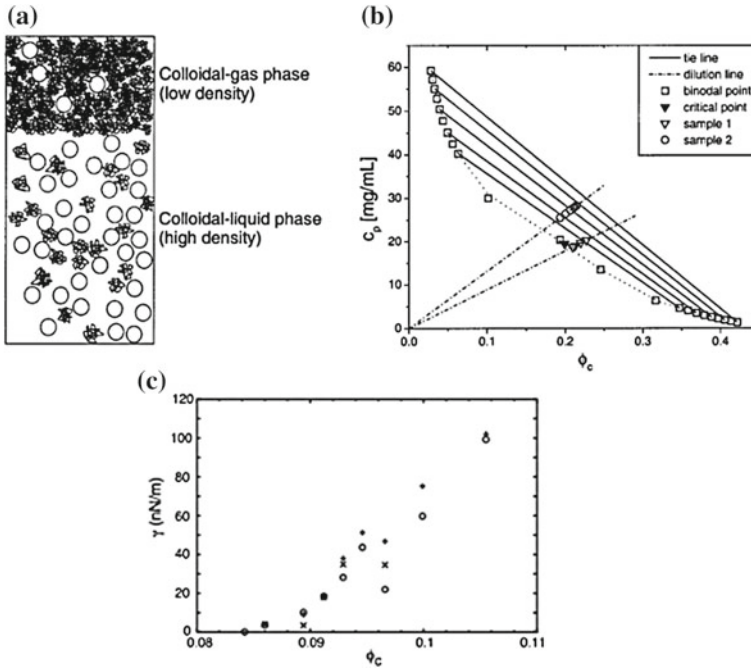


**Fig. 4.3** Liquid/liquid interface in binary systems of partial miscibility in the liquid state: Systems with an upper critical solution temperature (*left*) or a lower critical solution temperature (*right*). The graphs show the liquid/liquid coexistence curve (*top*), the temperature dependence of the interfacial tension  $\gamma$  (*middle*), and the temperature dependence of the surface excess entropy  $s^{(1,2)}$  (*bottom*) in the vicinity of the critical temperature  $T_c$ .

$\gamma \sim (\rho^l - \rho^g)^4$ , as the critical point is approached. This again is in agreement with the behaviour of simple liquids.

### 4.2.2 Adsorption at Fluid Interfaces

Adsorption at the liquid/vapour interface of a solvent (component 1) is expressed commonly by the relative surface excess concentrations  $\Gamma_k^{(1)}$  of the solutes ( $k = 2, 3, \dots$ ). Hence at constant temperature the Gibbs adsorption equation takes the form



**Fig. 4.4** A colloid–polymer suspension separated into a ‘colloidal gas’ and a ‘colloidal liquid’ phase: **a** sketch of the two-phase system; **b** phase diagram (polymer concentration  $c_P$  versus colloid volume fraction  $\phi_C$ ) showing coexistent colloid-rich (*liquid-like*) and polymer-rich (*gas-like*) phases and the critical point of the binodal curve (Reproduced from Ref. [8] with permission. Copyright 1999, American Chemical Society); **c** interfacial tension  $\gamma$  versus colloid volume fraction  $\phi_C$  near the critical point showing analogy with the behaviour of simple liquids near their liquid/vapour critical point (Reproduced from Ref. [9] with permission. Copyright 2004, American Association for the Advancement of Science)

$$d\gamma = - \sum_{k=2}^n \Gamma_k^{(1)} d\mu_k \quad (4.15)$$

The chemical potential of solutes in the bulk solution is given by

$$\mu_k^l = \mu_k^o + RT \ln a_k \quad (4.16)$$

The standard chemical potential  $\mu_k^o$  refers to the hypothetical state of an ideal dilute solution. The activity  $a_k$  can be expressed either as  $a_k = c_k f_k$  or  $a_k = x_k f_k$ , where  $c_k$  is the concentration,  $x_k$  the mole fraction and  $f_k$  the appropriate activity coefficient of component  $k$  in the unsymmetrical (Henry) convention ( $f_k \rightarrow 1$  as  $x_k \rightarrow 0$ ). Using the differential form of Eq. (4.16) at constant temperature,  $d\mu_k = RT \ln a_k$ , the Gibbs equation for a single nonionic solute (2) may be written

$$\Gamma_2^{(1)} = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a_2} \right)_T \quad (4.17)$$

According to this relation the relative surface excess  $\Gamma_2^{(1)}$  can be determined from the experimentally well accessible dependence of the surface tension on the activity of the solute. Because of the logarithmic activity scale, the choice of the concentration units (mol/L or mol/kg, etc.) is irrelevant, as long as the corresponding activity coefficient is used. The necessity of using activities in the Gibbs equation has been discussed in the literature [11]. For qualitative considerations the activity may be replaced by concentration. Equation 4.17 then indicates that solutes which lower the surface tension ( $d\gamma/dc_2 < 0$ ) are positively adsorbed ( $\Gamma_2^{(1)} > 0$ ), while solutes causing an increase in surface tension ( $d\gamma/dc_2 > 0$ ) are negatively adsorbed ( $\Gamma_2^{(1)} < 0$ ). At the surface of water, hydrophilic and well-hydrated solutes (inorganic salts, but also glycerine, glycine, etc.) are negatively adsorbed, while hydrophobic solutes (hexane, benzene) and amphiphilic substances (surfactants, etc.) are positively adsorbed.

For the adsorption of solutes at liquid/liquid interfaces it is convenient to express the Gibbs equation in terms of surface excess concentrations relative to the two solvents,  $\Gamma_k^{(1,2)}$  (see Sect. 4.1.3). For a single solute (component 3) this gives by analogy with Eq. (4.17)

$$\Gamma_3^{(1,2)} = -\frac{1}{RT} \left( \frac{\partial \gamma}{\partial \ln a_3} \right)_{T,p} \quad (4.18)$$

According to this relation it is the relative adsorption  $\Gamma_k^{(1,2)}$  that is directly accessible from measurements of the interfacial tension as a function of the activity  $a_k$ . Note that at equilibrium the concentration of a solute  $k$  in the two coexistent liquid phases  $\alpha$  and  $\beta$  can be grossly different, but the thermodynamic activity is equal, i.e.,  $a_k = c_k^\alpha f_k^\alpha = c_k^\beta f_k^\beta$ .

**Adsorption of surfactants from aqueous solutions:** As a case study we consider the determination of the adsorption of surfactants at the air/water interface [12–15]. Nonionic surfactants of alkyl chain length  $C_{12}$  or greater are strongly adsorbed at the air/water and oil/water interface. The surface tension derivative ( $d\gamma/d\ln c_2$ ) reaches a high negative limiting value, indicating a high limiting adsorption at bulk concentrations well below the critical micelle concentration (cmc). Above the cmc no further decrease in surface tension occurs ( $d\gamma/d\ln c_2 = 0$ ). This can be explained by the formation of micellar aggregates, so that the concentration of monomeric surfactant—and hence its activity  $a_2$ —remains constant above the cmc [16].

For an ionic surfactant,  $R^-Na^+$ , the general Gibbs equation (Eq. 4.7) takes the form ( $T = \text{const}$ ) [12]

$$-d\gamma = \Gamma_{Na^+}^\sigma d\mu_{Na^+} + \Gamma_{R^-}^\sigma d\mu_{R^-} + \Gamma_{H^+}^\sigma d\mu_{H^+} + \Gamma_{OH^-}^\sigma d\mu_{OH^-} + \Gamma_{H_2O}^\sigma d\mu_{H_2O} \quad (4.19)$$

where we consider all ionic species and the solvent. In the bulk solution the chemical potentials are interrelated by the Gibbs-Duhem relation

$$n_{Na^+} d\mu_{Na^+} + n_{R^-} d\mu_{R^-} + n_{H^+} d\mu_{H^+} + n_{OH^-} d\mu_{OH^-} + n_{H_2O} d\mu_{H_2O} = 0 \quad (4.20)$$

Combining these two relations and neglecting the terms in  $H^+$  and  $OH^-$  against the concentration of the surfactant ions leads to

$$-d\gamma = \left( \Gamma_{Na^+}^\sigma - \Gamma_{H_2O}^\sigma \frac{n_{Na^+}}{n_{H_2O}} \right) d\mu_{Na^+} + \left( \Gamma_{R^-}^\sigma - \Gamma_{H_2O}^\sigma \frac{n_{R^-}}{n_{H_2O}} \right) d\mu_{R^-} \quad (4.21)$$

For electrical neutrality in the solution and the surface we also have  $n_{Na^+} = n_{R^-} = n_{NaR}$  and  $\Gamma_{Na^+}^\sigma = \Gamma_{R^-}^\sigma = \Gamma_{NaR}^\sigma$ , so that

$$-d\gamma/RT = \left( \Gamma_{NaR}^\sigma - \Gamma_{H_2O}^\sigma \frac{n_{NaR}}{n_{H_2O}} \right) d\ln(a_{Na^+} a_{R^-}) \quad (4.22)$$

Introducing the mean activity  $a_{\pm} = (a_{Na^+} a_{R^-})^{1/2}$  and noting that the expression in brackets is the surface excess concentration of the surfactant relative to water,  $\Gamma_{NaR}^{(H_2O)} = \Gamma_{NaR}^{(1)}$ , we find

$$-d\gamma/RT = 2\Gamma_{NaR}^{(1)} d\ln(a_{\pm}) \quad (4.23)$$

The factor 2 in this relation arises because both the surfactant ion  $R^-$  and counterion  $Na^+$  must be adsorbed to maintain electroneutrality. Accordingly,  $d\gamma/d\ln a_{\pm}$  is twice as large as for a nonionic surfactant. The mean ion activity coefficient needed to evaluate the Gibbs relation can be taken from the extended Debye-Hückel equation in the form [15]

$$\log f_{\pm} = \frac{-0.5115|z_+ z_-| \sqrt{I}}{1 + 1.316 \sqrt{I}} + 0.055I \quad (4.24)$$

where  $z_+$  and  $z_-$  are the charge numbers of cation and anion,  $I$  is the ionic strength of the solution expressed in molar units, and the numerical constants apply for a temperature of 25 °C.

Is the adsorption of the ionic surfactant at the air/water interface affected by the addition of an inert electrolyte? If a non-adsorbed electrolyte (say, NaCl) is present in large excess, an increase in the concentration of  $R^-Na^+$  causes a negligible

increase of the  $\text{Na}^+$  concentration, so that  $d\mu_{\text{Na}^+}$  is negligible. Consideration of the Gibbs-Duhem equation then shows that  $d\mu_{\text{Cl}^-}$  is also negligible, and thus

$$-d\gamma/RT = \Gamma_R^{(1)} d\ln(a_{R^-}) \quad (4.25)$$

The activity coefficient  $f_{R^-}$  depends on the ionic strength which is determined by the excess of NaCl and is therefore constant, so that

$$-d\gamma/RT = \Gamma_R^{(1)} d\ln(c_{\text{Na}R}) \quad (4.26)$$

where  $\Gamma_R^{(1)}$  is again the surface excess of the surfactant relative to water and  $c_{\text{Na}R}$  is its concentration in solution. Hence the factor 2 in the Gibbs equation has disappeared and the ionic surfactant in excess electrolyte is adsorbed as if it was a nonionic surfactant.

### 4.2.3 Surface Phase Model

A concept adopted explicitly or implicitly in many treatments of adsorption from solution is that of a distinct *surface phase*, i.e., a layer of finite thickness located between the two bulk phases and affected by the interfacial tension [17, 18]. The surface phase is usually supposed to be of uniform composition. On the basis of such a model the measured surface excess concentrations can be expressed by the concentration or mole fraction difference between the surface phase (superscript  $s$ ) and bulk liquid phase (superscript  $l$ ). Specifically, if the surface phase consists of an amount  $n^s$  of solvent plus solute, with a mole fraction  $x_2^s$  of the solute, then the reduced surface excess  $\Gamma_2^{(n)}$  and the relative surface excess  $\Gamma_2^{(1)}$  of the solute can be expressed as

$$\Gamma_2^{(n)} = (1 - x_2^l)\Gamma_2^{(1)} = (x_2^s - x_2^l)n^s/A \quad (4.27)$$

where  $A$  is the surface area and  $x_2^l$  is the mole fraction of solute in the bulk solution. If  $n^s$  is known, Eq. (4.27) may be used to calculate  $x_2^s$  from the measured surface excess concentration. However, the value of  $n^s$  depends on what assumptions are made about the nature of the surface phase. In practice, meaningful results can be obtained by this approach only if there is independent evidence that the surface phase consists of a single monolayer of molecules. For adsorption from binary mixtures the condition that this surface layer is completely covered is then that

$$\Gamma_1^s \underline{a}_{1,0} + \Gamma_2^s \underline{a}_{2,0} = 1 \quad (4.28)$$

Here,  $\Gamma_1^s$  and  $\Gamma_2^s$  represent the (absolute) surface concentrations (amount per unit area), given by  $\Gamma_k^s = n_k^s/A = x_k^s n^s/A$ , and the quantities  $\underline{a}_{k,0}$  denote the partial molar

areas of solvent and solute in the surface phase. These cross-sectional areas may be estimated from molecular models. By combining Eqs. (4.27) and (4.28) we obtain an explicit expression to convert surface excess concentrations  $\Gamma_2^{(n)}$  to absolute surface concentrations  $\Gamma_2^s$  of the solute in the monolayer surface phase:

$$\Gamma_2^s = \frac{x_2^j + \underline{a}_{1,0} \Gamma_2^{(n)}}{1 - (\underline{a}_{2,0} - \underline{a}_{1,0}) \Gamma_2^{(n)}} \frac{n^s}{A} \quad (4.29)$$

In the particular case when the two components have the same size ( $\underline{a}_{1,0} = \underline{a}_{2,0} = \underline{a}_0$ ), then  $n^s = A/\underline{a}_0$  and Eq. (4.29) leads to

$$\underline{a}_0 \Gamma_2^s = x_2^j + \underline{a}_0 \Gamma_2^{(n)} \quad (4.30)$$

This relation shows that in the case of strong adsorption from dilute solutions, when  $\underline{a}_0 \Gamma_2^{(n)} \gg x_2^j$ , the surface excess concentration becomes nearly equal to the absolute concentration of the solute in the surface phase, i.e.,  $\Gamma_2^{(n)} \cong \Gamma_2^{(1)} \cong \Gamma_2^s$ . Hence in such cases it is justified to treat surface excess concentrations as true concentrations of the solute in the topmost layer of the liquid phase. If the condition  $\underline{a}_0 \Gamma_2^{(n)} \gg x_2^j$  does not apply, Eq. (4.29) may be used to calculate  $\Gamma_2^s$  from the measured surface excess concentration.

#### 4.2.4 Surface Equation of State and Adsorption Isotherm

Monolayers of strongly adsorbed substances have some resemblance with insoluble monolayers of lipids at the water surface [17]. The decrease in surface tension from the value of pure water,  $\gamma_0$ , to a value  $\gamma$  corresponding to a given surface concentration  $\Gamma^s$ , can be interpreted as a lateral pressure  $\Pi = \gamma_0 - \gamma$  exerted by the monolayer film. In the case of water-insoluble monolayers (so-called *Langmuir films*) a certain amount of lipid, commonly expressed by the number of molecules  $N$  is placed on a well-defined surface area  $A$ , and the surface concentration  $\Gamma^s = N/A$  of the lipid can be varied by increasing or decreasing  $A$  using suitable barriers to keep all the lipid molecules within the area  $A$ . The dependence of the film pressure  $\Pi$  on the area  $A$  at constant temperature and constant number of lipid molecules ( $\Pi - A$  isotherm) has a formal analogy with the pressure-volume diagram of a given amount of gas at constant temperature ( $P - V$  isotherm). In the case of water-soluble substances (e.g., surfactants) the surface concentration of the substance is independent of the surface area but can be controlled via the adsorption isotherm  $\Gamma^s = \Gamma^s(c)$ , i.e., by changing its concentration  $c$  in the subphase. Surface films of this kind are called *Gibbs films*. In this section we explore the functional dependence  $\Pi = \Pi(\underline{a})$ , where  $\underline{a} = A/N = 1/\Gamma^s$  is the mean area per adsorbed molecule in the Gibbs film at the given concentration  $c$  in the subphase. The relation

$\Pi = \Pi(a, T)$  is called the *monolayer equation of state* or two-dimensional (2D) equation of state of the adsorbed substance [19], by analogy with the equation of state  $p = p(V, T)$  of a fluid in the bulk (3D) state.

Experimentally, the monolayer equation of state is obtained by the following sequence of steps:

- (i) Determination of the film pressure isotherm  $\Pi = \Pi(c, T)$  by surface tension measurements as a function of the concentration  $c$ .
- (ii) Calculation of the appropriate surface excess concentration isotherm, e.g.,  $\Gamma^{(1)} = \Gamma^{(1)}(c, T)$  from the surface tension data by application of the Gibbs equation.
- (iii) Choice of a surface phase model and conversion of the surface excess concentrations to the model-based surface concentrations  $\Gamma^s(c, T)$ .
- (iv) Determination of the monolayer equation of state  $\Pi = \Pi(\underline{a}, T)$  by correlating film pressure  $\Pi(c, T)$  and surface concentration  $\Gamma^s(c, T)$  data corresponding to the same bulk concentration  $c$ , noting that  $\underline{a} = 1/\Gamma^s$ .

**Model equations of state and adsorption isotherms:** Drawing on the analogy between ‘two-dimensional’ (2D) monolayers and three-dimensional (3D) bulk fluids, monolayer equations of state of increasing complexity have been proposed:

$$\begin{array}{ll}
 \Pi \underline{a} = k_B T & \text{2D perfect gas} \\
 \Pi(\underline{a} - \underline{a}_0) = k_B T & \text{2D Volmer} \\
 \left(\Pi + \frac{\alpha}{\underline{a}^2}\right)(\underline{a} - \underline{a}_0) = k_B T & \text{2D van-der-Waals}
 \end{array} \quad (4.31)$$

In these relations  $k_B$  is the Boltzmann constant,  $\underline{a}_0$  represents the cross-sectional area of a molecule in the monolayer (analogous to the ‘co-volume’ in the 3D equation of state), and  $\alpha$  is a measure of attractive lateral interaction between adsorbed molecules. Each of these equations of state can be converted to a corresponding adsorption isotherm with the Gibbs adsorption equation. For ideal solution behaviour of the bulk phase all model adsorption isotherm equations can be expressed in the form  $Kc = f(\Gamma^s) = \tilde{f}(\underline{a})$ , where  $K$  is a constant which depends on the units in which the equilibrium concentration  $c$  of the solute in the bulk phase is expressed (molar concentration, mole fraction, etc.). Specifically, at low surface concentration, when the surface film behaves as a *2D perfect gas*, the adsorption isotherm becomes

$$Kc = \Gamma^s = \frac{1}{\underline{a}} \quad (4.32)$$

Low surface concentration means that  $1/\Gamma^s = \underline{a} \gg \underline{a}_0$ . If this condition is no longer met, deviations from linear adsorption isotherms occur. In this regime it is convenient to express the adsorption isotherm and monolayer equation of state in terms of  $\theta = \underline{a}_0/\underline{a}$ , the fraction of surface occupied by the adsorbed molecules.

For mobile monolayer films without long-range lateral interactions (2D Volmer) the adsorption isotherm and equation of state are

$$K_V c = \frac{\theta}{1-\theta} \exp \frac{\theta}{1-\theta} \quad (4.33)$$

$$\Pi \underline{a}_0 = k_B T \frac{\theta}{1-\theta}$$

For monolayer films with long-range interactions (2D van-der-Waals or Hill-deBoer) these relations are modified to

$$K_V c = \frac{\theta}{1-\theta} \exp \left[ \frac{\theta}{1-\theta} - \frac{2\alpha}{\underline{a}_0 k_B T} \theta \right] \quad (4.34)$$

$$\Pi \underline{a}_0 = k_B T \frac{\theta}{1-\theta} - \frac{\alpha}{\underline{a}_0} \theta^2$$

The following important conclusions emerge from these model isotherms:

(1) An adsorbate conforming to the 2D perfect gas exhibits a linear adsorption isotherm. This is a generic behaviour at very low surface concentrations ( $\underline{a} \gg \underline{a}_0$ ). Accordingly, all adsorption systems must exhibit a linear adsorption isotherm at sufficiently low concentrations  $c$ . If the surface concentration  $\Gamma^s$  and bulk concentration  $c$  are both expressed on a molar basis, then the adsorption constant  $K$  has the dimension of a length. The adsorption constant  $K_V$  appearing in Eqs. (4.33) and (4.34) can be converted to  $K$  by  $K = K_V / \underline{a}_0$ .

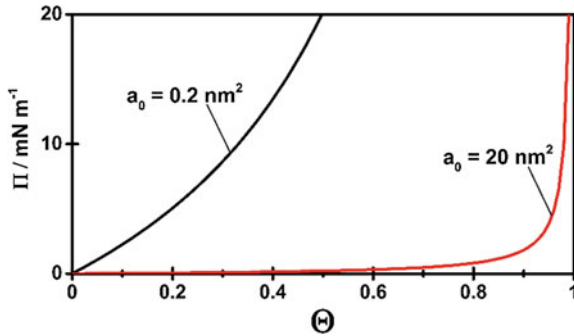
(2) At higher surface concentrations the interaction between the adsorbed molecules comes into play. The Volmer equation applies when the adsorbed molecules interact only by short-range repulsive forces. This can be tested experimentally by writing the Volmer equation of state in the form,  $k_B T / \Pi = \underline{a} - \underline{a}_0$ . Hence, a graph of  $k_B T / \Pi$  versus  $\underline{a}$  should be linear down to the lowest values of  $\underline{a}$  and the extrapolation to  $k_B T / \Pi = 0$  gives the co-area  $\underline{a}_0$  of the adsorbed molecules.

(3) In the absence of attractive lateral interactions the film pressure at a given surface coverage  $\theta$  is inversely proportional to the size of the adsorbed molecules (co-area  $\underline{a}_0$ ):

$$\Pi = \frac{k_B T}{\underline{a}_0} \frac{\theta}{1-\theta} \quad (4.35)$$

Figure 4.5 shows the film pressure as a function of surface coverage for two different values of the co-area:  $\underline{a}_0 = 0.2 \text{ nm}^2$  (typical of amphiphiles with small head groups, e.g. alkanols), and  $\underline{a}_0 = 20 \text{ nm}^2$  (typical for globular proteins) [20]. It can be seen that at half-coverage of the surface ( $\theta = 0.5$ ) the film pressure of the small amphiphile is already high ( $20 \text{ mN m}^{-1}$ ), while for the protein it is still very low ( $0.2 \text{ mN m}^{-1}$ ), and a marked increase of  $\Pi$  occurs only at very high surface coverage. This example shows that for proteins and other large adsorbate molecules



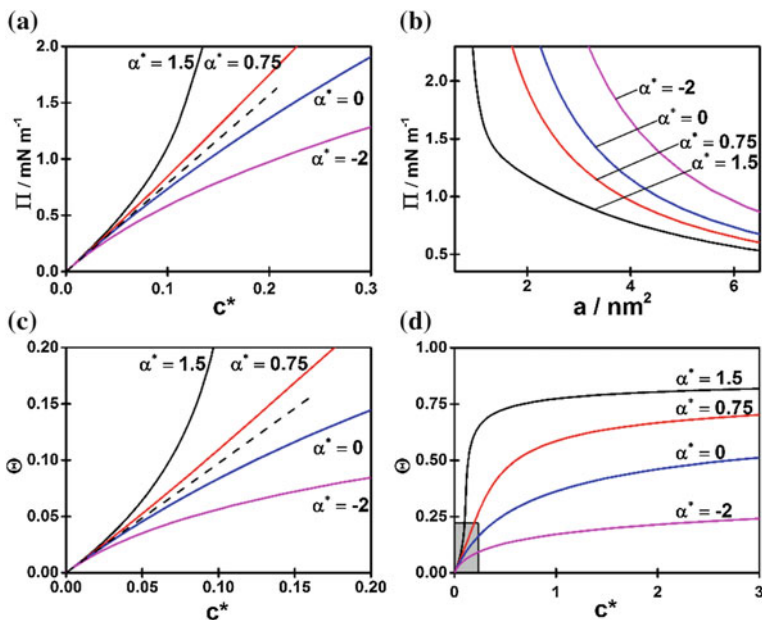


**Fig. 4.5** Surface pressure  $\Pi$  as a function of surface coverage  $\theta$  for adsorbed films of molecules with small or large cross-sectional area  $\underline{a}_0$ . When  $\underline{a}_0$  is small ( $0.2 \text{ nm}^2$ ),  $\Pi$  rises steeply with  $\theta$ ; when  $\underline{a}_0$  is large ( $20 \text{ nm}^2$ ),  $\Pi$  stays very low up to high surface coverage  $\theta$  (results for the Volmer model, Eq. (4.35), for  $20^\circ\text{C}$ )

it can be dangerous to draw conclusions about the adsorbed amount from film pressure measurements.

(4) The 2D van-der-Waals equation can be used to represent systems in which attractive lateral interactions between adsorbed molecules cannot be neglected. Figure 4.6 shows results for the surface pressure  $\Pi(c)$ , the surface equation of state  $\Pi(\underline{a})$ , and the adsorption isotherm  $\theta(c)$  for the 2D vdW model (Eq. 4.34), computed for several values of the reduced interaction parameter  $\alpha^* = \alpha/\underline{a}_0 k_B T$ . The isotherms for  $\alpha^* = 0$  represent the 2D Volmer model. Positive values of  $\alpha^*$  correspond to attractive lateral interactions between the molecules in the film. It can be seen that increasing  $\alpha^*$  causes higher values of the surface pressure  $\Pi$  and adsorption (surface coverage  $\theta$ ) at given concentration  $c^* = c * K_V$ . On the other hand, at a given mean area per adsorbed molecule ( $\underline{a}$ ), increasing lateral interaction between the molecules (increasing  $\alpha^*$ ) causes a decrease in the surface pressure  $\Pi$ , as can be seen in the graphs showing the surface equation of state  $\Pi(\underline{a})$ . Attractive lateral interactions are commonly observed for amphiphilic substances (e.g., fatty alcohols) adsorbed at the air/water interface. These molecules are adsorbed even more strongly at oil/water interfaces, but in that case the adsorbed film can be represented by the Volmer equation [21]. This remarkable behaviour is attributed to the fact that the attractive interactions between the alkanol chains are screened when they are surrounded by hydrocarbon molecules of the oil phase.

**Models of localized monolayer adsorption:** In many cases adsorption involves some sort of *binding* to specific adsorption sites. Hence adsorbed molecules are no longer free to move (“mobile”) but “localized”. The Langmuir equation is the prototype of isotherms for localized monolayer adsorption. It assumes that the surface constitutes  $M$  equivalent adsorption sites, each of which can accommodate one adsorbed molecule. If  $N^s$  molecules are adsorbed, the surface coverage is  $\theta = N^s/M$ . The Langmuir model assumes that no lateral interactions between adsorbed molecules exist. For this reason it is also called *2D ideal lattice gas* model.



**Fig. 4.6** Behaviour of adsorbed surface films according to the van der Waals model (Eq. 4.34): surface pressure  $\Pi(c)$  (upper left), surface equation of state  $\Pi(a)$  (upper right), and adsorption isotherm  $\theta(c)$  (lower left and right; where the graph at the left shows the low concentrations region enlarged). All results refer to 20 °C and a molecular co-area  $a_0 = 0.5 \text{ nm}^2$ . The values of the interaction parameter  $\alpha$  are given in reduced units ( $\alpha^* = \alpha/a_0 k_B T$ ), the bulk concentration is expressed in dimensionless units ( $c^* = K_V c$ )

The adsorption isotherm and monolayer equation of state of the Langmuir model are [14, 19]

$$K_L c = \frac{\theta}{1 - \theta} \quad (4.36)$$

$$\Pi a_0 = -k_B T \ln(1 - \theta)$$

When lateral interactions are introduced in this model on a mean-field basis, the Frumkin-Fowler-Guggenheim (FFG) isotherm is obtained:

$$K_L c = \frac{\theta}{1 - \theta} \exp\left(-\frac{2\alpha}{k_B T} \theta\right) \quad (4.37)$$

$$\Pi a_0 = -k_B T \left[ \ln(1 - \theta) + \frac{\alpha}{k_B T} \theta^2 \right]$$

As in the van-der-Waals equation (Eq. 4.34), positive values of the interaction parameter  $\alpha$  correspond to attractive lateral interactions, negative  $\alpha$  to repulsive

lateral interactions. Repulsive interactions can be significant in the adsorption of polyions (proteins, etc.). Attractive lateral interactions can play a role, for example, in the adsorption of ionic surfactants to an oppositely charged surface, when the hydrophobic tails tend to aggregate due to the hydrophobic effect. Like the van-der-Waals isotherm, the Frumkin isotherm indicates that a phase separation into a dilute and a dense 2D phase occurs at low temperatures, when  $|\alpha/k_B T|$  exceeds some critical value. This phase separation causes a step-wise increase of the surface coverage.

### 4.2.5 Standard Free Energy of Adsorption

Standard free energies of adsorption are used to characterize the strength of adsorption to interfaces. Of particular interest are values for very dilute systems, when interactions between adsorbed solute molecules are absent. From the Gibbs equation we obtain for 1 mol of adsorbate

$$-d\gamma = d\Pi = \Gamma_2^{(1)} d\mu_2 \cong \frac{1}{N_A a} d\mu_2 \quad (4.38)$$

where the last relation applies only to the regime of the 2D perfect gas ( $N_A$  is the Avogadro constant). Inserting the equation of state,  $N_A a = RT/\Pi$ , gives after integration

$$\mu_2^a = \mu_2^{o,a} + RT \ln \Pi \quad (4.39)$$

At equilibrium  $\mu_2^a$  is equal to the chemical potential of the component in the bulk solution (Eq. 4.16). For highly dilute solutions the activity can be replaced by the concentration and we obtain the following expression for the standard free energy of adsorption

$$\Delta_a G^o \equiv \mu_2^{o,a} - \mu_2^{o,l} = -RT \ln (\Pi/c_2)_{c_2 \rightarrow 0} \quad (4.40)$$

$$(\Pi/c_2)_{c_2 \rightarrow 0} = \exp(-\Delta_a G^o / RT)$$

where  $\mu_2^{o,a}$  and  $\mu_2^{o,l}$  represent the standard chemical potential of the solute in the surface and bulk solution. The standard enthalpy and standard entropy of adsorption can be obtained from the temperature dependence of  $\Delta_a G^o$ , viz.

$$\Delta_a H^o = \frac{d(\Delta_a G^o / T)}{d(1/T)} \quad (4.41)$$

$$T \Delta_a S^o = \Delta_a H^o - \Delta_a G^o$$

Experimentally this is achieved by measuring the initial slope of film pressure isotherms  $(\Pi/c_2)_{c_2 \rightarrow 0}$  at a number of temperatures  $T$  and using Eq. (4.40) to

**Table 4.1** Standard free energies  $\Delta_a G^o$ , enthalpies  $\Delta_a H^o$  (in units of  $\text{J mol}^{-1}$ ), and entropies  $T\Delta_a S^o$  (in units of  $\text{J K}^{-1} \text{mol}^{-1}$ ) of adsorption of n-carboxylic acids at the air/water interface ( $20^\circ\text{C}$ );  $n$  is the number of carbon atoms in the tail group (from Ref. [12])

acid	$n$	$-\Delta_a G^o$	$\Delta\Delta_a G^o$	$-\Delta_a H^o$	$T\Delta_a S$
propionic	2	6.8		24.4	-17.6
butyric	3	10.1	3.3	17.8	-7.7
pentanoic	4	13.4	3.3	12.1	1.3
hexanoic	5	15.6	2.1	7.5	8.1
heptanoic	6	19.0	3.4	10.1	8.9
octanoic	7	22.7	3.7		
nonanoic	8	25.6	2.9		
decanoic	9	29.7	4.1		

determine  $\Delta_a G^o(T)$ . Care must be taken to ascertain that all film pressure data correspond to the initial linear regime of the film pressure isotherm.

Table 4.1 shows results for the adsorption of carboxylic acids at the free water surface [12]. It can be seen that  $-\Delta_a G^o$  increases nearly linearly with the chain length ( $n$ ) of the hydrophobic tail, with an average increment  $\Delta\Delta_a G^o$  of ca.  $-3 \text{ kJ mol}^{-1}$  per  $\text{CH}_2$  group.  $\Delta_a H^o$  is negative, indicating that adsorption of a carboxylic acid molecule at the water surface is an exothermic process, but the values become less exothermic with increasing chain length.  $T\Delta_a S^o$  shows a most interesting dependence on the chain length: It is negative for short chains, indicating a loss of degrees of freedom upon adsorption. With increasing chain length  $T\Delta_a S^o$  becomes less negative and assumes high positive values for hexanoic and heptanoic acid. This is attributed to the *hydrophobic effect*: Highly oriented water molecules forming a hydrogen-bonded ‘cage’ around the hydrophobic tails of the solute molecule in solution are released when the hydrocarbon tail leaves the aqueous medium on adsorption. The average increment in entropy  $\Delta\Delta_a S^o$  is about  $23 \text{ JK}^{-1} \text{mol}^{-1}$  per  $\text{CH}_2$  group. If two water molecules are oriented at each  $\text{CH}_2$  group, the entropy of orientation per water molecule ( $\Delta_{or} S/R \cong 1.3$ ) is about half the entropy of melting of ice ( $\Delta_{sl} S/R \cong 2.6$ ). The results of Table 4.1 suggest that for longer chain lengths  $n$  the entropy term  $T\Delta_a S^o$  becomes larger in magnitude than the enthalpy term  $\Delta_a H^o$ . Hence, there is a predominantly entropic driving force for adsorption of the higher alkanolic acids at the water surface, due to the release of  $2n$  oriented water molecules on adsorption.

### 4.3 Liquid/Solid Interfaces

Adsorption of surfactants and polymers to solid/liquid interfaces is a broad field with a diversity of applications, from controlling the wettability of macroscopic surfaces to the stabilization of colloidal dispersions. Adsorption of biomolecules

onto micron- or nano-sized particles is used to immobilize biomarkers and drugs and many recent studies deal with methods to control the release of adsorbed drugs for applications in the pharmaceutical field. Traditionally, solid surfaces have been classified into hydrophilic and hydrophobic, or ‘high-energy’ (inorganic) and ‘low-energy’ (organic), but many surfaces are heterogeneous and combine hydrophilic and hydrophobic behaviour. For example, carbons or organic polymer surfaces may contain ionizable surface groups (like  $-\text{COOH}$ ) which at higher pH will be ionized and form a hydrophilic site. In this short article only a few aspects of adsorption of *soft matter* from aqueous solutions to solid surfaces can be touched.

### 4.3.1 Measurement of Adsorption

A wide variety of experimental methods is available to study adsorption at solid/liquid interfaces [22]. Adsorption onto flat macroscopic surfaces can be measured by ellipsometry and optical reflectometry (also by neutron or X-ray reflectometry in favourable cases, see chapter D.12 by J. Daillat), surface spectroscopic methods (see chapter D.15 by M. Hoffmann et al.) and quartz microbalance techniques. Adsorption onto particulate solids (powders and colloids) with high specific surface area can be determined directly from the adsorption-induced change in composition of the liquid phase. The reduced surface excess concentration  $\Gamma_k^{(n)}$  of a component  $k$  (defined in Sect. 4.1.3) is directly related to the change in composition and given in terms of the mole fraction before and after equilibration,  $x_k^0$  and  $x_k^l$ , by [18]

$$\Gamma_k^{(n)} = \frac{n^l(x_k^0 - x_k^l)}{m_s a_s} \quad (4.42)$$

where  $n^l$  is the amount of solution,  $m_s$  is the mass and  $a_s$  the specific surface area of the adsorbent. For solutions of polymers and other large molecules it is more convenient to express adsorption by the *volume-reduced* surface excess concentration  $\Gamma_k^{(v)}$  which is defined operationally by

$$\Gamma_k^{(v)} = \frac{V^l(c_k^0 - c_k^l)}{m_s a_s} \quad (4.43)$$

where  $V^l$  is the volume of a given amount of solution,  $c_k^0$  and  $c_k^l$  are the concentrations of component  $k$  before and after equilibration with the adsorbent. With some simplification (additivity of the volumes of the components on mixing, no adsorption-induced volume changes),  $\Gamma_k^{(v)}$  is related to the volume fraction profile  $\varphi_k(z)$  of the component in the boundary layer

$$\Gamma_k^{(v)} = \frac{1}{V_k^*} \int_0^\infty [\varphi_k(z) - \phi_k^l] dz \quad (4.44)$$

where  $V_k^*$  is the molar volume of component  $k$ . For a two-component system of solvent (1) and solute (2) this implies that  $V_1^* \Gamma_1^{(v)} = -V_2^* \Gamma_2^{(v)}$ , i.e., the ratio of the volume-reduced surface excess concentrations of solvent and solute is inversely proportional to the ratio of their molar volumes. This conforms to the intuitive picture of adsorption as a displacement of solvent molecules by the solute. For example, a protein molecule of a volume 1000 times the volume of water molecules will displace 1000 water molecules from the surface region, and  $\Gamma_{water}^{(v)} = -1000 \Gamma_{protein}^{(v)}$ .

### 4.3.2 Thermodynamic Relations

We have seen that for fluid interfaces the interfacial tension  $\gamma$  and its dependence on temperature and concentration of the components represents the primary experimental source of information on the interface. The interfacial tension of a liquid phase against a solid, which in the following will also be denoted by  $\gamma$ , is experimentally not accessible. However, the Gibbs equation forms a basis to determine  $\gamma$  from the measured adsorption. For a binary mixture at constant temperature we have

$$-d\gamma = \Gamma_1^{(n)} d\mu_1 + \Gamma_2^{(n)} d\mu_2 = \Gamma_2^{(n)} (d\mu_2 - d\mu_1) \quad (4.45)$$

because  $\Gamma_1^{(n)} = -\Gamma_2^{(n)}$ . With the Gibbs-Duhem relation  $x_1^l d\mu_1 + x_2^l d\mu_2 = 0$  this yields

$$-d\gamma = \Gamma_2^{(n)} d\mu_2 (1 + x_2^l/x_1^l) = \frac{\Gamma_2^{(n)}}{1 - x_2^l} d\mu_2 \quad (4.46)$$

Integration of this relation over the composition range from pure solvent (component 1) to a solution of mole fraction  $x_2^l$  then yields

$$\gamma_1^* - \gamma(x_2^l) = RT \int_0^{x_2^l} \frac{\Gamma_2^{(n)}}{1 - x_2^l} d \ln(x_2^l f_2^l) \quad (4.47)$$

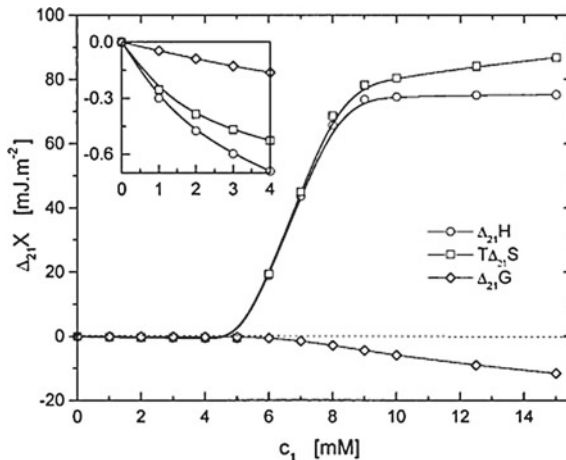
In this relation,  $\gamma_1^*$  is the interfacial tension of the solid against pure liquid 1 and  $\gamma(x_2^l)$  the tension against the solution of composition  $x_2^l$ . It can be shown [18] that  $\gamma_1^* - \gamma(x_2^l)$  is equivalent to the difference in Gibbs free energies of wetting of the

solid by pure solvent and a solution of composition  $x_2^l$ . This difference, in turn, corresponds to the free energy change of displacement of pure solvent by the solution that causes the adsorption  $\Gamma_2^{(n)}$ . Accordingly, the left-hand side of Eq. (4.47) is called the *Gibbs free energy of displacement* and is denoted by  $\Delta_{12}G$  ( $\text{J m}^{-2}$ ). An equivalent relation for  $\Delta_{12}G$  can be derived when the adsorption is expressed by the volume-reduced surface excess. In the limit of ideal dilute solutions (when  $x_2^l \ll 1$ ) this relation simplifies to

$$\Delta_{12}G(c_2) = -RT \int_0^{c_2} \frac{\Gamma_2^{(v)}}{c_2^l} dc_2^l \quad (4.48)$$

This relation can be used to determine Gibbs free energies of displacement from measured surface excess isotherms. When such isotherm measurements have been performed for several temperatures, the enthalpy and entropy of displacement,  $\Delta_{12}H$  and  $\Delta_{12}S$ , can be determined by relations analogous to Eq. (4.41). However, for solid/liquid interfaces the enthalpies of wetting and enthalpies of displacement can also be determined directly by isothermal titration calorimetry (ITC) or isothermal flow calorimetry (IFC). By combining adsorption measurement with calorimetric studies the thermodynamics of the adsorption system can be fully characterized.

As an example, Fig. 4.7 shows the thermodynamic functions  $\Delta_{12}G$ ,  $\Delta_{12}H$  and  $T\Delta_{12}S$  for the displacement of water by a short-chain nonionic surfactant ( $\text{C}_8\text{E}_4$ ) at a hydrophilic glass surface [23]. The Gibbs free energy  $\Delta_{12}G$  decreases with increasing concentration (i.e., with increasing adsorption) of the surfactant.



**Fig. 4.7** Thermodynamic characterization of the adsorption of the surfactant  $\text{C}_8\text{E}_4$  from aqueous solutions onto CPG silica: enthalpy ( $\Delta_{12}H$ ), entropy ( $T\Delta_{12}S$ ), and Gibbs free energy ( $\Delta_{12}G$ ) as functions of the displacement of water (2) by surfactant (1) at 25 °C. The *inset* shows the behaviour at low concentrations  $c_1$  on an enlarged scale (Reproduced from Ref. [23] with permission. Copyright 1997, American Chemical Society)

However, the overall change in  $\Delta_{12}G$  is rather small, due to enthalpy/entropy compensation. In the low-concentration region (shown by the inset in Fig. 4.7) the displacement of water by the surfactant is dominated by the exothermic enthalpy of displacement, which is attributed to a direct contact of the head groups with the hydrophilic surface. This initial adsorption step is connected with a decrease in entropy. At higher concentrations the enthalpy and entropy both change sign and the displacement of water by surfactant becomes entropy-controlled. This is a signature of the hydrophobic aggregation of the surfactant tails at the surface [23].

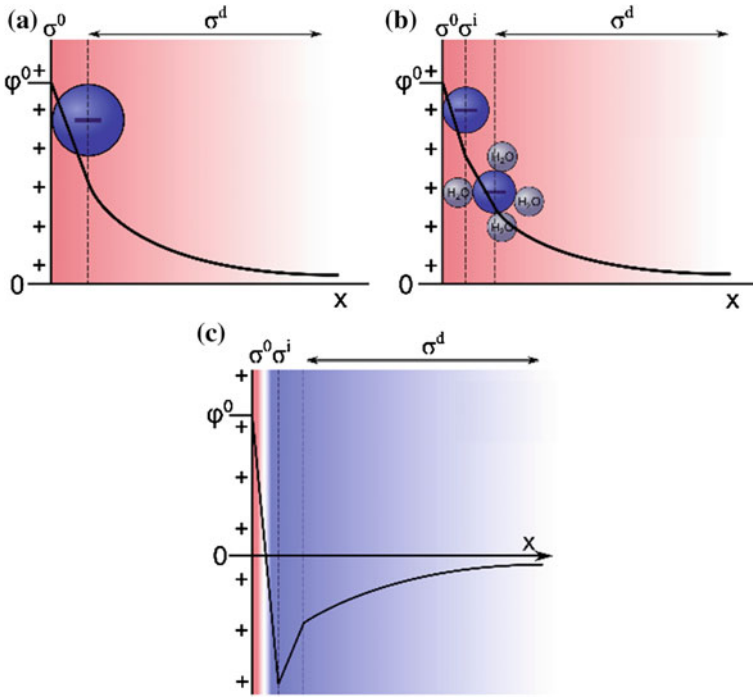
### 4.3.3 Electrical Nature of Solid/Aqueous Solution Interfaces

Electrostatic interactions between surface charges and oppositely charged ionic groups of solute molecules are often determinant for the adsorption from aqueous media. For instance, in ionic solids (e.g., silver halides) ions of one charge dissolve preferentially, leaving behind a surface of opposite charge. Alternatively, one type of ions of the solution may be adsorbed preferentially, again causing a charge separation at the surface. Many inorganic oxide surfaces ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ , etc.), exhibit a pH dependent surface charge according to the scheme



In all cases the charge on the solid surface (characterized by a charge density  $\sigma^0$ ) must be neutralized by oppositely charged counterions in the nearby solution, thus creating an *electric double layer*. The structure of this layer is sketched in Fig. 4.8. According to the classical Stern model [24, 25] the solution side of the double layer is subdivided somewhat artificially into two parts: the inner part (Stern layer) and the outer part (Gouy layer or diffuse layer). The Stern layer, in the words of J. Lyklema [25], is ‘where all the complications regarding finite ion size, specific adsorption, discrete charge, surface heterogeneity etc. reside’, while the diffuse layer is by definition ideal, obeying Poisson-Boltzmann statistics. The border line between the Stern layer (thickness  $d$ ) and the diffuse layer is called the outer Helmholtz (oH) plane. The net charge per unit area of this diffuse layer is  $\sigma^d$ . In modern treatments the Stern layer is further subdivided into an inner and an outer region. The centres of specifically adsorbed ions (i.e., ions adsorbed by non-electrostatic interactions) are located in the inner Helmholtz plane (iH), with a charge density  $\sigma^i$ . Ions which are not specifically adsorbed and remain hydrated can approach the surface no closer than the outer Helmholtz plane. In some cases, *super-equivalent* specific adsorption can lead to a change in sign of the potential  $\psi^i$  at the iH plane, connected with a charge reversal of the diffuse ion layer (see Fig. 4.8c). This can occur, for instance, in the adsorption of highly charged





**Fig. 4.8** Examples of Gouy-Stern layers: **a** only finite counterion size (*upper left*); **b** ion size and specific adsorption (*upper right*); **c** ion size and super-equivalent specific adsorption. All double layers have the same surface potential  $\psi^0$ , while the surface charge  $\sigma$  increases from **(a)** to **(c)** (after Ref. [25])

polymers to an oppositely charged surface. In any case, however, charge neutrality requires that

$$\sigma^0 + \sigma^i + \sigma^d = 0 \tag{4.49}$$

The situation when  $\sigma^0 = 0$  is called the *point of zero charge* (pzc), and when the solid surface plus specifically adsorbed ions has zero net charge (i.e., when  $|\sigma^0| = |\sigma^i|$ ) is called *isoelectric point* (iep). At the isoelectric point the potential  $\psi^d$  (Fig. 4.8) is zero. The potential at the slip plane (zeta-potential  $\zeta$ ) is very similar to  $\psi^d$  and also zero at the iep.

A central part of the Stern theory is to determine the specifically adsorbed charge  $\sigma^i$  as a function of the surface charge  $\sigma^0$ . For the adsorption of small ions  $i$ , the Langmuir adsorption equation can be adopted for this purpose, i.e.,  $K_i c_i = \theta_i / (1 - \theta_i)$ , where  $\theta_i = N_i / N_s$  is the fraction of adsorption sites occupied by the ions and  $c_i$  is the concentration in the solution. For a charged adsorbate the electrostatic contribution to the free energy of adsorption,  $z_i F \psi^i$ , has to be

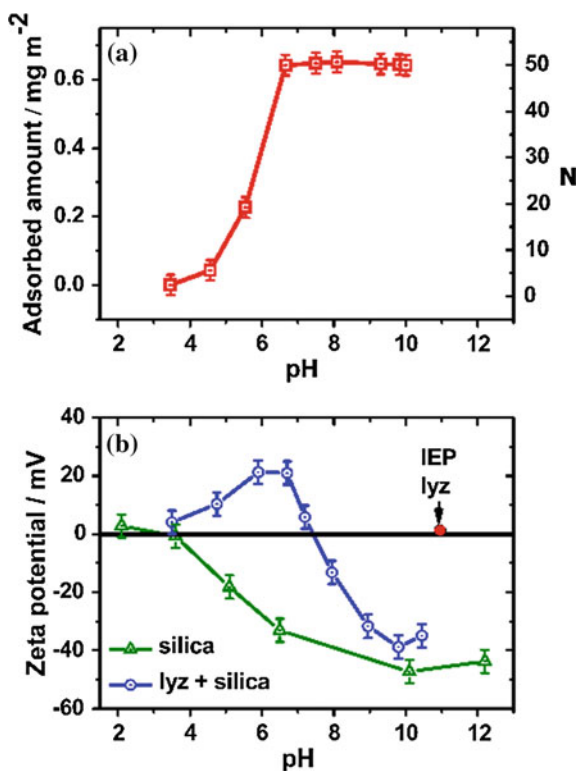
introduced, so that instead of  $K_i$  we have  $K_i \exp(-z_i F \psi^i / RT)$ . Writing the Langmuir equation explicit in  $\theta_i$  and introducing  $\sigma^i = z_i e N_i$ , we obtain the Stern equation

$$\sigma^i = z_i e N_s \frac{c_i K_i \exp(-z_i y^i)}{1 + c_i K_i \exp(-z_i y^i)} \quad (4.50)$$

where  $e$  is the elementary charge,  $F$  is the Faraday constant, and  $y^i = F \psi^i / RT$ . Hence it is possible to calculate  $\sigma^i$  once the surface potential  $\psi^i$  is known. This, however, generally requires some model assumptions [25], and is beyond the scope of this article.

As an example of super-equivalent specific adsorption, Fig. 4.9 shows results for the binding of the basic protein lysozyme to silica nanoparticles [26]. The silica surface is nearly uncharged below pH 4, but becomes negatively charged at higher pH due to the deprotonation of silanol groups. Lysozyme has a positive net charge up to its isoelectric point at pH 11. Figure 4.9a shows that binding of the protein starts when the silica surface becomes negatively charged, and it leads to an over-charging of the surface, as indicated by the positive zeta-potential of the silica

**Fig. 4.9** Binding of lysozyme to silica nanoparticles for a fixed overall amount of protein (corresponding to 50 molecules per particle), and the effect on the zeta potential of the particles, as a function of pH: **a** adsorbed amount expressed as protein mass per unit area and number of protein molecules per particle; **b** zeta potential of the particles in the absence and presence of lysozyme (Reproduced from Ref. [26] with permission. Copyright 2011, American Chemical Society)

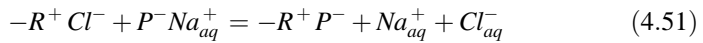


particles in the presence of the protein, although the silica particles without protein have a negative zeta potential. At higher pH the zeta potential decreases and becomes negative. This can be attributed to the increasing negative charge density of the silica surface and the decreasing positive net charge of the adsorbed protein as its isoelectric point is approached [26].

### 4.3.4 Adsorption as Ion Exchange

Ion exchange represents an important mechanism for adsorption to charged surfaces. This process can be dominated by electrostatic attraction of the ionic group of the adsorbate with an oppositely charged surface site. In this case adsorption is expected to be accompanied by a high exothermic adsorption enthalpy. However, in the case of protein or polyelectrolyte adsorption onto oxide surfaces, in many cases only weakly exothermic or even endothermic enthalpies of adsorption are observed, indicating that the driving force must include an entropic contribution that outweighs the enthalpic contribution. This can be rationalized from the fact that adsorption of the ionic group at the oppositely charged surface site involves the formation of an ion pair and the release of two counterions. In addition, it may also involve the release of water molecules hydrating the counterions. Models for this process indicate that the entropy gain amounts to ca.  $k_B T$  for each counterion or water molecule released [27].

The adsorption of a charged species on a charged site can be represented by an ion equilibrium reactions. For example, for a negative protein group  $P^-$  adsorbing to a positive site  $-R^+$



Here, the species are depicted with the counterions associated with the charges. The equilibrium constant of this reaction expressed in concentration units is [28]

$$K_{ads} = \frac{RP[NaCl]_{aq}^2}{R[P^- Na^+]_{aq}} \quad (4.52)$$

where  $RP$  represents the fraction of sites occupied by the protein and  $R$  is the fraction of vacant sites. In the absence of specific attractive interactions between  $P^-$  and  $-R^+$  the adsorption is driven by the release of the counterions  $Na^+$  and  $Cl^-$ . According to Eq. (4.52) the fraction of occupied sites should decrease when the salt concentration is increased, as it is indeed often observed.

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