Chapter 2
The Structure of the Metal-Solution Interface

2.1 Introduction: Spatial Separation of Electric Charge

The electrodeposition of metals or alloys occurs within a spatial region of finite thickness at the interface (or, more precisely, an interphase) between the growing material and the solution. The structure of this region, in particular the distribution of ions, solvent molecules and other uncharged species, and the resulting distribution of electric charges and potential, has an important bearing on the interface energy of the system, the nature and rate of charge transfer processes, and on the processes of nucleation and growth of metallic crystals. In general, charge separation occurs at this interface as a result of the different nature of the mobile charges in the two regions considered: electrons in the solid and ions in the electrolytic solution. The electronic charge distribution in the electrode extends into the solution farther than the charges generated by the ionic cores, and this excess of charges must be balanced by an opposite charge in the electrolyte. In the simplest approximation this separation of charges can be thought of as a parallel arrangement of opposite charges; for this reason, this region is also called *double layer*.

Many comprehensive and thorough discussions of the double layer are available in the literature [1]; our objective in this chapter is limited to a discussion of how and why the double layer influences the deposition process and how quantitative calculations of the properties of interest can be performed using experimental data. Practitioners in the area of electrodeposition often underestimate the role of double layer and surface phenomena in the electrode processes; here we try to highlight this role.

The presence of a metal/electrolyte interface not only results in charge separation, but also makes it possible for the exchange of charged particles between the two phases to occur: electrons and metallic ions may enter the solution, while ions transfer to the metal surface and may adsorb there. As a result of these processes an interfacial region is generated, which includes both charged and uncharged (dipolar or multipolar) species. The name electrical double layer (for brevity Double Layer, DL) underlines that the positively and negatively charged layers become spatially separated. More precisely, regions are formed having predominantly positive or negative charges.

Upon immersion of an electrode in an electrolyte, the DL forms by rearrangements of surface charges. An important characteristic of the DL is the potential drop $\Delta\varphi$ between the solid and electrolyte phases. Experimentally the presence of a DL is manifested as an electrical capacitance at the interface. In other words, the rearrangement of charges can be modeled as an electrical capacitor made up of oppositely charged conductors placed at the metallic and electrolyte sides, respectively, which generate a potential drop. The capacitance of the DL is usually of the order of $C_{DL} \approx 0.1\,\mathrm{Fm}^{-2}$. Since maximum values of $\Delta\varphi$ are about 1 V, this corresponds to a charge density of about 0.1 C/m² or 10 µC/cm².

It is necessary to distinguish between the real interface structure and the various models developed to simplify quantitative calculations of the DL properties. Usually the real system is modeled by replacing the discrete charge distribution with a continuous medium, and the dipole layer of the solvent with a continuous dielectric.

In order to describe current flow through the electrochemical cell, the complicated system of atoms, electrons, ions and molecules is replaced by a set of capacitors and resistors connected in a predetermined order (*equivalent circuit*), Fig. 2.1, which reproduces the electrical response of the real system. In this equivalent circuit, each element has its real equivalent; refinement and improvement of the model circuit can be achieved by comparison of the theoretical and experimental electrical responses at different frequencies. The overall impedance (i.e. complex resistance) of the system is measured in a wide range of frequencies (from 10^{-2} to 10^6 Hz), and the analysis of the data set permits to extract substantial amount of information on C_{DL} and other electrochemical quantities [2].

The value of capacitance C_{DL} is of immediate practical importance when imposing currents or voltages at the interface. For example, a step-like variation of the voltage applied at an electrode results in an exponential transient of the resulting current, which achieves a new steady state value only after a time of the order of the time constant $\tau = R \cdot C_{DL}$, where R is the equivalent resistance of the interface. In other processes of interest, an Alternating Current (AC) $I(t) = I^0 \cos(2\pi f t)$ may be superimposed to a constant current during metal deposition. At high frequencies this superimposed current does not influence the electrode processes. The reason is that DL charging by the superimposed AC current occurs over a finite time, of the order of:
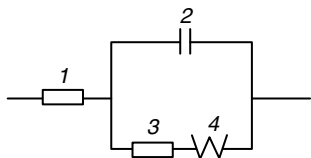
$$\tau = (RT/nF) \cdot C_{DL}/I^0 \tag{2.1}$$

Fig. 2.1 Equivalent circuit of the electrode. The double layer capacitance (*2*), charge transfer resistance (*3*) and diffusion impedance (*4*) along with the Ohmic electrolyte resistance (*1*) are taken into account

where $RT/nF = 25.7/n$ mV at 25°C. The quantity τ must be less than $1/f$, otherwise the alternate current will be damped due to DL charging and discharging. It follows that the condition

$$f < (nF/RT) \cdot I^0/C_{DL} \tag{2.2}$$

determines the upper frequency limit that can be utilized to study double layer processes.

A change in the potential drop across the DL by using an external power source results in a change of the charge density at both the liquid and solid surfaces; under certain conditions the charge may even change sign, from negative to positive or vice versa. The electrode potential φ_M^0 at which this change in the sign of surface charge occurs is termed *Potential of Zero Charge* (PZC); its value depends on the chemical identity of the electrode and on the chemistry of the solution. This situation corresponds to the absence of free charges on the surface. Among other contributions, the difference between the actual electrode potential and the PZC determines the nature of the species adsorbing at the surface: at more negative potentials positively charged species are adsorbed, and vice versa. It is essential in practical electrodeposition processes to predict which species adsorb at various electrode potentials since these substances may influence the process. Values of PZC for some metals are given in the Table 2.1.

From the experimental viewpoint, the DL may be characterized by measuring its capacitance as a function of electrode voltage. Various models of the DL have been

Table 2.1 Zero charge potentials

Metal	Solution	ZCP, Volts
Ag	0.0025 M Na$_2$SO$_4$	−0.67
Au	Calculated value	+0.20
Bi	0.002 M KF	−0.39
Cd	0.001 M NaF	−0.75
Co	Calculated value	−0.40
Cr	Calculated value	−0.45
Cu	0.01 M NaF	+0.09
Fe	Calculated value	−0.35
Ga	0.01 M HClO$_4$	−0.69
Hg	0.01 M NaF	−0.193
In	0.003 M NaF	−0.65
Ni	Calculated value	−0.25
Pb	0.001 M NaF	−0.56
Pd	0.05 M Na$_2$SO$_4$+0.001 M H$_2$SO$_4$	+0.26 (full charge)
Pd	0.05 M Na$_2$SO$_4$+0.001 M H$_2$SO$_4$	+0.10 (free charge)
Pt	0.03 M HF+0.12 M KF	+0.235 (full charge)
Pt	0.03 M HF+0.12 M KF	+0.185 (free charge)
Sb	0.002 M KClO$_4$	−0.15
Sn	0.00125 M Na$_2$SO$_4$	−0.43
Zn	Calculated value	−0.60

developed to describe the observed experimental behavior; they are discussed in the following. These models are able to describe and predict also other DL characteristics, such as volume and surface charge density, potential distribution and interface energy. Capacitance data in particular enable the determination of the extent of adsorption of ions and organic substances (Sect. 2.4).

2.2 Compact Part of the Double Layer: Helmholtz Layer

An electric charge q_m at the metal surface in contact with the solution is induced by the excess or deficiency of electrons in the surface layer. This charge must be compensated by an equal and opposite charge $q_2=-q_m$ at the solution side; q_2 is provided by ions present in the solution layer adjacent to metal surface.

The simplest model of DL consists of two charges q_m and q_2 distributed on two parallel planes, separated by a dielectric layer of solvent molecules (dipoles); in this model the charges are assumed to be point-like and spaced by a distance x_o, determined by the size of the solvation sheath generated by the solvent dipoles between the ionic layer and the metal surface; this region is of the order of 0.3 nm.

This model is referred to as compact DL or Helmholtz layer. It describes rigorously the DL structure at the interface of concentrated solutions and normal metals. It is similar to the familiar electric capacitor with one of the "plates" being liquid. The development of this concept is due to Helmholtz and Kohlrausch.

The capacitance per unit area of said capacitor is

$$C_1 = \varepsilon_0 \varepsilon_1 / d \tag{2.3}$$

where d is the distance between the charged planes; if the origin is placed at the metallic surface, then $d=x_o$; ε_0 is the permittivity of free space.

In Eq. (2.3) ε_1 is the relative permittivity in the region between the two charged layers; this space is filled by dipole molecules of the solvent but, due to the limited mobility of these dipoles, its permittivity is much less than that of the free solvent and assumed to be constant in $0<x<d$.

The electric potential within the DL varies linearly since no volume charge is present. At each point x

$$\varphi(x) = \varphi_0 + q(x_0 - x)/\varepsilon_0 \varepsilon_1 \tag{2.4}$$

where φ_0 is the potential at the plane where the ionic charges are located.

The outlined model is a strong simplification of the real structure and severely limited in its predictive capabilities. In order to improve on this model it is important to list such limitations, as follows.

1. The actual electron density in the metal near the interface cannot change sharply but does so gradually. As a result, the charged metal layer has a finite thickness of about 0.1 nm, and the charge distribution depends on the nature of the metal; semimetals and semiconductors for example are characterized by a much wider

distribution of the electronic charge. Moreover, the electron density decreases exponentially in the solution region adjacent to the metal surface, causing a non-linear drop of potential in the DL.

The penetration depth of the electric field into the metal (the Thomas–Fermi length l_{TF}) is given by

$$l_{TF} \approx \left(\varepsilon_0 E_F / e^2 n_e\right)^{1/2} \tag{2.5}$$

where E_F is the Fermi energy of the metal, and n_e its electronic density. Typical values are 5 eV and 10^{29} m^{-3}, respectively, giving for $l_{TF} \approx 0.05$ nm. In the case of semiconductors l_{TF} can be 2–4 orders of magnitude higher. It is apparent from this result that the metallic plate of the capacitor is not localized at the interface but has a finite thickness; this will affect the actual value of the capacitance.

2. The value of the relative dielectric constant ε_1 depends on the properties of metal and solvent and on the electric field in the DL, and is in fact a function of both metal and solution. Also, the thickness d in Eq. (2.3) is obviously not identical to x_o; whereas x_o is the minimum distance of the ions centers from the metallic surface, d corresponds to the thickness of the layer having said specific value of ε_1 [3, 4].

   Interestingly, the overall C_1 does not depend on solution concentration [5] (up to concentrations of about 0.1 M) but only on q: a change in q implies a change in ε_1/d.

3. Finally, the Helmholtz model assumes that the ions in the solution are frozen in a predetermined configuration; this is true only at the absolute zero temperature. At any other temperature, thermal motion should be considered; this is discussed in the next section.
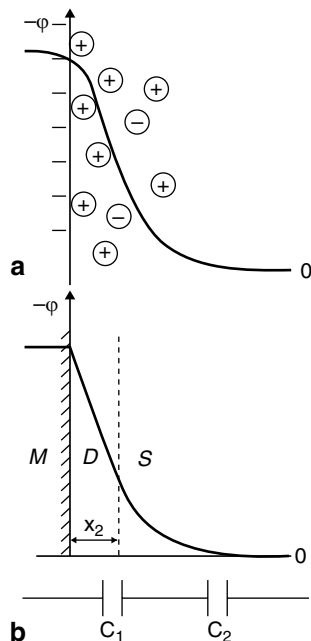
2.3 Diffuse Layer: Gouy-Chapman Layer

At any finite temperature, the thermal motion of the ions results in a shift of the center of charges from the fixed plane considered above, thus delocalizing the charge distribution. Part of the ions move from the surface into the bulk of solution, generating a volume charge distribution, or a *diffuse layer*.

The diffuse layer consists of ions of both signs, with one sign being present in some excess, which gradually reduces with increasing distance from the electrode (Fig. 2.2). It is common to represent the ionic atmosphere as a continuum characterized by a charge density ρ function of position, its integral value (the overall charge) being q_2. The permittivity of this medium is equal to the bulk value of the solvent. This region conventionally starts at a distance x_o from the electrode; closer to the electrode charged particles are absent.

The interface between the compact and diffuse layers is called *Outer Helmholtz Plane* (OHP). This plane can be thought of as the location where the point-like

Fig. 2.2 Distribution of the
electrical charge and potential
in the case of diluted solu-
tion. **a** compact and diffuse
layers: M – metal, D –
dielectric, S – solution; **b** the
electric model of the double
layer with compact and dif-
fuse parts

charges adsorbed on the electrode at zero temperature are concentrated; while some
models assume that a certain charge is located at this plane also at finite tempera-
ture, other models consider that the surface charge is zero at the plane itself, and
that the OHP represents the boundary between the double layer, where no charge is
present, and the diffuse layer, with a finite volume charge density q_v. In this latter
depiction, for $x < x_o q_v = 0$ while for $x \geq x_o |q_v| > 0$, gradually decreasing in the direc-
tion of the solution bulk. Due to the sharp change in the medium properties at the
OHP, this model requires a discontinuous jump in permittivity. This discontinuity
in permittivity is unrealistic; as a consequence, while the model often describes
adequately the potential and charge distributions in the DL, such description cannot
be completely rigorous.

The overall capacitance C_{DL} (or, for simplicity, C) of the system consisting of
the compact and diffuse layers is determined by the series capacitances of the two
layers, C_1 and C_2 as [6]:

$$C^{-1} = C_1^{-1} + C_2^{-1}, \text{ or } C = C_1 C_2 / (C_1 + C_2) \tag{2.6}$$

From the electrostatic standpoint this picture is analogous to placing in the plane x_o
a conductive non-charged plate. This introduces no changes to the charge and po-
tential distribution and is needed only to develop a model with two capacitors. Actu-
ally these two capacitors model the dense layer and the diffuse layer, respectively
(Fig. 2.2). The charge of the latter is distributed across a finite thickness.

The capacitance C_2 can be determined by calculating the potential distribution in the diffuse layer. This was first accomplished independently by Gouy and Chapman, approximately 100 years ago; the calculation is based on the assumption that the position of the ions is determined by a Poisson–Boltzmann distribution and has an important standing in electrochemistry; this is why we include here the corresponding derivation.

Assuming point-like ionic charges, the volume charge density can be written as an algebraic sum of all the ionic charges:

$$\rho = \Sigma c_i z_i F = F \Sigma c_i^0 z_i \exp\left(-z_1 f \varphi\right) \tag{2.7}$$

When c_i is expressed in moles per liter, ρ is in Coulombs/liter. The local concentration of ions i is assumed to depend on the local potential as $c_i\,(\varphi) = c_i^0 \exp\left(-z_1 f \varphi\right)$; this corresponds to assuming that i) only electrostatic forces are important, and ii) the electrostatic field is not influenced by the ion under consideration.

The volume charge density ρ is related to the potential φ by the Poisson equation $d_2\varphi/dx^2 = -\rho/\varepsilon_0\varepsilon$; together with Eq. (2.7) this gives

$$d^2\varphi/dx^2 = -\left(F/\varepsilon_0\varepsilon\right) \Sigma c_i^0 z_i \exp\left(-z_1 f \varphi\right). \tag{2.8}$$

Here, $f=F/RT$.

We consider here a one-dimensional configuration, where the field changes only normal to the surface. Contrary to Eq. (2.3), ε is now the bulk dielectric permittivity of the solution. Equation (2.8) has the form $\varphi'' = f(\varphi)$; it can be integrated using a standard method, by multiplying both sides with $2\varphi'dx = 2d\varphi$, therefore obtaining exact differentials.

As a result of the integration two quantities are obtained. The first is the potential φ as a function of distance from the OHP; for a symmetrical z, z-charged electrolyte (that is, an electrolyte obtained by dissolution of a $A^{z+}B^{z-}$ salt), $\varphi(x)$ is given for $x>x_o$ by the Stern formula [7]:

$$\varphi = 4z^{-1} f^{-1} \arctan\left\{\tan\left(z f \varphi_o/4\right) \cdot \exp\left[(x_o - x)/\lambda_D\right]\right\} \tag{2.9}$$
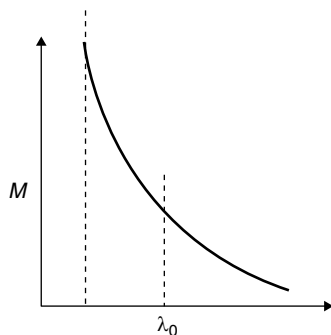
φ_o is the potential at the OHP, $\lambda_D = |z|^{-1} F^{-1}(RT\varepsilon\varepsilon_0/2c)^{\frac{1}{2}}$ has the dimensions of a length and is termed *Debye length*. When $q_m=0$ this is the length at which the potential falls by $e\approx2.7$ times (for $x>2x_o$ Eq. (2.9) corresponds practically to an exponential decrease as shown in Fig. 2.3).

For nonsymmetrical electrolytes the solutions of Eq. (2.8) can also be derived by the method of the auxiliary functions of φ [8].

The second result of the integration is a relationship between φ_o and q_2:

$$(q_2)^2 = 2RT\varepsilon\varepsilon_0\Sigma c_i^0\left[\exp\left(-z_1 f \varphi_o\right) - 1\right] \tag{2.10}$$

or for a z,z-electrolyte

$$q_2 = q_D \sinh (z f \varphi_o/2) \tag{2.11}$$

where $q_D = (8RTc\varepsilon\varepsilon_0)^{1/2} = 2\varepsilon\varepsilon_0/(\lambda_0 |z| f)$; this quantity has the dimensions of a charge per square meter and can be called *Debye charge*. In other reference books a different notation is often used: $A = \frac{1}{2}q_D$.

The overall charge consists in the sum of cationic charges

$$q_2^{(+)} = q_D \left[\exp (-z f \varphi_o/2) - 1\right] \tag{2.12}$$

and of anionic charges

$$q_2^{(-)} = q_D \left[\exp (-z f \varphi_o/2) - 1\right]. \tag{2.13}$$

Furthermore, φ_o can also be expressed in terms of q:

$$\varphi_o = 2z^{-1} f^{-1} \arcsin h (q_2/q_D). \tag{2.14}$$

This very important expression has two limiting cases: when $q_2 \ll q_D$

$$\varphi_o = 2q_2/ |z| f q_D = q_2\lambda_D/\varepsilon\varepsilon_0 \tag{2.15}$$

and when $q_2 \gg q_D$

$$|\varphi_o| = \text{const} + (2/zf) \ln |q_2| - (1/zf) \ln c \tag{2.16}$$

Equation (2.16) permits to find the capacitance of the diffuse layer as $C_2 = dq_2/d\varphi_o$:

$$C_2 = \frac{1}{2} |z| f q_2 \cosh (\frac{1}{2} z f \varphi_o) = (\varepsilon\varepsilon_0/\lambda_D) \cosh (\frac{1}{2} z f \varphi_o) \tag{2.17}$$

or, as a function of charge:

$$C_2 = \frac{1}{2} |z| f (q_2 + q_D)^{1/2} \tag{2.18}$$

We can see from Eq. (2.15) that $\varphi_o=0$ when $q_2=0$. Under these conditions also $q_m=0$, i.e. the metal surface is at its zero charge potential. At $q_m=0$, C_2 goes through its minimum:

$$C_2 = \tfrac{1}{2}\,|z|\,f q_D = |z|\,F(2\varepsilon\varepsilon_0 c/RT)^{1/2} = \varepsilon\varepsilon_0/\lambda_D \qquad (2.19)$$

This minimum becomes deeper the more diluted is the solution.

The above formulae give the capacitance of the diffuse layer; the total C_{DL} may be measured experimentally, and then the capacitance of the dense layer is obtained as

$$C_1^{-1} = C^{-1} - C_2^{-1}, \qquad (2.20)$$

If C_1 does not depend on potential then C_{DL} has its minimum at the same potential as C_2, i.e. at the PZC. In reality, in symmetric electrolytes as $c \to 0$ the minimum in C_{DL} is obtained at the PZC [6]. In most cases the minimum is somewhat shifted from the PZC (Fig. 2.4). Curves of this sort are obtained with low melting metal electrodes such as Hg, Pb, Cd, Bi, Ga etc.

Considering the diffuse layer as a conventional capacitor with $C=C_2$ and permittivity ε it is possible to determine its equivalent thickness λ; i.e., by placing the overall charge at this distance from the OHP we obtain a capacitor with the same capacitance. When $q_2=0$ this thickness is equal to

$$\lambda = \varepsilon\varepsilon_0/C_2 = |z|^{-1}F^{-1}(RT\varepsilon\varepsilon_0/2c)^{1/2} \qquad (2.21)$$

This coincides with the Debye length λ_D. At $q_2 \neq 0$

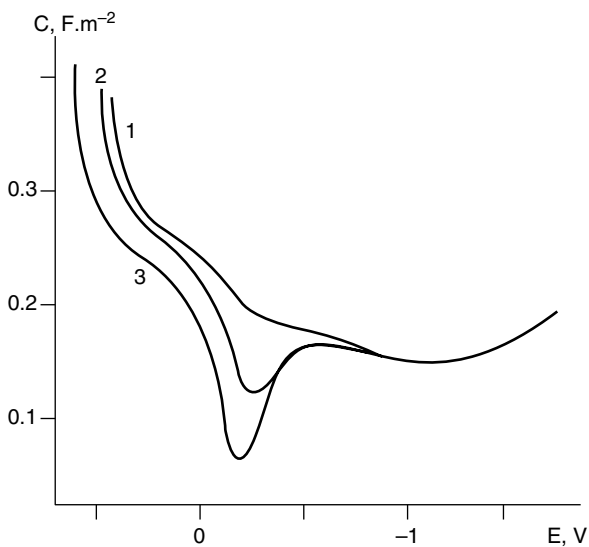$$\lambda = \lambda_D/ch\,(|z|\,f\varphi) \qquad (2.22)$$

Fig. 2.4 Differential DL capacity at mercury in NaF solutions: *1* 0.1 M, *2* 0.001 M. The minima are close to PZC

As the concentration and/or q increase, λ_D diminishes. In concentrated solutions $\lambda_D \rightarrow 0$ and the overall volume charge concentrates near the OHP; in this case the model of two capacitors in series simplifies to that of a compact layer. In this limiting case the charge of the "liquid plate" is attributed to the OHP.

2.4 Adsorption at Electrodes

Before proceeding further, it is necessary to discuss the process of adsorption of electrolyte species at the electrode. Several types of adsorption phenomena and the corresponding interactions should be considered, namely: (a) the adsorption of surface-active substances, (b) the adsorption of ions (including specific adsorption), (c) the adsorption of electroactive species: reagents, products and intermediates, and (d) the formation of adsorbed ionic or molecular layers.

The thermodynamic analysis of adsorption is based on the *Gibbs adsorption equation*; this description is most general and is independent of any model of the interface. At the boundary between two phases 1 and 2, the thermodynamic properties of these two phases change gradually across the boundary. Assume that this transition occurs within a narrow region 3 between 1 and 2 (Fig. 2.5), which is bounded by the planes I and II; the thickness of this region is of molecular dimensions. In this region the concentrations of the various species differ from those in the regions 1 and 2. For each species i we define the "surface excess" Γ_i as the excess of the surface concentration (number of moles n_i per unit area A) of component i in the region 3 relative to 1 or 2. The planes I and II are named the Gibbs planes, and $\Gamma_i = n_i/A$ is referred to as "adsorption" (moles per unit surface). In the case of adsorption at a metal electrode from solution only one Gibbs plane is necessary since the second one coincides with the metal surface.

Under conditions of constant temperature and pressure (conditions characteristics of electrochemical systems) the Gibbs adsorption equation has the form
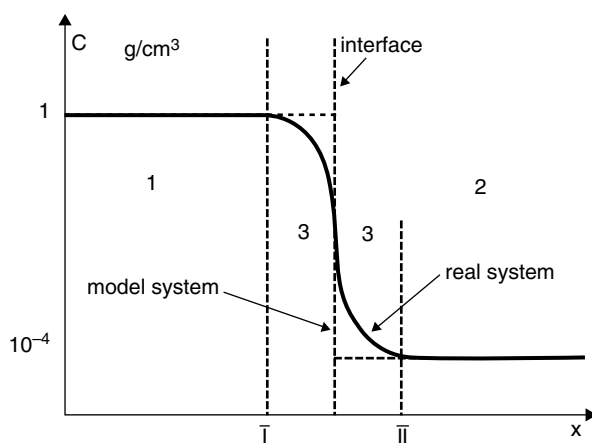

Fig. 2.5 Intermediate region (3) between the phases 1 and 2

$$d\gamma = -\Sigma_i \Gamma_i d\mu_i, \tag{2.23}$$

In particular, for a two-component system

$$d\gamma = -\Gamma_1 d\mu_1 - \Gamma_2 d\mu_2. \tag{2.24}$$

Another important equation is the Gibbs–Duhem equation for the chemical potential:

$$x_1 d\mu_1 + x_2 d\mu_2 = 0 \tag{2.25}$$

In these equations γ is the solid/electrolyte interface energy, and x_i is the molar fraction of the component i in the solution. The Gibbs Eq. (2.23) may be considered as the surface analogue of Eq. (2.25).

If we consider Eq. (2.23) for the case of a solute (sol) and the solvent (water) it is possible to write

$$d\gamma = -\Gamma_{sol} d\mu_{sol} - \Gamma_w d\mu_w \tag{2.23'}$$

and, assuming that Γ_w is zero, this simplifies further to

$$d\gamma = -\Gamma_{sol} d\mu_{sol} \tag{2.23''}$$

This equation relates the adsorption of a solute species to the change in interface energy of the electrode; the driving force for adsorption is therefore a decrease in interface energy.

The extent of adsorption of the various species in general depends on the concentration of the species in solution and on the interactions between these species. A different set of assumptions will therefore result in different forms for the adsorption isotherms, describing the dependence of adsorption of a certain species on the above variables.

2.4.1 Model Adsorption Isotherms

2.4.1.1 The Langmuir Isotherm

The simplest and most commonly used adsorption equation, suitable for the description of both gas adsorption and adsorption from solutions is the *Langmuir isotherm*

$$Bc = \theta / (1 - \theta), \tag{2.26}$$

which relates the electrode coverage $\theta = \Gamma / \Gamma_\infty$ by a certain species to the concentration of that species in solution, c. Γ_∞ is the limiting adsorption when $c \rightarrow \infty$, and B is a constant. This equation can also be written as:

$$Bc = \Gamma / (\Gamma_\infty - \Gamma). \tag{2.27}$$

In many cases the limiting adsorption Γ_∞ is equal to the number of active electrode sites per unit surface n_s/N_A, but this correspondence may not always be cor-

rect; a large molecule for example may occupy several active centers, and then $\Gamma_\infty \neq n_s/N_A$. The adsorption constant B depends on temperature, and in the case of electrochemical systems also on the electrode potential.

The kinetic derivation of the Langmuir isotherm equation is well known; the constant B is derived as the ratio of the rate constants for adsorption and desorption. Both rates are equal at equilibrium, therefore:

$$K_{ads}c\,(1 - \theta) = K_{des}\theta$$

and:

$$K_{ads}c/K_{des} = \theta/\,(1 - \theta)\,, \tag{2.28}$$

or

$$B = K_{ads}/K_{des}. \tag{2.29}$$

The Langmuir equation however can also be derived without resorting to any kinetic considerations, only on the basis of thermodynamic and statistical methods. In this way, it can be found that the value of B depends on the adsorption energy ΔG_{ads}:

$$B = B_o \exp\,(-\Delta G_{ads}/RT); \tag{2.30}$$

this expression separates explicitly the temperature dependence from the dependence on the electrode potential (as will be seen later, ΔG_{ads} depends on potential).

Obviously, in the Langmuir isotherm the value of B does not depend on the coverage θ. This isotherm is usually considered valid only for localized adsorption, i.e. when the species are adsorbed at fixed sites; in the case of adsorption from solution however this feature has limited significance because adsorption is actually a replacement process: the solute substitutes for the molecules of the solvent at the surface. At low concentrations this isotherm becomes the linear Henry isotherm, whereas at sufficiently high concentrations of the adsorbed substance $\theta \to 1$.

The adsorption isotherm corresponds to a two-dimensional equation of state for the interface energy: $\Delta\gamma = f(T, \theta)$, that generalizes the usual three-dimensional equation of state $P = f(T,V)$. The quantity $\Delta\gamma$ is the change in interface energy upon adsorption. This two-dimensional equation of state can be derived using the Gibbs adsorption isotherm for one component. By approximating the thermodynamic activity with the concentration:

$$d\gamma = -\Gamma d\mu = -RT \cdot \Gamma dlnc. \tag{2.31}$$

Combining this equation with the Langmuir equation leads to

$$d\gamma = -RT\Gamma\theta dln\,(\theta/\,(1 - \theta)) \tag{2.32}$$

(B=const, and then $d\,lnB=0$).

After integration, and taking $\gamma_o = \gamma\,(\theta = 0)$

$$\gamma - \gamma_o = \Delta\gamma = -RT\Gamma_\infty ln\,(1 - \theta)\,, \tag{2.33}$$

This result is obtained through a change of variables: $\theta/(1-\theta)=z$, or $\theta=z/(1+z)$, from which

$$d\gamma = -RT\Gamma_\infty z/(1+z) \cdot dz/z = -RT\Gamma_\infty dz/(1+z),$$

and then

$$\int d\gamma = -RT\Gamma_\infty \int dz/(1+z), \text{ or} \tag{2.34}$$

$$\gamma = \gamma_0 + RT\Gamma_\infty \ln(1+z) = \gamma_0 - RT\Gamma_\infty \ln(1-\theta). \tag{2.35}$$

This two-dimensional equation of state for the Langmuir isotherm describes the ideal two-dimensional adsorbed layer, whose behavior corresponds to that of the ideal gas.

2.4.1.2   The Frumkin Isotherm

In the three-dimensional case a deviation from the ideal gas law is usually taken into account by the Van der Waals equation of state, in which two coefficients a and b are included. For N particles in the system this equation has the form:

$$(p + aN^2/V^2)(V - bN) = Nk_BT. \tag{2.36}$$

The coefficient a takes into account interparticle interactions. A statistical analysis shows that a can be expressed as

$$a = 2\pi \int |u| r^2 dr, \tag{2.37}$$

where $u(r_{ik})$ is the interaction energy between particle pairs, and the integration is carried out for all the pairs in the system. Then the total variation of potential energy (as compared with that of the ideal gas) is proportional to $N(N-1)$, which at high N can be approximated by N^2.

The same procedure can be generalized to take into account pair-wise interactions in the two-dimensional case. The resulting correction must be proportional to the square of the number of the adsorbed species, and it can therefore be expressed in terms of coverage as $a\theta^2$.

This derivation was first performed by Frumkin in 1926. He wrote the corrected equation as:

$$\Delta\gamma = -RT\Gamma_\infty \ln(1-\theta) + a\theta^2, \tag{2.38}$$

the quadratic dependence resulting from taking into account all the interacting particle pairs.

The combination of this new equation of state with the Gibbs adsorption equation results in the *Frumkin adsorption isotherm*:

$$Bc = [\theta/(1-\theta)] \exp(-2a\theta). \tag{2.39}$$

The quantity B, as in the Langmuir isotherm, depends on temperature and electric potential. As experiments have shown, this is true also for the value of a, which is called *attraction constant*. $a<0$ describes repulsive interactions, whereas $a>0$ corresponds to attractive interactions between the adsorbed species.

The Frumkin isotherm is most frequently used in the coverage range $0.2<\theta<0.8$. This is one of the most widely used adsorption isotherms in electrochemistry, particularly to describe the adsorption of surface-active organic molecules at electrodes. This isotherm takes into account the variation of the adsorption energy (enthalpy) at varying coverage, the reason for this dependence being the lateral interactions existing in the adsorbed layer.

2.4.1.3 The Stern Isotherm

The Stern isotherm generalizes the Langmuir isotherm to the case of electrically charged species. It does not take into account any lateral or dipolar interactions, but includes the work done on the charged species to transfer them from $\varphi=0$ to the potential φ. In this case the adsorption energy ΔG_{ads} can be written as

$$\Delta G_{ads} = \Delta G_0 + z_s F \varphi. \tag{2.40}$$

Thus the "adsorption constant" B depends in this case not only on temperature and on the specific chemical energy of adsorption ΔG_0 but also on the potential φ. The resulting isotherm takes the form

$$B_o exp\left(-\Delta G_0/RT + z_s F \varphi_i/RT\right) c = \theta/\left(1-\theta\right), \text{ or} \tag{2.41}$$

$$Bc = \theta/\left(1-\theta\right) exp(-z_s F \varphi/RT) \tag{2.42}$$

This equation is a simplified form of a more complicated expression originally derived by Stern for the adsorption of two different species.

2.4.1.4 Adsorption, Double Layer Capacitance and Interfacial Tension

The Gibbs adsorption isotherm does not consider explicitly any effect linked to charges and electrostatic fields. These effects can be included however by substituting the chemical with the electrochemical potential, or, equivalently, by taking into account the work $z_s F \varphi_i$, in a similar way as it was done in the derivation of the Stern isotherm:

$$d\gamma = -\Gamma d\mu - q d\varphi \tag{2.43}$$

where $q = d\gamma/d\varphi$.

This relates the dependence of the interface energy on potential to the surface charge and can be rewritten in terms of the interface capacitance C_{DL}:

$$d^2\gamma/d\varphi^2 = -dq/d\varphi = -C_{DL} \tag{2.44}$$

Assume C_{DL} is constant (this is valid under the Helmholtz or the linear Gouy-Chapman approximation, or far away from the PZC). Integrating this relationship we obtain:

$$q = -C_{DL}\,(\varphi - \varphi_{PZC}) \tag{2.45}$$

$$\gamma = -C_{DL}(\varphi - \varphi_{PZC})^2/2 + \gamma_{PZC}, \text{ or} \tag{2.46}$$

$$\gamma_{PZC} - \gamma = C_{DL}(\varphi - \varphi_{PZC})^2/2. \tag{2.47}$$

This shows that γ is maximum at the PZC, and that under the approximation of constant C_{DL}, it changes quadratically with potential. Experimental results agree with this prediction, as shown for example in Fig. 2.6, depicting the capacitance and interfacial tension vs. applied potential for NaF solutions. In this figure, it should also be noted that the PZC remains approximately unchanged with electrolyte concentration.

These predictions however fail when adsorption of anions occurs at the surface. Figure 2.7 shows for example the measured capacitance and interface energy for KBr solutions. In this case, no clear minimum in the capacitance is observed, and at potentials positive with respect to the PZC the capacitance increases to very high values, of the order of 200 $\mu F/cm^2$. The interface energy still follows an approximately parabolic behavior, but the PZC shifts to negative values with increasing electrolyte concentration.

Finally, Fig. 2.8 illustrates an example of adsorption of neutral molecules. Neutral molecules can adsorb due to their polar nature or due to local, specific interactions. The capacitance is very small in the range of potentials corresponding to the adsorption of the neutral molecule, due to the fact that no change in surface charge occurs at potentials where the molecule is adsorbed. Peaks in capacitance are observed at the potentials where the molecules desorb. The interface energy correspondingly shows a deformed parabolic behavior.
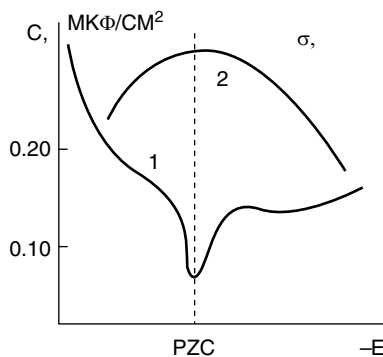

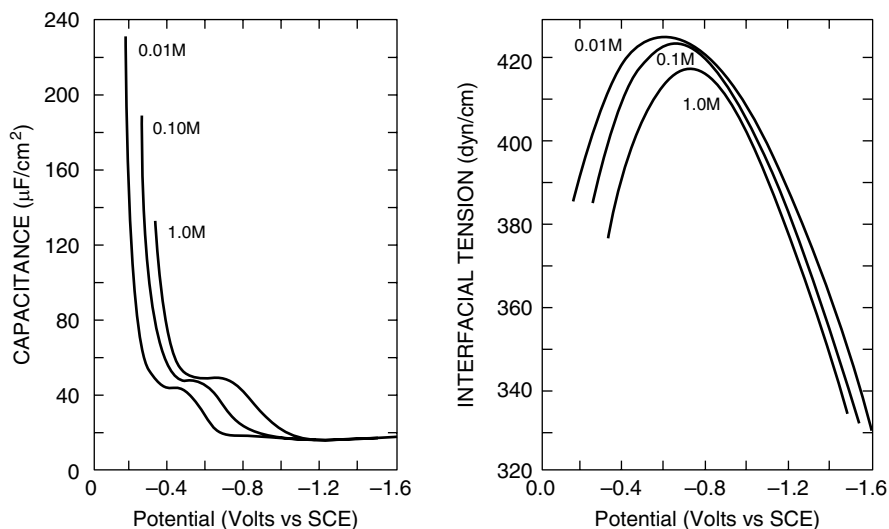**Fig. 2.6** Capacitance (a) and surface energy (interfacial tension) measured for NaF solutions

Fig. 2.7 Differential capacitance and interfacial tension for aqueous KBr solutions. (Adapted from E. Gileadi "Interfacial electrochemistry: an experimental approach" Addison-Wesley (1975))
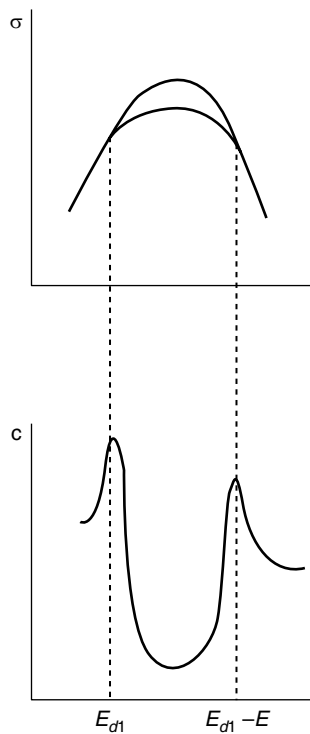

Fig. 2.8 Adsorption of neutral molecules: electrocapillary curve and capacity

2.5 Specific Adsorption

Now we return to the Gouy–Chapman model and consider ion adsorption in detail. Most ions upon adsorption can approach the electrode surface only up to the Outer Helmholtz Plane (OHP). Some of the ions in solution however actually approach the metal surface at a distance closer than the OHP; this may occur as a consequence of partial dehydration or when the ion interacts with the surface not only through electrostatic forces but also for example by forces of chemical origin. In such case these species form a *specifically adsorbed* layer; under the assumption of point-like species, this is located at a distance x_i from the electrode surface, where $x_i < x_o$. This distance determines the *Inner Helmholtz Plane* (IHP), hence the index *i*. Different species may in principle have different x_i, but usually only one inner plane is considered. This extended model of the double layer was introduced by Grahame.

   In the following chapters we will discuss the process of charge transfer through the interface. During this process, the species that undergo charge transfer (the *electroactive* species) are located within the compact (Helmholtz) layer, either at the OHP, the IHP or somewhere in between. For this reason, a precise description of the potential distribution in this region is important in electrochemical kinetics.

   Said system is schematically shown in Fig. 2.9. The charge at the metallic surface q_m is equal to the sum of charge q_1 at the IHP, and the remaining charge in the diffuse layer, q_2; this provides for the electroneutrality of the overall system:

$$q_m + q_1 + q_2 = 0 \tag{2.48}$$

The value of q_1 is determined by the quantity of specifically adsorbed species Γ: $q_1 = z_s F\Gamma$ where z_s is the charge of the specifically adsorbed ions and Γ their surface concentration (moles per area unit), as determined by the Stern adsorption isotherm, where the potential is that of the inner Helmholtz plane φ_i:

$$B_o exp\left(-\Delta G_0/RT + z_s F\varphi_i/RT\right) c = \Gamma / \left(\Gamma_\infty - \Gamma\right), \tag{2.49}$$

In this equation Γ_∞ is the limiting adsorption and the potential φ_i is equal to the sum of the potential at the OHP φ_0 which was found earlier and the potential drop between the two Helmholtz planes. This potential drop is determined by the charges
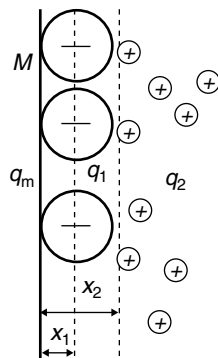

Fig. 2.9 Charge distribution at specific adsorption

(1) on the metal surface and (2) at the IHP. The former contributes the amount $q_m(x_o - x_i)/\varepsilon_0\varepsilon_1$ while the latter adds a term $q_1(x_o - x_i)/\varepsilon_0\varepsilon_1$. Consequently,

$$\varphi_i = \varphi_0 + [q_m(x_o - x_i) + q_1(x_o - x_i)]/\varepsilon_0\varepsilon_1. \qquad (2.50)$$

One can see that the amount of specifically adsorbed species Γ depends on the potential at the IHP, but in addition this potential is also determined by the charge q_1 which is equal to $z_sF\Gamma$.

This result shows that the calculation of charge and potential distribution in the DL for a specific adsorption is not simple. Nevertheless, experimental data enable determination of the charge and potential distribution in this case. Several specific experimental and mathematical methods have been developed for their determination [9]. Here we only state that the simultaneous solution of Eqs. (2.49) and (2.50) can give in implicit form the dependence of q_1 (and consequently of φ_i) on the concentration of the specifically adsorbed species. The value of φ_0 was found in Sect. 2.3, in the discussion of the Gouy–Chapman model.

The overall potential difference between the solution bulk and the metal surface is

$$\varphi_m = \varphi_0 + [q_m x_o + q_1(x_o - x_i)]/\varepsilon_0\varepsilon_1. \qquad (2.51)$$

The equations reported in Sects. 2.2–2.5 give the distribution of charge and potential at the Helmholtz planes and in the diffuse layer; a complete description of the system requires in addition knowledge of the parameters B_0, x_i, x_o etc., and allows a fit of most experimental data. These parameters may be estimated by using experimental data of DL capacitance over a wide range of potentials and of ionic concentrations (see Sect. 2.8).

It is necessary to note that the specific adsorption of ions can change significantly the potential distribution in the double layer. For example, at potentials more positive than PZC the value of φ_0 is positive; however, if anions do adsorb specifically, their overall charge $|q_1|$ exceeds the metal charge $|\varphi_m|$. This leads consequently to a positive adsorption of the cations, as seen from Eq. (2.48). Then, the diffuse layer contains an excess of cations, leading to the potential distribution shown in Fig. 2.10. Phenomena of this sort explain the shift of PZC shown in Fig. 2.7, resulting from specific adsorption (in this case of Br$^-$).
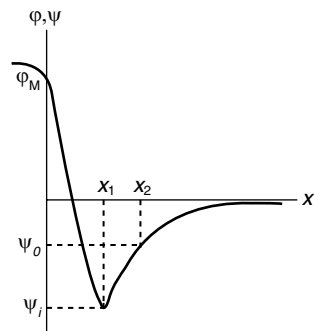

Fig. 2.10 One type of the potential distribution in the double at specific adsorption

A complete theory gives an explicit expression for this potential shift: $d\varphi_{ZCP}/d\ln c = RT/zF$ for the specific adsorption of z-charged ions (c is the concentration of the said ions); in reality the actual shift is often larger than this value. This is due to the discrete character of the charge distribution at the IHP.

2.6 Adsorption of Uncharged Organic Species

The structure of the DL is determined not only by the distribution of charged species but also by the presence of neutral surface-active, predominantly organic, substances. Such substances are usually employed in practical electrodeposition processes. Surface adsorption of these species does not change radically the electrical potential configuration, but influences the distribution of the charged species and also the permittivity in the dense layer. Adsorbed molecules may be modeled as electric dipoles oriented by the DL field; consequently, these do not contribute to the overall charge, but re-distribute it in the vicinity of the sites where they are adsorbed. The charge at free sites on the other hand does not change, leading to a *model of two parallel capacitors* for the interface [6]. In this model one capacitor is originated by the charge distributed over free sites (filled by the solvent molecules), and the other by the charge distribution at the sites covered by organic molecules. The overall charge is thus obtained as a sum over the two regions:

$$q = q_{\theta=0}(1-\theta) + q_{\theta=1}\theta \qquad (2.52)$$

Here $q_{\theta=0}$ is the charge (per area unit) of the free sites and $q_{\theta=1}$ is that for covered sites; θ is the fractional coverage by organic molecules as it was introduced earlier. We will indicate these two contributions as C_0 and C'. The value of θ is governed by the adsorption isotherm which in this case depends on potential (or charge) of the electrode. As it was noted in Sect. 2.4, the Frumkin isotherm is best suited to describe the adsorption of organic species:

$$Bc = \theta(1-\theta)^{-1}\,exp(-2a\theta). \qquad (2.53)$$

In most cases in fact it adequately describes experimental data. In this formula however the value of B is dependent on potential because the effects of replacing water in the DL with organics must be included into the treatment. When the DL capacitance changes from C_0 to C' the electrostatic work expended for this replacement (per mole of adsorbed species) is

$$W = (C_0 - C')(\varphi - \varphi_{PZC})^2/2\Gamma_\infty \qquad (2.54)$$

At the PZC this work is equal to zero, ant therefore B must have its maximum at this potential. In reality, the adsorbed species may have a non-zero dipole moment, thus shifting the potential of maximum adsorption to some point $\varphi_{PZC}+\Delta\varphi$ just as a polarized dielectric volume produces a potential drop at an uncharged capacitor.

As a result,

$$B = B_0 exp \left[-\left(C_0 - C'\right) \left(\varphi - \varphi_{PZC} - \Delta\varphi\right)^2 / \left(2RT\Gamma_\infty\right) \right]. \qquad (2.55)$$

The PZCs for different metals are rather different, thus leading to the adsorption of the same organics within different potential ranges.

The shape of the adsorption isotherm slightly varies with a potential shift; this effect can be usually accounted for by including a linear dependence of the parameter a on potential.

Thus, by measurements of the DL capacitance as a function of electric potential and of the concentration of organic species it is possible to determine all the parameters describing the adsorption of organics. An interesting phenomenon is observed when performing these measurements: this consists in the presence of capacitance maxima at the edges of the adsorption region (Fig. 2.8), which is related to the sharp decay of adsorption in these regions.

Indeed, if the charge of the surface fraction partially covered by organics is $q(\varphi,\theta)$, then the differential capacitance is equal to

$$C = dq/d\varphi = (dq/d\varphi)_\theta + (dq/d\theta)_\varphi (d\theta/d\varphi) \qquad (2.56)$$

The first contribution (the conventional capacitance) is equal, as seen from (2.52), to

$$(dq/d\varphi)_\theta = (dq_{\theta=0}/d\varphi)(1 - \theta) + (dq_{\theta=1}/d\varphi)\theta = q = C_0 (1 - \theta) + C'\theta, \qquad (2.57)$$

The second contribution is, as seen from (2.52)

$$(q_{\theta=1} - q_{\theta=0}) d\theta/d\varphi, \qquad (2.58)$$

which allows to rewrite (2.56) as

$$C = C_0 (1 - \theta) + C'\theta + (q_{\theta=1} - q_{\theta=0}) d\theta/d\varphi. \qquad (2.59)$$

This differs from the simple model of two capacitors in parallel by the third term, which is always positive (since both factors have the same sign). This term becomes important at the edges of the adsorption region due to the high value of $d\theta/d\varphi$; this explains the origin of the said maxima in Fig. 2.8.

Finally, it should be stressed that the discussion in this section concerns not only inert species simply blocking the surface but also neutral electroactive species, the surface concentration of which may govern the rate of the electrochemical process of interest.

2.7 Double Layer on Polycrystalline Solid Surfaces

Up to this point the surface was assumed to be macroscopically uniform. This is indeed the case for a liquid or monocrystalline electrode; in a polycrystalline electrode instead the various crystallographic facets have different properties, and at the

same potential the charges and capacitances of these facets may by different. These effects are particularly important for the compact layer. The diffuse layer on the contrary can be considered to be the same for the overall surface when the crystal grains are sufficiently small; with coarse grains having a size larger than the Debye length however each facet should also have its own diffuse layer.

There are attempts in the literature to describe a polycrystalline surface as uniform but having a finite roughness k_r (Sect. 1.4). In this case the roughness thus determined does not reflect an actual geometric roughness, but rather crystallographic features of the real surface, for example the existence of particular crystal facets, dislocations and other defects responsible for surface inhomogeneities.

Upon transition from the liquid to the solid state the double layer of the same electrode changes moderately; this was established by measuring the DL properties of a Ga electrode slightly below and above its melting point (about 30°C). Most studies of the double layer at solid surfaces require the use of well characterized structures such as dislocation-free monocrystalline surfaces, or surfaces with well-known step density. The opposite case however may also be of interest: very important information is found in fact through the use of a highly imperfect, liquid-type surface. This can be achieved by shearing or grinding. A freshly cut surface relaxes very quickly; therefore one should perform the measurements of interest very quickly. The cylindrical "cutting" electrode specifically designed for these investigations [10] is a very convenient electrochemical tool. The cutting of a thin metallic layer can be made immediately in the solution (with the potential applied), and measurements can be performed at any moment after surface renewal.

At sufficiently negative potentials C_{DL} depends weakly both on the surface state (solid or liquid) and on the chemical identity of the metal; under these conditions the roughness coefficient may be determined by correlating the results for a solid electrode with those measured on a mercury or amalgam electrode. For this process to be accurate however it is necessary that no adsorption of surface-active species occurs; this depends strongly on the metal identity.

In general, adsorption over dissimilar metal electrodes is significantly different; we have already noted that this is partly connected with the change of PZC; this can shift the region of adsorption up to 1 V. Additionally, the interaction of various metals with water may vary widely, resulting in a different width of the adsorption region. Finally, the adsorption energy as expressed by the parameter B_0 is determined by the electronic structure of both metal and adsorbate; in this respect, it has been established that maximum values of B_0 belong to species having definite ionization potentials I, which are specific for each metal ("*resonance potentials*" [11]). This statement is based mostly on the statistical treatment of the experimental data and has no deep theoretical foundation.

The most typical magnitude of I is 7.70–7.90 eV; this is characteristic for Cd, Sn, Bi, Pb and Cr. The approximate characteristic values experimentally found for copper, mercury, silver and zinc are correspondingly 7.2, 8.8, 9.0 and 9.4 eV; these values are close but not identical to the first ionization potentials of the metals. Oxidized areas of the surfaces have different "resonance potentials". Unfortunately, no data are available in the literature for other metals. The reported data provide a

guideline in choosing which substances may be strongly adsorbing at definite metal electrodes.

In comparing the *compact parts* of the double layer on different metals we recommend to divide the values of the corresponding capacitance into two contributions, one depending on the metal C_m and the other depending on the solvent C_s [12] as it is done for two capacitors in series (since the corresponding potential drops are additive):

$$C_1^{-1} = C_m^{-1} + C_s^{-1} \qquad\qquad (2.60)$$

In this formula C_m does not depend on the electrical charge q_m nor on the solution properties, but, as the experiment shows, varies with the metal identity as

$$C_{m2}^{-1} = C_{m1}^{-1} + const, \qquad\qquad (2.61)$$

the constant depending on the metal considered; m1 (e.g. mercury) can be taken as the standard.

C_s depends also on the charge, as follows

$$C_s^{-1}(m2) = C_s^{-1}(m1) + f(q) \qquad\qquad (2.62)$$

As a first approximation, $f(q)=K(q-q_1)$; K depends on the metal identity, and the charge q_1 corresponds to $f(q)=0$, i.e. at the potential when all the solvent dipoles have the same orientation on all metals. Such analysis has no firm theoretical base but it provides a method to correlate available data on the behavior of surface-active compounds at different metal surfaces, a very important task in electrodeposition.

2.8   Some Calculations of Double Layer Parameters

Experimental data on C_{DL} as a function of potential allow determination of the charge q by integration:

$$q(\varphi) = \int C_{DL}d\varphi, \qquad\qquad (2.63)$$

If the measurement is made in a given potential scale E (relatively to a definite reference electrode)

$$q(E) = \int C_{DL}dE \qquad\qquad (2.64)$$

This is the analogue of the expression (2.45) for a variable C_{DL}. Integration is performed from the PZC to a generic potential value and gives the charge of the metal surface as a function of potential. Sometimes it is more convenient to integrate in the reverse direction from some negative potential (at which no adsorption takes place); in this case however one has to find the integration constant.

Table 2.2 Specific surface energies of metals (in J/m^2)

Ag	Al	Au	Bi	Co	Cu	Fe	Hg	Mg	Ni	Pb	Pt	W	Zn
1.0	0.95	1.3	0.42	2.0	1.5	2.0	0.51	0.60	2.0	0.51	2.0	2.8	0.97

The surface/interface energy γ is a significant quantity in the field of electrocrystallization because it determines the character of nucleation processes. As shown in Sect. (2.4), its value is related to the electrode potential as $q = d\gamma/d\varphi$; in a given potential scale E

$$d\gamma/dE = -q \tag{2.65}$$

at constant activities of the components. This is Lippman's *electrocapillarity equation*.

It is therefore possible to calculate the surface energy by double integration:

$$\gamma = \gamma_0 - \int\int C_{DL} dE^2. \tag{2.66}$$

The constant γ_0 corresponds to PZC. At this potential the surface energy has its maximum. Approximate values of γ for different metals at room temperature are given in Table 2.2. It should be noted that Eq. (2.65) is not completely general. First, it must be corrected by the contribution from the adsorption of the electrolyte components (Eq. 2.43):

$$d\gamma = -qdE - \Sigma\Gamma_i d\mu_i, \tag{2.67}$$

where Γ_i is the adsorption (surface excess) of component i, and μ_i its chemical potential. The effect of interface energy change is most pronounced in presence of specific adsorption, especially when covalent bonding of the adsorbed species with the metal occurs.

In the case of a solid electrode the reversible surface work σ does not coincide with the overall surface energy γ; instead:

$$\gamma = \sigma + d\sigma/d\ln S, \tag{2.68}$$

the second term being the work done against the crystal bonds to change the electrode surface S; this term may be minimized by performing a very slow plastic deformation. As a consequence of this additional work term, Eq. (2.65) becomes:

$$(d\gamma/dE) = -q - dq/d\ln S. \tag{2.69}$$

Based on Eq. (2.69), it is additionally possible to determine the characteristics of the compact layer. Equations (2.17–2.18) allow calculation of the capacitance of the diffuse layer C_2 at any concentration, charge or potential; the value of C is experimentally measured, and by use of Eq. (2.20) we can find the capacitance of the compact layer C_1, and therefore $\varepsilon_1/d = C_1/\varepsilon_0$.

The plot of $1/C$ vs. $1/C_2$ for solutions of different concentrations at constant charge is a straight line with slope equal to 1 (Fig. 2.11) intercepting the y-axis at the value of $1/C_2$ corresponding to the given charge. This value does not depend on

Fig. 2.11 Parsons–Zobel plot
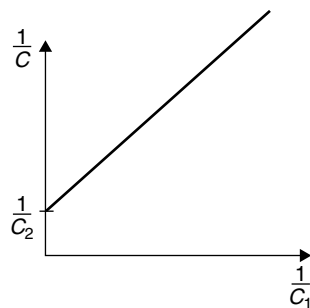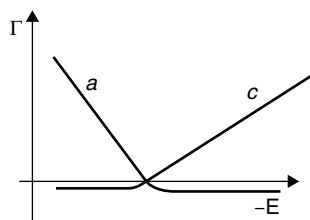of $1/C$ on $1/C_2$

Fig. 2.12 Dependences of
charges of cations and anions
on the electrode potential

concentration, being only charge dependent. This plot (Parsons and Zobel [13]) is
often used to determine the roughness coefficient k_f; for the case of a rough elec-
trode the slope is k_f instead of 1.

Once the total charges are known, one may find the partial charges of the anions
and cations in the diffuse layer. The dependence of such charges on electrode poten-
tial is shown in Fig. 2.12. Then, from the data for the electrolytes with and without
surface-active species and specifically adsorbed species it is possible to calculate
the variations in C, q and σ introduced by their presence.

For example, one can verify the validity of the DL model presented earlier for a
given system by the following method [14]. The difference $C_{DL}^{-1}(q, c_1) - C_{DL}^{-1}(q, c_2)$
found from experimental data acquired at two different concentrations c (but at the
same charge q) must be equal to the difference $C_2^{-1}(q, c_1) - C_2^{-1}(q, c_2)$ between
the capacitances of the diffuse parts of the DL. This follows from Eq. (2.6) if we take
into account that the capacitance of the compact layer depends only on q and not on
the concentration. The latter difference can be easily calculated with Eq. (2.18) for
any combination of c and q. Then if the two differences closely coincide one can
conclude that the overall model is adequate.

There is one further important thermodynamic formula which is used to calcu-
late the adsorption, derived from the expression for the chemical potential in an
ideal solution $d\mu = RT\ln c$:

$$\Gamma = -(1/RT)\,(\partial\gamma/\partial \ln c)_E \tag{2.70}$$

The methods of calculation of the various charge components and potential drops in
the double layer have been extensively developed; these methods enable the deter-

mination of the set of parameters corresponding to the above models starting from experimental data. Details of these methods can be found elsewhere [15].

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