ELECTRICAL PHENOMENA AT INTERFACES AND BIOINTERFACES
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PREFACE

This book is based on a joint project of the Center for Colloid and Interface Science, Research Institute for Science and Technology, Tokyo University of Science, and the Electrokinetic Society of Japan. Kunio Furusawa and I edited *Electrical Phenomena at Interfaces* (1990; 2nd Edition, 1998); although this book has a similar title, it is on completely different concepts. This book is written for scientists, engineers, and graduate students who want to study theoretical and experimental aspects of electrical phenomena at interfaces and bioInterfaces. The principal purpose of this book is to bridge three different fields: nano-, bio-, and environmental sciences. As a basis of these three different fields, the understanding of electrical phenomena at interfaces and bioInterfaces is becoming more and more important.

This book is divided into three parts. Part I contains the fundamentals of electrical phenomena at interfaces and bioInterfaces. Parts II and III treat many topics in this field, including applications in nano- and environmental sciences (Part II) and applications in biosciences (Part III).

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PART I

FUNDAMENTALS
POTENTIAL AND CHARGE OF A HARD PARTICLE AND A SOFT PARTICLE

HIROYUKI OHSHIMA

1.1 INTRODUCTION

When a charged colloidal particle is immersed in an electrolyte solution, mobile electrolyte ions form an ionic cloud around the particle. As a result of electrostatic interaction between electrolyte ions and particle surface charges, in the ionic cloud the concentration of counterions (electrolyte ions with charges of the sign opposite to that of the particle surface charges) becomes very high, while that of coions (electrolyte ions with charges of the same sign as the particle surface charges) is very low. Figure 1.1 schematically shows the distribution of ions around a charged spherical particle of radius $a$. The ionic cloud together with the particle surface charge forms an electrical double layer. Such an electrical double layer is often called an electrical diffuse double layer since the distribution of electrolyte ions in the ionic cloud takes a diffusive structure due to the thermal motion of ions. The electrostatic interaction between colloidal particles and the motion of colloidal particles in an external field (e.g., electric field and gravitational field) depend strongly on the distributions of electrolyte ions and of the electric potential across the electrical double layer around the particle surface [1–5].
1.2 THE POISSON–BOLTZMANN EQUATION

Consider a uniformly charged particle immersed in a liquid containing $N$ ionic species with valence $z_i$ and bulk concentration (number density) $n_i^\infty$ ($i = 1, 2 \ldots N$) (in units of cubic meter). From the electroneutrality condition, we have

$$\sum_{i=1}^{N} z_i n_i^\infty = 0. \quad (1.1)$$

The electric potential $\psi(r)$ at position $r$ outside the particle, measured relative to the bulk solution phase, where $\psi$ is set equal to zero, is related to the charge density $\rho_\text{el}(r)$ at the same point by the Poisson equation, viz.,

$$\Delta \psi(r) = -\frac{\rho_\text{el}(r)}{\varepsilon_r \varepsilon_0}, \quad (1.2)$$

where $\Delta$ is the Laplacian, $\varepsilon_r$ is the relative permittivity of the electrolyte solution, and $\varepsilon_0$ is the permittivity of a vacuum. We assume that the distribution of the electrolyte ions $n_i(r)$ obeys Boltzmann’s law, viz.,

$$n_i(r) = n_i^\infty \exp \left( -\frac{z_i e \psi(r)}{kT} \right). \quad (1.3)$$

Figure 1.1. Electrical double layer of thickness $1/\kappa$ around a spherical charged particle of radius $a$. 
where \( n_i(r) \) is the concentration (number density) of the \( i \)th ionic species at position \( r \), \( e \) is the elementary electric charge, \( k \) is Boltzmann’s constant, and \( T \) is the absolute temperature. The charge density \( \rho_{el}(r) \) at position \( r \) is thus given by

\[
\rho_{el}(r) = \sum_{i=1}^{N} z_i n_i(r) = \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(r)}{kT}\right).
\] (1.4)

Combining Equations 1.2 and 1.4 gives

\[
\Delta \psi(r) = -\frac{1}{\varepsilon_i \varepsilon_0} \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(r)}{kT}\right).
\] (1.5)

This is the Poisson–Boltzmann equation for the potential distribution \( \psi(r) \), which is subject to the following boundary conditions:

\[
\psi(r) = \psi_o \text{ at the particle surface}
\] (1.6)

and

\[
\psi(r) \to 0 \text{ as } r = |r| \to \infty.
\] (1.7)

If the internal electric fields inside the particle can be neglected, then the surface charge density \( \sigma \) of the particle is related to the potential derivative normal to the particle surface as

\[
\frac{\partial \psi}{\partial n} = -\frac{\sigma}{\varepsilon_i \varepsilon_0},
\] (1.8)

where \( n \) is the outward normal at the particle surface.

### 1.3 LOW POTENTIAL CASE

If the potential \( \psi \) is low, viz.,

\[
\left|\frac{z_i e \psi}{kT}\right| \ll 1,
\] (1.9)

then Equation 1.5 reduces to the following linearized Poisson–Boltzmann equation (Debye–Hückel equation):

\[
\Delta \psi = \kappa^2 \psi
\] (1.10)

with

\[
\kappa = \left(\frac{1}{\varepsilon_i \varepsilon_0 kT} \sum_{i=1}^{N} z_i^2 e^2 n_i^\infty\right)^{1/2},
\] (1.11)
TABLE 1.1. Debye–Hückel Parameter for Various Electrolytes

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<tr>
<td>Symmetrical electrolyte of valence (z) and bulk concentration (n)</td>
<td>(\kappa = \left( \frac{2z^2e^2n}{\varepsilon n \varepsilon kT} \right)^{1/2} )</td>
</tr>
<tr>
<td>2-1 electrolyte of bulk concentration (n)</td>
<td>(\kappa = \left( \frac{6e^2n}{\varepsilon n \varepsilon kT} \right)^{1/2} )</td>
</tr>
<tr>
<td>Mixed solution of 1-1 electrolyte of bulk concentration (n_1) and 2-1 electrolyte of bulk concentration (n_2)</td>
<td>(\kappa = \left( \frac{2(n_1 + 3n_2)e^2}{\varepsilon n \varepsilon kT} \right)^{1/2} )</td>
</tr>
</tbody>
</table>

where \(\kappa\) is called the Debye–Hückel parameter. The reciprocal of \(\kappa\) (i.e., \(1/\kappa\)), which is called the Debye length, corresponds to the thickness of the double layer. Note that \(n_i^\infty\) in Equations 1.5 and 1.10 is given in units of cubic meter. If one uses the units of \(M\) (mole per liter), then \(n_i^\infty\) must be replaced by \(1000 N_A n_i^\infty\), \(N_A\) being Avogadro’s number. Expressions for \(\kappa\) for various types of electrolytes are explicitly given in Table 1.1.

Linearized Equation 1.10 can be solved for particles of various shapes. Table 1.2 gives the potential distribution for a planar surface, a sphere of radius \(a\), and a cylinder of radius \(a\), which can be obtained by solving Equation 1.10 (with \(\Delta = d^2/dx^2\) for a planar surface, \(\Delta = d^2/dr^2 + 2/r\cdot d/dr\) for a sphere, and \(\Delta = d^2/dr^2 + 1/r\cdot d/dr\) for a cylinder) subject to Equations 1.6 and 1.7, where \(x\) is the distance from the planar surface located at \(x = 0\) and \(r\) is the distance from the sphere center or the cylinder axis. Table 1.2 also shows the surface potential \(\psi\)/surface charge density \(\sigma\) relationship, which can be obtained by substituting \(\psi\) into Equation 1.8.

1.4 ARBITRARY POTENTIAL CASE

The nonlinear Poisson–Boltzmann Equation 1.5 (with \(\Delta = d^2/dx^2\)) for a planar surface can be solved analytically. For a planar surface in contact with a \(z\)-\(z\) symmetrical electrolyte solution, a 2-1 electrolyte solution, or a mixed solution of 1-1 electrolyte of bulk concentration \(n_1\) and 2-1 electrolyte of bulk concentration \(n_2\), the potential distribution \(\psi(x)\) and the surface potential \(\psi_s\)/surface charge density \(\sigma\) relationship are given in Table 1.3.

Consider the asymptotic behavior of the potential distribution at large distances, which will also be used for calculating the electrostatic inter-
**TABLE 1.2. Solution to the Linearized Poisson–Boltzmann Equation**

<table>
<thead>
<tr>
<th>Potential Distribution</th>
<th>Surface Potential $\psi_o$/Surface Charge Density $\sigma$ Relationship</th>
</tr>
</thead>
<tbody>
<tr>
<td>Planar surface</td>
<td>$\psi(x) = \psi_o e^{-\kappa x}$</td>
</tr>
<tr>
<td></td>
<td>$\psi_o = \frac{\sigma}{\varepsilon \varepsilon_0 \kappa}$</td>
</tr>
<tr>
<td>Sphere of radius $a$</td>
<td>$\psi(r) = \psi_o \frac{a}{r} e^{-\kappa(r-a)}$</td>
</tr>
<tr>
<td></td>
<td>$\psi_o = \frac{\sigma}{\varepsilon \varepsilon_0 \kappa(1+1/\kappa a)}$</td>
</tr>
<tr>
<td>Cylinder of radius $a$</td>
<td>$\psi(r) = \psi_o \frac{K_0(\kappa r)}{K_0(\kappa a)}$</td>
</tr>
<tr>
<td></td>
<td>$\psi_o = \frac{\sigma}{\varepsilon \varepsilon_0 \kappa} K_1(\kappa a)$</td>
</tr>
</tbody>
</table>

**Note:** $x (>0)$ is the distance from the planar surface and $r (>a)$ is the distance from the center $O$ of the sphere or that from the axis of the cylinder. $K_n(z)$ is the modified Bessel function of the second kind of order $n$.

action between two particles. When a planar surface is in contact with a $z$-symmetrical electrolyte, the potential distribution $\psi(x)$ around the surface (see Table 1.3) in the region far from the surface, that is, at large $\kappa x$, takes the form

$$\psi(x) = \frac{4kT}{ze} \gamma e^{-\kappa x} = \frac{4kT}{ze} \tanh \left( \frac{z e \psi_o}{4kT} \right) e^{-\kappa x}. \quad (1.12)$$
<table>
<thead>
<tr>
<th>Electrolytes</th>
<th>$\psi(x)$</th>
<th>$\psi_o/\sigma$ Relationship</th>
<th>$\psi_{\text{eff}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>z-z</td>
<td>$\psi(x) = \frac{2kT}{ze} \ln \left( \frac{1 + \gamma e^{-kx}}{1 - \gamma e^{-kx}} \right)$</td>
<td>$\sigma = \frac{2e_i e_o e z \psi_o}{2kT} \sinh \left( \frac{ze \psi_o}{2kT} \right)$</td>
<td>$\psi_{\text{eff}} = \frac{4kT}{ze} \gamma$</td>
</tr>
<tr>
<td>2-1</td>
<td>$\psi(x) = \frac{kT}{e} \ln \left( \frac{\frac{2}{3} \gamma' e^{-kx} + \frac{1}{2}}{1 - \frac{1}{3} \gamma' e^{-kx}} \right) - \frac{1}{2}$</td>
<td>$\sigma = \frac{e_i e_o kT}{e} \left{ 1 - \exp \left( -\frac{e \psi_o}{kT} \right) \right}$</td>
<td>$\psi_{\text{eff}} = \frac{4kT}{e} \gamma'$</td>
</tr>
<tr>
<td>1-1 plus 2-1</td>
<td>$\psi(x) = \frac{kT}{e} \ln \left( \frac{1}{1 - \eta/3} \right) \left{ \frac{1 + (1 - \eta/3) \gamma'' e^{-kx}}{1 - (1 - \eta/3) \gamma'' e^{-kx}} \right}$</td>
<td>$\sigma = \frac{e_i e_o kT}{e} (1 - e^{-\eta})$</td>
<td>$\psi_{\text{eff}} = \frac{4kT}{e} \gamma''$</td>
</tr>
</tbody>
</table>

Note: $\gamma = \tanh \left( \frac{ze \psi_o}{4kT} \right) = \frac{\exp(ze \psi_o/2kT) - 1}{\exp(ze \psi_o/2kT) + 1}$

$$\gamma' = \frac{3}{2} \left[ \left( \frac{2}{3} e^{\eta/3} + \frac{1}{3} \right)^{1/2} - 1 \right]$$
$$\gamma'' = \left( \frac{1}{1 - \eta/3} \right) \left[ \left( \frac{1 - \eta/3}{3} \right)^{1/2} + 1 \right] - 1$$
$$\eta = \frac{3n_2}{n_1 + 3n_2}$$
$$y_0 = \frac{e \psi_o}{kT}$$
Comparing Equation 1.12 with the linearized form $\psi(x) = \psi_o \exp(-\kappa x)$ (see Table 1.2), we find that the effective surface potential $\psi_{\text{eff}}$ of the plate is given by

$$\psi_{\text{eff}} = \frac{4kT}{ze} \gamma = \frac{kT}{ze} \cdot 4 \tanh \left( \frac{z e \psi_o}{4kT} \right),$$

(1.13)

This result, together with those for other types of electrolytes, is given in Table 1.3.

For a sphere, the nonlinear Poisson–Boltzmann equation has not been solved analytically. Loeb et al. [6] tabulated numerical computer solutions to the nonlinear spherical Poisson–Boltzmann equation and approximate analytic solutions are given in References 7–9 (Table 1.4). For the case of an infinitely long cylindrical particle of radius $a$, approximate solutions are derived in References 7 and 10 (Table 1.5).

### Table 1.4. Potential Distribution $\psi(r)$ and Surface Potential $\psi_o$/Surface Charge Density $\sigma$ Relationship for a Sphere of Radius $a$ with Arbitrary Surface Potential

**Potential distribution** $\psi(r) = \frac{2kT}{ze} \ln \left[ \frac{(1 + Bs)(1 + \frac{Bs}{2ka + 1})}{(1 - Bs)(1 - \frac{Bs}{2ka + 1})} \right] (z-z)$

**Surface potential $\psi_o$/surface charge density $\sigma$ relationship**

$$\sigma = \frac{2e_s e_o kT}{ze} \sinh \left( \frac{ze \psi_o}{2kT} \right) \times \left[ 1 + \frac{1}{\kappa a \cosh^2(ze \psi_o / 4kT)} + \frac{1}{(\kappa a)^2} \frac{8 \ln \cosh(z e \psi_o / 4kT)}{\sinh^2(ze \psi_o / 2kT)} \right]^{1/2} (z-z)$$

(2-1)

**Note:** $s = \frac{a}{r} \exp(-\kappa(r-a))$, $B = \frac{(2ka + 1)}{1 + \frac{2ka + 1}{\kappa a + 1} \tanh \left( \frac{ze \psi_o}{4kT} \right)}$, $p = 1 - \exp(-e \psi_o / kT)$, $q = \left[ \frac{2}{3} \exp(e \psi_o / kT) + 1 \right]^{1/2}$, $t = \left( \frac{1 - \eta}{3} \right) \exp \left( \frac{e \psi_o}{kT} \right) + \frac{\eta}{3}^{1/2}$, $\eta = \frac{3n_z}{n_1 + 3n_2}$. 


1.5 SOFT PARTICLES

We consider the case where the particle core is covered by an ion-penetrable surface layer of polyelectrolytes, which we term a surface charge layer (or, simply, a surface layer). Polyelectrolyte-coated particles are often called soft particles (Fig. 1.2) [3–5]. Soft particles serve as a model for biocolloids such as cells. Figure 1.3 gives a schematic representation of ion and potential distributions around a hard surface (Fig. 1.3a) and a soft surface (Fig. 1.3b), which shows that the potential deep inside the surface layer is practicably equal to the Donnan potential \( \psi_{\text{DON}} \), if the surface layer is much thicker than the Debye length \( 1/\kappa \). Also we term \( \psi_o \equiv \psi(0) \) (which is the potential at the boundary...