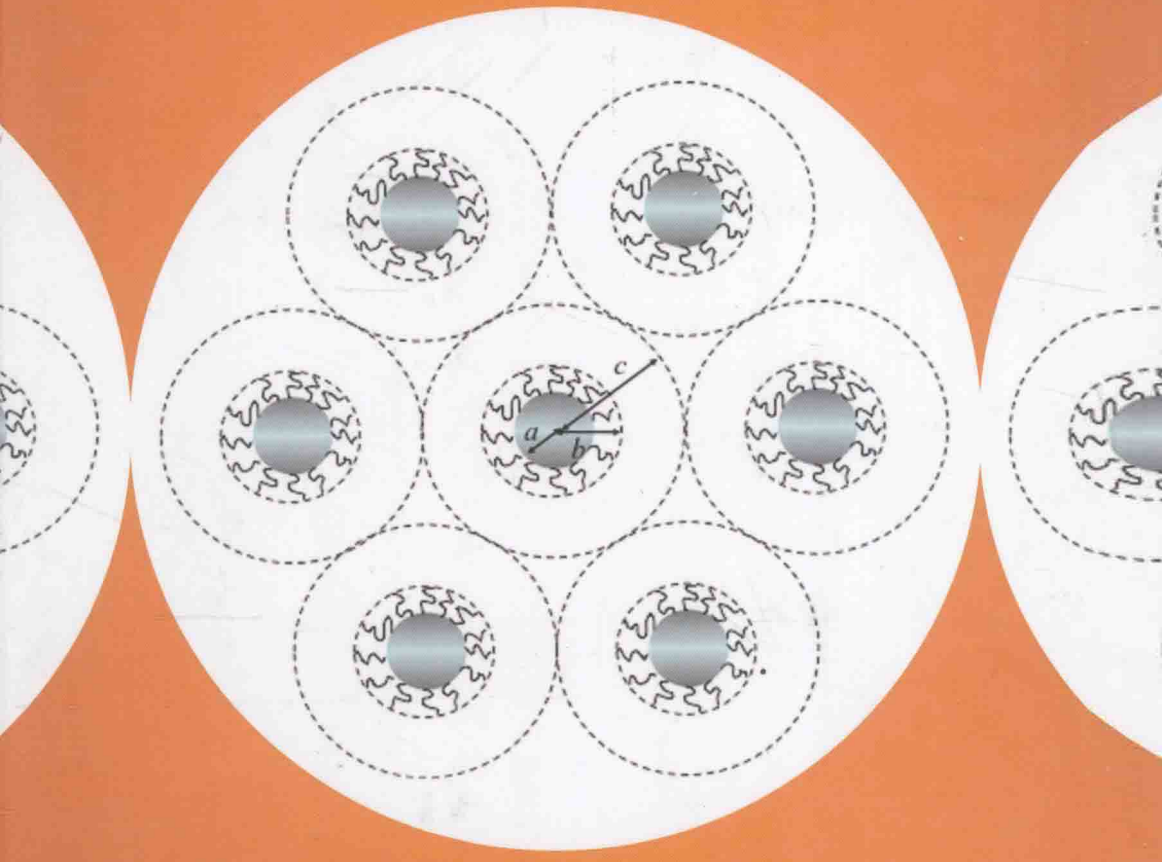
BIOPHYSICAL CHEMISTRY of BIOINTERFACES



HIROYUKI OHSHIMA

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BIOPHYSICAL CHEMISTRY OF BIOINTERFACES

Hiroyuki Ohshima

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PREFACE

The principal aim of this book is to provide a tool for discussing various phenomena at biointerfaces such as the surface of cells on the basis of biophysical chemistry. For nonbiological interfaces, colloid and interface science, one of the major branches of physical chemistry, forms a powerful basis for understanding various interfacial phenomena. The Derjaguin–Landau–Verwey–Overbeek (DLVO) theory explains well the stability of colloidal suspensions in terms of the electrostatic and van der Waals interactions between the particles. The behavior of colloidal particles in an applied electric filed is analyzed by electrophoresis theories of Smoluchowski, Hückel, and Henry. The charge or potential of the particle surface plays an essential role in the above-mentioned phenomena. It must be noted here that the particle-fixed charges are assumed to be located only at the particle surface (of zero thickness). This model, however, is by no means a good approximation for biocolloids such as biological cells. For such particles, fixed charges are distributed over some depth on the particle surface, or the particle surface is covered with a polyelectrolyte layer. We call polyelectrolyte-coated particles soft particles. In this book, we discuss various phenomena at biointerfaces, that is, potential and charge at interfaces, electrokinetic phenomena at interfaces, and interactions between surfaces, on the basis of the soft particle model. We will see that the Donnan potential as well as the surface potential is an important factor controlling electric properties of soft particles or soft surfaces.

I would like to express my sincere thanks to Professor Tom Healy and Professor Lee White, who introduced me into the field of electrokinetic phenomena when I stayed as a postdoctoral fellow at the University of Melbourne in 1981–1983. I would like to thank Professor Shinpei Ohki at the State University of New York at Buffalo, where I stayed as a postdoctoral fellow. He pointed out to me the important role of the Donnan potential in electric phenomena of soft particles. I am happy to thank my sons Manabu and Nozomu and their wives Yumi and Michiyo for their understanding and help during the writing of this book.

Finally, I would like to gratefully acknowledge the assistance provided by Ms. Anita Lekhwani, Senior Acquisitions Editor, and Ms. Rebekah Amos, Editorial Program Coordinator.

HIROYUKI OHSHIMA

LIST OF SYMBOLS

a	particle radius
d	thickness of the surface charge layer
e	elementary electric charge
g	gravity
k	Bolzmann's constant
K^{∞}	electrical conductivity of an electrolyte solution in the absence of particles
K^{*}	complex conductivity of an electrolyte solution
n_i^{∞}	bulk concentration (number density) of the ith ionic species
N	number density of ionized groups in the surface charge layer
N_A	Avogadro's constant
p	pressure
T	absolute temperature
u	liquid velocity
U	electrophoretic velocity
U_{SED}	sedimentation velocity
y	scaled electric potential
z_i	valence of the ith ionic species
Z	valence of ionized groups in the surface charge layer
ε_o	permittivity of a vacuum
ε_r	relative permittivity of an electrolyte solution
ϕ	particle volume fraction
γ	frictional coefficient of the forces exerted by the polymer segments on the liquid flow
η	viscosity
η_s	effective viscosity of a suspension of particles
κ	Debye–Hückel parameter
κ_m	Debye–Hückel parameter in the surface charge layer
λ	$(\gamma/\eta)^{1/2}$
λ_i	Drag coefficient of the ith ionic species
$1/\lambda$	softness parameter
μ	electrophoretic mobility
ρ_{el}	volume charge density resulting from electrolyte ions

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ρ_{fix}	volume density of fixed charges distributed in the surface charge layer
ρ_{o}	mass density of a medium
σ	surface charge density
ω	angular frequency
ψ	electric potential
$\psi^{(0)}$	equilibrium electric potential
ψ_{o}	surface potential
ψ_{DON}	Donnan potential
ζ	zeta potential

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PART I
Potential and Charge at Interfaces

1 Potential and Charge of a Hard Particle

1.1 INTRODUCTION

The potential and charge of colloidal particles play a fundamental role in their interfacial electric phenomena such as electrostatic interaction between them and their motion in an electric field [1–4]. When a charged colloidal particle is immersed in an electrolyte solution, mobile electrolyte ions with charges of the sign opposite to that of the particle surface charges, which are called counterions, tend to approach the particle surface and neutralize the particle surface charges, but thermal motion of these ions prevents accumulation of the ions so that an ionic cloud is formed around the particle. In the ionic cloud, the concentration of counterions becomes very high while that of coions (electrolyte ions with charges of the same sign as the particle surface charges) is very low, as schematically shown in Fig. 1.1, which 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 thermal motion of ions. The electric properties of charged colloidal particles in an electrolyte solution strongly depend on the distributions of electrolyte ions and of the electric potential across the electrical double layer around the particle surface. The potential distribution is usually described by the Poisson–Boltzmann equation [1–4].

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^∞ $(i = 1, 2, \ldots, N)$ (in units of m^{-3}). From the electroneutrality condition, we have

$$\sum_{i=1}^{N} z_i n_i^\infty = 0 \tag{1.1}$$

Usually we need to consider only electrolyte ions as charged species. The electric potential $\psi(\boldsymbol{r})$ at position $\boldsymbol{r}$ outside the particle, measured relative to the bulk

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