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
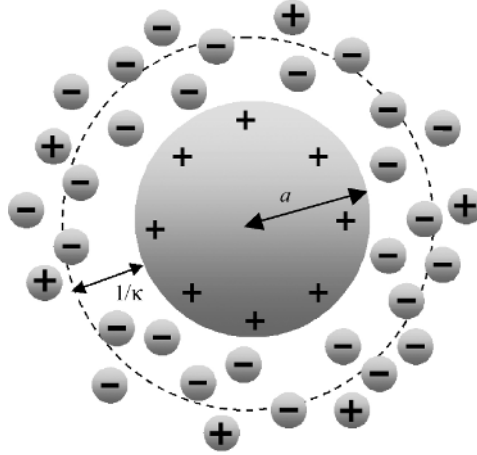
FIGURE 1.1   Electrical double layer around a positively charged colloidal particle. The particle is surrounded by an ionic cloud, forming the electrical double layer of thickness $1/\kappa$, in which the concentration of counterions is greater than that of coions.

solution phase, where ψ is set equal to zero, is related to the charge density $\rho_{el}(r)$ at the same point by the Poisson equation, namely,

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

where Δ is the Laplacian, ε_r is the relative permittivity of the electrolyte solution, and ε_0 is the permittivity of the vacuum. We assume that the distribution of the electrolyte ions $n_i(r)$ obeys Boltzmann's law, namely,

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

where $n_i(r)$ is the concentration (number density) of the ith 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

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

which is the required relation between $\psi(r)$ and $\rho_{el}(r)$.

Combining Eqs. (1.2) and (1.4) gives

$$\Delta\psi(r) = -\frac{1}{\varepsilon_r\varepsilon_0} \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e\psi(r)}{kT}\right) \tag{1.5}$$

This is the Poisson–Boltzmann equation for the potential distribution $\psi(r)$. The surface charge density σ of the particle is related to the potential derivative normal to the particle surface as

$$\varepsilon_p \frac{\partial \psi}{\partial n} - \varepsilon_r \frac{\partial \psi}{\partial n} = \frac{\sigma}{\varepsilon_o} \qquad (1.6)$$

where ε_p is the relative permittivity of the particle and n is the outward normal at the particle surface. If the internal electric fields inside the particle can be neglected, then the boundary condition (1.6) reduces to

$$\frac{\partial \psi}{\partial n} = -\frac{\sigma}{\varepsilon_r \varepsilon_o} \qquad (1.7)$$

If the potential ψ is low, namely,

$$\left| \frac{z_i e \psi}{kT} \right| \ll 1 \qquad (1.8)$$

then Eq. (1.5) reduces to

$$\Delta \psi = \kappa^2 \psi \qquad (1.9)$$

with

$$\kappa = \left(\frac{1}{\varepsilon_r \varepsilon_o kT} \sum_{i=1}^{N} z_i^2 e^2 n_i^\infty \right)^{1/2} \qquad (1.10)$$

Equation (1.9) is the linearized Poisson–Boltzmann equation and κ in Eq. (1.10) is the Debye–Hückel parameter. This linearization is called the Debye–Hückel approximation and Eq. (1.9) is called the Debye–Hückel equation. The reciprocal of κ (i.e., $1/\kappa$), which is called the Debye length, corresponds to the thickness of the double layer. Note that n_i^∞ in Eqs. (1.5) and (1.10) is given in units of m^{-3}. If one uses the units of M (mol/L), then n_i^∞ must be replaced by $1000 N_A n_i^\infty$, N_A being Avogadro's number.

Expressions for κ for various types of electrolytes are explicitly given below.

(i) For a symmetrical electrolyte of valence z and bulk concentration n,

$$\kappa = \left(\frac{2z^2 e^2 n}{\varepsilon_r \varepsilon_o kT} \right)^{1/2} \qquad (1.11)$$

(ii) For a 1-1 symmetrical electrolyte of bulk concentration n,

$$\kappa = \left(\frac{2e^2 n}{\varepsilon_r \varepsilon_o kT} \right)^{1/2} \qquad (1.12)$$

(iii) For a 2-1 electrolyte of bulk concentration n,

$$\kappa = \left(\frac{6e^2 n}{\varepsilon_r \varepsilon_o kT}\right)^{1/2} \tag{1.13}$$

(iv) For a mixed solution of 1-1 electrolyte of bulk concentration n_1 and 2-1 electrolyte of bulk concentration n_2,

$$\kappa = \left(\frac{2(n_1 + 3n_2)e^2}{\varepsilon_r \varepsilon_o kT}\right)^{1/2} \tag{1.14}$$

(v) For a 3-1 electrolyte of bulk concentration n,

$$\kappa = \left(\frac{12e^2 n}{\varepsilon_r \varepsilon_o kT}\right)^{1/2} \tag{1.15}$$

(vi) For a mixed solution of 1-1 electrolyte of concentration n_1 and 3-1 electrolyte of concentration n_2,

$$\kappa = \left(\frac{2(n_1 + 6n_2)e^2}{\varepsilon_r \varepsilon_o kT}\right)^{1/2} \tag{1.16}$$

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Consider the potential distribution around a uniformly charged plate-like particle in a general electrolyte solution composed of N ionic species with valence z_i and bulk concentration (number density) n_i^∞ ($i = 1, 2, \ldots, N$) (in units of m^{-3}). We take an x-axis perpendicular to the plate surface with its origin $x = 0$ at the plate surface so that the region $x < 0$ corresponds to the internal region of the plate while the region $x > 0$ corresponds to the solution phase (Fig. 1.2). The electric potential $\psi(x)$ at position x outside the plate, measured relative to the bulk solution phase, where ψ is set equal to zero, is related to the charge density $\rho_{el}(x)$ of free mobile charged species by the Poisson equation (Eq. (1.2)), namely,

$$\frac{d^2\psi(x)}{dx^2} = -\frac{\rho_{el}(x)}{\varepsilon_r \varepsilon_o} \tag{1.17}$$

We assume that the distribution of the electrolyte ions $n_i(x)$ obeys Boltzmann's law, namely,

$$n_i(x) = n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \tag{1.18}$$
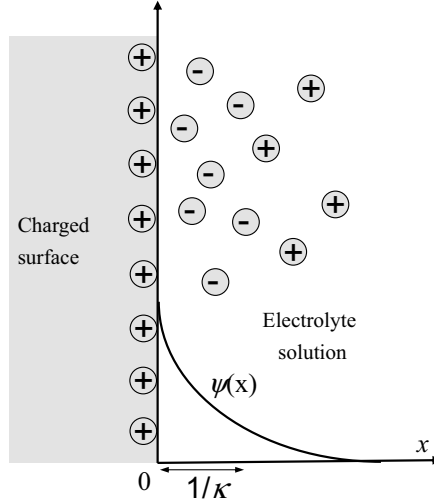
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FIGURE 1.2 Schematic representation of potential distribution $\psi(x)$ near the positively charged plate.

where $n_i(x)$ is the concentration (number density) of the ith ionic species at position x. The charge density $\rho_{el}(x)$ at position x is thus given by

$$\rho_{el}(x) = \sum_{i=1}^{N} z_i e n_i(x) = \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \tag{1.19}$$

Combining Eqs. (1.17) and (1.19) gives the following Poisson–Boltzmann equation for the potential distribution $\psi(x)$:

$$\frac{d^2\psi(x)}{dx^2} = -\frac{1}{\varepsilon_r \varepsilon_o} \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e \psi(x)}{kT}\right) \tag{1.20}$$

We solve the planar Poisson–Boltzmann equation (1.20) subject to the boundary conditions:

$$\psi = \psi_o \quad \text{at} \quad x = 0 \tag{1.21}$$

$$\psi \to 0, \ \frac{d\psi}{dx} \to 0 \quad \text{as} \quad x \to \infty \tag{1.22}$$

where ψ_o is the potential at the plate surface $x = 0$, which we call the surface potential.

If the internal electric fields inside the particle can be neglected, then the surface charge density σ of the particle is related to the potential derivative normal to the

particle surface by (see Eq. (1.7))

$$\frac{d\psi}{dx}\bigg|_{x=0^+} = -\frac{\sigma}{\varepsilon_r \varepsilon_o} \tag{1.23}$$

1.3.1   Low Potential

If the potential ψ is low (Eq. (1.8)), then Eq. (1.20) reduces to the following linearized Poisson–Boltzmann equation (Eq. (1.9)):

$$\frac{d^2\psi}{dx^2} = \kappa^2 \psi \tag{1.24}$$

The solution to Eq. (1.24) subject to Eqs. (1.21) and (1.22) can be easily obtained:

$$\psi(x) = \psi_o e^{-\kappa x} \tag{1.25}$$

Equations (1.23) and (1.25) give the following surface charge density–surface potential $(\sigma-\psi_o)$ relationship:

$$\psi_0 = \frac{\sigma}{\varepsilon_r \varepsilon_o \kappa} \tag{1.26}$$

Equation (1.26) has the following simple physical meaning. Since ψ decays from ψ_o to zero over a distance of the order of κ^{-1} (Eq. (1.25)), the electric field at the particle surface is approximately given by ψ_o/κ^{-1}. This field, which is generated by σ, is equal to $\sigma/\varepsilon_r \varepsilon_o$. Thus, we have $\psi_o/\kappa^{-1} = \sigma/\varepsilon_r \varepsilon_o$, resulting in Eq. (1.26).

1.3.2   Arbitrary Potential: Symmetrical Electrolyte

Now we solve the original nonlinear Poisson–Boltzmann equation (1.20). If the plate is immersed in a symmetrical electrolyte of valence z and bulk concentration n, then Eq. (1.20) becomes

$$\begin{aligned}
\frac{d^2\psi(x)}{dx^2} &= -\frac{zen}{\varepsilon_r \varepsilon_o}\left[\exp\left(-\frac{ze\psi(x)}{kT}\right) - \exp\left(\frac{ze\psi(x)}{kT}\right)\right] \\
&= \frac{2zen}{\varepsilon_r \varepsilon_o}\sinh\left(\frac{ze\psi(x)}{kT}\right)
\end{aligned} \tag{1.27}$$

We introduce the dimensionless potential $y(x)$

$$y = \frac{ze\psi}{kT} \tag{1.28}$$

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then Eq. (1.27) becomes

$$\frac{d^2y}{dx^2} = \kappa^2 \sinh y \tag{1.29}$$

where the Debye–Hückel parameter κ is given by Eq. (1.11). Note that $y(x)$ is scaled by kT/ze, which is the thermal energy measured in units of volts. At room temperatures, kT/ze (with $z = 1$) amounts to ca. 25 mV. Equation (1.29) can be solved by multiplying dy/dx on its both sides to give

$$\frac{dy}{dx}\frac{d^2y}{dx^2} = \kappa^2 \sinh y \frac{dy}{dx} \tag{1.30}$$

which is transformed into

$$\frac{1}{2}\frac{d}{dx}\left\{\left(\frac{dy}{dx}\right)^2\right\} = \kappa^2 \frac{d}{dx}\cosh y \tag{1.31}$$

Integration of Eq. (1.31) gives

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa^2 \cosh y + \text{constant} \tag{1.32}$$

By taking into account Eq. (1.22), we find that $\text{constant} = -2\kappa^2$ so that Eq. (1.32) becomes

$$\left(\frac{dy}{dx}\right)^2 = 2\kappa^2(\cosh y - 1) = 4\kappa^2 \sinh^2\left(\frac{y}{2}\right) \tag{1.33}$$

Since y and dy/dx are of opposite sign, we obtain from Eq. (1.33)

$$\frac{dy}{dx} = -2\kappa \sinh(y/2) \tag{1.34}$$

Equation (1.34) can be further integrated to give

$$\int_y^{y_o} \frac{dy}{2\sinh(y/2)} = \kappa \int_0^x dx \tag{1.35}$$

where

$$y_o = \frac{ze\psi_o}{kT} \tag{1.36}$$

is the scaled surface potential. Thus, we obtain

$$y(x) = 4\operatorname{arctanh}(\gamma e^{-\kappa x}) = 2\ln\left(\frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}}\right) \tag{1.37}$$

or

$$\psi(x) = \frac{2kT}{ze}\ln\left(\frac{1 + \gamma e^{-\kappa x}}{1 - \gamma e^{-\kappa x}}\right) \tag{1.38}$$

with

$$\gamma = \tanh\left(\frac{ze\psi_o}{4kT}\right) = \frac{\exp(ze\psi_o/2kT) - 1}{\exp(ze\psi_o/2kT) + 1} = \frac{\exp(y_o/2) - 1}{\exp(y_o/2) + 1} \tag{1.39}$$

Figure 1.3 exhibits γ as a function of y_o, showing that γ is a linearly increasing function of y_o for low y_o, namely,

$$\gamma \approx \frac{y_o}{4} = \frac{ze\psi_o}{4kT} \tag{1.40}$$

but reaches a plateau value at 1 for $|y_o| \geq 8$.

Figure 1.4 shows $y(x)$ for several values of y_o calculated from Eq. (1.37) in comparison with the Debye–Hückel linearized solution (Eq. (1.25)). It is seen that the Debye–Hückel approximation is good for low potentials ($|y_o| \leq 1$). As seen from Eqs. (1.25) and (1.37), the potential $\psi(x)$ across the electrical double layer varies nearly
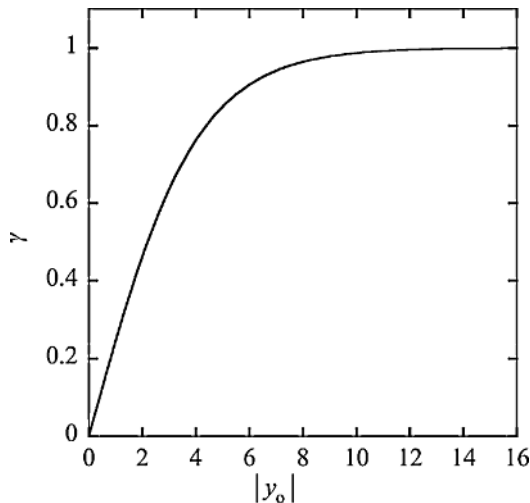

FIGURE 1.3 γ as a function of $|y_o|$ (Eq. (1.39)).

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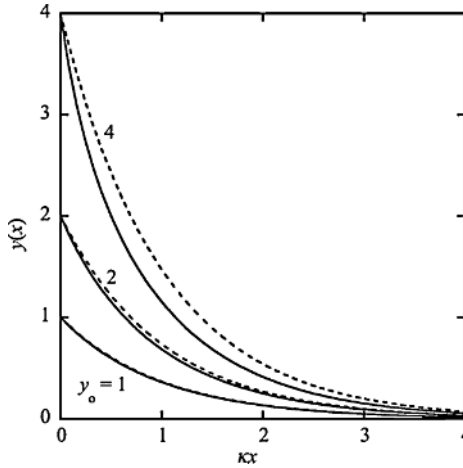
FIGURE 1.4 Potential distribution $y(x) \equiv ze\psi(x)/kT$ around a positively charged plate with scaled surface potential $y_o \equiv ze\psi_o/kT$. Calculated for $y_o = 1$, 2, and 4. Solid lines, exact solution (Eq. (1.37)); dashed lines, the Debye–Hückel linearized solution (Eq. (1.25)).

exponentially (Eqs. (1.37)) or exactly exponentially (Eq. (1.25)) with the distance x from the plate surface, as shown in Fig. 1.4. Equation (1.25) shows that the potential $\psi(x)$ decays from ψ_o at $x = 0$ to ψ_o/e ($\psi_o/3$) at $x = 1/\kappa$. Thus, the reciprocal of the Debye–Hückel parameter κ (the Debye length), which has the dimension of length, serves as a measure for the thickness of the electrical double layer. Figure 1.5 plots the
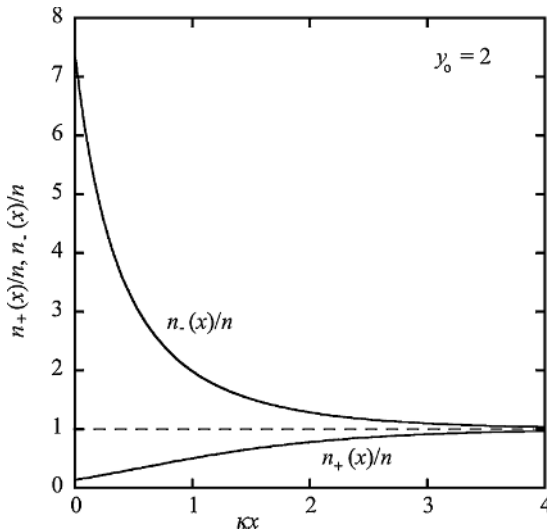
FIGURE 1.5 Concentrations of counterions (anions) $n_-(x)$ and coions (cations) $n_+(x)$ around a positively charged planar surface (arbitrary scale). Calculated from Eqs. (1.3) and (1.26) for $y_o = 2$.

concentrations of counterion ($n_-(x) = n\exp(y(x))$) and coions ($n_+(x) = n\exp(-y(x))$) around a positively charged plate as a function of the distance x from the plate surface, showing that these quantities decay almost exponentially over the distance of the Debye length $1/\kappa$ just like the potential distribution $\psi(x)$ in Fig. 1.4.

By substituting Eq. (1.38) into Eq. (1.23), we obtain the following relationship connecting ψ_o and σ:

$$\sigma = \frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\sinh\left(\frac{ze\psi_o}{2kT}\right) = (8n\varepsilon_r\varepsilon_o kT)^{1/2}\sinh\left(\frac{ze\psi_o}{2kT}\right) \qquad (1.41)$$

or inversely,

$$\begin{aligned}\psi_o &= \frac{2kT}{ze}\operatorname{arcsinh}\left(\frac{\sigma}{\sqrt{8n\varepsilon_r\varepsilon_o kT}}\right) = \frac{2kT}{ze}\operatorname{arcsinh}\left(\frac{ze\sigma}{2\varepsilon_r\varepsilon_o\kappa kT}\right) \\ &= \frac{2kT}{ze}\ln\left[\frac{ze\sigma}{2\varepsilon_r\varepsilon_o\kappa kT} + \left\{\left(\frac{ze\sigma}{2\varepsilon_r\varepsilon_o\kappa kT}\right)^2 + 1\right\}\right]\end{aligned} \qquad (1.42)$$

If σ is small and thus ψ_o is low, that is, the condition (Eq. (1.8)) is fulfilled, then Eq. (1.38) reduces to Eq. (1.25) with the surface potential given by Eq. (1.26). Figure 1.6 shows the σ–ψ_o relationship calculated from Eq. (1.42) in comparison with the approximate results (Eq. (1.26)). The deviation of Eq. (1.26) from Eq. (1.42) becomes significant as the charge density σ increases.
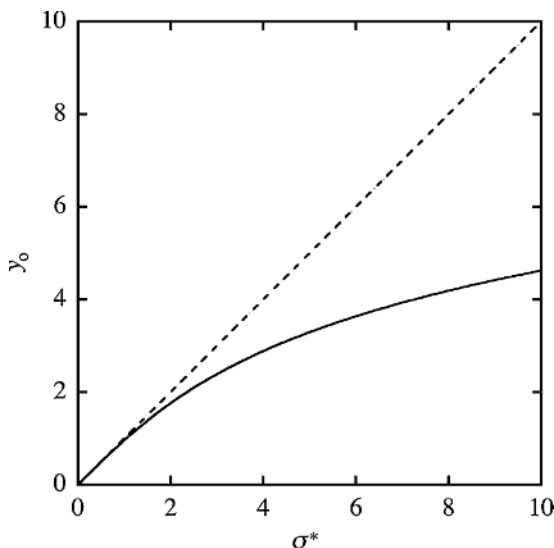
FIGURE 1.6 Scaled surface potential $y_o = ze\psi_o/kT$ as a function of the scaled surface charge density $\sigma^* = ze\sigma/\varepsilon_r\varepsilon_o\kappa kT$ for a positively charged planar plate in a symmetrical electrolyte solution of valence z. Solid line, exact solution (Eq. (1.41)); dashed line, Debye–Hückel linearized solution (Eq. (1.26)).

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1.3.3   Arbitrary Potential: Asymmetrical Electrolyte

When a charged plate is immersed in a 2-1 electrolyte (e.g., $CaCl_2$) of bulk concentration n, the Poisson–Boltzmann equation (1.20) becomes

$$\frac{d^2\psi(x)}{dx^2} = -\frac{2en}{\varepsilon_r \varepsilon_o}\left[\exp\left(-\frac{2e\psi(x)}{kT}\right) - \exp\left(\frac{e\psi(x)}{kT}\right)\right] \tag{1.43}$$

where the first term on the right-hand side of Eq. (1.43) corresponds to divalent cations while the second to monovalent anions. Equation (1.43) subject to the boundary conditions (1.21) and (1.22) can be integrated by multiplying dy/dx on both sides of Eq. (1.43) to give

$$\psi(x) = \frac{kT}{e}\ln\left[\frac{3}{2}\left(\frac{1 + \frac{2}{3}\gamma' e^{-\kappa x}}{1 - \frac{2}{3}\gamma' e^{-\kappa x}}\right)^2 - \frac{1}{2}\right] \tag{1.44}$$

with

$$\gamma' = \frac{3}{2}\left\{\frac{\left(\frac{2}{3}e^{y_o} + \frac{1}{3}\right)^{1/2} - 1}{\left(\frac{2}{3}e^{y_o} + \frac{1}{3}\right)^{1/2} + 1}\right\} \tag{1.45}$$

$$y_o = \frac{e\psi_o}{kT} \tag{1.46}$$

where y_o is the scaled surface potential and κ is given by Eq. (1.13). By substituting Eq. (1.44) into Eq. (1.23), we obtain the following relationship between the surface potential ψ_o and the surface charge density σ:

$$\sigma = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e}\left\{1 - \exp\left(-\frac{e\psi_o}{kT}\right)\right\}\left\{\frac{2}{3}\exp\left(\frac{e\psi_o}{kT}\right) + \frac{2}{3}\right\}^{1/2} \tag{1.47}$$

If σ is small and thus ψ_o is low, then the potential distribution $\psi(x)$ (Eq. (1.44)) and the σ–ψ_o relationship (Eq. (1.47)) are given by Eqs. (1.25) and (1.26), respectively, which also hold for general electrolytes.

Next consider the case of a mixed solution of 1-1 electrolyte of bulk concentration n_1 and 2-1 electrolyte of bulk concentration n_2. The Poisson–Boltzmann equation (1.5) becomes

$$\frac{d^2\psi(x)}{dx^2} = -\frac{e}{\varepsilon_r \varepsilon_o}\left[n_1\exp\left(-\frac{e\psi(x)}{kT}\right) + 2n_2\exp\left(-\frac{2e\psi(x)}{kT}\right) - (n_1 + 2n_2)\exp\left(\frac{e\psi(x)}{kT}\right)\right] \tag{1.48}$$

Equation (1.48) subject to the boundary conditions (1.21) and (1.22) can be easily integrated to give

$$\psi(x) = \frac{kT}{e} \ln\left[\left(\frac{1}{1-\eta/3}\right)\left\{\frac{1+(1-\eta/3)\gamma''e^{-\kappa x}}{1-(1-\eta/3)\gamma''e^{-\kappa x}}\right\}^2 - \left(\frac{\eta/3}{1-\eta/3}\right)\right] \qquad (1.49)$$

with

$$\eta = \frac{3n_2}{n_1 + 3n_2} \qquad (1.50)$$

$$\gamma'' = \left(\frac{1}{1-\eta/3}\right)\left[\frac{\{(1-\eta/3)e^{y_o} + \eta/3\}^{1/2} - 1}{\{(1-\eta/3)e^{y_o} + \eta/3\}^{1/2} + 1}\right] \qquad (1.51)$$

where y_o is the scaled surface potential defined by Eq. (1.46) and κ is given by Eq. (1.14).

The relationship between σ and ψ_o, which is derived from Eqs. (1.23) and (1.49), is given by

$$\sigma = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}(1 - e^{-y_o})\left[\left(1 - \frac{\eta}{3}\right)e^{y_o} + \frac{\eta}{3}\right]^{1/2} \qquad (1.52)$$

1.3.4   Arbitrary Potential: General Electrolyte

In the case of a charged plate immersed in a general electrolyte, the Poisson–Boltzmann equation (1.20), in terms of the scaled potential $y(x) = e\psi/kT$, is rewritten as

$$\frac{d^2y}{dx^2} = -\frac{\kappa^2 \sum_{i=1}^{N} z_i n_i e^{-z_i y}}{\sum_{i=1}^{N} z_i^2 n_i} \qquad (1.53)$$

where the Debye–Hückel parameter κ is given by Eq. (1.10). The boundary conditions are given by Eqs. (1.21) and (1.22). Since y_o and dy/dx are of opposite sign, integration of Eq. (1.53) gives

$$\frac{dy}{dx} = -\mathrm{sgn}(y_o)\kappa\left[\frac{2\sum_{i=1}^{N} n_i(e^{-z_i y} - 1)}{\sum_{i=1}^{N} z_i^2 n_i}\right]^{1/2} \qquad (1.54)$$

where $\mathrm{sgn}(y_o) = +1$ for $y_o > 0$ and -1 for $y_o < 0$. Note that the sign of $1 - \exp(-y)$ equals that of y_o. Equation (1.54) is thus rewritten as

$$\frac{dy}{dx} = -\kappa f(y) \qquad (1.55)$$

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with

$$f(y) = \text{sgn}(y_0) \left[\frac{2 \sum_{i=1}^{N} n_i (e^{-z_i y} - 1)}{\sum_{i=1}^{N} z_i^2 n_i} \right]^{1/2} = (1 - e^{-y}) \left[\frac{2 \sum_{i=1}^{N} n_i (e^{-z_i y} - 1)}{(1 - e^{-y})^2 \sum_{i=1}^{N} z_i^2 n_i} \right]^{1/2}$$

$$(1.56)$$

Note that as $y \to 0$, $f(y) \to y$. Explicit expressions for $f(y)$ for some simple cases are given below.

(i) For a symmetrical electrolyte of valence z,

$$f(y) = 2 \sinh(zy/2) \tag{1.57}$$

(ii) For a monovalent electrolyte,

$$f(y) = 2 \sinh(y/2) \tag{1.58}$$

(iii) For a 2-1 electrolyte,

$$f(y) = (1 - e^{-y}) \left(\frac{2}{3} e^y + \frac{1}{3} \right)^{1/2} \tag{1.59}$$

(iv) For a mixed solution of 2-1 electrolyte of concentration n_2 and 1-1 electrolyte of concentration n_1,

$$f(y) = (1 - e^{-y}) \left[\left(1 - \frac{\eta}{3} \right) e^y + \frac{\eta}{3} \right]^{1/2} \tag{1.60}$$

with

$$\eta = \frac{3 n_2}{n_1 + 3 n_2} \tag{1.61}$$

(v) For a 3-1 electrolyte,

$$f(y) = (1 - e^{-y}) \left(\frac{1}{2} e^y + \frac{1}{3} + \frac{1}{6} e^{-y} \right)^{1/2} \tag{1.62}$$

(vi) For a mixed solution of 3-1 electrolyte of concentration n_2 and 1-1 electrolyte of concentration n_1,

$$f(y) = (1 - e^{-y}) \left[\left(1 - \frac{\eta'}{2} \right) e^y + \frac{\eta'}{3} + \frac{\eta'}{6} e^{-y} \right]^{1/2} \tag{1.63}$$

with

$$\eta' = \frac{6n_2}{n_1 + 6n_2} \tag{1.64}$$

By integrating Eq. (1.55) between $x = 0$ ($y = y_o$) and $x = x$ ($y = y$), we obtain

$$\kappa x = \int_y^{y_o} \frac{dy}{f(y)} \tag{1.65}$$

which gives the relationship between y and x. For a symmetrical electrolyte of valence z, 2-1 electrolytes, and a mixed solution of 2-1 electrolyte of concentration n_2 and 1-1 electrolyte of concentration n_1, Eq. (1.65) reproduces Eqs. (1.38), (1.44), and (1.49), respectively.

The surface charge density–surface potential (σ–y_o) relationship is obtained from Eqs. (1.23) and (1.55) and given in terms of $f(y_o)$ as

$$\sigma = -\varepsilon_r \varepsilon_o \frac{d\psi}{dx}\bigg|_{x=0^+} = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} f(y_o) \tag{1.66}$$

or

$$\sigma = \frac{\varepsilon_r \varepsilon_0 \kappa kT}{e} \operatorname{sgn}(y_o) \left[\frac{2\sum_{i=1}^{N} n_i(e^{-z_i y_0} - 1)}{\sum_{i=1}^{N} z_i^3 n_i} \right]^{1/2}$$

$$= \frac{\varepsilon_r \varepsilon_0 \kappa kT}{e} \operatorname{sgn}(y_o)(1 - e^{-y_0}) \left[\frac{2\sum_{i=1}^{N} n_i(e^{-z_i y_0} - 1)}{(1 - e^{-y_0})^2 \sum_{i=1}^{N} z_i^2 n_i} \right]^{1/2} \tag{1.67}$$

Note that as $y_o \to 0$, $f(y_o) \to y_o$ so that for low y_o Eq. (1.67) reduces to Eq. (1.26). For a symmetrical electrolyte of valence z, 2-1 electrolytes, and a mixed solution of 2-1 electrolyte of concentration n_2 and 1-1 electrolyte of concentration n_1, Eq. (1.67) combined with Eqs. (1.57), (1.59), and (1.60) reproduces Eqs. (1.41), (1.47), and (1.52), respectively.

1.4   SPHERE

Consider a spherical particle of radius a in a general electrolyte solution. The electric potential $\psi(r)$ at position r obeys the following spherical Poisson–Boltzmann equation [3]:

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = -\frac{1}{\varepsilon_r \varepsilon_o} \sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e \psi}{kT}\right) \tag{1.68}$$
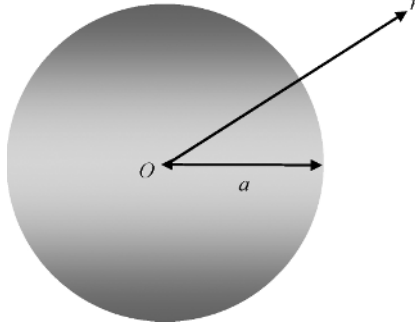
FIGURE 1.7   A sphere of radius a.

where we have taken the spherical coordinate system with its origin $r = 0$ placed at the center of the sphere and r is the distance from the center of the particle (Fig. 1.7). The boundary conditions for $\psi(r)$, which are similar to Eqs. (1.21) and (1.22) for a planar surface, are given by

$$\psi = \psi_o \quad \text{at} \quad r = a^+ \tag{1.69}$$

$$\psi \to 0, \ \frac{d\psi}{dr} \to 0 \quad \text{as} \quad zr \to \infty \tag{1.70}$$

1.4.1   Low Potential

When the potential is low, Eq. (1.68) can be linearized to give

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = \kappa^2\psi \tag{1.71}$$

The solution to Eq. (1.71) subject to Eqs. (1.69) and (1.70) is

$$\psi(r) = \psi_o \frac{a}{r} e^{-\kappa(r-a)} \tag{1.72}$$

If we introduce the distance $x = r - a$ measured from the sphere surface, then Eq. (1.72) becomes

$$\psi(x) = \psi_o \frac{a}{a+x} e^{-\kappa x} \tag{1.73}$$

For $x \ll a$, Eq. (1.73) reduces to the potential distribution around the planar surface given by Eq. (1.19). This result implies that in the region very near the particle surface, the surface curvature may be neglected so that the surface can be regarded as planar. In the limit of $\kappa \to 0$, Eq. (1.72) becomes

$$\psi(r) = \psi_o \frac{a}{r} \tag{1.74}$$

which is the Coulomb potential distribution around a sphere as if there were no electrolyte ions or electrical double layers. Note that Eq. (1.74) implies that the potential decays over distances of the particle radius a, instead of the double layer thickness $1/\kappa$.

The surface charge density σ of the particle is related to the particle surface potential ψ_o obtained from the boundary condition at the sphere surface,

$$\left.\frac{\partial \psi}{\partial r}\right|_{r=a^+} = -\frac{\sigma}{\varepsilon_r \varepsilon_o} \tag{1.75}$$

which corresponds to Eq. (1.23) for a planar surface. By substituting Eq. (1.72) into Eq. (1.75), we find the following ψ_o–σ relationship:

$$\psi_o = \frac{\sigma}{\varepsilon_r \varepsilon_o \kappa (1 + 1/\kappa a)} \tag{1.76}$$

For $\kappa a \gg 1$, Eq. (1.76) tends to Eq. (1.26) for the ψ_o–σ relationship for the plate case. That is, for $\kappa a \gg 1$, the curvature of the particle surface may be neglected so that the particle surface can be regarded as planar. In the opposite limit of $\kappa a \ll 1$, Eq. (1.76) tends to

$$\psi_o = \frac{\sigma a}{\varepsilon_r \varepsilon_o} \tag{1.77}$$

If we introduce the total charge $Q = 4\pi a^2$ on the particle surface, then Eq. (1.77) can be rewritten as

$$\psi_o = \frac{Q}{4\pi \varepsilon_r \varepsilon_o a} \tag{1.78}$$

which is the Coulomb potential. This implies that for $\kappa a \ll 1$, the existence of the electrical double layer may be ignored. Figures 1.8 and 1.9, respectively, show that Eq. (1.76) tends to Eq. (1.26) for a planar ψ_o–σ relationship for $\kappa a \gg 1$ and to the Coulomb potential given by Eq. (1.78) for $\kappa a \ll 1$. It is seen that the surface potential ψ_o of a spherical particle of radius a can be regarded as ψ_o of a plate for $\kappa a \geq 10^2$ (Fig. 1.8) and as the Coulomb potential for $\kappa a \leq 10^{-2}$ (Fig. 1.9). That is, for $\kappa a \leq 10^{-2}$, the presence of the electrical double layer can be neglected.

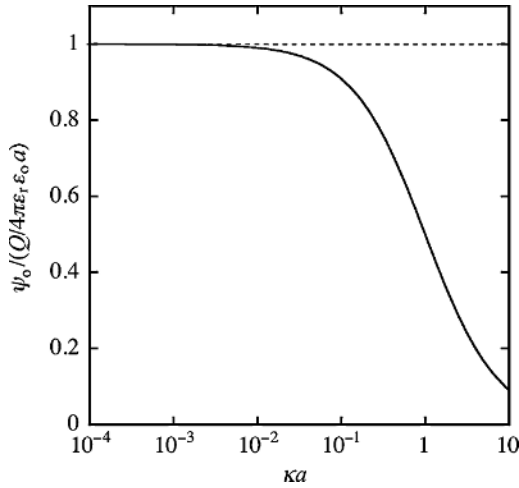### 1.4.2   Surface Charge Density–Surface Potential Relationship: Symmetrical Electrolyte

When the magnitude of the surface potential is arbitrary so that the Debye–Hückel linearization cannot be allowed, we have to solve the original nonlinear spherical Poisson–Boltzmann equation (1.68). This equation has not been solved but its approximate analytic solutions have been derived [5–8]. Consider a sphere of radius a with a
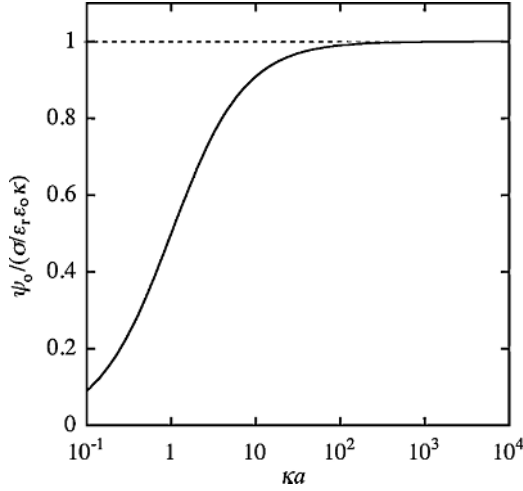
FIGURE 1.8 Surface potential ψ_o and surface charge density σ relationship of a spherical particle of radius a as a function of κa calculated with Eq. (1.76). For $\kappa a \geq 10^2$, the surface potential ψ_o can be regarded as $\psi_o = \sigma/\varepsilon_r\varepsilon_o\kappa$ for the surface potential of a plate.

surface charge density σ immersed in a symmetrical electrolyte solution of valence z and bulk concentration n. Equation (1.68) in the present case becomes

$$\frac{d^2\psi}{dr^2} + \frac{2}{r}\frac{d\psi}{dr} = \frac{2zen}{\varepsilon_r\varepsilon_o}\sinh\left(\frac{ze\psi}{kT}\right) \tag{1.79}$$

FIGURE 1.9 Surface potential ψ_o and surface charge density σ relationship of a spherical particle of radius a as a function of κa calculated with Eq. (1.76). For $\kappa a \leq 10^{-2}$, the surface potential ψ_o can be regarded as the Coulomb potential $\psi_o = Q/4\pi\varepsilon_r\varepsilon_o a$.

Loeb et al. tabulated numerical computer solutions to the nonlinear spherical Poisson–Boltzmann equation (1.63). On the basis of their numerical tables, they discovered the following empirical formula for the σ–ψ_o relationship:

$$\sigma = \frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\left[\sinh\left(\frac{ze\psi_o}{2kT}\right) + \left(\frac{2}{\kappa a}\right)\tanh\left(\frac{ze\psi_o}{4kT}\right)\right] \tag{1.80}$$

where the Debye–Hückel parameter κ is given by Eq. (1.11). A mathematical basis of Eq. (1.80) was given by Ohshima et al. [7], who showed that if, on the left-hand side of Eq. (1.79), we replace $2/r$ with its large a limiting form $2/a$ and $d\psi/dr$ with that for a planar surface (the zeroth-order approximation given by Eq. (1.34)), namely,

$$\frac{2}{r}\frac{d\psi}{dr} \rightarrow \frac{2}{a}\frac{d\psi}{dr}\bigg|_{\text{zeroth-order}} = -\frac{4\kappa}{a}\sinh\left(\frac{ze\psi}{2kT}\right) \tag{1.81}$$

then Eq. (1.63) becomes

$$\frac{d^2y}{dr^2} = \kappa^2\left(\sinh y + \frac{4}{\kappa a}\sinh\left(\frac{y}{2}\right)\right) \tag{1.82}$$

where $y = ze\psi/kT$ is the scaled potential (Eq. (1.28)). Since the right-hand side of Eq. (1.82) involves only y (and does not involve r explicitly), Eq. (1.82) can be readily integrated by multiplying dy/dr on its both sides to yield

$$\frac{dy}{dr} = -2\kappa\sinh\left(\frac{y}{2}\right)\left[1 + \frac{2}{\kappa a\,\cosh^2(y/4)}\right]^{1/2} \tag{1.83}$$

By expanding Eq. (1.83) with respect to $1/\kappa a$ and retaining up to the first order of $1/\kappa a$, we obtain

$$\frac{dy}{dr} = -2\kappa\sinh\left(\frac{y}{2}\right)\left[1 + \frac{1}{\kappa a\,\cosh^2(y/4)}\right] \tag{1.84}$$

Substituting Eq. (1.84) into Eq. (1.75), we obtain Eq. (1.80), which is the first-order σ–ψ_o relationship.

A more accurate σ–ψ_o relationship can be obtained by using the first-order approximation given by Eq. (1.84) (not using the zeroth-order approximation for a planar surface given by Eq. (1.34)) in the replacement of Eq. (1.81), namely,

$$\frac{2}{r}\frac{dy}{dr} \rightarrow \frac{2}{a}\frac{dy}{dr}\bigg|_{\text{first-order}} = -\frac{4}{a}\kappa\sinh\left(\frac{y}{2}\right)\left[1 + \frac{1}{\kappa a\,\cosh^2(y/4)}\right] \tag{1.85}$$
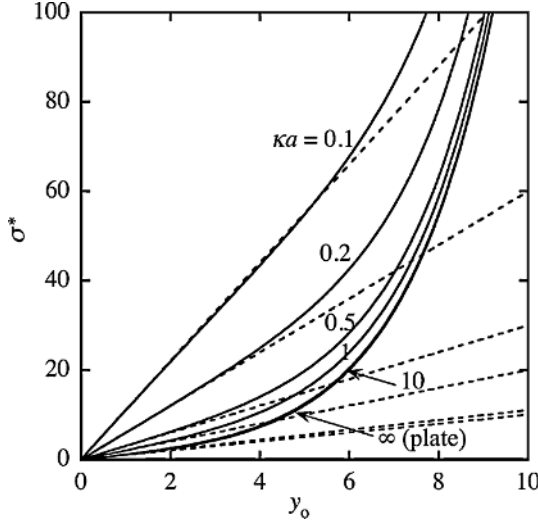
FIGURE 1.10   Scaled surface charge density $\sigma^* = ze\sigma/\varepsilon_r\varepsilon_o\kappa kT$ as a function of the scaled surface potential $y_o = ze\psi_o/kT$ for a positively charged sphere in a symmetrical electrolyte solution of valence z for various values of κa. Solid line, exact solution (Eq. (1.86)); dashed line, Debye–Hückel linearized solution (Eq. (1.76)).

The result is

$$\sigma = \frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\sinh\left(\frac{ze\psi_o}{2kT}\right)\left[1 + \frac{1}{\kappa a}\frac{2}{\cosh^2(ze\psi_o/4kT)} + \frac{1}{(\kappa a)^2}\frac{8\ln[\cosh(ze\psi_o/4kT)]}{\sinh^2(ze\psi_o/2kT)}\right]^{1/2}$$

(1.86)

which is the second-order σ–ψ_o relationship [4]. The relative error of Eq. (1.80) is less than 1% for $\kappa a \geq 5$ and that of Eq. (1.86) is less than 1% for $\kappa a \geq 1$. Note that as y_o increases, Eqs. (1.80) and (1.86) approach Eq. (1.41). That is, as the surface potential y_o increases, the dependence of y_o on κa becomes smaller. Figure 1.10 gives the σ–ψ_o relationship for various values of κa calculated from Eq. (1.86) in comparison with the low-potential approximation (Eq. (1.76)).

1.4.3   Surface Charge Density–Surface Potential Relationship: Asymmetrical Electrolyte

The above approximation method can also be applied to the case of a sphere in a 2-1 symmetrical solution, yielding [4]

$$\sigma = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}\left[pq + \frac{2\{(3-p)q - 3\}}{\kappa apq}\right]$$

(1.87)

as the first-order σ–ψ_o relationship and

$$\sigma = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} pq \left[1 + \frac{4}{\kappa a} \frac{(3-p)q-3}{(pq)^2} + \frac{4}{(\kappa a)^2 (pq)^2} \left\{ 6\ln\left(\frac{q+1}{2}\right) + \ln(1-p) \right\} \right]^{1/2}$$

(1.88)

as the second-order σ–ψ_o relationship, where

$$p = 1 - \exp(-e\psi_o/kT)$$

(1.89)

$$q = \left[\frac{2}{3}\exp\left(\frac{e\psi_o}{kT}\right) + \frac{1}{3} \right]^{1/2}$$

(1.90)

and κ is the Debye–Hückel parameter for a 2-1 electrolyte solution (Eq. (1.13)).

For the case of a mixed solution of 1-1 electrolyte of concentration n_1 and 2-1 electrolyte of concentration n_2, the first-order σ–ψ_o relationship is given by [7]

$$\sigma = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e}$$
$$\left[pt + \frac{2}{\kappa a p t} \left\{ (3-p)t - 3 - \frac{3^{1/2}(1-\eta)}{2\eta^{1/2}} \ln\left(\frac{\{1+(\eta/3)^{1/2}\}\{t-(\eta/3)^{1/2}\}}{\{1-(\eta/3)^{1/2}\}\{t+(\eta/3)^{1/2}\}} \right) \right\} \right]$$

(1.91)

with

$$t = \left[\left(1 - \frac{\eta}{3}\right)\exp\left(\frac{e\psi_o}{kT}\right) + \frac{\eta}{3} \right]^{1/2}$$

(1.92)

$$\eta = \frac{3n_2}{n_1 + 3n_2}$$

(1.93)

where κ is the Debye–Hückel parameter for a mixed solution of 1-1 and 2-1 electrolytes (Eq. (1.14)) and p is given by Eq. (1.89).

1.4.4 Surface Charge Density–Surface Potential Relationship: General Electrolyte

The above method can be extended to the case of general electrolytes composed of N ionic species with valence z_i and bulk concentration (number density) n_i^∞ ($i = 1, 2, \ldots, N$) (in units of m^{-3}) [8]. The spherical Poisson–Boltzmann equation (1.68) can be rewritten in terms of the scaled potential $y \equiv e\psi/kT$ as

$$\frac{d^2 y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = -\frac{\kappa^2 \sum_{i=1}^{N} z_i n_i e^{-z_i y}}{\sum_{i=1}^{N} z_i^2 n_i}$$

(1.94)

where κ is the Debye–Hückel parameter of the solution and defined by Eq. (1.10). In the limit of large κa, Eq. (1.94) reduces to the planar Poisson–Boltzmann equation (1.53), namely,

$$\frac{d^2y}{dr^2} = -\frac{\kappa^2 \sum_{i=1}^{N} z_i n_i e^{-z_i y}}{\sum_{i=1}^{N} z_i^2 n_i} \tag{1.95}$$

Integration of Eq. (1.95) gives

$$\frac{dy}{dr} = -\text{sgn}(y_o)\kappa \left[\frac{2 \sum_{i=1}^{N} n_i (e^{-z_i y} - 1)}{\sum_{i=1}^{N} z_i^2 n_i} \right]^{1/2} \tag{1.96}$$

Equation (1.96) is thus rewritten as

$$\frac{dy}{dr} = -\kappa f(y) \tag{1.97}$$

where $f(y)$ is defined by Eq. (1.56). Note that as $y \to 0$, $f(y)$ tends to y and the right-hand side of Eq. (1.94) is expressed as $\kappa^2 f(y) df/dy$. By combining Eqs. (1.75) and (1.97), we obtain

$$\sigma = -\varepsilon_r \varepsilon_o \frac{d\psi}{dr}\bigg|_{r=a^+} = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} f(y_o) \tag{1.98}$$

where $y_o \equiv e\psi/kT$ is the scaled surface potential. Equation (1.98) is the zeroth-order σ–y_o relationship.

To obtain the first-order σ–y_o relationship, we replace the second term on the left-hand side of Eq. (1.94) by the corresponding quantity for the planar case (Eq. (1.88)), namely,

$$\frac{2}{r}\frac{dy}{dr} \to \frac{2}{a}\frac{dy}{dr}\bigg|_{\text{zeroth-order}} = -\frac{2\kappa}{a} f(y) \tag{1.99}$$

Equation (1.94) thus becomes

$$\frac{d^2y}{dr^2} = \frac{2\kappa}{a} f(y) + \kappa^2 f(y)\frac{df}{dy} \tag{1.100}$$

which is readily integrated to give

$$\frac{dy}{dr} = -\kappa f(y) \left[1 + \frac{4}{\kappa a f^2(y)} \int_0^y f(u)\,du \right]^{1/2} \tag{1.101}$$

By expanding Eq. (1.101) with respect to $1/\kappa a$ and retaining up to the first order of $1/\kappa a$, we have

$$\frac{dy}{dr} = -\kappa f(y)\left[1 + \frac{2}{\kappa a f^2(y)} \int_0^y f(u)du\right] \tag{1.102}$$

From Eqs. (1.75) and (1.102) we obtain the first-order σ–y_o relationship, namely,

$$\sigma = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}f(y_o)\left[1 + \frac{2}{\kappa a f^2(y_o)} \int_0^{y_o} f(u)du\right] \tag{1.103}$$

Note that since $f(y_o) \to y_o$ as $y_o \to 0$, Eq. (1.103) tends to the correct form in the limit of small y_o (Eq. (1.76)), namely,

$$\sigma = \varepsilon_r\varepsilon_o\kappa\left(1 + \frac{1}{\kappa a}\right)\psi_o \tag{1.104}$$

We can further obtain the second-order σ–y_o relationship by replacing the second term on the left-hand side of Eq. (1.94) by the corresponding quantity for the first-order case (i.e., by using Eq. (1.101) instead of Eq. (1.97)), namely,

$$\frac{2}{r}\frac{dy}{dr} \to \frac{2}{a}\frac{dy}{dr}\bigg|_{\text{first-order}} = -\frac{2\kappa}{a}f(y)\left[1 + \frac{2}{\lambda\kappa a f^2(y)} \int_0^y f(u)du\right] \tag{1.105}$$

where we have introduced a fitting parameter λ. Then, Eq. (1.94) becomes

$$\frac{d^2y}{dr^2} = \frac{2\kappa}{a}f(y)\left[1 + \frac{2}{\lambda\kappa a f^2(y)} \int_0^y f(u)du\right] + \kappa^2 f(y)\frac{df}{dy} \tag{1.106}$$

which is integrated to give

$$\sigma = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}f(y_o)\left[1 + \frac{4}{\kappa a f^2(y_o)} \int_0^{y_o} f(y)dy + \frac{8}{\lambda(\kappa a)^2 f^2(y_o)} \int_0^{y_o} \frac{1}{f(y)}\left\{\int_0^y f(u)du\right\}dy\right]^{1/2} \tag{1.107}$$

In the limit of small y_o, Eq. (1.107) tends to

$$\sigma = \varepsilon_r\varepsilon_o\kappa\psi_o\left[1 + \frac{2}{\kappa a} + \frac{2}{\lambda(\kappa a)^2}\right]^{1/2} \tag{1.108}$$

We thus choose $\lambda = 2$ to obtain Eq. (1.104). Therefore, Eq. (1.107) becomes

$$\sigma = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}f(y_o)\left[1 + \frac{4}{\kappa af^2(y_o)}\int_0^{y_o} f(y)dy + \frac{4}{(\kappa a)^2 f^2(y_o)}\int_0^{y_o}\frac{1}{f(y)}\left\{\int_0^y f(u)du\right\}dy\right]^{1/2}$$

(1.109)

which is the required second-order σ–y_o relationship.

For some simple cases, from Eqs. (1.103) and (1.109) with Eq. (1.56) one can derive explicit expressions for the σ–y_o relationship. Indeed, for 1-1 and 2-1 electrolyte solutions and their mixed solution, Eqs. (1.103) and (1.109) with Eqs. (1.58)–(1.60) yield Eqs. (1.80) and (1.86)–(1.88). As another example, one can derive expressions for the σ–y_o relationship for the case of 3-1 electrolytes of concentration n. In this case, the Debye–Hückel parameter κ and $f(y)$ are given by Eqs. (1.15) and (1.62), respectively. By substituting Eq. (1.62) into Eqs. (1.103) and (1.109) and carrying out numerical integration, we can derive the first-order and second-order σ–y_o relationships, respectively. The relative error of Eq. (1.103) is less than 1% for $\kappa a \geq 5$ and that of Eq. (1.109) is less than 1% for $\kappa a \geq 1$.

1.4.5 Potential Distribution Around a Sphere with Arbitrary Potential

By using an approximation method similar to the above method and the method of White [6], one can derive an accurate analytic expression for the potential distribution around a spherical particle. Consider a sphere of radius a in a symmetrical electrolyte solution of valence z and bulk concentration n[7]. The spherical Poisson–Boltzmann equation (1.68) in this case becomes

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \kappa^2\sinh y$$

(1.110)

where $y = ze\psi/kT$ is the scaled potential. Making the change of variables

$$s = \frac{a}{r}\exp(-\kappa(r-a))$$

(1.111)

we can rewrite Eq. (1.110) as

$$s^2\frac{d^2y}{ds^2} + s\frac{dy}{ds} = \sinh y - \frac{2\kappa a + 1}{(\kappa a + 1)^2}G(y)$$

(1.112)

where

$$G(y) = \left(\frac{2\kappa r + 1}{2\kappa a + 1}\right)\left(\frac{\kappa a + 1}{\kappa r + 1}\right)^2\left(\sinh y - s\frac{dy}{ds}\right)$$

(1.113)

and the boundary conditions (1.69) and (1.70) as

$$y = y_o \text{ for } s = 1 \tag{1.114}$$

$$y = \frac{dy}{ds} = 0 \text{ for } s = 0 \tag{1.115}$$

When $\kappa a \gg 1$, Eq. (1.112) reduces to

$$s^2 \frac{d^2 y}{ds^2} + s \frac{dy}{ds} = \sinh y \tag{1.116}$$

with solution

$$y(r) = 2 \ln \left[\frac{1 + \tanh(y_o/4)s}{1 - \tanh(y_o/4)s} \right] \tag{1.117}$$

an approximate expression obtained by White [6].

To obtain a better approximation, we replace $G(y)$ in Eq. (1.112) by its large κa limiting value

$$\begin{aligned} \lim_{\kappa a \to \infty} G(y) &= \sinh y - \lim_{\kappa a \to \infty} \left(s \frac{dy}{ds} \right) \\ &= \sinh y - 2 \sinh(y/2) \end{aligned} \tag{1.118}$$

to obtain

$$s^2 \frac{d^2 y}{ds^2} + s \frac{dy}{ds} = \sinh y - \frac{2\kappa a}{\kappa a + 1} \left\{ y - 2 \sinh\left(\frac{y}{2}\right) \right\} \tag{1.119}$$

This equation can be integrated once to give

$$s \frac{dy}{ds} = \frac{2\kappa a + 1}{(\kappa a + 1)^2} \sinh\left(\frac{y}{2}\right) \left[1 + \frac{2\kappa a + 1}{(\kappa a)^2 \cosh^2(y/4)} \right]^{1/2} \tag{1.120}$$

which is further integrated to give

$$y(r) = 2\ln \left[\frac{(1 + Bs)(1 + Bs/(2\kappa a + 1))}{(1 - Bs)(1 - Bs/(2\kappa a + 1))} \right] \tag{1.121}$$

or

$$\psi(r) = \frac{2kT}{ze} \ln \left[\frac{(1 + Bs)(1 + Bs/(2\kappa a + 1))}{(1 - Bs)(1 - Bs/(2\kappa a + 1))} \right] \tag{1.122}$$

where

$$B = \frac{((2\kappa a + 1)/(\kappa a + 1))\tanh(y_o/4)}{1 + \left\{ 1 - ((2\kappa a + 1)/(\kappa a + 1)^2)\tanh^2(y_o/4) \right\}^{1/2}} \tag{1.123}$$
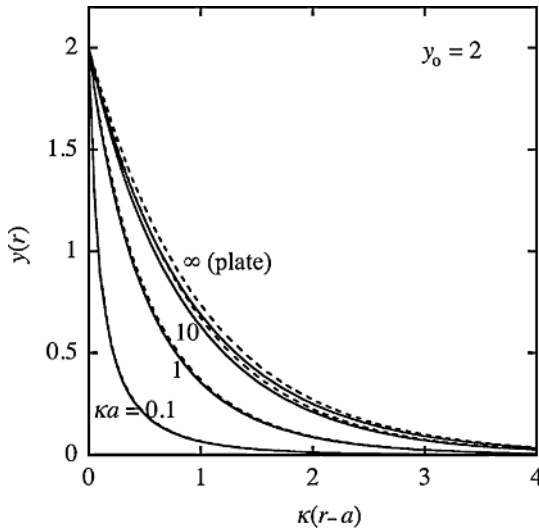
The relative error of Eq. (1.122) is less than 1% for $\kappa a \geq 1$. Note also that Eq. (1.121) or (1.122) exhibits the correct asymptotic form, namely,

$$y(r) = \text{costant} \times s \tag{1.124}$$

Figure 1.11 gives the scaled potential distribution $y(r)$ around a positively charged spherical particle of radius a with $y_o = 2$ in a symmetrical electrolyte solution of valence z for several values of κa. Solid lines are the exact solutions to Eq. (1.110) and dashed lines are the Debye–Hückel linearized results (Eq. (1.72)). Note that Eq. (1.122) is in excellent agreement with the exact results. Figure 1.12 shows the plot of the equipotential lines around a sphere with $y_o = 2$ at $\kappa a = 1$ calculated from Eq. (1.121). Figures 1.13 and 1.14, respectively, are the density plots of counterions (anions) $(n_-(r) = n \exp(+y(r)))$ and coions (cations) $(n_+(r) = n \exp(-y(r)))$ around the sphere calculated from Eq. (1.121).

Note that one can obtain the σ–y_o relationship from Eq. (1.120),

$$
\begin{aligned}
\sigma &= -\varepsilon_r \varepsilon_o \frac{dy}{dr}\bigg|_{r=a^+} = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} \frac{\kappa a + 1}{\kappa a} s \frac{dy}{ds}\bigg|_{s=1} \\
&= \frac{2\varepsilon_r \varepsilon_o \kappa kT}{e} \sinh\left(\frac{y_o}{2}\right)\left[1 + \frac{2\kappa a + 1}{(\kappa a)^2 \cosh^2(y_o/4)}\right]^{1/2}
\end{aligned}
\tag{1.125}
$$

FIGURE 1.11   Scaled potential distribution $y(r)$ around a positively charged spherical particle of radius a with $y_o = 2$ in a symmetrical electrolyte solution of valence z for several values of κa. Solid lines, exact solution to Eq. (1.110); dashed lines, Debye–Hückel linearized solution (Eq. (1.72)). Note that the results obtained from Eq. (1.122) agree with the exact results within the linewidth.
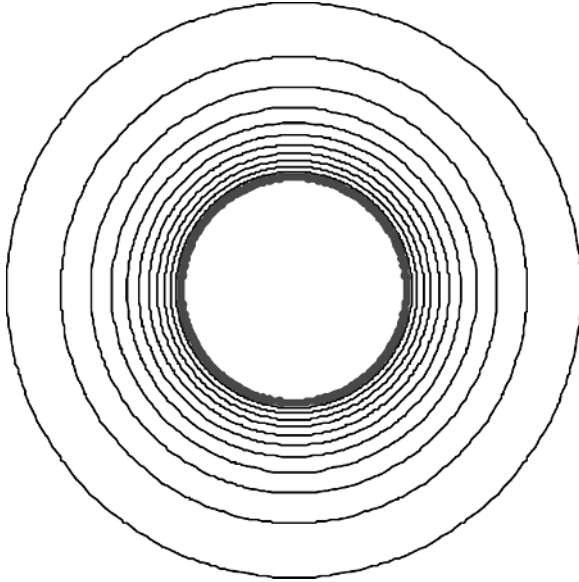
FIGURE 1.12   Contour lines (isopotential lines) for $\psi(r)$ around a positively charged sphere with $y_o = 2$ at $\kappa a = 1$. Arbitrary scale.
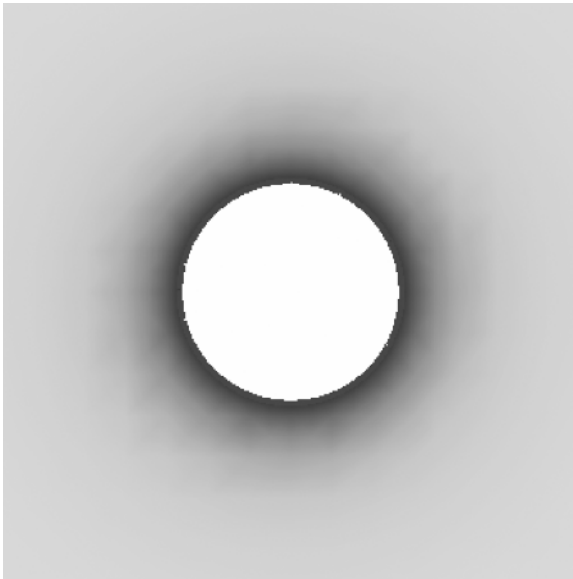
FIGURE 1.13   Density plots of counterions (anions) around a positively charged spherical particle with $y_o = 2$ at $\kappa a = 1$. Calculated from $n_-(r) = n \exp(+y(r))$ with the help of Eq. (1.121). The darker region indicates the higher density and $n_-(r)$ tends to its bulk value n far from the particle. Arbitrary scale.

FIGURE 1.14   Density plots of coions (cations) around a positively charged spherical particle with $y_o = 2$ at $\kappa a = 1$. Calculated from $n_+(r) = n \exp(-y(r))$ with the help of Eq. (1.121). The darker region indicates the higher density and $n_+(r)$ tends to its bulk value n far from the particle.

which corresponds to Eq. (1.80), but one cannot derive the second-order σ–y_o relationship by this method. The advantage in transforming the spherical Poisson–Boltzmann equation (1.79) into Eq. (1.112) lies in its ability to yield the potential distribution $y(r)$ that shows the correct asymptotic form (Eq. (1.124)).

We obtain the potential distribution around a sphere of radius a having a surface potential ψ_o immersed in a solution of general electrolytes [9]. The Poisson–Boltzmann equation for the electric potential $\psi(r)$ is given by Eq. (1.94), which, in terms of $f(r)$, is rewritten as

$$\frac{d^2y}{dr^2} + \frac{2}{r}\frac{dy}{dr} = \kappa^2 f(y)\frac{dy}{dr} \tag{1.126}$$

with $f(r)$ given by Eq. (1.56). We make the change of variables (Eq. (1.111)) and rewrite Eq. (1.126) as

$$s^2\frac{d^2y}{ds^2} + s\frac{dy}{ds} = f(y)\frac{df}{dy} - \frac{2\kappa r + 1}{(\kappa r + 1)^2}\left\{f(y)\frac{df}{dy} - s\frac{dy}{ds}\right\} \tag{1.127}$$

which is subject to the boundary conditions: $y = y_o$ at $s = 1$ and $y = dy/ds = 0$ at $s = 0$ (see Eqs. (1.114) and (1.115)). When $\kappa a \gg 1$, Eq. (1.127) reduces to

$$s^2\frac{d^2y}{ds^2} + s\frac{dy}{ds} = f(y)\frac{df}{dy} \tag{1.128}$$

which is integrated once to give

$$s\frac{dy}{ds} = f(y) \tag{1.129}$$

We then replace the second term on the right-hand side of Eq. (1.127) with its large κa limiting form, that is, $\kappa r \to \kappa a$ and $s\, dy/ds \to f(y)$ (Eq. (1.120)),

$$\frac{2\kappa r + 1}{(\kappa r + 1)^2}\left\{f(y)\frac{df}{dy} - s\frac{dy}{ds}\right\} \to \frac{2\kappa a + 1}{(\kappa a + 1)^2}\left\{f(y)\frac{df}{dy} - f(y)\right\} \tag{1.130}$$

Equation (1.127) then becomes

$$s^2\frac{d^2 y}{ds^2} + s\frac{dy}{ds} = +f(y)\frac{df}{dy} - \frac{2\kappa a + 1}{(\kappa a + 1)^2}\left\{f(y)\frac{df}{dy} - s\frac{dy}{ds}\right\} \tag{1.131}$$

and integrating the result once gives

$$s\frac{dy}{ds} = F(y) \tag{1.132}$$

with

$$F(y) = \frac{\kappa a}{\kappa a + 1}f(y)\left[1 + \frac{2(2\kappa a + 1)}{(\kappa a)^2}\frac{1}{f^2(y)}\int_0^y f(u)du\right]^{1/2} \tag{1.133}$$

Note that $F(y) \to y$ as $y \to 0$ and that $F(y) \to f(y)$ as $\kappa a \to \infty$. Expressions for $F(y)$ for several cases are given below.

(i) For a 1-1 electrolyte solution,

$$F(y) = \frac{2\kappa a}{\kappa a + 1}\sinh\left(\frac{y}{2}\right)\left[1 + \frac{2(2\kappa a + 1)}{(\kappa a)^2}\frac{1}{\cosh^2(y/4)}\right]^{1/2} \tag{1.134}$$

(ii) For the case of 2-1 electrolytes,

$$F(y) = \frac{\kappa a}{\kappa a + 1}(1 - e^{-y})\left(\frac{2}{3}e^y + \frac{1}{3}\right)^{1/2}$$
$$\left[\frac{1 + 2(2\kappa a + 1)(2 + e^{-y})(\frac{2}{3}e^y + \frac{1}{3})^{1/2} - 3}{(\kappa a)^2(1 - e^{-y})^2(\frac{2}{3}e^y + \frac{1}{3})}\right]^{1/2} \tag{1.135}$$

(iii) For the case of a mixed solution of 1-1 electrolyte of concentration n_1 and 2-1 electrolyte of concentration n_2,

$$
\begin{aligned}
F(y) = {}& \frac{\kappa a}{\kappa a + 1}(1 - e^{-y})\left[\left(1 - \frac{\eta}{3}\right)e^y + \frac{\eta}{3}\right]^{1/2} \\
& \times \left[1 + \frac{2(2\kappa a + 1)}{(\kappa a)^2(1 - e^{-y})^2\{(1 - \eta/3)e^y + \eta/3\}}\right. \\
& \times \left\{(2 + e^{-y})\sqrt{\left(1 - \frac{\eta}{3}\right)e^y + \frac{\eta}{3}} - 3 - \frac{\sqrt{3}(1 - \eta)}{2\sqrt{\eta}}\right. \\
& \left.\left.\times \ln\left(\frac{\{\sqrt{(1 - \eta/3)e^y + \eta/3} - \sqrt{\eta/3}\}(1 + \sqrt{\eta/3})}{\{\sqrt{(1 - \eta/3)e^y + \eta/3} + \sqrt{\eta/3}\}(1 - \sqrt{\eta/3})}\right)\right\}\right]^{1/2}
\end{aligned}
$$

$$(1.136)$$

where η is defined by Eq. (1.61).

Equation (1.132) is integrated again to give

$$
-\ln s = \int_y^{y_o} \frac{dy}{F(y)} \tag{1.137}
$$

Substituting Eq. (1.134) into Eq. (1.137), we obtain Eq. (1.122) with $z = 1$. For a 2-1 electrolyte and a mixture of 1-1 and 2-1 electrolytes, one can numerically calculate $y(r)$ from Eq. (1.137) with the help of Eqs. (1.135) and (1.136) for $F(y)$. For a 3-1 electrolyte and a mixture of 1-1 and 3-1 electrolytes, one can numerically calculate $F(y)$ from $f(y)$ (Eqs. (1.62) and (1.63)) with the help of Eq. (1.133) and then calculate $y(r)$ from Eq. (1.137).

1.5   CYLINDER

A similar approximation method can be applied for the case of infinitely long cylindrical particles of radius a in a general electrolyte composed of N ionic species with valence z_i and bulk concentration n_i ($i = 1, 2, \ldots, N$). The cylindrical Poisson–Boltzmann equation is

$$
\frac{d^2\psi}{dr^2} + \frac{1}{r}\frac{d\psi}{dr} = -\frac{1}{\varepsilon_r\varepsilon_o}\sum_{i=1}^{N} z_i e n_i^\infty \exp\left(-\frac{z_i e\psi}{kT}\right) \tag{1.138}
$$

where r is the radial distance measured from the center of the cylinder (Fig. 1.15). The conditions (1.69), (1.70), and (1.75) for a spherical particle of radius a are also
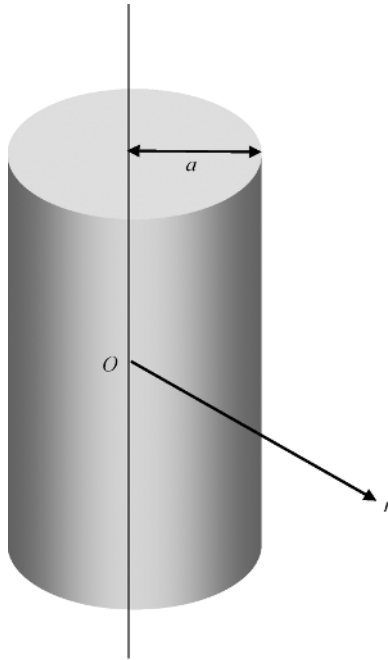
FIGURE 1.15   A cylinder of radius a.

applied for a cylindrical particle of radius a, namely,

$$\psi = \psi_\mathrm{o} \text{ at } r = a^+ \tag{1.139}$$

$$\psi \to 0, \ \frac{d\psi}{dr} \to 0 \text{ as } r \to \infty \tag{1.140}$$

$$\left.\frac{\partial\psi}{\partial r}\right|_{r=a^+} = -\frac{\sigma}{\varepsilon_r\varepsilon_\mathrm{o}} \tag{1.141}$$

where σ is the surface charge density of the cylinder.

1.5.1   Low Potential

For low potentials, Eq. (1.128) reduces to

$$\frac{d^2\psi}{dr^2} + \frac{1}{r}\frac{d\psi}{dr} = \kappa^2\psi \tag{1.142}$$

where κ is given by Eq. (1.10). The solution is

$$\psi(r) = \psi_\mathrm{o}\frac{K_0(\kappa r)}{K_0(\kappa a)} \tag{1.143}$$

where ψ_o is the surface potential of the particle and $K_n(z)$ is the modified Bessel function of the second kind of order n. The surface charge density σ of the particle is obtained from Eq. (1.141) as

$$\sigma = \varepsilon_r \varepsilon_o \kappa \psi_o \frac{K_1(\kappa a)}{K_0(\kappa a)} \tag{1.144}$$

or

$$\psi_o = \frac{\sigma}{\varepsilon_r \varepsilon_o \kappa} \frac{K_0(\kappa a)}{K_1(\kappa a)} \tag{1.145}$$

In the limit of $\kappa a \to \infty$, Eq. (1.145) approaches Eq. (1.26) for the plate case.

1.5.2 Arbitrary Potential: Symmetrical Electrolyte

For arbitrary ψ_o, accurate approximate analytic formulas have been derived [7,10], as will be shown below. Consider a cylinder of radius a with a surface charge density σ immersed in a symmetrical electrolyte solution of valence z and bulk concentration n. Equation (1.138) in this case becomes

$$\frac{d^2 y}{dr^2} + \frac{1}{r} \frac{dy}{dr} = \kappa^2 \sinh y \tag{1.146}$$

where $y = ze\psi/kT$ is the scaled potential. By making the change of variables [6]

$$c = \frac{K_0(\kappa r)}{K_0(\kappa a)} \tag{1.147}$$

we can rewrite Eq. (1.146) as

$$c^2 \frac{d^2 y}{dc^2} + c \frac{dy}{dc} = \sinh y - (1 - \beta^2) H(y) \tag{1.148}$$

where

$$H(y) = \left[\frac{1 - \{K_0(\kappa r)/K_1(\kappa r)\}^2}{1 - \beta^2} \right] \left(\sinh y - c \frac{dy}{dc} \right) \tag{1.149}$$

$$\beta = \frac{K_0(\kappa a)}{K_1(\kappa a)} \tag{1.150}$$

and the boundary conditions (1.139) and (1.140) as

$$y = y_o \quad \text{for } c = 1 \tag{1.151}$$

$$y = \frac{dy}{ds} = 0 \quad \text{for } c = 0 \tag{1.152}$$

In the limit $\kappa a \gg 1$, Eq. (1.148) reduces to

$$c^2\frac{d^2y}{dc^2} + c\frac{dy}{dc} = \sinh y \tag{1.153}$$

with solution

$$y(c) = 2\ln\left[\frac{1 + \tanh(y_o/4)c}{1 - \tanh(y_o/4)c}\right] \tag{1.154}$$

an expression obtained by White [6]. We note that from Eq. (1.149)

$$H(y) \underset{\kappa a \to \infty}{=} \sinh y - 2\sinh(y/2) \tag{1.155}$$

and replacing $H(y)$ in Eq. (148) by its large κa limiting form (Eq. (1.155)) we obtain

$$c^2\frac{d^2y}{dc^2} + c\frac{dy}{dc} = \sinh y - (1 - \beta^2)\{\sinh y - 2\sinh(y/2)\} \tag{1.156}$$

This equation can be integrated to give

$$y(r) = 2\ln\left[\frac{(1 + Dc)\{1 + ((1 - \beta)/(1 + \beta))Dc\}}{(1 - Dc)\{1 - ((1 - \beta)/(1 + \beta))Dc\}}\right] \tag{1.157}$$

and

$$\sigma = \frac{2\varepsilon_r\varepsilon_o\kappa kT}{ze}\sinh\left(\frac{y_o}{2}\right)\left[1 + \left(\frac{1}{\beta^2} - 1\right)\frac{1}{\cosh^2(y_o/4)}\right]^{1/2} \tag{1.158}$$

with

$$D = \frac{(1 + \beta)\tanh(y_o/4)}{1 + \{1 - (1 - \beta^2)\tanh^2(y_o/4)\}^{1/2}} \tag{1.159}$$

where $y_o = ze\psi_o/kT$ is the scaled surface potential of the cylinder. For low potentials, Eq. (1.158) reduces to Eq. (1.144).

1.5.3   Arbitrary Potential: General Electrolytes

We start with Eq. (1.138), which can be rewritten as

$$\frac{d^2y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = -\frac{\kappa^2\sum_{i=1}^{N}z_in_ie^{-z_iy}}{\sum_{i=1}^{N}z_i^2n_i} \tag{1.160}$$

where $y = e\psi/kT$

Equation (1.160) may further be rewritten as

$$\frac{d^2y}{dr^2} + \frac{1}{r}\frac{dy}{dr} = \kappa^2 f(y)\frac{df}{dy} \tag{1.161}$$

where $f(y)$ is defined by Eq. (1.56). Making the change of variables (Eq. (1.147)), we can rewrite Eq. (1.161) as

$$c^2\frac{d^2y}{dc^2} + c\frac{dy}{dc} = f(y)\frac{df}{dy} - \left[1 - \left\{\frac{K_0(\kappa r)}{K_1(\kappa r)}\right\}^2\right]\left\{f(y)\frac{df}{dy} - c\frac{dy}{dc}\right\} \tag{1.162}$$

When $\kappa a \gg 1$, Eq. (1.162) reduces to

$$c^2\frac{d^2y}{dc^2} + c\frac{dy}{dc} = f(y)\frac{df}{dy} \tag{1.163}$$

Equation (1.163) is integrated once to give

$$c\frac{dy}{dc} = f(y) \tag{1.164}$$

We then replace the second term on the right-hand side of Eq. (1.162) with its large κa limiting form, namely,

$$\left[1 - \left\{\frac{K_0(\kappa r)}{K_1(\kappa r)}\right\}^2\right]\left\{f(y)\frac{df}{dy} - c\frac{dy}{dc}\right\} \to (1 - \beta^2)\left\{f(y)\frac{df}{dy} - f(y)\right\} \tag{1.165}$$

Equation (1.162) then becomes

$$c^2\frac{d^2y}{dc^2} + c\frac{dy}{dc} = f(y)\frac{df}{dy} - (1 - \beta^2)\left\{f(y)\frac{df}{dy} - f(y)\right\} \tag{1.166}$$

and integrating the result once gives

$$c\frac{dy}{dc} = F(y) \tag{1.167}$$

with

$$F(y) = \beta f(y)\left[1 + 2\left(\frac{1}{\beta^2} - 1\right)\frac{1}{f^2(y)}\int_0^y f(u)du\right]^{1/2} \tag{1.168}$$

Note that $F(y) \to y$ as $y \to 0$ and that $F(y) \to f(y)$ as $\kappa a \to \infty$. Expressions for F (y) for several cases are given below.

(i) For a 1-1 electrolyte solution,

$$F(y) = 2\beta \sinh\left(\frac{y}{2}\right)\left[1 + \left(\frac{1}{\beta^2} - 1\right)\frac{1}{\cosh^2(y/4)}\right]^{1/2} \tag{1.169}$$

(ii) For the case of 2-1 electrolytes,

$$F(y) = \beta(1 - e^{-y})\left(\frac{2}{3}e^y + \frac{1}{3}\right)^{1/2}\left[1 + 2\left(\frac{1}{\beta^2} - 1\right)\frac{(2 + e^{-y})(\frac{2}{3}e^y + \frac{1}{3})^{1/2} - 3}{(1 - 2^{-y})^2(\frac{2}{3}e^y + \frac{1}{3})}\right]^{1/2} \tag{1.170}$$

(iii) For the case of a mixed solution of 1-1 electrolyte of concentration n_1 and 2-1 electrolyte of concentration n_2,

$$
\begin{aligned}
F(y) \;=\; & \beta(1 - e^{-y})\left[\left(1 - \frac{\eta}{3}\right)e^y + \frac{\eta}{3}\right]^{1/2} \\
& \times\left[1 + \frac{2(\beta^{-2} - 1)}{(1 - e^{-y})^2\{(1 - \eta/3)e^y + \eta/3\}}\right. \\
& \times\left\{(2 + e^{-y})\sqrt{\left(1 - \frac{\eta}{3}\right)e^y + \frac{\eta}{3}} - 3 - \frac{\sqrt{3}(1 - \eta)}{2\sqrt{\eta}}\right. \\
& \left.\left.\times\ln\left(\frac{\{\sqrt{(1 - \eta/3)e^y + \eta/3} - \sqrt{\eta/3}\}(1 + \sqrt{\eta/3})}{\{\sqrt{(1 - \eta/3)e^y + \eta/3} + \sqrt{\eta/3}\}(1 - \sqrt{\eta/3})}\right)\right]\right\}^{1/2}
\end{aligned}
\tag{1.171}
$$

where η is defined by Eq. (1.61).

The relationship between the reduced surface charge density σ and the reduced surface potential $y_o = e\psi_o/KT$ follows immediately from Eq. (1.141), namely [10],

$$
\begin{aligned}
\sigma \;=\; & -\varepsilon_r\varepsilon_o\frac{\partial\psi}{\partial r}\bigg|_{r=a^+} = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}\frac{K_1(\kappa r)}{K_0(\kappa a)}\frac{dy}{dc}\bigg|_{c=1} \\
\;=\; & \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}\frac{1}{\beta}c\frac{dy}{dc}\bigg|_{c=1} = \frac{\varepsilon_r\varepsilon_o\kappa kT}{e}\frac{1}{\beta}F(y_o)|
\end{aligned}
\tag{1.172}
$$

Note that when $|y_o| \ll 1$, Eq. (1.172) gives the correct limiting form (Eq. (1.144)), since $F(y) \to y$ as $y \to 0$.

For the case of a cylinder having a surface potential y_o in a 1-1 electrolyte solution, $F(y)$ is given by Eq. (1.169). Substitution of Eq. (1.169) into Eq. (1.172) yields Eq. (1.158) with $z = 1$. For the case of 2-1 electrolytes, $F(y)$ is given by Eq. (1.170). The σ–y_o relationship is thus given by

$$\sigma = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} pq \left[1 + 2 \left(\frac{1}{\beta^2} - 1 \right) \frac{(3-p)q - 3}{(pq)^2} \right]^{1/2} \tag{1.173}$$

For a mixed solution of 1-1 electrolyte of concentration n_1 and 2-1 electrolyte of concentration n_2, $F(y)$ is given by Eq. (1.171). The σ–y_o relationship is thus given by

$$\sigma = \frac{\varepsilon_r \varepsilon_o \kappa kT}{e} pt$$
$$\left[1 + \frac{2(\beta^{-2} - 1)}{(pt)^2} \left\{ (3-p)t - 3 - \frac{\sqrt{3}(1-\eta)}{2\sqrt{\eta}} \ln \left(\frac{(t - \sqrt{\eta/3})(1 + \sqrt{\eta/3})}{(t + \sqrt{\eta/3})(1 - \sqrt{\eta/3})} \right) \right\} \right]^{1/2} \tag{1.174}$$

with

$$t = \sqrt{\left(1 - \frac{\eta}{3} \right) e^{y_o} + \frac{\eta}{3}} \tag{1.175}$$

Similarly, for the case of 3-1 electrolytes, $F(y)$ is calculated from $f(y)$ (Eq. (1.62)). For a mixed solution of 3-1 electrolyte of concentration n_2 and 1-1 electrolyte of concentration n_1, $F(y)$ is calculated from $f(y)$ (Eq. (1.63)). By substituting the obtained expressions for $F(y)$ into Eq. (1.172) and carrying out numerical integration, we can derive the σ–y_o relationship.

Equation (1.167) is integrated again to give

$$-\ln c = \int_y^{y_o} \frac{dy}{F(y)} \tag{1.176}$$

Equation (1.176) gives the general expression for the potential distribution around a cylinder. For the special case of a cylinder in a 1-1 electrolyte, in which case $F(y)$ is given by Eq. (1.134), we obtain Eq. (1.157) with $z = 1$. For other types of electrolytes, one can calculate by using Eq. (1.176) with the help of the corresponding expression for $F(y)$.

1.6   ASYMPTOTIC BEHAVIOR OF POTENTIAL AND EFFECTIVE SURFACE POTENTIAL

Consider here the asymptotic behavior of the potential distribution around a particle (plate, sphere, or cylinder) at large distances, which will also be used for calculating the electrostatic interaction between two particles.

1.6.1 Plate

Consider a charged plate with arbitrary surface potential ψ_o in a symmetrical electrolyte solution of valence z and Debye–Hückel parameter κ. We take an x-axis perpendicular to the plate surface with its origin at the plate surface so that the region $x > 0$ corresponds to the solution phase while the region $x < 0$ to the plate interior. Equation (1.37) (or Eq. (1.38)) for the potential distribution $\psi(x)$ around the surface in the region far from the surface, that is, at large κx, takes the form

$$\psi(x) = \frac{4kT}{ze} \gamma e^{-\kappa x} = \frac{4kT}{ze} \tanh\left(\frac{ze\psi_o}{4kT}\right) e^{-\kappa x} \tag{1.177}$$

or

$$y(x) \equiv \frac{ze\psi(x)}{kT} = 4\gamma e^{-\kappa x} = 4 \tanh\left(\frac{ze\psi_o}{4kT}\right) e^{-\kappa x} \tag{1.178}$$

Comparing Eqs. (1.25) and (1.177), we find that the effective surface potential ψ_{eff} of the plate is given by

$$\psi_{\text{eff}} = \frac{4kT}{ze} \gamma = \frac{kT}{ze} \cdot 4 \tanh\left(\frac{ze\psi_o}{4kT}\right) \tag{1.179}$$

and the scaled effective surface potential $Y = zey_{\text{eff}}/kT$ is given by

$$Y = 4\gamma = 4 \tanh\left(\frac{ze\psi_o}{4kT}\right) \tag{1.180}$$

where γ is defined by Eq. (1.39). For small potentials, the effective surface potential ψ_{eff} tends to the real surface potential ψ_o. Figure 1.16 shows the asymptotic solution (Eq. (1.178)) in comparison with the exact solution (Eq. (1.37)).

For a sphere in a 2-1 electrolyte solution, it follows from Eq. (1.44) that $\psi(x)$ asymptotes

$$\psi(x) = \frac{4kT}{e} \gamma' e^{-\kappa x} = \frac{kT}{e} \cdot 6 \left\{ \frac{(\frac{2}{3} e^{y_o} + \frac{1}{3})^{1/2} - 1}{(\frac{2}{3} e^{y_o} + \frac{1}{3})^{1/2} + 1} \right\} e^{-\kappa x} \tag{1.181}$$

where γ' is defined by Eq. (1.45). The effective surface potential ψ_{eff} is thus given by

$$\psi_{\text{eff}} = \frac{4kT}{e} \gamma' = \frac{kT}{e} \cdot 6 \left\{ \frac{(\frac{2}{3} e^{y_o} + \frac{1}{3})^{1/2} - 1}{(\frac{2}{3} e^{y_o} + \frac{1}{3})^{1/2} + 1} \right\} \tag{1.182}$$
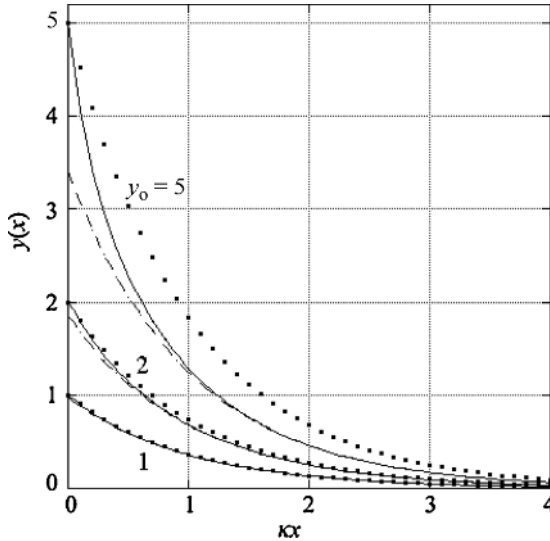
FIGURE 1.16   Potential distribution $y(x)$ around a positively charged plate with scaled surface potential $y_o \equiv ze\psi_o/kT$ in a symmetrical electrolyte solution for $y_o = 1$, 2, and 5. Solid lines are exact results (Eq. (1.37)), dashed lines are asymptotic results (Eq. (1.178)), and dotted lines are the Debye–Hückel approximation (Eq. (1.25)).

and the scaled effective surface potential $Y = zey_{eff}/kT$ is given by

$$Y = 4\gamma' = 6\left\{\frac{(\frac{2}{3}e^{y_o} + \frac{1}{3})^{1/2} - 1}{(\frac{2}{3}e^{y_o} + \frac{1}{3})^{1/2} + 1}\right\} \tag{1.183}$$

For the case of a mixed solution of 1-1 electrolyte of bulk concentration n_1 and 2-1 electrolyte of bulk concentration n_2, Eq. (1.48) in the region far from the surface, that is, at large κx, takes the form

$$\psi(x) = \frac{4kT}{e}\gamma''e^{-\kappa x} = \frac{4kT}{e}\left(\frac{1}{1 - \eta/3}\right)\left[\frac{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} - 1}{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} + 1}\right]e^{-\kappa x} \tag{1.184}$$

where η and γ'' are defined by Eqs. (1.50) and (1.51), respectively. The effective surface potential ψ_{eff} is thus given by

$$\psi_{eff} = \frac{4kT}{e}\gamma'' = \frac{4kT}{e}\left(\frac{1}{1 - \eta/3}\right)\left[\frac{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} - 1}{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} + 1}\right] \tag{1.185}$$

and the scaled effective surface potential $Y = zey_{eff}/kT$ is given by

$$Y = 4\gamma'' = 4\left(\frac{1}{1 - \eta/3}\right)\left[\frac{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} - 1}{\{(1 - \eta/3)e^{y_o} + \eta/3\}^{1/2} + 1}\right] \tag{1.186}$$

We obtain the scaled effective surface potential Y for a plate having a surface potential ψ_o (or scaled surface potential y_o) immersed in a solution of general electrolytes [9]. Integration of the Poisson–Boltzmann equation for the electric potential $\psi(x)$ is given by Eq. (1.65), namely,

$$\kappa x = \int_y^{y_o} \frac{dy}{f(y)} \tag{1.187}$$

where $y = e\psi/kT$ and $f(x)$ is defined by Eq. (1.56). Equation (1.187) can be rewritten as

$$
\begin{aligned}
\kappa x &= \int_y^{y_o} \left\{ \frac{1}{f(y)} - \frac{1}{y} \right\} dy + \int_y^{y_o} \frac{1}{y} dy \\
&= \int_y^{y_o} \left\{ \frac{1}{f(y)} - \frac{1}{y} \right\} dy + \ln|y_o| - \ln|y|
\end{aligned}
\tag{1.188}
$$

Note here that the asymptotic form $y(x)$ must be

$$y(x) = \text{constant} \times \exp(-\kappa x) \tag{1.189}$$

or

$$\kappa x = \text{constant} - \ln|y| \tag{1.190}$$

Therefore, the integral term of (1.188) must become independent of y at large x. Since y tends to zero in the limit of large x, the lower limit of the integration may be replaced by zero. We thus find that the asymptotic form $y(x)$ satisfies

$$\kappa x = \int_0^{y_o} \left\{ \frac{1}{f(y)} - \frac{1}{y} \right\} dy + \ln|y_o| - \ln|y| \tag{1.191}$$

It can be shown that the asymptotic form of $y(x)$ satisfies

$$y(x) = Ye^{-\kappa x} \tag{1.192}$$

with

$$Y = y_o \exp\left[\int_0^{y_o} \left\{ \frac{1}{f(y)} - \frac{1}{y} \right\} dy \right] \tag{1.193}$$

Equation (1.193) is the required expression for the scaled effective surface potential (or the asymptotic constant) Y. Wilemski [11] has derived an expression for Y (Eq. (15) with Eq. (12) in his paper [11]), which can be shown to be equivalent to Eq. (1.193). For a planar surface having scaled surface potentials y_o in a z-z symmetrical electrolyte solution, Eq. (1.193) reproduces Eq. (1.180). Similarly, for the case of a

planar surface having a scaled surface potential y_o in a 2-1 electrolyte solution, Eq. (1.193) reproduces Eq. (1.183), while for the case of a mixed solution of 1-1 electrolyte of concentration n_1 and 2-1 electrolyte of concentration n_2, it gives Eq. (1.186).

1.6.2 Sphere

The asymptotic expression for the potential of a spherical particle of radius a in a symmetrical electrolyte solution of valence z and Debye–Hückel parameter κ at a large distance r from the center of the sphere may be expressed as

$$\psi(r) = \psi_{\text{eff}} \frac{a}{r} e^{-\kappa(r-a)} \tag{1.194}$$

$$y(r) = \frac{ze}{kT}\psi(r) = Y\frac{a}{r}e^{-\kappa(r-a)} \tag{1.195}$$

where r is the radial distance measured from the sphere center, ψ_{eff} is the effective surface potential, and $Y = ze\psi_{\text{eff}}/kT$ is the scaled effective surface potential of a sphere. From Eq. (1.122) we obtain

$$\psi_{\text{eff}} = \frac{kT}{ze} \cdot \frac{8\tanh(y_o/4)}{1 + \{1 - ((2\kappa a + 1)/(\kappa a + 1)^2)\tanh^2(y_o/4)\}^{1/2}} \tag{1.196}$$

or

$$Y = \frac{8\tanh(y_o/4)}{1 + \{1 - ((2\kappa a + 1)/(\kappa a + 1)^2)\tanh^2(y_o/4)\}^{1/2}} \tag{1.197}$$

It can be shown that ψ_{eff} reduces to the real surface potential ψ_o in the low-potential limit.

We obtain an approximate expression for the scaled effective surface potential Y for a sphere of radius a having a surface potential ψ_o (or scaled surface potential $y_o = e y_o/kT$) immersed in a solution of general electrolytes [9]. The Poisson–Boltzmann equation for the scaled electric potential $y(r) = e\psi/kT$ is approximately given by Eq. (1.137), namely,

$$-\ln s = \int_y^{y_o} \frac{dy}{F(y)} \tag{1.198}$$

with

$$s = \frac{a}{r}\exp(-\kappa(r-a)) \tag{1.199}$$

where $F(y)$ is defined by Eq. (1.133). It can be shown that the scaled effective surface potential $Y = e\psi_{\text{eff}}/kT$ is given by

$$Y = y_o\exp\left[\int_0^{y_o}\left\{\frac{1}{F(y)} - \frac{1}{y}\right\}dy\right] \tag{1.200}$$

Equation (1.200) is the required expression for the scaled effective surface potential (or the asymptotic constant) Y and reproduces Eq. (1.197) for a sphere of radius a having a surface potential ψ_o in a symmetrical electrolyte solution of valence z. The relative error of Eq. (1.200) is less than 1% for $\kappa a \geq 1$.

1.6.3   Cylinder

The effective surface potential ψ_{eff} or scaled effective surface potential $Y = ze\psi_{eff}/kT$ of a cylinder in a symmetrical electrolyte solution of valence z can be obtained from the asymptotic form of the potential around the cylinder, which in turn is derived from Eq. (1.157) as [7]

$$y(r) = Yc \tag{1.201}$$

with

$$c = \frac{K_0(\kappa r)}{K_0(\kappa a)} \tag{1.202}$$

and

$$Y = \frac{8\tanh(y_o/4)}{1 + \{1 - (1 - \beta^2)\tanh^2(y_o/4)\}^{1/2}} \tag{1.203}$$

where r is the distance from the axis of the cylinder and

$$\beta = \frac{K_0(\kappa a)}{K_1(\kappa a)} \tag{1.204}$$

We obtain an approximate expression for the scaled effective surface potential Y for a cylinder of radius a having a surface potential ψ_{eff} (or scaled surface potential $Y = e\psi_{eff}/kT$) immersed in a solution of general electrolytes . The Poisson–Boltzmann equation for the scaled electric potential $y(r) = e\psi/kT$ is approximately given by Eq. (1.176), namely,

$$-\ln c = \int_y^{y_o} \frac{dy}{F(y)} \tag{1.205}$$

where $F(y)$ is defined by Eq. (1.168). It can be shown that the scaled effective surface potential $Y = e\psi_{eff}/kT$ is given by

$$Y = y_o\exp\left[\int_0^{y_o} \left\{\frac{1}{F(y)} - \frac{1}{y}\right\}dy\right] \tag{1.206}$$

Equation (1.206) reproduces Eq. (1.203) for a cylinder in a symmetrical electrolyte solution of valence z. The relative error of Eq. (1.206) is less than 1% for $\kappa a \geq 1$.

1.7 NEARLY SPHERICAL PARTICLE

So far we have treated uniformly charged planar, spherical, or cylindrical particles. For general cases other than the above examples, it is not easy to solve analytically the Poisson–Boltzmann equation (1.5). In the following, we give an example in which one can derive approximate solutions.

We give below a simple method to derive an approximate solution to the linearized Poisson–Boltzmann equation (1.9) for the potential distribution $\psi(r)$ around a nearly spherical spheroidal particle immersed in an electrolyte solution [12]. This method is based on Maxwell's method [13] to derive an approximate solution to the Laplace equation for the potential distribution around a nearly spherical particle.

Consider first a prolate spheroid with a constant uniform surface potential ψ_o in an electrolyte solution (Fig. 1.17a). The potential ψ is assumed to be low enough to obey the linearized Poisson–Boltzmann equation (1.9). We choose the z-axis as the axis of symmetry and the center of the prolate as the origin. Let a and b be the major and minor axes of the prolate, respectively. The equation for the surface of the prolate is then given by
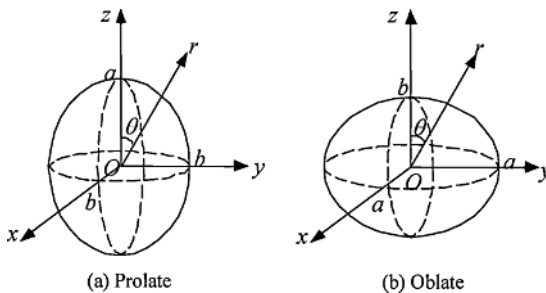
$$\frac{x^2 + y^2}{b^2} + \frac{z^2}{a^2} = 1 \tag{1.207}$$

We introduce the spherical polar coordinate (r, θ, ϕ), that is, $r^2 = x^2 + y^2 + z^2$ and $z = r\cos\theta$, and the eccentricity of the prolate

$$e_p = \sqrt{1 - (b/a)^2} \tag{1.208}$$

Then, when the spheroid is nearly spherical (i.e., for low e_p), Eq. (1.207) becomes

$$r = a\left(1 - \frac{e_p^2}{2}\sin^2\theta\right) = a\left[1 + \frac{e_p^2}{3}\left\{\frac{1}{2}(3\cos^2\theta - 1) - 1\right\}\right] \tag{1.209}$$

FIGURE 1.17 Prolate spheroid (a) and oblate spheroid (b). a and b are the major and minor semiaxes, respectively. The z-axis is the axis of symmetry.

which is an approximate equation for the surface of the prolate with low eccentric-ity e_p (which is correct to order e_p^2).

The solution to Eq. (1.9) must satisfy the boundary conditions that ψ tends to zero as $r \to \infty$ and $\psi = \psi_o$ at the prolate surface (given by Eq. (1.209)). We thus obtain

$$\psi(r,\theta) = \psi_o \frac{a}{r} e^{-\kappa(r-a)} - \psi_o \frac{(1+\kappa a)}{3} e_p^2 \left\{ \frac{a}{r} e^{-\kappa(r-a)} - \frac{k_2(\kappa r)}{4k_2(\kappa a)} (3\cos^2\theta - 1) \right\}$$

(1.210)

where $k_n(z)$ is the modified spherical Bessel function of the second kind of order n.

We can also obtain the surface charge density $\sigma(\theta)$ from Eq. (1.210), namely,

$$\sigma(\theta) = -\varepsilon_r \varepsilon_o \frac{\partial \psi}{\partial n} = -\varepsilon_r \varepsilon_o \cos\alpha \frac{\partial \psi}{\partial r} \text{ at } r = a \left[1 + \frac{e_p^2}{3} \left\{ \frac{1}{2}(3\cos^2\theta - 1) - 1 \right\} \right]$$

(1.211)

where α is the angle between n and r. It can be shown that $\cos\alpha = 1 + O(e_p^4)$. Then we find from Eqs. (1.210) and (1.211) that

$$\begin{aligned}
\frac{\sigma(\theta)}{\varepsilon_r \varepsilon_o \kappa \psi_o} &= 1 + \frac{1}{\kappa a} + \frac{e_p^2}{3\kappa a} \left[1 - \left\{ 2 + 2\kappa a + (\kappa a)^2 \right. \right. \\
&\left. \left. -(1+\kappa a)\frac{\{9 + 9\kappa a + 4(\kappa a)^2 + (\kappa a)^3\}}{2\{3 + 3\kappa a + (\kappa a)^2\}}(3\cos^2\theta - 1) \right\} \right]
\end{aligned}$$

(1.212)

Figure 1.18 shows equipotential lines (contours) around a prolate spheroid on the z–x plane at $y = 0$, calculated from Eq. (1.210) at $\kappa a = 1.5$ and $\kappa b = 1$.
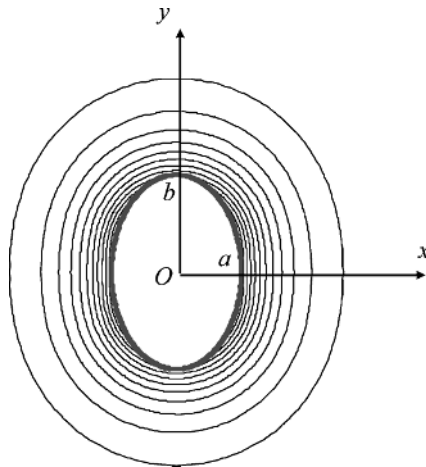
FIGURE 1.18   Equipotential lines (contours) around a prolate spheroid on the z–x plane at $y = 0$. Calculated from Eq. (1.210) at $\kappa a = 1.5$ and $\kappa b = 1$ (arbitrary size).

We next consider the case of an oblate spheroid with constant surface potential ψ_o (Fig. 1.17b). The surface of the oblate is given by

$$\frac{x^2 + y^2}{a^2} + \frac{z^2}{b^2} = 1 \qquad (1.213)$$

where the z-axis is again the axis of symmetry, a and b are the major and minor semiaxes, respectively. Equation (1.213) can be approximated by

$$r = a\left(1 + \frac{e_o^2}{2}\sin^2\theta\right) = a\left[1 - \frac{e_o^2}{3}\left\{\frac{1}{2}(3\cos^2\theta - 1) - 1\right\}\right] \qquad (1.214)$$

where the eccentricity e_o of the oblate is given by

$$e_o = \sqrt{(a/b)^2 - 1} \qquad (1.215)$$

After carrying out the same procedure as employed for the case of the prolate spheroid, we find that $\psi(r, \theta)$ and the σ–ψ_o relationship, both correct to order e_o^2, are given by

$$\psi(r,\theta) = \psi_o \frac{b}{r} e^{-\kappa(r-b)} - \psi_o \frac{(1+\kappa b)}{3} e_o^2 \left\{\frac{b}{r} e^{-\kappa(r-b)} - \frac{k_2(\kappa r)}{4k_2(\kappa b)}(3\cos^2\theta - 1)\right\} \qquad (1.216)$$

$$\frac{\sigma(\theta)}{\varepsilon_r\varepsilon_0\kappa\psi_o} = 1 + \frac{1}{\kappa b} - \frac{e_o^2}{3\kappa b}\Big[1 - \big\{2 + 2\kappa b + (\kappa b)^2$$
$$-(1+\kappa b)\frac{\{9 + 9\kappa b + 4(\kappa b)^2 + (\kappa b)^3\}}{2\{3 + 3\kappa b + (\kappa b)^2\}}(3\cos^2\theta - 1)\big\}\Big] \qquad (1.217)$$

which can also be obtained directly from Eqs. (1.210) and (1.212) by interchanging $a \leftrightarrow b$ and replacing e_p^2 by $-e_o^2$.

The last term on the right-hand side of Eqs. (1.210), (1.212), (1.216), and (1.217) corresponds to the deviation of the particle shape from a sphere.

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