Biophysical Chemistry, 47 (1993) 53–59
Elsevier Science Publishers B.V., Amsterdam

BIOCHE 01749

Surface potential of a particle in an electrolyte solution containing rodlike zwitterions

Hiroyuki Ohshima [a,*], Katsu Natamori [b] and Tamotsu Kondo [a]

[a] *Faculty of Pharmaceutical Sciences and Institute of Colloid and Interface Science, Science University of Tokyo, Shinjuku-ku, Tokyo 162 (Japan)*
[b] *Taisho Pharmaceutical Co., Ltd., Omiya-shi, Saitama 330 (Japan)*

(Received 15 October 1992; accepted in revised form 7 December 1992)

Abstract

The surface potential of charged colloidal particles is calculated for the case where they are suspended in an electrolyte solution containing zwitterions of concentration C_z as well as univalent pointlike ions of concentration C_1. A zwitterion is regarded as a rod of length a carrying two charges $+e$ and $-e$ (e is the elementary electric charge) at its ends. Equations determining the surface potential are derived which are based on the theory of Carnie and McLaughlin (*Biophys. J.* 44 (1983) 325) on the effects of large divalent cations on the particle surface potential. It is found that when $\kappa a \ll 1$, zwitterions behave as neutral species and when $\kappa a \gg 1$, they behave like univalent electrolytes of concentration $C_z/2$ (not C_z), where κ is the Debye–Hückel parameter at zero zwitterionic concentration. Approximate expressions for the surface potential as a function of σ (the surface charge density of the particles), C_1, C_z, and a are derived.

Keywords: Surface potential; Rodlike zwitterions

1. Introduction

One of the deficiencies of the Poisson–Boltzmann equation for the electric potential in the vicinity of the surface of colloidal particles in an electrolyte solution is that electrolyte ions are treated as point charges: in other words, the size effects of ions are neglected [1]. Carnie and McLaughlin [2] proposed a modified Poisson–Boltzmann equation taking into account the size effects of large divalent cations and demonstrated that the neglect of the size effects leads to serious errors in estimating the surface potential from the charge density of the particle surface. Ohshima and Ohki [3] devised a simple numerical procedure for solving this modified Poisson–Boltzmann equation and extended the approach by Carnie and McLaughlin [2] to the case where divalent cations can absorb on the particle surface.

In this paper, on the basis of the method of Carnie and McLaughlin [2], we calculate the surface potential of colloidal particles immersed in an electrolyte solution containing rodlike zwitteri-

---

[*] To whom correspondence should be addressed at the Faculty of Pharmaceutical Sciences, Science University of Tokyo, 12 Ichigaya Funagawara-machi, Shinjuku-ku, Tokyo 162, Japan.

ons, as well as univalent pointlike electrolyte ions. Since zwitterions carry no net charges, any effects of zwitterions on the particle surface potential cannot be expected from the original Poisson–Boltzmann approach in which ions are all treated as point charges. This is the case only in the limit of small zwitterions. Obviously, however, this approach would not be a good approximation for systems involving large zwitterions such as neutral amino acids. In the limit of large zwitterions their behavior becomes similar to that of two separate charges. In the present paper we regard zwitterions as rods and give general equations determining the particle surface potential in the presence of rodlike zwitterions of arbitrary length.

2. Basic equations

Consider a charged colloidal particle immersed in an electrolyte solution composed of univalent pointlike electrolytes of concentration $C_1(M)$ and zwitterions of concentrations $C_z(M)$. The zwitterion is regarded as a rod of length a, carrying two point charges $+e$ and $-e$ at its ends (Fig. 1). We assume that the particle is large, so that the particle surface can be regarded as planar. Let the charge density of the particle surface be σ. We also assume that neither pointlike electrolyte ions nor zwitterions can adsorb the particle surface. We take an x-axis perpendicular to the particle surface with its origin at the surface so that the region $x > 0$ corresponds to the electrolyte solution and $x < 0$ to the particle interior, as shown in Fig. 2.

On the basis of the theory of Carnie and McLaughlin [2] the Poisson–Boltzmann equation for the electric potential $\psi(x)$ (relative to the bulk solution phase, where $\psi(x)$ is set equal to zero) can be modified in the present case as follows. Consider the end of a rod that carries the $+e$ charge. The probability of finding this end at position x is inevitably influenced by the other end carrying the $-e$ charge. That is, when the $+e$ end is located at position x, the other end (i.e., the $-e$ end) can exist only in the region $(x-a, x+a)$ if $x > a$, or in the region $(0, x-a)$ if $x < a$ (these two regions can be combined in the form $(\max[0, x-a], x+a)$, as is seen in Fig. 2. Thus the probability of finding the $+e$ end of a rod at position x is the product of probabilities P_1 and P_2. Here P_1 is the probability that the $+e$ end would be found at position x if it existed alone (i.e., in the absence of the other end) and P_2 is the probability of finding the $-e$ end at an arbitrary point in the region $(\max[0, x-a], x+a)$ with the location of the $+e$ end kept at position x. The probability P_1 is proportional to

$$C_z \exp\left[-\frac{e\psi(x)}{kT}\right], \tag{1}$$

and P_2 is proportional to

$$\frac{1}{2a}\int_{\max[0,x-a]}^{x+a} \exp\left[+\frac{e\psi(x')}{kT}\right] \mathrm{d}x'. \tag{2}$$

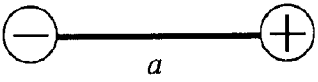

Fig. 1. Rodlike zwitterion of length a carrying $+e$ and $-e$ at its ends.

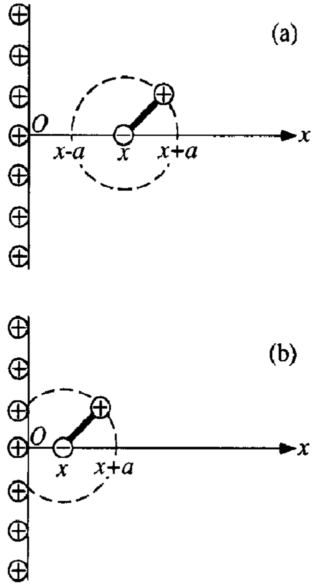

Fig. 2. Rodlike ions near the charged surface. (a) $x \geq a$, and (b) $0 < x < a$.

Here we have assumed a Boltzmann distribution for charged species. Thus the concentration $C_z^+(x)$ of the $+e$ end of the rods at position x, is given by the product of eqs. (1), (2) and the bulk concentration C_z, viz.,

$$C_z^+(x) = C_z \exp\left[-\frac{e\psi(x)}{\mathrm{kT}}\right] \times \left\{\frac{1}{2a}\int_{\max[0,x-a]}^{x+a} \exp\left[+\frac{e\psi(x')}{kT}\right] \mathrm{d}x'\right\}. \tag{3}$$

Similarly, the concentration of the $-e$ end at position x, $C_z^-(x)$, is given by

$$C_z^-(x) = C_z \exp\left[+\frac{e\psi(x)}{kT}\right] \times \left\{\frac{1}{2a}\int_{\max[0,x-a]}^{x+a} \exp\left[-\frac{e\psi(x')}{kT}\right] \mathrm{d}x'\right\}. \tag{4}$$

The electric potential $\psi(x)$ is related to the charge density $\rho(x)$ at position x via the Poisson equation, viz.,

$$\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{\rho(x)}{\varepsilon_r\varepsilon_0}, \tag{5}$$

where ε_r is the relative permittivity of the electrolyte solution and ε_0 is the permittivity of a vacuum. The charge density $\rho(x)$ at position x is given by

$$\rho(x) = 1000\, N_A e\left[C_z^+(x) - C_z^-(x) + C_1^+(x) - C_1^-(x)\right]. \tag{6}$$

where N_A is Avogadro's number, $C_1^+(x)$ and $C_1^-(x)$ are, respectively, the concentrations of coexisting univalent cations and anions. If we assume a Boltzmann distribution for these ions, then $C_1^+(x)$ and $C_1^-(x)$ are given by

$$C_1^+(x) = C_1 \exp\left[-\frac{e\psi(x)}{kT}\right],$$

$$C_1^-(x) = C_1 \exp\left[+\frac{e\psi(x)}{kT}\right]. \tag{7}$$

Combining eqs. (3)–(7), we obtain

$$\begin{aligned}\frac{\mathrm{d}^2\psi}{\mathrm{d}x^2} = -\frac{1000 N_A e}{\varepsilon_r\varepsilon_0} &\times \Bigg(C_z \exp\left[-\frac{e\psi(x)}{kT}\right] \\ &\times \frac{1}{2a}\int_{\max[0,x-a]}^{x+a} \exp\left[+\frac{e\psi(x')}{kT}\right] \mathrm{d}x' \\ &- C_z \exp\left[+\frac{e\psi(x)}{kT}\right] \\ &\times \frac{1}{2a}\int_{\max[0,x-a]}^{x+a} \exp\left[-\frac{e\psi(x')}{kT}\right] \mathrm{d}x' \\ &+ C_1 \exp\left[-\frac{e\psi(x)}{kT}\right] \\ &- C_1 \exp\left[+\frac{e\psi(x)}{kT}\right]\Bigg).\end{aligned} \tag{8}$$

Equation (8) is the Poisson–Boltzmann equation modified by taking into account the finite size of zwitterions. The boundary conditions at the particle surface $x = 0$ and at $x = a$ are given by

$$\left.\frac{\mathrm{d}\psi}{\mathrm{d}x}\right|_{x=+0} = -\frac{\sigma}{\varepsilon_r\varepsilon_0}, \tag{9}$$

and

$\psi(x)$ and $\mathrm{d}\psi/\mathrm{d}x$ are, respectively, continuous at $x = a$. (10)

Equation (9) relates the potential derivative at $x = +0$ to the surface charge density σ.

3. Results and discussion

Equation (8) subject to the boundary conditions (9) and (10) can be solved numerically to provide the potential distribution $\psi(x)$. The relationship between the surface charge density σ and the surface potential $\psi_0 \equiv \psi(0)$ is derived as follows.

Multiplying $\mathrm{d}\psi/\mathrm{d}x$ on both sides of eq. (8) and integrating the result once, we have

$$\begin{aligned}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \kappa^2\Bigg[& \mathrm{e}^{y(x)} + \mathrm{e}^{-y(x)} - 2 \\ & + \frac{r}{2a}\Bigg\{(\mathrm{e}^{-y(x)} - 1)\int_0^{x+a} \mathrm{e}^{y(x')}\,\mathrm{d}x' \\ & + \int_x^a (\mathrm{e}^{-y(x')} - 1)\ \mathrm{e}^{y(x'+a)}\,\mathrm{d}x' \\ & + \int_a^\infty (\mathrm{e}^{-y(x')} - 1) \\ & \times (\mathrm{e}^{y(x'+a)} - \mathrm{e}^{y(x'-a)})\,\mathrm{d}x' \\ & + (\mathrm{e}^{y(x)} - 1)\int_0^{x+a} \mathrm{e}^{-y(x')}\,\mathrm{d}x' \\ & + \int_x^a (\mathrm{e}^{y(x')} - 1)\ \mathrm{e}^{-y(x'+a)}\,\mathrm{d}x' \\ & + \int_a^\infty (\mathrm{e}^{y(x')} - 1) \\ & \times (\mathrm{e}^{-y(x'+a)} - \mathrm{e}^{-y(x'-a)})\,\mathrm{d}x'\Bigg\}\Bigg], \\ & 0 < x \le a, \qquad (11)\end{aligned}$$

$$\begin{aligned}\left(\frac{\mathrm{d}y}{\mathrm{d}x}\right)^2 = \kappa^2\Bigg[& \mathrm{e}^{y(x)} + \mathrm{e}^{-y(x)} - 2 \\ & + \frac{r}{2a}\Bigg\{(\mathrm{e}^{-y(x)} - 1)\int_{x-a}^{x+a} \mathrm{e}^{y(x')}\,\mathrm{d}x' \\ & + \int_x^\infty (\mathrm{e}^{-y(x')} - 1) \\ & \times (\mathrm{e}^{y(x'+a)} - \mathrm{e}^{y(x'-a)})\,\mathrm{d}x' \\ & + (\mathrm{e}^{y(x')} - 1)\int_{x-a}^{x+a} \mathrm{e}^{-y(x')}\,\mathrm{d}x' \\ & + \int_x^\infty (\mathrm{e}^{y(x')} - 1) \\ & \times (\mathrm{e}^{-y(x'+a)} - \mathrm{e}^{-y(x'-a)})\,\mathrm{d}x'\Bigg\}\Bigg], \\ & x \ge a, \qquad (12)\end{aligned}$$

with

$$y(x) = e\psi(x)/kT, \qquad (13)$$

$$\kappa = \sqrt{\frac{2000 N_A e^2 C_1}{\varepsilon_r \varepsilon_0 kT}}, \qquad (14)$$

$$r = C_z/C_1, \qquad (15)$$

where $y(x)$ is the scaled potential, $y_0 \equiv y(0) = e\psi_0/kT$ is the scaled surface potential, κ is the Debye–Hückel parameter of the electrolyte solution in the absence of rodlike zwitterions (i.e., when $C_z = 0$), and r is the concentrations ratio of rodlike zwitterions and univalent pointlike electrolytes.

Evaluating eq. (11) at $x = +0$

$$\begin{aligned}&\left(\frac{\mathrm{d}y}{\mathrm{d}x}\bigg|_{x=+0}\right)^2 \\ &= \kappa^2\Bigg[e^{y_0} + \mathrm{e}^{-y_0} - 2 + \frac{r}{2a}\int_0^a (\mathrm{e}^{-y_0+y(x')} \\ &\quad + \mathrm{e}^{y_0-y(x')} - 2)\,\mathrm{d}x'\Bigg]. \qquad (16)\end{aligned}$$

Combining this result with eq. (9), we obtain

$$\begin{aligned}\left(\frac{e\sigma}{\varepsilon_r\varepsilon_0 kT}\right)^2 = \kappa^2\Bigg[& \mathrm{e}^{y_0} + \mathrm{e}^{-y_0} - 2 \\ & + \frac{r}{2a}\int_0^a (\mathrm{e}^{-y_0+y(x')} \\ & + \mathrm{e}^{y_0-y(x')} - 2)\,\mathrm{d}x'\Bigg]. \qquad (17)\end{aligned}$$

Equation (17) is the required relationship between y_0 and σ. The second term in the brackets on the right-hand side of eq. (17) represents the contribution from rodlike zwitterions. Calculation of y_0 as a function of C_1 and C_z for given σ via eq. (17) requires $y(x)$, which is obtained numerically from the solution to eq. (8). Figures 3 and 4, respectively, show some results of the calculation of the surface potential ψ_0 as a function of the rod length a and the concentration C_z of zwitterions.

In order to see the behavior of rodlike zwitterions in more detail, we derive approximate analytic expressions for the relationship between y_0 and σ. Some limiting solutions can be derived from eqs. (16) or (17) without numerical calculations, as will be shown below. Consider first the

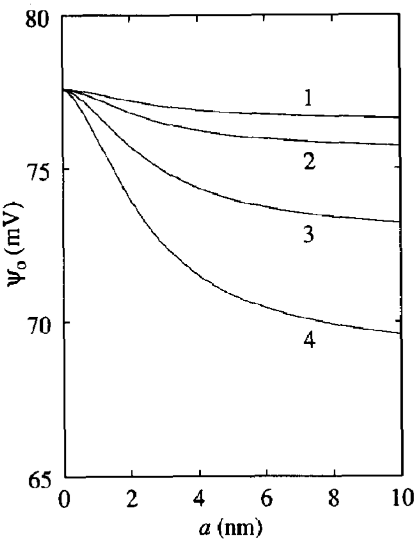

Fig. 3. Surface potential ψ_0 of a plate immersed in a mixed solution of a univalent electrolyte of concentration $C_1 = 0.1$ *M* and rodlike zwitterions of length *a* and concentration C_z as a function of *a* for several values of C_z. Calculated with $\sigma = 0.08$ C/m^2, $T = 298.15$ K, and $\varepsilon_r = 78.5$. Curves: 1, $C_z = 0.01$ *M*; 2, $C_1 = 0.02$ *M*; 3, $C_1 = 0.05$ *M*; and 4, $C_1 = 0.1$ *M*.

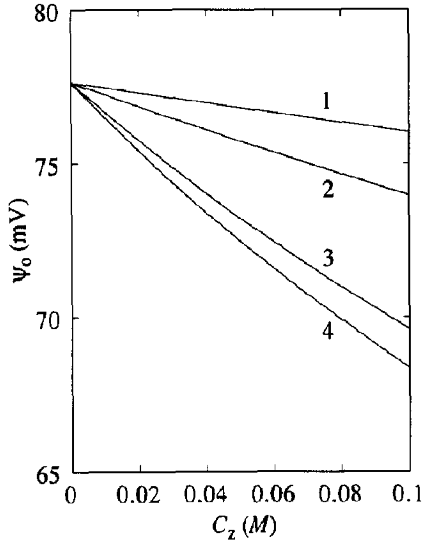

Fig. 4. Surface potential ψ_0 of a plate immersed in a mixed solution of a univalent electrolyte of concentration $C_1 = 0.1$ *M* and rodlike zwitterions of length *a* and concentration C_z as a function of C_z for several values of *a*. Calculated with $\sigma = 0.08$ C/m^2, $T = 298.15$ K, and $\varepsilon_r = 78.5$. Curves: 1, $a = 1$ nm; 2, $a = 2$ nm; 3, $a = 5$ nm; and 4, a = 10 nm.

limiting case of small *a*. In this case one may expand $\exp(\pm y(x))$ around $x = 0$ in the integrand of eq. (16) to give

$$\mathrm{e}^{\pm y(x)} = \mathrm{e}^{\pm y_0}\left[1 \pm \left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=0} x + \frac{1}{2}\left\{\left(\left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=0}\right)^2 \pm \left.\frac{\mathrm{d}^2y}{\mathrm{d}x^2}\right|_{x=0}\right\}x^2 + \cdots\right] \tag{18}$$

Substituting eq. (18) into eq. (16) yields

$$\left(\left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=0}\right)^2 = \kappa^2\left[\mathrm{e}^{y_0} + \mathrm{e}^{-y_0} - 2 + \frac{r}{6}\left(\left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=0}\right)^2 a^2\right], \tag{19}$$

or

$$\left(\left.\frac{\mathrm{d}y}{\mathrm{d}x}\right|_{x=0}\right)^2 = \frac{\kappa^2}{1 - \frac{r}{6}(\kappa a)^2}(\mathrm{e}^{y_0} + \mathrm{e}^{-y_0} - 2) \approx \kappa^2\left[1 + \frac{r}{6}(\kappa a)^2\right](\mathrm{e}^{y_0} + \mathrm{e}^{-y_0} - 2). \tag{20}$$

By combining with eq. (8), we thus obtain

$$\left(\frac{e\sigma}{\varepsilon_r\varepsilon_0 kT}\right)^2 = \kappa^2\left[1 + \frac{r}{6}(\kappa a)^2\right](\mathrm{e}^{y_0} + \mathrm{e}^{-y_0} - 2). \tag{21}$$

Equation (21) is valid for $\kappa a \ll 1$. For $a \to 0$, eq. (21) becomes

$$\left(\frac{e\sigma}{\varepsilon_r\varepsilon_0 kT}\right)^2 = \kappa^2(\mathrm{e}^{y_0/2} - \mathrm{e}^{-y_0/2})^2, \tag{22}$$

which agrees with the relationship between y_0 and σ for the electrolyte solution containing only univalent electrolytes. This is physically obvious because for $a \to 0$, zwitterions become neutral species so that they exert no electrostatic effects on the potential distribution. Also it follows from comparison between eqs. (21) and (22) that in the case of $\kappa a \ll 1$, the effective Debye–Hückel parameter is given by

$$\kappa_{\mathrm{eff}} = \kappa\left[1 + \frac{r}{6}(\kappa a)^2\right]^{1/2}. \tag{23}$$

Consider next the opposite limiting case of $a \to \infty$. Note that $y(x)$ should rapidly tend to zero beyond the electrical double layer (or beyond a distance of the order of $1/\kappa$ from the particle surface), i.e., $y(x) \to 0$ as $x \to \infty$, so that

$$\frac{1}{a}\int_0^a \mathrm{e}^{\pm y(x')}\,\mathrm{d}x' \to 1 \text{ as } a \to \infty. \tag{24}$$

Equation (17) thus becomes

$$\left(\frac{e\sigma}{\varepsilon_r\varepsilon_0 kT}\right)^2 = \kappa^2\left(1 + \frac{r}{2}\right)\left(\mathrm{e}^{y_0/2} - \mathrm{e}^{-y_0/2}\right)^2, \tag{25}$$

which is the relationship between y_0 and σ at $\kappa a \gg 1$. Equation (25) implies that the effective Debye–Hückel parameter is given by

$$\kappa_{\mathrm{eff}} = \kappa\left(1 + \frac{r}{2}\right)^{1/2} = \left[\frac{2000 N_A e^2 (C_1 + C_z/2)}{\varepsilon_r\varepsilon_0 kT}\right]^{1/2}. \tag{26}$$

This means that for $\kappa a \gg 1$ zwitterions behave like univalent electrolytes of concentration $C_z/2$ instead of C_z. That is, the probability of finding of one of the rod ends near the particle surface is half that for the case of point charges due to the presence of the other end.

The numerical procedure to find the relationship between ψ_0 and σ on the basis of eqs. (8), (11), (12) and (17), involving numerical integration and iteration, is quite tedious. We give below a simple method to obtain an approximate relationship between ψ_0 and σ. In the iteration procedure, the zeroth-order solution is the one for the case of no divalent cations. The next-order solution is obtained by replacing $y(x)$ in eq. (17) by the potential distribution $y_1(x)$ for the case of $C_z = 0$, which is given by

$$y_1(x) = 2\ln\left[\frac{1 + \gamma\exp(-\kappa x)}{1 - \gamma\exp(-\kappa x)}\right], \tag{27}$$

with

$$\gamma = \frac{\exp(y_0/2) - 1}{\exp(y_0/2) + 1}. \tag{28}$$

Substituting eq. (27) into eq. (17) and integrating, we obtain

$$\left(\frac{e\sigma}{\varepsilon_r\varepsilon_0 kT}\right)^2 = \kappa^2\left[\left(1 + \frac{r}{2}\right)\left(\mathrm{e}^{y_0/2} - \mathrm{e}^{-y_0/2}\right)^2 + \frac{2r}{\kappa a}\left\{\mathrm{e}^{y_0}\left(\frac{1}{1+\gamma} - \frac{1}{1+\gamma\,\mathrm{e}^{-\kappa a}}\right) + \mathrm{e}^{-y_0}\left(\frac{1}{1-\gamma} - \frac{1}{1-\gamma\,\mathrm{e}^{-\kappa a}}\right)\right\}\right]. \tag{29}$$

Equation (29) is a transcendental equation for y_0. The solution of eq. (29) can easily be obtained numerically for given values of σ, C_1, and C_z. Eq. (29) is found to provide a quite accurate relationship between y_0 and σ for practical purposes. The reason for this is that the solution to eq. (29) yields correct limiting forms both at $\kappa a \gg 1$ and $\kappa a \ll 1$, i.e., eqs. (21) and (25).

Finally we give below an approximate explicit expression for ψ_0 applicable for small y_0 obtained by linearizing eq. (29) with respect to ψ_0, viz.,

$$\psi_0 = \frac{\sigma}{\varepsilon_r\varepsilon_0\kappa}\,\frac{1}{\left[1 + \frac{r}{2} - \frac{r}{\kappa a}\left\{1 - \mathrm{e}^{-\kappa a} - \frac{1}{4}\left(1 - \mathrm{e}^{-2\kappa a}\right)\right\}\right]^{1/2}}. \tag{30}$$

In the limit of small κa, we have

$$\psi_0 = \frac{\sigma}{\varepsilon_r\varepsilon_0\kappa}\,\frac{1}{\left[1 + \frac{r}{6}(\kappa a)^2\right]^{1/2}}. \tag{31}$$

In the opposite limit of large κa, eq. (24) reduces to

$$\psi_0 = \frac{\sigma}{\varepsilon_r \varepsilon_0 \kappa} \frac{1}{\left(1 + \frac{r}{2}\right)^{1/2}}. \qquad (32)$$

We again see that in the limit of small κa, the effective Debye–Hückel parameter is given by eq. (23) and that in the limit of large κa, rodlike zwitterions behave like univalent electrolytes of concentration $C_z/2$ and the effective Debye–Hückel parameter is given by eq. (26).

Acknowledgment

One of us (H.O.) acknowledges SUT Special Grant for Research Promotion 1992.

References

1 E.J.W. Verwey and J.Th.G. Overbeek, Theory of the stability of lyophobic colloids (Elsevier, Amsterdam, 1948).
2 S. Carnie and McLaughlin, Biophys. J. 44 (1983) 325.
3 H. Ohshima and S. Ohki, J. Colloid Interface Sci., 142 (1991) 596.