Hiroyuki Ohshima

Faculty of Pharmaceutical
Sciences and Institute
of Colloid and Interface Science,
Science University of Tokyo,
Tokyo, Japan

Electrophoretic mobility of a charged spherical colloidal particle covered with an uncharged polymer layer

A general expression is derived for the electrophoretic mobility of a spherical charged colloidal particle covered with an uncharged polymer layer in an electrolyte solution in an applied electric field for the case where the particle zeta potential is low. It is assumed that electrolyte ions as well as water molecules can penetrate the polymer layer. Approximate analytic expressions for the electrophoretic mobility of particles carrying low zeta potentials are derived for the two extreme cases in which the particle radius is very large or very small.

1 Introduction

The motion of charged colloidal particles in an applied electric field is called particle electrophoresis [1–4]. The electrophoretic mobility (*i.e.*, the particle velocity per unit applied electric field) of a charged colloidal particle depends on the zeta potential of the particle. The zeta potential ζ is defined as the potential at the plane where the liquid velocity relative to the particle is zero. This plane, which is called the slipping plane or shear plane, does not necessarily coincide with the particle surface. Only if the slipping plane is located at the particle surface, the zeta potential ζ becomes equal to the particle surface potential Ψ_o.

The most widely employed formula relating the electrophoretic mobility μ of a colloidal particle to its zeta potential ζ is Smoluchowski's formula [1]:

$$\mu = \frac{\varepsilon_r \varepsilon_o}{\eta} \zeta \qquad (1)$$

where ε_r and η are, respectively, the relative permittivity and the viscosity of the electrolyte solution and ε_o is the permittivity of a vacuum. Smoluchowski's equation (1) is the correct limiting mobility equation for very large particles and is valid irrespective of the shape of the particle provided that the dimension of the particle is much larger than the Debye length $1/\kappa$ and thus the particle surface can be considered to be locally planar. For a sphere with radius a, this condition is expressed by $\kappa a \gg 1$. The electrophoretic mobility of very small spheres ($\kappa a \ll 1$), on the other hand, is given by Hückel's equation [2], *viz.*,

Correspondence: Professor Dr. Hiroyuki Ohshima, Faculty of Pharmaceutical Sciences, Science University of Tokyo, 12 Ichi-gaya Funagawara-machi, Shinjuku-ku, Tokyo 162-0826, Japan
E-mail: ohshima@ps.kagu.sut.ac.jp
Fax: +81-3-3268-3045

$$\mu = \frac{2\varepsilon_r \varepsilon_o}{3\eta} \zeta \qquad (2)$$

which differs from Smoluchowski's equation (1) by a factor of 2/3. Henry [3] derived a general mobility formula for a spherical particle of radius a that is applicable for low zeta potentials and all values of κa.

The above Eqs. (1) and (2) can be employed for hard particles with no surface structures. There are, however, other types of colloidal particles than hard particles. Colloidal particles covered with polymers are an example. Coating of colloidal particles with polymers is an efficient method to stabilize suspensions of colloidal particles. Colloidal particles found in biological systems such as cells also have surfaces covered with polymers. Colloidal particles coated with a layer of polymers or polyelectrolytes are termed soft particles. The author has developed a theory of electrophoresis of soft particles and derived approximate analytic expressions for the mobility of soft particles for the case where the particles are covered with a layer of polyelectrolytes, *i.e.*, charged polymers [5–11]. This theory unites the electrophoresis theories of hard particles [1–4] and of polyelectrolytes [12], since a soft particle tends to a hard particle in the absence of the polymer layer and to a polyelectrolyte in the absence of the particle core. A number of electrophoresis measurements have been carried out on various types of soft particles [13–26], which include hydrogel coated latex particles [13–16] and biological cells [17–25], showing that the electrophoretic behaviors of these particles can be explained well by the electrophoresis theory of soft particles.

In the present paper we treat the case of a soft colloidal particle consisting of a charged core covered with a layer of ion-penetrable uncharged polymers and derive approximate mobility expressions for the two extreme cases of very large or very small particles corresponding to Eqs. (1) and (2).

2 Fundamental electrokinetic equations

Notation

a	radius of the core of a soft particle
b	radius of a soft particle (the particle core plus the polymer layer)
d	thickness of the polymer layer, $d = b - a$
e	elementary electric charge
E	applied electric field
$G(r)$	function defined by Eq. (13)
$h(r)$	function defined by Eq. (6)
k	Boltzmann's constant
L_1-L_4	functions defined by Eqs. (17)–(20)
L	differential operator defined by Eq. (12)
$n_i^{(0)}$	Equilibrium concentration (number density) of the i-th ionic species
n_i^∞	bulk concentration (number density) of the i-th ionic species
T	absolute temperature
u(r)	liquid velocity
U	particle velocity
y	scaled equilibrium electric potential
z_i	valence of the i-th ionic species
ε_r	relative permittivity of the electrolyte solution
ε_o	permittivity of a vacuum
$\phi_i(r)$	function defined by Eq. (7)
γ	frictional coefficient of the forces exerted by the polymer segments on the liquid flow
η	viscosity of the electrolyte solution
κ	Debye-Hückel parameter
λ	$= (\gamma/\eta)^{1/2}$
λ_i	drag coefficient of the i-th ionic species
μ	electrophoretic mobility
$\mu_i(\mathbf{r})$	electrochemical potential of the i-th ionic species
$\Psi^{(0)}$	equilibrium electric potential
ζ	zeta potential
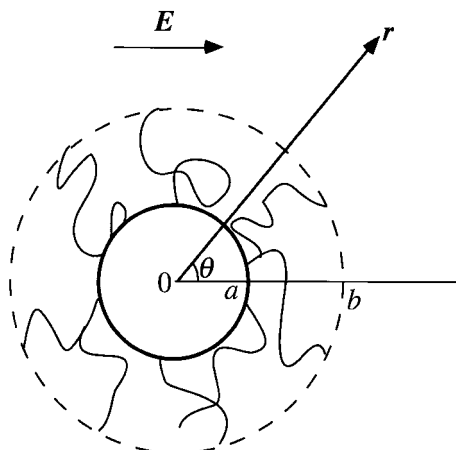
Figure 1. A spherical soft particle composed of a charged core covered with an uncharged polymer layer moving steadily with velocity U in an applied electric field E. a, radius of the particle core; d, thickness of the polymer layer covering the particle core. $b = a + d$.

Consider a charged spherical colloidal particle covered with an uncharged polymer layer moving with a velocity U in a liquid containing a general electrolyte in an applied electric field E. We assume that the charged particle core of radius a is coated with an ion-penetrable layer of uncharged polymers with a thickness d. The polymer-coated particle has thus an inner radius a and an outer radius $b \equiv a + d$ (Fig. 1). The origin of the spherical polar coordinate system (r, θ, φ) is held fixed at the center of the particle core and the polar axis ($\theta = 0$) is set parallel to E. Let the electrolyte be composed of N ionic mobile species of valence z_i, bulk concentration (number density) n_i^∞, and drag coefficient λ_i ($i = 1, 2, \ldots, N$). We assume that electrolyte ions as well as water molecules can penetrate the polymer layer, which corresponds to not very high densities of polymer segments in the polymer layer, and adopt the model of Debye-Bueche [27] in which the polymer segments are regarded as resistance centers distributed in the polymer layer, exerting frictional forces $-\gamma u$ on the liquid flowing in the polymer layer, where u is the liquid velocity and γ is the frictional coefficient, which is assumed to be constant across the polymer layer.

The other assumptions in our analysis are as follows. (i) The Reynolds numbers of the liquid flows outside and inside the polymer layer are small enough to ignore inertial terms in the Navier-Stokes equations and the liquid can be regarded as incompressible. (ii) The applied field E is weak so that the particle velocity U is proportional to E and terms of higher order in E may be neglected. (iii) The slipping plane is located on the particle core (at $r = a$). (iv) No electrolyte ions can penetrate the particle core.

(v) The polymer layer is permeable to mobile charged species. (vi) The relative permittivity ε_r takes the same value both inside and outside the polymer layer.

The fundamental electrokinetic equations, *i.e.*, the Navier-Stokes equations combined with the Poisson equation, can be expressed in terms of the liquid velocity **u(r)** at position **r** relative to the particle (**u(r)** $\rightarrow$ **–U** as $r \rightarrow \infty$) and the deviation $d\mu_i(\mathbf{r})$ of the electrochemical potential $d\mu_i(\mathbf{r})$ of the *i*-th ionic species due to the applied field **E**. These equations are given by [5]

$$\eta \nabla \times \nabla \times \nabla \times \mathbf{u} + \gamma \nabla \times u = \sum_{i=1}^{N} \nabla \delta n_i \times \nabla n_i^{(0)} \quad a < r < b \quad (3)$$

$$\eta \nabla \times \nabla \times \nabla \times \mathbf{u} = \sum_{i=1}^{N} \nabla \delta n_i \times \nabla n_i^{(0)} \quad r > b \quad (4)$$

and

$$\nabla \left(n_i^{(0)} \mathbf{u} - \frac{1}{\lambda} n_i^{(0)} \nabla \delta \mu_i \right) = 0 \quad (5)$$

where $n_i^{(0)}$ is the equilibrium concentration (number density) of the *i*-th ionic species and a function of $r = |\mathbf{r}| \left(n_i^{(0)} \rightarrow n_i^{\infty} \text{ as } r \rightarrow \infty \right)$.

Further, symmetry considerations permit us to write [5, 14]

$$\mathbf{u}(\mathbf{r}) = \left(-\frac{2}{r} h(r) E \cos\theta, \frac{1}{r} \frac{d}{dr} (rh(r)) E \sin\theta, 0 \right) \quad (6)$$

$$\delta \mu_i(\mathbf{r}) = -z_i e \phi_i(r) E \cos\theta \quad (7)$$

where $E = |\mathbf{E}|$. Equations (3)–(5) can then be rewritten in terms of h and ϕ_i as

$$L(Lh - \lambda^2 h) = G(r) \quad a < r < b \quad (8)$$

$$L(Lh) = G(r) \quad r > b \quad (9)$$

$$L\phi_i = \frac{dy}{dr} \left(z_i \frac{d\phi_i}{dr} - \frac{2\lambda_i}{e} \frac{h}{r} \right) \quad (10)$$

with

$$\lambda = (\gamma/\eta)^{1/2} \quad (11)$$

$$L \equiv \frac{d}{dr} \frac{1}{r^2} \frac{d}{dr} r^2 = \frac{d^2}{dr^2} + \frac{2}{r} \frac{d}{dr} - \frac{2}{r^2} \quad (12)$$

$$G(r) = -\frac{e}{\eta r} \frac{dy}{dr} \sum_{i=1}^{N} z_i^2 n_i^{\infty} \exp(-z_i y) \phi_i \quad (13)$$

where

$$y(r) = \frac{e \psi^{(0)}(r)}{kT} \quad (14)$$

is the scaled equilibrium potential outside the particle core, k is the Boltzmann's constant, and T is the absolute temperature.

The boundary conditions for the above electrokinetic equations are as follows. (i) **u** = 0 at $r = a$, (ii) the normal and tangential components of **u** are continuous at $r = b$,

(iii) the normal and tangential components of the stress tensor are continuous at $r = b$. (iv) In the stationary state the net force acting on the particle (the particle core plus the polymer layer) or an arbitrary volume enclosing the particle must be zero.

3 General mobility expression

The electrophoretic mobility $\mu = U/E$ (where $U = |\mathbf{U}|$) can be calculated from [5, 10]

$$\mu = 2 \lim_{r \to \infty} \frac{h(r)}{r} \quad (15)$$

with the result that

$$\mu = \frac{b^2}{9} \int_b^{\infty} \left[3 \left(1 - \frac{r^2}{b^2} \right) - \frac{2L_2}{L_1} \left(1 - \frac{r^3}{b^3} \right) \right] G(r) dr +$$
$$+ \frac{2L_3}{3\lambda^2 L_1} \int_a^{\infty} \left(1 + \frac{r^3}{2b^3} \right) G(r) dr -$$
$$- \frac{2}{3\lambda^2} \int_a^b \left[1 - \frac{3a}{2\lambda^2 b^3 L_1} \{ (L_3 + L_4 \lambda r) \cosh[\lambda(r - a)] - \right.$$
$$\left. - (L_4 + L_3 \lambda r) \sinh[\lambda(r - a)] \} \right] G(r) dr \quad (16)$$

where

$$L_1 = \left(1 + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} - \frac{3a^2}{2\lambda^2 b^4} \right) \cosh[\lambda(b - a)] -$$
$$- \left(1 - \frac{3a^2}{2b^2} + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} \right) \frac{\sinh[\lambda(b - a)]}{\lambda b} \quad (17)$$

$$L_2 = \left(1 + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} \right) \cosh[\lambda(b - a)] +$$
$$+ \frac{3a^2}{2b^2} \frac{\sinh[\lambda(b - a)]}{\lambda b} - \frac{3a}{2\lambda^2 b^3} \quad (18)$$

$$L_3 = \cosh[\lambda(b - a)] - \frac{\sinh[\lambda(b - a)]}{\lambda b} - \frac{a}{b} \quad (19)$$

$$L_4 = \sinh[\lambda(b - a)] - \frac{\cosh[\lambda(b - a)]}{\lambda b} + \frac{\lambda a^2}{3b} + \frac{2\lambda b^2}{3a} + \frac{1}{\lambda b} \quad (20)$$

Further, we assume that the equilibrium potential $\Psi^{(0)}(r)$ satisfies the Poisson-Boltzmann equation. If the particle zeta potential ζ is low, then the Poisson-Boltzmann equation may be linearized to give

$$\frac{d^2 \psi^{(0)}}{dr^2} + \frac{2}{r} \frac{d\psi^{(0)}}{dr} = \kappa^2 \psi^{(0)} \quad (21)$$

where κ is the Debye-Hückel parameter defined by

$$\kappa = \left(\frac{1}{\varepsilon_r \varepsilon_0 kT} \sum_{i=1}^{N} z_i^2 e^2 n_i^\infty \right)^{1/2} \qquad (22)$$

The Debye length, which expresses the thickness of the electrical double layer, is $1/\kappa$. The solution to Eq. (21) is given by

$$\psi^{(0)}(r) = \zeta \frac{a}{r} \exp[-\kappa(r-a)] \qquad (23)$$

Also, in the low zeta potential approximation, the function $\phi_i(r)$ is given by

$$\phi_i(r) = r + \frac{a^2}{2r^2} \qquad (24)$$

Thus, $G(r)$ in Eq. (16) becomes

$$G(r) = -\frac{\varepsilon_r \varepsilon_0 \kappa^2}{\eta} \left(1 + \frac{a^3}{2r^3} \right) \frac{d\psi^{(0)}}{dr} \qquad (25)$$

Equation (16) as combined with Eqs. (23) and (25) is the required general expression for the electrophoretic mobility μ of a charged spherical colloidal particle covered with a layer of uncharged polymer layer for the case where the zeta potential is low.

4 Approximate mobility expressions

We now derive analytic approximate mobility expressions for the two extreme cases: (a) very large particles with $a \to \infty$ (*i.e.*, $\kappa a \gg 1$ and $\lambda a \gg 1$) and (b) vary small particles with $\kappa a \ll 1$ (λa may be arbitrary) from Eqs. (16) (with Eqs. (23) and (25)). The results are given below.

(a) The case $a \to \infty$ (*i.e.*, $\kappa a \gg 1$ and $\lambda a \gg 1$). In this case the electrophoretic mobility μ can be expressed as

$$\mu = \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} H_1(\kappa d, \lambda d) \qquad (26)$$

where

$$H_1(\kappa d, \lambda d) =$$

$$\frac{1}{1-(\lambda/\kappa)^2} \left[\frac{1}{\cosh(\lambda d)} - \frac{\lambda}{\kappa} \exp(-\kappa d) \left\{ \frac{\lambda}{\kappa} + \tanh(\lambda d) \right\} \right] \qquad (27)$$

Note that Eq. (26) (as combined with Eq. 27) agrees with a plate-like charged particle covered with an uncharged polymer layer [6, 29]. The function $H_1(\kappa d, \lambda d)$ is the ratio of the electrophoretic mobilities of very large particles in the presence and absence of the polymer layer. That is, $H_1(\kappa d, \lambda d)$ is a correction factor for Smoluchowski's formula [1] due to the presence of the polymer layer. Figure 2 shows the function $H_1(\kappa d, \lambda d)$ as a function of κd and λd. It is seen that H_1 decreases with increasing κd and/or λd and takes values between 0 and 1, demonstrating that the presence of the polymer layer always decreases the electrophoretic mobility.

Consider several further limiting cases for Eq. (26). In the limit $\lambda \to 0$, in which case the polymer layer vanishes, H_1 tends to 1 so that Eq. (26) reduces to Smoluchowski's formula (1), as expected, *viz.*,
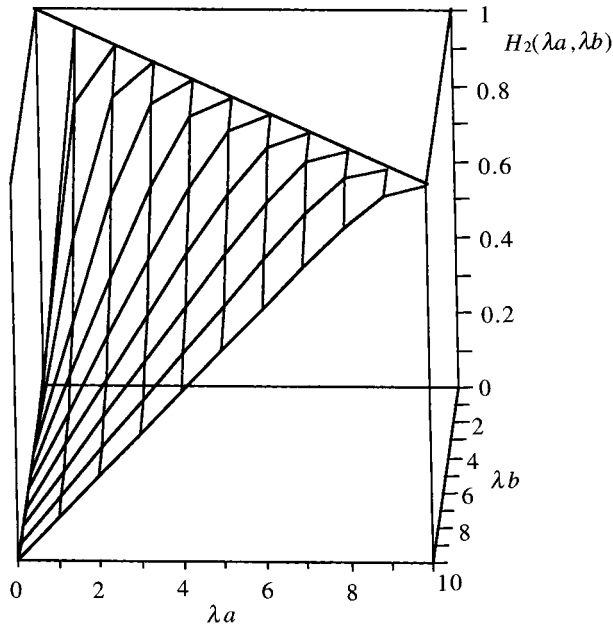
$$\mu \to \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \quad \text{as } \lambda \to 0 \qquad (28)$$

In the opposite limit $\lambda \to \infty$, H_1 tends to $\exp(-\kappa d)$ so that Eq. (25) becomes

$$\mu \to \frac{\varepsilon_r \varepsilon_0 \zeta}{\eta} \exp(-\kappa d) \quad \text{as } \lambda \to \infty \qquad (29)$$
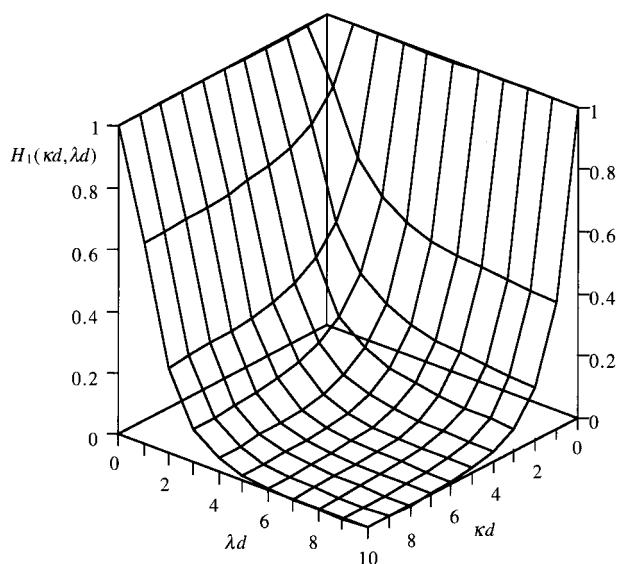
Figure 2. The ratio $H_1(\kappa d, \lambda d)$ of the electrophoretic mobilities of a charged spherical colloidal particle with $a \to \infty$ in the presence and absence of an uncharged polymer layer as a function of κd and λd.

Figure 3. The ratio $H_2(\lambda a,\ \lambda b)$ of the electrophoretic mobilities of a charged spherical colloidal particle with $\kappa a \ll 1$ in the presence and absence of an uncharged polymer layer as a function of λa and λb ($a \leq b$).

This corresponds to the situation in which the polymer layer becomes rigid so that the slipping plane is shifted outward from $r = a$ to $r = b$. At $r = b$ (*i.e.*, at the front edge of the polymer layer), the electric potential is

$$\psi^{(0)}(r) = \zeta \exp(-\kappa d) \tag{30}$$

which is obtained from Eq. (23) when $\kappa a \gg 1$. The electric potential given by Eq. (30) corresponds to a zeta potential of a particle covered with a polymer layer of thickness d with $\lambda \to \infty$.

(b) The case of $\kappa a \ll 1$ (λa may be arbitrary). In this case the electrophoretic mobility is given by

$$\mu = \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta} H_2(\lambda a, \lambda b) \tag{31}$$

where

$$H_2(\lambda a, \lambda b) = \frac{a}{b}\left(\frac{L_2}{L_1} + \frac{3L_3}{2\lambda^2 b^2 L_1}\right) \tag{32}$$

where L_1, L_2 and L_3 are given by Eqs. (17)–(19). The function $H_2(\lambda a, \lambda b)$ is the ratio of the electrophoretic mobilities of very small particles in the presence and absence of the polymer layer. That is, $H_2(\lambda a, \lambda b)$ is a correction factor to Hückel's formula (2) due to the presence of the polymer layer. Note that Eq. (31) can be directly derived from the condition of balance between the electric force and the drag force acting on the particle, by using an expression for the drag force acting on a particle covered with an

uncharged polymer layer derived by Masliyah *et al.* [30]. Figure 3 shows the function $H_2(\lambda a, \lambda b)$ as a function of λa and λb. As in the case (a), the correction factor H_2 takes values between 0 and 1, implying that the presence of the polymer layer always decreases the electrophoretic mobility.

Consider several further limiting cases. In the limit $a \to b$, the polymer layer vanishes so that $H_2(\lambda a, \lambda b) \to 1$ and Eq. (31) tends back to Hückel's formula (2), *viz.*,

$$\mu \to \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta} \quad \text{as } a \to b \tag{33}$$

In the limit $\lambda \to 0$, the polymer layer also vanishes so that $H_2(\lambda a, \lambda b) \to 1$ and Eq. (31) becomes

$$\mu \to \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta} \quad \text{as } \lambda \to 0 \tag{34}$$

In the opposite limit $\lambda \to \infty$, $H_2(\lambda a, \lambda b) \to a/b$ and Eq. (30) becomes

$$\mu \to \frac{2\varepsilon_r\varepsilon_0\zeta}{3\eta}\ \frac{a}{b} \quad \text{as } \lambda \to \infty \tag{35}$$

This corresponds to the situation in which the polymer layer becomes rigid so that the slipping plane is shifted outward from $r = a$ to $r = b$. At $r = b$ (*i.e.*, at the front edge of the polymer layer), the electric potential is

$$\psi^{(0)}(b) = \zeta\frac{a}{b} \tag{36}$$

which is obtained from Eq. (23) when $\kappa \to 0$ and corresponds to a zeta potential of a particle covered with a polymer layer of thickness $d = b - a$ with $\lambda \to \infty$.

5 Concluding remarks

We have derived the general mobility expression (16) (as combined with Eqs. 23 and 25) for a charged spherical colloidal particle covered with an uncharged polymer layer for the case of low zeta potentials. On the basis of this expression, we have derived approximate analytic expressions (26) and (31) for the mobility for the limiting cases where the particle radius is very large (case (a)) and very small (case (b)). We have introduced two functions H_1 and H_2, which are the ratio of the electrophoretic mobilities in the presence and absence of the polymer layer for the respective cases (a) and (b). The functions H_1 and H_2, both of which take values between 1 and 2, show how the presence of the uncharged polymer layer decreases the magnitude of the electrophoretic mobility for cases (a) and (b). Note finally that there is a significant difference between the electrophoretic mobility of charged polymer-coated particles developed in previous papers [5–11] and that of uncharged polymer-coated parti-

cles. As demonstrated in the present paper, the mobility is proportional to the zeta potential when the polymer layer is uncharged, while the concept of zeta potential loses its meaning for charged polymer-coated particles provided that the thickness of the polymer layer is much greater than $1/\kappa$, which is the case for typical soft particles.

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6 References

[1] von Smoluchowski, M., *Electrische Endosmose und Strömungsströme*, in: Greatz, L., (Ed.), Handbuch der Elektrizität und des Magnetismus, Barth, Leipzig 1921, Vol. 2, p. 366.

[2] Hückel, E., *Phys. Z*. 1924, *25*, 204–214.

[3] Henry, D. C., *Proc. R. Soc. London, Ser. A* 1931, *133*, 106–129.

[4] Ohshima, H., in: Ohshima, H., Furusawa, K. (Eds.), *Electrical Phenomena at Interfaces,* Marcel Dekker, New York 1998, Chapter 2.

[5] Ohshima, H., *J. Colloid Interface Sci*. 1994, *163*, 474–483.

[6] Ohshima, H., *Adv. Colloid Interface Sci*. 1995, *62*, 189–235.

[7] Ohshima, H., *Colloids and Surfaces A: Physicochemical and Engineering Aspects* 1995, *103*, 249–255.

[8] Ohshima, H., *Electrophoresis* 1995, *16*, 1360–1363.

[9] Ohshima, H., *Colloid Polym Sci*. 1997, *275*, 480–485.

[10] Ohshima, H., *J. Colloid Interface Sci*. 2000, *228*, 190–193.

[11] Ohshima, H., *Colloid Polym Sci*. 2001, *279*, 88–91.

[12] Hermans J. J., Fujita, H., *Koninkl. Ned. Akad. Wetenschap. Proc*. 1955, *B58*, 182–187.

[13] Ohshima, H., Makino, K., Kato, T., Fujimoto, K, Kondo, T., Kawaguchi, H., *J. Colloid Interface Sci*. 1993, *159*, 512–514.

[14] Makino, K., Taki, T., Ogura, M., Handa, S., Nakajima, M., Kondo, T., Ohshima, H., *Biophys. Chem*. 1993, *47*, 261–265.

[15] Makino, M., in: Ohshima, H., Furusawa, K. (Eds.), *Electrical Phenomena at Interfaces,* Marcel Dekker, New York 1998, Chapter 31.

[16] Rasmusson, M., Vincent, B., Marston, N., *Colloid Polym. Sci*. 2000, *278*, 253–258.

[17] Makino, K., Ikekita, M., Kondo, T., Tanuma, S., Ohshima, H., *Colloid Polym. Sci*. 1994, *272*, 487–492.

[18] Mazda, T., Makino, K., Ohshima, H., *Colloids and Surfaces B: Biointerfaces* 1995, *5*, 75–80; Erratum *ibid*. 1998, *10*, 303.

[19] Takashima S. H., Morisaki, H., *Colloids and Surfaces B: Biointerfaces* 1997, *9*, 205–212.

[20] Bos, R., van der Mei, H. C., Busscher, H. J., *Biophys. Chem*. 1998, *74*, 251–255.

[21] Kondo, T., in: Ohshima, H., Furusawa, K. (Eds.), *Electrical Phenomena at Interfaces,* Marcel Dekker, New York 1998, Chapter 30.

[22] Torimura, M., Ito, S., Kano, K., Ikeda, T., Esaka, Y., Ueda, T., *J. Chromatogr. B* 1999, *721*, 31–37.

[23] Morisaki, H., Nagai, S., Ohshima, H., Ikemoto, E., Kogure, K., *Microbiology* 1999, *145*, 2797–2802.

[24] Kiers, P. J. M., Bos, R., van der Mei, H. C., Busscher, H. J., *Microbiology* 2001, *147*, 757–762.

[25] Hayashi, H., Tsuneda, S., Hirata, A., Sasaki, H., *Colloids and Surfaces B: Biointerfaces* 2001, *22*, 149–157.

[26] Larsson, A., Rasmusson, M., Ohshima, H., *Carbohydr. Res.* 1999, *317*, 223–228.

[27] Debye, P., Bueche, A., *J. Chem. Phys.* 1948, *16*, 573–579.

[28] Ohshima, H., Healy, T. W., White, L. R., *J. Chem. Soc. Faraday Trans. 2* 1983, *79*, 1613–1628.

[29] Donath E., Pastuschenko, V., *Bioelectrochem. Bioenerg*. 1979, *6*, 543–554.

[30] Masliyah, J. H., Neale, G., Malysa, K., van de Ven, T. G. M., *Chem. Sci*. 1987, *42*, 245–253.