Colloid Polym Sci 275:480–485 (1997)

ORIGINAL CONTRIBUTION

H. Ohshima

Electrophoretic mobility of cylindrical soft particles

Received: 29 August 1996
Accepted: 7 November 1996

Prof. Dr. H. Ohshima (✉)
Faculty of Pharmaceutical Sciences
Science University of Tokyo
12 Ichigaya Funagawara-machi
Shinjuku-ku, Tokyo 162, Japan

Abstract A general theory for the electrophoresis of a cylindrical soft particle (i.e., a cylindrical hard colloidal particle coated with a layer of ion-penetrable polyelectrolytes) in an electrolyte solution in an applied transverse or tangential electric field is proposed. This theory unites two different electrophoresis theories for cylindrical hard particles and for cylindrical polyelectrolytes. That is, the general mobility expression obtained in this paper tends to the mobility expression for a cylindrical hard particle for the case where the polyelectrolyte layer is absent or the frictional coefficient in the polyelectrolyte layer becomes infinity, whereas it tends to that for a cylindrical polyelectrolyte in the absence of the particle core. Simple approximate analytic mobility expressions are also presented.

Key words Electrophoretic mobility – cylindrical particle – soft particle

Introduction

In previous papers [1–3] we have proposed a theory of electrophoresis of a spherical soft colloidal particle (i.e., a spherical particles covered with a layer of polyelectrolytes). This theory unites the previous theories of the electrophoresis of spherical hard colloidal particles, of spherical polyelectrolytes, and of plate-like soft particles. In the present paper we develop the above theory to derive mobility expressions for cylindrical soft particles.

Theory

Cylinder in a transverse field

Consider an infinitely long cylindrical colloidal particle moving with a velocity **U** in a liquid containing a general electrolyte in an applied electric field **E**. The origin of the cylindrical polar coordinate system (r, θ, ϕ) is held fixed at the particle. In this section we treat the case where the cylinder axis coincides with the z-axis and the polar axis $(\theta = 0)$ is set parallel to **E** so that **E** is perpendicular to the cylinder axis (Fig. 1). We assume that the particle core of radius a is coated with an ion-penetrable layer of polyelectrolytes with a thickness d. The polyelectrolyte-coated particle has thus an inner radius a and an outer radius $b \equiv a + d$. The relative permittivity ε_r takes the same value both inside and outside the polyelectrolyte layer. 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 also assume that fixed charges are distributed with a density of $\rho_{\text{fix}}(r)$, which is a cylindrically symmetrical function of $r = |\mathbf{r}|$ only. We adopt the model of Debye–Bueche [4] that the polymer segments are regarded as resistance centers distributed uniformly in the polyelectrolyte layer, exerting frictional forces on the liquid flowing in the polyelectrolyte layer. Here we denote the frictional coefficient by γ.

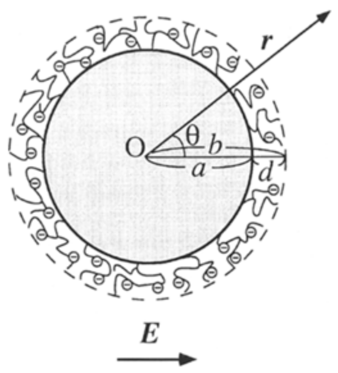

Fig. 1 A cylindrical soft particle moving in a transverse electric field $\boldsymbol{E}$. a = radius of the particle core. d = thickness of the polyelectrolyte layer covering the particle core. $b = a + d$

The fundamental electrokinetic equations are [1–3]

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

$$\eta\nabla\times\nabla\times\nabla\times\mathbf{u}=\sum_{i=1}^{N}\nabla\delta\mu_i\times\nabla n_i^{(0)},\quad r>b\,,\tag{2}$$

$$\nabla\cdot\left(n_i^{(0)}\mathbf{u}-\frac{1}{\lambda_i}n_i^{(0)}\nabla\delta\mu_i\right)=0\,.\tag{3}$$

Here $\mathbf{u}$ is the flow velocity of the liquid relative to the particle, $\delta\mu_i$ is the deviation of the electrochemical potential of the ith ionic species due to the applied electric field $\mathbf{E}$ and $n_i^{(0)}$ is the equilibrium concentration (number density) of ith ionic species. Equations (1) and (2) are essentially the Navier–Stokes equations for the liquid flows inside and outside the polyelectrolyte layer and Eq. (3) is the continuity equation for the ith ionic species. The distribution of electrolyte ions at equilibrium $n_i^{(0)}$ obeys the Boltzmann equation and the equilibrium potential $\psi_i^{(0)}$ satisfies the Poisson–Boltzmann equation, both being functions of r only, viz.,

$$n_i^{(0)}=n_i^{\infty}\exp\left(-\frac{z_ie\psi^{(0)}}{kT}\right),\tag{4}$$

$$\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}\left(r\frac{\mathrm{d}\psi^{(0)}}{\mathrm{d}r}\right)=-\frac{\rho^{(0)}(r)}{\varepsilon_r\varepsilon_0}\,,\tag{5}$$

with

$$\rho^{(0)}(r)=\begin{cases}\displaystyle\sum_{i=1}^{N}z_ien_i^{\infty}\exp\left(-\frac{z_ie\psi^{(0)}}{kT}\right)+\rho_{\mathrm{fix}}(r), & a<r<b\,,\\ \displaystyle\sum_{i=1}^{N}z_ien_i^{\infty}\exp\left(-\frac{z_ie\psi^{(0)}}{kT}\right), & r>b\,.\end{cases}\tag{6}$$

By analogy with the case of spherical particles [5, 6, 1–3], we may write [7]

$$\delta\mu_i(\mathbf{r})=-z_ie\phi_i(r)\mathbf{E}\cdot\hat{\mathbf{r}}=-z_ie\phi_i(r)E\cos\theta\,,\tag{7}$$

$$\delta\psi(\mathbf{r})=-Y(r)\mathbf{E}\cdot\hat{\mathbf{r}}=-Y(r)E\cos\theta\,,\tag{8}$$

$$\mathbf{u}(\mathbf{r})=(u_r,u_\theta,0)=\left(-\frac{h(r)}{r}E\cos\theta,\frac{\mathrm{d}h(r)}{\mathrm{d}r}E\sin\theta,0\right),\tag{9}$$

with $\hat{\mathbf{r}}=\mathbf{r}/r$ and $E=|\mathbf{E}|$. Substituting Eqs. (7–9) into Eqs. (1–3) gives

$$L\phi_i=\frac{\mathrm{d}y}{\mathrm{d}r}\left(z_i\frac{\mathrm{d}\phi_i}{\mathrm{d}r}-\frac{\lambda_i}{e}\frac{h}{r}\right),\tag{10}$$

$$L(Lh-\lambda^2h)=G(r),\quad a\le r<b\,,\tag{11}$$

$$L(Lh)=G(r),\quad r>b\,,\tag{12}$$

with

$$\lambda=(\gamma/\eta)^{1/2}\,,\tag{13}$$

where

$$L\equiv\frac{\mathrm{d}}{\mathrm{d}r}\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}r=\frac{\mathrm{d}^2}{\mathrm{d}r^2}+\frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}-\frac{1}{r^2}\tag{14}$$

is a differential operator and $G(r)$ is defined by

$$G(r)=-\frac{e}{\eta r}\frac{\mathrm{d}y}{\mathrm{d}r}\sum_{i=1}^{N}n_i^{\infty}z_i^2\exp(-z_iy)\phi_i(r)\,.\tag{15}$$

Here $y\equiv e\psi^{(0)}/kT$ is the scaled equilibrium potential. The solutions to Eqs. (10–12) must satisfy the following boundary conditions: (1) no electrolyte ions can penetrate into the particle core; (2) $\mathbf{u}=\mathbf{0}$ at $r=a$ and $\mathbf{u}\to-\mathbf{U}$ as $r\to\infty$; (3) the normal and tangential components of $\mathbf{u}(\mathbf{r})$ and the hydrodynamic stress tensor must be continuous at $r=b$; and (4) the net force acting on the particle must be zero in the stationary state.

The electrophoretic mobility, defined by $\mu_\perp=U/E$, where $U=|\mathbf{U}|$, is obtained from the solution to Eqs. (11 and 12) via

$$\mu=\lim_{r\to\infty}\frac{h(r)}{r}\tag{16}$$

(see Eq. (9)). We thus obtain the following general expression for the electrophoretic mobility $\mu_\perp$ of a cylindrical soft particle in a transverse field:

$$\begin{aligned}\mu_\perp=&\frac{H(\lambda b)}{bF(\lambda b)}h(b)+\frac{b^2}{8}\int_b^{\infty}\left[1-\frac{r^2}{b^2}\left\{1-2\ln\left(\frac{r}{b}\right)\right\}\right]G(r)\,\mathrm{d}r\\&-\frac{W}{\lambda^2F(\lambda b)}\int_b^{\infty}\left(1-\frac{r^2}{b^2}\right)G(r)\,\mathrm{d}r+\frac{1}{2\lambda^2}\int_a^{b}H(\lambda r)G(r)\,\mathrm{d}r\\&+\frac{H(\lambda b)}{2\lambda^2F(\lambda b)}\int_a^{b}\left\{1-\frac{r^2}{b^2}-F(\lambda r)\right\}G(r)\,\mathrm{d}r\end{aligned}\tag{17}$$

with

$$H(x) = x\{I_0(\lambda a)K_1(x) + K_0(\lambda a)I_1(x)\} - 1 \,, \tag{18}$$

$$F(x) = xI_1(x)\left\{K_0(\lambda a) - \frac{a^2}{b^2}K_2(\lambda a)\right\} + xK_1(x)\left\{I_0(\lambda a) - \frac{a^2}{b^2}I_2(\lambda a)\right\} , \tag{19}$$

$$W = 1 + \frac{(\lambda b)^2}{4}\left[I_2(\lambda b)K_0(\lambda a) - K_2(\lambda b)I_0(\lambda a) - \frac{a^2}{b^2}\{I_0(\lambda b)K_2(\lambda a) - K_0(\lambda b)I_2(\lambda a)\}\right] , \tag{20}$$

where $I_n(z)$ and $K_n(z)$ are, respectively, the nth order modified Bessel functions of the first and second kinds.

In Eq. (17) $h(b)$ can be obtained from the force balance on the polyelectrolyte layer, viz.,

$$h(b) = \frac{1}{\eta\lambda^2 b}\int_a^b \rho_{\text{fix}}(r)\frac{\mathrm{d}}{\mathrm{d}r}(r^2 Y)\,\mathrm{d}r \,, \tag{21}$$

which is obtained from the constraint that the net force acting on the resistance centers in the polyelectrolyte layer must be zero, i.e., the electric force acting on the fixed charges must be balanced by the frictional force. Here $Y(r)$ can be obtained as follows. From Eqs. (7 and 8) we find that

$$\delta\rho(\mathbf{r}) = \sum_{i=1}^{N} z_i e\delta n_i(\mathbf{r}) = -\varepsilon_r\varepsilon_0\Delta\delta\psi(\mathbf{r}) = \varepsilon_r\varepsilon_0 E\cos\theta\cdot LY \tag{22}$$

and

$$LY = \frac{1}{\varepsilon_r\varepsilon_0 kT}\sum_{i=1}^{N} z_i^2 e^2 n_i^{(0)}(r)\cdot(Y - \phi_i) \,. \tag{23}$$

Thus, if the double layer potential remains cylindrically symmetrical in the presence of the applied electric field (the relaxation effect is neglected), i.e., $\delta\rho(\mathbf{r}) = 0$, then it follows from Eqs. (22 and 23) that

$$LY = 0 \text{ and } Y = \phi_i \tag{24}$$

which gives

$$Y(r) = \phi_i(r) = r + \frac{a^2}{r} \,. \tag{25}$$

Thus, when $\rho_{\text{fix}}(r) = \rho_{\text{fix}}$ (=constant), Eq. (21) becomes

$$h(b) = \frac{\rho_{\text{fix}}(b^2 - a^2)}{\eta\lambda^2 b} \,. \tag{26}$$

In this case Eq. (15) reduces to

$$G(r) = -\frac{e}{\eta}\frac{\mathrm{d}y}{\mathrm{d}r}\left(1 + \frac{a^2}{r^2}\right)\sum_{i=1}^{N} n_i^\infty z_i^2 \exp(-z_i y) \,. \tag{27}$$

Approximate expressions for $\mu_\perp$

Let us consider several limiting cases of the general mobility expression (17). In the limit $a \to b$, the polyelectrolyte layer vanishes and the particle should become a rigid paricle. Indeed, in this limit Eq. (17) tends to

$$\mu_\perp = \frac{b^2}{8}\int_b^\infty \left[1 - \left(\frac{r}{b}\right)^2\left\{1 - 2\ln\left(\frac{r}{b}\right)\right\}\right]G(r)\,\mathrm{d}r \,. \tag{28}$$

Equation (28) is the general mobility expression for a cylindrical rigid particle with a radius b in a transverse field obtained in the previous paper [7], which leads to Henry's mobility formula if the potential is linearized [8]. Also, in the limit $\lambda \to \infty$, the polyelectrolyte-coated particle behaves like a rigid particle with a radius of b and the slipping plane is shifted outward from $r = a$ to $r = b$. Indeed, in this limit Eq. (17) tends to Eq. (28), although the potential distribution $\psi^{(0)}(r)$ in $G(r)$ is different from the limiting case $a \to b$, since for the case of $\lambda \to \infty$, electrolyte ions can penetrate the particle surface and the particle-fixed charges are distributed not only at $r = a$ (i.e., at the surface of the particle core) but also throughout the polyelectrolyte layer ($a < r < b$). Thus the mobility values are in general different for these two cases.

In the limit $a \to 0$, the particle core vanishes and the particle becomes a cylindrical polyelectrolyte (a porous charged cylinder) of radius b. For the case where $a \to 0$ and the polyelectrolyte is uniformly charged, i.e., $\rho_{\text{fix}}(r) = \rho_{\text{fix}}(=\text{constant})$, Eq. (17) (as combined with Eq. (26)) becomes

$$\mu_\perp = \frac{\rho_{\text{fix}}}{\eta\lambda^2} + \frac{b^2}{8}\int_b^\infty\left[1 - \left(\frac{r}{b}\right)^2\left\{1 - 2\ln\left(\frac{r}{b}\right)\right\}\right]G(r)\,\mathrm{d}r - \frac{1}{2\lambda^2}\int_0^b\left[\frac{r^2}{b^2} - \frac{rI_1(\lambda r)}{bI_1(\lambda b)}\right]G(r)\,\mathrm{d}r + \frac{1}{2\lambda^2}\left[1 - \frac{\lambda b I_0(\lambda b)}{2I_1(\lambda b)}\right]\int_b^\infty\left(1 - \frac{r^2}{b^2}\right)G(r)\,\mathrm{d}r \,. \tag{29}$$

Further, for low potentials, $\psi^{(0)}(r)$ can be explicitly obtained from the linearized Poisson–Boltzmann equations (5) (with Eq. (6)), viz.,

$$\psi^{(0)}(r) = \frac{\rho_{\text{fix}}}{\varepsilon_r\varepsilon_0\kappa^2}[1 - \kappa bK_1(\kappa b)I_0(\kappa r)], \quad 0 \le r \le b \,, \tag{30}$$

$$\psi^{(0)}(r) = \frac{\rho_{\text{fix}}}{\varepsilon_r\varepsilon_0\kappa^2}\kappa bI_1(\kappa b)K_0(\kappa r), \quad r \ge b \,, \tag{31}$$

where

$$\kappa = \left(\frac{1}{\varepsilon_r\varepsilon_0 kT}\sum_{i=1}^{N} z_i^2 e^2 n_i^\infty\right)^{1/2} \tag{32}$$

is the Debye–Hückel parameter. By substituting Eqs. (30 and 31) into the general mobility formula (17), we obtain

$$\mu_{\perp} = \frac{\rho_{\text{fix}}}{\eta\lambda^2} + \frac{\rho_{\text{fix}} b}{2\eta\kappa}\Bigg[I_1(\kappa b)K_0(\kappa b)$$

$$+ \frac{\kappa}{\kappa^2 - \lambda^2}\left\{\kappa I_0(\kappa b) - \lambda\frac{I_0(\lambda b)}{I_1(\lambda b)} I_1(\kappa b)\right\}K_1(\kappa b)\Bigg] . \quad (33)$$

If, further, $\kappa b \gg 1$ and $\lambda b \gg 1$, then Eq. (33) becomes

$$\mu_{\perp} = \frac{\rho_{\text{fix}}}{\eta\lambda^2}\left[1 + \frac{1}{2}\left(\frac{\lambda}{\kappa}\right)^2 \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\right] . \quad (34)$$

Note that replacement of 1/2 in the brackets on the right-hand side by 2/3 leads to the mobility expression for a spherical polyelectrolyte derived by Hermans and Fujita [9].

Next consider a plate-like particle, that is, the limiting case of $a \to \infty$, but the magnitude of $\lambda d = \lambda(b - a)$ is arbitrary. Then, Eq. (17) (as combined with Eq. (26)) becomes

$$\mu_{\perp} = \frac{\varepsilon_r\varepsilon_0}{\eta}\frac{1}{\cosh(\lambda d)}\left[\psi(-d) + \lambda\int_{-d}^{0}\psi(x)\sinh\{\lambda(x + d)\}\,\mathrm{d}x\right]$$

$$+ \frac{1}{\eta\lambda}\frac{1}{\cosh(\lambda d)}\int_{-d}^{0}\rho_{\text{fix}}(x)\sinh\{\lambda(x + d)\}\,\mathrm{d}x , \quad (35)$$

with $x = r - b$. Consider further the case where $\lambda d \gg 1$ and $\kappa d \gg 1$. If the electrolyte is symmetrical with a valence z and bulk concentration n^{∞} and $\rho_{\text{fix}}(r) = \rho_{\text{fix}}$ (= constant), then the potential inside the polyelectrolyte layer can be approximated by [1–3]

$$\psi(x) = \psi_{\text{DON}} + (\psi_0 - \psi_{\text{DON}})\exp(-\kappa_m|x|) \quad (36)$$

with

$$\psi_{\text{DON}} = \frac{kT}{ze}\ln\left[\frac{\rho_{\text{fix}}}{2zen^{\infty}} + \left\{\left(\frac{\rho_{\text{fix}}}{2zen^{\infty}}\right)^2 + 1\right\}^{1/2}\right] \quad (37)$$

$$\psi_0 = \frac{kT}{ze}\left(\ln\left[\frac{\rho_{\text{fix}}}{2zen^{\infty}} + \left\{\left(\frac{\rho_{\text{fix}}}{2zen^{\infty}}\right)^2 + 1\right\}^{1/2}\right]\right.$$

$$\left. + \frac{2zen^{\infty}}{\rho_{\text{fix}}}\left[1 - \left\{\left(\frac{\rho_{\text{fix}}}{2zen^{\infty}}\right)^2 + 1\right\}^{1/2}\right]\right) , \quad (38)$$

where ψ_{DON} is the Donnan potential in the polyelectrolyte layer, ψ_0 is the potential at the boundary $x = 0$ (or, $r = b$) between the polyelectrolyte layer and the surrounding solution, which we call the surface potential of the soft particle, and

$$\kappa_m = \kappa\left[1 + \left(\frac{\rho_{\text{fix}}}{2zen^{\infty}}\right)^2\right]^{1/4} \quad (39)$$

is the Debye–Hückel parameter of the polyelectrolyte layer. By substituting Eq. (36) into Eq. (35) (with $\rho_{\text{fix}}(x) = \rho_{\text{fix}}$), we obtain

$$\mu_{\perp} = \frac{\varepsilon_r\varepsilon_0}{\eta}\frac{\psi_0/\kappa_m + \psi_{\text{DON}}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{\rho_{\text{fix}}}{\eta\lambda^2} . \quad (40)$$

For low potentials, Eq. (40) becomes

$$\mu_{\perp} = \frac{\rho_{\text{fix}}}{\eta\lambda^2}\left[1 + \left(\frac{\lambda}{\kappa}\right)^2\frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\right] , \quad (41)$$

which differs from Eq. (34) by a factor 1/2 in the second term in the brackets. The reason for this is given later.

Finally, consider the case where $\lambda a \gg 1$, $\kappa a \gg 1$ (and thus $\lambda b \gg 1$, $\kappa b \gg 1$), $\lambda d = \lambda(b - a) \gg 1$, $\kappa d = \kappa(b - a) \gg 1$ and $\rho_{\text{fix}}(r) = \rho_{\text{fix}}$. In this case, Eq. (17) (with Eq. (26)) becomes

$$\mu_{\perp} = \frac{\rho_{\text{fix}}}{\eta\lambda^2} + \frac{1}{4}\int_b^{\infty}\left[(r - b)^2 + \frac{2}{\lambda}(r - b)\right]G(r)\,\mathrm{d}r$$

$$- \frac{1}{2\lambda^2}\int_a^b\{1 - \mathrm{e}^{\lambda(r-b)}\}G(r)\,\mathrm{d}r . \quad (42)$$

For the case in which the electrolyte is symmetrical with a valence z and bulk concentration n^{∞} and $\rho_{\text{fix}}(r) = \rho_{\text{fix}}$, the potential inside the polyelectrolyte layer can be approximated by Eq. (36) with Eqs. (37–39). Note that the potential is in practice equal to the Donnan potential ψ_{DON} inside the polyelectrolyte layer and varies only in the region near the boundary $r = b$ between the polyelectrolyte layer and the surrounding solution. That is, y changes most appreciably near $r = b$, in other words, $\mathrm{d}y/\mathrm{d}r$ is practically zero expect in the region near $r = b$. Then we can approximately replace $(1 + a^2/r^2)$ in the expression (27) for $G(r)$ by $(1 + a^2/b^2)$, giving

$$G(r) = -\left(1 + \frac{a^2}{b^2}\right)\frac{z^2en^{\infty}}{\eta}\frac{\mathrm{d}y}{\mathrm{d}r}(e^{-zy} + e^{-zy}) . \quad (43)$$

By using Eq. (43) and the potential distribution given by Eq. (36), we obtain from Eq. (17)

$$\mu_{\perp} = \frac{\varepsilon_r\varepsilon_0}{2\eta}\frac{\psi_0/\kappa_m + \psi_{\text{DON}}/\lambda}{1/\kappa_m + 1/\lambda}\left[1 + \frac{1}{(1 + d/a)^2}\right] + \frac{\rho_{\text{fix}}}{\eta\lambda^2} . \quad (44)$$

For low potentials, Eq. (44) reduces to

$$\mu_{\perp} = \frac{\rho_{\text{fix}}}{\eta\lambda^2}\left[1 + \frac{1}{2}\left(\frac{\lambda}{\kappa}\right)^2\frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\left\{1 + \frac{1}{(1 + d/a)^2}\right\}\right] . \quad (45)$$

In the limit of $d \ll a$. Eq. (44) (or Eq. (45)) reduces to Eq. (40) (or Eq. (41)), while in the opposite limit of $d \gg a$, Eq. (45) becomes Eq. (34). Namely, Eq. (45) connects Eq. (34) with Eq. (41).

Cylinder in a tangential field

Henry [8] showed that the electrophoretic mobility $\mu_\parallel$ of an infinitely long cylindrical hard particle in a tangential field is independent of the cylinder radius a and is equal to that for a plate-like particle with the applied field being parallel to the particle surface. It can readily be proven that the same is true for the mobility of a cylindrical soft particle. The mobility expression for a tangential field $\mu_\parallel$ is thus given by Eq. (35). For the case where $\lambda a \gg 1$, $\kappa a \gg 1$, $\lambda d \gg 1$, $\kappa d \gg 1$ and $\rho_{\text{fix}}(r) = \rho_{\text{fix}}$, this is given by Eq. (40), viz.,

$$\mu_\parallel = \frac{\varepsilon_r \varepsilon_0}{\eta} \frac{\psi_0/\kappa_m + \psi_{\text{DON}}/\lambda}{1/\kappa_m + 1/\lambda} + \frac{\rho_{\text{fix}}}{\eta\lambda^2} \tag{46}$$

or Eq. (41) for low potentials, viz.,

$$\mu_\parallel = \frac{\rho_{\text{fix}}}{\eta\lambda^2}\left[1 + \left(\frac{\lambda}{\kappa}\right)^2 \frac{1 + \lambda/2\kappa}{1 + \lambda/\kappa}\right] . \tag{47}$$

Results and discussion

In the present paper we have presented a theory of the electrophoresis of a cylindrical soft particle and derived simple approximate mobility formulas (44) for $\mu_\perp$ and (46) for $\mu_\parallel$, which are applicable when $\lambda a \gg 1$, $\kappa a \gg 1$, $\lambda d \gg 1$ and $\kappa d \gg 1$. These mobility formulas consist of two terms, as in the case of spherical soft particles [1–3]. The first term on the right-hand side of each of Eqs. (44 and 46) is proportional to a weighted average of ψ_0 and ψ_{DON} and the second term arises from the balance of forces acting directly on the resistance centers in the polyelectrolyte layer. This second term, which is not subject to the ionic shielding effect, tends to a non-zero value in the limit of high electrolyte concentrations. The existence of a non-zero limiting mobility value is a characteristic of electrophoresis theories based on the Debye–Bueche model [4], which is valid as long as the size of the polymer segments is much smaller than $1/\kappa$.

The mobility expressions (44) and (46) can be combined, by introducing a function $f(d/a)$, as

$$\mu = \frac{\varepsilon_r \varepsilon_0}{\eta} \frac{\psi_0/\kappa_m + \psi_{\text{DON}}/\lambda}{1/\kappa_m + 1/\lambda} f\left(\frac{d}{a}\right) + \frac{\rho_{\text{fix}}}{\eta\lambda^2} . \tag{48}$$

That is, when a cylinder is oriented perpendicular to the applied electric field, $f(d/a)$ is given by

$$f\left(\frac{d}{a}\right) = \frac{1}{2}\left[1 + \frac{1}{(1 + d/a)^2}\right] \tag{49}$$

which varies from 1 to 1/2 as d/a increases. If, on the other hand, a cylinder is parallel to the applied field, then $f(d/a)$ is always equal to unity, i.e.,

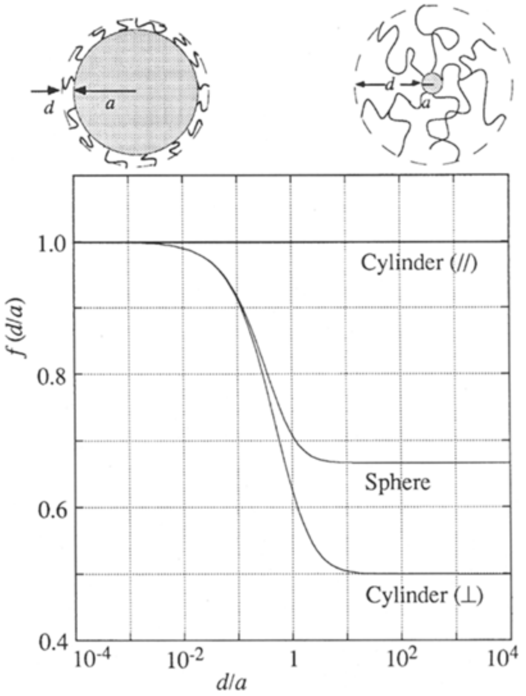

Fig. 2 $f(d/a)$ for a cylinder in a transverse field (⊥) (given by Eq. (49)) or in a tangential field (‖) (Eq. (50)) in comparison with that for a sphere (Eq. (51))

$$f\left(\frac{d}{a}\right) = 1 . \tag{50}$$

It is to be noted that for a spherical soft particle (a spherical particle core of radius a covered with a polyelectrolyte layer of thickness d), $f(d/a)$ is given by [1–3]

$$f\left(\frac{d}{a}\right) = \frac{2}{3}\left[1 + \frac{1}{2(1 + d/a)^3}\right] , \tag{51}$$

which varies from 1 to 2/3 as d/a increases.

The function $f(d/a)$ essentially represents the effects of the distortion of an applied electric field due to the presence of the particle core and thus it corresponds to Henry's function for a rigid cylinder [7] and for a rigid sphere [10]. Indeed, the thickness d of the polyelectrolyte layer plays a role of the thickness of the electrical double layer ($1/\kappa$) for the case of rigid particles. In Fig. 2 we plot the function $f(d/a)$ for a cylinder in a transverse field (Eq. (49)) or in a tangential field (Eq. (50)) in comparison with that for a sphere (Eq. (51)). In the case of a cylinder in a transverse field (Eq. (49)), for $d/a < 10^{-2}$ ($f(d/a) \approx 1$), the cylindrical soft particle behaves like a planar soft particle. On the other hand, for $d/a > 10$ ($f(d/a) \approx 1/2$), the cylindrical soft particle behaves like a cylindrical polyelectrolyte with no particle core. That is, in the latter case the effect of the presence of the particle core (i.e., the field-distortion effect) can be ignored. For a cylindrical soft particle oriented at an arbitrary angle between its axis and the applied electric field, its electrophoretic mobility averaged over a random distribution of orientation is given by, as in the case of hard cylinders [11, 12],

$$\mu_{\mathrm{av}} = \tfrac{1}{3}\,\mu_{\parallel} + \tfrac{2}{3}\,\mu_{\perp}\ . \qquad (52)$$

Conclusions

The principal result of the present paper is Eq. (48) (with Eqs. (49 and 50)). This expression gives the electrophoretic mobility of cylindrical soft particles (i.e., a cylindrical hard colloidal particle of radius a coated with a layer of ion-penetrable polyelectrolytes of thickness d) in an electrolyte solution in an applied transverse or tangential electric field. Equation (48) tends to the mobility expression for a cylindrical hard particle for $d \to 0$ or the frictional coefficient in the polyelectrolyte layer becomes infinity ($\lambda \to \infty$). It also tends to the mobility expression for a cylindrical polyelectrolyte for $d/a \to \infty$ and to that for a plate-like soft particle for $d/a \to 0$.

Acknowledgment This work was supported in part by a Grant-in-Aid (08672486) from the Ministry of Education, Science and Culture, Japan.

References

1. Ohshima H (1994) J Colloid Interface Sci 163:474
2. Ohshima H (1994) Adv Colloid Interface Sci 62:189
3. Ohshima H (1994) Colloids Surfaces A: Physicochemical and Engineering Aspects 103:249
4. Debye P, Bueche A (1948) J Chem Phys 16:573
5. O'Brien RW, White LR (1978) J Chem Soc Faraday Trans 2 74:1607
6. Ohshima H, Healy TW, White LR (1983) J Chem Soc Faraday Trans 2 79:1613
7. Ohshima H (1996) J Colloid Interface Sci 180:299
8. Henry DC (1931) Proc R Soc London Ser A133:106
9. Hermans JJ, Fujita H (1955) Koninkl Ned Akad Wetenschap Proc B58:182
10. Ohshima H (1994) J Colloid Interface Sci 168:269
11. Keizer A, de van der Drift WPJT, Overbeek JThG (1975) Biophys Chem 3:107
12. Stigter D (1978) J Phys Chem 82:1424