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ORIGINAL CONTRIBUTIONS

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Approximate expression for the electrophoretic mobility of a spherical colloidal particle covered with an ion-penetrable uncharged polymer Layer

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Abstract An approximate analytic expression is derived for the electrophoretic mobility of a charged spherical colloidal particle covered with an ion-penetrable uncharged polymer layer in an electrolyte solution by taking into account the relaxation effects. This expression is applicable for all values of zeta potentials at large $\kappa a (\kappa a \geq$ ca. 30), where κ is the Debye–Huckel parameter and a is the radius of the particle core. A simple expression for the ratio of the electrophoretic mobility of a polymer-coated particle to that of a bare particle without a polymer layer is also given.

Keywords Electrophoretic mobility · Colloidal particle · Uncharged polymer layer

Introduction

It has been shown theoretically [1–5] that the electrophoretic mobility of a colloidal particle covered with an ion-penetrable uncharged polymer is quite different from that of a bare particle without a polymer layer. Recently, the author derived an approximate analytic expression for the electrophoretic mobility [3, 4], which corresponds to a modification of Henry's function [6] by taking into account the presence of the polymer layer. This expression is applicable for all values of κa (where κ is the Debye–Hückel parametr and a is the particle radius), but it is correct to the first order of the particle zeta potential and thus can be used only when the particle zeta potential is low. The purpose of the present study is to extend the previous theory [3], and derive an approximate analytic expression of the electrophoretic mobility of a charged spherical particle covered with an ion-penetrable uncharged polymer layer that is applicable for large κa but for all values of the particle zeta potential. Our theory is based on our previous theory [3] as well as on theories for the electrophoretic mobility of polyelectrolyte-coated particles, which are called soft particles [7–9]. The approximation method used in the present work is similar to that of our previous studies on electrophoresis of a bare particle without a polymer layer [10].

Fundamental electrokinetic equations

Consider a charged spherical colloidal particle covered with an ion-penetrable uncharged polymer layer moving with a velocity **U** in a symmetrical electrolyte solution of bulk concentration n^{∞} and valence z in an applied electric field **E**. We may assume that the particle core is positively charged without loss of generality. We regard the potential at the surface of the particle core as the particle zeta potential ζ. We also assume that the charged particle core of radius a is coated with an ion-penetrable layer of uncharged polymers with 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 drag coefficient of

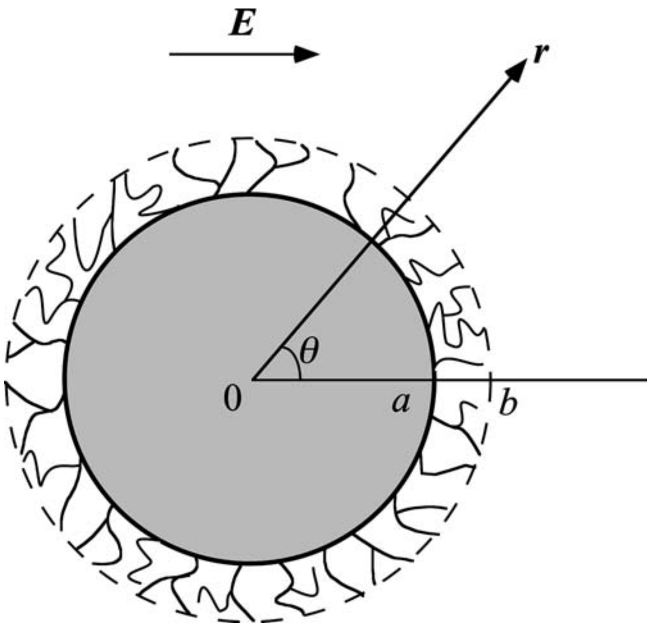

Fig. 1 A spherical particle composed of a charged core covered with an ion-penetrable uncharged polymer layer moving steadily with velocity U in an applied electric field E. a radius of the particle core. d thickness of the polymer layer covering the particle core. $b = a + d$

cations (co-ions) be λ_+ and that of anions (counterions) be λ_-, respectively. We adopt the model of Debye–Bueche [11, 12], in which the polymer segments are regarded as resistance centers distributed uniformly in the polymer layer, exerting frictional forces on the liquid flowing in the polymer layer.

The main assumptions in our analysis are as follows. (1) 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. (2) 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. (3) The slipping plane is located on the particle core. (4) No electrolyte ions can penetrate the particle core. (5) The polymer layer is permeable to mobile charged species. (6) The relative permittivity ε_r takes the same value both inside and outside the polymer layer.

The fundamental electrokinetic equations are given by

$$\eta\nabla \times \nabla \times \mathbf{u} + \gamma\mathbf{u} + \nabla p + \rho_{\mathrm{el}}\nabla\psi = \mathbf{0}, \quad a<r<b, \tag{1}$$

$$\eta\nabla \times \nabla \times \mathbf{u} + \nabla p + \rho_{\mathrm{el}}\nabla\psi = \mathbf{0}, \quad r > b, \tag{2}$$

$$\nabla \cdot \mathbf{u} = 0, \tag{3}$$

$$\mathbf{v}_\pm = \mathbf{u} - \frac{1}{\lambda_\pm}\nabla\mu_\pm, \tag{4}$$

$$\nabla \cdot (n_\pm \mathbf{v}_\pm) = \mathbf{0}, \tag{5}$$

$$\rho_{\mathrm{el}}(\mathbf{r}) = ze\{n_+(\mathbf{r}) - n_-(\mathbf{r})\}, \tag{6}$$

$$\mu_\pm(\mathbf{r}) = \mu_\pm^\infty \pm ze\,\psi(\mathbf{r}) + kT\ln n_\pm(\mathbf{r}), \tag{7}$$

$$\Delta\psi(\mathbf{r}) = -\frac{\rho_{\mathrm{el}}(\mathbf{r})}{\varepsilon_r\varepsilon_o}, \tag{8}$$

where $\mathbf{u}(\mathbf{r})$ is the liquid velocity at position $\mathbf{r}$ relative to the particle, $\mathbf{v}_+$ and $\mathbf{v}_-$ are, respectively, the velocity of cations and anions, $p(\mathbf{r})$ the pressure, $\rho_{\mathrm{el}}(\mathbf{r})$ the space charge density at position $\mathbf{r}$ resulting from electrolyte ions, given by Eq. 6, $\psi(\mathbf{r})$ the electric potential, $\mu_+(\mathbf{r})$ and $n_+(\mathbf{r})$ are, respectively, the electrochemical potential and the concentration (the number density) of cations, and $\mu_-(\mathbf{r})$ and $n_-(\mathbf{r})$ are those for anions, and $\mu_\pm{}^\infty$ is a constant term in $\mu_\pm(\mathbf{r})$. Equations 1, 2 and 3 are the Navier–Stokes equations and the equation of continuity for an incompressible flow under assumption (1). The term $\gamma\mathbf{u}$ in Eq. 1 represents the frictional forces exerted on the liquid flow by the polymer segments in the polymer layer, where γ is the frictional coefficient [11, 12]. Equation 4 expresses that the flow $\mathbf{v}_\pm(\mathbf{r})$ of electrolyte ions is caused by the liquid flow $\mathbf{u}$ $(\mathbf{r})$ and the gradient of the electrochemical potential $\mu_\pm(\mathbf{r})$, given by Eq. 7. Equation 5 is the continuity equation for electrolyte ions and Eq. 8 is Poisson's equation. The drag coefficients $\lambda_\pm$ of cations and anions are further related to the limiting conductances $\Lambda_\pm{}^\circ$ of cations and anions by

$$\lambda_\pm = \frac{N_A e^2 z}{\Lambda_\pm^\circ}. \tag{9}$$

For K^+ and Cl^- ions, the values of Λ° are 73.5×10^{-4} and 76.3×10^{-4} $m^2\ \Omega^{-1}\ mol^{-1}$, respectively.

We assume that the slipping plane, at which the liquid velocity **u** relative to the particle is zero, coincides the particle core surface at $r = a$ (assumption (3)). Then, the above electrokinetic equations must be solved under the following boundary conditions.

$$\mathbf{u} = \mathbf{0} \quad \text{at } r = a, \tag{10}$$

$$\mathbf{u} \to -\mathbf{U} \quad \text{as } r \to \infty. \tag{11}$$

In the stationary state, the net force acting on the particle or an arbitrary volume enclosing the particle must be zero. Consider a large sphere S of radius r containing the particle (plus the electrical double layer around the particle) at its center. The radius r of S is taken to be sufficiently large, so that the net electric charge within S is zero. There is then no electric force acting on S, and we need to consider the only hydrodynamic force $\mathbf{F}_\mathrm{H}$, which must be zero, i.e.,

$$\mathbf{F}_\mathrm{H} = \int_S \sigma \cdot \hat{\mathbf{n}}\, \mathrm{d}S \to 0 \quad \text{as } r \to \infty, \tag{12}$$

where the integration is carried out over the surface of S, σ is the hydrodynamic stress tensor and $\widehat{n}$ is the outward normal to S. Finally, the boundary condition for the velocity of the ionic flow $v_\pm$ is given by

$$\mathbf{v}_\pm \cdot \hat{\mathbf{n}}|_{r=a} = 0, \tag{13}$$

which states that no electrolyte ions can penetrate the particle surface (assumption (4)). The boundary conditions for $\mathbf{u}(\mathbf{r})$ and $\mathbf{v}_\pm(\mathbf{r})$ at the boundary at $r = b$ between the polymer layer and the surrounding solution are given as follows. The normal and tangential components of the velocity $\mathbf{u}(\mathbf{r})$ are continuous at $r = b$. The normal and tangential components of the stress tensor are continuous at $r = b$. The potential $\psi(\mathbf{r})$ and the electric field $-\nabla\psi(\mathbf{r})$ are continuous at $r = b$. The continuity of $-\nabla\psi(\mathbf{r})$ results from the assumption (6). Thus, the normal and tangential components of Maxwell's stress are continuous at $r = b$. Therefore, the normal and tangential components of the hydrodynamic stress must be continuous at $r = b$.

Linearized equations

Under assumption (2), we may write

$$n_\pm(\mathbf{r}) = n_\pm^{(0)}(r) + \delta n_\pm(\mathbf{r}), \tag{14}$$

$$\psi(\mathbf{r}) = \psi^{(0)}(r) + \delta\psi(\mathbf{r}), \tag{15}$$

$$\mu_\pm(\mathbf{r}) = \mu_\pm^{(0)} + \delta\mu_\pm(\mathbf{r}), \tag{16}$$

$$\rho(\mathbf{r}) = \rho^{(0)}(r) + \delta\rho(\mathbf{r}), \tag{17}$$

where the quantities with superscript (0) refer to those at equilibrium, i.e., in the absence of $\mathbf{E}$, and $\mu_\pm{}^{(0)}$ is a constant independent of r.

We assume that the distribution of electrolyte ions at equilibrium $n^{(0)}$ (r) obeys the Boltzmann equation and the equilibrium potential $\psi^{(0)}$ (r) outside the particle core satisfies the Poisson–Boltzmann equation, both being functions of r $(=|\mathbf{r}|)$ only, viz.,

$$n_\pm^{(0)}(r) = n^\infty \exp\left(\mp \frac{ze\psi^{(0)}}{kT}\right), \tag{18}$$

$$\frac{1}{r^2}\frac{\mathrm{d}}{\mathrm{d}r}\left(r^2\frac{\mathrm{d}\psi^{(0)}}{\mathrm{d}r}\right) = -\frac{\rho_\mathrm{el}^{(0)}(r)}{\varepsilon_\mathrm{r}\varepsilon_\mathrm{o}} \tag{19}$$

with

$$\begin{aligned}\rho_\mathrm{el}^{(0)}(r) &= ze\left\{n_+^{(0)}(r) - n_-^{(0)}(r)\right\}\\ &= zen^\infty\left\{\exp\left(-\frac{ze\psi^{(0)}}{kT}\right) - \exp\left(\frac{ze\psi^{(0)}}{kT}\right)\right\}.\end{aligned} \tag{20}$$

The boundary condition for $\psi^{(0)}(r)$ are

$$\psi^{(0)}(a) = \zeta, \tag{21}$$

$$\psi^{(0)}(r) \to 0 \quad \text{as } r \to \infty, \tag{22}$$

where ζ is the potential at the surface of the particle core, i.e., the zeta potential of the particle.

Further, symmetry considerations permit us to write

$$\mathbf{u}(\mathbf{r}) = \left(-\frac{2}{r}h(r)E\cos\theta, \frac{1}{r}\frac{\mathrm{d}}{\mathrm{d}r}(rh(r))E\sin\theta, 0\right), \tag{23}$$

$$\delta\mu_\pm(\mathbf{r}) = \mp ze\phi_\pm(r)E\cos\theta, \tag{24}$$

where $E = |\mathbf{E}|$ and e is the elementary electric charge. The fundamental electrokinetic Eqs. 1, 2, 3, 4 and 5 can be transformed into equations for $h(r)$ and $f(r)$, which are expressed as [7–9]

$$L\phi_\pm = \pm\frac{\mathrm{d}y}{\mathrm{d}r}\left(\frac{\mathrm{d}\phi_\pm}{\mathrm{d}r} \mp \frac{2\lambda_\pm}{ze}\frac{h}{r}\right), \tag{25}$$

$$L(Lh - \lambda^2 h) = G(r), \quad a<r<b, \tag{26}$$

$$L(Lh) = G(r), \quad r > b \tag{27}$$

with

$$G(r) = -\frac{\varepsilon_\mathrm{r}\varepsilon_\mathrm{o}\kappa^2}{2\eta}\left(\frac{kT}{ze}\right)\frac{\mathrm{d}y}{\mathrm{d}r}\left\{\mathrm{e}^{-y}\frac{\phi_+(r)}{r} + \mathrm{e}^{y}\frac{\phi_-(r)}{r}\right\}, \tag{28}$$

$$\lambda = \left(\frac{\gamma}{\eta}\right)^{1/2}, \tag{29}$$

$$y(r) = \frac{ze\psi^{(0)}(r)}{kT}, \tag{30}$$

$$\kappa = \left(\frac{2n^\infty z^2 e^2}{\varepsilon_\mathrm{r}\varepsilon_\mathrm{o}kT}\right)^{1/2}. \tag{31}$$

Here, $L = \mathrm{d}^2/\mathrm{d}\,r^2 + (2/r)\mathrm{d}/\mathrm{d}\,r - 2/r^2$, y is the scaled equilibrium potential and κ is the Debye–Hückel parameter.

The boundary conditions for $\mathbf{u}(\mathbf{r})$ and $\mathbf{v}_\pm(\mathbf{r})$ are expressed in terms of h and $\phi_\pm$ as follows [9].

$$\left.\frac{\mathrm{d}\phi_\pm}{\mathrm{d}r}\right|_{r=a} = 0, \tag{32}$$

$$\phi_{\pm}(r) \to r \quad \text{as } r \to \infty, \tag{33}$$

$$h = \frac{\mathrm{d}h}{\mathrm{d}r} = 0 \quad \text{at } r = a, \tag{34}$$

$$h(r) \to \frac{U}{2E} r + O\left(\frac{1}{r}\right) \quad \text{as } r \to \infty, \tag{35}$$

$$h(b^{+}) = h(b^{-}), \tag{36}$$

$$\left.\frac{\mathrm{d}h}{\mathrm{d}r}\right|_{r=b^{+}} = \left.\frac{\mathrm{d}h}{\mathrm{d}r}\right|_{r=b^{-}}, \tag{37}$$

$$\left.\frac{\mathrm{d}^2h}{\mathrm{d}r^2}\right|_{r=b^{+}} = \left.\frac{\mathrm{d}^2h}{\mathrm{d}r^2}\right|_{r=b^{-}}, \tag{38}$$

$$\left.\frac{\mathrm{d}}{\mathrm{d}r}[r(Lh)]\right|_{r=b^{+}} = \left.\frac{\mathrm{d}}{\mathrm{d}r}\left[r(Lh - \lambda^2 h)\right]\right|_{r=b^{-}}, \tag{39}$$

where $U = |\mathbf{U}|$.

Equation 25 subject to boundary conditions (32) and (33) can formally be integrated to give

$$\begin{aligned} \phi_{\pm}(r) = \quad & r + \tfrac{a^3}{2r^2} \mp \tfrac{1}{3}\left(r + \tfrac{a^3}{2r^2}\right) \int_a^\infty \tfrac{\mathrm{d}y}{\mathrm{d}x}\left(\tfrac{\mathrm{d}\phi_{\pm}}{\mathrm{d}x} \mp \tfrac{2\lambda_{\pm}}{ze}\tfrac{h}{x}\right)\mathrm{d}x \\ & \pm \tfrac{1}{3}\int_a^r \left(r - \tfrac{x^3}{r^2}\right) \tfrac{\mathrm{d}y}{\mathrm{d}x}\left(\tfrac{\mathrm{d}\phi_{\pm}}{\mathrm{d}x} \mp \tfrac{2\lambda_{\pm}}{ze}\tfrac{h}{x}\right)\mathrm{d}x. \end{aligned} \tag{40}$$

Similarly, integration of Eqs. 26 and 27 subject to boundary conditions (34) and (35) yields

$$\begin{aligned} h(r) = & \frac{1}{3\lambda^2}\left[-r\int_b^r G(r')\,\mathrm{d}r' + \frac{1}{r^2}\int_b^r r'^3 G(r')\,\mathrm{d}r'\right] - \frac{C_1 r}{\lambda^2} \\ & - \frac{C_2}{\lambda^2 r^2} + \frac{1}{\lambda^3}\int_b^r \left\{\left(\frac{r'}{r} - \frac{1}{\lambda^2 r^2}\right)\sinh[\lambda(r - r')]\right. \\ & \left. - \left(\frac{r'}{\lambda r^2} - \frac{1}{\lambda r}\right)\cosh[\lambda(r - r')]\right\} G(r')\,\mathrm{d}r' \\ & + C_3\left\{\frac{\lambda\cosh[\lambda(r-b)]}{r} - \frac{\sinh[\lambda(r-b)]}{r^2}\right\} \\ & + C_4\left\{\frac{\lambda\sinh[\lambda(r-b)]}{r} - \frac{\cosh[\lambda(r-b)]}{r^2}\right\}, \quad a \leqslant r \leqslant b, \end{aligned} \tag{41}$$

and

$$\begin{aligned} h(r) = & \frac{U}{2E} r + \frac{D_1}{r^2} + \frac{r^3}{30}\int_\infty^r G(r')\,\mathrm{d}r' - \frac{r}{6}\int_\infty^r r'^2 G(r')\,\mathrm{d}r' \\ & + \frac{1}{6}\int_\infty^r r'^3 G(r')\,\mathrm{d}r' - \frac{1}{30r^2}\int_\infty^r r'^5 G(r')\,\mathrm{d}r' \quad r > b. \end{aligned} \tag{42}$$

The integration constants C_1–C_4 and D_1 in Eqs. 41 and 42 are determined so as to satisfy the boundary conditions (34), (35), (36), (37), (38) and (39).

General expression for electrophoreric mobility

The electrophoretic mobility $\mu = U/E$ (where $U = |\mathbf{U}|$) can be calculated from Eq. 42 as

$$\mu = 2\lim_{r\to\infty}\frac{h(r)}{r}. \tag{43}$$

The result is [9]

$$\begin{aligned} \mu = & \frac{b^2}{9}\int_b^\infty \left[3\left(1 - \frac{r^2}{b^2}\right) - \frac{2L_2}{L_1}\left(1 - \frac{r^3}{b^3}\right)\right] G(r)\,\mathrm{d}r \\ & + \frac{2L_3}{3\lambda^2 L_1}\int_a^\infty \left(1 + \frac{r^3}{2b^3}\right) G(r)\,\mathrm{d}r \\ & - \frac{2}{3\lambda^2}\int_a^b \left[1 - \frac{3a}{2\lambda^2 b^3 L_1}\{(L_3 + L_4\lambda r)\cosh[\lambda(r-a)]\right. \\ & \qquad \left. -(L_4 + L_3\lambda r)\sinh[\lambda(r-a)]\}\right] G(r)\,\mathrm{d}r \end{aligned} \tag{44}$$

with

$$\begin{aligned} L_1 = & \left(1 + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3} - \frac{3a^2}{2\lambda^2 b^4}\right)\cosh[\lambda(b-a)] \\ & - \left(1 - \frac{3a^2}{2b^2} + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3}\right)\frac{\sinh[\lambda(b-a)]}{\lambda b}, \end{aligned} \tag{45}$$

$$\begin{aligned} L_2 = & \left(1 + \frac{a^3}{2b^3} + \frac{3a}{2\lambda^2 b^3}\right)\cosh[\lambda(b-a)] \\ & + \frac{3a^2}{2b^2}\frac{\sinh[\lambda(b-a)]}{\lambda b} - \frac{3a}{2\lambda^2 b^3}, \end{aligned} \tag{46}$$

$$L_3 = \cosh[\lambda(b-a)] - \frac{\sinh[\lambda(b-a)]}{\lambda b} - \frac{a}{b}, \tag{47}$$

$$L_4 = \sinh[\lambda(b-a)] - \frac{\cosh[\lambda(b-a)]}{\lambda b} + \frac{\lambda a^2}{3b} + \frac{2\lambda b^2}{3a} + \frac{1}{\lambda b}. \tag{48}$$

Approximate mobility expression for large κa

In a previous study (3), we derived an analytic approximate expression for the electrophoretic mobility μ applicable for all values of κa at low zeta potential ζ on the basis of the general expression (44) for the electrophoretic mobility μ. In the present study, we derive an approximate expression applicable for all values of ζ at large κa with the help of an approximation method as developed in a previous study [10] for the electrophoretic mobility of a bare particle.

For large κa, since the principal contribution to the integral in Eq. 44 comes from the region $r - a \approx 1/\kappa$, we may regard $(r - a)/a$ as of the order of $1/\kappa a$ and expand the integrand of Eq. 44 around $r = a$, obtaining

$$\mu = \frac{a(L_3 + \lambda a L_4)}{2\lambda^2 b^3 L_1} \int_a^\infty (r-a)^2 G(r)\,\mathrm{d}r + O\left(\frac{1}{\kappa a}\right). \tag{49}$$

Further, for large κ a, the Poisson–Boltzmann Eq. (19) as combined with Eq. 20 becomes the following planar Poisson–Boltzmann equation:

$$\frac{\mathrm{d}^2 y}{\mathrm{d}r^2} = \kappa^2 \sinh y. \tag{50}$$

The solution to Eq. 50 is given by

$$y(r) = 2\ln\left[\frac{1+\gamma \mathrm{e}^{-\kappa(r-a)}}{1-\gamma \mathrm{e}^{-\kappa(r-a)}}\right], \tag{51}$$

where

$$\gamma = \tanh\left(\frac{ze\zeta}{4kT}\right). \tag{52}$$

It can be shown from Eq. 40 that

$$\frac{\phi_\pm(r)}{a} = \frac{\phi_\pm(a)}{a} + O\left(\frac{1}{\kappa a}\right) \tag{53}$$

with

$$\begin{aligned}\frac{\phi_\pm(a)}{a} &= \frac{3}{2} \mp \frac{1}{2}\int_a^\infty \frac{\mathrm{d}y}{\mathrm{d}r}\left(\frac{\mathrm{d}\phi_\pm}{\mathrm{d}r} \mp \frac{2\lambda_\pm}{ze}\frac{h}{r}\right)\mathrm{d}r \\ &= \frac{3}{2} + \int_a^\infty (1-\mathrm{e}^{\mp y})\left[\frac{\phi_\pm(a)}{a^2} \mp \frac{\lambda_\pm}{ze}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{h}{r}\right)\right]\mathrm{d}r \\ &\quad + O\left(\frac{1}{\kappa a}\right).\end{aligned} \tag{54}$$

We again note that for large κ a, we may regard $(r - a)/a$ as of the order of $1/\kappa a$ and expand the quantity in the integrand of Eq. 42, obtaining

$$\begin{aligned}\frac{\mathrm{d}}{\mathrm{d}r}\left(\frac{h}{r}\right) &= \frac{1}{2a}\int_a^r (r-a)^2 G(r)\,\mathrm{d}r - \frac{1}{2a}(r-a)^2 \\ &\quad \times \int_r^\infty G(r)\,\mathrm{d}r + \frac{1}{a}(r-a)\int_r^\infty (r-a)G(r)\,\mathrm{d}r.\end{aligned} \tag{55}$$

By substituting Eq. 55 into Eq. 54 and using Eq. 51, we have

$$\frac{\phi_+(a)}{a} = \frac{3}{2} + O\left(\frac{1}{\kappa a}\right), \tag{56}$$

$$\frac{\phi_-(a)}{a} = \frac{3}{2(1+F)} + O\left(\frac{1}{\kappa a}\right) \tag{57}$$

with

$$F = \frac{2}{\kappa a}(1+3m_-)\left\{\exp\left(\frac{ze\zeta}{2kT}\right) - 1\right\}, \tag{58}$$

where

$$m_- = \frac{2\varepsilon_r\varepsilon_o kT}{3\eta z^2 e^2}\lambda_- \tag{59}$$

is the scaled drag coefficient of anions (counterions) and F corresponds to Dukhin's number. Note that Eqs. 56 and 57 are the same as the leading terms of the corresponding expressions for $\phi_\pm(a)$ for a bare particle (correct to $O(1/\kappa a)$) [10]. By substituting Eqs. 56, 57, and 51 into Eq. 49, we finally obtain, by neglecting terms of order $1/\kappa a$,

$$\begin{aligned}\mu &= \frac{3a(L_3 + \lambda a L_4)\varepsilon_r\varepsilon_o}{2\eta\lambda^2 b^3 L_1} \\ &\quad \times \left\{\zeta - \frac{2F}{1+F}\left(\frac{kT}{ze}\right)\ln\left[\frac{1+\exp(ze\zeta/2kT)}{2}\right]\right\},\end{aligned} \tag{60}$$

which is the required expression for the large κa mobility formula for a spherical particle coated with a neutral polymer layer. Equation (60), which is obtained by neglecting terms of $O(1/\kappa a)$, is correct to $O(1)$.

Results and discussion

We have derived an approximate analytic expression (60) for the electrophoretic mobility μ of a spherical particle coated with a neutral polymer layer. It is shown that the mobility depends not only on the particle zeta potential ζ (which is the surface potential of the particle core) and κa, but also on the thickness d and the frictional coefficient γ (or λ) of the polymer layer. If each polymer segment exerts the Stokes resistance $6\pi\eta$ $a_\mathrm{p}\mathbf{u}$ on the liquid flow in the polymer layer, then γ is given by $\gamma = 6\pi\eta a_\mathrm{p} N_\mathrm{p}$, where N_p and a_p are the number per unit volume and the radius of a polymer segment composing the polymer layer, respectively. The parameter λ is thus given by $(6\pi a_\mathrm{p} N_\mathrm{p})^{1/2}$. When $a_\mathrm{p} = 0.7$ nm and $N_\mathrm{p} = 0.1$ M, for example, λ amounts to 8.9×10^8 m^{-1}, i.e., $1/\lambda = 1.1$ nm. The relaxation effects, which become appreciable for high zeta potentials, are taken into account through the parameter F, given by Eq. 58 (which corresponds to Duhkin's number). Equation (60) is an approximate formula applicable for all values of ζ at large κa. Since Eq. 60 is derived by neglecting terms of the order of $1/\kappa a$, it is expected to be applicable for $\kappa a \geq$ca. 30 with tolerable errors.

In Fig. 2, we give some examples of the calculations of the electrophoretic mobility μ of a spherical particle covered with an uncharged polymer layer in an aqueous KCl solution at 25 °C ($\eta = 0.891$ mPa s, $\varepsilon_r = 78.54$, and $m_- = 0.169$, corresponding to Cl^- ions) as a function of the scaled zeta potential $ze\zeta/kT$ for $\lambda d = 0$ (bare particle), 1 and 2 for $\lambda a = 100$ and $\kappa a = 100$, where E_m is the scaled electrophoretic mobility defined as

$$E_m = \frac{3\eta ze}{2\varepsilon_r\varepsilon_o kT}\mu \tag{61}$$

so that

$$E_m = \frac{9a(L_3 + \lambda a L_4)}{4\lambda^2 b^3 L_1} \times \left\{ \left(\frac{ze\zeta}{kT}\right) - \frac{2F}{1+F}\ln\left[\frac{1+\exp(ze\zeta/2kT)}{2}\right] \right\}. \tag{62}$$

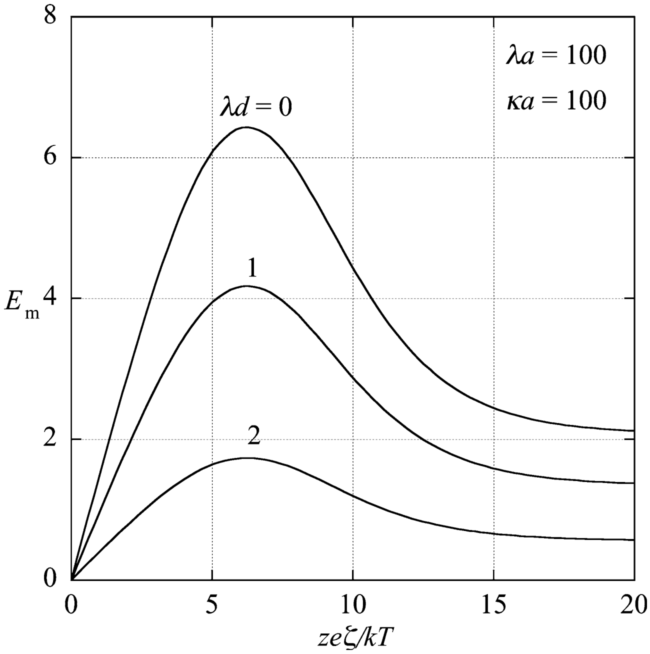

Fig. 2 Scaled electrophoretic mobility E_m of a spherical particle covered with an ion-penetrable uncharged polymer layer as a function of the scaled zeta potential $ze\zeta/kT$ for $\lambda d = 0$ (bare particle), 1 and 2. Calculated with Eq. 60 for $\lambda a = 100$ and $\kappa a = 100$ in an aqueous KCl solution at 25 °C ($\eta = 0.891$ mPa s, $\varepsilon_r = 78.54$, and $m_- = 0.169$, corresponding to Cl^- ions)

Figure 2 shows that E_m depends strongly on λd and that E_m of a polymer-coated particle exhibits a maximum as in the case of a bare particle ($\lambda d \to 0$) due to the relaxation effects. When $a \to b$, the surface polymer layer disappears so that the particle becomes a bare particle and Eq. 60 becomes

$$\mu = \frac{\varepsilon_r\varepsilon_o}{\eta}\left\{ \zeta - \frac{2F}{1+F}\left(\frac{kT}{ze}\right)\ln\left[\frac{1+\exp(ze\zeta/2kT)}{2}\right] \right\}, \tag{63}$$

which agrees with the leading term of an accurate mobility expression for a bare particle correct to $O(1/\kappa a)$ (Eq. 57 in Ref. [10]). Also, when $\lambda \to 0$, the particle becomes a bare particle and Eq. 60 reduce to (63), as expected. On the other hand, for large λa Eq. 60 further reduces to

$$\mu = \frac{\varepsilon_r\varepsilon_o}{\eta\cosh\lambda d}\left\{ \zeta - \frac{2F}{1+F}\left(\frac{kT}{ze}\right)\ln\left[\frac{1+\exp(ze\zeta/2kT)}{2}\right] \right\}. \tag{64}$$

We thus see that for large λa, the effect of the presence of the neutral polymer layer is expressed simply by a factor $1/\cosh(\lambda d)$.

It follows from Eqs. 60 and 63 that the ratio of the electrophoretic mobility μ of a polymer-coated particle to that of a bare particle μ_o is given by the following simple relation:

$$\frac{\mu}{\mu_o} = \frac{3a(L_3 + \lambda a L_4)}{2\lambda^2 b^3 L_1}, \tag{65}$$

which is independent of κa. Equation (65) again becomes for large λa

$$\frac{\mu}{\mu_o} = \frac{1}{\cosh(\lambda d)}. \tag{66}$$

Figure 3 shows the ratio μ/μ_o as a function of λd for several values of λa. For large λa, μ/μ_o approaches the value given by Eq. 66 independent of λa.

In the limit of $\kappa a \to \infty$, where F tends to 0 so that the relaxation effects become negligible (Smoluchowski's limit), Eq. 60 becomes

$$\mu = \frac{3\varepsilon_r\varepsilon_o a(L_3 + \lambda a L_4)}{2\eta\lambda^2 b^3 L_1}\zeta, \quad (\kappa a \to \infty). \tag{67}$$

When $\lambda \to 0$ or $d \to 0$, the polymer-coated particle becomes a bare particle without a polymer layer and Eq. 67 becomes

$$\mu = \frac{\varepsilon_r\varepsilon_o\zeta}{\eta}, \quad (\kappa a \to \infty). \tag{68}$$

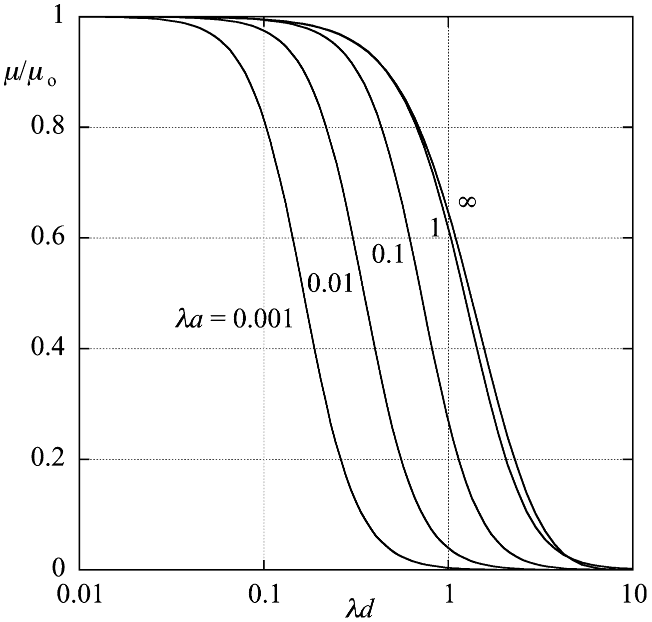

Fig. 3 The ratio μ/μ_o of the electrophoretic mobility μ of a polymer-coated particle to that of a bare particle μ_o as a function of the scaled thickness of the polymer layer λd at $\lambda a = 100$. Calculated Eq. 65

That is, Eq. 67 is a modification of Smoluchowski's formula (68) by taking into account the presence of an uncharged polymer layer. For low zeta potential, Eq. 60 again reduces to Eq. 67, viz.,

$$\mu = \frac{3\varepsilon_r\varepsilon_o a(L_3 + \lambda a L_4)}{2\eta\lambda^2 b^3 L_1}\zeta, \quad \left(\frac{ze\zeta}{kT} \ll 1\right), \tag{69}$$

which agrees with the result obtained in a previous study [3] (Note that the quantity on the right-hand side of Eq. 28 in Ref. [3] is equivalent to $3a\,(L_3 + \lambda a L_4)/2\lambda^2 b^2\,L_1$ appearing in Eqs. 67 and 69).

Finally, it should be noted that in the limit of very high zeta potential ζ, the mobility μ tends to the following limiting value independent of ζ:

$$\mu = \frac{3\varepsilon_r\varepsilon_o a(L_3 + \lambda a L_4)}{2\eta\lambda^2 b^3 L_1} \cdot \left(\frac{kT}{ze}\right) 2\ln 2, \quad (\zeta \to \infty). \tag{70}$$

By comparing with Eq. 69, we see that the highly charged particle behaves as if the zeta potentials were $(kT/ze)2\ \ln\ 2$, just as in the case of bare particles [13, 14].

Conclusion

We have derived an approximate analytic expression (Eq. 60) for the electriophoretic mobility μ of a charged spherical colloidal particle covered with an ion-penetrable uncharged polymer layer in an electrolyte solution by taking into account the relaxation effects. This expression is applicable for all values of zeta potential at large κa ($\kappa a \geq$ca. 30). A simple expression (Eq. 65) is also derived for the ratio of the electrophoretic mobility of a polymer-coated particle to that of a bare particle without a polymer layer.

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