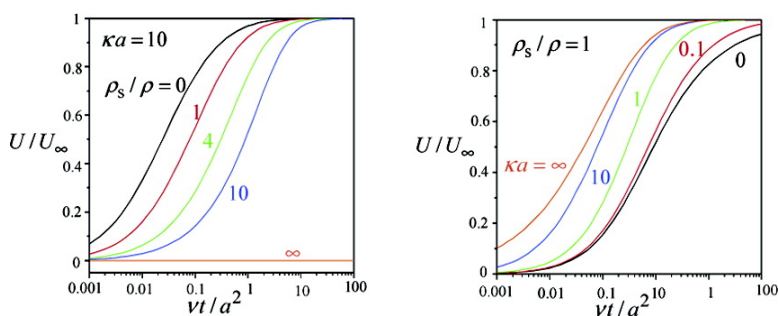


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Transient Electrophoresis of Spherical Particles at Low Potential and Arbitrary Double-Layer Thickness

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A theoretical study is presented for the dynamic electrophoretic response of a charged spherical particle in an unbounded electrolyte solution to a step change in the applied electric field. The electric double layer surrounding the particle may have an arbitrary thickness relative to the particle radius. The transient Stokes equations modified with the electrostatic effect which govern the fluid velocity field are linearized by assuming that the system is only slightly distorted from equilibrium. Semianalytical results for the transient electrophoretic mobility of the particle are obtained as a function of relevant parameters by using the Debye–Huckel approximation. The results demonstrate that the electrophoretic mobility of a particle with a constant relative mass density at a specified dimensionless time normalized by its steady-state quantity decreases monotonically with a decrease in the parameter κa , where κ^{-1} is the Debye screening length and a is the particle radius. For a given value of κa , a heavier particle lags behind a lighter one in the development of the electrophoretic mobility. In the limits of $\kappa a \rightarrow \infty$ and $\kappa a = 0$, our results reduce to the corresponding analytical solutions available in the literature. The electrophoretic acceleration of the particle is a monotonic decreasing function of the time for any fixed value of κa . In practical applications, the effect of the relaxation time for the transient electrophoresis is negligible, regardless of the value of κa or the relative mass density of the particle.

1. Introduction

When a charged particle suspended in an electrolyte solution is subjected to an external electric field, the particle begins to move. This motion is termed electrophoresis and has been one of the most widely applied experimental methods for the characterization and separation of colloidal particles. Although the basic relationships involved in electrophoretic phenomena were derived mainly for the steady state,^{1–11} the transient behavior of these phenomena is perhaps as important as their steady-state behavior insofar as an evaluation of their usefulness or an efficient design of the relevant equipment is concerned. When a colloidal particle moves through a constant but nonuniform electric field, the field measured in the frame of the particle is unsteady. In several applications, the use of alternating electric fields has been proposed for measurements of the electrophoretic mobility of suspended particles.^{12,13} Knowledge of the dynamic

response of charged particles to a time-variant electric field can be used to interpret experimental observations or to develop new separation technologies.

Through the use of the “ad hoc” assumption that the fluid in the electric double layer surrounding the particle attains its full electroosmotic velocity instantaneously when the constant electric field is imposed, Morrison obtained exact solutions for the transient electrophoresis of a dielectric sphere¹⁴ and of an arbitrarily oriented long cylinder¹⁵ for the limit of vanishingly thin double layers ($\kappa a \rightarrow \infty$, where κ^{-1} is the Debye screening length defined by eq 8 and a is the particle radius). Later, Ivory¹⁶ made a correction to Morrison’s solution for the electrophoresis of a sphere by applying the interfacial boundary condition derived from the integral form of the momentum equation governing the fluid motion in the double layer, but this model failed to predict the transient response of the particle mobility as a function of the parameter κa . Recently, the transient electrophoresis due to a sudden application of a constant electric field has been analyzed approximately for the case of a dielectric sphere with a thin but finite double layer (say, $\kappa a > 10$) by taking the effect of the dynamic response of the electroosmotic flow in the double layer into account.¹⁷ In that work, exact expressions for the time-dependent electrophoretic mobility of a spherical particle with a very thick double layer ($\kappa a \rightarrow 0$) were also obtained in closed forms.

In most real situations of electrophoresis of small charged particles, the thickness of the electric double layer can be comparable to their size and the dependence of the dynamic response of an electrophoretic particle on κa in

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(1) Henry, D. C. *Proc. R. Soc. London, Ser. A* **1931**, *133*, 106.
 (2) Booth, F. *Proc. R. Soc. London, Ser. A* **1950**, *203*, 514.
 (3) Wiersema, P. H.; Loeb, A. L.; Overbeek, J. Th. G. *J. Colloid Interface Sci.* **1966**, *22*, 78.
 (4) Morrison, F. A. *J. Colloid Interface Sci.* **1970**, *34*, 210.
 (5) Dukhin, S. S.; Derjaguin, B. V. In *Surface and Colloid Science*; Matijevic, E., Ed.; Wiley: New York, 1974; Vol. 7.
 (6) O’Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1978**, *74*, 1607.
 (7) Hunter, R. J. *Zeta Potential in Colloid Science*; Academic Press: London, 1981.
 (8) Ohshima, H.; Healy, T. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2* **1983**, *79*, 1613.
 (9) O’Brien, R. W. *J. Colloid Interface Sci.* **1983**, *92*, 204.
 (10) Chen, S. B.; Keh, H. J. *J. Fluid Mech.* **1992**, *238*, 251.
 (11) Masliyah, J. H. *Electrokinetic Transport Phenomena*; AOSTRA: Edmonton, Alberta, Canada, 1994.
 (12) O’Brien, R. W.; Cannon, D. W.; Rowlands, W. N. *J. Colloid Interface Sci.* **1995**, *173*, 406.

(13) Rasmusson, M.; Akerman, B.; *Langmuir* **1998**, *14*, 3512.

(14) Morrison, F. A. *J. Colloid Interface Sci.* **1969**, *29*, 687.

(15) Morrison, F. A. *J. Colloid Interface Sci.* **1971**, *36*, 139.

(16) Ivory, C. F. *J. Colloid Interface Sci.* **1984**, *100*, 239.

(17) Keh, H. J.; Huang, Y. C. *J. Colloid Interface Sci.* **2005**, *291*, 282.

a broad range must be considered. In this paper, we present a theoretical investigation for the transient electrophoresis due to a sudden application of a constant electric field for the case of a dielectric sphere with an arbitrary thickness of its double layer. The zeta potential (or surface charge density) of the particle is assumed to be uniform and small. The transient response of the electrophoretic mobility of the particle to a step change in the applied electric field as a function of the relevant parameters such as κa is obtained semianalytically.

2. Analysis

We consider the transient electrophoretic motion of a charged spherical particle of radius a in an unbounded liquid solution containing M ionic species. At the time $t = 0$, the uniform electric field is imposed in the positive z direction and maintains a constant strength E_∞ throughout the system. The origin of the spherical coordinate system (r, θ, ϕ) is taken at the center of the particle and the polar axis $\theta = 0$ points toward the positive z direction. Gravitational effects on the particle are ignored. Obviously, the problem is axially symmetric about the z axis.

Because the Reynolds number of electrokinetic flows is small, the velocity field \mathbf{u} of the incompressible Newtonian fluid at time t is governed by the transient Stokes equations modified with the electrostatic effect

$$-\rho \frac{\partial \mathbf{u}}{\partial t} + \eta \nabla^2 \mathbf{u} = \nabla p + \sum_{m=1}^M z_m e n_m \nabla \psi \quad (1)$$

$$\nabla \cdot \mathbf{u} = 0 \quad (2)$$

Here, n_m and z_m are the concentration (number density) distribution and valence, respectively, of species m , p is the hydrodynamic pressure distribution, ψ is the electrostatic potential distribution, ρ and η are the mass density and viscosity, respectively, of the fluid, and e is the elementary electric charge.

It is assumed that the magnitude of the particle velocity is not large and hence that the electric double layer surrounding the particle is only slightly distorted from the equilibrium state, where there is no applied electric field and the particle and fluid are at rest. Therefore, n_m , ψ , and p can be expressed as

$$n_m = n_m^{(\text{eq})} + \delta n_m \quad (3a)$$

$$\psi = \psi^{(\text{eq})} + \delta \psi \quad (3b)$$

$$p = p^{(\text{eq})} + \delta p \quad (3c)$$

where $n_m^{(\text{eq})}$, $\psi^{(\text{eq})}$, and $p^{(\text{eq})}$ are the equilibrium distributions of the concentration of species m , the electrostatic potential, and the pressure, respectively, and δn_m , $\delta \psi$, and δp are the corresponding small deviations from the equilibrium state. The equilibrium concentration of each ionic species is related to the equilibrium potential by the Boltzmann distribution.

Substituting eq 3 into eq 1, canceling their equilibrium components, using Poisson's equation, and neglecting the

products of the small perturbed quantities δn_m and $\delta \psi$, one obtains

$$-\frac{1}{\nu} \frac{\partial \mathbf{u}}{\partial t} + \nabla^2 \mathbf{u} = \frac{1}{\eta} \nabla \delta p - \frac{\epsilon}{4\pi\eta} [\nabla^2 \psi^{(\text{eq})} \nabla \delta \psi + \nabla^2 \delta \psi \nabla \psi^{(\text{eq})}] \quad (4)$$

where $\nu = \eta/\rho$ is the kinematic viscosity of the fluid, and $\epsilon = 4\pi\epsilon_0\epsilon_r$, where ϵ_r is the relative permittivity of the electrolyte solution and ϵ_0 is the permittivity of a vacuum.

When the zeta potential $\zeta [= \psi^{(\text{eq})}(r = a)]$ of the particle is small (say, $|\zeta|e/kT \leq 2$, where k is the Boltzmann constant and T is the absolute temperature), eq 4 can be further linearized (correct to the first order of ζ , known as the Debye-Hückel approximation) as

$$-\frac{1}{\nu} \frac{\partial \mathbf{u}}{\partial t} + \nabla^2 \mathbf{u} = \frac{1}{\eta} \nabla \delta p - \frac{e\sigma}{\eta\kappa kT} \nabla^2 \psi_{\text{eq1}} \nabla \psi_0 \quad (5)$$

where¹⁸

$$\psi_{\text{eq1}} = \frac{kT}{e} \left(\frac{\kappa a}{\kappa a + 1} \right) \frac{a}{r} \exp[-\kappa(r - a)] \quad (6)$$

$$\psi_0 = -E_\infty \left(\frac{a^3}{2r^2} + r \right) \cos \theta \quad (7)$$

$$\kappa = \left(\frac{4\pi e^2}{\epsilon kT} \sum_{m=1}^M z_m^2 n_m^\infty \right)^{1/2} \quad (8)$$

which is the Debye screening parameter, and σ is the surface charge density of the particle, which is related to ζ by

$$\sigma = \frac{\epsilon(\kappa a + 1)}{4\pi a} \zeta \quad (9)$$

Note that the perturbed potential given by eq 7 satisfies the Laplace equation $\nabla^2 \psi_0 = 0$. We have assumed that there are no transients of any kind in the electrostatic potential; that is, the potential is assumed to develop immediately upon application of the external electric field and is unaffected by the particle motion. Evidently, this assumption is valid in most practical situations of electrophoresis.

Since the flow field is axially symmetric, it is convenient to introduce the Stokes stream function $\Psi(r, \theta, t)$ which satisfies eq 2 and is related to the velocity components in the spherical coordinate system by

$$v_r = -\frac{1}{r^2 \sin \theta} \frac{\partial \Psi}{\partial \theta} \quad (10a)$$

$$v_\theta = \frac{1}{r \sin \theta} \frac{\partial \Psi}{\partial r} \quad (10b)$$

Taking the curl of eq 5 and applying eq 10 give a fourth-order linear partial differential equation for Ψ

$$E_S^2 \left(E_S^2 - \frac{1}{\nu} \frac{\partial}{\partial t} \right) \Psi = \frac{\kappa e \sigma}{\eta k T} E_\infty \left(\frac{a^3}{2r^2} + r \right) \frac{d\psi_{\text{eq1}}}{dr} \sin^2 \theta \quad (11)$$

where the axisymmetric Stokes operator E_S^2 is given by

$$E_S^2 = \frac{\partial^2}{\partial r^2} + \frac{\sin \theta}{r^2} \frac{\partial}{\partial \theta} \left(\frac{1}{\sin \theta} \frac{\partial}{\partial \theta} \right) \quad (12)$$

The initial and boundary conditions for the fluid velocity field around the particle are

$$t = 0: v_r = v_\theta = 0 \quad (13)$$

$$r = a: v_r = U \cos \theta \quad (14a)$$

$$v_\theta = -U \sin \theta \quad (14b)$$

$$r \rightarrow \infty: v_r = v_\theta = 0 \quad (15)$$

where U is the time-dependent electrophoretic velocity of the particle to be determined. Clearly, $U(t = 0) = 0$ and

$$U(t \rightarrow \infty) \equiv U_\infty = \frac{\epsilon \zeta E_\infty}{4\pi\eta} \{1 - [5E_7(\kappa a) - 2E_5(\kappa a)] \exp(\kappa a)\} \quad (16)$$

which is the steady-state particle velocity obtained by Henry¹ and

$$E_n(x) = \int_1^\infty y^{-n} \exp(-xy) dy \quad (17)$$

It is well understood that the steady electrophoretic mobility given by eq 16 is a monotonic increasing function of the electrokinetic parameter κa for a charged sphere with a constant surface potential and is a monotonic decreasing function of κa for a particle with a constant surface charge density.¹¹ Inspection of eqs 10–15 shows that the stream function must be of the form

$$\Psi = g(r,t) \sin^2 \theta \quad (18)$$

The Laplace transform, which is defined by an over-bar for a function of time $f(t)$ as

$$\bar{f}(s) = \int_0^\infty f(t) \exp(-st) dt \quad (19a)$$

and

$$f(t) = \frac{1}{2\pi i} \int_{\gamma-i\infty}^{\gamma+i\infty} \bar{f}(s) \exp(st) ds \quad (19b)$$

with $i = \sqrt{-1}$, will be used to solve for the flow field and particle velocity. Then, the transform of eq 11 with the substitution of eq 18 becomes

$$\left(\frac{d^2}{dr^2} - \frac{2}{r^2} \right) \left(\frac{d^2}{dr^2} - \frac{2}{r^2} - \frac{s}{\nu} \right) \bar{g}(r,s) = -\frac{3r}{sa^2} G(r) \quad (20)$$

where

$$G(r) = -\frac{\kappa a^2 e \sigma}{6\eta k T} E_\infty \left[2 + \left(\frac{a}{r} \right)^3 \right] \frac{d\psi_{eq1}}{dr} \quad (21)$$

The general solution of eq 20 in the form of $\bar{\Psi}(r, \theta, s)$ defined by eqs 18 and 19 can be expressed as

$$\bar{\Psi} = \left[C_1 \left(\frac{r}{a} \right)^2 + C_2 \left(\frac{r}{a} \right)^{-1} + C_3 \left(1 - \sqrt{\frac{\nu 1}{sr}} \right) \exp\left(\sqrt{\frac{s}{\nu}} r \right) + C_4 \left(1 + \sqrt{\frac{\nu 1}{sr}} \right) \exp\left(-\sqrt{\frac{s}{\nu}} r \right) + \bar{g}_p(r,s) \right] \sin^2 \theta \quad (22)$$

with the particular solution

$$\bar{g}_p = \frac{1}{s} \left[\left(\frac{r}{a} \right)^2 \int_a^\infty \frac{\nu}{s} G dr - \frac{a}{r} \int_a^\infty \frac{\nu(r/a)^3}{s} G dr - \frac{3}{2a^2} \left(\frac{\nu}{s} \right)^2 \left(1 - \sqrt{\frac{\nu 1}{sr}} \right) \exp\left(\sqrt{\frac{s}{\nu}} r \right) \int_a^\infty \left(1 + \sqrt{\frac{s}{\nu}} r \right) \exp\left(-\sqrt{\frac{s}{\nu}} r \right) G dr - \frac{3}{2a^2} \left(\frac{\nu}{s} \right)^2 \left(1 + \sqrt{\frac{\nu 1}{sr}} \right) \exp\left(-\sqrt{\frac{s}{\nu}} r \right) \int_a^\infty \left(1 - \sqrt{\frac{s}{\nu}} r \right) \exp\left(\sqrt{\frac{s}{\nu}} r \right) G dr \right] \quad (23)$$

The coefficients $C_1, C_2, C_3,$ and C_4 in eq 22 are to be determined from the boundary conditions given by eqs 14 and 15, with the result

$$C_1 = -\frac{\nu}{s^2} \int_a^\infty G dr \quad (24a)$$

$$C_2 = -2C_3 \exp\left(a \sqrt{\frac{s}{\nu}} \right) - \frac{1}{2a^2} \left(\frac{\nu}{s} \right) (2C_1 + a^2 \bar{U}) \left(3 + 3a \sqrt{\frac{s}{\nu}} + a^2 \frac{s}{\nu} \right) \quad (24b)$$

$$C_3 = \frac{3}{2a^2} \left(\frac{\nu}{s} \right)^2 \frac{1}{s} \int_a^\infty \left(1 + \sqrt{\frac{s}{\nu}} r \right) \exp\left(-\sqrt{\frac{s}{\nu}} r \right) G dr \quad (24c)$$

$$C_4 = C_3 \exp\left(2a \sqrt{\frac{s}{\nu}} \right) + \frac{3}{2a} \sqrt{\frac{\nu}{s}} (2C_1 + a^2 \bar{U}) \exp\left(a \sqrt{\frac{s}{\nu}} \right) \quad (24d)$$

With the solution of the stream function given by eqs 22–24, the fluid velocity components can be determined using eq 10.

The total force exerted on a charged spherical particle undergoing electrophoresis in an electrolyte solution can be expressed as the sum of the electric force and the hydrodynamic drag force. The electric force acting on the charged sphere can be represented by the integral of the electrostatic force density over the fluid volume outside the particle. Due to the fact that the net electric force acting on the particle at the equilibrium state is zero, the electric force in the Debye–Huckel approximation is given by

$$F_e = -\frac{2\pi e \sigma}{\kappa k T} \int_0^\pi \int_a^\infty \nabla^2 \psi_{eq1} \nabla \psi_0 \cdot \mathbf{e}_z r^2 \sin \theta dr d\theta \quad (25)$$

where \mathbf{e}_z is the unit vector in the positive z direction. Substituting eqs 6 and 7 into eq 25, we obtain

$$F_e = -4\pi\eta a \int_a^\infty \left(\frac{r}{a} \right)^3 G dr - 2\pi\kappa a^3 \sigma E_\infty \frac{\kappa a}{\kappa a + 1} \quad (26)$$

which is time-independent.

The transient hydrodynamic drag force acting on the sphere is given by the general expression¹⁹

$$F_h = \pi \left[r^2 \int_0^\pi \frac{\partial p}{\partial \theta} \sin^2 \theta d\theta - 2\eta r \int_0^\pi E_S^2 \Psi \sin \theta d\theta \right]_{r=a} \quad (27)$$

After the application of eqs 3c and 5 knowing that the equilibrium hydrodynamic pressure is not a function of

(19) Happel, J.; Brenner, H. *Low Reynolds Number Hydrodynamics*; Martinus Nijhoff: Dordrecht, The Netherlands, 1983.

θ to get rid of the pressure term, the previous expression becomes

$$F_h = \pi \int_0^\pi \left[\eta r^4 \sin \theta \frac{\partial}{\partial r} \left(\frac{E_S^2 \Psi}{r^2 \sin^2 \theta} \right) - \rho r^3 \frac{\partial v_\theta}{\partial t} + \kappa r^2 \frac{e\sigma}{kT} \frac{\partial}{\partial \theta} (\psi_{\text{eq1}} \psi_0) \right]_{r=a} \sin^2 \theta d\theta \quad (28)$$

The substitution of eqs 6 and 7 into eq 28 yields

$$F_h = \pi \int_0^\pi \left[\eta r^4 \sin^3 \theta \frac{\partial}{\partial r} \left(\frac{E_S^2 \Psi}{r^2 \sin^2 \theta} \right) - \rho r^3 \sin^2 \theta \frac{\partial v_\theta}{\partial t} \right]_{r=a} d\theta + 2\pi \kappa a^3 \sigma E_\infty \frac{\kappa a}{\kappa a + 1} \quad (29)$$

The total force is equal to the rate of change of the particle momentum with respect to time

$$F_e + F_h = \frac{4}{3} \pi a^3 \rho_s \frac{dU}{dt} \quad (30)$$

where ρ_s is the mass density of the particle. Evidently, there are two key factors that govern the transients in this system: the first is the transient involved in the development of the velocity profile around the particle and the second is the transient associated with the inertial acceleration of the particle. When t is small, the second factor is more important, but when t is relative large, the first factor becomes more important.

After taking the Laplace transform of eqs 26, 29, and 30 and using eqs 22–24 and 10b, we obtain the general equation of motion of an electrophoretic sphere in response to the application of a step-function electric field

$$\bar{U}^*(S) = \frac{2}{S^2 \left[1 + \sqrt{S} + \frac{1}{9} \left(1 + 2 \frac{\rho_s}{\rho} \right) S \right]} \int_a^\infty \left\{ 1 + \sqrt{S} + \frac{1}{3} S - \left(1 + \sqrt{S} \frac{r}{a} \right) \exp \left[-\sqrt{S} \left(\frac{r}{a} - 1 \right) \right] - \frac{S}{3} \left(\frac{r}{a} \right)^3 \right\} G dr \quad (31)$$

where

$$T = vt/a^2 \quad (32a)$$

and

$$S = a^2 s/\nu \quad (32b)$$

are the dimensionless time and its Laplace-transform variable, respectively, and

$$\bar{U}^*(S) = \bar{U}(s)\nu/a^2 \quad (33)$$

The time-dependent electrophoretic velocity U of the dielectric sphere in response to the application of a step-function electric field can be obtained by the numerical inverse transform of eq 31. The result, which will be presented in the next section, indicates that the transient electrophoretic velocity is not only a function of the dimensionless time T but also a function of the parameters κa and ρ_s/ρ . In the limits of $\kappa a \rightarrow \infty$ and $\kappa a \rightarrow 0$, the inverse transform of eq 31 can be performed analytically, and the results reduce to the corresponding closed-form formulas

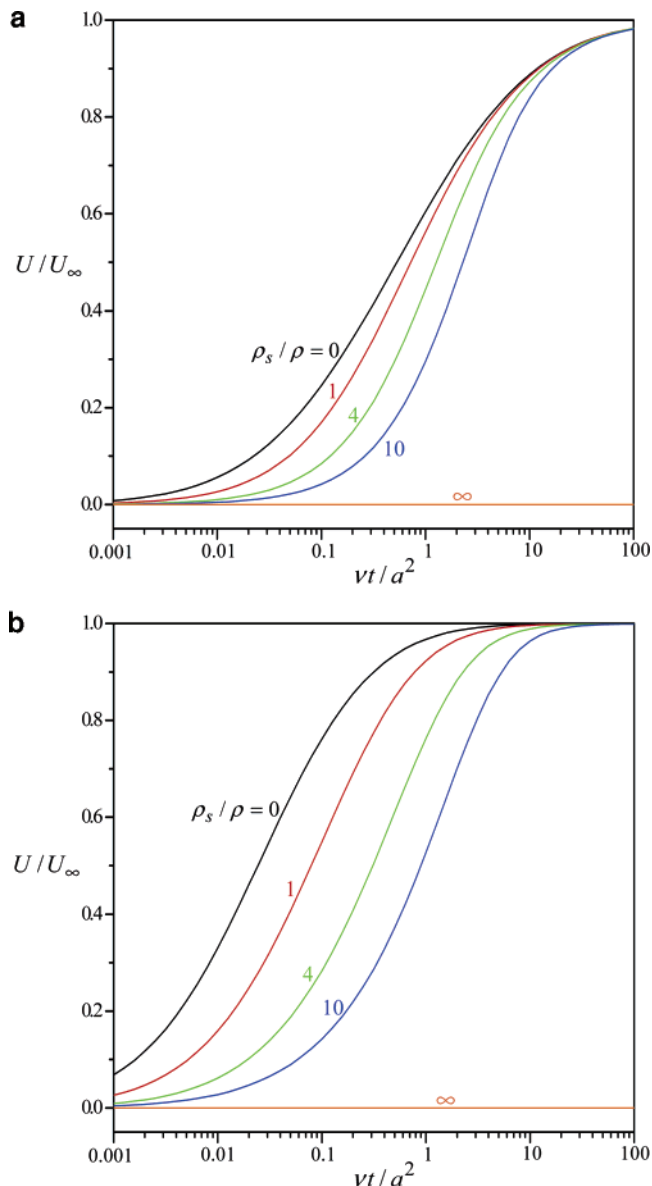


Figure 1. Plots of the normalized electrophoretic mobility U/U_∞ versus the dimensionless time vt/a^2 with ρ_s/ρ as a parameter: (a) $\kappa a = 0.1$; (b) $\kappa a = 10$.

given in the literature.^{14,17} Note that the relaxation (polarization) effect of the diffuse ions in the electric double layer surrounding the particle is not included in eq 31, and its validity demands that the diffusion time scale for the ions across the double layer is much shorter than the viscous time scale.

3. Results and Discussion

When a spherical dielectric particle of radius a in an electrolyte solution is subjected to an applied electric field of a constant strength E_∞ from the time $t = 0$, the transient electrophoretic velocity U can be obtained by the numerical inverse transform of eq 31. In Figures 1–4, this time-dependent particle velocity normalized by its steady-state quantity U_∞ given by eq 16 is plotted versus the dimensionless time vt/a^2 , the mass density ratio ρ_s/ρ , and the electrokinetic parameter κa . As expected, the electrophoretic mobility of the particle increases monotonically with the time from zero at $t = 0$ to its steady-state

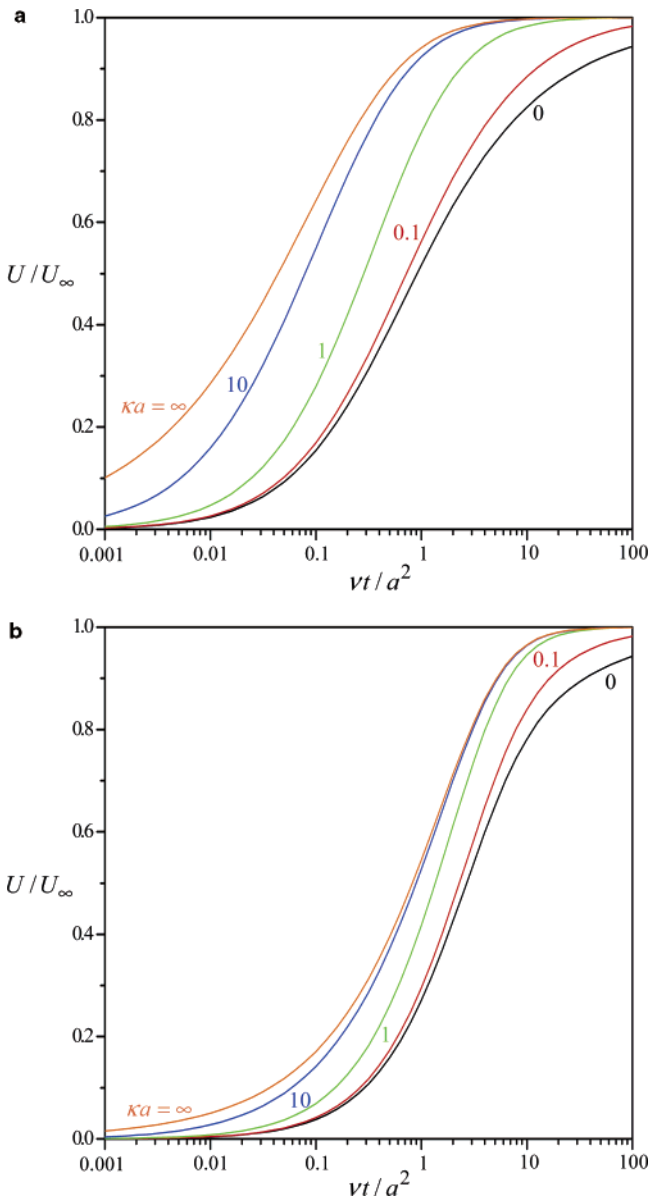


Figure 2. Plots of the normalized electrophoretic mobility U/U_∞ versus the dimensionless time vt/a^2 with κa as a parameter: (a) $\rho_s/\rho = 1$; (b) $\rho_s/\rho = 10$.

magnitude as $t \rightarrow \infty$ for any specified value of κa and finite value of ρ_s/ρ .

For constant values of κa and vt/a^2 , as shown in Figures 1, 3a, and 4, the normalized electrophoretic mobility of the dielectric sphere is a monotonic decreasing function of ρ_s/ρ , meaning that a heavier particle lags behind a lighter one in the development of the electrophoretic velocity. In the limiting case of $\rho_s/\rho \rightarrow \infty$, the particle mobility vanishes regardless of the values of κa and vt/a^2 . For fixed values of ρ_s/ρ and vt/a^2 , as illustrated in Figures 2, 3, and 4a, U/U_∞ decreases monotonically with a decrease in κa , indicating that a particle with a thicker double layer is trailing behind the same particle with a thinner double layer in the development of the normalized electrophoretic mobility (although the actual mobility U/E_∞ of the particle might still increase with a decrease in κa for the case of constant surface charge density, because the steady mobility in this case is higher at thicker double layer). This behavior is expected knowing that the transient

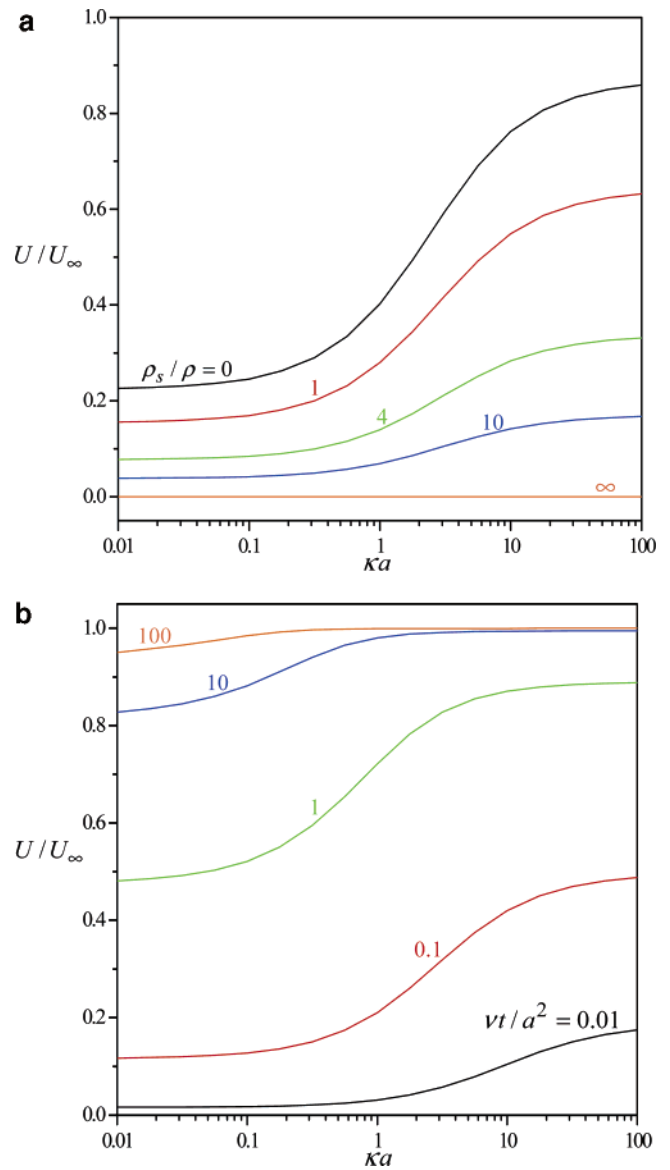


Figure 3. Plots of the normalized electrophoretic mobility U/U_∞ versus the parameter κa : (a) $vt/a^2 = 0.1$; (b) $\rho_s/\rho = 2$.

electroosmotic velocity of an electrolyte solution adjacent to a charged solid surface relative to its steady quantity becomes smaller when the thickness of the double layer increases, regardless whether the surface potential or the surface charge density is constant.²⁰

Figures 5 and 6 show plots of the dimensionless acceleration $(a^2/\nu U_\infty) dU/dt$ of a spherical particle undergoing transient electrophoresis versus the dimensionless time vt/a^2 with ρ_s/ρ and κa as parameters. As expected, the acceleration is a monotonic decreasing function of the time from a maximum at $t = 0$ to zero as $t \rightarrow \infty$ for any fixed value of κa and finite value of ρ_s/ρ . For a given value of κa , as exhibited in Figure 5, the dimensionless acceleration first (say, as $vt/a^2 < 0.05$) decreases with an increase in ρ_s/ρ but later may become an increasing function of ρ_s/ρ . For a specified value of ρ_s/ρ , as shown in Figure 6, the dimensionless acceleration first decreases with a decrease in κa but later may increase with a decrease in κa . For the limiting case of $\kappa a \rightarrow \infty$, the acceleration is infinite at the instant the electric field is

(20) Keh, H. J.; Tseng, H. C. *J. Colloid Interface Sci.* **2001**, *242*, 450.

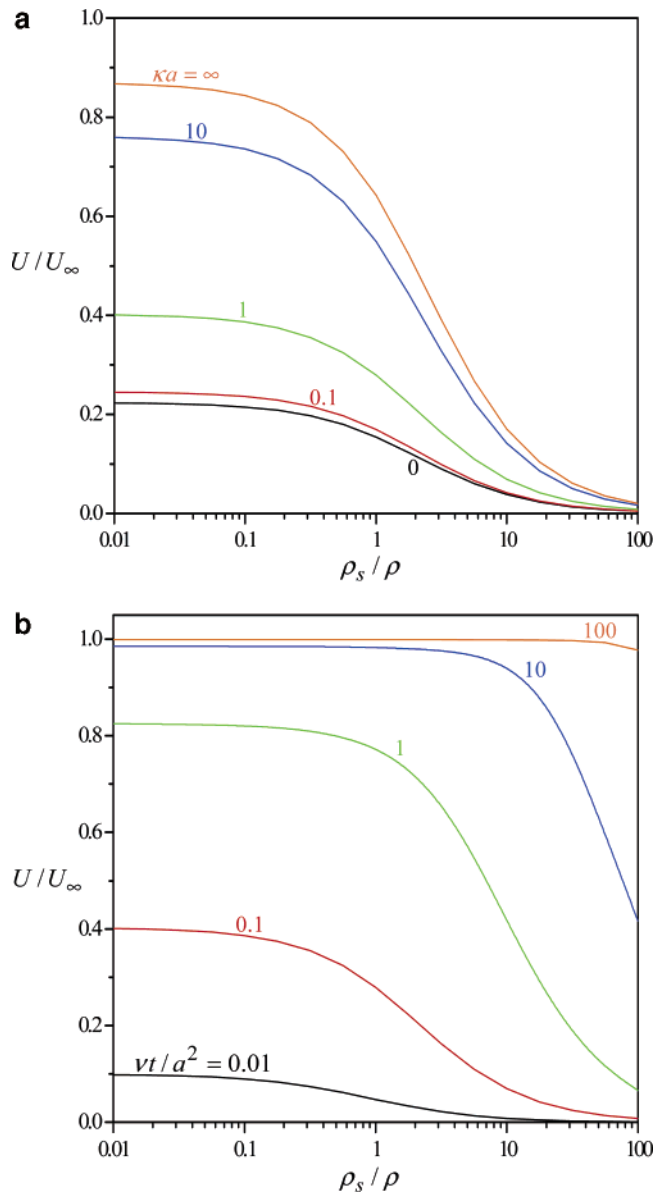


Figure 4. Plots of the normalized electrophoretic mobility U/U_∞ versus the parameter ρ_s/ρ : (a) $vt/a^2 = 0.1$; (b) $\kappa a = 1$.

imposed, and this singular result is due to the finite electroosmotic slip velocity at the particle surface, which drives the electrophoretic movement of the particle, even at the time $t = 0$. For the limiting case of $\kappa a = 0$, the initial dimensionless acceleration is a finite value equal to $9/(1 + 2\rho_s/\rho)$, which can be derived from the available analytical solution for the relevant transient electrophoretic mobility.¹⁷ As $vt/a^2 > 0.5$, in general, the inertial acceleration of the particle given by the right-hand side of eq 30 is negligible and the instantaneous particle velocity could be evaluated by simply setting the sum of the force acting on the particle equal to zero.

As a typical example, we now consider the situation of a neutrally buoyant spherical particle (with $\rho_s/\rho = 1$) shown in Figure 2a. The instantaneous electrophoretic mobility of the particle reaches 95% of its terminal value in the dimensionless time vt/a^2 equal to about 1.2 and 127 for the limiting cases of a thin double layer ($\kappa a \rightarrow \infty$) and of a thick double layer ($\kappa a \rightarrow 0$), respectively (a particle of thicker double layer tails one with a thinner double layer in the

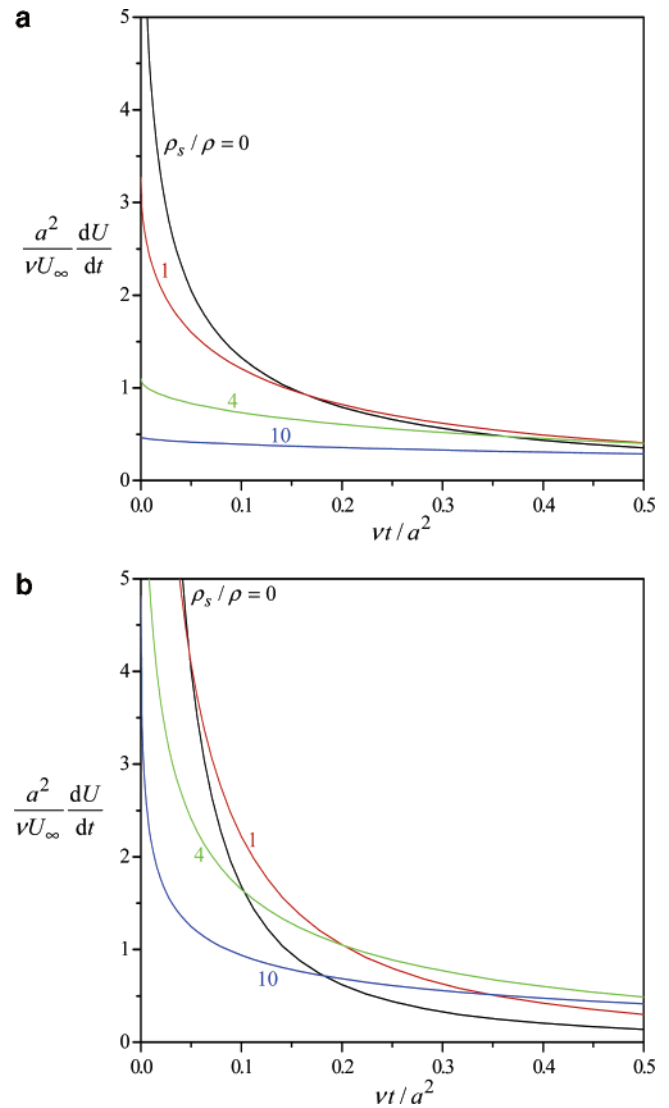


Figure 5. Plots of the normalized electrophoretic acceleration ($a^2/vU_\infty dU/dt$) versus the dimensionless time vt/a^2 with ρ_s/ρ as a parameter: (a) $\kappa a = 0.1$; (b) $\kappa a = 10$.

development of the normalized mobility U/U_∞), which can also be predicted from the relevant analytical solutions,¹⁷ independent of the applied electric field and the zeta potential of the particle. When the particle is suspended in an aqueous solution (with ν of the order 10^{-6} m²/s) and has a radius of the order 1 μm (for the case of a thin double layer) or 0.1 μm (for the case of a thick double layer), these relaxation responses correspond to time scales on the order of microseconds. For a particle with a greater value of ρ_s/ρ , the relaxation time for transient electrophoresis can be an order of magnitude longer, but this response time is still negligible in practical applications. Consequently, the electrophoretic velocity of a dielectric sphere will closely follow the Henry equation (eq 16) with the instantaneous applied electric field.

4. Concluding Remarks

In this paper, an analysis of the transient electrophoresis of a spherical dielectric particle with a low zeta potential suspended in an electrolyte solution with an arbitrary value of κa in response to a step change in the applied electric field is presented. Solving the linearized unsteady

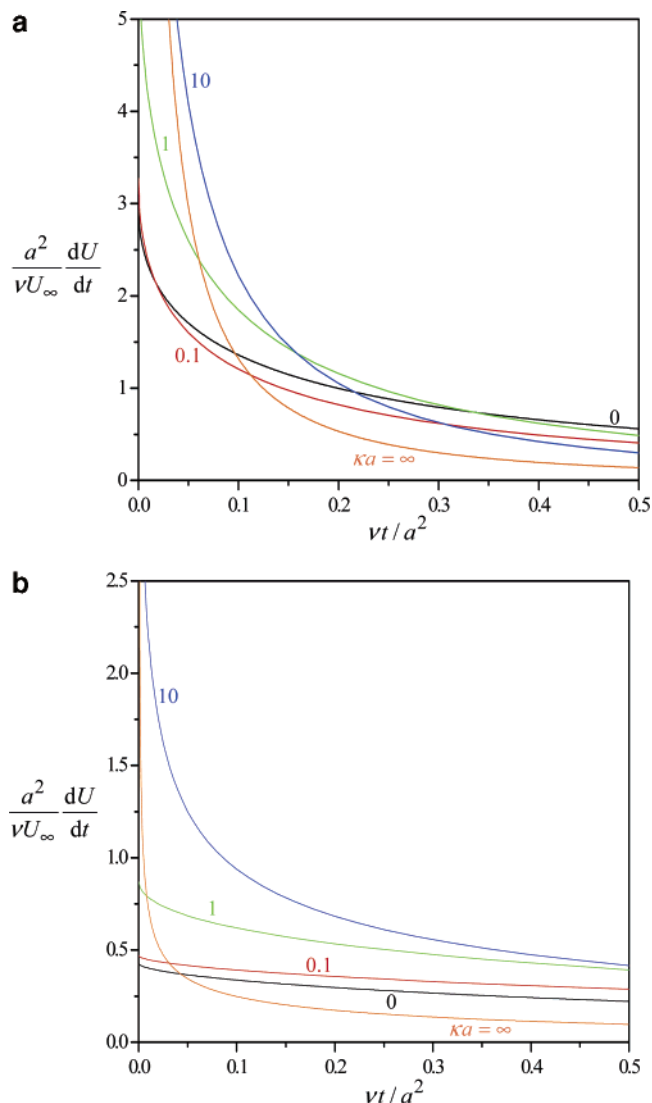


Figure 6. Plots of the normalized electrophoretic acceleration ($a^2/\nu U_\infty$) dU/dt versus the dimensionless time $\nu t/a^2$ with κa as a parameter: (a) $\rho_s/\rho = 1$; (b) $\rho_s/\rho = 10$.

equation of motion applicable to the system, we have obtained semianalytical solutions for the dynamic re-

sponse of the flow field of the suspending fluid and the electrophoretic mobility of the particle as a function of the relevant parameters. These results show that the particle mobility decreases monotonically with a decrease in the electrokinetic particle radius κa for fixed values of the mass density ratio ρ_s/ρ and the dimensionless time $\nu t/a^2$. The acceleration of the particle decreases monotonically with the time and vanishes in the limit $\nu t/a^2 \rightarrow \infty$. Our results, which provide useful insight into the actual phenomena regarding the transient response of a charged particle to a sudden application of a constant electric field, indicate that the effect of the relaxation time for transient electrophoresis in general is negligible, irrespective of the applied electric field, the zeta potential, and the value of κa .

It is worth repeating that the above-mentioned semianalytical solutions are obtained on the basis of the Debye–Huckel approximation. This means that these results are satisfactory only when used for low values of $\psi^{(eq)}$. Comparing with the numerical results for the steady-state electrophoretic mobility of a charged sphere in a KCl solution obtained by O’Brien and White⁶ valid for an arbitrary value of zeta potential; however, one can find that eq 16 for the mobility of a charged sphere with a low zeta potential in an electrolyte solution is quite accurate for reasonably high zeta potentials (with errors less than 4% for $|\zeta|e/kT \leq 2$). Therefore, our results might be used tentatively for the situation of reasonably high electric potential. To see whether our approximate solution can be extended to the general case with higher values of the electric potential, a numerical solution to the unsteady electrokinetic differential equations with no assumption on the magnitude of electric potential, allowing the polarization effect of the mobile ions in the double layer, would be needed to compare it with the approximate solution.

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