Electrokinetic Behavior of Colloidal Particles with Thin Ionic Double Layers

The phenomenological equations that govern the nonequilibrium behavior of the ionic diffuse double layer surrounding an isolated, charged colloidal particle are considered. An approximate solution is constructed that is valid when the ratio of the Debye length to the characteristic particle dimension is small. This solution is applicable to a particle that is subjected to an external perturbation composed of an arbitrary linear combination of steady, axisymmetric electrical, hydrodynamical, or concentration gradient fields. Hence, this analysis provides a unified approach to the treatment of the entire class of admissible problems in the thin double layer approximation. Specific applications are shown to the problems of electrophoresis and dilute shear viscosity of a suspension of uniform, noninteracting spherical colloidal particles. Comparison with the numerical results of previous investigators shows that the solutions are accurate over much of the parameter range of practical interest in colloidal suspensions. The role of the zeta potential and the mobilities, valences, and concentrations of the dissolved ions on electrokinetic phenomena are examined.

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Introduction

At the boundary of an electrolyte in contact with a charged solid surface there is a diffuse layer of free ionic charge present as a consequence of the balance between electrostatic forces and thermal fluctuations (Verwey and Overbeek, 1948). At equilibrium this ionic diffuse double layer is characterized by sharp variations in the ion concentrations, charge density, and electric potential normal to the solid surface. This equilibrium can be perturbed by a wide variety of steady or time-dependent fields that originate in the macroscopic gradients of the ionic concentrations and electric potential or in the hydrodynamic flows of the solvent. The electrokinetic phenomena that arise are important in several technological applications as well as in fundamental experiments to study the nature and properties of the solid–electrolyte interface.

Smoluchowski (1921) first studied these phenomena theoretically, and his results for electrophoresis, electroosmosis, and other cognate problems are widely used to interpret experimental data (Hunter, 1981). There are two key assumptions that are implicit in Smoluchowski's results. The first is that the ratio of the thickness of the diffuse double layer (i.e., the Debye length) to the characteristic macroscopic dimension (i.e., the particle or capillary pore size) is infinitesimally small. The second assumption is that the modifying effect of the electroosmotic convection, ionic diffusion, and electromigration fluxes that occur transverse to the solid surface within the double layer region is negligible. The first of these assumptions is invariably satisfied in experimental systems involving aqueous electrolytes. These systems are of the greatest interest from the practical point of view. It turns out that if the first assumption is valid, then the second is not crucial unless the electric potential at the particle surface (the zeta potential) is fairly large.

Subsequent theoretical research in electrokinetic phenomena has dealt with the removal of one or both of these assumptions. Hermans (1938), Overbeek (1943), and Booth (1950a,b, 1954) presented a phenomenological set of transport equations for the solvent velocity, electric potential, and concentrations of the various ionic species. In the absence of any perturbing fields their formulation reduces to the Gouy–Chapman equilibrium model of the ionic diffuse double layer. These equations, which are described here in the Problem Formulation section, are nonlinear and strongly coupled in the field variables. In practical applications, the applied perturbing fields are sufficiently weak that only the linear response to these fields needs to be considered. However, the essential difficulty in the problem arises from the nonlinear dependence of the ionic concentrations on the electric potential in the double layer region. Even at equilibrium, this leads to the well-known Poisson–Boltzmann equation,

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the solution of which must in general be obtained either numerically (Loeb et al., 1961) or by approximate methods (Natarajan and Schechter, 1984, 1986).

Two approaches have been used to obtain approximate solutions to the electrokinetic equations. The first approach (Overbeek, 1943; Booth 1950a,b, 1954) removes Smoluchowski's thin double layer approximation and linearizes the equation set by assuming a small zeta potential. This is akin to the Debye–Hückel linearization of the equilibrium equations. Higher order effects in the zeta potential are calculated by a regular perturbation procedure; however, this rapidly becomes cumbersome and it is impractical to calculate more than about two terms in the solution expansion. The radius of convergence of these series solutions is not well defined, and this is important in view of the fact that the measurable deviations from the Smoluchowski theory in the thin double layer limit occur at fairly large values of the zeta potential.

The second approach, which has been taken by several recent investigators (Dukhin and Derjaguin, 1974; Dukhin and Shilov, 1974; Ohshima et al., 1982; O'Brien, 1983; Fixman, 1980, 1983; Chew and Sen, 1982; Chew, 1983; O'Brien and Hunter, 1981; Hinch and Sherwood 1983), retains the thin double layer assumption while removing the restriction to small zeta potentials of the previous approach. Here, the solvent is divided into two regions—an inner region just adjacent to the solid surface where the charge density and ionic concentrations vary sharply normal to the surface, and an outer electroneutral region further away that is characterized by more gradual variations in the field variables. This approach is not a linearization, and its success is due entirely to the fact that even though the perturbing fields give rise to gradual variations in the ionic concentrations parallel to the solid surface, the normal variations are as if there were a local equilibrium. This enables the use of the only exact solution of the equilibrium equations that is valid for all zeta potential, namely, for the case of a binary, symmetric electrolyte adjacent to a flat solid surface (Loeb et al., 1961).

The latter approach is due to Dukhin and coworkers (Dukhin and Derjaguin, 1974; Dukhin and Shilov, 1974), but their intuitive formulation has led to several alternative derivations (Ohshima et al., 1982; Fixman, 1983; O'Brien and Hunter, 1981). All of these studies lead to essentially the same results. The primary purpose of this paper is to show this consensus and to provide definitive results that are applicable to a wide variety of boundary value problems in the thin double layer approximation. Considering only linear effects in the perturbing fields, the solution to the electrokinetic equations is obtained in the form of integrals. Then, as in the previous work (Natarajan and Schechter, 1984, 1986), we consider a binary symmetric electrolyte and analytically evaluate these integrals to obtain exact solutions. The novelty here is that these solutions are applicable to all linear combinations of axisymmetric perturbing fields whether originating from imposed electric gradients, concentration gradients, or hydrodynamic flows.

The results are specialized to consider two well-known problems—electrophoresis of a single colloidal particle, and the dilute shear viscosity of a colloidal suspension. Although extensively studied, these two problems together illustrate all the calculations required for the general case. They also permit a comparison with the numerical work of previous investigators (O'Brien and White, 1981; Watterson and White 1981). Such comparisons have also been carried out by others (O'Brien and Hunter, 1981; Fixman, 1983) and show the analytical results of the thin double layer approximation to be accurate over much of the parameter range of practical interest in colloidal suspensions. It is hence a simple and very useful generalization of the Smoluchowski theory.

Problem Formulation

Consider a charged spherical colloidal particle that is fixed at the origin and is completely immersed in an electrolyte solvent. The particle is surrounded by a diffuse layer of compensating free ionic charge whose density decays exponentially from the particle surface. The Debye length κ^{-1}, which is an estimate for the length scale of this decay is defined as

$$\kappa^{-1} = \left(\frac{\epsilon_m kT}{\Sigma_i \, n_{i\infty} e^2 z^2{}_i} \right)^{1/2} \tag{1}$$

where ϵ_m is the solvent electric permittivity; k, T, and e are Boltzmann's constant, absolute temperature, and protonic charge; $n_{i\infty}$, z_i, and $\mathcal{D}_i$ are the reference bulk electroneutral concentrations, valences, and diffusivities, respectively, of ionic species i. In an aqueous univalent symmetric electrolyte, for example, we have $\kappa^{-1} = 3.04 \times 10^{-8}\ \mathrm{M}^{-1/2}$ cm, where M is the molar concentration of electrolyte. In addition, we let η_0 and U denote the solvent viscosity and a characteristic measure of the ambient fluid velocity distant from the particle surface, respectively.

The dimensionless particle radius a, pressure p, velocity $\boldsymbol{u}$, electric potential ϕ, charge density ρ, and the concentration of ionic species i, n_i are all defined with respect to the scales, κ^{-1}, $\eta_0 U\kappa$, U, kT/e, $\Sigma_i n_{i\infty} e z_i^2$, and $n_{i\infty}$, respectively. Under steady conditions the required field equations are given by

$$0 = -\nabla p + \nabla^2 \boldsymbol{u} - \mathcal{H} \rho \nabla \phi \tag{2}$$

$$\nabla \cdot \boldsymbol{u} = 0 \tag{3}$$

$$\nabla^2 \phi = -\rho \tag{4}$$

$$\nabla^2 n_i + \nabla \cdot (z_i n_i \nabla \phi) = \mathcal{P}_i \boldsymbol{u} \cdot \nabla n_i \quad \text{for all } i \tag{5}$$

where the index i in Eq. 5 runs over all the dissolved ionic species. Equation 2 describes the solvent flow, and in addition to the usual creeping flow terms contains a term that corresponds to the electrical body force. The continuity equation and Poisson's equation for the electric potential are given in Eqs. 3 and 4. Species conservation Eq. 5 contains terms corresponding to diffusion, electromigration and convection, respectively. The quantities $\mathcal{H}$ and $\mathcal{P}_i$ are the Hartmann number and the individual ionic Peclet numbers respectively,

$$\mathcal{H} = \frac{kT \sum_i n_{i\infty} z_i^2}{\kappa \eta_0 U}, \quad \mathcal{P}_i = \frac{U}{\kappa D_i} \tag{6}$$

These quantities are defined here in a convenient but more or less arbitrary choice of scales; hence their magnitudes are not significant and they do not appear as such in the final results. The boundary conditions associated with Eqs. 2–5 are

$$\phi = \phi^*, \quad r = a \tag{7}$$

$$u = 0, \quad r = a \tag{8}$$

$$z_i n_i \frac{\partial \phi}{\partial r} + \frac{\partial n_i}{\partial r} = 0 \quad \text{for all } i,\ r = a \tag{9}$$

$$\rho \longrightarrow 0, \quad r \longrightarrow \infty \tag{10}$$

The condition in Eq. 7 is that the electric potential on the particle surface is given by the zeta potential, i.e. $\phi^* = e\zeta/kT$; Eqs. 8 and 9 are the no-slip condition for the solvent velocity and the no-flux condition for ion species transport at the particle surface. The condition in Eq. 10 is that the ionic charge density vanishes far away from the particle. There are additional boundary conditions on the field variables as $r \longrightarrow \infty$ associated with the applied perturbations to which the particle is subjected. These are left unspecified for the present.

The basic assumptions in the set of model equations given above are:

1. The solvent is uniform and has a constant viscosity and electric permittivity up to the particle surface
2. There are no finite size effects associated with the ions in the electrolyte
3. The electric potential at the no-slip surface is uniform
4. There is no transfer of ionic species between the electrolyte and the Stern layer of strongly adsorbed ions on the particle surface

In the absence of any perturbing fields, the convective terms in the ionic transport Eq. 5 are zero. The remaining terms integrate to give Boltzmann distributions for the various ionic species

$$n_i = \exp(-z_i \phi) \tag{11}$$

The charge density is then given by

$$\rho = \frac{\sum_i e z_i n_i n_{i\infty}}{\sum_i e z_i^2 n_{i\infty}} = \frac{\sum_i e z_i n_{i\infty} \exp(-z_i \phi)}{\sum_i e z_i^2 n_{i\infty}} \tag{12}$$

In this case, the terms involving the electric body forces in Eq. 2 can be written as the gradient of a scalar potential

$$-\rho \nabla \phi = \nabla \left[\frac{\sum_i e n_{i\infty} \exp(-z_i \phi)}{\sum_i e z_i^2 n_{i\infty}} \right] \tag{13}$$

showing that at equilibrium the electric body forces can be balanced by a isotropic pressure field.

Axisymmetric Solution to the Velocity Field

In this section, we obtain a general axisymmetric solution to Eqs. 2 and 3 for the solvent flow with the boundary conditions of Eq. 8. The solution is implicit since the charge density ρ and the electric potential ϕ are unknown and themselves depend on the velocity field through the convective terms in Eq. 5. We consider a Cartesian system of axes with base vectors (e_1, e_2, e_3) with the axis of symmetry in the e_3 direction, as well as a polar coordinate system (r, θ, φ), where θ is the angle measured from the symmetry axis and φ is the azimuthal angle.

The velocity field in the solvent is decomposed in the form

$$u = u^{ex} + u^{in} \tag{14a}$$

$$p = p^{ex} + p^{in} \tag{14b}$$

so that (u^{ex}, p^{ex}) satisfy the homogenous Stokes equation, the no-slip condition on the particle surface, and the appropriate specified velocity boundary condition far away from the particle. The particular solution (u^{in}, p^{in}) satisfies the no-slip condition on the particle surface but decays to zero far away from the particle. The first solution is associated with the externally imposed flow field, while the second solution corresponds to the electroosmotic flows generated by the electrical body forces in the double layer region.

The methods for solving the homogenous Stokes equations for the flow external to a sphere are well known (Happel and Brenner, 1973; Chwang and Wu, 1975). In a later section, to calculate the dilute shear viscosity, we consider the case when the distant flow is an axisymmetric, pure shear flow with the symmetric rate of strain tensor D given by

$$D = -\frac{1}{2} e_1 \otimes e_1 - \frac{1}{2} e_2 \otimes e_2 + e_3 \otimes e_3 \tag{15}$$

The solution to the velocity field u^{ex} with this ambient flow is

$$u_i^{ex} = u^{ex} \cdot e_i = D_{ij} r_j \left(1 - \frac{a^5}{r^5}\right) - \frac{5}{2} D_{jk} \frac{r_j r_k r_i}{r^2} \left(\frac{a^3}{r^3} - \frac{a^5}{r^5}\right) \tag{16}$$

The velocity components of the solution (u^{in}, p^{in}) are given in terms of the Stokes stream function Ψ^{in} as

$$u_r^{in} = \frac{1}{r^2} \frac{\partial \Psi^{in}}{\partial \mu}, \quad u_\theta^{in} = \frac{1}{r(1 - \mu^2)^{1/2}} \frac{\partial \Psi^{in}}{\partial r} \tag{17}$$

where $\mu = \cos \theta$. Taking the curl of Eq. 2, we obtain

$$E^2 E^2 \Psi^{in} \equiv \left[\frac{\partial^2}{\partial r^2} + \frac{(1 - \mu^2)}{r^2} \frac{\partial^2}{\partial \mu^2} \right]^2 \Psi^{in} = -\mathcal{H}(1 - \mu^2) \left(\frac{\partial \rho}{\partial r} \frac{\partial \phi}{\partial \mu} - \frac{\partial \phi}{\partial r} \frac{\partial \rho}{\partial \mu} \right) \tag{18}$$

along with the boundary conditions

$$\Psi^{in} = \frac{\partial \Psi^{in}}{\partial r} = 0, \quad r = a \tag{19}$$

$$\Psi^{in} \longrightarrow 0, \quad r \longrightarrow \infty \tag{20}$$

The operator E^2 in Eq. 18 is separable in spherical coordinates (Happel & Brenner, 1973) and the eigenfunctions of the angular part are given by the set $[C_p(\mu)]_{p=2}^{\infty}$, where $C_p(\mu)$ are the Gegenbauer polynomial of degree p and order $-1/2$. These functions form a complete, orthogonal set on the interval $(-1, 1)$ with respect to an inner product with weight function (1 –

$\mu^2)^{-1}$. The orthogonality condition is given by

$$\int_{-1}^{1} (1 - \mu^2)^{-1} C_p(\mu) C_q(\mu)\, d\mu = \frac{2}{p(p-1)(2p-1)} \delta_{pq} \quad \text{for } p, q > 2 \tag{21}$$

The solution to Eq. 18 is obtained by taking the expansions

$$\rho = \sum_{n=0}^{\infty} \bar{\rho}_n(r) P_n(\mu),$$

$$\phi = \sum_{n=0}^{\infty} \bar{\phi}_n(r) P_n(\mu),$$

$$\Psi^{in} = \sum_{p=2}^{\infty} \Theta_p(r) C_p(\mu) \tag{22}$$

where $P_n(\mu)$ is the Legendre polynomial of order n, and we again note that the radial variations of ρ and ϕ are as yet undetermined. Substituting Eq. 22 into Eq. 18 yields

$$\left[\frac{d^2}{dr^2} - \frac{p(p-1)}{r^2}\right]^2 \Theta_p(r) = F_p(r) \tag{23}$$

where

$$F_p(r) = -\mathcal{H} \sum_{n=0}^{\infty} \sum_{m=0}^{\infty} \left(\frac{\partial \bar{\rho}_n}{\partial r} \bar{\phi}_m - \bar{\rho}_m \frac{\partial \bar{\phi}_n}{\partial r} \right) a_{pmn} \tag{24}$$

with the coefficients a_{pmn} given by

$$a_{pmn} = \frac{1}{2} p(p-1)(2p-1) \int_{-1}^{1} \frac{dP_m(\mu)}{d\mu} P_n(\mu) C_p(\mu)\, d\mu \tag{25}$$

Explicit values of a_{pmn} are required in this paper in only two special cases, which are

$$a_{p0n} = 0, \quad a_{pm0} = m(m+1)\delta_{m,p-1} \tag{26}$$

Equation 23 is solved in terms of a complementary function Θ_p^h and a particular integral Θ_p^p. We have

$$\Theta_p^h(r) = A_p^{(1)} r^{p+2} + A_p^{(2)} r^p + A_p^{(3)} r^{-p+3} + A_p^{(4)} r^{-p+1} \tag{27}$$

where the $A_p^{(i)}$ are arbitrary constants. The particular integral is obtained by the method of variation of parameters as

$$\Theta_p^p(r) = G_p^{(1)} r^{p+2} + G_p^{(2)} r^p + G_p^{(3)} r^{-p+3} + G_p^{(4)} r^{-p+1} \tag{28}$$

where the coefficients $G_p^{(i)}$ are given by

$$\frac{dG_p^{(1)}}{dr} = \frac{\frac{1}{2} F_p(r)}{(4p^2 - 1)} r^{-p+1} \tag{29a}$$

$$\frac{dG_p^{(2)}}{dr} = \frac{-\frac{1}{2} F_p(r)}{(4p^2 - 8p + 3)} r^{-p+3} \tag{29b}$$

$$\frac{dG_p^{(3)}}{dr} = \frac{\frac{1}{2} F_p(r)}{(4p^2 - 8p + 3)} r^{p} \tag{29c}$$

$$\frac{dG_p^{(4)}}{dr} = \frac{-\frac{1}{2} F_p(r)}{(4p^2 - 1)} r^{p+2} \tag{29d}$$

$$G_p^{(1)}(a) = G_p^{(2)}(a) = G_p^{(3)}(a) = G_p^{(4)}(a) = 0 \tag{29e}$$

The constants in Eq. 27 are now determined from the boundary conditions of Eqs. 19 and 20,

$$A_p^{(1)} a^{p+2} + A_p^{(2)} a^p + A_p^{(3)} a^{-p+3} + A_p^{(4)} a^{-p+1} = 0 \tag{30a}$$

$$(p+2) A_p^{(1)} a^{p+1} + p A_p^{(2)} a^{p-1} + (-p+3) A_p^{(3)} a^{-p+2} + (-p+1) A_p^{(4)} a^{-p} = 0 \tag{30b}$$

$$A_p^{(1)} + G_p^{(1)}(\infty) = 0 \tag{30c}$$

$$A_p^{(2)} + G_p^{(2)}(\infty) = 0 \tag{30d}$$

Therefore, in principle the solution to the flow field can be completed once the form of the function $F_p(r)$ is explicitly known. This requires the calculation of the ionic charge density and electric potential and is considered further in the next section.

Perturbation Theory

When $a \gg 1$, the free ionic charge is found in the region just adjacent to the particle surface which we denote the "inner" region. Further away from the particle, the ionic charge density is exponentially small; this electroneutral region is denoted the "outer" region.

In the outer region, the rescaled radial variable $s = r/a$ is used and the dependent variables are written in the form

$$\phi = \phi', \quad n_i = 1 + n_i', \quad u = u' \tag{31}$$

The primed qualities defined above are exponentially small at equilibrium and are proportional to the applied perturbing field under nonequilibrium conditions. Substituting from Eq. 31 into Eqs. 4 and 5, those terms involving products of primed quantities are neglected as we are only interested in the linear response to the perturbing fields. It is then easily seen that ϕ' and n_i' satisfy Laplace's equation and are harmonic functions. Thus, their solution is written as

$$\phi' = \phi^* \sum_{n=0}^{\infty} \left(H_{0,n} s^n + \frac{h_{0,n}}{s^{n+1}} \right) P_n(\mu) \tag{32a}$$

$$\overline{z_i^{l-1} n_i'} = \phi^* \sum_{n=0}^{\infty} \left(H_{l,n} s^n + \frac{h_{l,n}}{s^{n+1}} \right) P_n(\mu) \tag{32b}$$

where the overbars denote the averages

$$\overline{\langle\ \rangle_i} = \frac{\sum_i z_i^2 \langle\ \rangle_i n_{i\infty}}{\sum_i z_i^2 n_{i\infty}} \tag{33}$$

From the electroneutrality condition we have $\overline{z_i^{-1}n_i'} = 0$. The constants $H_{l,n}$ are determined by the boundary conditions that are specified far away from the particle. For example, $H_{0,1}$ corresponds to a uniform axial electric field, $H_{0,2}$ corresponds to an axisymmetric quadrupole at infinity, and so on. Similarly, the quantities $H_{l,1}$ for $l \geq 1$ correspond to uniform concentration gradient perturbing fields. The constants $h_{l,n}$ are determined from the matching conditions as $s \longrightarrow 1$ and thus represent the response of the particle and double layer region to the applied fields.

In the inner region, we define the boundary layer variable

$$x = r - a = a(s - 1) \tag{34}$$

in terms of which the axisymmetric gradient and Laplacian are

$$\nabla = \frac{\partial}{\partial x} e_r + a^{-1} \frac{\partial}{\partial \theta} e_\theta - a^{-2} x \frac{\partial}{\partial \theta} e_\theta + O(a^{-3}) \tag{35a}$$

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + 2a^{-1} \frac{\partial}{\partial x} + a^{-2} \left[-2x \frac{\partial}{\partial x} + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial}{\partial \mu} \right] + O(a^{-3}) \tag{35b}$$

The inner expansions are taken in the form

$$\phi = \phi_1 + a^{-1}\phi_2 + O(a^{-2}) \tag{36a}$$

$$\rho = \rho_1 + a^{-1}\rho_2 + O(a^{-2}) \tag{36b}$$

$$n_i = n_{i,1} + a^{-1}n_{i,2} + O(a^{-2}) \tag{36c}$$

The scaling for the fluid velocity is obtained upon noting that the no-slip boundary condition, Eq. 8, along with the incompressibility condition, Eq. 3, requires that the first normal derivative of the u_θ and the first two normal derivatives of u_r vanish at the particle surface. Thus

$$u_\theta = a^{-1}\hat{u}_\theta + O(a^{-2}), \quad u_r = a^{-2}\hat{u}_r + O(a^{-3}) \tag{36d}$$

The formal matching conditions that the inner and outer expansions must satisfy to $O(a^{-1})$ are then given for $l \geq 0$ by

$$\lim_{x \to \infty} \overline{z_i^{l-1} n_{i,1}} + \overline{z_i^l}\phi_1 = \lim_{s \to 1} \overline{z_i^{l-1} n_i'} + \overline{z_i^l}\phi' \tag{37a}$$

$$\lim_{x \to \infty} \frac{\partial}{\partial x} (\overline{z_i^{l-1} n_{i,1}} + \overline{z_i^l}\phi_1) = 0 \tag{37b}$$

$$\lim_{x \to \infty} \frac{\partial}{\partial x} (\overline{z_i^{l-1} n_{i,2}} + \overline{z_i^l}\phi_2) = \lim_{s \to 1} \frac{\partial}{\partial s} (\overline{z_i^{l-1} n_i'} + \overline{z_i^l}\phi') \tag{37c}$$

The reason for writing the matching conditions in this form that the linear combinations given above appear somewhat naturally in the analysis. Substituting the expansions in Eqs. 36a–36d into Eqs. 4 and 5 and the boundary conditions in Eqs. 7 and 9 yields to leading order

$$\frac{\partial^2 \phi_1}{\partial x^2} = -\rho_1 \tag{38a}$$

$$\frac{\partial^2 n_{i,1}}{\partial x^2} + z_i \left[\frac{\partial}{\partial x} \left(n_{i,1} \frac{\partial \phi_1}{\partial x} \right) \right] = 0 \tag{38b}$$

$$\phi_1 = \phi^* \tag{38c}$$

$$\frac{\partial n_{i,1}}{\partial x} + z_i n_{i,1} \frac{\partial \phi_1}{\partial x} = 0, \quad x = 0 \tag{38d}$$

Equation 38b is integrated twice and Eq. 38d used to yield

$$\ln n_{i,1} + z_i\phi_1 = \ln [1 + \phi^* A_i(\mu)] + z_i\phi^* B(\mu) \tag{39}$$

The righthand side in Eq. 39 is a function of the angular coordinate only and is chosen so that as $x \longrightarrow \infty$

$$n_{i,1} \longrightarrow 1 + \phi^* A_i(\mu), \quad \phi_1 \longrightarrow \phi^* B(\mu) \tag{40}$$

The implications of Eq. 39 follow upon noting that, except for a factor of kT, the lefthand side is the electrochemical potential of the ionic species i. This electrochemical potential is constant in the direction normal to the particle surface and equal to its value in the electrically neutral region of the solvent just beyond the double layer region. The variations of the electrochemical potential laterally along the particle surface are indicated by the dependence of A_i and B on the polar angle. These lateral variations are not only due to the externally imposed gradients but also reflect the nonequilibrium response of the diffuse double layer to these imposed fields. Equation 5 and the boundary condition of Eq. 9 in the inner region at $O(a^{-1})$ are given by

$$\begin{aligned} \frac{\partial^2 n_{i,2}}{\partial x^2} + 2 \frac{\partial n_{i,1}}{\partial x} + {} & z_i \left[\frac{\partial}{\partial x} \left(n_{i,1} \frac{\partial \phi_2}{\partial x} \right) + \frac{\partial}{\partial x} \left(n_{i,2} \frac{\partial \phi_1}{\partial x} \right) + 2n_{i,1} \frac{\partial \phi_1}{\partial x} \right] \\ & = \mathcal{P}_i a^{-1} \left(\hat{u}_r \frac{\partial n_{i,1}}{\partial x} + \hat{u}_\theta \frac{\partial n_{i,1}}{\partial \theta} \right) - \\ & a^{-1} \left[-2x \frac{\partial n_{i,1}}{\partial x} + \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial n_{i,1}}{\partial \mu} \right] \\ & -a^{-1} z_i \left[-2x n_{i,1} \frac{\partial \phi_1}{\partial x} + (1 - \mu^2) \frac{\partial n_{i,1}}{\partial \mu} \frac{\partial \phi_1}{\partial \mu} \right. \\ & \left. + n_{i,1} \frac{\partial}{\partial \mu} (1 - \mu^2) \frac{\partial \phi_1}{\partial \mu} \right] \end{aligned} \tag{41a}$$

$$\frac{\partial n_{i,2}}{\partial x} + z_i \left(n_{i,1} \frac{\partial \phi_2}{\partial x} + n_{i,2} \frac{\partial \phi_1}{\partial x} \right) = 0, \quad x = 0 \tag{41b}$$

The terms on the righthand side of Eq. 41a include the leading order contributions of convection and of tangential ionic diffusion and electromigration in the double layer. These contain the factor a^{-1}, and hence they are generally negligibly small. However, for sufficiently large values of the surface potential ϕ^*, they become $O(1)$ and are basically responsible for the deviations from the Smoluchowski theory.

For matching purposes only, the asymptotic behavior of $n_{i,2}$ and ϕ_2 as $x \longrightarrow \infty$ is required and is obtained as follows. After using Eq. 39 to eliminate terms from Eq. 41a, it is integrated once and the conditions of Eqs. 37b and 41b are applied to yield

$$\lim_{x\to\infty} \frac{\partial n_{i,2}}{\partial x} + z_i n_{i,1} \frac{\partial \phi_2}{\partial x} =$$

$$\lim_{x\to\infty} Pe_i a^{-1} \int_0^x \left(\hat{u}_r \frac{\partial n_{i,1}}{\partial x} + \hat{u}_\theta \frac{\partial n_{i,1}}{\partial \theta} \right) dx$$

$$- \lim_{x\to\infty} a^{-1} \int_0^x \left[\frac{\partial}{\partial \mu} (1-\mu^2) \left(\frac{\partial n_{i,1}}{\partial \mu} + z_i n_{i,1} \frac{\partial \phi_1}{\partial \mu} \right) \right] dx \quad (42)$$

Equation 42 is further simplified by retaining only those terms that are proportional to the applied fields to obtain

$$\lim_{x\to\infty} \frac{\partial n_{i,2}}{\partial x} + z_i n_{i,1} \frac{\partial \phi_2}{\partial x} = z_i \phi^* [D_i^{ex}(\mu) + D_i^{in}(\mu) + E_i(\mu)] \quad (43)$$

where

$$z_i \phi^* D_i^{ex}(\mu) = \lim_{x\to\infty} \mathcal{P}_i a^{-1} \int_0^x \hat{u}_r^{ex} \frac{dn_{i,1}^{eq}}{dx} dx \quad (44a)$$

$$z_i \phi^* D_i^{in}(\mu) = \lim_{x\to\infty} \mathcal{P}_i a^{-1} \int_0^x \hat{u}_r^{in} \frac{dn_{i,1}^{eq}}{dx} dx \quad (44b)$$

$$z_i \phi^* E_i(\mu) = \lim_{x\to\infty} -a^{-1} \phi^* \frac{\partial}{\partial \mu} (1-\mu^2) \frac{\partial}{\partial \mu} (A_i + z_i B) \int_0^x n_{i,1}^{eq}\, dx \quad (44c)$$

where $n_{i,1}^{eq}$ is the equilibrium portion of the leading order solution $n_{i,1}$. We define the expansions

$$\overline{z_i^{l-1} A_i} + \overline{z_i^l} B = \sum_{n=0}^{\infty} \alpha_{l,n} P_n(\mu) \quad (45a)$$

$$\overline{z_i^l D_i^{ex}(\mu)} + \overline{z_i^l D_i^{in}(\mu)} + \overline{z_i^l E_i(\mu)} = \sum_{n=0}^{\infty} \beta_{l,n} P_n(\mu) \quad (45b)$$

so that the matching conditions, Eqs. 37a and 37c, now become

$$\begin{aligned} H_{0,n} + h_{0,n} &= \alpha_{0,n} \\ H_{l,n} + h_{l,n} &= \alpha_{l,n} - \overline{z_i^l} \alpha_{0,n}, \quad l \geq 1 \end{aligned} \quad (46a)$$

$$\begin{aligned} nH_{0,n} - (n+1) h_{0,n} &= \beta_{0,n} \\ nH_{l,n} - (n+1) h_{l,n} &= \beta_{l,n} - \overline{z_i^l} \beta_{0,n}, \quad l \geq 1 \end{aligned} \quad (46b)$$

These conditions then lead to a complete determination of the dependent variables correct to leading order. The basic unknowns in Eqs. 46a,b are $\alpha_{l,n}$ and $h_{l,n}$, whereas the coefficients $H_{l,n}$ are specified by the boundary conditions and $\beta_{l,n}$ are obtained in terms of the other coefficients from the definite integrals in Eqs. 43 and 44. The evaluation of these integrals requires the solution to the $O(1)$ problem on the inner scales as given in Eq. 38. This equation is a variant of the one-dimensional, planar, nonlinear Poisson-Boltzmann equation and has no known analytical solution for a general electrolyte. One possible recourse is to construct approximate solutions by expansions in the zeta potential. Since we are solving the problem only in a planar geometry these expansions can be calculated to a high order somewhat more easily than is possible in the spherical geometry. The choice of the averaged quantities in Eq. 32, which might have seemed arbitrary, is now seen to be appropriate since these are precisely the quantities that appear in a solution by expansion in powers of the zeta potential (Natarajan, 1984).

Rather than consider approximate methods for the solution of Eq. 38, we concentrate here on the one case for which an analytical solution to these equations is known, i.e., for a binary, symmetric (z:z) electrolyte. We denote quantities associated with the cations and anions by the subscripts + and −, respectively. Then, $z_+ = -z_- = z$, and from the electroneutrality condition in the outer region, $A_+ = A_- = A$. Thus Eqs. 38 and 39 together give

$$\frac{\partial^2 \phi_1}{\partial x^2} = -\frac{1}{z}(1 + \phi^* A) \sinh(z\phi_1 - z\phi^* B) \quad (47)$$

This is integrated along with the boundary conditions of Eqs. 37b and 38c to give

$$\frac{\tanh\left[\frac{1}{4} z(\phi_1 - \phi^* B)\right]}{\tanh\left[\frac{1}{4} z\phi^*(1 - B)\right]} = \exp\left[-(1 + \phi^* A)^{1/2} x\right] \quad (48)$$

Retaining only linear terms in A and B, we have

$$\phi_1 = \frac{4}{z} \tanh^{-1}(Qe^{-x}) - \frac{\phi^* A}{z} \left(\frac{2Qxe^{-x}}{1 - Q^2 e^{-2x}} \right) + \phi^* B \left[\frac{1 - e^{-x} - Q^2(e^{-2x} - e^{-x})}{1 - Q^2 e^{-2x}} \right] \quad (49)$$

where

$$Q = \tanh\left(\frac{1}{4} z\phi^*\right) \quad (50)$$

The corresponding charge density is easily found to be

$$\begin{aligned} \rho_1 = &-\frac{1}{z} \sinh[4 \tanh^{-1}(Qe^{-x})] \\ &- \frac{\phi^* A}{z} \left\{ \sinh[4 \tanh^{-1}(Qe^{-x})] - \frac{2Qxe^{-x}}{1 - Q^2 e^{-2x}} \cosh[4 \tanh^{-1}(Qe^{-x})] \right\} \\ &+ \frac{\phi^* B(1 - Q^2) e^{-x}}{1 - Q^2 e^{-2x}} \cosh[4 \tanh^{-1}(Qe^{-x})] \end{aligned} \quad (51)$$

The results of the preceding section are now used to determine the electroosmotic velocity field. The quantity $F_p(r)$ defined in Eq. 24 is exponentially small except on the scales $x \sim O(1)$.

Thus, using Eq. 45a and Eqs. 49–51 we have

$$F_p(x) = -\phi^*\mathcal{H}\sum_{n=1}^{\infty} n(n+1)\delta_{n,p-1}\frac{4Qe^{-x}}{1-Q^2e^{-2x}} \times \left\{\frac{\alpha_{0,n}}{z}\cosh\left[4\tanh^{-1}(Qe^{-x})\right] - \frac{\alpha_{1,n}}{z^2}\sinh\left[4\tanh^{-1}(Qe^{-x})\right]\right\} \quad (52)$$

In order to evaluate the integral in Eq. 44a, we require electroosmotic flow field only on the scales $x \sim O(1)$. Then, Θ_p^h and Θ_p^p in Eqs. 27 and 28 when expressed in terms of the inner variable x become

$$\Theta_p^h = \int_0^{\infty}\left(\frac{x^2x'}{2!} - \frac{x^3}{3!}\right)F_p(x')dx' + O(a^{-1}) \quad (53a)$$

$$\Theta_p^p = \int_0^{x}\left(\frac{x^3}{3!} - \frac{x^2x'}{2!} + \frac{xx'}{2!} - \frac{x'^3}{3!}\right)F_p(x')dx' + O(a^{-1}) \quad (53b)$$

Evaluating these integrals, the final form of the stream function Ψ^{in} is

$$\Psi^{in} = 2\phi^*Ha\sum_{n=1}^{\infty} n(n+1)\left\{\frac{\alpha_{0,n}}{z}\int_0^x \ln\left[\frac{(1+Qe^{-x'})(1-Q)}{(1-Qe^{-x'})(1+Q)}\right]dx' + \frac{\alpha_{1,n}}{z^2}\int_0^x \ln\left[\frac{1-Q^2e^{-2x'}}{(1-Q^2)}\right]dx'\right\} C_{n+1}(\mu) \quad (54)$$

From Eqs. 39 and 49, the equilibrium ionic concentrations in the double layer to leading order are

$$n_{\pm,1}^{eq} = \left(\frac{1 \mp Qe^{-x}}{1 \pm Qe^{-x}}\right)^2 \quad (55)$$

The only remaining difficulty is that Eq. 44c diverges as x for $x \to \infty$. The matching condition of Eq. 37c cannot be directly applied since the outer expansion as defined in Eq. 32 does not have a corresponding term as $s \to 1$. This is not surprising since this matching condition was formulated so that terms which had a factor of a^{-1} were elevated to $O(1)$ when the zeta potential became large. In fact, the coefficient of the diverging term remains $O(a^{-1})$ as the zeta potential increases and hence would be matched by a corresponding term in the outer expansion to the equivalent order. Therefore, this term can be neglected here without loss of accuracy and this is most easily done by replacing the integrand $n_{i,1}^{eq}$ in Eq. 44c by $(n_{i,1}^{eq} - 1)$. The required integrals are then

$$D_{\pm}^{in} = -\frac{3}{2}m_{\pm}a^{-1}\sum_{n=1}^{\infty} n(n+1)\left[\frac{\alpha_{0,n}}{z^2}f_1(\pm Q) \pm \frac{\alpha_{1,n}}{z^3}f_2(\pm Q)\right]P_n(\mu) \quad (56)$$

$$E_{\pm} = -a^{-1}\sum_{n=1}^{\infty} n(n+1)\left(\alpha_{0,n} \pm \frac{\alpha_{1,n}}{z}\right)f_3(\pm Q)P_n(\mu) \quad (57)$$

where

$$m_{\pm} = \frac{2}{3}\frac{\epsilon_m}{\eta_0\mathcal{D}_{\pm}}\left(\frac{kT}{e}\right)^2 \quad (58)$$

$$f_1(Q) = \frac{8Q}{1+Q} - 4\ln\left(\frac{1+Q}{1-Q}\right) \quad (59a)$$

$$f_2(Q) = \frac{8Q}{1+Q} - 4\ln(1-Q) - 8\ln(1+Q) \quad (59b)$$

$$f_3(Q) = \frac{4Q}{1+Q} \quad (59c)$$

The dimensionless quantities $m_{\pm}$ defined above are the reciprocal ion diffusivities (Wiersema, 1966). These typically have values between 0.1 and 0.65 for various ions in aqueous electrolytes. The functions, f_1, f_2, f_3 are shown in Figure 1. The use of Eqs. 36, 56, and 57 along with the specification of the applied field leads directly to the solution in the thin double layer approximation. This procedure is demonstrated with specific examples in the following sections.

Application to Electrophoresis

A particle placed in a uniform electric field $\mathcal{E}$ moves rectilinearly with a constant velocity $\mathcal{U}$ parallel to the field direction. Smoluchowski's well-known result for the electrophoretic mobility is

$$\frac{\mathcal{U}}{\mathcal{E}} = \frac{\epsilon_m\zeta}{\eta_0} \quad (60)$$

We calculate the required corrections to this result using the theory developed in the previous section. The analysis there was in a frame of reference fixed to the particle; to make it applicable here we assume that, far away from the particle, there is also

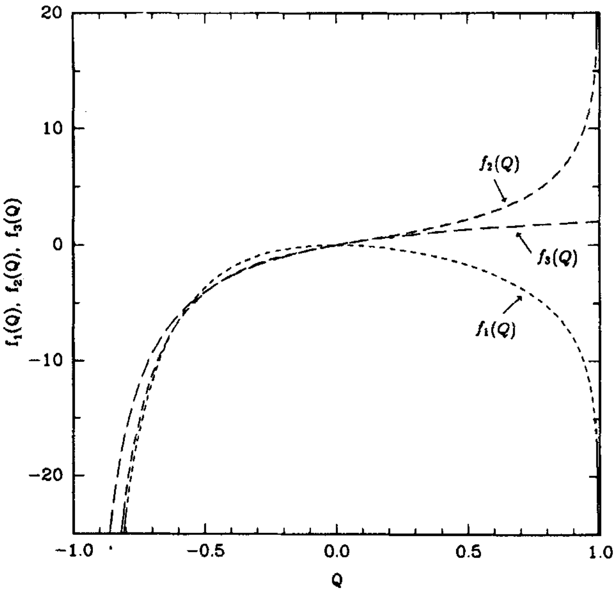

Figure 1. Functions $f_1(Q)$, $f_2(Q)$, and $f_3(Q)$ defined in Eq. 59.
$Q = \tanh(\frac{1}{4}z\phi^*)$

simultaneously a uniform streaming flow of a magnitude such that the net force on the particle is zero.

Since the net force on the particle is the same over any surface that completely encloses the particle, we choose a surface $\mathcal{S}$ large enough that it completely encloses the particle and the double layer region. Then the net charge within the surface is zero, and from elementary electrostatic considerations the total electrical force on $\mathcal{S}$ is zero. Consequently the force on $\mathcal{S}$ is purely hydrodynamic and can be calculated from the strength of the stokeslet in the exterior flow by using a formula due to Payne and Pell (1960)

$$\mathcal{F} = 6\pi a + 8\pi \lim_{r\to\infty} \frac{\Psi^{in}}{r(1-\mu^2)} \tag{61}$$

The first term represents the stokeslet strength due to the uniform flow far away from the particle, while the second term is due to the electroosmotic flow field. From the results obtained in Eqs. 22, 27, and 28 we get

$$\mathcal{F} = 6\pi a + 4\pi \left[\frac{5}{2} a^3 G_2^{(1)}(\infty) + \frac{3}{2} a G_2^{(2)}(\infty) + G_2^{(3)}(\infty)\right] \tag{62}$$

Using Eq. 29, this is expressed in the form

$$\mathcal{F} = 6\pi a + \pi \int_0^\infty x^2 F_2(x)dx \tag{63}$$

where the integrand is given in Eq. 52, and upon evaluation of the integral this yields

$$\mathcal{F} = 6\pi a - 8\pi\phi^* \mathcal{H} \left[\frac{\alpha_{0,1}}{z} \ln\left(\frac{1+Q}{1-Q}\right) + \frac{\alpha_{1,1}}{z^2} \ln(1-Q^2)\right] \tag{64}$$

The only remaining task is the determination of the coefficients $\alpha_{0,1}$ and $\alpha_{1,1}$ using the matching conditions in Eq. 46. These take the form

$$H_{0,1} + h_{0,1} = \alpha_{0,1} \quad h_{1,1} = \alpha_{1,1} \tag{65a}$$

$$H_{0,1} - 2h_{0,1} = \beta_{0,1}, \quad -2h_{1,1} = \beta_{1,1} \tag{65b}$$

where $H_{0,1} = \mathcal{E}a/\zeta$. The quantities $\beta_{0,1}$ and $\beta_{1,1}$ are obtained from their definitions in Eq. 45b and Eqs. 56–59. The contribution from D_i^{ex} in Eq. 45b is omitted as the typical eletrophoretic velocities are small and their convective effects negligible. Eliminating $h_{0,1}$ and $h_{1,1}$ from Eq. 65 then yields

$$X_{11}\alpha_{0,1} + X_{12}\alpha_{1,1} = \frac{3}{2} H_{0,1} \tag{66a}$$

$$X_{21}\alpha_{0,1} + X_{22}\alpha_{1,1} = 0 \tag{66b}$$

where

$$X_{11} = 1 - \frac{3}{4az^2}[m_+ f_1(Q) + m_- f_1(-Q)] - \frac{1}{2a}[f_3(Q) + f_3(-Q)] \tag{67a}$$

$$X_{12} = -\frac{3}{4az^3}[m_+ f_2(Q) - m_- f_2(-Q)] - \frac{1}{2az}[f_3(Q) - f_3(-Q)] \tag{67b}$$

$$X_{21} = -\frac{3}{4az}[m_+ f_1(Q) - m_- f_1(-Q)] - \frac{z}{2a}[f_3(Q) - f_3(-Q)] \tag{67c}$$

$$X_{22} = 1 - \frac{3}{4az^2}[m_+ f_2(Q) + m_- f_2(-Q)] - \frac{1}{2a}[f_3(Q) + f_3(-Q)] \tag{67d}$$

Solving for $\alpha_{0,1}$ and $\alpha_{1,1}$ the condition $\mathcal{F} = 0$ is applied to give for the reduced electrophoretic mobility,

$$E_m = \frac{3\eta_0 e \mathcal{U}}{2\epsilon_m kT\mathcal{E}} = \frac{3}{z} \frac{(X_{22} - X_{21}/z)\ln(1+Q) - (X_{22} + X_{21}/z)\ln(1-Q)}{X_{11}X_{22} - X_{12}X_{21}} \tag{68}$$

The predictions of Eq. 68 are compared with some numerical results of O'Brien and White in Figures 2 and 3. The agreement is excellent in the parameter region $\phi^* < 10$ and $a > 20$ and should suffice for the majority of the colloidal systems encountered in practise.

A rough estimate for the range of validity of Eq. 68 due to the neglect of higher order terms in a^{-1} may be obtained from Henry's results, which are valid only for $\phi^* \ll$ and can be expressed

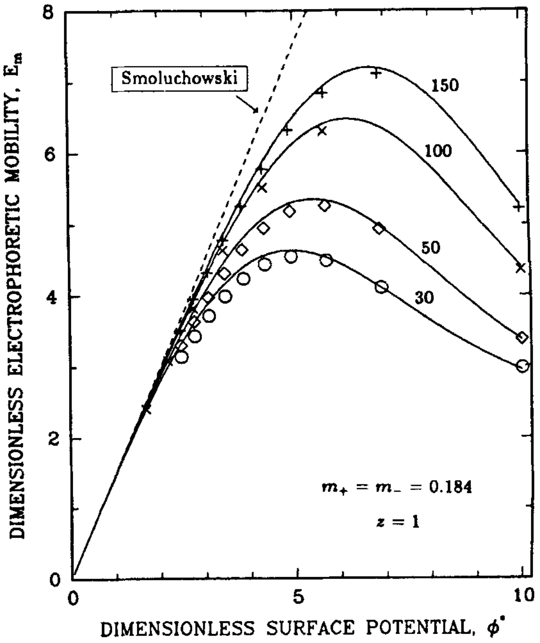

Figure 2. Electrophoretic mobility v. zeta potential for a typical (1:1) electrolyte.

_Calculated from Eq. 68. + × ◇ ○ Numerical results of O'Brien and White (1981), tabulated in O'Brien and Hunter (1981).

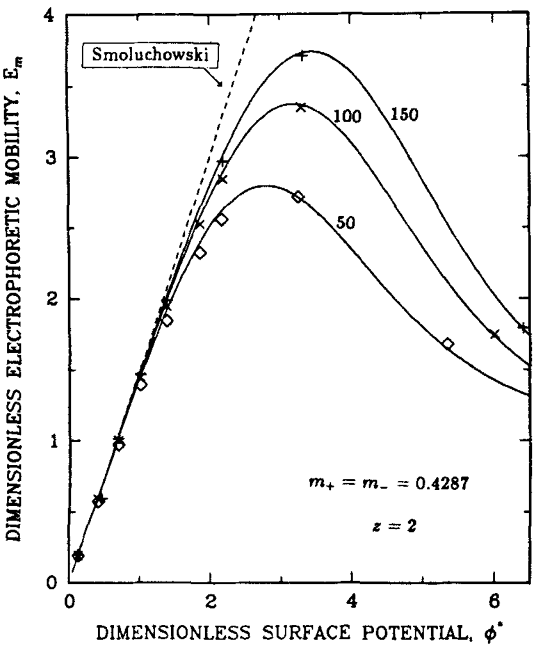

Figure 3. Electrophoretic mobility v. zeta potential for a typical (2:2) electrolyte.

_From Eq. 68. + × ◇ Numerical results of O'Brien and White (1981), tabulated in O'Brien and Hunter (1981).

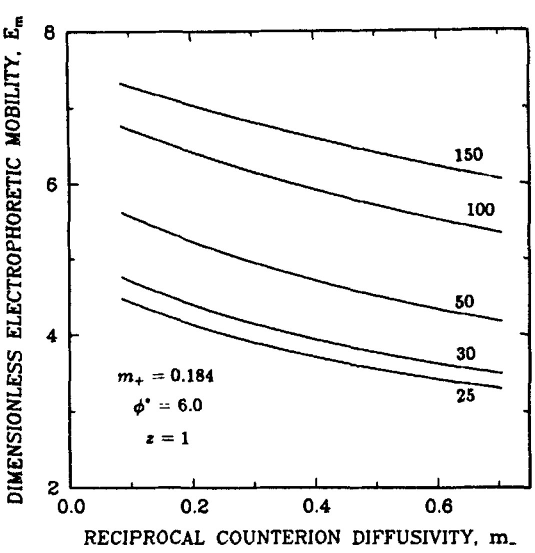

Figure 4. Effect of variation of counterion mobility on electrophoretic mobility of a positively charged particle in a (1:1) electrolyte.

in the form (Henry, 1931; Ohshima et al., 1982)

$$E_m = \frac{3}{2}\phi^*[1 - 3a^{-1} + O(a^{-2})] \tag{69}$$

The first correction term is seen to become significant for $a < 20$. However, Figures 2 and 3 indicate that Eq. 68 may be more accurate at higher zeta potentials, where the above estimate is inapplicable.

There have been several previous analytical studies of electrophoresis in the thin double layer approximation. No attempt has been made here manipulate Eq. 68 to reproduce any of the several different final results that have been quoted, but a qualitative comparison shows good agreement. The key results of the earlier section on the velocity field solution (4) include the matching condition, Eq. 46, the potential in the nonequilibrium double layer, Eq. 49, and the electroosmotic flow field, Eq. 54. These results, when specialized to electrophoresis, are latent in the work of Dukhin and Derjaguin (1974) and Fixman (1983). The best comparison is with the results of O'Brien and Hunter (1981) since the equivalent of Eqs. 64 and 66 above appears in their work. However, their equivalent of the coefficients defined in Eq. 67 above neglects terms that do not grow exponentially with ϕ^*. This simplifies the final results somewhat without greatly affecting the accuracy at large zeta potentials.

In Eq. 64 the force on the particle due to the electroosmotic flow appears as the sum of two terms that involve the coefficients $\alpha_{0,1}$ and $\alpha_{1,1}$, respectively, and hence represent the separate contributions to the electroosmotic flow of the variations in electric potential and ion concentrations beyond the double layer region. Of course, this is not a strict decomposition if there is significant tangential ionic transport in the double layer, since $\alpha_{0,1}$ and $\alpha_{1,1}$ are then related to each other from Eq. 66. However, it points to the fact that it is equally possible to move a charged colloidal particle by placing it in a macroscopic concentration gradient of neutral electrolyte as by placing it in a macroscopic electric field (Dukhin and Derjaguin, 1974; Prieve et al., 1984).

In the present problem, the Smoluchowski theory entirely neglects the tangential ionic transport within the double layer. This we see is justifiable only for small to moderate values of the surface potential. Hence, the theory takes $\alpha_{1,1}$ to be identically zero and $\alpha_{0,1} = 3/2H_{0,1}$; the latter value is just that obtained for an uncharged particle in the applied electrical field. Thus, an independently determined electric field acts on the free ionic charge in the double layer to drive an electroosmotic flow. Increasing the surface potential or equivalently the free ionic charge leads to a stronger electroosmotic flow and hence to higher electrophoretic mobilities.

The inclusion of tangential ionic transport within the double layer alters this picture in two ways. First, ion transfer between the electroneutral outer region and the double layer region is necessary to balance the variations in the tangential ionic transport along the particle surface, and this leads to gradients in the ion concentrations in the outer region. Second, the local variations of the free ionic charge density along the particle surface lead to a polarization electric field that acts so as to decrease the effectiveness of the applied electric field. Again, in view of Eq. 66 these two effects are not strictly separable; however, in terms of their contributions to the electrophoretic mobility in Eq. 68 the calculations show that both these effects tend to retard the particle and lead to a decrease in the rate of growth of the electrophoretic mobility with increasing surface potential. At sufficiently large surface potentials the first of these retarding effects can become so large that the mobility, apparently paradoxically, begins to decrease with increasing surface potential.

The effect of varying the counterion and coion diffusivities on the electrophoretic mobility are shown in Figures 4 and 5 for a particle with a surface potential sufficiently large that tangential ion transport effects are important. In both cases decreasing

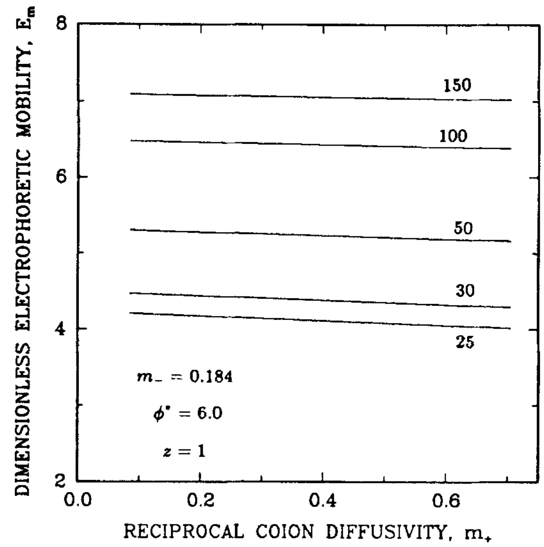

Figure 5. Effect of variation of coion mobility on electrophoretic mobility of a positively charged particle in a (1:1) electrolyte.

the ionic diffusivity at a fixed overall electrolyte concentration leads to a decrease in the mobility, although the effect is very slight in the case of the coions due to their lower concentrations. This is as expected, for the larger concentration gradients that arise when the ion diffusivities are decreased lead to a stronger retardation.

Finally, in Figure 6 we consider the influence of the electrolyte valence on the electrophoretic mobility. The results are shown for uni-, di-, and trivalent electrolytes with the same ionic diffusivities and the same overall electrolyte concentration. This last fact leads to a trivial variation in the Debye length and if this were all, from Figure 1 we might expect E_m to increase in going from a univalent to a trivalent electrolyte. However, the actual result is the contrary and gives an indication the strong dependence of the mobility on the electrolyte valence.

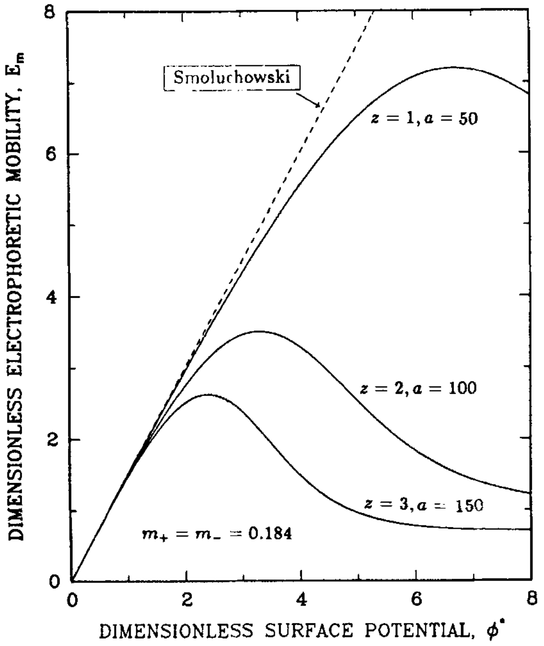

Figure 6. Effect of varying electrolyte valence on electrophoretic mobility.

Ion mobilities and overall concentration held constant.

Application to the Dilute Shear Viscosity

The intrinsic shear viscosity of a dilute suspension of uncharged, noninteracting particles is given by the well known Einstein relation

$$\frac{\eta_{susp} - \eta_0}{\eta_0 \Phi} = 5/2 \tag{70}$$

where η_{susp} is the suspension viscosity and Φ is the volume fraction of particles in the suspension. If in addition the particles are charged so that they are surrounded by diffuse ionic double layers, the intrinsic viscosity will be enhanced over the value of 2.5. This is known as the primary electroviscous effect, and a general theory for its calculation has been given by Russel (1976). According to this theory, the average stress in a representative volume of the suspension can be written as a sum of the contribution of the solvent alone and that due to the presence of particles in the suspension. The latter is denoted as $T_{jk}^{(p)}$ and in the dilute noninteracting limit (Sherwood, 1980; Natarajan, 1984) is given by

$$T_{jk}^{(p)} = 5\Phi \left[D_{jk} + \frac{3\mathcal{H}}{20\pi a^3} \int_v A_{jkl}(\mathbf{r}) \rho(\mathbf{r}) \frac{\partial \phi(\mathbf{r})}{\partial r_l} \, dV \right] \tag{71}$$

where D_{jk} is the spatial mean of the symmetric rate of strain tensor in the suspension and

$$\begin{aligned} A_{jkl}(\mathbf{r}) = \frac{1}{2}\left(r_k \delta_{jl} + r_j \delta_{kl} - \frac{2}{3} r_l \delta_{jk}\right) + \frac{5}{6} a^3 \left(\frac{r_l \delta_{jk}}{r^3} - \frac{3 r_j r_k r_l}{r^5}\right) \\ - \frac{1}{2} a^5 \left(\frac{r_j \delta_{kl} + r_k \delta_{jl} + r_l \delta_{jk}}{r^5} - \frac{5 r_j r_k r_l}{r^7}\right) \end{aligned} \tag{72}$$

The integral in Eq. 71 extends over the volume $\mathcal{V}$ external to a single isolated particle. The first term in the equation is just the Einstein correction, while the second term gives the electroviscous contribution to the dilute shear viscosity. The evaluation of the integral in Eq. 71 requires the nonequilibrium charge density and electric potential distributions to be calculated for an isolated colloidal particle that is placed in an ambient flow field with the same mean shear rate as that of the suspension as a whole.

The calculation of a Newtonian shear viscosity correction should be independent of the exact form of the ambient shear flow; hence there is no loss of generality in taking this flow to be axisymmetric, as in Eqs. 2 and 3. Using the divergence theorem it is seen that any portion of the vector $\rho \nabla \phi$ that is expressible as the gradient of a scalar will make no contribution to the value of the integral in Eq. 71. Hence, omitting such terms we obtain to leading order

$$\rho(\mathbf{r}) \nabla \phi = \frac{\sum_i n_{i\infty}(A_i + z_i B) \nabla n_{i,1}^{eq}}{\sum_i n_{i\infty} z_i^2} \tag{73}$$

In the present problem, the expansions for A_i and B in Eq. 45a will contain only those terms proportional to $P_2(\mu)$. Substituting in Eq. 71, the angular integrations are easily completed, and noting that the integrand is nonzero only on the scales $x = r - a \sim O(1)$, we obtain

$$T_{jk}^{(p)} = 5\Phi D_{jk}\left[1 - \frac{3\phi^*\mathcal{H}}{2a\sum_i n_{i\infty}z_i^2} \sum_i n_{i\infty}\int_{-1}^{1} \cdot (A_i + z_iB)P_2(\mu)d\mu \int_0^\infty x^2\frac{\partial n_{i,1}^{eq}}{\partial x}dx\right] \quad (74)$$

This result is valid for a general electrolyte. Specializing it to a binary, symmetric electrolyte and using Eqs. 45a and 55, the definite integrals are evaluated to yield for the intrinsic viscosity

$$\frac{5}{2} - \frac{6\phi^*\mathcal{H}}{az}\left[\alpha_{0,2}\ln\left(\frac{1+Q}{1-Q}\right) + \frac{\alpha_{1,2}}{z}\ln(1-Q^2)\right] \quad (75)$$

The coefficients $\alpha_{0,2}$ and $\alpha_{1,2}$ are obtained from the matching conditions, Eq. 46, which take the form

$$\alpha_{0,2} = h_{0,2} = -\frac{1}{3}\beta_{0,2} \quad (76a)$$

$$\alpha_{1,2} = h_{1,2} = -\frac{1}{3}\beta_{1,2} \quad (76b)$$

As in the previous section, the values of $\beta_{0,2}$ and $\beta_{1,2}$ are obtained from their definitions in Eq. 45b. The value of D_i^{ex}, which gives the convective ion flux within the double layer due to the imposed shear flow, can be obtained from Eq. 44a. In this case

$$\hat{u}_r^{ex} = \frac{15}{2}x^2P_2(\mu) \quad (77)$$

so that

$$D_\pm^{ex} = \pm\frac{60\mathcal{P}_\pm a^{-1}}{z\phi^*}\ln(1 \pm Q)P_2(\mu) \quad (78)$$

Substituting this along with Eqs. 56 and 57 into Eq. 76 yields

$$Y_{11}\alpha_{0,2} + Y_{12}\alpha_{1,2} = -\frac{10}{z\phi^*}[\mathcal{P}_+\ln(1+Q) - \mathcal{P}_-\ln(1-Q)] \quad (79a)$$

$$Y_{21}\alpha_{0,2} + Y_{22}\alpha_{1,2} = -\frac{10}{z\phi^*}[\mathcal{P}_+\ln(1+Q) - \mathcal{P}_-\ln(1-Q)] \quad (79b)$$

where the coefficients that appear above are related to those appearing in Eq. 67 as

$$Y_{11} = 2X_{11} - 1, \quad Y_{12} = 2X_{12}, \quad Y_{21} = 2X_{21}, \quad Y_{22} = 2X_{22} - 1 \quad (80)$$

Solving for $\alpha_{0,2}$ and $\alpha_{1,2}$ from Eq. 79 and substituting into Eq. 75 finally gives the intrinsic viscosity

$$\frac{\eta_{susp} - \eta_0}{\eta_0\Phi} = \frac{5}{2} + \frac{90[m_+\mathcal{A}\ln(1+Q) - m_-\mathcal{B}\ln(1-Q)]}{a^2z^2(Y_{11}Y_{22} - Y_{12}Y_{21})} \quad (81)$$

where

$$\mathcal{A} = (Y_{22} - Y_{12}z)\ln\left(\frac{1+Q}{1-Q}\right) + (Y_{11} - Y_{21}/z)\ln(1-Q^2) \quad (82)$$

$$\mathcal{B} = (Y_{22} + Y_{12}z)\ln\left(\frac{1+Q}{1-Q}\right) - (Y_{11} + Y_{21}/z)\ln(1-Q^2) \quad (83)$$

At low surface potentials, the intrinsic viscosity reduces to

$$\frac{5}{2}\left[1 + \frac{9(m_+ + m_-)\phi^{*2}}{2a^2}\right] \quad (84)$$

which is consistent with the results of the Smoluchowski-Booth theory (Booth, 1950b) in the thin double layer, low surface potential limit.

The variation of the intrinsic viscosity with surface potential from Eq. (81) is shown in Figure 7 for $20 < a < 200$. A comparison with similar figures in the numerical work of Watterson and White (1981) shows excellent agreement. The results show that at low surface potentials the intrinsic viscosity grows quadratically as predicted by Eq. (84). However, the effects of electroosmotic convection and of tangential diffusion and elec-

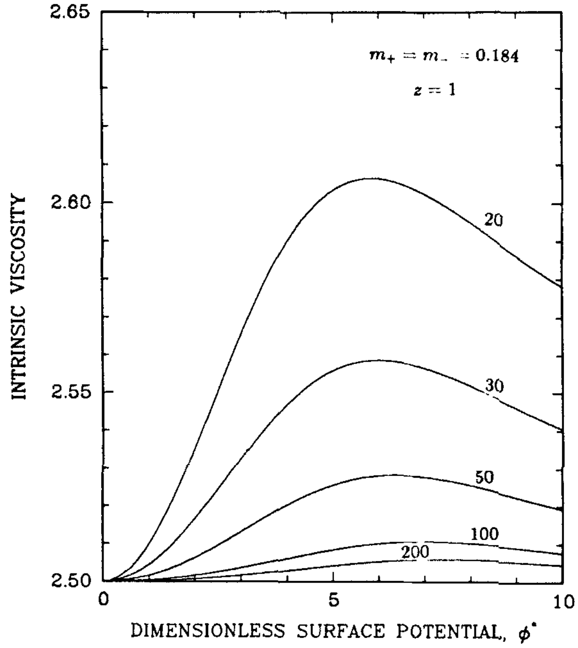

Figure 7. Effect of variation of surface potential on intrinsic viscosity for a (1:1) electrolyte.

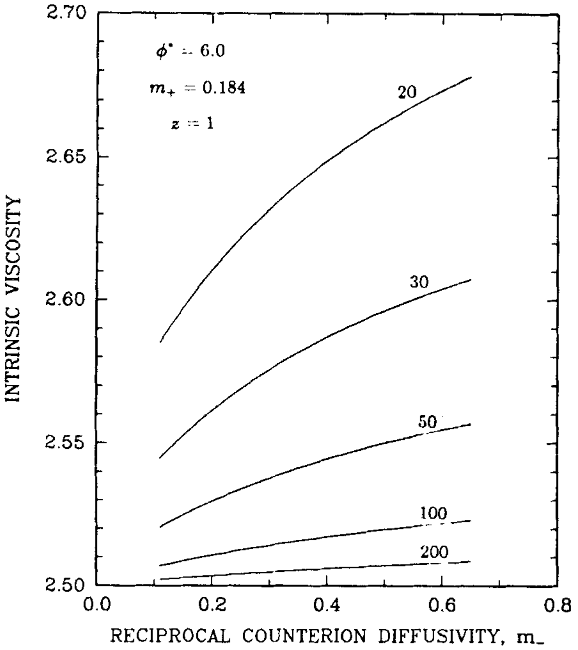

Figure 8. Intrinsic viscosity v. counterion mobility for a positively charged particle in a (1:1) electrolyte.

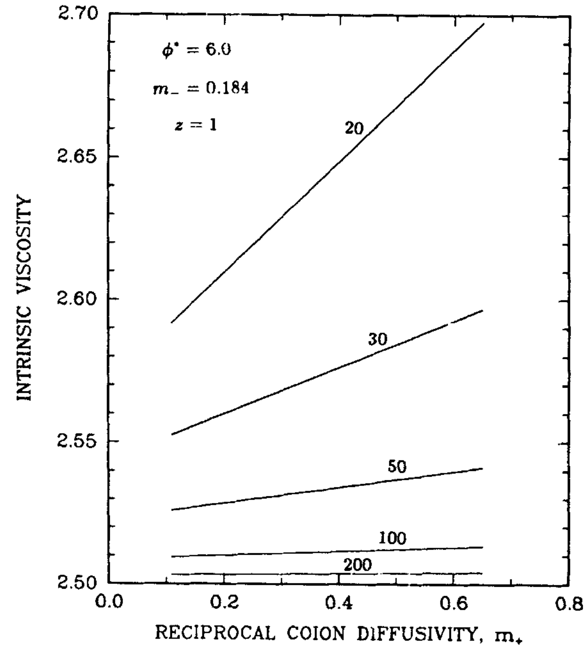

Figure 9. Intrinsic viscosity v. coion mobility for a negatively charged particle in a (1:1) electrolyte.

tromigration which are, once again, neglected in Eq. 84, become important at higher surface potentials. This leads eventually to a decrease in the intrinsic viscosity with increasing surface potential. The magnitude of the electroviscous contribution is seen to be small and points to the need for careful experimentation in its measurement.

The effect of varying the ion diffusivities is shown in Figures 8 and 9. According to Eq. 84, the intrinsic viscosity should increase linearly with the decreasing diffusivity of either type of ions. This is more or less true in the case of the coions, which is consistent with the fact that the coions do not significantly contribute to the modifying ion fluxes. In the case of the counterions, however, the rate of increase of the intrinsic viscosity decreases significantly as diffusivity decreases.

In Figure 10 we show the effect of changing the electrolyte valence. Increasing the valence at a constant overall concentration of the electrolyte leads to a compression of the diffuse double layer. However, comparing Figure 10 with Figure 7 we see that the decrease in the intrinsic viscosity is much greater than would be predicted on this basis alone.

Concluding Remarks

The solution of the electrokinetic equations in the thin double layer approximation is obtained in the Perturbation Theory section and the results are applied to the two problems of electrophoresis and the dilute shear viscosity of a colloidal suspension in the succeeding two sections. The fact that the classical results of Smoluchowski (1921) must be modified due to substantial tangential ionic fluxes within the double layer at higher zeta potentials has been pointed out by several previous authors. In that sense, the present paper is a consolidation of much of the previous work along with some new results, especially with regard to applications to the dilute shear velocity. It is evident that an analysis such as that presented here is essential in calculating multiparticle interactions in electrokinetic phenomena. For example, in the electrophoresis of moderately concentrated suspensions of charged particles, the interactions will involve not only the macroscopic electric potential gradients but also macroscopic ion concentration gradients that arise solely due to the tangential ion fluxes within the double layers of each individual particle.

The perturbation theory is limited to a binary, symmetric

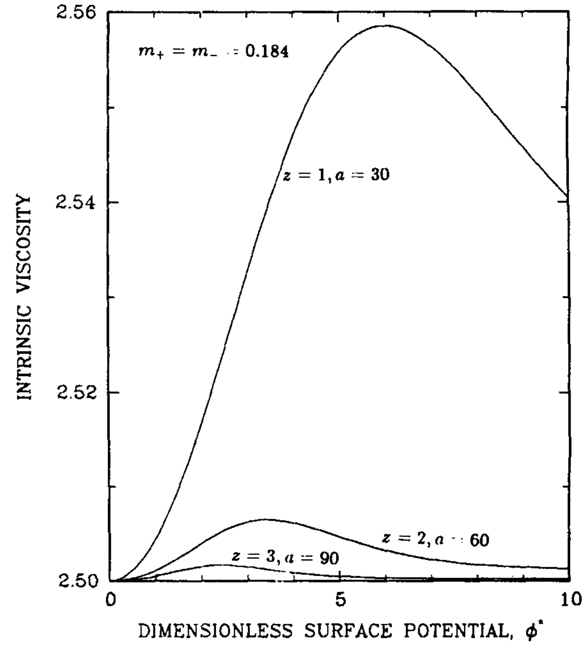

Figure 10. Effect of varying electrolyte valence on intrinsic viscosity.

Ion mobilities and overall concentration held constant.

electrolyte, and its extension to a general electrolyte is frustrated by the lack of a solution to the nonlinear Poisson-Boltzmann equation that is valid for all zeta potentials. The limited influence of the coions on the results for electrophoresis, Figure 5, suggests a heuristic extension of the present theory to general electrolytes by symmetricizing with respect to the counterions with the maximum valence (O'Brien, 1983). However, the accuracy of such an assumption will be poor if the counterions of lesser valence have substantially larger bulk concentrations. The only general recourse is to obtain solutions in series expansions in powers of the surface potential. This has not been pursued here, but it may be pointed out that the accuracy of this procedure will be limited by the number of terms in the expansion that can reasonably be evaluated and the extent to which these terms yield a convergent asymptotic expansion at the large values of the surface potentials of interest.

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Notation

a – dimensionless particle radius
C_p – Gegenbauer polynomial of degree p and order $-1/2$
$\mathcal{D}_i$ – diffusivity of ion species i
D – symmetric rate of strain tensor
e – protonic charge
E_m – dimensionless electrophoretic mobility
$\mathcal{E}$ – electrophoretic field
f_1, f_2, f_3 – functions of the zeta potential, Eqs. 59a–c
$\mathcal{F}$ – dimensionless force on particle
$\mathcal{H}$ – Hartmann number
k – Boltzmann's constant
$m_{\pm}$ – dimensionless reciprocal ion diffusivities, Eq. 58
M – molar concentration of electrolyte
n_i – concentration of ion species i
p – dimensionless pressure
P_n – Legendre polynomial of order n
$\mathcal{P}_i$ – Péclet number of ion species i
Q – as defined in Eq. 50
r – radial variable in spherical polar coordinates
T – absolute temperature
T^p_{jk} – contribution of the particles to average suspension stress
U – characteristic fluid velocity
$\mathcal{U}$ – electrophoretic velocity
$\mathbf{u}$ – dimensionless velocity
z_i – valence of ion species i

Greek letters

ϵ_m – solvent permittivity
ζ – zeta potential
η_{susp} – suspension viscosity
η_0 – solvent viscosity
θ – polar angle in spherical polar coordinates
κ – reciprocal Debye length
μ – $\cos\theta$
ρ – dimensionless charge density
ϕ – dimensionless electric potential
ϕ^* – dimensionless zeta potential
Φ – volume fraction of particles in suspension
φ – azimuthal angle in spherical polar coordinates
Ψ – Stokes stream function

subscripts

$+$ – cation in a binary symmetric electrolyte
$-$ – anion in a binary symmetric electrolyte
∞ – values of the field variables in the bulk, electroneutral region

superscripts

ex – homogenous solution of the field equations
in – particular solution of the field equations

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