Nonlinear effects on migration of charged spherical rigid/soft particle in an unbounded electrolyte solution

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Abstract In this paper we have studied the migration of a colloidal particle under the influence of an external electric field in an electrolyte solution. The colloidal particle is considered to be rigid or a composite particle. The composite particle, the "soft particle", consist an inner hard core coated with a concentric porous layer containing uniformly distributed fixed charges. Situations in which the particle translates along the direction of the imposed electric field with electrophoretic velocity as well as velocity higher than that, is considered. The nonlinear electrokinetic motion and forces experienced by the particle is evaluated through solving the Navier-Stokes, Nernst-Planck and Poisson equations. A pressure correction based iterative algorithm is adopted for the numerical computations. The effect of nonlinear inertial terms in Navier-Stokes equations on the polarization of the EDL and ion distribution near the particle is analyzed. The dependence of hydrodynamic drag and electrostatic force experienced by the particle under several flow conditions is studied. Our results show that as the particle velocity rises from its electrophoretic velocity the hydrodynamic drag gradually approaches the Stokes drag and the electric force diminishes. At large translational speed of the particle, the net charge distribution around the particle is governed by both diffusion and advection mechanisms.

Keywords: Colloidal particle, Electrophoresis, Numerical simulation.

1 Introduction

The transport behavior of colloidal particles under the influence of electric field in a continuous medium at low Reynolds numbers is of much fundamental and practical interest such as, colloidal, biological, biomedical, and biochemical sciences, to name a few. When the colloidal suspension involved is very dilute so that the interaction between particles can be neglected, this configuration obviously resembles the actual system in the sense of geometric similarity. The surface charge of the colloidal particle affects the ion concentration in the host electrolyte and a thin layer, the electrochemical double layer (EDL), forms around the particle in which a spatial gradient of ions develops. In the presence of an external electric field, both the charges on the particle and the ions in the EDL interact with the overall electric field near the particle, resulting in electrostatic forces acting on both the particle and the fluid. The overall electric field is superposition of the external field applied and that in the EDL generated as a result of the charged particle. The electroosmotic motion of ions close to the charged particle produces a retardation effect. The particle movement is determined by the balance between the electric force and the electroosmotically induced retardation drag.

When charged colloidal particles are moving relative to an electrolyte solution, the electric double layer surrounding each particle is distorted by the fluid flow around the particle. The deformation of the double layer resulting from the fluid motion is usually referred to as the relaxation (or polarization) effect. To determine the current density distribution and transport properties, it is necessary to find out not only the local electric potential but also the local ionic densities and fluid velocity. Therefore, for mathematical modeling, it is necessary to solve the nonlinear coupled set of equations based on the Navier-Stokes equation for fluid flow, Poisson equation for electric potential and Nernst-Planck equation for the distribution of each ionic species.

The double layer deformation and the mobility of charged colloidal particle has been addressed by O'Brien and White (1978). They considered the problem is divided into two sub-problems. In the first problem the particle is allowed to move at a constant speed without any electric field and in the second problem the particle is held fixed under an external electric field. There they concluded that if the double layer is either very thin or very thick, the effect of its polarization is negligible. The double layer deformation and mobility of a uniformly as well as non-uniformly charged particle in presence of a solid boundary, has been investigated by several authors namely, Hsu and Ku (2005), Joo et al. (2008), Hsu and Chen (2007) and the references there-in. In all those studies, the convection effects on flow and ionic concentration distribution is neglected.

In all the foregoing studies the flow field is modeled through the linear Stokes equations and the ion distribution is obtained either by solving the Nernst-Planck or Poisson-Boltzmann equation. Recently, Keller et al. (2010) investigated the settling process of a colloidal particle under the influence of a gravitational or centrifugal field. There they have shown that the fluid Reynolds number have a strong influence on the drag force and hence on settling velocity. Yang et al. (2010) studied the advective flow of a permeable sphere subjected to an incoming flow and an external electric field. They modeled the flow by introducing an electric body force term in the Navier-Stokes equations without taking into account the EDL polarization. Chein and Dutta (2009) studied numerically the nonlinear electrophoretic motion of a particle through a nanopore located in chraged membrane.

In the present study, we consider the dispersion of charged spherical particle with arbitrary velocity in an electrolyte under an axial electric field. The main objective of the present study is to investigate the influence of fluid Reynolds number on the electrokinetic motion and forces experienced by the charged particle. The flow field is considered to be axi-symmetric with finite Reynolds number. The external electric field is applied along the flow direction. The coupled set of partial differential equations is computed through a pressure correction based iterative algorithm.

2 Governing Equations

We consider a charged spherical particle moving at a constant velocity, u_0 , in a quiescent electrolyte. The particle is located at the center of a large cylinder filled with a Newtonian fluid moving in the direction along the axis of the cylinder which comprises the computational domain. A uniform electrical field E_0 is applied along the moving direction of the sphere and causes an electro-osmotic flow. This problem is equivalent to that of a fixed sphere experiencing an incoming flow at a velocity

of u_0 . For the present problem the electric field, the concentration field, and the flow field need to be solved simultaneously. A spherical polar coordinate (r, θ, ϕ) is considered with origin at the center of the sphere and z-axis along the direction of the applied electric field.

The net electric field is decomposed into two parts, one is the external electric field and the other is the induced electric field developed due to migration of ions. The electric potential ϕ_{ext} due to the imposed electric field is obtained by solving the Laplace equation. The induced electric field is governed by the Poisson equation $\nabla^2 \phi = -(\kappa a)^2 \bar{\rho}_e/2$. The Nernst-Planck equation governing the distribution of ions is given by

$$\frac{Re \ Sc}{2} \frac{\partial n_i}{\partial t} + \frac{Re \ Sc}{2} \left[v \frac{\partial n_i}{\partial r} + \frac{u}{r} \frac{\partial n_i}{\partial \theta} \right] - \nabla^2 n_i - \\
z_i \left[\frac{\partial n_i}{\partial r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial n_i}{\partial \theta} \frac{\partial \phi}{\partial \theta} \right] - z_i \left[\frac{\partial n_i}{\partial r} \frac{\partial \phi_{ext}}{\partial r} \right] \\
+ \frac{1}{r^2} \frac{\partial n_i}{\partial \theta} \frac{\partial \phi_{ext}}{\partial \theta} + \frac{(\kappa a)^2}{2} z_i n_i \bar{\rho}_e = 0 \tag{1}$$

The electric potential is scaled by $\phi_0 (= RT/F)$ and the ionic concentration by bulk ionic number n_0 . We choose $U_0 = \epsilon_e \phi_0^2 / a\mu$ as velocity scale, $\tau = a/U_0$ as time scale, where a is the particle radius taken as length scale. We consider symmetric electrolytes and the non-dimensional concentrations of cations and anions are denoted by n_1 and n_2 with valencies $z_1 = -z_2 = 1$, respectively. The net scaled ionic concentration is denoted by $\bar{\rho}_e = (n_1 - n_2)$. Different parameters arising in the non-dimensional governing equations are inverse of the EDL thickness, $\kappa = \sqrt{2e^2n_0/\varepsilon_e k_BT}$, Reynolds Number $Re = 2U_0 a/\mu$, Schmidt number $Sc = \nu/D$, Peclet Number Pe = ReSc. Here ϵ_e is permittivity of the medium, e is elementary electric charge, k_B is Boltzmann constant, R is gas constant, T is absolute temperature, F is Faraday can stant, μ is dynamic viscosity, ρ is fluid density, $\nu = \mu/\rho$ is kinematic viscosity and D is diffusivity.

The non-dimensional form of the Navier-Stokes equations describing the motion of the ionized fluid with electric body force in axi-symmetric form is governed by

$$\frac{1}{r sin\theta} \frac{\partial}{\partial \theta} (u sin\theta) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v) = 0 \qquad (2)$$

$$\frac{\partial v}{\partial t} + v \frac{\partial v}{\partial r} - \frac{u^2}{r} + \frac{u}{r} \frac{\partial v}{\partial \theta} = -\frac{\partial p}{\partial r} + \frac{2}{Re} (\nabla^2 v - \frac{2}{r^2} \frac{\partial u}{\partial \theta} - \frac{2v}{r^2} - \frac{2}{r^2} u cot\theta) - B \bar{\rho}_e (\frac{\partial \phi}{\partial r} + \frac{\partial \phi_{ext}}{\partial r}) \quad (3)$$

$$\frac{\partial u}{\partial t} + v \frac{\partial u}{\partial r} + \frac{uv}{r} + \frac{u}{r} \frac{\partial u}{\partial \theta} = -\frac{1}{r} \frac{\partial p}{\partial \theta} + \frac{2}{Re} (\nabla^2 u)$$

$$+ \frac{2}{r^2} \frac{\partial v}{\partial \theta} - \frac{u}{r^2 sin^2 \theta}) - B \bar{\rho}_e (\frac{1}{r} \frac{\partial \phi}{\partial \theta} + \frac{1}{r} \frac{\partial \phi_{ext}}{\partial \theta}) \quad (4)$$

where V = (v, u) is velocity vector, v is the radial and u cross-radial velocity component.

We choose $U_0 = \varepsilon_e \phi_0^2/a\mu$ as the velocity scale, time is scaled by $\tau = a/U_0$, length is scaled by a, the radius of the sphere and pressure is non-dimensionalized by ρU_0^2 , where ρ is fluid density. Different parameters arising in non-dimensionliation of the governing equations are inverse of the EDL thickness, $\kappa = \sqrt{2e^2n_0a^2/\varepsilon_ek_BT}$ Reynolds Number $Re = 2U_0a/\mu$, Schmidt number $Sc = \nu/D$, Peclet Number Pe = ReSc and the parameter $B = \kappa^2/Re$.

Along the upstream boundary $(\frac{\pi}{2} \leq \theta \leq \pi)$, $u = -\alpha \Lambda \mu_E sin\theta$, $v = \alpha \Lambda \mu_E cos\theta$, $\frac{\partial \phi}{\partial r} = 0$, $n_i = 1$, $\phi_{ext} = -\Lambda r cos\theta$. Along the downstream boundary $(0 \leq \theta \leq \frac{\pi}{2})$ and on the axis of symmetry $(\theta = 0 \text{ or } \pi)$, the variables are considered to satisfy the symmetry conditions. On the surface of the particle (r = 1), we apply noslip boundary condition for velocity component. The particle surface is considered as ion-impenetrable with constant ζ potential. Here ζ is non-dimensional surface potential, \hat{n} is unit normal on the surface of the particle, $\Lambda = E_0 a/\phi_0$, μ_E is scaled mobility discussed later in details.

For a composite particle a 'single domain' formulation, where a single set of equation are used to describe the fluid flow in the porous as well as the fluid region with appropriate switching term, is adopted. Porous media is considered to be pseudo-fluid in which the intrinsic velocity is V and the filter velocity \mathbf{v} are related with each other by the relation $V = \epsilon \mathbf{v}$, where ϵ is the porosity of the medium.

For a rigid no slip, nonconducting particle, maintained at constant surface potential, the nondimensional electrostatic body force and hydrodynamic forces can be expressed respectively, as

$$F_E = -\epsilon_e \phi_0^2 \int \int_S \frac{\partial \phi}{\partial r} \frac{\partial \phi_{ext}}{\partial z} dS \tag{5}$$

$$F_D = \epsilon_e \phi_0^2 \int \int_S \left(-\frac{Re}{2} p \cos\theta - \sin\theta \frac{\partial u}{\partial r} \right) dS \quad (6)$$

The forces F_E and F_D are scaled by $\epsilon_e \phi_0^2$.

3 Numerical Methods

The equations for fluid flow and ion distribution are solved numerically using a control volume approach (1998) over a staggered grid system. The discretized form of the governing equations is obtained by integrating the governing equations over each control volume. Different control volumes are used to integrate different equations. At each interface of the control volume, the Quadratic Upstream Interpolation for Convective Kinematics (QUICK) scheme, proposed by Leonard (1979), is used to discretise the convective terms of the unsteady

equations, while the second order central difference scheme is used for the diffusion terms. The QUICK scheme uses a quadratic interpolation/extrapolation between three nodal values to estimate the variables at the interface of the control volume. The pressure link between the continuity and momentum equations are accomplished by transforming the discretized continuity equation into a Poisson equation for pressure correction. This Poisson equation implements a pressure correction for a divergent velocity field. At each iteration, the Poisson equation for induced electric potential and Laplace equation for external electric field are solved through successive overral axation (SOR) technique. We considered a nonuniform grid distribution along the radial direction but a uniform grid is considered along the θ -direction. A timedependent numerical solution is achieved by advancing the flow field variables through a sequence of short time steps. At the initial stage of the motion, the time step is taken to be 0.001 which has been subsequently increased to 0.005 after the transient state. In order to access the accuracy of our numerical methods, we have compared our results for electrophoretic mobility with the numerical / analytical results due to Ohshima (2002), Hill et al. (2003), and Henry (2001) and found them in good agreement (Fig.1).

4 Results and Discussions

We considered the migration of a positively charged particle along the direction of the imposed electric field. The balance between the electrostatic force. the hydrodynamic drag due to electroosmosis and induced pressure field determines the motion of the particle. The diffusivity of ions are assumed to be same as $D = 2 \times 10^{-9} m^2/s$, and Schmidt number is assumed as Sc = 500 for all computations presented here. Results are presented for the solid colloidal particle case only. We have presented the electrophoretic mobility of the particle of radius $0.1\mu m$ for different values of the double layer thickness (κ a) and surface potential (ζ) in Fig. 1. The electrophoretic mobility of the particle is evaluated based on the procedure used by OBrien and White (1978).

The variation of the scaled drag on the particle in electrophoresis with κa is shown in Fig. 2(a) at different values of the surface potential (ζ) for a fixed value of the particle radius. The drag force is balanced by the electric force experienced by the sphere. It is clear from this result that the drag force increases as the EDL thickness decreases, however, the variation is not linear. As the molarity of the electrolyte is raised, the Debye layer ($\lambda = 1/\kappa$) becomes thinner and the retardation effect caused

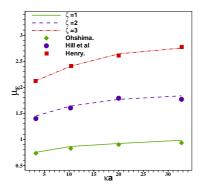


Figure 1: Variation of scaled electrophoretic mobility with EDL thickness for different values of surface potential ζ when $a=0.1\mu$ and $E_0=2.58\times 10^5 V/m$. Comparison with the results due to Ohshima (1978), Hill et al. (2003), and Henry (2001) is also made.

by the electroosmosis becomes higher. However, the variation in scaled drag F_D with the increase of κ is prominent at higher values of surface potential. At lower surface potentials the polarization of EDL is weak compare to higher ζ -potential case. The retardation force which arise due to polarization of EDL, is thus less perturbed by the change of EDL thickness at lower values of ζ -potential. When the electrolyte concentration is low i.e., κ is small, the drag force is almost equal to the drag due to Stokes flow at $\zeta = 1$. Drag force increases monotonically with the increase of surface potential. The strength of the induced electric field increases as the surface charge of the particle is increased. The induced electric field also depends on the molarity of the solution and hence on κ . The variation of the scaled electric force F_E with the EDL thickness at different values of the applied electric field for the case of electrophoresis is presented in Fig. 2b. Electric force, and hence Drag force, is higher at higher values of the external electric field. Our results show that the electric force has relatively less affected by the variation of EDL thickness at lower values of applied electric field. The variation of the electrophoretic mobility is qualitatively same as the varication of electric force (or magnitude of F_D) with κ .

The variation of the drag factor (Ω) with the migration speed of the charged particle is presented in Fig.3(a) and (b). Here Ω is the ratio of the drag experienced by the charged particle with the corresponding Stokes drag when an uncharged particle is assumed to migrate at the same speed. Our result shows that the drag factor is greater than one when particle is migrating along the direction of the imposed electric field. Thus, the viscous drag is larger than the Stokes drag when the particle moves along

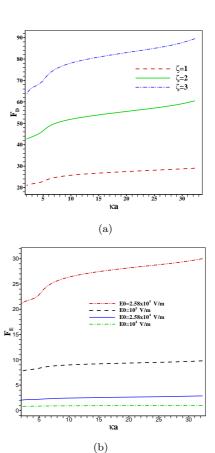
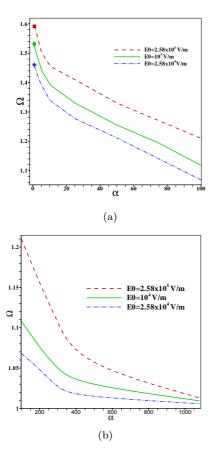
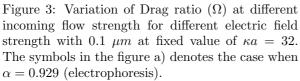


Figure 2: The variation of a) scaled drag force with κa when $a=0.1\mu m$ for $\zeta=1,2,3$; b) scaled electric force with κa for different electric field strength with $\zeta=1$.

the direction of applied electric field. The electroosmotic flow due to the EDL around the positively charged particle is in the opposite direction to the applied electric field. Hence, the drag experienced by the particle becomes higher than the Stokes drag when it moves opposite to the EOF. The effect of EDL polarization diminishes as the magnitude of α increases. We find that as α becomes large, the drag factor tends to one i.e., the drag on the charged particle translating at high speed is the same as the drag experienced by an uncharged particle. Our results show that at $\alpha = 1000$ (i.e., Re = 0.929), the drag factor is almost 1. In Fig. 4a and b we present the electric force ratio (F_m) , which is the ratio between the electric force F_E and the electric force for the electrophoretic case, as a function of α when EDL thickness $\lambda = 3.1nm$ and imposed electric field $E_0 = 2.58 \times 10^5 \text{V/m}, E_0 = 10^4 \text{V/m} \text{ and}$ $E_0 = 2.58 \times 10^4 \text{V/m}$. Our finding shows that the electric body force is highest when the particle is moving at the electrophoretic velocity. The electrostatic force on the particle is evaluated through the Maxwell stress tensor . we find from figs. 4 that





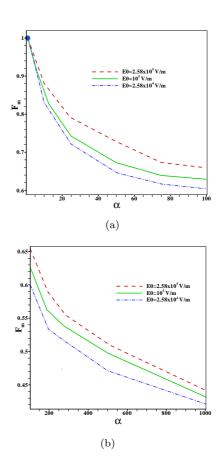


Figure 4: Variation of electric body force ratio (F_m) at different incoming flow strength for different electric field strength with 0.1 μm at fixed value of $\kappa a=32$. The symbols in the figure a) denotes the case when $\alpha=0.929$ (electrophoresis).

as the migration speed of the particle increases, the electric body force diminishes. The electric force becomes negligible as the magnitude of α becomes large.

We discuss the polarization of the EDL around the particle for three different cases namely, electrophoresis ($\alpha = 1$), $\alpha = 500$ and $\alpha = 1000$ in Figs. 5-6. The polarization of the EDL around the particle arises from the motion of ions in the EDL induced by both electroosmosis in the EDL and the induced pressure gradient due to migration of the particle. For the electrophoresis of the positively charged particle, the excessive counter-ions in the particle's EDL region are negative ions. In presence of an electric field, the particle will move towards the cathode (the positive z-direction) whereas the counter-ions will migrate towards the anode (negative z-direction). The migration of counter-ions will initiate the electroosmotic flow, which results in retardation of the mobility of the particle. This phenomenon is called the electrophoretic retardation effect. The electrostatic force responding to the external potential difference and the hydrodynamic drag due to electroosmosis contributes among others to determine the phoretic motion of the particle.

When the particle translates along the direction of the applied electric field (positive z-axis), the counter-ions (anions) clusters downstream of the sphere. When the particle moves at a velocity higher than the electrophoretic velocity ($\alpha > 1$), we find that the accumulation of counter-ions downstream of the particle is higher (Fig. 5b). Thus the EDL is further asymmetric compared to the electrophoretic case. Fig.5b and c show that as the translational speed of the particle is higher than the electrophoretic velocity, the thickness of the EDL is greater in the downstream region compare to the electrophoresis case (Fig. 5a). As the double layer thickens, the induced electric field strength reduces and thus the electric force, which is the surface integral of $\frac{\partial \phi}{\partial r}$ also reduces. This observation supports the findings of Fig. 4a and b, where we have shown that F_E reduces as α increases. The distribution

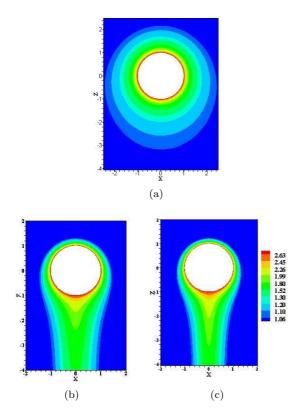


Figure 5: Distribution of concentration of counterion for a) $\alpha=1$ (electrophoresis), b) $\alpha=500$ c) $\alpha=1000$, around the spherical particle of radius 0.1 μm , EDL thickness $\lambda=3.1~nm$ for electric field strength $E_0=2.58\times 10^5 V/m$ with surface potential $\zeta=1$.

of counter-ions near the particle for electrophoretic case (Fig. 5a) shows ring-like structure as the ion transport is mostly governed by the diffusion mechanism. However, Fig. 5b and c show that ion distribution is affected by the advection of the particle as well

The polarization of the EDL perturbs the ionic concentration distributions away from the equilibrium, which, in turn, induces changes of the local net charge density and electric field that affect the electrostatic forces acting on both the particle and the fluid. The polarization of the EDL is evident from the distribution of net scaled ionic concentration. The net ionic concentration is negative around the particle. When the particle migrates along the direction of the applied electric field (positive zaxis) the negative value of the net ionic distribution along the downstream region (z < 0) of the particle is much higher than the upstream region (z > 0). It is evident from the Poisson equation for potential that as the value of κ^2 is as great as about 1024, a small difference between the concentrations of the counter-ion and co-ion can induce a significant change of the electric field. The induced

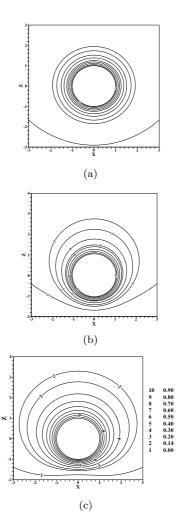


Figure 6: Variation scaled induced potential for a) $\alpha = 0.929$ (electrophoresis), b) $\alpha = 500$ c) $\alpha = 1000$, around the spherical particle of radius $0.1 \ \mu m$ for electric field strength $E_0 = 2.58 \times 10^5 V/m$ with surface potential $\zeta = 1$ at fixed value of $\kappa a = 32$.

electric field is directed from the particle towards the fluid i.e., opposite of the direction of applied electric field. The induced electric field is strong in the z<0 region close to the particle surface where the net charge density is enhanced. This is evident from the Figs.6a-c, as the induced electric potential has a steep gradient in the z<0 region. Region in which the electric potential gradient is strong becomes narrower, and hence the Maxwell stress is lower and electric force lower, as fluid Reynolds number increases.

5 Conclusions

The nonlinear electrokinetics of a charged particle through an electrolyte under an axial electric field is studied. The complete set of Navier-Stokes, Poisson and Nernst-Planck equations are solved through the

control volume approach. The electrophoretic mobility of the particle is compared with several published results and found them in agreement. We have presented the drag force for electrophoretic case, which is balanced by the electric force, as a function of EDL thickness at different values of wall potential and external electric field. The forces experienced by the particle moving in electrophoretic velocity rises as the ζ -potential increases. However, the effect of EDL thickness on the forces has less impact at lower values of ζ -potential and E_0 . As the migration speed of the particle is higher than the electrophoretic velocity, the drag and electric forces reduces with the rise of migration speed. For high fluid Reynolds numbers the hydrodynamic forces dominate while the electric effect becomes more significant as the fluid velocity reduces. The advection effects on ionic distribution and induced electric field is evident from the results for higher values of α .

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