

Double layer polarization and non-linear electroosmosis in and around a charged permeable aggregate

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Abstract—We have studied the migration of a charged permeable aggregate in electrolyte under the influence of an axial electric field and pressure gradient. The migration of the positively charged aggregate leads to a deformation of the anionic cloud around it. The hydrodynamics of the aggregate is governed by the interaction of electroosmotic flow in and around the particle, hydrodynamic friction and electric force experienced by the aggregate. We have computed the non-linear Nernst-Planck equations coupled with the Darcy-Brinkman extended Navier-Stokes equations and Poisson equation for electric field through a finite volume method. The permeability of the aggregate enable the counterion penetration. The penetration of counterions depends on the volume charge density of the aggregate and ionic concentration of electrolytes at a fixed field strength. The retardation effect due to the double layer polarization increases the drag force compared to an uncharged aggregate. Increase in migration speed from the electrophoretic velocity of the aggregate produces further asymmetry in charge cloud and reduces the electric body force exerted on the particle. The permeability of the particle have relatively little influence on the electric body force when Double layer is relatively thin. The impact of the key parameters of electrokinetics on the hydrodynamics of the aggregate is analyzed.

Keywords—Electrophoresis, Advective flow, Polarization effect, Numerical solution.

I. INTRODUCTION

STUDIES of electrokinetics of charged porous particle is important in the context of electrophoresis of polymer gels or polyelectrolyte as well as sedimentation, electroosmotic dewatering and aggregation of waste water sludge. The electroosmotic flow and ion penetration inside the aggregate leads to characteristic difference in hydrodynamics compared to a rigid particle. A charged particle which is immersed in electrolyte is surrounded by diffused charged layer enriched with ions of opposite sign (counterions) to that of the particle surface charge. This ionic cloud around the charged particle is deformed due to the electroosmosis of electrolytes under an imposed electric field. This effect is referred as the double-layer polarization (DLP). The DLP effect leads to an electric field opposite to the imposed field for a positively charged particle. When the particle is permeable to fluids, the counterions penetrate inside the particle and simultaneously the coions are expelled from it, resulting in further imbalance to the charge cloud surrounding the particle.

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Hermans and Fujita [1] studied the electrophoresis of an isolated charged porous sphere and provided an expression for the electrophoretic mobility in terms of the volume charge density, electrolyte concentration and softness of the particle. Their analysis is based on thin Debye length and electric potential of the particle so that the DLP effect is negligible. Subsequently, several authors (Keh and Chen [2] and the references there-in) studied the electrophoresis of fully porous particle and soft particle under several electrokinetic conditions. In a recent review article, H. Ohshima [3] provided a brief account on those studies. In most of the theoretical studies reported in the forgoing review article the ion distribution is assumed to follow the linearized Poisson-Boltzmann distribution. The DLP effect on electrophoresis of polyelectrolytes was studied by Yeh and Hsu [4] and Huang et al. [5] by solving the non-linear Poisson-Boltzmann equation for ion distribution. Our literature survey suggest that all the previous studies have neglected the non-linear convection effects in fluid flow as well as ion distribution. Nonlinearities, however, can greatly affect the polarization and hence the forces experienced by the aggregate.

In the present paper we have investigated the nonlinear electrokinetics of the permeable aggregate migrating at an arbitrary velocity. The particle can be transported either through a centrifugal field or by imposing a pressure gradient, combined with the electric field. The non-linear effects on ion distribution, fluid flow and forces experienced by the particle are investigated numerically. The mathematical model considered here is based on the Navier-Stokes-Nernst-Planck-Poisson equations. Based on the Brinkman model for porous media, the flow field and ion distribution is computed both inner and outer region of the particle. The flow field is analyzed through a single domain approach in which the porous region is considered as a pseudo-fluid and the composite region as a continuum. A pressure correction based control volume approach is adopted for computing the governing equations. In the single-domain formulation with finite volume discretization, the variable values from both sides of the interface are used to obtain solutions, and therefore the matching of variable values is inherent. Our algorithm is validated by comparing with several published results.

The aggregate is assumed to have a fixed charge density and homogenous porosity. The deformation of electric field around the aggregate due to the convection of ions leads to the polarization effect. This polarization effect depends on the ion

concentration of the electrolyte (i.e., Debye length), charge density of the aggregate, its permeability as well as Reynolds number. A detailed investigation on the hydrodynamics and force field is investigated in the present analysis. We have compared the hydrodynamic drag experienced by the aggregate with the corresponding uncharged case.

II. GOVERNING EQUATIONS

We consider a permeable micro-sized sphere of radius a moving at a constant velocity, U_0 , in a quiescent electrolyte. The sphere is located at the center of a large cylinder filled with a Newtonian fluid and 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 direction of translation of the sphere. This problem is equivalent to that of a fixed sphere experiencing an incoming flow at a velocity of U_0 . When the cylinder diameter is much bigger than that of the sphere, the wall confinement effect on the electrokinetics of the sphere can be neglected. The porous sphere is assumed to be composed of charged monomers and have a uniform porosity ϵ and permeability k_p . As the present configuration involves porous-solid and fluid-porous interfaces, the Brinkman model is used to account for the jump in shear stress. The fluid velocity q is related to the intrinsic (average over the fluid volume only) velocity V by $q = \epsilon V$. We adopt a unified single-domain approach (Bhattacharyya et al. [6] and the references therein). In this approach, the two sets of equations for the fluid and the porous regions are combined into one set using appropriate switching terms. When this single set of equations is integrated over control volumes, it automatically takes care of the interfacial conditions. Thus, the present approach does away with the need for separate interface conditions. A spherical polar coordinate (r, θ, ψ) is adopted with the origin located at the center of the sphere and the direction of the applied electric field is along the initial line (z -axis).

The equations governing this electrokinetic phenomena are the Navier-Stokes equations for fluid flow, Nernst-Planck equations for ion transport and Poisson equation for electric field. We assume an axisymmetric flow with z -axis as the axis of symmetry. The radius of the sphere a is assumed to be the length scale, the free-stream velocity U_0 is the velocity scale, $\tau = a/U_0$ as time scale, $\phi_0 (= RT/F)$ is the potential scale and the bulk ionic number n_0 is the scale for ionic concentration. The structure of the polyelectrolyte is assumed to be homogeneous with a constant fixed charge density ρ_{fix} throughout porous aggregate. We have considered the fluid as incompressible Newtonian fluid with constant physical properties. The non-dimensional form of the Navier-Stokes equations describing the motion of the ionized fluid in and around the porous aggregate is

$$\frac{\partial v}{\partial t} + \frac{1}{\epsilon} \left(v \frac{\partial v}{\partial r} - \frac{u^2}{r} + \frac{u}{r} \frac{\partial v}{\partial \theta} \right) = -\epsilon \frac{\partial p}{\partial r} - B_1 \rho_e \frac{\partial \phi}{\partial r} + \frac{2\epsilon}{Re} \left(\nabla^2 v - \frac{2}{r^2} \frac{\partial u}{\partial \theta} - \frac{2v}{r^2} \right) - B \frac{2\epsilon}{Re Da} v \quad (1)$$

$$\frac{\partial u}{\partial t} + \frac{1}{\epsilon} \left(v \frac{\partial u}{\partial r} + \frac{uv}{r} + \frac{u}{r} \frac{\partial u}{\partial \theta} \right) = -\epsilon \frac{1}{r} \frac{\partial p}{\partial \theta} - \epsilon B_1 \bar{\rho}_e \frac{1}{r} \frac{\partial \phi}{\partial \theta} + \frac{2\epsilon}{Re} \left(\nabla^2 u + \frac{2}{r^2} \frac{\partial v}{\partial \theta} - \frac{u}{r^2 \sin^2 \theta} \right) - B \frac{2\epsilon}{Re Da} u \quad (2)$$

where the binary parameter B is 1 in the porous zone and 0 in fluid zone. The equation of continuity is given by

$$\frac{1}{r \sin \theta} \frac{\partial}{\partial \theta} (u \sin \theta) + \frac{1}{r^2} \frac{\partial}{\partial r} (r^2 v) = 0 \quad (3)$$

where $V = (v, u)$ is velocity vector, v is the radial and u cross-radial velocity component. Based on the Gauss law, the electric potential Φ is determined by the following Poisson equation

$$\nabla^2 \phi = -\frac{(\kappa a)^2}{2} \bar{\rho}_e - B Q_{fix} \quad (4)$$

where the net scaled ionic concentration is denoted by $\bar{\rho}_e = (n_1 - n_2)$, the inverse of the EDL thickness is given by $\kappa = \sqrt{2e^2 n_0 / \epsilon_e K_B T}$ and $Q_{fix} = \rho_{fix} a^2 / \epsilon_e \phi_0$. Here ϵ_e is the permittivity of the medium, e is the elementary electric charge, K_B is Boltzmann constant, R is gas constant, T is absolute temperature, F is Faraday constant.

The Nernst-Planck equations governing the distribution of ions in non-dimensional form is given by

$$\frac{Re Sc}{2} \frac{\partial n_i}{\partial t} + \frac{Re Sc}{2} \left[v \frac{\partial n_i}{\partial r} + \frac{u}{r} \frac{\partial n_i}{\partial \theta} \right] - \nabla^2 n_i - z_i \left[\frac{\partial n_i}{\partial r} \frac{\partial \phi}{\partial r} + \frac{1}{r^2} \frac{\partial n_i}{\partial \theta} \frac{\partial \phi}{\partial \theta} \right] + \left[\frac{(\kappa a)^2}{2} z_i n_i \bar{\rho}_e + z_i n_i B Q_{fix} \right] = 0 \quad (5)$$

Here $i=1, 2$ and $z_1 = 1, z_2 = -1$. The pressure is non-dimensionalized by ρU_0^2 . Different parameters arising in the non-dimensional governing equations are Reynolds Number $Re = 2\rho U_0 a / \mu$, Schmidt number $Sc = \nu / D$, Peclet Number $Pe = Re Sc$ and Darcy number $Da = \kappa_p / a^2$. Here μ is the dynamic viscosity, $\nu = \mu / \rho$ is the kinematic viscosity and D is diffusivity.

The Laplacian operator in spherical polar co-ordinate system with axi-symmetry is given by

$$\nabla^2 = \frac{1}{r^2} \frac{\partial}{\partial r} \left(r^2 \frac{\partial}{\partial r} \right) + \frac{1}{r^2 \sin \theta} \frac{\partial}{\partial \theta} \left(\sin \theta \frac{\partial}{\partial \theta} \right) \quad (6)$$

In the fluid region Darcy number Da , is assumed to be infinity and the porosity ϵ is 0 outside the porous zone and $0 < \epsilon < 1$ with in the porous zone. The dimensionless parameter B_1 arises in the momentum equation is actually represents the ratio of ionic pressure to dynamic pressure as $B_1 = \epsilon n_0 \phi_0 / \rho_f U_0^2$. In the far field, the gradient of the potential must approach the applied electric field, E_0 . Far away from the particle the velocity is along the axial direction and is U_0 . Along the outer boundary, the concentration of ionic species and electric potential is considered to be independent of radial coordinate. A symmetry condition is imposed along the axis of symmetry $\theta = 0$ and π .

When the charged particle migrates under the influence of electric field, the forces acting on the particle are electrostatic

force and the hydrodynamic force. The axi-symmetric nature of our problem suggests that only the z-component of these forces need to be considered. The electrostatic body force and the hydrodynamic force along the flow direction can be calculated by integrating on the surface S of the particle the Maxwell stress tensor and hydrodynamic stress tensor, respectively and are given by

$$F_E = \int \int_S (\sigma^E \cdot \hat{n}) e_z dS \quad (7)$$

$$F_D = \int \int_S (\sigma^H \cdot \hat{n}) e_z dS \quad (8)$$

where e_z is the unit vector along z-axis and

$$\sigma^E = \epsilon_e [EE - 1/2E^2 I], \quad (9)$$

$$\sigma^H = -pI + \mu[\nabla V + (\nabla V)^T] \quad (10)$$

For spherical porous aggregate, the non-dimensional electrostatic body force and hydrodynamic forces can be expressed respectively, as

$$F_E = -\epsilon_e \phi_0^2 \int \int_S \left[\frac{\partial \phi}{\partial r} \frac{\partial \phi}{\partial z} - \frac{1}{2} \left(\left(\frac{\partial \phi}{\partial r} \right)^2 + \left(\frac{1}{r} \frac{\partial \phi}{\partial \theta} \right)^2 \right) \right] dS \quad (11)$$

$$F_D = \mu U_0 a \int \int_S \left[\left(-\frac{Re}{2} p + 2 \frac{\partial v}{\partial \theta} \cos \theta \right) - \sin \theta \left(\frac{\partial u}{\partial r} + \frac{1}{r} \frac{\partial v}{\partial \theta} - \frac{u}{r} \right) \right] dS \quad (12)$$

The forces F_E and F_D are scaled by $\epsilon_e \phi_0^2$ and $\mu U_0 a$, respectively. We considered the migration of the charged porous particle with $Q_{fix} > 0$, which implies that the particle migrates along the direction of the external electric field.

III. NUMERICAL METHODS

The equations for fluid flow and ion distribution are solved in a coupled manner through a control volume approach [7] over a staggered grid system. In the staggered grid arrangement, the velocity components are stored at the midpoints of the cell sides to which they are normal. The scalar quantities such as the pressure and concentrations are stored at the center of the cell. 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 every iteration, the Poisson equations for electric potential is solved by a successive-over-relaxation (SOR) technique.

IV. RESULTS AND DISCUSSIONS

The electrophoresis of the permeable aggregate is governed by the fixed charge density (ρ_{fix}), permeability (κ_p), ionic concentration of the electrolyte (I), field strength and radius of the spherical particle. The charge density and permeability depends on the form of the aggregate under consideration i.e., the size of the monomers and the number of monomers. The ionic concentration of the electrolyte is specified via the

Debye layer thickness $\lambda = \sqrt{\epsilon_e K_B T / 2e^2 n_0}$. We considered the migration of a positively charged porous particle along the direction of the imposed electric field. When the porous sphere is convecting through the electrolyte it will attract counterions and repelled the coions. The imposed electric field will induce an electroosmotic flow in the diffused charges present surrounding the particle. The balance between the electrostatic force, the hydrodynamic drag due to electroosmosis and induced pressure field determines the motion of the particle.

We present results for $a = 2.5 \mu m$ at different values of Da and $Q_{fix} > 0$. The diffusivity of ions are considered to be $D_+ = 1.33 \times 10^{-9} m^2/s$ and $D_- = 2.03 \times 10^{-9} m^2/s$ with field strength $E_0 = 10^4 V/m$. The softness of the particle is determined by $\lambda_s = 1/\kappa_p$. If we consider the permeable sphere as an aggregate of charged monomers of size close to 5nm and the Darcy number is assumed to vary between 1 to 0.1, this implies that Q_{fix} to lie between 1 to 10.

We have compared our computed result for electrophoretic mobility of the porous sphere of size $a = 2.5 \mu m$ with the expression provided by Ken and Chen [2] as well as Herman and Fujita [1] for different values κa and Q_{fix} and found them in good agreement (Fig.1a,b). The electrophoretic mobility is obtained based on the two problem method as described by OBrien and White[8]. Our computed results found to be in good agreement with the theoretical analysis. The analytic expression for scaled mobility, scaled by $\epsilon_e \phi_0 / \mu$ as described by Hermann and Fujita [1] for thin EDL is given by

$$\mu_E = \frac{2}{3} Q_{fix} Da \left[1 + \frac{1}{2} P^2 \frac{2+P}{1+P} \right] \quad (13)$$

where $P = \beta/\kappa a$ with $\beta = 1/\sqrt{Da}$. When the EDL thickness comparable to the particle radius, the scaled mobility of charged colloidal particle is due to Keh and Chen [2]

$$\mu_E = Q_{fix} Da \left[1 + \frac{1}{3} P^2 \left(1 + e^{-2\kappa a} - \frac{1 - e^{-2\kappa a}}{\kappa a} \right) + \frac{1}{3} \left(\frac{P^2}{P^2 - 1} \right) \left(1 + \frac{1}{\kappa a} \right) \left(P^2 \frac{\kappa a (1 + e^{-2\kappa a}) - 1 + e^{-2\kappa a}}{\beta \coth \beta - 1} \right) \right] \quad (14)$$

Note that as $\kappa a \rightarrow \infty$, the nondimensional mobility approaches to $Q_{fix} Da$, the electrophoretic mobility of an individual polymer segment or monomer. We find from Fig.1a that the scaled electrophoretic mobility of the sphere tends to 1 as κa becomes large when Q_{fix} is taken to be 1. For sufficiently thin Debye layer (large κa), the shielding effect due to electrolytes vanishes and the mobility becomes independent of the ionic concentration of electrolytes. This critical value of κa depends on Q_{fix} . We have also evaluated the electric body force and drag exerted (not presented here) on the particle when it is in electrophoresis. The forces are found to be equal and opposite, which further justifies the correctness of the present algorithm.

When a charged aggregate is convected through the electrolyte, the retardation force created by the induced electric field results in larger drag compared to an uncharged particle. This retardation force is directly proportional to the volume

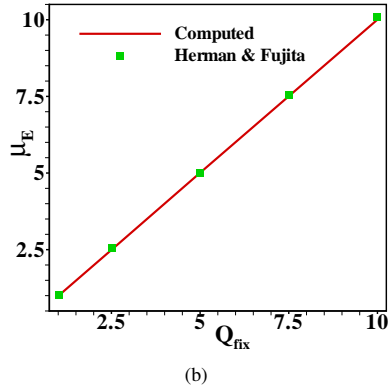
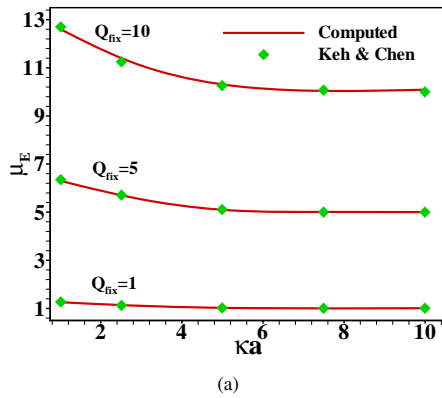


Fig. 1. Variation of scaled electrophoretic mobility by varying the (a) double layer thickness parameter (κa) for different values of Q_{fix} and (b) fixed charge Q_{fix} with in the porous zone for $\kappa a = 10$ when $a = 2.5 \mu m$ and $Da = 1$. Comparison with the results due to Herman and Fujita [1] and Keh and Chen [2] is also made.

charge density of the positively charged particle. The drag force experienced by the particle varies with the permeability of the particle. In Fig.2, we have shown the variation of drag factor with $\beta = 1/\sqrt{(Da)}$ at different Q_{fix} for the charged porous sphere convecting with Reynolds number $Re = 0.1$. We have also computed the drag with the corresponding uncharged porous sphere. We present the drag factor (Ω_E) which is the ratio of the drag exerted on a charged porous aggregate with the corresponding Stokes drag of a rigid uncharged sphere. For an uncharged permeable sphere, Neale et al. [9] obtained the relation for the drag factor, Ω , of an uncharged permeable aggregate as

$$\Omega = \frac{F_d^P}{F_d^H} = \frac{2\beta^2[1 - \frac{\tanh\beta}{\beta}]}{2\beta^2 + 3[1 - \frac{\tanh\beta}{\beta}]} \quad (15)$$

For any permeable sphere with intermediate values of permeability, $0 < \Omega < 1$. Our computed solution for Ω for uncharged permeable sphere is in agreement with the relation (15). Note that as $\beta \rightarrow \infty$ (i.e., $Da \rightarrow 0$), $\Omega \rightarrow 1$. Fig.2 shows that the drag factor Ω_E is essentially larger than Ω , as expected. However, as the particle permeability increases, the drag force appreciably deviates from the Stokes value. The results show that the drag is enhanced at the same rate as the charge density

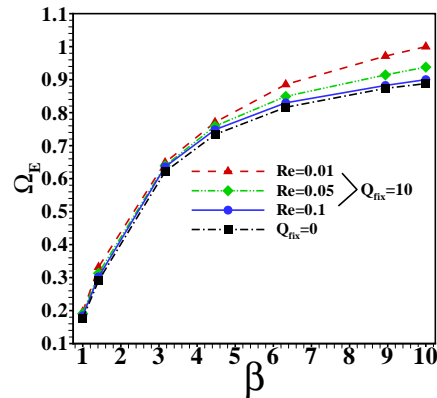


Fig. 2. Variation of drag factor Ω_E by varying the Darcy number for different values of Q_{fix} with fixed $\kappa a = 10$ when the particle radius $a = 2.5 \mu m$ and electric field applied $E_0 = 10^4 V/m$.

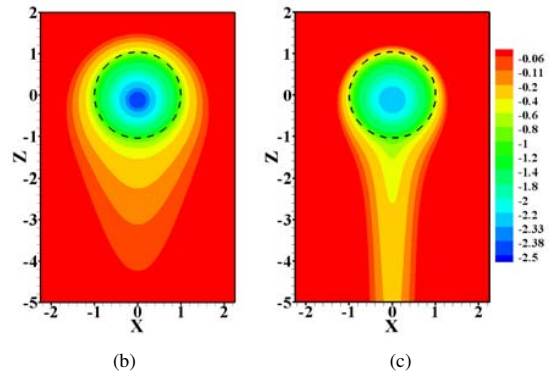
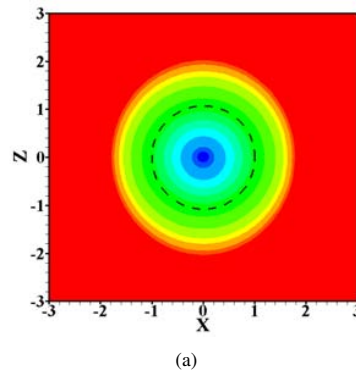
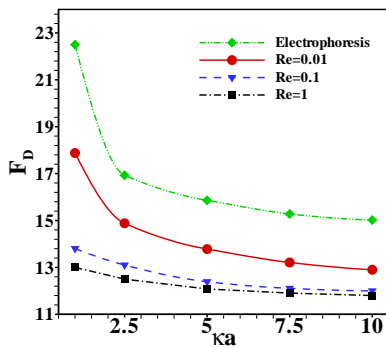


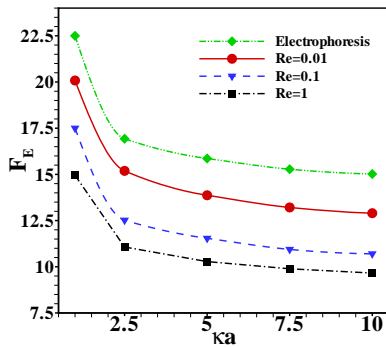
Fig. 3. Distribution of counterion concentration for (a) $Re = 9.29 \times 10^{-4}$; (b) $Re = 0.1$ and (c) $Re = 1$. Here the fixed charge is taken to be $Q_{fix} = 10$ with in the porous zone for $\kappa a = 10$ when the particle radius $a = 2.5 \mu m$ and electric field applied $E_0 = 10^4 V/m$. Here Darcy number is taken to be $Da = 0.1$

is enhanced. We find that the presence of the fixed charge in the aggregate increases its settling velocity compared to an uncharged porous sphere.

The effect of the migration speed (Re) of the porous sphere on the net charge density and body forces exerted on the particle is presented in Fig.3a-c and Fig.4a,b. When the particle translates along the direction of the applied electric field (E_0)



(a)



(b)

Fig. 4. Variation of nondimensional (a) drag force F_D and (b) electric body force (F_E) by varying κa for different values of Re at fixed charge $Q_{fix} = 10$ with in the porous zone when the particle radius $a = 2.5 \mu m$ and electric field applied $E_0 = 10^4 V/m$. Here the Darcy number is taken to be 0.1.

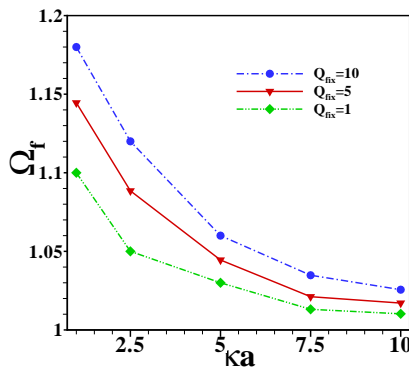


Fig. 5. Variation of drag factor Ω_f at $Re = 0.1$ by varying κa for different values of Q_{fix} .

positive z-axis), the counter-ions (anions) cluster downstream of the sphere. When the particle moves at a velocity higher than the electrophoretic velocity, we find that the accumulation of counterions downstream of the particle is higher. Thus the EDL is further asymmetric compared to the electrophoretic case. With the rise of the convection speed i.e., increase of Re , the counterion penetration inside the aggregate occurs at

a faster rate. With the rise of Re , the advection mechanism becomes stronger and the double layer around the aggregate is distorted. With the rise of migration speed both the viscous drag and electrostatic force decreases rapidly (Fig.4a,b).

We have shown before that the electrophoretic mobility of a charged aggregate becomes independent of the ionic concentration beyond a critical value of the double layer thickness. This critical value of the EDL thickness depends on the fixed charge density. We present the drag factor (Ω_f) which is the ratio of the drag exerted on a charged porous aggregate with the corresponding uncharged one. In Fig.5 we have investigated the effect on drag factor Ω_f due to variation of κa for different values of the fixed charge density Q_{fix} when $Re = 0.1$ and the aggregate radius is $2.5 \mu m$, where Ω_f represents the ratio of the drag experienced by the charged porous aggregate by corresponding uncharged one. It is evident from the results that the friction drag assume a constant value as the double layer becomes thin. Fig.5 also suggest that the drag exerted on the sphere increases linearly with the increase of the fixed charge density of the sphere.

V. CONCLUSIONS

We have computed the Darcy-Brinkman extended Navier-Stokes equations coupled with the Nernst-Planck equations and Poisson equation for electric field to determine the nonlinear electrokinetics of a charged permeable aggregate translating under an axial electric field. The fixed charge density of the aggregate produces a retardation effect due to DLP and this retardation effect increases with the rise of charge density of the aggregate. As the ionic concentration of the electrolytes becomes large, both drag and electric body force experienced by the sphere reduces. However, both the body forces become independent of κa beyond a critical value of the double layer thickness. Our results suggest that the variation of drag experienced by the charged aggregate with the variation of its permeability follow the same trend as that of an uncharged aggregate.

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