Abstract

This thesis presents a numerical as well as theoretical study on the phoretic motion of a charged dielectric colloid under the influence of an external electric field or concentration gradient of solute molecules through an electrolyte or hydrogel medium considering finite ion size effects and ion-solvent interactions. The mathematical model is based on the conservation principle, which leads to the coupled set of Navier-Stokes-Poisson-Nernst-Planck equations (PNP-model) and their modified forms to account for the finite ion size effects. The Brinkman extended Navier-Stokes model is used to formulate the flow through the gel medium. Governing equations are solved numerically based on a control volume approach. A theoretical analysis for certain limiting situations is also made.

Chapter 1 of the thesis is introductory. In **Chapter** 2, we analyze the electrophoresis of a hydrophobic particle, considering ion steric interactions, dielectric decrement effects, and viscosity modification. We establish that ion steric interactions and dielectric decrement create counterion saturation in the Debye layer, leading to enhanced mobility compared to the standard PNP-model. However, the dependence of medium viscosity and, consequently, ion diffusivity on the ionic volume fraction reduces particle mobility compared to the standard PNP-model. We also develop a simplified model for a thin Debye layer based on first-order perturbation on the applied electric field, significantly reducing computational time. This model can be implemented for any number of ionic species as well as non-$z:z$ electrolytes.

In **Chapter** 3, we present the diffusiophoresis of a rigid particle by considering the ion steric interactions and the variation of viscosity with the ionic volume fraction. The counterion saturation in the Debye layer due to the ion steric interaction enhances the surface potential by attenuating the shielding effect, diminishes the surface conduction, and magnifies the induced electric field. These in combination create a larger mobility at a thinner Debye length compared with the PNP-model. This increment in mobility attenuates when the ionic volume fraction dependent viscosity is considered. Semi-analytical expressions for mobility based on a linear perturbation technique under a thinner Debye length is presented which is valid for a lower ionic volume fractions.

In **Chapter** 4, we analyze the diffusiophoresis of a rigid particle in a hydrogel media accounting the ion steric interactions. The impact of the finite ion size effect is found to be significant when the bulk ionic concentration is large enough to create a Debye length thinner than the particle size. We have considered the impact of the hindered diffusivity of ions in the gel medium, which is shown to be significant for low porosity and high charge density situations. We also proposed an empirical formula for the diffusiophoretic mobility in a hydrogel media in

PNP-model which matches well with our numerical results at thinner Debye length.

Subsequently in **Chapter** 5, we consider the electrophoresis of a rigid particle in a weakly non-Newtonian media accounting the ion steric interactions. Our analysis shows that the non-Newtonian part of mobility exhibits a non monotonic variation with surface potential similar to the Newtonian part. We express the non-Newtonian correction in mobility relating to both the non-Newtonian properties of the fluid and the electrokinetic parameters. We have established that when the flow behavior index is low, and the relaxation time of the fluid is high, the fluid behaves like a Newtonian one.

Finally, in **Chapter** 6, we provide a comprehensive summary of the entire thesis with addressing our limitations and future scopes.

Keywords : Electrophoresis; Diffusiophoresis; Chemiphoresis; Double layer polarization; Nernst-Planck equations; Numerical solution; Asymptotic analysis; Debye-Hückel approximation; Surface conduction; Hydrophobicity; Ion steric effect; Dielectric decrement; Viscosity modification; Hydrogel; Non-Newtonian fluid.