Abstract

This thesis presents a detailed numerical investigation supported by theoretical analysis on the electrokinetic transport of colloidal particles and ionized fluids, subjected to externally applied fields. Moving beyond the classical mean-field based Poisson-Nernst-Planck (PNP) framework, an improved mathematical model is developed by incorporating non-local electrostatic correlations and ion-solvent interactions of finite-sized hydrated ions. The Nernst-Planck equation is modified to include these effects and the consideration of non-local electrostatic correlations results in a fourth-order modified Poisson equation for an electric field. The viscosity of the ionized fluid is assumed to vary spatially due to the volume exclusion of finite-sized ions. The complete set of non-linear governing equations is solved using the finite volume method, without imposing limitations on Debye layer thickness, surface charge density, or external field strength. Additionally, simplified models consisting of coupled boundary value problems and semi-analytical solutions are derived for limiting cases such as weak external fields or high electrolyte concentrations. The outcomes of this thesis provide valuable insights with potential applications in biomedical technologies and industrial processes.

Chapter 1 introduces the fundamental theory of electrokinetic phenomena. In **Chapter 2** we study the diffusiophoresis of a soft particle consisting of a hydrophobic rigid core enveloped by a charged polyelectrolyte layer (PEL), subjected to an externally imposed ionic concentration gradient. A change in the dielectric constant between the PEL and the surrounding medium induces ion partitioning, which modifies the ion transport. We have adopted the Brinkman extended Navier-Stokes equation for fluid flow through the PEL. A simplified model based on the perturbation technique under a small concentration gradient is developed. The impact of the core hydrophobicity and PEL permittivity on the mobility is analyzed. The hydrodynamic slip at the core amplifies the effect of surface charge. Ion partitioning reduces counterion concentration in the PEL and attenuates the screening of the surface charge and hence an increased mobility is achieved. Positive mobility is observed at high ionic strength for mixed electrolytes.

Chapter 3 provides a numerical study along with a weak field analysis on the diffusiophoresis of charge-regulated rigid particles accounting for finite ion size and electrostatic correlations. The surface charge of the particle is considered to depend on the pH and bulk concentration of the electrolyte. The influence of pH-dependent surface charge on the ion transport and particle mobility is elucidated. Ion steric interactions are modeled using the Carnahan-Starling (CS) equation of state and the local viscosity is assumed to vary with the ionic volume fraction. We have analyzed the impact of steric interactions and ion-ion correlations on the diffusiophoresis for both monovalent and multivalent electrolytes. The ion steric effects cause counterion saturation and reduce surface charge screening which significantly affects the mobility of the particle. The electrostatic correlations create a layered structure of the electric double layer (EDL) through overscreening of the surface charge, leading to mobility reversal in multivalent electrolytes. In **Chapter 4** we have studied the diffusiophoresis of a highly charged diffuse soft particle in multivalent electrolytes through a modified mean-field based electrokinetic model (MNPC) which incorporates steric interactions and electrostatic correlations of finite-sized ions as well as the spatial variation of electrolyte viscosity. In this chapter we have employed the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation of state for the volume exclusion effect arising due to finite ion size consideration. Under weak field approxima-

tion we have derived a simplified model which is further refined into a semi-analytical formulation for symmetric electrolytes in the thin EDL limit. An in-depth analysis on the role of ion sterics and electrostatic correlations on the diffusiophoretic mobility of a soft particle is detailed in this chapter. The PEL fixed charge density plays a crucial role in modulating diffusiophoresis and may suppress the influence of ion-ion correlations at a higher bulk concentration.

In **Chapter 5**, we present a numerical study, supported by theoretical analysis, on the electrophoresis of highly charged soft particles in trivalent electrolyte solutions under the action of an applied electric field. A continuum-based model (MNPDC), extending the classical mean-field theory, is developed to incorporate ion-ion electrostatic correlations, ion-solvent interactions, and hydrodynamic steric effects of finite-sized ions. The governing equations are derived from the system's volumetric free energy, accounting for non-local electrostatics, entropy due to ion sterics, and Born energy due to permittivity variations. Viscosity and ion diffusivity are modeled as functions of local ion volume fraction. The study reveals mobility reversal of soft particles with like-charged core and PEL. This mechanism explains like-charge attraction, such as DNA condensation. At a higher ionic concentration, the ion sterics interactions and dielectric decrement creates a saturation in ion density. An enhanced fixed charge density of the PEL increases screening and suppresses the impact of ion correlations. The influence of counterion size and mixed electrolytes of different valency on the mobility are also elaborated. In **Chapter 6**, we analyze the electroosmotic flow (EOF) of multivalent asymmetric electrolytes through a conical nanopore embedded in a polarizable material, using the same modified mathematical model (MNPDC). Dielectric polarization induces a non-uniform surface charge along the pore wall, leading to a bipolar EDL. This chapter provides a detailed analysis on charge inversion, counterion condensation, and EOF reversal. The dielectric polarization is significantly reduced in the present modified model which aligns better with experiments than standard models, capturing EOF reversal beyond a critical trivalent electrolyte concentration (C_0) and its enhancement with increasing C_0. However, higher surface charge can suppress the reversal due to ion crowding. Additionally, we have also analyzed ion concentration polarization (ICP) and ion selectivity of the nanopore. A semi-analytical solution for EOF through a long cylindrical pore is also provided.

Chapter 7 presents the key conclusions drawn from this thesis and outlines potential directions for future research.

Keywords: Electrophoresis; Diffusiophoresis; Electroosmosis; Hydrophobic surface; Soft particle; Ion steric interaction; Electrostatic correlations; Dielectric polarization; Numerical simulation; Control volume method; QUICK scheme; Poisson-Fermi equation; Nernst-Planck equations; Navier-Stokes equations; Simplified models; Thin layer analysis.