

Abstract

This thesis presents a detailed numerical investigation supported by theoretical analysis on the electrokinetic transport of multivalent electrolytes in charged nanopores and nanochannels, subjected to three external driving mechanisms namely, an imposed electric field, a pressure gradient, and a concentration gradient. Moving beyond the classical mean-field based Poisson-Nernst-Planck (PNP) framework, a modified electrokinetic model, referred to as the MNPC (Modified Nernst-Planck with Correlations) model, is developed by incorporating ion-ion electrostatic correlations, steric interactions of finite-sized ions, and concentration-dependent medium viscosity and ion diffusivity. The electrostatic correlations are modeled through a fourth-order modified Poisson equation, the steric interactions are incorporated via the Boublik-Mansoori-Carnahan-Starling-Leland (BMCSL) equation of state, and the viscosity variation is described by the Batchelor-Green equation. The analysis also incorporates hydrodynamic slippage along hydrophobic channel walls and the lateral mobility of physisorbed surface charges, which significantly modify the slip-velocity condition and the resulting electrokinetic transport. The complete set of nonlinear governing equations is solved numerically using finite volume method on a nonuniform staggered grid. Additionally, simplified models, semi-analytical, and analytical solutions are derived for limiting cases such as, thin Debye layer or a low surface potential. This thesis provides valuable insights on the electrokinetics involving multivalent electrolytes in nanofluidic systems, leading to potential applications in biomedical technologies, energy harvesting, and water purification.

Chapter 1 introduces the fundamental theory of electrokinetic transport phenomena, the governing equations, and their applications in nanofluidic systems. **Chapter 2** presents a numerical investigation on electroosmotic flow of multivalent electrolytes through a reservoir connected cylindrical nanopore using the MNPC model. The results demonstrate that strong ion-ion correlations lead to the formation of a condensed counterion layer adjacent to the charged surface, resulting in surface charge overscreening and a layered EDL structure with oscillatory charge density. Beyond a critical surface charge density, this overscreening of surface charge creates a charge inversion in the electric double layer to drive a reversal in the direction of electroosmotic flow. Smaller counterions are found to produce stronger correlation effects, leading to a more pronounced EOF reversal. The ion selectivity and conductance of the nanopore differ significantly from the predictions of the standard PNP model. It is further demonstrated that EOF reversal induced by multivalent electrolytes can be suppressed by mixing with a monovalent salt.

Chapter 3 presents a numerical and analytical investigation on electroosmotic flow of multivalent electrolytes in a hydrophobic slit channel with laterally mobile surface charges. A modified slip velocity condition is derived through the balance of hydrodynamic friction and the tangential electric force on the laterally mobile ions at the hydrophobic interface. A simplified model is developed under the thin Debye layer consideration so as to neglect the surface conduction, which are solved analytically under the Debye-Hückel linearization. The results show that the hydrodynamic friction and electromigration of adsorbed surface ions reduce the fluid slip at the charged hydrophobic interface. The hydrophobic slip suppresses the EOF reversal by providing additional momentum to the fluid, while the lateral mobility of the surface charge enhances the channel conductivity. Under a strong ion crowding, the condensed counterion layer exhibits diffuse characteristics, suppressing charge inversion in the EDL.

Chapter 4 reports a numerical analysis supplemented by analytical solutions for streaming potential and electrochemical energy conversion efficiency in a soft nanochannel, where the hydrophobic channel walls are coated with a diffuse polyelectrolyte layer (PEL) carrying a fixed volumetric charge. The ion partitioning effect arising from the lower dielectric permittivity of the PEL is incorporated through the Born energy difference of ions, and the laterally mobile surface charges modify the slip velocity condition. The results demonstrate that coating the channel walls with a PEL of lower dielectric constant significantly enhances the streaming current and energy conversion efficiency. Contrary to prior studies, the lateral mobility of the surface charge is found to enhance the streaming current and energy conversion efficiency under certain combinations of PEL charge density and surface charge polarity. The electromigration contribution of mobile surface ions to the streaming current, neglected in earlier studies, is shown to be non-negligible at thicker Debye layers.

In **Chapter 5**, a numerical and analytical investigation is made on pressure-driven flow of multivalent electrolytes in a hydrophobic nanochannel with laterally mobile surface charges, employing the full MNPC model. A simplified model is developed under the thin Debye layer approximation and closed-form analytical solutions are derived under the Debye-Hückel linearization for two distinct regimes of the scaled correlation length. The MNPC model accurately captures the experimentally observed reversal of the streaming current in multivalent electrolytes, which the standard PNP model fails to predict. Overlapping EDLs are found to suppress charge inversion, while hydrophobic slip suppresses the polarity inversion of the streaming current by enhancing the cationic streaming current near the wall. The lateral mobility of the surface charge amplifies the reversal by generating an additional negative surface current. The analytical solutions are shown to successfully capture the correlation-induced reversal in streaming current, constituting a novel and experimentally accessible benchmark.

Chapter 6 deals with the diffusioosmotic flow of multivalent electrolytes in a charged nanochannel, employing the MNPC model. Governing electrokinetic equations are solved in their full form using a finite-volume based numerical scheme. A simplified model is developed under the thin Debye layer approximation, which are solved analytically under the Debye-Hückel linearization for symmetric electrolytes. The results demonstrate that multivalent counterions significantly alter the diffusioosmosis, with strong ion-ion correlations leading to a reversal of the diffusioosmotic mobility. The chemiosmotic contribution is found to be significantly suppressed in multivalent electrolytes, with the electroosmotic contribution becoming dominant and driving the fluid opposite to the applied concentration gradient. Comparisons with the standard PNP model highlight the critical importance of incorporating short-range ion-ion correlations and steric effects for an accurate description of diffusioosmosis in non-dilute multivalent electrolytes.

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

Keywords: Electroosmotic flow; Streaming potential; Diffusioosmosis; Multivalent electrolytes; Electric double layer; Ion-ion correlations; Ion steric interactions; Hydrophobic slip; Mobile surface charge; Polyelectrolyte layer; Ion partitioning; Non-local electrostatics; BMCSL equation of state; Finite volume method; QUICK scheme; TVD scheme; Simplified models; Analytical solutions.