

ABSTRACT

We address some fundamental considerations in the determination of streaming potential in the ionic transport through micro- and nano-channels. Streaming potential refers to the induced electrical potential generated due to an advective transport of net charge in order to maintain an overall zero current. We first describe the general description of fluid flow with due consideration of the electrical body force. We then describe the structure of the electrical double layer in narrow confinements with impermeable walls, and those with cation selective walls. We also portray the electrokinetic energy conversion efficiency, which is the efficiency with which mechanical energy is converted into electrical energy through streaming potential, and the nature of the effective viscosity, which is the perceived viscosity for such flows.

We investigate the transport through nano-pores by first developing an analytical approach for the proper resolution of the electrical double layer with finite sized ions. We present the streaming potential and effective viscosity in various parametric limits of the pertinent physicochemical parameters. We then focus on the ion-selective transport through nano-pores. The consideration of finite sized ions, through a free-energy based continuum model and validated through molecular dynamics simulations, leads to non-trivial alteration in the condensation of counterions close to the wall which bears tremendous implication of the pressure driven transport in nano-pores in the presence of streaming potential. We then account for the influence of wall-ion and ion-ion non-electrostatic interactions apart from the electrostatic (Coulombic) interactions towards estimating streaming potential and energy conversion efficiencies, which are consistent with existing experimental findings.

We then discuss the influence of the fluid rheology towards altering the velocity profile and streaming potential in a non-trivially coupled manner. Apart from this, we investigate the influence of solution rheology and ionic packing, especially in the region near the wall, to estimate the variation of ionic conductivity of the fluid which is consistent with the classical empirical estimates of it.

We next consider the impact of the solvent dipole orientation in regions of high electric fields near the region close to the wall towards altering streaming potential. Apart from affecting the structure of the electrical double layer, the spatial alteration in the relative permittivity and presence of dielectric friction are shown to dramatically alter the calculations of streaming potential in narrow confinements. We also assess the impact of solvent polarization and finite ionic size towards determining the structure of the electrical double

layer, current response and impedance of a system with an aqueous electrolyte in between two cation selective surfaces, thereby highlighting the fundamental physics underlying devices such as electrodialysis, deionization etc.

The analytical findings in this Thesis may prove important for benchmarking numerical solutions involving transport in various electrokinetic scenarios. The results and conclusions from the Thesis are of tremendous importance for better understanding of membrane processes, better interpretation of streaming potential data, designing better electrokinetic conversion devices, mass-flow controllers and so on.

Keywords: electrokinetics, electrical double layer, streaming potential, ion-selective channel, steric effects, non-electrostatic effects, Yukawa potential, solvent polarization, cation selective electrode