

## ABSTRACT

The demands of clinical, environmental, and pharmaceutical applications have long driven the advancement of analytical techniques towards improved limits of detection (LOD), greater specificity, and decreased analysis time. Despite these efforts, low analyte concentration, limited sample volume, and the complexity of matrices still present major challenges and motivate the development of more advanced sample preparation. Lab-on-a-chip (LOC) devices integrate micro-to nanoscale fluidic structures with electrodes or chemically-modified surfaces to confer several distinct advantages including efficient handling of small volumes, rapid analysis, and access to surface-driven physical phenomena. In this context, electrokinetic forces are ideal for performing fluidic operations and for manipulating charged species and/or biological objects such as DNA, proteins, and cells.

Ion concentration polarization (ICP) is an electrokinetic phenomenon brought about by selective charge transport, such as occurs in a nanofluidic channel that links two microfluidic compartments. This asymmetric process results in the accumulation of charged species in one compartment (ion enrichment) and ion depletion in the other. The key feature of this process is that charge transport is selective, for example only cations are able to carry charge across the pore. An ion depletion zone (IDZ) develops as cations are removed *via* the pore, and the migration of anions, away from this end of the pore is enhanced by the locally high electric field strength (due to decreased ionic conductivity). At the other end of the pore, cations accumulate and anions migrate inward, creating an ion enrichment zone (IEZ). A key feature of any ICP device is the current due to selective charge transport, which is directly proportional to the rate of IDZ and IEZ growth.

Despite significant recent advances in the field, however, several critical aspects like ion concentration polarization in a straight nanochannel with varying surface charge and ion concentration polarization of electrorheological and magnetorheological fluids remain unexplored which are the central considerations of this dissertation. The dissertation commences by investigating ion concentration polarization within a nanochannel, where the surface charge is varied along the length of the channel. By considering several surface patches with differing charge densities across predetermined axial spans, it is demonstrated how these effects can be utilized to create selectively ion-enriched and ion-depleted regions. This phenomenon is ascribed to the establishment of an axial concentration gradient, which arises from ionic advection resulting from the synergistic effects of an externally applied electric field and an induced back-pressure gradient along the channel axis, as well as electro-migration influenced by both the applied and induced electrostatic fields.

The next part of the dissertation deals with rheology of the fluid medium undergoing ion concentration polarization. A look is taken at electrorheological and magnetorheological fluids. This study highlights the distinctive function of electrorheological or magnetorheological fluids in facilitating the selective enrichment and depletion of charged species within microfluidic channels of varying areas. The phenomenon reported is fundamentally distinct from other nonlinear electrokinetic effects previously documented, as the dependence of flow rheology on the electric field or magnetic field is the central mechanism orchestrating the observed nonlinear ion transport.