

Project Report (Period: 2017 – 2018)

Objectives: This proposal concerns with the development of a multiscale computational approach to unravel the fundamental mechanisms of wettability alteration and dynamics of imbibition of brine solutions in combination with surfactants. Our ideas was to use atomistic simulations to study the organization of water, oil and salt molecules near chemically realistic models of rock surfaces, and use the results to parametrize the surface-component interactions for coarse-grained representations of the problem. Longer term, we envisioned using such coarse-grained representations to study kinetics of imbibition which are inaccessible to the length and time scales of atomistic simulations.

In the previous reporting period, we were primarily concerned with the development of the multiscale simulation approach for multicomponent systems containing surfactants, polymers etc. For this purpose, we developed a coarse-grained approach which relies on coarse-graining only the intermolecular interactions. Such interactions were parametrized by a comparison of the long-range structural characteristics of the multicomponent system with the coarse-grained simulations. The coarse-grained simulation approach is then used to effect simulations of long length and time scales which can capture the morphological characteristics of the system. Subsequently, the finer scale details are reintroduced into the morphologies so generated and are followed by a shorter time scale simulation. To test the efficacy of the above methodology, we implemented the above approach on a simpler system of block copolymer solvated with salt. As a consequence of microphase separation, such systems display morphological characteristics at nanoscale. We implemented our above methodology to such a system to identify the differences in the ion coordination behavior arising from the nanoscale separation. In addition, we used such ideas to identify the impact of microphase separation on polymer dynamical characteristics.

In the present reporting period, we embarked on a few different problems relating to the transport of water and salt in charged polymeric systems. Such investigations were motivated by experimental observations which have demonstrated that the transport properties of salt ions and water in in such systems exhibit an

intriguing dependence on salt concentration that is opposite to that seen in electrolyte solutions. Further, insights gained in such contexts were expected to influence the thinking in the context of water and salt transport in confinement and pore geometries.

Motivated by the above experimental results, we studied, using atomistic simulations, the dynamics of water and a variety of salt ions in polymer electrolytes. We found a reversal in the salt concentration dependence of the mobilities of Na⁺, Cl⁻ ions salt ions and water molecules when compared with aqueous solutions. Our results show that diffusion of salt ions and water in charged polymer membranes are in general influenced by their association with polymer charge groups and ion pairing effects. Divalent ions were more strongly coupled with the polymeric ionic groups compared to monovalent salt ions, and exhibited diffusivity trends which are distinct relative to monovalent salts. Further, we demonstrated that the mobility of water molecules were influenced by coordination of water with polymer charge groups and their ion pairing tendencies, and also exhibited distinct trends in monovalent and divalent salt solutions.

The above results shed light on some of the phenomena which may arise in the context of water and salt ion transport in charged confinements (such as may arise in rock geometries). To provide a more direct characterization of the influence of pore size on such a phenomena, we have now embarked on an effort in which the polymer membranes are construed to contain ordered pores of specified sizes. Such morphologies typically arise in block copolymer membranes. Using such a construct, we are investigating the pressure driven flow of water and salt ions.