Ion Dehydration Under Operating Conditions for Brine Treatment

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High-salinity brine treatment is critical to increase water supplies and minimize waste discharge. Membrane-based desalination processes such as reverse osmosis and nanofiltration are being increasingly considered for brine treatment due to their high energy efficiency compared to thermal processes. However, brine treatment exposes membranes to extremely high pressures and salinities that alter membrane transport properties, impairing the water-salt selectivity and water productivity of a given membrane. The underlying mechanisms by which pressure and salinity affect the rejection of ions have not been determined. Specifically, ion dehydration energies have been correlated with ion rejection as larger penalties to strip waters from the hydration shell correspond to higher ion rejection. We study ion dehydration at the operating salinity and pressure for brine treatment using atomistic molecular simulations of ions in solution and ions within polymeric membranes. We use simulations biased in the coordination number to estimate free energies as a function of dehydration for monovalent and divalent ions. Additionally, we characterize the structure of hydration shells of varying size in bulk water and in membrane voids, since moving between membrane voids will require stripping and rearranging the hydration shell. We compare dehydration energies to experimentally-determined energy barriers to membrane transport to determine whether ion dehydration is the primary mechanism governing ion rejection in these polymeric membranes. We study trends in dehydration energies and structure in high salinity and pressure environments in order to better understand the necessary rearrangements for rejection in brine treatment membranes.