Dielectric spectroscopy of water and ions in clay interlayer nanopores from experiments and molecular dynamics simulation

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Fluids exhibit distinct properties when confined in narrow spaces. In the case of liquid water, this confinement effect is most significant in pores narrower than 2 nm. Confinement alters the hydrogen bonding network of liquid water, leading to changes in thermodynamic properties as well as long-timescale dynamics. Confinement likely also has significant effects on the properties of solutes, as the alteration of the static dielectric constant directly alters the enthalpies of ion hydration. Presently, however, the chemical effects of confinement are poorly understood.

One potential useful method for studying these confinement effects is provided by dielectric relaxation spectroscopy (DRS). DRS probes the frequency-dependent polarizability and conductivity of a medium in response to an oscillating electric field. In hydrated clays, the dielectric response reflects the collective relaxation of water dipoles and counterion currents. DRS is emerging as a powerful tool for probing water content and water-surface interactions in porous media. To the best of our knowledge, however, only two previous studies have reported DRS spectra for water in clay interlayer nanopores, and those results were note interpreted using molecular simulations.

Here, we reported DRS complemented by molecular dynamics (MD) simulation for synthetic swelling clays differing in structural charge as a function of hydration state, including one- and two-layer hydrates. The DRS data show that the main dielectric relaxation mode of water is strongly slowed in confinement by a factor of ~30. In addition, two further dielectric relaxation modes are observed. The MD simulations reproduce the main features of the experimental DRS data and provide support for our interpretations of the interlayer water species of different mobility.