Effect of mineral confinement on water dielectric response in concentrated electrolyte solutions

PIOTR ZARZYCKI[1], CHRISTOPHER A. COLLA[1], MARZENA PRUS[2], BENJAMIN GILBERT[1]

[1]Energy Geosciences Division, Lawrence Berkeley National Laboratory, Berkeley, California, United States

[2]Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

Dielectric relaxation spectroscopy is a unique probe of subtle solvent relaxation phenomena and behavior of water in various states of interactions [1,2]. However, spectra interpretation remains problematic [3,4].

Here, we show how molecular modeling can help to unambiguously decompose spectra into individual relaxation modes and relate them to the underlying physical processes of water in concentrated electrolyte solutions (e.g., brines). By combining molecular modeling and experimental methods, we can explain the effect of crowding and mineral confinement on dielectric, and conductive properties of aqueous solutions. Here, we present the results obtained using classical and first-principles molecular dynamics, dielectric and infrared spectroscopy of a series of chlorides solutions. To test mineral confinement we chose a few swelling and non-swelling clays. We conclude that the water dielectric response is governed by the interplay between solvation and hydrogen-bond network dynamics.

Our results are relevant for understanding the properties of high-concentration aqueous solutions that are common in energy-relevant Earth, atmospheric and technological systems — ranging from saturated solutions at the onset of mineral nucleation to saline waters in geological formations.

[1] Buchner, R.; Hefter, G. *Phys. Chem. Chem. Phys.* **2009**, *11*, 8984–16.

[2] Kaatze, U.; Behrends, R.; Pottel, R. *J. Non-Cryst. Solids* **2002**, *305* (1-3), 19–28.

[3] Kremer, F. and A. Schönhals Broadband Dielectric Spectroscopy. **2003**, Berlin, Springer.

[4] Raicu, V. and Y. Feldman Dielectric Relaxation in Biological Systems. **2015** Oxford, Oxford University Press.