Contribution ID: **702** Type: **Oral Presentation**

Ion Pairing of Ca2+, Zn2+, and La3+ with Acetate is Enhanced in Nanopores

Wednesday 21 May 2025 09:50 (15 minutes)

Nanoscale confined systems are common in the environment and in many technological innovations. Recent studies have shown that the fundamental properties and reactivity of bulk water or unconfined surfaces change under nanoscale confinement. These confinement-imposed changes, in turn, influence several nanoscale processes. Understanding nanoscale processes within confined systems is important for predicting the fate and transport of chemical species, water treatment by nano-filtration, and the fixation of contaminants in porous materials. In this study, we investigated the impact of nanoscale confinement on the ion pairing involving Ca^{2+}, Zn^{2+}, and La^{3+} with CH_3COO^- anions. By modeling the Raman spectra of bulk and confined solutions, we quantified the complexed and uncomplexed acetate species in aqueous solutions and then in the same solutions confined within mesoporous silica with 4 nm cylindrical pores. From these values, we estimated the binding constants and standard Gibbs free energy of ion formation in solution versus in nanopores. The equilibrium constants increased by 0.09, 1.70, and 2.5 units for Ca^{2+}–, Zn^{2+}–, and La^{3+}–CH_3COO^-, respectively, when compared to analogous constants measured for bulk solutions. Hence, ion pair formation is more favorable in nanopores than in bulk aqueous solutions. Through density functional theory (DFT) calculations, we predicted the stabilization of ion pairs in confined and aqueous environments. In agreement with the experimental findings, the DFT-calculated thermodynamic values for the free energy of formation predict the stabilization of contact ion pairs in confined systems compared to the bulk aqueous environment. These findings have broad implications on the fate and transport of chemical species in soils and other terrestrial environments and can improve the predictive geochemical modeling of cation-anion complexes in confined systems.

Acknowledgement: SNL is managed and operated by NTESS under DOE NNSA contract DE-NA0003525.

Country

United States

Acceptance of the Terms & Conditions

Click here to agree

Student Awards

Water & Porous Media Focused Abstracts

This abstract is related to Water

References

Authors: FASHINA, Bidemi (Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico); BALDO, Anthony (Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico); WATTS, Heath (Department of Earth, Environmental & Resource Sciences, University of Texas at El Paso, El Paso, Texas); LEUNG, Kevin (Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico); KUBICKI, James (Department of Earth, Environmental & Resource Sciences, University of Texas at El Paso, El Paso, Texas); ILGEN, Anastasia (Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico)

Presenter: FASHINA, Bidemi (Geochemistry Department, Sandia National Laboratories, Albuquerque, New Mexico)

Session Classification: MS17

Track Classification: (MS17) Complex fluid and Fluid-Solid-Thermal coupled process in porous media: Modeling and Experiment