

Background & Objective

• The molecular scale structure and dynamics of water and dissolved aqueous species in bulk solutions, at interfaces, and in nano-scale pore spaces of various materials play a critically determinative role in the performance and quality of water purification and desalination systems, and constitutes one of the **Grand Challenges of the WaterCAMPWS**.

• **The objective of our research** is to combine several experimental spectroscopic and computational molecular dynamics (MD) techniques to advance the fundamental understanding of the interaction of aqueous solutions with hydrated inorganic and organic materials, individual components and integrated membrane systems: adsorption and binding of molecules on surfaces; energetics of adsorption and transport of water, ions, and organic molecules through material systems.

• We have extensive experience in MD modeling and experimental characterization of these materials (Kirkpatrick et al, 1999, 2005; Kalinichev et al., 2001, 2007; Kalinichev and Kirkpatrick, 2002, 2007).

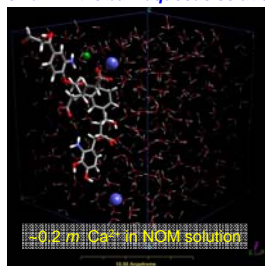
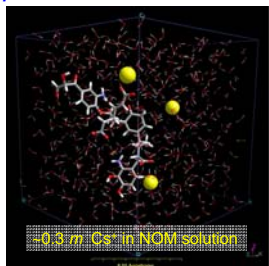
• **The combination of MD simulations with NMR spectroscopy is especially important** here, because NMR is element-specific; can readily explore water-solid systems *in situ* and over a wide range of hydration states, temperatures and pressures; and is the only simultaneous probe of molecular scale structure and the relatively low-frequency dynamics often relevant to water-solid systems.

Results for 2006 and Implications

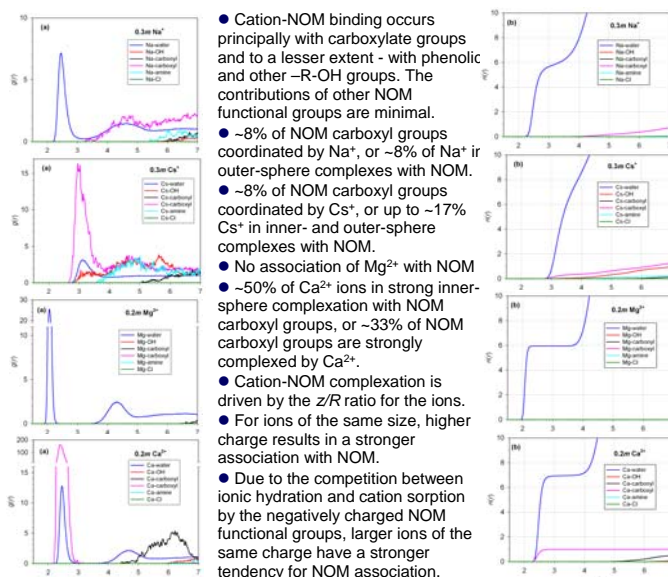
• MD simulations of the interaction of natural organic matter (NOM) with dissolved monovalent (Na^+ , Cs^+) and divalent (Mg^{2+} , Ca^{2+}) cations show that Na^+ forms only outer-sphere complexes with NOM, much weaker than Cs^+ . Mg^{2+} interacts little with NOM due to its strongly held hydration shell, Ca^{2+} has the strongest association with NOM and forms inner-sphere complexes with NOM carboxylate groups.

Two Cs^+ ions (yellow balls) in outer-sphere coordination to the NOM molecule, and one remains in the bulk aqueous solution.

One Ca^{2+} ion (blue ball) in inner-sphere coordination to the NOM molecule; the other Ca^{2+} and the Cl^- ion (green ball) remain in the bulk aqueous solution.

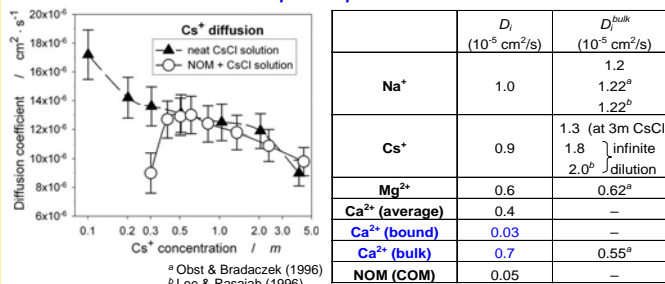


Atom-atom radial distribution functions (left) and running coordination numbers (right) quantifying the cation-NOM complexation in aqueous solutions



• The diffusional mobility of NOM-bound cations is ~20% (NOM- Na^+ outer-sphere complex) to ~2000% (NOM- Ca^{2+} inner-sphere complex) less than in neat aqueous solutions (without NOM).

Diffusion coefficients of aqueous species in NOM solutions



• MD simulation results confirm previous conclusions based on the NMR measurements (Xu et al., 2006) and show that Cs^+ is associated with the NOM principally as outer sphere complexes and that this interaction significantly reduces the Cs^+ diffusion coefficient.

• MD simulation results support the idea of supramolecular, Ca-mediated NOM aggregation as the mechanism of the formation of compact fouling layers on the surfaces of nanofiltration and RO membranes (e.g., Li & Elimelech, 2004).

• Preliminary MD computer simulations of a polyethersulfone (PES) membrane surface interacting with aqueous solutions containing NOM, and Na^+ , Ca^{2+} or Mg^{2+} ions (in collaboration with Won-Young Ahn, a student of Prof. M.Clark, CEE, UIUC) indicate that only the divalent ions are effectively bound to the carboxyl groups of NOM, thus lowering their diffusion coefficients and promoting cation-NOM supramolecular aggregation.

• No significant cation binding to the sulfonfyl groups of the membrane surface is observed, and the evidence that stronger NOM-surface interaction in the presence of divalent metal ions contributes to the membrane fouling still remains inconclusive.

• Larger-scale MD simulations are currently in progress and will help to clarify and quantify the possible role of cation facilitated adsorption and supramolecular aggregation on the membrane surfaces.

WaterCAMPWS Collaborations

• Our NMR and molecular modeling efforts heavily rely on the collaboration with other CAMPWS participants who are providing experimental atomistic characterization of the surfaces and substrates by other kinds of physical and chemical analysis, such as IR, SFG spectroscopy (Shen, Waychunas). New collaborations with Profs. M.Clark, B.Mariñas, and H.Nguyen (CEE, UIUC) are currently being established to work on the experimental characterization and molecular modeling of the interactions of organic molecules (NOM, DNA, viral capsid proteins) with inorganic and organic surfaces in aqueous salt solutions.

• Our group also has a long-standing collaboration with researchers at Sandia National Laboratories who are participants in the recently established Sandia Water Initiative (SWI), which has a mission parallel to the WaterCAMPWS.

Publications

• J.Wang, A.G.Kalinichev, R.J.Kirkpatrick (2006) Effects of substrate structure and composition on the structure, dynamics, and energetics of water at mineral surfaces. *Geochim.Cosmochim.Acta*, **70**, 562-582.

• G.V.Bondarenko, Y.E.Gorbaty, A.V.Okhulkov, A.G. Kalinichev (2006) Structure and hydrogen bonding in liquid and supercritical aqueous NaCl solutions: A comprehensive experimental and computational study. *J.Phys.Chem.A*, **110**, 4042-4052.

• X.Xu, R.J.Kirkpatrick (2006) NaCl interaction with interfacially polymerized polyamide films of reverse osmosis membranes: A solid-state ²³Na NMR study. *J.Membrane Science*, **280**, 226-233.

• X.Xu, A.G.Kalinichev, R.J.Kirkpatrick (2006) ¹³³Cs and ³⁵Cl NMR spectroscopy and MD modeling of Cs^+ and Cl^- complexation with natural organic matter. *Geochim.Cosmochim.Acta*, **70**, 4319-4331.

• A.G.Kalinichev, R.J.Kirkpatrick (2007) Molecular dynamics modeling of cationic complexation with natural organic matter, *Eur. J. Soil Sci.*, **58**, in press.

• I.S.Ufimtsev, A.G.Kalinichev, T.J.Martinez, R.J.Kirkpatrick (2007) A charged ring model for classical OH(aq) simulations. *J.Amer.Chem.Soc.*, (submitted).

Human Resource Development & Knowledge Transfer

• A.G.Kalinichev is a Research Mentor in the WaterCAMPWS REU and SRQP programs and presented a seminar "The anatomy of a research paper" for the REU students in the Spring and Summer 2006 semesters at UIUC.

• A.G.Kalinichev has developed a new course GEOL593MM "Molecular modeling of water and interfaces" (<http://online.engr.uiuc.edu/webcourses/geol593mm/>). The course was taught at UIUC during the Spring Semester 2005 for CAMPWS graduate students, and is now offered on-line as one of the engineering web-based courses. An extended version of this course is currently (Spring 2006, 2007) taught as GEOL593J2 and includes, in addition to lectures and discussions, a series of hands-on computer exercises on molecular modeling of aqueous interfaces.

• A.G.Kalinichev was an invited instructor at the "Workshop on Molecular Modeling Fundamentals in Water Treatment Applications" - a technology-transfer workshop organized in April 2006 by AquaMem Scientific Consultants for specialists in water purification industry (<http://www.desertwildlands.com/AquaMem/AquaMem/>).