# Molecular-scale thermodynamics of aqueous NaCl to hydrothermal conditions

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Heat and mass transfer by hydrothermal convection at mid-ocean ridges, formation of magmatic-hydrothermal ore deposits and other geochemical processes involve high-temperature, aqueous, saline fluids at low to intermediate densities as key agent. However, quantitative modelling of chemical reactions in these fluids is severely hampered by the lack of a proper thermodynamic model. Conventional models such as HKF do not apply at these conditions because they fail to incorporate the effect of solvent compressibility on solute thermodynamics.

A potential way out is the study of such system via molecular simulation in order to understand the molecular-scale origin of macroscopic thermodynamic properties. A strict framework for this approach has been provided by Chialvo and co-workers [1] by analysing the molecular-scale structural changes that solutes induce in the solvent. This formalism has, however, never been tested for its feasibility to quantitatively explain solute thermodynamics from molecular simulations over wide ranges of states.

Here I present the result from classical molecular dynamics simulations of systems of either 16384 SPCE water molecules or 16382 SPCE plus 1 NaCl over a wide range of temperatures (T = 373 K to 873 K) and densities ($\rho = 0.05$ to $1$ g cm$^{-3}$). On the technical side, the influence of cut-off schemes (0.9 to 3 nm) for the short-range potentials and the long-range electrostatic part (simulated via the Particle Mesh Ewald approach) as well as simulation duration (up to 50 ns) to obtain sufficiently accurate statistics in pair correlation functions is discussed. Trends of for the length scale, over which the 'solvation number', $N_{ex}$, develops as a function of T and $\rho$, can be related to the solvent's compressibility. $N_{ex}$ can directly be related to the generalized Krichesvkii parameter, which is the key to solute thermodynamics in the near- and supercritical regions. Finally, the simulated trends in $N_{ex}$ are discussed on the basis of the molecular-scale fluid structure and possible implications for the derivation of novel thermodynamic models for high-temperature, low-density fluids are discussed.

[1] Chialvo et al. (1999) J. Chem. Phys. 110, 1075-1086.

# Permeability reduction, calcium and sulfur isotope fractionation during uranium bioremediation

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Subsurface immobilization of aqueous uranium via electron donor amended bioreduction has been successfully demonstrated at the Integrated Field Scale Subsurface Research Challenge (IFRC) site at Rifle, Colorado, USA [1]. During a 2009 field-scale stimulation experiment, hydrologic conductivity measurements were made in adjacent injection wells prior to, during and after electron donor amendment to monitor the effects of mineral precipitation on electron donor delivery. The pre-injection conductivity was 4 m/day in all wells. In well G-51 conductivity dropped four orders of magnitude to a post-amendment value of 0.0001 m/day while in well G-53, installed 2 m away from G-51, the post-amendment conductivity was 1 m/day. Samples collected for chemical and isotopic analysis in these wells present a unique opportunity to observe open versus closed system effects on the chemistry of biostimulation. In well G-51, acetate and bromide concentrations persisted for more than 100 days after injection was stopped, whereas both were undetectable immediately following the end of the injection in G-53. In G-51, after acetate addition ceased both sulfate and calcium concentrations dropped from 9 mM to 0 mM and from 6 mM to 1 mM, respectively. In well G-53 during the amendment sulfate concentrations varied between 11 mM and 6 mM and calcium between 7 mM and 5 mM, both returning to background values of 8 mM and 6 mM, respectively, after injection stop. The fractionation of sulfur isotopes has been shown to decrease significantly as sulfate becomes limited during electron donor addition at Rifle [2]. The samples collected for this study will provide an opportunity to observe the full range of fractionation effects for conditions ranging from abundant sulfate to fully sulfate limited. For calcium isotopes, preliminary data shows a shift of approximately 2‰ during calcite precipitation at Rifle. This effect is expected to be even more pronounced in the closed G-51 samples, and will be used to correlate fractionation with the mass balance of calcite precipitation.

[1] Anderson et al. (2003) Appl. Environ. Microbiol. 69, 5884–5891. [2] Druhan et al. (2008) Environ. Sci. Technol. 42, 7842–7849.