

Linking structural and thermodynamic properties of solutes in high-temperature fluids

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In geochemical modeling of hydrothermal fluids, solute standard state properties are most commonly represented using the landmark Helgeson-Kirkham-Flowers equation of state (HKF-EOS) [1]. However, the HKF-EOS becomes unreliable at PT conditions of low solvent (H_2O) density, and especially near the critical point of H_2O . This limitation stems primarily from treating the solvent as an incompressible dielectric medium, without explicitly accounting for the volumetric consequences of hydration [2].

In an effort to improve predictions of the standard state properties of solutes in compressible (including near critical) fluids, we conduct molecular simulations of electrolyte and non-electrolyte solvation at high temperatures. The aim of the simulations is two-fold: to characterize the structural environment of dissolved species, as well as to calculate the solvation free energies using λ -dynamics [3]. Thus, the simulations allow us to assess the thermodynamic properties of solutes as functions of the PT conditions, while also yielding insights into how these properties relate to the local density perturbations associated with solvation [4].

The hydration free energies of solutes vary systematically with solvent density. These trends can be linked to the temperature- and density-driven variation in the solute hydration shell [5], as well as the volumetric perturbations resulting from the density difference between the hydration shell versus the "bulk" solvent [4]. These results help to establish a basis for new correlations for solute thermodynamic properties in compressible, low-density fluids.

[1] Helgeson *et al* (1981) *Am. J. Sci.* **281**, 1249-1516. [2] Driesner (2013) *Rev. Mineral.* **76**, 5-33. [3] Kong & Brooks (1996) *J. Chem. Phys.* **105**, 2414-2423. [4] Chialvo *et al* (1999) *J. Chem. Phys.* **110**, 1075-1086. [5] Driesner & Cummings (1999) *J. Chem. Phys.* **111**, 5141-5149.