Molecular Modeling of Ion Solvation and Thermodynamics in Aqueous Solution at Extreme Temperature and Pressure

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The thermodynamics of electrolytes plays a key role in the design and optimization of systems ranging from refining and chemical processing to extreme deep-water oil and gas extraction. Current models have limited predictive capabilities as they rely on correlating data at moderate conditions. This limitation becomes acute when the predictions are sought at conditions very removed from conditions where model parameters were obtained, such as in extreme high temperature and pressure (HTHP) conditions of interest in describing mineral scaling and corrosion. Further, at HTHP conditions where dielectric screening is reduced, it becomes essential to acknowledge the molecular nature of the solvent and ion-solvent and ion-ion interactions. Achieving this within a consistent framework remains an outstanding challenge in both basic science and engineering. We are creating a meso-scale theory of electrolytes that draws upon molecular level insights from simulations at classical and quantum mechanical levels on the one hand and macroscopic experimental data on the other. A new statistical mechanics based model has been introduced to describe molecular aspects of ion solvation and ion-ion association. The statistical associating fluid theory (SAFT) is used to model solvent association and long-range effects are obtained using an integral equation method. Hydration shell structure with the new approach agrees well with molecular simulation results and the prediction for solution densities at HTHP shows good agreement with experimental data. We are working on refining the reference fluid for estimating packing around an ion to better describe ion-hydration with the new approach. Results from these studies will be presented. We will also discuss other extensions of the model to predict properties at HTHP conditions.