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Los Alamos
NATIONAL LABORATORY

# Salts in Hot Water: Developing a Scientific Basis for Supercritical Desalination and Strategic Metal Recovery

Katie Maerzke, PI

The w21_superdesal project is part of an LDRD-DR on supercritical desalination (20190057DR). The goal of the simulation work is to use atomistic simulations to understand at a molecular level the changes in hydrogen bonding and ion solvation that occur as we increase the temperature and/or pressure and change the density and ion concentration. Our simulation results will also aid in the interpretation of experimental data and guide the development of applied thermodynamic models for engineering design calculations.

New project member Richard Messerly led the first principles simulation work (in collaboration with Katie Maerzke). This work used the bulk of our allocation. He followed up on our previous work on CuCl hydration in high temperature water vapors by examining AgCl over a wider range of temperatures (and the same density range) using the nested Monte Carlo framework of Jadrich and Leiding (LANL T-1). Experimental estimates of the temperature and density dependence of the AgCl hydration numbers are inconclusive and possibly even contradictory. We find a monotonic temperature dependence, with the hydration number decreasing slightly with increasing temperature. In addition, our predicted hydration numbers steadily increase with increasing density. These temperature and density trends are in agreement with some of the experimental data sets. By incorporating bootstrap resampling and fitting the simulation results to the same empirical model used in the experimental data analysis, we are able to reduce uncertainties in our predictions. We find that a complexed water molecule around AgCl typically forms a distorted linear structure that is not as persistent as the nearly linear O-Cu-Cl structure found in our earlier work. The Ag-O bond is also slightly longer and weaker than the corresponding Cu-O bond. These differences are consistent with lower solubility for AgCl than CuCl in high-temperature water vapors. Consistent with experiment, our simulation results predict that the hydration numbers (and thus solubilities) for AgCl are lower than CuCl by approximately a factor of two under the same conditions.

Staff scientist Katie Maerzke (formerly T-1, currently XTD-IDA), the PI for this IC allocation, has performed classical Monte Carlo simulations using an in-house code called MCCCS-MN from her former PhD group. She has used this code to simulate phase equilibria, including the vapor-liquid coexistence curve for several water models as well as pressure-composition diagrams at two temperatures for different combinations of water and NaCl force fields. This work is to aid in the evaluation of force field accuracy under near supercritical conditions, in conjunction with the work of postdoc Lara Patel (performed under our previous allocation). This work has resulted in a publication to be submitted soon.

Graduate student Diego Gomez (Tulane University, mentor Lawrence Pratt) is an external collaborator on this LDRD-DR project. He has run some CP2K calculations at

LANL as part of his work on quasi-chemical theory. He was unable to get CP2K to compile at his university, but we have it compiled at LANL.

Publications:

R. A. Messerly, T. J. Yoon, R. B. Jadrich, R. P. Currier, and K. A. Maerzke "Elucidating the temperature and density dependence of silver chloride hydration numbers in high-temperature water vapor: A first principles molecular simulation study," *Chemical Geology*, **594**, 120766 (2022).

K. A. Maerzke, T. J. Yoon, R. P. Currier, "Monte Carlo simulations of NaCl-$H_2O$ mixtures: Comparison of classical force fields," in preparation for *J. Chem. Eng. Data*.

Conference presentations:

R. A. Messerly, T. J. Yoon, R. B. Jadrich, R. P. Currier, and K. A. Maerzke "Predicting silver chloride hydration numbers in high-temperature water vapor with machine learning and first-principles molecular simulations," Goldschmidt 2022, July 2022

Financial Impact:

The IC computer resources are supporting the theory/simulation work for an LDRD-DR. This includes 25% of a staff scientist (KAM), approximately 25% of another postdoc (TJY), and 10% of second postdoc/later 5% of a staff scientist (RAM). We also supported part of a graduate student at Tulane. All told, this is approximately 20% of the DR budget.