

Project ID: **54506**

Project Title: **Acid-Base Behavior in Hydrothermal Processing of Wastes**

Lead Principal Investigator:

Dr. Keith P. Johnston
Matthew van Winkle Regents Professorship in Chem. Eng.
Department of Chemical Engineering
University of Texas at Austin
26th and Speedway
Austin, Texas 78712--1062
Telephone: 512-471-4617
e-mail: kpj@che.utexas.edu

Co Principal Investigators:

Peter Rossky
Professor
Dept. Chemistry
University of Texas
Austin TX 78712

RESEARCH OBJECTIVE

A new technology, hydrothermal oxidation (also called supercritical water oxidation), is being developed to treat high level nuclear wastes. Nitrates are reduced to nitrogen; furthermore, phosphates, alumina sludge, and chromium are solubilized, and the sludge is reconstituted as fine oxide particles. A major obstacle to development of this technology has been a lack of scientific knowledge of chemistry in hydrothermal solution above 350 C, particularly acid-base behavior, and transport phenomena, which is needed to understand corrosion, metal-ion complexation, and salt precipitation and recovery. Our objective is to provide this knowledge with in-situ UV-vis spectroscopic measurements and fully molecular computer simulation.

On the theoretical side, we have focused on the study of the transport properties of aqueous ions in supercritical water. The motivation for these studies is two fold. First, although transport coefficients are fundamental to solution chemistry reaction rates, the behavior of such transport properties over wide ranges of density and temperature are not well established experimentally, particularly at the densities typically of interest (< 0.5 g/cc). Second, due to practical challenges, ionic association equilibria in SCW is typically accessed via measurements of conductivity followed by analysis through a theoretical model that incorporates ion pairing. The results of these analyses in the interesting low density region have yielded results for the limiting infinite dilution conductivity of alkali halides which are not consistent among labs. However, the most common result suggests a nearly constant ionic diffusion constant with decreasing density, which is further rather insensitive to temperature. This is in contrast to the typical behavior at higher densities, where there is agreement on a linear increase with decreasing density. Either this surprising behavior is a physical result of a balance of forces that is different at the lower densities, or the model used to extrapolate to infinite dilution, and to extract the association constants, is not accurate for these cases. Our goal is to determine independently via computer simulation what one should expect of these transport coefficients.

RESEARCH PROGRESS AND IMPLICATIONS

This report summarizes work after the third year of a 3-year project, which has been extended to include a fourth year. Many of the DOE wastes contain high concentrations of nitrates, and the equilibrium of these species is of interest in hydrothermal oxidation. To address this, UV-Vis spectroscopy was utilized to measure the decomposition of aqueous HNO₃ solutions above 300 °C, in some cases with added NaOH, H₂O₂, and/or NaNO₂, to form NO₂, HNO₂, NO, N₂O and oxygen. Optimization models have been developed to determine equilibrium constants from the spectra for dissociation, redox and disproportionation reactions involving nitric and nitrous acid, NO₂, NO, N₂O, NO₃⁻, and oxygen in supercritical at temperatures of 380°C and 400°C and at pressures of 276 to 414 bar. A constrained nonlinear programming (NLP) model of moderate size has been developed to estimate equilibrium constants and extinction coefficients. This model is optimized using an implementation of the generalized reduced gradient (GRG) algorithm. Although it was only possible to measure the absorbance of two of the twelve species by UV-Vis spectroscopy, six equilibrium constants and two extinction coefficients could be optimized. Significant improvements of these values are obtained

with a Jackknife Statistical implementation. Linear extrapolation of the log K versus density plots to zero density results in values which are very close to independent gas-phase values.

On the theoretical side, we have completed a very important simulation study of ion transport in water under extreme conditions and also initiated a highly novel investigation of hydrolysis reactions in SCW.

The motivation for the study of transport is based on the facts that 1) transport coefficients are fundamental to solution reaction rates, but the behavior of such transport properties over wide ranges of density and temperature are not well understood, and 2) ionic association equilibria under extreme conditions in SCW is typically accessed indirectly via interpretations of conductivity measurements through ion pairing models. Although there is some variation, results suggest a linear increase in ionic diffusion constant with decreasing density at higher densities, turning over to a plateau in the most interesting region of SCW densities. We have for the first time developed a complete physical explanation of the conductivity data, using computer simulation to analyze the transport coefficients. We have demonstrated that the plateau in the data is reproduced computationally and is associated with an increasing imbalance between water-water forces and the stronger solvent-solute forces acting on the solvent in the ionic hydration shell. This shell remains intact throughout the measured density region but exerts an increasing friction on the ion with decreasing density. At densities below those measured experimentally to date, the hydration shell does begin to degrade, in accord with our earlier interpretation as solvent adsorption, and the transport rate is predicted to resume an increase. Of perhaps most importance, the calculated results have led to a suggested manner in which to analyze purely experimental data in order to best elucidate the physical content. The results of this work are currently being prepared for publication.

PLANNED ACTIVITIES

We plan to study carbonate/bicarbonate/ carbonic acid equilibria in supercritical water as these species play a central role in hydrothermal oxidation. Chemical equilibria for these species will be monitored with novel pH indicators developed in our lab. The behavior of the equilibrium constants will be analyzed in terms of our previous studies of ion solvation in supercritical water.

We have initiated modeling and simulation of aqueous hydrolysis reactions in SCW due to their ubiquitous presence in SCW oxidation reactions. Under ambient aqueous conditions, the first step of an S_N1 reaction occurs by initial separation into an *ion* pair, with typical further reaction of a carbocation. However, the relative stability of the ion pair and the alternative reaction path involving separation into a *neutral* radical pair depends very directly on the solvent polarity. Even in ambient water, it has been demonstrated that a free energy barrier to separation arises due to the transition from a covalent to a separated ionic state. As is widely appreciated in other contexts, SCW offers *tunable* polarity. Thus, one should expect not only that reaction barriers depend on solvent density, but also that the underlying mechanism itself will vary. In order to understand this variation in mechanism in detail, we are in the process of investigating the active mechanism and free energy associated with dissociation of the model reactant, *t*-butyl chloride. The details of dissociation of this model system have been studied theoretically in considerable detail in ambient water in the past, so there is an excellent base of models from which to start.

INFORMATION ACCESS

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