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Acid-Base Behavior in Hydrothermal Processing of Wastes

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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.

A major objective of the experimental studies has been to determine the equilibria for Cr(VI) up to 420° C as this is a key species to be removed from nuclear wastes. A wide range of concentrations of KOH and perchloric acid were utilized to manipulate the acid-base equilibria and to understand the effects of ion solvation and ion pairing. The second system is the equilibria between nitric acid, nitrous acid, nitrogen dioxide, nitrite and nitrate ions and oxygen. For both of these systems, chemical equilibria has not been measured previously in hydrothermal solution at these temperatures.

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 second year of a 3-year project. Equilibria of nitric acid in supercritical water (SCW) were studied by using UV-Vis spectroscopy. It was found that nitric acid reversibly decomposes in supercritical water (380 - 400° C) to form NO_2, nitrous acid, nitrite ion and oxygen. The extent of decomposition increases with temperature. The reaction occurs to an immeasurable degree in pure sodium nitrate solution which demonstrates that the acidic medium is necessary for decomposition. At constant temperature, the contribution of nitrogen in the +3 oxidation state versus that in the +4 oxidation state (nitrogen dioxide) increases with increasing pressure (density).

To model transport coefficients, we have taken two different approaches. In the first (see publication list), we have used a model of solvent induced friction to infer ionic transport. The model assumes

that the viscosity of the solvent is different in the first solvation shell of the ion compared to the bulk, a division of the solvent that we have earlier demonstrated captures the main elements of solvation thermodynamics. Simulation of solvent rotational dynamics is used as a measure of the excess viscosity in the region near the ion, from which one can infer a radial viscosity profile. We then use an approximate relation between the viscosity profile and the ionic friction to determine conductivity. According to this treatment, when phrased in conventional terms, the effective Stokes radius of ions tends to be enhanced at low solvent densities so that a simple application of Stokes law with physical ionic radii and bulk viscosity is a gross overestimate of the contribution to conductivity. However, the decrease in solvent viscosity with decreasing density is such that the limiting equivalent conductivity is found to increase approximately linearly from subcritical through supercritical conditions, with no apparent plateau in low density SCW.

In order to test this result, we have also pursued a full dynamical simulation of ion diffusion coefficients in SCW. These simulations are computationally demanding, since relatively long runs are required to obtain statistically accurate results. Although these studies are not complete, the results for NaCl at a series of SCW densities (0.087g/cc - 0.5g/cc; 673K) show a remarkable feature. In all cases, the velocity correlation function, whose integral determines the diffusion rate, exhibits two time regimes. For very early times (< 0.5 ps), the frictional decay of the velocity is rapid and nearly constant with density for a given ion. However, there is a relatively slowly decaying tail in the velocity that is increasingly more distinct with decreasing density. This contribution would lead to increasing diffusion rates with decreasing density.

Planned Activities

The following planned activities will be performed in the last year. For the nitrogen oxide chemical equilibria, we are developing sophisticated optimization techniques to determine quantitative equilibrium constants for this complex reaction network. We also plan to study other equilibrium reactions with novel in-situ pH indicators developed in our laboratory for supercritical water.

On the theory side, we are now working on obtaining statistically precise results for the decays in the velocity correlation functions so that the behavior of conductivity with solvent density can be pinned down. It is also of considerable interest to determine the physical origin of the time scale that characterizes the slowest decay. One candidate is the dynamical time scale for sampling over alternative solvation structures in the solvated ion cluster, and we will also be pursuing an analysis of this hypothesis.

Other Access To Information

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