

Informal Progress Report: Acid-Base Behavior in Hydrothermal Processing of Wastes DE-FG07-96ER14687

A major obstacle to the development of hydrothermal technology for treating DOE wastes has been a lack of scientific knowledge of solution chemistry, thermodynamics and transport phenomena. Our progress over the last year is highlighted in the following four abstracts from manuscripts which have been submitted to journals. We also have made considerable progress on a spectroscopic study of the acid-base equilibria of Cr(VI).

Experimental studies

We have utilized novel spectroscopic indicators to study acid-base equilibria up to 380°C. Until now, very few systems have been studied at such high temperatures, although this information is vital for hydrothermal processing of wastes.

1. Boric Acid Equilibria in Near-Critical and Supercritical Water

The pH values of aqueous solutions of boric acid and KOH were measured with the optical indicator 2-naphthol at temperatures from 300 to 380°C. The equilibrium constant K_b^{-1} for the reaction $B(OH)_3 + OH^- = B(OH)_4^-$ was determined from the pH measurements and correlated with a modified Born model. The titration curve for the addition of HCl to sodium borate exhibits strong acid-strong base behavior even at 350°C and 24.1 MPa. At these conditions, aqueous solutions of sodium borate buffer the pH at 9.6 ± 0.25 .
submitted to Ind. Eng. Chem. Res.

2. Neutralization of Acids and Bases in Subcritical and Supercritical Water: Acetic Acid and HCl

Acid-base titrations for the KOH-acetic acid or NH_3 -acetic acid systems were monitored with the optical indicator 2-naphthoic acid at 350°C and 34 MPa, and those for the HCl- Cl^- system with acridine at 380 °C and up to 34 MPa (5000 psia). KOH remains a much stronger base than NH_4OH at high temperature. From 298 K to the critical temperature of water, the dissociation constant for HCl decreases by 13 orders of magnitude, and thus, the basicity of Cl^- becomes significant. Consequently, the addition of NaCl to HCl raises the pH. The pH titration curves may be predicted with reasonable accuracy from the relevant equilibrium constants and Pitzer's formulation of the Debye-Hückel equation for the activity coefficients.

submitted to J. Supercritical Fluids

Theoretical studies

To understand solvation in supercritical water, computer simulation studies of solution structure and solvation free energies of ions are being carried out. The simulation results

have been used to develop a thermodynamic model of ion solvation which may be applied to treat reaction equilibria and phase equilibria for process design and development. In addition, simulations are being used to understand the how hydration in highly compressible supercritical solutions influences ion transport.

1. Ion Solvation in Supercritical Water Based on an Adsorption Analogy

The solvation structure and free energy for Li^+ , Na^+ , K^+ , F^- , Cl^- , Be^{2+} , Mg^{2+} , and Ca^{2+} in supercritical aqueous solutions are described by a dielectric concentric shell model incorporating solvent adsorption analogous to a Langmuir model. The ratio of solvent bulk density to the local density in the first coordination shell of alkali and halide ions obtained from molecular dynamics simulation is shown to be linear in bulk density at supercritical temperatures, justifying the model. The model utilizes two parameters: a maximum local density, which is found to be insensitive to temperature and correlated with the surface field, and a desorption constant, which we find may be approximated as zero in the free energy calculations. In comparison to the Born model, free energies of solvation predicted by the concentric shell model show far better agreement with values from full molecular simulation and with those from a compressible continuum model.

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2. Aqueous Ion Transport Properties and Water Reorientation Dynamics from Ambient to Supercritical Conditions

Ion transport properties including the friction coefficient, Walden product (product of conductivity and viscosity), and the limiting equivalent conductance are predicted in water at elevated temperatures using a semi-continuum model. Molecular dynamics computer simulation is used to determine water rotational reorientation times in the first coordination shell compared to the bulk, and the results are incorporated into a hydrodynamic expression for the ionic friction coefficient. Along the coexistence curve of water, the effective Stokes-Einstein radius implied by the model is relatively constant, but it increases in supercritical water where the motion of the first shell water molecules is coupled more closely to that of the ion. The limiting equivalent conductance is found to increase approximately linearly with decreasing solvent density in the supercritical regime, in qualitative accord with the experimental extrapolations of Quist and Marshall and in contrast to the plateau with decreasing density inferred from much more recent experiments by Zimmerman *et al.*

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