FINAL REPORT

Title: Development of an Experimental Data Base and Theories for Prediction of Thermodynamic Properties of Aqueous Electrolytes and Nonelectrolytes of Geochemical Significance at Supercritical Temperatures and Pressures.
Register #: ER14080
Core research area: Geosciences Research
Program Manager: Woodward, Nicholas
Institution: DELAWARE, UNIVERSITY OF
End Date:5/14/2005
Keywords: Aqueous geochemistry, Electrical Conductivity, Numerical simulation/modeling, Organic Geochemistry, Precipitation, Solubility, Speciation

Lead Investigator
Robert Wood
Email: rwood@udel.edu

OBJECTIVES: The objective of this research was to combine new experimental measurements on heat capacities, volumes, and association constants of key compounds with theoretical equations of state and with first principles quantum mechanical calculations to generate predictions of thermodynamic data. The resulting thermodynamic data allow quantitative models of geochemical processes at high temperatures and pressures.

Research funded by a DOE grant to Prof. Robert Wood at the University of Delaware involved the development of new theoretical equations of state for aqueous solutions of electrolytes and non-electrolytes, methods to estimate thermodynamic data not available from experiments, collection of data on model compounds through experiments and predictions of properties using *ab initio* quantum mechanics. During the last three and a half years, with support from our DOE grant, 16 papers have been accepted or published, and 3 more are in preparation. Results of this research have been reported in numerous invited and contributed presentations at national and international meetings. For this report, we will briefly comment on the highlights of the last 3 and a half years and give a complete list of papers published, accepted, or submitted during these years.

Association Constants by Conductance

Our use of conductance measurements to get equilibrium association constants for a variety of aqueous electrolytes at high temperature has been going very well. We have published the interpretation of our high concentration NaCl results as well as high concentration literature data on KCl (SHARYGIN et al., 2002). This work indicated that for most geochemical environments there is no need to invoke multi-ion clusters at concentrations up to 2 or 3 mole/kg because pair-wise association with mean spherical approximation activity coefficients fits the conductance data .

We have published the interpretation of our sodium acetate and sodium acetate/acetic acid mixture results (ZIMMERMAN and WOOD, 2002). This work measured complexing of sodium ion by acetate at temperatures to 470 K. These are the first results that we have obtained on the assocciation constants of alkali metals with organic anions.

Processing our aqueous Li_2SO_4 and K_2SO_4 results to get the first and second association constants for these salts has been delayed because we needed association constants from our new measurements on H_2SO_4, $NaHSO_4$, and Na_2SO_4 in our analysis of the earlier data. We have finished the analysis of the new data and the results have been accepted by the Journal of Physical Chemistry (HNEDKOVSKY et al., 2005). This paper reports the first and second association constants of H^+ with SO_4^{--}, Na^+ with SO_4^{--} as well as the association of H^+ with $NaSO_4^-$, and Na^+ with HSO_4^-. These results also determined the limiting equivalent conductance of the H^+, HSO_4^-, and SO_4^- ions, and extend our knowledge of the first association constants to high temperatures.

We are ready to submit our results on Li_2SO_4 and K_2SO_4 (BALASHOV et al., in preparation). There are no previous measurements of the second association constants for Li^+, and K^+ with SO_4^{--}. . These association constants are important in determining the activity of these salts at high temperatures and will enable a better understanding of high temperature sulfate brines.

Using our new apparatus (with a diamond shield to prevent corrosion of the sapphire insulator by acids) we have also made new measurements on HCl but these measurements are not yet interpreted.

We have completed measurements on magnesium chloride, magnesium acetate, calcium chloride, and calcium acetate in order to understand the complexing of organic ligands to these ions at high temperatures. The paper on the calcium measurements has been accepted (Mendez De Leo and Wood 2005)

Semi-empirical Equations of State

The utility of our previous model for predicting the thermodynamic properties of aqueous nonelectrolytes has been greatly increased by deriving parameters for predicting a number of compounds including ones of high polarity (alcohols, amides, acids, and amides) and/or large size (hexane and benzene) (PLYASUNOV et al., 2001).

In collaboration with Everett Shock and coworkers at Arizona State University we have used our recent experimental data to reparameterize the revised HKF model (SCHULTE et al., 2001). In collaboration with Everett Shock and Andrey Plyasunov at Arizona State University we have developed methods for predicting second cross viral coefficients for interactions involving water (PLYASUNOV et al., 2003). These predictions are needed in our new equation of state.

In collaboration with Jason Myers and Stanley Sandler we have developed an equation of state for electrolytes that has few adjustable parameters so it should be useful for engineering and geochemical calculations at high temperatures (MYERS et al., 2002). We have used this equation to explore the magnitude of the anomalous activity coefficients that are expected near the critical point of

water (MYERS et al., 2003). The effects are large and not included in the usual Debye-Huckel equations so that the usual equilibrium calculations in this region can have large errors.

A Helmholtz Energy model coupled with chemical association was used near the critical point for simultaneous correlation of density and heat capacity measurements together with association constants determined from conductance measurements (SEDLBAUER and WOOD 2004).

We have collaborated in the construction of a new heat capacity calorimeter at the University Blaise Pascal in France so that Vladimir Majer and co-workers can continue measurements on this important property (HNEDKOVSKY et al., 2002). This paper shows the systematic errors that can be present in these measurements and makes recommendations about how to minimize these errors.

Theoretical Predictions of Structure and Free Energy

We have further developed our new method of predicting free energies of hydration where experimental measurements are impossible. This method uses molecular dynamic simulation and *ab initio* quantum mechanics to make the predictions. We have shown that our new method can predict hydration free energies of ions at high temperatures with good accuracy (LIU et al., 2002). For instance; we predicted the free energy of hydration of sodium ion plus chloride ion at 573 K as -657 kJ/mole whereas the experimental value is -661 kJ/mole. In this last year, we have used this method to predict the hydration free energies of sodium ion and chloride ion at infinite dilution at a variety of state points: 723 K and 973 K with densities from 0.01 gm/cm^3 to 0.5 gm/cm^3 (LIU et al., 2003b). These results will allow the development of accurate semi-empirical equations of state for ions at supercritical temperatures.

We have predicted the free energy of hydration of water at extremes of temperature and pressures using this new method (up to 2400 K and densities of 1.8 gms/cm^3; (SAKANE et al., 2001).

This new method has been used to calculate the potential of mean force for NaCl at 973 K and density of 0.535 gms/cm^3 (LIU et al., 2003b). Our value for the log of the association constant is -2.3 whereas the conductance data of Quist and Marshall yield a value of -2.6. This demonstrates that we can predict association constants with reasonable accuracy using this method. We have calculated the potential of mean force and the association constant for NaCl(aq) at a variety of high temperature state points and are preparing the results for publication (LIU et al., in preparation-b).

The new method has also been adapted to predict coordination numbers and pair correlation functions (WOOD et al., 2002). We are presently doing calculations on Na+ and Cl- at a variety of state points (Dang et al. In preparation).

It seems clear that using this new method we can now predict free energies of hydration with an accuracy of about 5 kJ/mole for any reasonably simple solute containing elements as heavy as Cl^{-} at temperatures to about 2000 K and water densities to about 1.8 g/cm^3. The accuracy of this new method will improve as better quantum methods are developed and computers become faster. Methods can be developed to predict heavier elements and more complex solutes (with naturally larger expenditures of computer time). If this new method is used to refine semi-empirical models under conditions where experiments are impossible, it will allow quantitative predictions of many geochemical phenomena at extreme temperatures and/or pressures.

List of publications in the last 3 years resulting from this grant and in preparation

Sakane S., Liu W., Doren D. J., Shock E. L., and Wood R. H. (2001) Prediction of the Gibbs energies and an improved equation of state for water at extreme conditions from *ab initio* energies with classical simulations. *Geochimica. Cosmo. Acta* **65**, 4067-4075.

Schulte M. D., Shock E. L., and Wood R. H. (2001) The temperature dependence of the standard-state thermodynamic properties of aqueous nonelectrolytes. *Geochimica. Cosmo. Acta* **65**, 3919-3930.

Plyasunov A. V., O'Connell J. P., Wood R. H., and Shock E. L. (2001) Semiempirical equation of state for the infinite dilution thermodynamic functions of hydration of nonelectrolytes over wide ranges of temperature and pressure. *Fluid Phase Equlibria*, 183-184, 133-142.

Sharygin A. V., Wood R. H., Zimmerman G. H., and Balashov V. N. (2002) Multiple Ion Association versus Redissociation in Aqueous NaCl and KCl at High Temperatures. *J. Phys. Chem. B* **106**(28), 7121 - 7134.

Myers J. A., Sandler S. I., and Wood R. H. (2002) An Equation of State for Electrolyte Solutions Covering Wide Ranges of Temperature, Pressure, and Composition. *Ind. Eng. Chem. Res.* **41**, 3282-3297.

Hnedkovsky L., Hynek V., Majer V., and Wood R. H. (2002) A new version of differential flow heat capacity calorimeter; tests of heat loss corrections and heat capacities of aqueous NaCl from T = 300 K to T = 623 K. *Journal Chem. Thermodynamics* **34**, 755-782.

Zimmerman G. H. and Wood R. H. (2002) Conductance of dilute sodium acetate solutions to 469 K and of acetic acid and sodium acetate/acetic acid mixtures to 548 K and 20 MPa. *J. Solution Chem.* **31**, 995-1017.

Wood R. H., Liu W., and Doren D. J. (2002) Rapid Calculation of the Structures of Solutions with *Ab Initio* Interaction Potentials. *J. Phys. Chem. A* **106**, 10906-10911.

Liu W., Sakane S., Wood R. H., and Doren D. J. (2002) The Hydration Free Energy of Aqueous Na^+ and Cl^- at High Temperatures Predicted by *ab initio*/Classical Free Energy Perturbation at 973.15 K with 0.535 g/cm^3 and 573.15 K with 0.725 g/cm^3. *J. Phys. Chem. A* **106**, 1409-1418.

Myers J. A., Sandler S. I., Wood R. H., and Balashov V. N. (2003) Ion Activities in Dilute Solutions Near the Critical Point of Water. *J. Phys. Chem. B* **107**, 10906 - 10911.

Liu W., Wood R. H., and Doren D. J. (2003a) The Hydration Free Energy and the potential of mean force of a model of the sodium chloride ion pair in supercritical water with ab initio solute-solvent interactions. *J. Chem. Phys.* **118**, 2837-2844.

Plyasunov A. V., Shock E. L., and Wood R. H. (2003) Second cross virial coefficients for interactions involving water. Correlations and group contribution values. *J. Chem. Eng. Data* **48**, 1463-1470.

Liu W., Wood R. H.,   and Doren D. J., (2003) Density and Temperature Dependance of Hydration

Free Energy of Na$^+$ and Cl$^-$ at Supercritical Conditions Predicted by *ab initio*/Classical Free Energy Perturbation , J. Phys. Chem. B, 107, 9505-9513.

Hnedkovsky L., Wood R. H., and Balashov, V. N., (2005) Conductance of Aqueous Na$_2$SO$_4$, H$_2$SO$_4$, and their mixtures: Limiting Equivalent Ion Conductances , Dissociation Constants, and Speciation to 673K ah 28 MPa, J. Phys. Chem. B, 2005 accepted.

Sedlbauer J., and Wood R. H., (2004) Thermodynamic properties of dilute NaCl(aq) solutions near the critical point of water, J. Phys. Chem. B, 108

Méndez De Leo L. P. , and Wood R. H., (2005), Conductance study of association in aqueous CaCl$_2$, Ca(CH$_3$COO)$_2$, and Ca(CH$_3$COO)$_2$.nCH$_3$COOH from 348 to 523 K at 10 MPa, J. Phys. Chem. B, accepted.

Balashov V. N., Sharygin A V., Wood R. H., Grafton B. K., and Xiao C., (2005) Multiple ion association and sulfate ion mobility in aqueous Li2SO4 and K2SO4 from measurement of conductance at temperatures from 523 to 673K, in Preparation

Liu W., Wood R. H., and Doren D. J., (2005), Potential of Mean Force and Association Constants of the Sodium Chloride Ion Pair in 973.15K and 723.15K with Various Water Densities Using the *ab initio* / Classical Free Energy Perturbation Method In Preparation.

Dong H., Liu W., Wood R. H., and Doren D. J., (2005), Coordination Number and Pair Correlation Function of models of aqueous Na$^+$ and Cl$^-$ ions with First Principles Interactions: Results at 723 and 573 K with densities of 0.01 and 0.725 g/cm^3 respectively . In Preparation.