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11. SUPPLEMENTARY NOTES

The views, opinions and/or findings contained in this report are those of the author(s) and should not be construed as an official Department of the Army position, policy or decision, unless so designated by other documentation.

12 a. DISTRIBUTION / AVAILABILITY STATEMENT Approved for public release; distribution unlimited.	12 b. DISTRIBUTION CODE

13. ABSTRACT (Maximum 200 words)

The specific aim of the research was to develop a model based on Helmholtz energy that can be used to describe the thermodynamics of aqueous uni-univalent electrolyte solutions in the water critical region. A model describing the thermodynamics of NaCl solutions in this region was developed using literature heat of dilution ($\Delta_{dil}H$) data as a function of temperature (T = 350 to 402 ^{o}C), pressure (P = 18 to 41 MPa), and solute concentration (m = 0 to 5 molal) and tested using $\Delta_{dil}H$ values for NaCl solutions measured by us within these T, P, and m ranges. Agreement between calculated and measured $\Delta_{dil}H$ values is good. Model calculations show that the apparent log K', Δ_rH, Δ_rS, and Δ_rC_p values change significantly with m, T, and solution density. The model can be used to determine speciation in aqueous NaCl solutions under the above conditions. Values of $\Delta_{dil}H$ for sodium acetate and acetic acid were measured at the above T, P, and m ranges. These acetate systems involve more than one significant reaction. The acetate results will be used to extend the model to more complex electrolyte solutions. The method of sealing the calorimeter was improved resulting in less down time.

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1. Foreword

None

2. Table of Contents

3. List of Appendices, Figures, and Tables

a. Appendices

None

b. Figures

c. Tables

4. Statement of the Problem Studied

The military has a large stockpile of chemical weapons that must be destroyed. This needs to be done as soon as possible to meet treaty obligations and to remove the danger of possible leakage of very hazardous materials. The standard method of destruction is by high-temperature incineration. Drawbacks[1] to incineration are the burning of fossil fuel, the high temperatures required (2000 to 3000 ^{o}C), the production of NO_x, the high residence times needed to get the required level of destruction, the large space requirements, and the high maintenance needs.

A promising alternative to incineration is super critical water oxidation (SCWO).[1,2] The following are advantages of SCWO as compared to incineration: there are no fossil fuel requirements other than for initial heating, SCWO proceeds at much lower operating temperatures (400 to 600 ^{o}C), there is no NO_x formation at these low temperatures, a 99.99% destruction efficiency is achieved at short residence times, the space requirements are much smaller due to the high density of the reactants, the residence time is short, the equipment is less complex, and it is less difficult to satisfactorily contain the hazardous material. However, a major drawback to SCWO is the corrosion of the equipment during the heat up and cool down phases of the process (300 to 400 ^{o}C).[3]

The problem studied was how to minimize the corrosion observed in SCWO processes. Possible solutions to this problem are use of materials of construction that are corrosion resistant, altering the flow in the equipment so that the corrosive solution does not impinge on the materials of construction, and changing the chemistry so that the resulting solution is less corrosive. Our work has been directed toward changing the chemistry of the solution. The easiest way to make the solution less corrosive is to reduce the hydrogen ion concentration to acceptable levels. This can be done by adding a base. Unfortunately, most bases form insoluble salts when they react with acids at SCWO conditions, thus plugging the apparatus. In order to find appropriate buffering agent(s) and conditions, a quantitative knowledge is needed of the speciation in the solution at the corrosive conditions. Our approach to the determination of speciation has been to develop a thermodynamic model which describes aqueous solutions at temperatures from 300 to 400 ^{o}C, as a function of pressure (density), and solute concentration. This model (valid for NaCl solutions) has been developed during the grant period. In order to test the model, we used density data and heat of dilution data taken from the literature as well as heat of dilution values that we measured during the grant period. Heat of dilution data provide a severe test of the model as heats of dilution depend both on the values of the parameters and their temperature derivatives.

5. Summary of the Most Important Results

During the grant period several important accomplishments were made. These are summarized in the following subsections.

a. Development of the RII Model

In the preceding grant period we developed the RI model[4] based on residual Helmholtz energy (A^{res}) which was an important improvement over other models describing the thermodynamics of NaCl solutions in the near critical region of water. This RI model quantitatively described dilute solutions, but was inadequate in describing the thermodynamics of aqueous solutions at high NaCl concentrations. An important achievement during the present grant period was the development of the RII model through incorporation of terms that account for the concentration dependence of the thermodynamic properties of ions in solution. The model development was aided by the use of literature heat of dilution ($\Delta_{dil}H$) data as a function of temperature (T = 350 to 402 °C), pressure (P = 18 to 41 MPa), and solute concentration (m = 0 to 5 molal).[5,6] Agreement between calculated and measured $\Delta_{dil}H$ values was good. A comparison of the ability of the RII model, the RI model and the model developed by Anderko and Pitzer[7] (AP) to predict literature $\Delta_{dil}H$ values is shown in Figure 1.

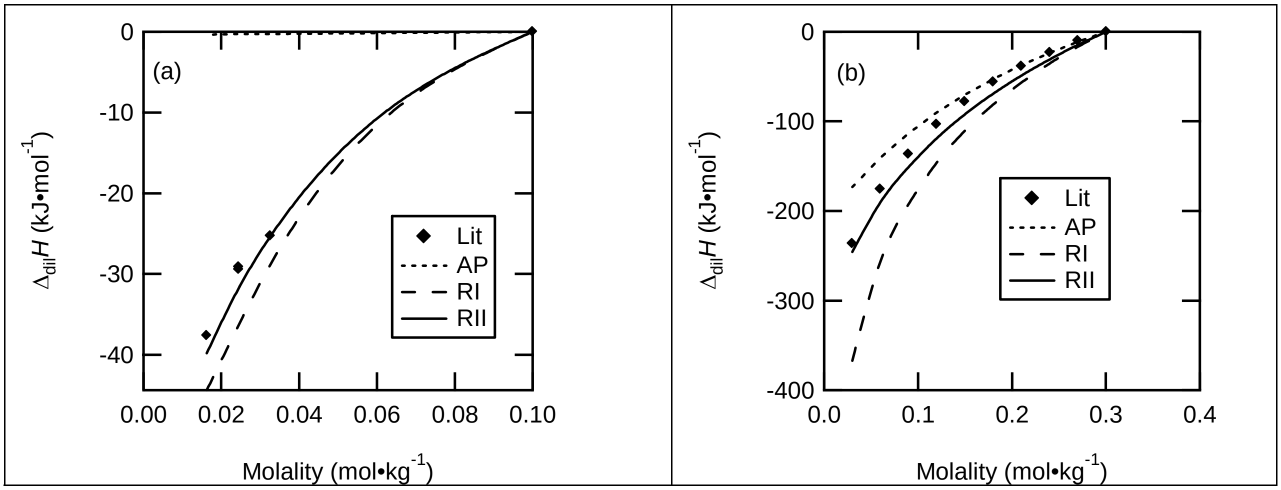

Figure 1. Plots of literature and calculated (see inset) $\Delta_{dil}H$ values. Temperature and pressure conditions for the literature values are (a) 350 °C, 20.5 MPa; (b) 380 °C, 24.7 MPa.

b. Calorimeter Modifications

We observed that as the temperature of measurement increased, more corrosion of the calorimeter occurred. This corrosion manifested itself in failure of the seals in the insert. As temperature increased, the life time of the seals decreased dramatically. In order to eliminate this problem, we replaced the O-ring seals with a cap that is welded to the cylinder. This has resulted in much less time spent in maintenance of the calorimeter and much improved operation and more consistent results.

c. Measurement of $\Delta_{dil}H$

i. Measurement of $\Delta_{dil}H$ Values for $NiCl_2$ and $Ni(NO_3)_2$ Solutions

The heats of dilution of $NiCl_2$ and $Ni(NO_3)_2$ solutions have been measured at 250, 275, and 300 °C. Measurements at these temperatures are important for two reasons. First, this temperature range is where corrosion begins to be appreciable. Second, it is important to develop a model valid over a wide temperature range in order to understand the processes which occur involving different electrolytes during the heat-up and cool-down periods that exist during supercritical water oxidation. Corrosion of metal containers results in divalent metal salts being present in supercritical water oxidation processes. Very little is known about the thermodynamic behavior, including speciation, of these salts in high temperature aqueous solutions. Activity coefficients, speciation, and heats of reaction are needed in order to extend the RII model to include solutions containing divalent metal salts. Nickel salts were chosen for initial study because nickel is a common component of corrosion-resistant containers and nickel salts do not have the undesirable redox properties of many of the other transition divalent metal ions. In Figure 2, representative results are given for the dilution of $NiCl_2$ at 300 °C. This study needs to be extended to 400 ^{o}C. Preliminary log *K* and $\Delta_r H$ values are given in Table 1.

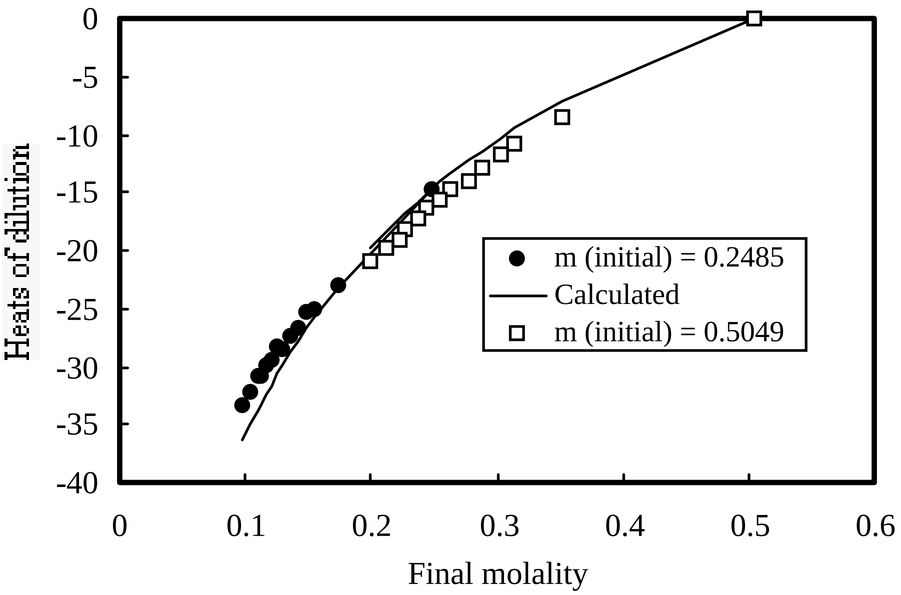

Figure 2. Plot of heats of dilution vs. final molality of $NiCl_2$ at 300 °C and 17 MPa.

Table 1. Log *K* and $\Delta_r H$ Values for the Aqueous Reaction, $Ni^{2+} + Cl^- = NiCl^+$

Temperature/^{o}C	Log *K*	$\Delta_r H$/kJ·mol^{-1}
250	1.54	69
275	1.89	90
300	2.34	129

ii. Measurement of $\Delta_{dil}H$ Values for NaCl and Sodium Acetate (NaOAc) Solutions

Heats of dilution for NaCl and NaOAc solutions have been determined at the following conditions: temperatures (pressures in parentheses) of 350 (17.5, 24, 26, 28 MPa), 360 (20, 23, 24, 26, 28 MPa), 370 (26, 28 MPa), 375 (24, 28, 32 MPa), and 380 ^{o}C (32 MPa) which includes 183 $\Delta_{dil}H$ data points. The temperatures and pressures of measurement were selected because they are near the critical point of water. As the critical point of water is approached, the compressibility of water approaches infinity. This results in dramatic changes in water properties. Therefore, in this region, small changes in T, density (ρ) and m cause large changes in fluid properties. These large changes in properties provide a severe test for any model designed to predict them.

Typical plots of $\Delta_{dil}H$ values for NaCl and NaOAc solutions versus m are shown in Figure 3.

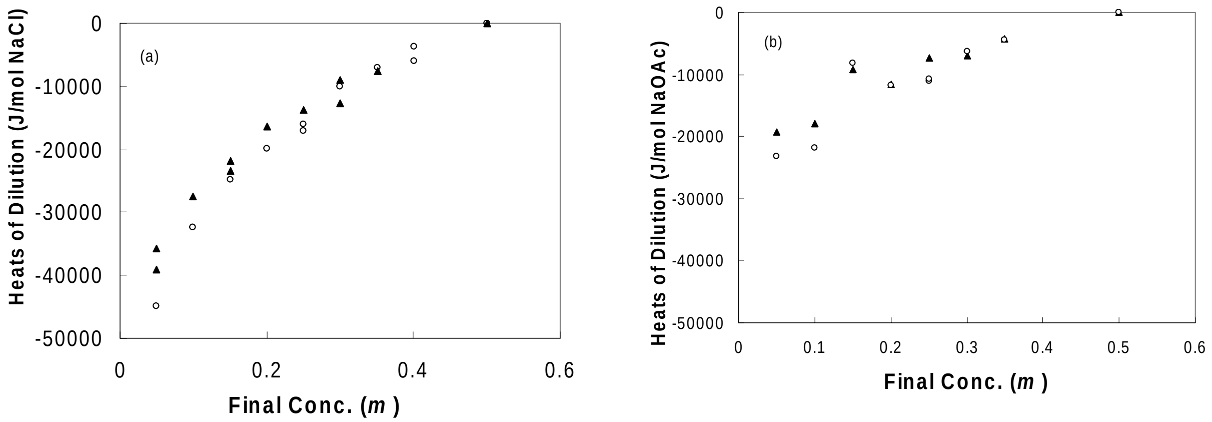

Figure 3. Plots of $\Delta_{dil}H$ versus final molality for (a) NaCl solutions and (b) NaOAc solutions at 360 ^{o}C at 26 (○) and 28 (▲) MPa.

The plots in Figure 3 show that the -$\Delta_{dil}H$ values are much larger at a given molality for NaCl than they are for NaOAc. This difference is due to two factors. First, NaOAc is more associated than NaCl. Second, more than one significant reaction occurs in the case of NaOAc, whereas only one occurs in the case of NaCl. The reactions occurring in both cases where $X^- = Cl^-$ or OAc^- include the following:

$$\mathrm{NaX(aq)} = \mathrm{Na^+} + \mathrm{X^-} \tag{1}$$
$$\mathrm{H^+} + \mathrm{OH^-} = \mathrm{H_2O} \tag{2}$$
$$\mathrm{HX(aq)} = \mathrm{H^+} + \mathrm{X^-} \tag{3}$$
$$\mathrm{Na^+} + \mathrm{OH^-} = \mathrm{NaOH(aq)} \tag{4}$$
$$\mathrm{X^-} + \mathrm{H_2O} = \mathrm{HX(aq)} + \mathrm{OH^-} \tag{5}$$

Equation 5 is a combination of Equations 2 and 3. The affinity of Cl^- for Na^+ and H^+ is much less than the affinity of OAc^- for Na^+ and H^+.[8] The K value for Reaction 3 is close to the K value for reaction 2 in the case of OAc^- but not in the case of Cl^-.[8] Therefore, the extent of Reaction 5 is much less in the case of NaCl than in the case of NaOAc. In the case of NaCl solutions, only Equation 1 is needed to adequately describe the system. However, in the case of NaOAc, all of the reactions are required to adequately describe the system. The balance of the exothermic (Equations 1, 3, and 5) and endothermic (Equations 2 and 4) reactions produces a smaller net $-\Delta_{dil}H$ value in the case of NaOAc.

iii Testing of the RII Model Using New $\Delta_{dil}H$ Values for NaCl Solutions

The RII model was developed using available $\Delta_{dil}H$ values[5,6] which were obtained over the ranges of 350 to 402 °C, 18 to 41 MPa, and 0 to 5 *m*. Measurements of $\Delta_{dil}H$ values for NaCl solutions made during the grant period were within the same *T*, *P*, and *m* ranges, but most were not at the same *T*, *P*, and *m* values as those used to develop the RII model. The purposes for making these measurements were to study the pressure dependence of the $\Delta_{dil}H$ values and to check the validity of the RII model at other temperatures and pressures within the model range. The $\Delta_{dil}H$ values predicted by the RII model are in good agreement with the present results as shown by the representative curves in Figure 4. This good agreement between measured and calculated $\Delta_{dil}H$ values gives credence to the validity of the model in the near-critical region of water.

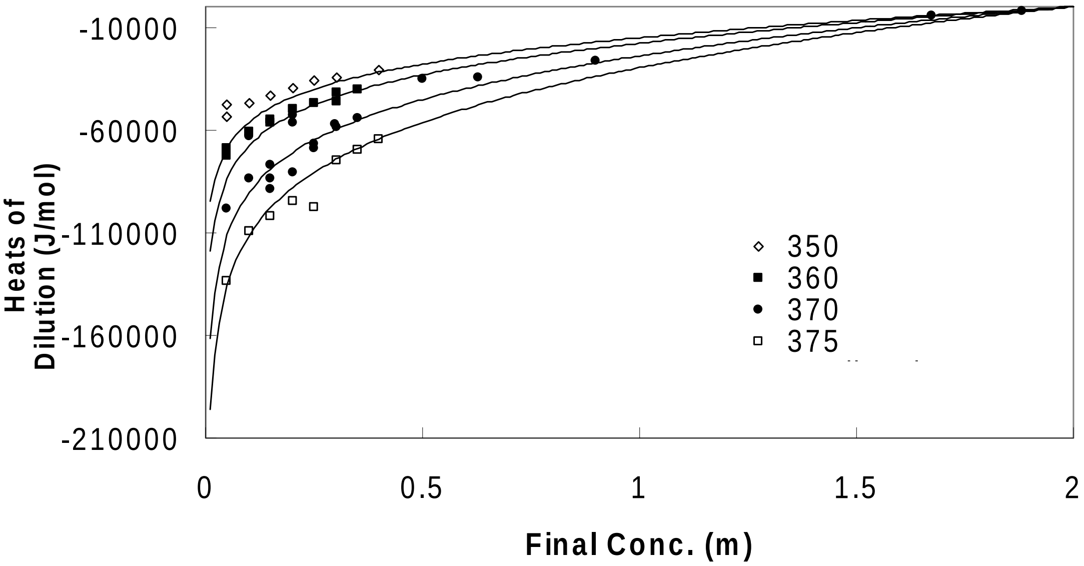

Figure 4. Plot of $\Delta_{dil}H$ values for dilution of NaCl solutions versus final NaCl concentration as a function of temperature at 28 MPa

d. Results from the RII Model

i. Model Fits $\Delta_{dil}H$ Values over a Wide Range of Densities

The good agreement between the measured $\Delta_{dil}H$ values and those calculated using the RII model is impressive considering the large changes of solution density with the changes in solute concentration at constant temperature and pressure conditions. For example, at 375 °C and 24 MPa, water has a density of 0.486 gm/cm^3, a 5 molal NaCl solution has a density of 0.862 gm/cm^3 while a 0.2 molal NaCl solution has a density of 0.504. At 400 °C and 30 MPa, water has a density of 0.357 gm/cm^3 and a 5 molal NaCl solution has a density of 0.862 gm/cm^3. The model accurately accounts for the enthalpy changes over these large solution density changes. At 374 °C and higher temperatures, the water being mixed with the salt solution is a supercritical fluid while the solution at the higher concentration ranges is a subcritical fluid. The model can be used to accurately calculate the density and enthalpy changes that occur with solute concentration changes in this situation.

ii. Thermodynamic Values as a Function of Solute Concentration

The model can be used to find the log of the apparent equilibrium constant valid at finite *m* values (log *K´*), $\Delta_r H$, $\Delta_r S$, and $\Delta_r C_p$ values for the reaction in Equation 6.

$$Na^+ + Cl^- = NaCl(aq) \qquad (6)$$

Log *K´* values are plotted in Figure 5 as a function of $m^{0.5}$ and *P* at 350, 375, and 400 °C. This plot shows significant trends.

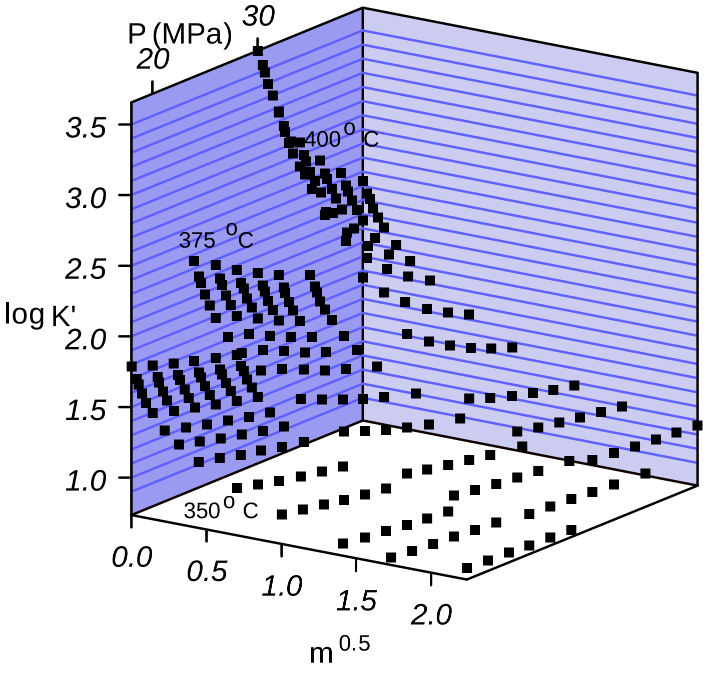

Figure 5. Plot of log *K´* for the reaction $Na^+ + Cl^- = NaCl(aq)$ versus $m^{0.5}$ (NaCl) and pressure (MPa) at 350, 375, and 400 °C.

First, at all *T* values, the log *K´* values decrease initially with increasing *m* and level off at high *m* values. At 350 °C, the log *K´* values increase slightly at the highest *m* values compared to the second highest *m* values. At 375 °C, the log *K´* values are essentially the same at the two highest *m* values. At 400 °C, the log *K´* values continue to decrease through the *m* range studied. Second, as *T* increases, the log *K´* values become larger at a given *m* and *P* value. This increase due to T is greatest at $m = 0$ and decreases with increasing m. Third, as P increases at the same T and m, the log K' values decrease. The decrease in log K' values with P is most pronounced at high T and low m. The decrease in log K' values due to increasing P becomes smaller as T decreases and m increases. Plots of $\Delta_r H$ and $\Delta_r S$ values versus P and m show trends similar to those found in the case of the log K' values. Explanations for these trends are available.[9]

The trends with T, P, and m for $\Delta_r C_p$ values are similar to those found for log K' $\Delta_r H$ and $\Delta_r S$. However, the $\Delta_r C_p$ values are more sensitive than either $\Delta_r H$ or $\Delta_r S$ to the changes in T, P, and m. The reasons for this have been presented and discussed.[9]

iii. Speciation

One of the significant contributions of the RII model is that it can be used to calculate the species distribution as a function of temperature, pressure/density, and solute concentration. Minimizing corrosion by changing the chemistry requires a knowledge of the speciation in the solution. As shown in Figure 6, the fraction of NaCl that is dissociated (F_{dis}^{NaCl}) into its ions varies dramatically with changes in solute concentration, temperature, and pressure/density.[9]

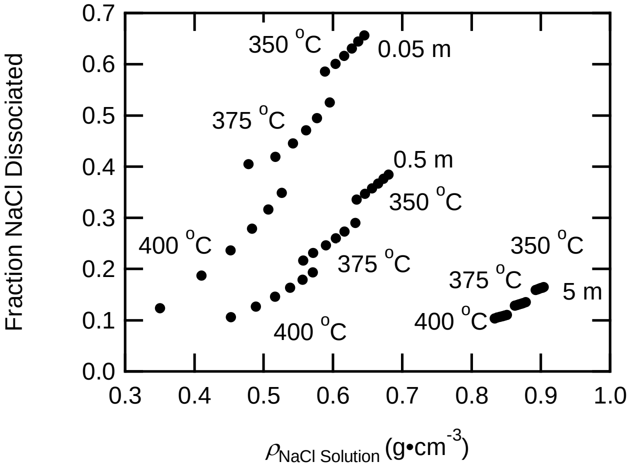

Figure 6. Plot of fraction of NaCl dissociated (F_{dis}^{NaCl}) versus NaCl solution density at 350, 375, and 400 °C and at 0.05, 0.5 and 5 *m* NaCl.

The F_{dis}^{NaCl} value increases significantly with ρ at a given T and m. At high m values, ρ and, therefore, F_{dis}^{NaCl} changes little with T. At low m values, ρ and F_{dis}^{NaCl} change dramatically with T. As m decreases, the change of F_{dis}^{NaCl} with T and ρ becomes larger. For example, at 0.05 m, F_{dis}^{NaCl} varies from about 0.12 to 0.66 as the density increases from about 0.35 to 0.65 g·cm^{-3}. The results in Figure 6 illustrate dramatically the important role of ρ in determining F_{dis}^{NaCl}.

e. Future Work

The next step is to extend this model to other systems, especially those that include more than one reaction. Once this is accomplished, one will be able to apply this model to describe systems that occur in SCWO processes. The goal is to have a computer program that can be used in the design and operation of SCWO processes. This program would be used in a way similar to that of the MULTEQ computer program written by us.[10] The MULTEQ code is used today in the nuclear power industry to describe the chemistry of the secondary water in the steam generators at temperatures around 280 °C. Application of the MULTEQ program has saved hundreds of millions of dollars for this industry during the past ten years as its use can tell the operators of the steam generators what changes must be made in the water chemistry. In practice this is a rapid and successful process.

Reliable thermodynamic data are needed in order to put the correct parameters in any code and to test the code. These data are sparse in the critical region of water over wide solute concentration ranges. That is why every effort should be made to collect data in this region for a variety of aqueous systems.

6. Listing of Publications

a. Papers Published in Peer-Reviewed Journals

(1) Oscarson, J.L.; Liu, B.; Izatt, R. M. A Model Incorporating Ion Dissociation, Solute Concentration, and Solution Density Effects to Describe the Thermodynamics of Aqueous Sodium Chloride Solutions Near the Critical Point of Water, *Ind. Eng. Chem. Res.* 2004, in press.

b. Papers Published in Non-Peer-Reviewed Journals or in Conference Proceedings

none

c. Papers Presented at Meetings but not Published in Conference Proceedings

(1) Peterson, C. J.; Oscarson, J. L.; Liu, B.; Cardenas-Garcia, J.; Izatt, R.M. “The Effect of Pressure on Heats of Dilution of Sodium Chloride Solutions Near the Critical Point of Water.” 59th Calorimetry Conference, Sante Fe NM, June 27 - July 1, 2004.

(2) Peterson, C. J.; Oscarson, J. L.; Liu, B.; Cardenas-Garcia, J.; Izatt, R.M. “The Effect of Pressure on Heats of Dilution of Sodium Acetate Solutions Near the Critical Point of Water.” 59th Calorimetry Conference, Sante Fe NM, June 27 - July 1, 2004.

(3) Liu, B.; Oscarson, J. L.; Izatt, R.M. “A Model Incorporating Ion Dissociation, Solute Concentration, and Solution Density Effects to Describe the Thermodynamics of Aqueous Sodium Chloride Solutions in the Critical Region of Water.” 59th Calorimetry Conference, Sante Fe, NM, June 27 - July 1, 2004.

(4) Oscarson, J. L.; Peterson, C.J.; Liu,,B.; Izatt, R.M. “Heats of Dilution as Predicted by an Extended Helmholtz Energy Model for Aqueous Solutions of NaCl near the Critical Point of Water.” 58th Calorimetry Conference, Laie, HI, July 27-August 1, 2003.

(5) Izatt, R. M.; Oscarson, J. L. “The World of High Temperature Aqueous Chemistry.” XXIV National Meeting of Calorimetry, Thermal Analysis, and Chemical Thermodynamics, Catania, Italy, December 15 - 18, 2002.

(6) Oscarson, J. L.; Izatt, R. M. “ΔC_p for Chemical Reactions in Aqueous Solutions as a Probe to Gain Insight into Water-Solute Interactions.” 56th Calorimetry Conference, Colorado Springs, CO, July 29 – August 2, 2001.

d. Manuscripts Submitted, but not Published

none

e. Technical Reports Submitted to ARO

none

7. List of All Participating Scientific Personnel Showing Any Advanced Degrees Earned by Them while Employed on the Project

Those who were supported partially and who worked on the research include:

1. Dr. Reed M. Izatt, Principal Investigator

2. Dr. John L. Oscarson, Co-principal Investigator
3. Dr. Jaime Cardenas-Garcia, Post-doctoral Associate
4. Sue Gillespie, Research Associate
5. Bing Liu, Graduate Student (Ph. D. expected in December 2004)
6. Craig Peterson, Graduate Student (Ph. D. expected in 2007)
7. Xiaoyun Lin, Graduate Student (M. S. expected in 2005)
8. Nathan Rytting, Undergraduate Student
9. Lynlee Southam Undergraduate Student
10. Andrew Dadson Undergraduate Student
11. Tyler Izatt Undergraduate Student

8. Report of Inventions

None

9. Bibliography

(1) Shaw, R. W., Dahmen, N. Destruction of Toxic Organic Materials Using Supercritical Water Oxidation: Current State of the Technology. In *Supercritical Fluids: Fundamentals and Applications*, Kiran, E.; Debenedetti, P. G.; Peters, C. J., Eds.; Kluwer Academic, Dordrecht, **2000**, 425-437.

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(9) Oscarson, J.L.; Liu, B.; Izatt, R. M. A Model Incorporating Ion Dissociation, Solute Concentration, and Solution Density Effects to Describe the Thermodynamics of Aqueous Sodium Chloride Solutions Near the Critical Point of Water, *Ind. Eng. Chem. Res.* 2004, in press.

(10)Oscarson, J.L.; Christensen, J.J.; Izatt, R.M. "Development and Uses of the EPRI Program (MULTEQ) for Predicting Concentrations and Partitioning of Chemical Species in High Temperature Aqueous Solutions"; Proceedings of the Symposium on Chemistry in High-temperature Water, Provo, UT, August 1987; Proceedings 1990, paper 4b*.

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