International Journal of Thermophysics, Vol. 16, No. 2, 1995

The Structure and Phase Equilibria of Salt–Water Solution at Supercritical Conditions[1]

S. T. Cui[2] and J. G. Harris[3,4]

We study the thermodynamic properties of the supercritical water and dilute aqueous salt solutions using molecular dynamics simulation. The sodium and chloride ions are found to show strong pairing at conditions corresponding to those of supercritical water oxidation. We also present the first prediction of the solubility of sodium chloride in supercritical water obtained directly from intermolecular interactions using molecular simulations.

KEY WORDS: chemical potential; potential of mean force; sodium chloride; solubility; supercritical water.

1. INTRODUCTION

There has been growing interest in aqueous solutions at supercritical conditions due to their importance in supercritical water oxidation technology and other industrial applications. The presence of salts in the oxidation products is one of the major considerations in reactor design. At present, very little is known about the molecular-level behavior of such solutions at the conditions encountered in supercritical water oxidation.

Typical conditions encountered in supercritical water oxidation are temperatures of 700–800 K and pressures around 250 bar. In this paper, we examine the properties of water and sodium chloride–water solutions under these conditions. Using molecular dynamics simulations, we investigate the

---

[1] Paper presented at the Twelfth Symposium on Thermophysical Properties, June 19–24, 1994, Boulder, Colorado, U.S.A.

[2] Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996, U.S.A.

[3] Department of Chemical Engineering, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, U.S.A.

[4] Author to whom correspondence should be addressed.

0195-928X/95/0300-0493$07.50/0 © 1995 Plenum Publishing Corporation

behavior of the ions in supercritical water and the thermodynamic properties of pure water as described by simple but physically reasonable potential models. We compare these calculations with experimental measurements and with the Born model, a simple continuum model. We then calculate the solubility of sodium chloride in supercritical water as predicted by these models. Further details of these calculations are reported in two other papers [1].

2. THE MODELS AND SIMULATION METHODS

We use the SPC model for water [2], and Pettit and Rossky's model of sodium and chloride ions, which consists of a Coulombic plus a Huggins–Mayer interaction [3]. For the interactions between the ions and the water molecules, we adopt the interaction potentials introduced by Pettit and Rosky, which are essentially a Coulombic plus a Lennard-Jones potential between an ion and a charge site on the water molecule [3]. We differ from Ref. 3 in using the SPC charges instead of TIPS charges on the water molecule. Other groups have used this model to explore the behavior of single ions in water very close to the critical point [4]. The SPC model of water predicts a reasonable dielectric constant and internal energy at ambient condition. It underpredicts the density at 1 bar by about 3%. The models of the sodium and chloride ions give a good description for the properties of internal energy and the lattice parameter for the sodium chloride crystal at ambient condition, as will be shown below from our simulation result.

We used an Ewald summation to treat the Coubombic part of the interactions in the solid, and the site–site reaction field method of Neumann and co-workers to treat them in the liquid [5]. In the site–site reaction field each Coulombic interactions is replaced by an effective potential,

$$V_{ij} = \begin{cases} q_i q_j \left(\dfrac{1}{r} + \dfrac{r^2}{2R_c^3} - \dfrac{3}{2R_c} \right), & r \leqslant R_c \\ 0, & r < R_c \end{cases} \tag{1}$$

where q_i and q_j are the charges of sites i and j, and R_c is the cutoff distance (9.5 Å in the solubility calculations and 12.66 Å in all other calculations).

We integrated the equations of motion using the velocity Verlet algorithm [6], with a time step of 0.0025 ps. Pressure and temperature were controlled by means of Nose–Andersen approaches [7]. We used 123–125 water molecules in each simulation. Tests on larger systems indicate that the finite-size effects are small [1]. Further details describing equilibration and sampling times are reported elsewhere [1].

3. THE PROPERTIES OF PURE WATER AT SUPERCRITICAL CONDITIONS

Table I lists some of the properties of SPC water at ambient and at a number of supercritical conditions. At supercritical conditions, the SPC model predicts the equation of state accurately, while the dielectric constant is slightly larger than the experimental value. This discrepancy is due to the SPC water dipole moment's (2.27 D) being larger than the actual dipole moment of an isolated water molecule (1.85 D). This enhanced dipole moment accounts for the polarization of the water molecule in the dense liquid. Reducing the dipole moment by either decreasing the charges or shortening the O–H bond to account for the much lower polarization of the water under supercritical conditions makes the prediction of the equation of state much less accurate.

4. THE POTENTIAL OF MEAN FORCE AND THE DISSOCIATION CONSTANT

Previous potential-of-means-force calculations show that at ambient conditions [8], the SPC model predicts a bound state and a dissociated state of the sodium chloride ion pair which are separated by a potential barrier. The free energy of binding of the Na–Cl pair is low enough so that the salt is almost completely dissociated.

To investigate the salt dissociation under the conditions encountered in supercritical water oxidation, we computed the potential of mean force between sodium and chloride ions at several state points. The potential-of-mean-force curves were computed by integrating the mean force between the sodium and chloride ions predicted at each ion pair separation. We used 112.5 ps of equilibrated NVT molecular dynamics simulations. Figure 1 shows the potential of mean force between sodium and chloride ions at 800 K and at a density at which pure water would have a pressure of 250 bar. The figure shows a single minimum in the potential of mean force at about 0.24 nm where the potential of mean force is $-208\ \mathrm{kJ \cdot mol^{-1}}$, a much shallower well than the $-522\ \mathrm{kJ \cdot mol^{-1}}$ one of an ion pair in free space. Because the well depth is about 31 $k_B T$, the sodium and chloride ions exist as a tightly bound ion pair in the supercritical aqueous solution at the conditions we have studied. This observation is supported by the computation of the dissociation constant from the potential-of-mean-force curve shown in Fig. 1, which is $10^{-12}\ \mathrm{mol \cdot L^{-1}}$.

Figure 1 also shows a calculation by a continuum approach, in which the potential of mean force between the ions is the non-Coulombic interaction between the ions plus the Coulombic interaction attenuated by the

Table I. The Properties of Pure SPC Water at Ambient and a Few Supercritical Conditions[a]

ρ (kg · m^{-3})	T (K)	P_{calc} (bar)	P_{ideal} (bar)	P_{exp} [13] (bar)	$\varepsilon_{\mathrm{calc}}$	$\varepsilon_{\mathrm{exp}}$ [14]	ε_{u} ($\mu = 2.27$ D)	ε_{u} ($\mu = 1.85$ D) [16]	U (kJ · mol^{-1})
125.2	700	246(2)	398	250	2.23(2)	2.06	1.95	1.63	−8.67(0.07)
83.26	800	245(3)	307	250	1.65(2)	1.54	1.55	1.36	−5.02(0.10)
67.43	900	244(4)	280	250	1.48(2)	1.37	1.39	1.26	−3.54(0.07)
57.94	1000	248(3)	267	250	1.33(2)	1.28	1.30	1.20	−2.64(0.04)
1000	298	932(25)	1375	1	76(5)	77.6	17.61	12.03	−41.24(0.07)

[a] ρ is the density of water. T is the temperature in kelvin. P_{calc}, P_{ideal}, P_{exp} are pressure calculated from our simulation, from the ideal gas law, and from experiment, respectively. Values in parentheses are the statistical uncertainties. $\varepsilon_{\mathrm{cal}}$ is the dielectric constant at the state point (T, ρ) predicted by our simulations, and $\varepsilon_{\mathrm{exp}}$ is the value from Archer and Wang's correlation of the experimental data in Ref. 14 at P_{exp}, ρ, and T (the correlation uses all three properties explicitly); their correlation fits the data of Ref. 15, but these dielectric constants are somewhat higher than those we employed in the comparison in Ref. 1. It is not clear which data are more accurate. ε_{u} ($\mu = 2.27$ D) and ε_{u} ($\mu = 1.85$ D) are the dielectric constants obtained for uncorrelated dipoles the SPC water dipole moment and the experimental water dipole moment, respectively. U is the average potential energy per molecule.

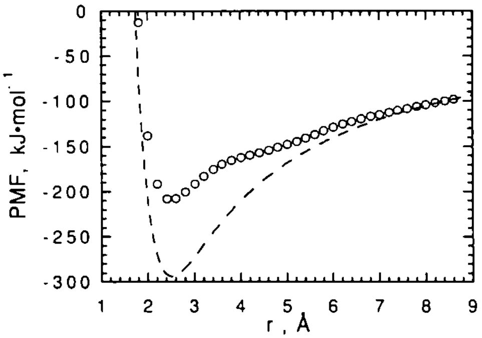

Fig. 1. The potential of mean force between Na^+ and Cl^- pair in supercritical water at $\rho = 83.26\ kg \cdot m^{-3}$, $T = 800$ K, at essentially infinite dilution. The dashed line is the prediction from a continuum picture in which the solvent effect is included by attenuating all Coulomb interactions by a dielectric constant $\varepsilon = 1.65$, the circles are our molecular dynamics simulation result.

dielectric constant predicted for the state point by our simulations. Such a continuum model agrees very well with the simulation at large ion separations, while substantially underestimating the solvation effect at smaller separations. This is expected because the continuum model neglects the molecular nature of the solvent molecules; this effect should be more severe at small ion separations.

5. THE SOLUBILITY OF SODIUM CHLORIDE IN SUPERCRITICAL WATER

When a supercritical water solution is saturated with sodium chloride, the chemical potential of the sodium chloride in the supercritical water must equal that of the solid sodium chloride at the same temperature and pressure. Because the sodium chloride at our state points exists as a bound ion pair, the solid-phase sodium chloride is in equilibrium with paired sodium chloride molecules in water. Thus, the sodium chloride solution is essentially a mixture of sodium chloride pairs in water. Because the sodium chloride potential of mean force has such a deep well, it is reasonable to fix the distance between the sodium and the chloride ions at 0.2293 nm, corresponding to the equilibrium bond distance for a sodium chloride ion pair in free space.

We break up the chemical potential change into three parts, using as our standard states the isolated Na^+ and Cl^- at fixed positions. The solid chemical potential is μ^{s}_{NaCl}. The chemical potential of a NaCl bound pair *in vacuo* is μ^{id}_{NaCl}. The insertion of the ion pair into water changes its chemical potential by $\Delta\mu^{l}_{NaCl}$. The equality of the chemical potentials in the two phases requires that

$$\mu^{s}_{NaCl} = \mu^{id}_{NaCl} + \Delta\mu^{l}_{NaCl} \tag{2}$$

μ^{id}_{NaCl} is given by

$$\mu^{id}_{NaCl} = k_B T \ln\left(\frac{\rho_{NaCl}\Lambda^{3}_{NaCl}}{q_I}\right) + u_{NaCl} \tag{3}$$

where ρ_{NaCl} is the density of the sodium chloride pair in water, $\Lambda_{NaCl} = (h^2/2\pi m k_B T)^{1/2}$ is the de Broglie wavelength of the sodium chloride molecule, m is the mass of the sodium chloride molecule, k_B is the Boltzmann constant, and T is its temperature. q_I is the partition function corresponding to the internal motion of the molecules, such as the rotational degrees of freedom and the vibrational degrees of freedom, and $-u_{NaCl}$ is the binding energy of the ion pair. The vibrational degrees of freedom add approximately $-0.5k_B T$ to the chemical potential, increasing the solubility by a factor of about 1.5. When the solubility is low, as is the case under the conditions we investigate, the excess chemical potential is essentially independent of composition. Thus we can compute it for a very low concentration and solve Eqs. (2)–(3) for the mole fraction of NaCl in the liquid phase.

The excess chemical potential, $\Delta\mu^{l}_{NaCl}$, can be calculated using the Kirkwood coupling-parameter method and/or the Widom test-particle method. In our simulations, we have used a combination of the two methods for its evaluation. In the Kirkwood method we attenuate the ion pair–water interaction by a factor of λ, so that setting $\lambda = 0$ turns the interaction between the ion pair and water completely off, while setting $\lambda = 1$ turns it completely on to its physical value. The difference between the excess chemical potentials of the ion pair and the fictitious molecule with the ion pair–water interactions attenuated by a factor λ_{min} is

$$\mu_{ex} = \int_{\lambda_{min}}^{1} \langle \phi \rangle_{\lambda}\, d\lambda \tag{4}$$

Because the integrand becomes singular at $\lambda = 0$, we find the chemical potential at $\lambda_{min} = 0.1$ using the Widom insertion method. This approach is more efficient than a Widom insertion at $\lambda = 1$, because the clustering of solvent molecules around the ions means that the configurations contributing to $\Delta\mu^{l}_{NaCl}$ are likely to be sampled infrequently. At the smaller coupling parameter, the clustering effect is substantially reduced, and the Widom method can more efficiently sample the appropriate configurations.

The chemical potential of the sodium chloride in the solid phase be written as $\mu^{s}_{\mathrm{NaCl}} = F/N + Pv$, where F is the Helmholtz free energy and v the volume per molecule of the system. For the solid system at the pressure considered in this work, the Pv term contributes only approximately $0.1k_{\mathrm{B}}T$ to the chemical potential and hence is negligible. Thus the calculation of the chemical potential reduces to that of the Helmholtz free energy.

There are several methods which can be used to calculate the free energy of solid systems. Lutsko et al. compared the relative merits for several commonly used methods [9]. We have chosen the quasiharmonic approximation (QHA) for its simplicity and computational efficiency. For the simple argon system, the QHA has been shown to be valid up to 75% of the melting temperature. The highest temperature considered in this paper is about 76% of the experimental melting temperature at 1 bar (1074 K). We compared our QHA predictions with those of a thermodynamic integration from very low temperature to verify the accuracy of the QHA approximation under our conditions. We also calculated the cohesive energy and the lattice parameter for the sodium chloride crystal at atmospheric pressure and 298 K, which gives $-759.3\ \mathrm{kJ \cdot mol^{-1}}$ for the cohesive energy and 0.285 nm for the distance between the sodium and chloride ions, as compared to the experimentally measured values of $-764.4\ \mathrm{kJ \cdot mol^{-1}}$ and 0.281 nm [10].

The Helmholtz free energy F for the NaCl crystal in the QHA is

$$F = k_{\mathrm{B}}T \ln\left\{\prod_{n=1}^{3N-3}\left(\frac{hv_n}{k_{\mathrm{B}}T}\right)\right\} + U_0 \tag{5}$$

where the product is over all of the normal modes of the solid, and U_0 is the static potential energy of the system. To find all of the vibrational frequencies, we performed a molecular dynamics simulation of the solid at constant pressure to find the average density of the solid. We then minimized the energy with respect to the particle positions holding the total volume fixed at the average obtained from the simulation. The normal mode frequencies were determined from the diagonal elements of the dynamical matrix,

$$D_{ij} = \left(\frac{\partial^2 U}{\partial r_{i\alpha}\,\partial r_{j\beta}}\right)_{\mathrm{eq}} \tag{6}$$

where U is the total potential energy and the $r_{i\alpha}$ are the spatial coordinates of the ions.

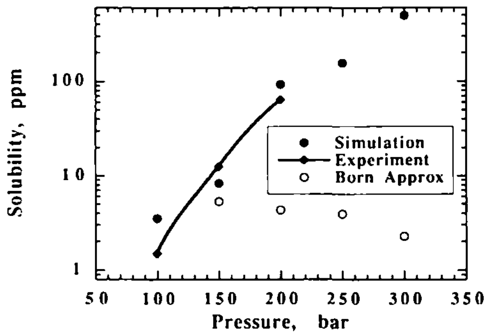

Fig. 2. The solubility of the sodium chloride in supercritical water at temperature 723 K. The solid circles are the simulation results, the diamonds are the experimental data from Ref. 11, and the open circles are the prediction of the Born approximation.

Figures 2 and 3 illustrate the pressure dependence of the solubility at temperatures 450 and 500°C as predicted by our simulations, the Born model [11], and experiments [12]. The figures show that the simulations predict the magnitude and pressure dependence of the solubility as well as we can expect. The slope of the plot of solubility versus pressure appears to be slightly lower than that seen in the experiments. The largest contribution to the statistical error in the logarithm of the solubility is approximately $0.5k_BT$ arising from the computation of the excess chemical potential in water.

A few factors may affect the accuracy of the solubility predicted from the simulation. The large dipole of the SPC water molecule causes an

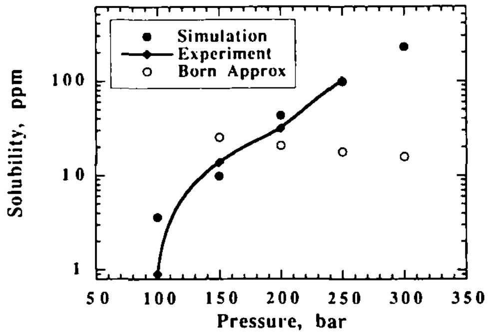

Fig. 3. The solubility of the sodium chloride in supercritical water at temperature 773 K. The symbols have the same meanings as in Fig. 2.

overestimate of the electrostatic attraction between the ions and the water molecules and an overestimate of the dielectric constant, both favoring solubilization of the ions. The potential models for the ions have been shown to give reasonably good predictions of the cohesive energy and lattice parameter for the sodium chloride crystal at ambient conditions. Because the well depth is on the order of $100k_BT$, a relatively small change in it can cause a large change in the solubility.

In Figs. 2 and 3, we also show a simple estimate of the solubility by the Born model [11]. In this continuum model, the sodium and the chloride ions are treated as charged hard spheres of radius R_{Na} and R_{Cl}, respectively. The Gibbs free energy change due to the insertion of a sphere into the solution, a continuum with dielectric constant ε, is

$$\Delta G = -\frac{(Ze)^2}{2R}\left(1-\frac{1}{\varepsilon}\right) \tag{7}$$

where Ze is the electric charge, R is the radius of the particle, and ε is the dielectric constant of the medium. In our application of the model to the ion pair, we insert the sodium sphere and the chloride sphere separately and then bring them to the desired distance of $d = 0.2293$ nm in the dielectric continuum. During this process, the dielectric constant of the medium remains fixed. The total change in the chemical potential during the procedure is

$$\Delta G_{\mathrm{NaCl}} = -\frac{e^2}{2R_{\mathrm{Na}}}\left(1-\frac{1}{\varepsilon}\right)-\frac{e^2}{2R_{\mathrm{Cl}}}\left(1-\frac{1}{\varepsilon}\right)-\frac{e^2}{\varepsilon d} \tag{8}$$

We estimated the radius of Na^+ in water from the interaction potential by assuming that the water molecule approaches the Na^+ with oxygen pointing toward the ion, and the ion is on the line of the bisector of the water molecule. Similarly, for Cl^- we assume the hydrogens approach the Cl^- ion first. In these cases we define the radius of the sphere to be the point where the potential crosses zero. This way, we obtain $R_{\mathrm{Na}} = 0.188$ nm, $R_{\mathrm{Cl}} = 0.188$ nm, $R_{\mathrm{Cl}} = 0.280$ nm. Substituting these values into Eq. (8) produces the Born estimate for the solubility presented in Fig. 3, which does not predict the pressure dependence of the solubility. Thus the molecular structure of the water plays a key role in the solubility of the salt in these supercritical solutions.

6. CONCLUSIONS

In summary, we conclude from this study that the SPC water model gives an accurate description of the equation of state for the conditions appropriate to the supercritical water oxidation. Sodium chloride ions are strongly paired at these conditions. We have also presented the first predictions of the solubility of a salt in supercritical water directly from intermolecular interactions. These particular interactions predict values of the solubility of sodium chloride in water which for such a sample model are in remarkable agreement with experiment.

ACKNOWLEDGMENTS

This work was supported by the Army Research Office under the University Research Initiative program. We also acknowledge the Pittsburgh Supercomputer Center for supercomputer time allocations to carry out some of this work.

REFERENCES

1. S. T. Cui and J. G. Harris, *Chem. Eng. Sci.* **49**:2749 (1994); *J. Chem. Phys.*, in press.
2. H. J. C. Berendsen, J. P. M. Potsma, W. F. von Gunsteren, and J. Hermans, in *Intermolecular Forces*, B. Pullman, ed. (Reidel, Dordrecht, 1981).
3. B. M. Pettitt and P. J. Rossky, *J. Chem. Phys.* **84**:5836 (1986).
4. P. T. Cummings, H. D. Cochran, J. M. Simonson, R. E. Mesmer, and S. Karboni, *J. Chem. Phys.* **94**:5606 (1991).
5. G. Hummer, D. M. Soumpasis, and M. Neumann, *Mol. Phys.* **77**:769 (1994).
6. H. C. Andersen, *Corp. Phys.* **52**:24 (1983).
7. G. Ciccotti and J. P. Ryckaert, *Phys. Rep.* **4**:345 (1986).
8. E. Guardia, R. Rey, and J. A. Padro, *J. Chem. Phys.* **95**:187 (1991).
9. J. F. Lutsko, D. Wolf, and S. Yip, *J. Chem. Phys.* **88**:6526 (1988).
10. L. Pauling, *The Nature of the Chemical Bond and the Structure of Molecules and Crystals: An Introduction to Modern Structural Chemistry* (Cornell University Press, Ithaca, New York, 1960), p. 526; F. G. Fumi and M. P. Tosi, *J. Phys. Chem. Solids* **25**:31 (1964).
11. M. Born, *Z. Phys.* **1**:45 (1920); T. P. Straatsma and H. J. C. Berendsen, *J. Chem. Phys.* **89**:5876 (1988).
12. F. J. Armellini and J. W. Tester, *Fluid Phase Equilibria* **84**:123 (1993).
13. R. H. Perry and D. Green, eds., *Perry's Chemical Engineer's Handbook*, 6th ed. (McGraw-Hill, New York, 1984).
14. D. G. Archer and P. Wang, *J. Phys. Chem. Ref. Data* **19**:371 (1990).
15. K. Heger, M. Uematsu, and E. U. Franck, *Ber. Bunsenges. Phys. Chem.* **84**:758 (1980).
16. H. J. C. Berendsen, J. R. Grigera, and T. P. Straatsma, *J. Phys. Chem.* **91**:6269 (1990).