SOLVATION IN SUPERCRITICAL WATER

H. D. Cochran
Oak Ridge National Laboratory
P. O. Box 2008
Oak Ridge, TN 37831-6224

P. T. Cummings and S. Karaborni
Department of Chemical Engineering
University of Virginia
Charlottesville, VA 22901

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ABSTRACT

The aim of this work is to determine the solvation structure in supercritical water compared with that in ambient water and in simple supercritical solvents. Molecular dynamics studies have been undertaken of systems that model ionic sodium and chloride, atomic argon, and molecular methanol in supercritical aqueous solutions using the simple point charge model of Berendsen for water. Because of the strong interactions between water and ions, ionic solutes are strongly attractive in supercritical water, forming large clusters of water molecules around each ion. Methanol is found to be a weakly-attractive solute in supercritical water. The cluster of excess water molecules surrounding a dissolved ion or polar molecule in supercritical aqueous solutions is comparable to the solvent clusters surrounding attractive solutes in simple supercritical fluids. Likewise, the deficit of water molecules surrounding a dissolved argon atom in supercritical aqueous solutions is comparable to that surrounding repulsive solutes in simple supercritical fluids. The number of hydrogen bonds per water molecule in supercritical water was found to be about one third the number in ambient water. The number of hydrogen bonds per water molecule surrounding a central particle in supercritical water was only mildly affected by the identity of the central particle—atom, molecule, or ion. These results should be helpful in developing a qualitative understanding of important processes that occur in supercritical water.

1. INTRODUCTION

Supercritical (SC) water has been proposed as a solvent or a reaction medium for a number of technological applications and is also important in power systems using SC steam cycles and in some geochemical processes. The technological applications in which SC water is considered as a solvent and/or reac-

fluids. Likewise, the deficit of water molecules surrounding a dissolved argon atom in supercritical aqueous solutions is comparable to that surrounding repulsive solutes in simple supercritical fluids. The number of hydrogen bonds per water molecule in supercritical water was found to be about one third the number in ambient water. The number of hydrogen bonds per water molecule surrounding a central particle in supercritical water was only mildly affected by the identity of the central particle—atom, molecule, or ion. These results should be helpful in developing a qualitative understanding of important processes that occur in supercritical water.

1. INTRODUCTION

Supercritical (SC) water has been proposed as a solvent or a reaction medium for a number of technological applications and is also important in power systems using SC steam cycles and in some geochemical processes. The technological applications in which SC water is considered as a solvent and/or reaction medium include destructive oxidation of hazardous wastes (Modell *et al.* 1982, Thomason and Modell 1984, Staszak *et al.* 1987); conversion of coal (Modell *et al.* 1978, Penninger 1985); and production of chemicals (Narayan and Antal 1989). Huang *et al.* (1989a,b) consider the technologically important corrosion processes of alloys in SC water.

By way of motivation, let us consider just one of the potentially important new technological applications of SC water—oxidation of hazardous wastes. Wibley and Tester (1989) found that the detailed oxidation kinetics of methanol in SC water could not be explained by accepted gas-phase elementary kinetic models corrected for high pressure. They speculated that clustering of the SC water molecules about reactant molecules might contribute to the unusual kinetic behavior. Penninger (1985) and Narayan and Antal (1989) concluded that ionic species (despite the relatively low degree of dissociation in SC water) play important roles in catalyzing some reactions that occur in SC water. We suggest that fundamental understanding of some of these technologically important applications of SC water might be substantially improved through understanding the solvation structures around solutes dissolved in SC water. For example, we believe that some solutes in SC water will be surrounded by local clusters of water molecules and that others will be surrounded by local regions of low water density. Most solutes will tend to aggregate with themselves and with one another. Obviously, if these speculations are accurate, pressure-corrected gas-phase kinetic models (based on the premise of uniform, random molecular distributions) cannot be accurate. Improved fundamental understanding may lead to improved processes or to solution of unanticipated future problems.

Through advances in both experiment and theory there has developed a greatly improved understanding of the structure and properties of solutions in simple solvents at SC conditions. It is now understood (*e.g.* Cochran and Lee 1989) that the striking properties of dilute solutions of relatively large solute molecules near the critical point (CP) of a simple SC solvent result from the formation of massive clusters of solvent molecules around these "attractive" solutes. Large numbers of excess solvent molecules (in comparison to the bulk average density) clustering around each solute molecule give rise to very large, negative values of the solute partial molar volume, rapid increase in the solubility, *etc.* as the CP is approached. In the unusual case of a small solute molecule in dilute solution in a relatively large SC solvent, regions of solvent deficit (again in comparison to the bulk average density) surround these "repulsive" solutes. The large, positive partial molar volumes of solutes such as argon, ethylene, and xenon in SC water (Biggerstaff and Wood 1988) provide dramatic evidence of the practical reality of such repulsive SC solutions.

Wheeler (1972) gave the first theoretical description of the behavior of dilute solutions near the CP of the solvent, and more recently, Kim and Johnston (1987) and Debenedetti (1987) presented molecular thermodynamic descriptions of clustering in SC solutions. Cochran, *et al.* (1988), Cochran and Lee (1989), Wu *et al.* (1990), and Cochran *et al.* (1990) have presented a thorough description of these structures at the level of molecular physics for solutions in simple SC fluids. An additional structural feature in dilute SC solutions found by Cochran and co-workers is the strong aggregation of solute molecules with one another. This behavior has been observed experimentally by Brennecke and Eckert (1989) and undoubtedly has important practical consequences, for example, in chemical reactions.

Likewise, there has developed a detailed understanding of the structure and properties of aqueous solutions at ambient conditions. In the pure state, ambient water is known (*e.g.*, Rossky 1985, Beveridge, *et al.* 1983, Franks 1979) to consist of a hydrogen-bonded network within which virtually all water molecules are hydrogen-bonded to other water molecules. The structure is distorted from the regular, tetrahedral array in ice I by the dynamics of bond bending and rotation in the liquid, so that orientational order persists only for two or three molecular diameters. Around a nonpolar solute ambient water molecules tend to maintain their hydrogen-bonded structure, the water molecules orienting so that the $\text{O} \cdots \text{H} - \text{O}$ groups straddle the weakly interacting nonpolar solute surface and maintain the degree of hydrogen-bonding available in the bulk (Rossky 1985). Polar solutes such as methanol can participate in the hydrogen-bonding network of ambient water. Around multifunctional solute molecules the solvation structure associated with each functional group is not qualitatively perturbed by the presence of other groups even in close proximity. In contrast, the strength of charge-dipole interactions is so strong that ionic solutes disrupt the hydrogen-bonding structure of ambient water and

simple SC fluids. An additional structural feature in dilute SC solutions found by Cochran and co-workers is the strong aggregation of solute molecules with one another. This behavior has been observed experimentally by Brennecke and Eckert (1989) and undoubtedly has important practical consequences, for example, in chemical reactions.

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We have sought to gain improved understanding of the solvation structures around solutes in SC water using molecular dynamics simulation of model solute particles in SC water; the solutes we have modeled so far include ionic Na⁺ and Cl⁻, atomic argon, and molecular methanol. Calculations were performed by the molecular dynamics technique in the canonical, isokinetic ensemble using a fourth order Gear predictor-corrector algorithm. The details have been presented by Cummings *et al.* (1990). Water interactions were modeled by the simple point charge (SPC) model of Berendsen *et al.* (1981) which consists of a spherical Lennard-Jones (LJ) potential centered on the oxygen atom with partial point charges located so as to result in good prediction of the properties and structure of ambient water. Ionic Na⁺ and Cl⁻ have been modeled as LJ spheres with central unit charges (Pettitt and Rossky 1986). Atomic Ar has been modeled as an LJ sphere (Straatsma *et al.* 1986). For molecular methanol in water we have used Haughney's H1 potential (Haughney *et al.* 1986). Details of these potential models and the potential parameters used are given by Cummings *et al.* (1990).

Long-range interactions have been handled by the reaction field technique (Neumann and Steinhäuser 1980). The simulations were performed with single solute particles in a bath of 215, 255, or 863 solvent particles, depending on the state. The time step was 1 fs, the equilibration time was 15 ps, and the simulation time was 30 or 45 ps. Calculations for each case took 3 to >12 CPU-hrs on the Oak Ridge Cray.

The calculation method was successfully tested by calculating thermodynamic and dielectric properties of ambient water. Calculations of the thermodynamic and dielectric properties of pure SC water at $T_r = 1.00$ and $\rho_r = 1.50$, the dense SC state, and at $T_r = 1.05$ and $\rho_r = 1.00$, the near-critical SC state, (Cummings *et al.* 1990, Cummings *et al.* 1991) demonstrated the remarkable accuracy of the SPC model even for SC states.

2. RESULTS AND DISCUSSION

Figure 1 presents the calculated g_{cc} (the centers pair correlation function) at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$ for water particles surrounding water, sodium, and chloride particles; Figure 2 presents similar results (but note the expanded y-axis) for water particles surrounding water, methanol, and argon particles. The strong charge-dipole interaction makes each ion a strongly attractive solute in supercritical water. The weaker dipole-dipole and Lennard-Jones interactions make the methanol a weakly-attractive solute and argon a repulsive solute in supercritical water.

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Figures 3 and 4 present the calculated number of excess (in comparison to the bulk average) water particles within a sphere of radius R surrounding the central particle for the same systems as above. The equation defining this excess number of surrounding water molecules is

$$N(R) = \rho \int_0^R 4\pi r^2 [g_{cc}(r) - 1] dr$$

where ρ is the water number density.

Again, one can clearly perceive that the Na^+ ion is a strongly attractive solute. The first solvation shell is distinct (containing about 4 excess water molecules), and the cluster contains at least 26 excess water molecules in all. The sodium-water centers correlation function shows that in the shell of nearest neighbors surrounding a Na^+ ion in SC water the local water density is about 20 times the bulk water density. When adjusted for density, however, the number of water molecules represented by the first maximum is the same as that observed in ambient water (Pettitt and Rossky 1986, Figure 1).

The Cl^- ion, in comparison is also strongly attractive. The first solvation shell contains about 4 excess water molecules, and the total cluster contains about 20 excess water molecules. The local water density in the first solvation shell around a Cl^- ion is about 10 times the bulk density. Again, when adjusted for density, the first maximum is the same as observed in ambient water (Pettitt and Rossky 1986, Figure 2).

Figure 3. Number of excess water particles surrounding a central water, sodium, and chloride particle at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$

Figure 4. Number of excess water particles surrounding a central water, argon, and methanol particle at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$

Because the system is at a reduced temperature of 1.05 (still relatively far from the CP) the cluster is not large. An attractive LJ solute in an LJ solvent at the same reduced temperature and density is surrounded by a comparable number of excess solvent molecules (Cochran and Lee 1989, Figure 4). The decrease in

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Because the system is at a reduced temperature of 1.05 (still relatively far from the CP) the cluster is not large. An attractive LJ solute in an LJ solvent at the same reduced temperature and density is surrounded by a comparable number of excess solvent molecules (Cochran and Lee 1989, Figure 4). The decrease in the number of excess water molecules after the maximum at about $R=3$ is an artifact of the canonical ensemble in a finite simulation cell; if there is an excess local density near the solute, a constant N and V system must have a deficit in local density distant from the solute by conservation of mass.

The local water density around a methanol molecule in SC water was found to be relatively small. At the near-critical state, the first maximum in the methanol-water centers distribution function (Figure 2) is about 1.5 compared, for example, with 2.7 for the water-water centers distribution function and about 23 for the sodium-water centers distribution function at this state. We speculate that dilute methanol in water at this state may behave as a weakly-attractive solute in the sense of Debenedetti and Mohamed (1989). That is, while there may be a small excess rather than a deficit of water molecules surrounding a dilute methanol molecule at this state (Figure 4), we might expect the infinite dilution partial molar volume of methanol in water to become large and positive at this state.

Unlike ionic solutes and the polar methanol solute, which behave as attractive and weakly-attractive solutes, respectively, in SC water, the argon atom clearly behaves as a repulsive solute. There is a deficit of about 3 water molecules surrounding an argon atom at the near-critical state. In Figure 2, it is striking that the first maximum in the centers correlation function for argon in SC water does not exceed unity; in contrast, simulation results (Tani 1983) and scattering results (Narten and Levy 1971, Thiessen and Narten 1982) for argon in ambient water show a first maximum equal to 2.0, a minimum of 0.8 and a small second maximum.

Similar results to those in Figures 1-4 but at $T_r = T/T_c = 1.00$ and $\rho_r = \rho/\rho_c = 1.50$ will be presented elsewhere (Cochran *et al.* 1991).

In contrast to simple solvents, water can exert strongly directional forces on neighboring molecules and exhibits extended hydrogen-bonded, network structures at ambient conditions. We have examined the degree to which water particles participate in hydrogen-bonding as a function of distance from a central (sodium, chloride, water, methanol, or argon) particle at supercritical conditions. The criterion for deciding whether a neighboring pair of water particles is or is not hydrogen-bonded is essentially arbitrary; however, prior study (Beveridge, *et al.* 1983, Rossky and Hirata, 1983) shows that results from geometric and energetic criteria are qualitatively consistent for ambient, pure water. We have employed the minimal geometric criterion of Beveridge, *et al.* (1983) to count, as a function of distance from a central particle, the number of hydrogen-bonds per water particle. The results are shown in Figures 5 and 6 at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$.

Figure 5. Number of hydrogen-bonds per water particle surrounding a central water particle at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$ and at ambient conditions.

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Figure 6. Number of hydrogen-bonds per water particle surrounding a central particle at $T_r = T/T_c = 1.05$ and $\rho_r = \rho/\rho_c = 1.00$

Figure 5 shows that at ambient conditions the number of hydrogen-bonds per water molecule surrounding a central water approaches about 2.3. We suspect that a less rigid criterion defining a hydrogen-bond might show the number to be closer to 4.0 but with distorted bond angles. In contrast, at supercritical conditions, the number of hydrogen-bonds per water molecule surrounding a central water is about 0.8. The decreased extent of hydrogen-bonding at supercritical conditions might result from both the lower density of water molecules and the greater kinetic energy of water molecules at supercritical temperature. Qualitatively, the observed result is consistent with the decreased dielectric constant of supercritical water compared with that of ambient water.

Figure 6 shows that the number of hydrogen-bonds per water molecule surrounding a central particle at supercritical conditions is only weakly affected by the identity of the central particle whether the central particle is a water or methanol molecule, a sodium or chloride ion, or an argon atom. This behavior is in contrast to that found surrounding solutes in ambient water. However, the relatively constant number of hydrogen-bonds per water molecule does not imply that the absolute number of hydrogen-bonds in water surrounding a central particle is relatively constant; recall the dramatic differences in local water density surrounding the different solutes shown in Figures 1 and 2. That the

number of hydrogen-bonds per water molecule in SC water is relatively unaffected by the identity of the central particle, despite the large differences in local water density around the different central particles, suggests that the high temperature of the SC systems is the key factor in the hydrogen-bonding. This would be consistent with the the observed dramatic increase in the rate of rotational relaxation of water with increasing temperature at constant density (Gordon and Goldman, 1989).

Similar results to those in Figures 5 and 6 but at $T_r = T/T_c = 1.00$ and $\rho_r = \rho/\rho_c = 1.50$ and more quantitative comparison at supercritical and ambient conditions of the effect of solutes on hydrogen-bonding will be presented elsewhere (Cochran *et al.* 1991b).

3. CONCLUDING REMARKS

We have used molecular dynamics calculations to explore the solvation structures which may be expected to surround solutes in SC water. Like solutions in simple SC fluids, SC aqueous solutions may exhibit long-range structure around a solute molecule characteristic of attractive, weakly-attractive, or repulsive interactions. In this sense, ions in SC water are strongly attractive solutes, methanol is weakly-attractive, and argon is a repulsive solute. The local water density is increased around attractive and weakly-attractive solutes and is reduced around repulsive solutes.

At close-range the solvation structures in SC water exhibit local water density and hydrogen-bonded structures different from solvation in ambient water. The strong interactions of water with dissolved ions within the longer-range water cluster create around the ion a local environment of very high water density. The local structure surrounding a dissolved methanol molecule is similar to that surrounding a water molecule in SC water. Around an argon atom in SC water the local density of water molecules is depressed from that of bulk SC water, to substantially lower local density than in the case of of ambient water. The number of hydrogen-bonds per water molecule surrounding a central particle in supercritical water is about one third the number observed in pure ambient water regardless of the identity of the central particle whether it was a water or methanol molecule, a sodium or chloride ion, or an argon atom. This hydrogen-bonding structure in supercritical water contrasts with the behavior found in ambient water.

We conclude from the results in Figures 1-4 that attractive solutes in SC water are surrounded by local regions of excess solvent density even at states substantially removed from the CP. These results are qualitatively the same as those seen for simple SC solvents and extensively explored in the prior work reviewed above. By extension, we might expect also to witness local solute-solute aggregation as has been seen for simple SC solvents, but this question could not be explored in the limited scope of the present work. Repulsive solutes in SC water, we conclude, are surrounded by local regions depleted in

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For simple SC fluids it has been possible to characterize, at a molecular level, what relative size and energy parameters will make a solute attractive or repulsive in a given solvent (Cochran and Johnson 1991), but this is not yet possible for solutes in SC water. Additional work is needed to answer this important question. Equally important for modeling reactions in SC water, following on the motivational remarks in the Introduction, is developing useful interaction models for reacting species (*e.g.*, free radicals) with SPC water. The complicated coupling between the electron density of the reactive species and the local water density fluctuations in the surrounding SC medium is will be challenging to model. We do not expect that pressure-corrected gas-phase kinetic models would be particularly successful in describing reactions in SC water inasmuch as some reacting species are likely to be found in a more liquid-like local environment if they are attractive solutes. Repulsive solutes would be surrounded by a local environment depleted in solvent but enriched in some solute species compared with the bulk average composition. Extending gas- or liquid-phase kinetic models to SC reaction systems appears to be fraught with danger and may prove impossible; an approach based on corrections for local water density for individual species might prove fruitful.

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