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Solvation Structure, Hydrogen Bonding, and Ion Pairing in Dilute Supercritical Aqueous NaCl Mixtures[1]

A. A. Chialvo,[2,3] P. T. Cummings,[2-4] and H. D. Cochran[2,3]

We review molecular dynamics simulations of infinitely dilute supercritical aqueous NaCl solutions to determine the solvation structure and the solute-induced effect on water–water hydrogen bonding and report new simulation results on the extent of the ion pairing. Our simulation studies indicate that Na^+ and Cl^- ions as a pair or as isolated infinitely dilute ions form strong solvation structures in SCW, even though the water–water hydrogen bonding is not affected. Within the context of the models we are using, there is strong indication of a high degree of Na^+/Cl^- ion pairing.

KEY WORDS: aqueous solutions; hydrogen bonding; ion pairing; molecular simulation; solute-induced effects; solvation; supercritical water.

1. INTRODUCTION

Supercritical water (SCW) is an attractive solvent and reaction medium for destructive oxidation of hazardous wastes [1,2], a process known as supercritical water oxidation (SCWO). The small dielectric [3] and ionic dissociation constants [4] of SCW make it possible for nonpolar compounds to be highly soluble in SCW, while polar and ionic compounds become barely soluble. The observed behavior indicates that the solvation of solutes in SCW differs markedly from that in water at ambient conditions and, therefore, requires a reexamination of the solvation phenomenon.

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[2] Department of Chemical Engineering, University of Tennessee, Knoxville, Tennessee 37996-2200, U.S.A.

[3] Chemical Technology Division, Oak Ridge National Laboratory, Oak Ridge, Tennessee 37831-6268, U.S.A.

[4] To whom correspondence should be addressed.

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Molecular-based simulations of aqueous solutions can substantially improve our understanding of the solvation mechanism in SCW and, consequently, help in the development of macroscopic correlations. For example, based on molecular-based simulation and theoretical results, we have pointed out that some solutes in SCW enhance the local water density around them and that others deplete it [5–8]. Obviously, if this interpretation stands, pressure-corrected-gas-phase kinetic models (based on the premise of uniform, random molecular distributions) are potentially inaccurate because they do not account for solute-induced local effects.

In this paper we focus on the short-range structure of SCW around the individual ions forming NaCl and the differences between the short-range behavior of the radial distribution functions $g_{\mathrm{UV}}(r)$ and $g_{\mathrm{VV}}(r)$ (where the subscripts UV and VV denote $\underline{\mathrm{u}}$te–sol$\underline{\mathrm{v}}$ent and sol$\underline{\mathrm{v}}$ent–sol$\underline{\mathrm{v}}$ent quantities) in terms of the excess number of solvent molecules surrounding either ion, $N^{\mathrm{ex}}(R)$, i.e.,

$$N^{\mathrm{ex}}(R) = 4\pi\rho_{\mathrm{V}} \int_0^R \left[g_{\mathrm{UV}}(r) - g_{\mathrm{VV}}(r)\right] r^2\, dr \tag{1}$$

which measures the excess of solvent molecules over what would be obtained if the ion were a solvent molecule. The sign of $N^{\mathrm{ex}}(R \to \infty) \equiv N^{\mathrm{ex}}$ is intimately connected to the sign of the solute partial molar volume at infinite dilution, $\bar{v}_{\mathrm{U}}^{\infty}$, since for an infinitely dilute solution [9]

$$N^{\mathrm{ex}} = -\kappa_{\mathrm{T}} \left(\frac{\partial P}{\partial x_{\mathrm{U}}}\right)_{T,\rho_{\mathrm{V}}}^{\infty} = 1 - \rho_{\mathrm{V}} \bar{v}_{\mathrm{U}}^{\infty} \tag{2}$$

where ρ_{V} is the density of the pure solvent, κ_{T} the isothermal compressibility of the solvent, P is the pressure, and x_{U} the mole fraction of the solute. We also study the hydrogen bonding in the solvent as a function of the distance from each ion to determine the extent to which the ions affect hydrogen bonding. Finally, we analyze the ion pairing at the state condition closest to the critical point of water.

2. INTERMOLECULAR POTENTIALS AND SIMULATION METHOD

The Newton–Euler equations of motion for the water molecules were integrated using a Gear's fourth-order predictor–corrector algorithm [10]. For the case of potential of mean-force calculations, the corresponding constrained equations of motion for the ion pair were integrated by means of a velocity Verlet algorithm, coupled to the analytic solution of the constraint via the method proposed by Palmer [11]. All simulations were performed in the canonical-isokinetic (NVT) ensemble, via a Gaussian thermostat, with $N = 256$ molecules ($N - 2$ water molecules plus an anion and a cation), the standard periodic boundary conditions, the minimum image criterion, and a spherical cutoff for the truncated intermolecular interactions [12]. Production runs for the mean-force calculations were extended to 10^5 time steps each, with constrained pair distances ranging from 1.5 to 9.9 Å, with increments of 0.2 Å. The thermodynamic properties as well as the anion–cation mean force $\Delta F(r)$ were evaluated by partitioning the run into 10 independent subruns from which averages and estimated standard deviation were obtained. Additional simulation details are given in Ref. 6.

SCW was described by the SPC model [13], which, based on our previous work [8,14], yields dielectric and thermodynamic properties for ambient and supercritical water in good agreement with experimental values. The ion–water interactions were described by the Pettitt and Rossky model [15], and the ion–ion interactions by the Fumi–Tosi model [16] (see Refs. 6–8 for more detail). The two state conditions studied were the same as those in our previous work, i.e., state 1, given by $\rho = 0.405\ \mathrm{g \cdot cm^{-3}}$ and $T = 587$ K, and state 2, given by $\rho = 0.27\ \mathrm{g \cdot cm^{-3}}$ and $T = 616$ K, corresponding, respectively, to ($T_r = 1$, $\rho_r = 1.5$) and ($T_r = 1.05$, $\rho_r = 1$). These reduced parameters are in terms of the critical point of pure SPC water.

2.1. Hydrogen Bonding

Here, as in our previous work [6–8], we used the minimal geometric criterion given by Beveridge et al. [17] to study the radial dependence of the number of neighboring water molecules which are H-bonded to a central water molecule, i.e., we report the average number of water molecules to which a water molecule located a distance r from a central molecule (either solvent or solute) is hydrogen bonded (see Ref. 6 for more detail).

2.2. Ion Pairing

Mean-force calculations were performed applying the method of constrains proposed by Ciccotti et al. [18]. The forces on each ion due to the ion–solvent interactions, i.e., $\mathbf{F}_{WA}$ and $\mathbf{F}_{WC}$, where WA and WC denote water–anion and water–cation, are determined directly during the simulation. Their contribution to the anion–cation mean force is the time average,

$$\Delta F(r) = 0.5 \langle \hat{r}_{AC} \cdot (\mathbf{F}_{WA} - \mathbf{F}_{WC}) \rangle \tag{3}$$

where $\hat{r}_{AC}$ is the unit vector along the direction of the anion–cation interactions. The total anion–cation mean force is given by

$$\begin{aligned} F(r) &\equiv -\frac{dW(r)}{dr} \\ &= F^{d}_{AC}(r) + \Delta F(r) \end{aligned} \tag{4}$$

where $F^{d}_{AC}(r)$ is the contributions of the direct anion–cation Coulombic and non-Coulombic interactions, and $W(r)$ is the potential of mean force, which is related to the anion–cation radial distribution function $g_{AC}(r)$,

$$W(r) = -kT \ln g_{AC}(r) \tag{5}$$

The potential of mean force is finally obtained by numerical integration of Eq. (4), i.e.,

$$W(r) = W(r_0) - \int_{r_0}^{r} F(r)\,dr \tag{6}$$

where we choose $r_0 \approx 8.1$ Å so that $W(r_0) \approx (q_A q_C/\varepsilon r_0)$ and ε is the dielectric constant of the pure SPC water as obtained by simulation at the same state conditions [8]. This procedure was recently used by Cui and Harris to study the behavior of NaCl aqueous solutions at supercritical conditions similar to those in the SCWO process [19].

3. SIMULATION RESULTS FOR SCW SOLUTIONS

The thermodynamic properties for the Na^+/Cl^- ion pair in supercritical water [6] are presented in Table I, along with the corresponding results for the isolated Na^+ion, Cl^-ion, and pure water [8]. (Note that these results were obtained in simulations in which the ion pair distance was unconstrained.) In contrast to the case of ions, which had a large effect on the pressure, the Na^+/Cl^- ion pair in supercritical water resulted in a small but noticeable decrease in pressure. Neither the ion pair nor the isolated ions show a large effect on the configurational internal energy.

The comparison between the structure of water around the Na^+ ion and the Cl^- ion indicates that the size of the first peak in the Na^+–water radial distribution function in the system Na^+/Cl^-–water is slightly reduced from that for the Na^+–water system (the isolated ion in water). Similary, the size of the first peak in the Cl^-–water radial distribution function in the system Na^+/Cl^-–water is reduced by about half from that for the Cl^-–water system (the isolated ion in water). This is shown in Figs. 1 and 2, where the Na^+–water and Cl^-–water radial distributions

Table I. Thermodynamic Properties of Infinitely Dilute NaCl–Water Solutions from Ref. 6[a]

System	Stat e	U_{conf} (kcal · gmol^{-1})[b]	U_{WW} (kcal · gmol^{-1})[c]	U_{NaW} (kcal · gmol^{-1})[d]	U_{ClW} (kcal · gmol^{-1})[d]	U_{NaCl} (kcal · gmol^{-1})[e]	P (atm)
NaCl–water	1	−5.77 ± 0.06	−4.62 ± 0.06	−175.3 ± 2.9	−119.4 ± 5.5	−96 ± 3	124 ± 20
Na^+–water[f]	1	−5.55 ± 0.08	−4.57	−216.3	—	—	−107 ± 50
Cl^-–water[f]	1	−5.54 ± 0.08	−4.67	—	−189.8	—	660 ± 50
Pure water[f]	1	−4.99 ± 0.07	−4.99 ± 0.07	—	—	—	185 ± 40
NaCl–water	2	−4.76 ± 0.08	−3.66 ± 0.04	−171.3 ± 5.5	−109.4 ± 5.1	−89 ± 3	170 ± 27
Na^+–water[f]	2	−4.53 ± 0.13	−3.68 ± 0.04	−220.6 ± 0.8	—	—	103 ± 7
Cl^-–water[f]	2	−4.41 ± 0.09	−3.71 ± 0.02	—	−182.4 ± 0.9	—	417 ± 30
Pure water[f]	2	−4.02 ± 0.09	−4.02 ± 0.09	—	—	—	205 ± 12

[a] Also given, for comparison, are the results from the simulations presented earlier [8] for pure water and Na^+ and Cl^- ions at infinite dilution in supercritical water.

[b] Per gmol of solution.

[c] Per gmol of water.

[d] Per gmol of ion.

[e] Per gmol of salt.

[f] From Ref. 8.

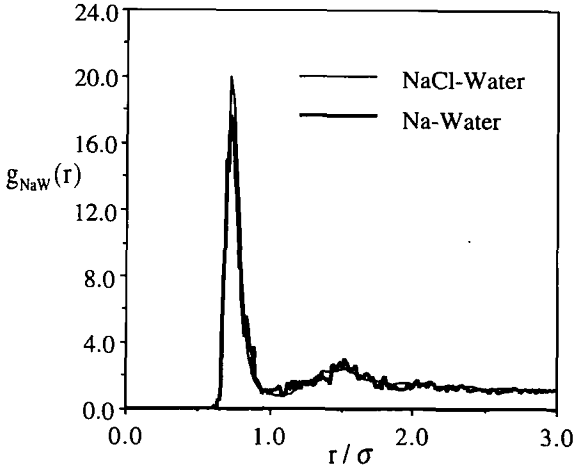

Fig. 1. Comparison between the sodium–water radial distribution function, $g_{UV}(r)$, for Na^+/Cl^- at infinite dilution in SPC water with the corresponding result for isolated Na^+ at infinite dilution, both at state 2. Distances are expressed in units of the water molecule diameter, $\sigma = 3.16$ Å.

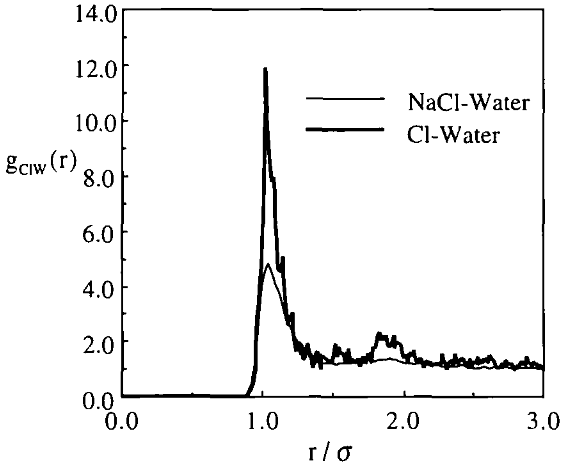

Fig. 2. Comparison between the chloride–water radial distribution function, $g_{UV}(r)$, for Na^+/Cl^- at infinite dilution in SPC water with the corresponding result for isolated Cl^- at infinite dilution, both at state 2. Distances are expressed in units of the water molecule diameter, $\sigma = 3.16$ Å.

functions, respectively, at state 2 calculated for a Na^+/Cl^- pair at infinite dilution are compared to the same quantities obtained from simulations of isolated ions at infinite dilution.

The origin of this reduction in the local density of water molecules surrounding the Cl^-ion in the case of the ion pair in comparison to the isolated ion result is not clear. One possible explanation may be the stronger ion–dipole force between Na^+ and water compared with that between Cl^- and water, brought about by the smaller size of the Na^+ion permitting closer approach of water molecules to Na^+. Thus, in the ion-pair case, the stronger Na^+/water attraction may result in a local environment around the Na^+ which is not very different from the isolated Na^+ case. From the size of the first peaks it is clear that the first nearest neighbors surrounding ionic solutes in supercritical water are highly localized and that the water molecules solvate the smaller Na^+ion more effectively. Consequently, the number of excess water molecules surrounding the Na^+ and Cl^-ions in the infinitely dilute ionic solution is positive for both cases, indicating that both Na^+ and Cl^- act as nonvolatile solutes in supercritical water at both states. Results for the hydrogen bonding around the Na^+ and Cl^- and other solutes (such as noble gases, methanol, and aromatic compounds) as a function of distance have been presented in detail elsewhere [6,8]. Here we simply quote the main conclusion: the identity of the solute appears to have little effect on the degree of H bonding in water molecules surrounding the solute. Thus, in particular, the ionic solutes do not appear to have a significant effect on the degree of hydrogen bonding.

Recent neutron scattering results [20] have suggested that the SPC model may overestimate the degree of hydrogen bonding in supercritical water. This criticism is based on measuring hydrogen bonding solely by the magnitude of the first peak in the oxygen–hydrogen pair correlation function. In contrast, we indicated that the geometry of the two molecules involved in the hydrogen bond must be taken into account, i.e., the angle-averaged pair correlation function may not provide a complete picture of the extent of the hydrogen bonding. We have adressed this issue in a recent paper [21] and concluded that a simple modification of the SPC model, one in which the Coulombic charges are scaled to match the gas phase dipole moment of water, can predict the neutron scattering results quite accurately. The rationale behind this scaling hinges upon the fact that the polarizability effects present at ambient (liquid-like) conditions, giving rise to a high effective dipole moment, are negligible at supercritical (gas-like) conditions (see Ref. 21 for details). However, the neutron scattering results await independent experimental confirmation and the resolution of some questions about the accuracy of the results.

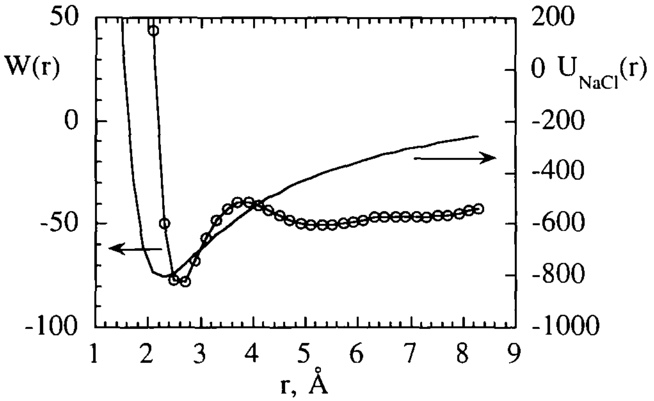

Fig. 3. Potential of mean force (left vertical axis) and bare interionic potential (right vertical axis) for the pair Na^+/Cl^- separated by a distance r at infinite dilution in SPC water at state 2. The energy values are reduced by the characteristic non-Coulombic interaction energy of the SPC water molecule, 1.08×10^{-14} erg per molecule.

The potential of mean force for state condition 2, displayed in Fig. 3, shows a deep minimum shifted ~0.3 Å to the right from the minimum of the solute–solute potential. This suggests that, for the chosen potential models, the Na^+/Cl^- ions are paired rather strongly at this near-critical, low-dielectric condition. Note that $W(r)$ shows also a very shallow minimum at $r \sim 5$ Å, which might be considered an intermediate behavior between the change of curvature found in this location by Cui and Harris for the same system at 700 K and 0.125 $g \cdot cm^{-3}$ (see Fig. 4 of Ref. 19) and the deeper minimum observed by Guardía et al. at ambient conditions (see Fig. 4 of Ref. 22). At ambient conditions, the potential of mean force shows two minima separated by a positive barrier, with the minimum at $r \sim 5$ Å deeper than the one coincident with the minimum of the Na–Cl potential, which is the signature of solvent-separated ion pairs [22].

4. CONCLUDING REMARKS

The solvation structures of ionic solutes (Na^+, Cl^-, and Na^+/Cl^-) in SCW indicate an enhancement of the local water density (first solvation shell) with respect to that for the pure water (ideal solution), i.e., a very strong solute solvation. This is macroscopically manifested as a negative value of the derivative $(\partial P/\partial x_U)^{\infty}_{T,\rho_v}$, or a decrease in the total pressure consistent with the idea of nonvolatile solutes, and the experimental evidence for NaCl in SCW [23]. As we noted from our previous studies

[6,8], the identity of a solute particle has little if any effect on the degree of hydrogen bonding among the surrounding water molecules at both the near-critical and the high-density supercritical states. Moreover, according to the potential-of-mean-force calculation, the chosen ion–ion and ion–water potentials predict the formation of Na^+/Cl^- ion pairing in near-critical SPC water. Similar conclusions were recently obtained by Gao [24] via a statistical perturbation approach for the system TIP4P–water with OPLS potentials for Na^+/Cl^-.

We conclude by noting that we have used the term "infinitely dilute" to describe our simulation, but in reality the solute is not at perfect infinite dilution. The mole fraction of salt is $\approx 4 \times 10^{-3}$; however, since there is only one ion pair in the periodically replicated simulation mixture, there are no anion–anion or cation–cation interactions. To obtain true infinite dilution properties from simulation would require a series of simulations at decreasing mole fractions of NaCl extrapolated to infinite dilution. Such simulations are under way in our group using the massively parallel computing facilities now available to us through Oak Ridge National Laboratory.

NOTE ADDED IN PROOF

A detailed study of the extent of pair association at near critical conditions has been presented elsewhere [25].

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