Supercritical Hydration of Organic Compounds. The Potential of Mean Force for Benzene Dimer in Supercritical Water

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Abstract: The diminishing hydrophobic effect in supercritical water has been examined through Monte Carlo simulations. The free energy profile was obtained for the association of the benzene dimer in supercritical water at 400 °C and 350 atm via statistical perturbation theory. In this report, it is first demonstrated that the TIP4P model can provide an adequate description of supercritical water in these simulations. Then, comparison is made with previous results for the benzene dimer in liquid benzene and ambient water at 25 °C and 1 atm. The results indicate that there is no hydrophobic enhancement of binding between benzene molecules in supercritical water with a much weaker association constant than that in ambient aqueous solution. Analysis of the computed potential of mean force suggests that solvent molecules do not form stable clusters near the solute. However, solvent–solvent clustering appears to be widespread. These findings provide the basis for further characterization of the supercritical hydration of organic compounds and modeling of reaction mechanisms in supercritical fluids.

In the past decade, supercritical fluids have emerged as an important medium for carrying out chemical reactions and have attracted numerous experimental studies.[1] The progress is especially impressive in the area of toxic waste destruction.[1,2] The industrial interest is stimulated by the observation that organic materials are oxidized in supercritical water (SCW) to yield primarily simple, environmentally clean products such as water, carbon dioxide, and other small molecules.[3] However, little is known about the reaction mechanism and the molecular picture of solvation under supercritical conditions. A remarkable property of SCW that accompanies it smaller dielectric constant at elevated temperatures is its ability to solvate nonpolar organic compounds.[4a] For example, above 350 °C and 250 atm, organic materials such as benzene and hydrocarbons and oxygen are completely miscible with water.[4] Consequently, oxidation processes can occur in a homogeneous phase. Another important issue in supercritical solvation is the extent of solvent clustering near the solute molecule.[5] In nonpolar supercritical fluids, enhanced solvent clustering has been noted from spectroscopic studies,[5,6] whereas a dynamic picture of the solute–solvent interaction appears to dominate in supercritical aqueous media.[1,5,7]

The present study examines the origin of the diminishing hydrophobic effect of organic molecules in SCW by computing the potential of mean force for a benzene dimer as a prototypical model in Monte Carlo simulations. Analysis of the theoretical results yields valuable insights on solute–solvent interactions in supercritical water.

Supercritical Fluid Water

The computation procedure follows previous work on aqueous solvation and chemical reactions with the BOSS program.[8,9] As usual, the critical issue in fluid simulations is the intermolecular potential functions. Well-proven potentials for benzene are available;[10,11] the 12-site model developed by Jorgensen and Severance was adopted along with the TIP4P potential for water in the present study.[10,12] Since the TIP4P model was developed to reproduce pure liquid properties at the ambient conditions, i.e., 25 °C and 1 atm,[12] it is important to verify that it is also appropriate to describe the properties of SCW. Consequently, five Monte Carlo simulations were carried out for a cubic cell consisting of 260 water monomers at 400 °C and pressures of 350, 500, 700, 1000, and 2000 atm. The isothermal–isobaric (NPT) ensemble is used along with periodic boundary conditions. The cutoff distances employed in these calculations are about one-half of the edge of the unit cell, ranging from 11 to 14 Å. In each case, at least 5×10^6 configurations were discarded for equilibration, followed by an additional 15×10^6 configurations of averaging. These long simulations are needed to provide adequate sampling of the dielectric relaxation to evaluate the fluid dielectric constant.[13]

The computed thermodynamic results along with the experimental data are listed in Table I. It should be noted that at the simulation conditions the fluid density changes significantly with small variations in temperature or pressure.[14] Furthermore, the

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[1] (a) Paulaitis, M. E.; Krukonis, V. J.; Kurnik, R. T.; Reid, R. C. *Rev. Chem. Eng.* **1983**, *1*, 179. (b) Bright, F. V., McNally, M. E. P., Eds. *Supercritical Fluid Technology: Theoretical and Applied Approaches in Analytical Chemistry*; ACS Symp. Ser. 488; American Chemical Society: Washington, DC, 1992. (c) Shaw, R. W.; Brill, T. B.; Clifford, A. A.; Eckert, C. A.; Franck, E. U. Supercritical Water, a Medium for Chemistry, *Chem. Eng. News* **1991**, *69(51)*, 26.

[2] (a) Thomason, T. B.; Modell, M. *Hazardous Waste* **1984**, *1*, 453. (b) Abraham, M. A.; Klein, M. T. *Ind. End. Chem. Prod. Res. Dev.* **1985**, *24*, 300.

[3] (a) Helling, R. K.; Tester, J. W. *Environ. Sci. Technol.* **1988**, *22*, 1319. (b) Tsao, C. C.; Zhou, Y.; Liu, X.; Houser, T. J. *J. Supercrit. Fluids* **1992**, *5*, 107. (c) Aaltonen, O.; Rantakyla, M. *CHEMTECH* **1991**, *21*, 240. (d) Eckert, C. A.; Van Alsten, J. G.; Stoicos, T. *Environ. Sci. Technol.* **1986**, *20*, 319. (e) Klesper, E. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 738.

[4] (a) Connelly, J. F. *J. Chem. Eng. Data* **1966**, *11*, 13. (b) Rebert, C. J.; Kay, W. B. *AIChE J.* **1959**, *5*, 285.

[5] Eckert, C. A.; Ziger, D. H.; Johnston, K. P.; Ellison, T. K. *Fluid Ph. Equil.* **1983**, *14*, 167.

[6] (a) Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 7821. (b) Betts, T. A.; Zagrobelny, J.; Bright, F. V. *J. Am. Chem. Soc.* **1992**, *114*, 8163. (c) Sun, Y.-P.; Fox, M. A.; Johnston, K. P. *J. Am. Chem. Soc.* **1992**, *114*, 1187. (d) Sun, Y.-P.; Bennett, G.; Johnston, K. P.; Fox, M. A. *J. Phys. Chem.* **1992**, *96*, 10001. (e) Kim, S.; Johnston, K. P. *Ind. Eng. Chem. Res.* **1987**, *26*, 1206. (f) Kajimoto, O.; Futakami, T.; Kobayashi, T.; Yamasaki, K. *J. Phys. Chem.* **1988**, *85*, 67.

[7] (a) Wu, R. S.; Lee, L. L.; Cochran, H. D. *Ind. Eng. Chem. Res.* **1990**, *29*, 977. (b) Petsche, I. B.; Debenedetti, P. G. *J. Chem. Phys.* **1989**, *91*, 7075.

[8] (a) Gao, J. *J. Am. Chem. Soc.* **1991**, *113*, 7796. (b) Gao, J.; Pavelites, J. J. *J. Am. Chem. Soc.* **1992**, *114*, 1912.

[9] Jorgensen, W. L. BOSS Version 2.9; Yale University, 1990.

[10] Jorgensen, W. L.; Severance, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 4768.

[11] (a) Karlstrom, G.; Linse, P.; Wallqvist, A.; Jonsson, B. *J. Am. Chem. Soc.* **1983**, *105*, 3777. (b) Allinger, N. L.; Lii, J.-H. *J. Comput. Chem.* **1987**, *8*, 1146. (c) Bartell, L. S.; Sharkey, L. R.; Shi, X. *J. Am. Chem. Soc.* **1988**, *110*, 7006.

[12] Jorgensen, W. L.; Chandrasekhar, J.; Madura, J. D.; Impey, R. W.; Klein, M. L. *J. Chem. Phys.* **1983**, *79*, 926.

[13] Neumann, M. *J. Chem. Phys.* **1986**, *85*, 1567.

0002-7863/93/1515-6893$04.00/0

Table I. Computed Thermodynamic Properties for Supercritical Water at 400 °C[a]

	P (atm) =				
	350	500	700	1000	2000
U_{int}	−3.07	−4.18	−4.68	−5.14	−5.82
ρ(calc)	0.232	0.404	0.501	0.592	0.737
ρ(expt)	0.475	0.578	0.638	0.693	0.793
ρ(expt, 450 °C)	0.202	0.402	0.529	0.614	0.743
ϵ(calc)	3.6	5.7	8.2	9.2	10.8
ϵ(expt)	9.3	12.2	14.2	16.1	19.7
ϵ(expt, 450 °C)	3.0	6.6	9.9	12.4	16.5

[a] Energies and densities are given in kcal/mol and g/cm^3, respectively. Standard deviations were estimated from separate averages over blocks of 5 × 10^5 configurations during the simulations; they are approximately ±0.03 kcal/mol for interaction energies U_{int}, ±1 for dielectric constants ϵ, and ±0.004 (at 2000 atm) to 0.057 (at 350 atm) g/cm^3 for densities ρ.

standard errors from the Monte Carlo simulations are also large due to greater volume fluctuations at the low-density region. Thus, it is difficult to predict the density of supercritical fluid water with empirical models. Although the simulations were carried out at 400 °C in the present study, the computed fluid densities are actually in good accord with the experimental data at 450 °C.[14] Since the reduced variables are the fundamental quantities used in fluid state functions,[15] the experimental reduced temperature ($T^* = T/T_c = 1.12$) may be compared with that corresponding to the simulation conditions. Consequently, the results in Table I suggest that the critical temperature (T_c) might be underestimated by 30 to 50 °C with the TIP4P model, which would yield a similar reduced temperature for the simulated fluid at 400 °C.

In Table I, the interaction energy of SCW is predicted to decrease as the density increases, whereas the calculated dielectric constants are much smaller than the experimental values at 400 °C. However, the dielectric constant of SCW depends critically on the fluid density.[16] Comparison of the computed and experimental values should be made corresponding to the same density. Thus, the agreement with the experimental data at 450 °C is good (Table I).[16] Note that the trend in Table I shows somewhat a progressive deterioration at higher pressures, i.e., higher densities; however, it should be remembered that the dielectric constant of TIP4P wate is 53 ± 2 at 20 °C and 1.0 g/cm^3, a value substantially smaller than the experimental value of 78.[13] The overall performance of the TIP4P model is remarkably good for SCW. Supercritical water and its ionic solutions have been investigated by Cummings et al. and others using the SPC potential in a canonical NVT ensemble molecular dynamics simulation.[17] Good agreement between computed and experimental dielectric constant was obtained. In that study, the estimated T_c is about 70 °C below the experimental value (374 °C).

Potential of Mean Force for the Benzene Dimer

The potential of mean force (pmf) for the benzene dimer was obtained by computing the free energy changes via statistical perturbation theory in the context of Monte Carlo simulations.[18] The reaction coordinate of the pmf is defined as the distance between the centers of the two benzene molecules in a rectangular cell (ca. 26.5 × 26.5 × 40 Å^3) containing 240 water molecules. The angular distribution of the benzene molecules is fully sampled in the Monte Carlo calculations.[10] The NPT ensemble at 400 °C and 350 atm was employed with periodic boundary conditions and Metropolis sampling. The double-wide sampling technique was used to compute the free energy changes with $\Delta R = \pm 0.15$ Å.[18b] Thus, a total of 22 simulations were carried out, each involving 10^6 configurations of equilibration and 4 × 10^6 configurations of averaging. A cutoff distance of 12 Å between the centers of mass was used to evaluate the solute–solvent and solvent–solvent interactions.

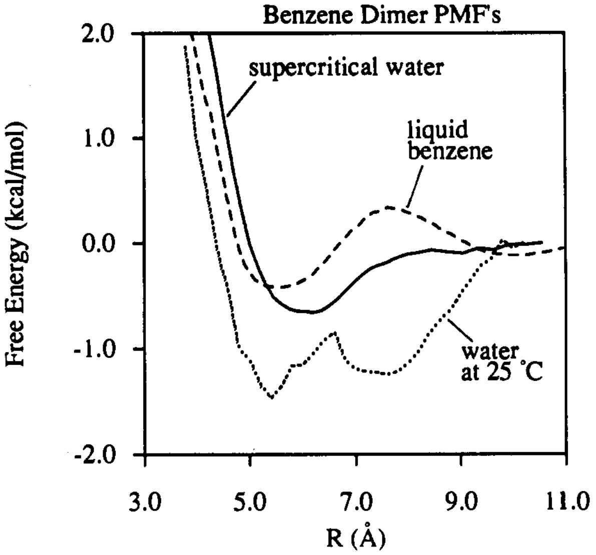

Figure 1. Computed potential of mean force for the benzene dimer in supercritical water at 400 °C and 350 atm (solid line), liquid benzene (dashed line), and ambient water (dotted line) at 25 °C and 1 atm. Data from ref 10 for liquid benzene and ambient water are kindly provided by W. L. Jorgensen and Dan Severance. R is the separation distance between the center of benzene rings.

Before the results are further analyzed, the issue of size dependency in the simulation should be addressed. Although the present system contains two benzene plus 240 water molecules, corresponding to a solution of solute mole fraction of 0.8%, it should be noted that the solute molecules do not interact with those in the periodic neighboring unit cells due to the use of a spherical cutoff, which is less than one-half of the edges of simulation box. Thus, the system may be viewed as a pseudo-infinite dilute solution.[10] Further, the computed pmf is unlikely to have a significant change if more water molecules are included in the simulation box since the density of SCW at the computation conditions is very low. The size of the central unit cell and the cutoff distance are both relatively large compared with the previous simulation of the benzene dimer in a box of 750 water molecules at 25 °C.[10] Early studies of liquid water at "normal" conditions also indicate that the size-dependence effect is not significant.[19]

Figure 1 displays the key results of the present study, which shows the free energy change along the separation distance between two benzene molecules in SCW at 400 °C and 350 atm. For comparison, the pmf's for the benzene dimer obtained by Jorgensen and Severance in ambient water and liquid benzene at 25 °C and 1 atm are also shown.[10] A number of special features of the supercritical hydration of benzene are readily revealed in Figure 1. First, the attractive force between benzene molecules is significantly weakened in SCW in comparison to that in ambient aqueous solution. The feature is now very similar to the pmf in pure liquid benzene at 25 °C and 1 atm, which may be attributed to the condensed phase effects due to solvent competition and entropic contributions associated with the thermal, configurational averaging.[10] The diminishing hydrophobic enhancement of binding in SCW, in contrast to that at ambient conditions,[10] is evident. This is consistent with the experimental observation of

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(14) Haar, L.; Gallagher, J. S.; Kell, G. S. *NBS/NRC Steam Tables*; Hemisphere: Washington, DC, 1984.

(15) Atkins, P. W. *Physical Chemistry*; W. H. Freeman and Co.: San Francisco, 1978; pp 43-47.

(16) Uematsu, M.; Franck, E. U. *J. Phys. Chem. Ref. Data* **1980**, *9*, 1291.

(17) (a) Cummings, P. T.; Cochran, H. D.; Simmonson, J. M.; Mesmer, R. E. *J. Chem. Phys.* **1991**, *94*, 5606. (b) Kataoka, Y. *J. Chem. Phys.* **1987**, *77*, 887. (c) Kalinichev, A. G. *Int. J. Thermophys.* **1986**, *7*, 887.

(18) (a) Zwanzig, R. W. *J. Chem. Phys.* **1954**, *22*, 1420. (b) Jorgensen, W. L.; Ravimohan, C. *J. Chem. Phys.* **1985**, *83*, 3050.

(19) Jorgensen, W. L.; Madura, J. D. *Mol. Phys.* **1985**, *56*, 1381.

Figure 2. Stereoplot of a random configuration for the benzene dimer in supercritical water at a separation distance of 8 Å.

complete miscibility of benzene in SCW.[4] In Figure 1, the computed well-depth in SCW is −0.66 kcal/mol, which may be compared with values of −0.4 and −1.5 kcal/mol in liquid benzene and ambient water determined in ref 10. A separate study by Beveridge and co-workers predicted a binding energy of −5 kcal/mol, though the importance sampling technique was employed in that study and only the face-to-face orientation was considered.[20]

Second, the only minimum in SCW is the contact dimer near 6.2 Å, while the second minimum corresponding to the solvent-separated configuration predicted by Jorgensen and Severance at room temperature disappears entirely.[10] Thus, there appears to be a progressive reduction of the solvent structure around the solute as the temperature and pressure of the system increase. The lack of structural features in the pmf indicates that solvent molecules do not form energetically more stable aggregates near the solute molecule than in the bulk. Further, the separation distance for the contact minimum in SCW is about 0.7 Å longer than those in liquid benzene and ambient water (both at 5.5 Å).[10] This is consistent with a lesser hydrophobic effect noted above. Strong hydrophobic interactions in the ambient environment favor a closer contact between the phenyl rings and a smaller exposure to the solvent.[10] Figure 2 shows a random example of the configuration at a separation distance of 8.0 Å in SCW, which is near the solvent-separated species in ambient water. It seems that the feature of water clusters bridging the two benzene molecules observed in ref 10 is no longer maintained at higher temperature and pressure. However, water molecules are seen to form aggregates and large cavities are present in the stereoview. In addition, gas-phase, low-energy face-solvating structures,[21] which are also observed in aqueous solution at 25 °C,[10] do not appear to occur.

Additional support for the weakening of the hydrophobic effect in SCW is provided by comparison of the computed association constants from eq 1:

$$K_a = 2\pi \int_0^{R_c} r^2 \exp[-\Delta G(r)/RT]\, dr \qquad (1)$$

where R_c is a distance defining the geometric limit of association.[22] Integration of the pmf in Figure 1 to a reasonable distance of about 8 Å yields a K_a of 1 M^{-1}, which represents a reduction of binding by a factor of 3 over that predicted by Jorgensen and Severance for the solution at 25 °C.[10]

Conclusion

The present results provide detailed structural and thermodynamic insights on the diminishing hydrophobic effect in supercritical water. The computed fluid density and dielectric constant at 400 °C are in agreement with the experimental data at 450 °C. The difference in temperature may be attributed to the possibility of an underestimate of the critical temperature for water with use of the TIP4P model. Further analysis of the potential of mean force for the benzene dimer in SCW suggests that there is no stable solvent aggregation near the benzene dimer. However, dynamic clustering of the solvent molecules is widespread. It is of interest to compare these findings for SCW solution with those of organic supercritical fluids, where enhanced solvent clustering around the solute molecules has been observed from spectroscopic experiments.[5,6] Our calculation presented here demonstrates the capability of computer simulations with the TIP4P model to study solvation of organic compounds in supercritical water.

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(20) Ravishanker, G.; Beveridge, D. L. *J. Am. Chem. Soc.* **1985**, *107*, 2565.

(21) Suzuki, S.; Green, P. G.; Bumgarner, R. E.; Dasgupta, S.; Goddard, W. A., III; Blake, G. A. *Science* **1992**, *257*, 942.

(22) Justice, M.-C.; Justice, J.-C. *J. Solution Chem.* **1976**, *5*, 543.