Theory of Hydrogen Bonding in Supercritical Fluids

Ram B. Gupta, Constantinos G. Panayiotou, Isaac C. Sanchez, and Keith P. Johnston
Dept. of Chemical Engineering, The University of Texas at Austin, Austin, TX 78712

The degree of hydrogen bonding and macroscopic thermodynamic properties for pure and mixed fluids are predicted with the hydrogen bonding lattice fluid (LFHB) equation of state over a wide range in density encompassing the gas, liquid and supercritical states. The model is successful for molecules forming complex self-associated networks, in this case pure methanol, ethanol, and water, and the mixture 1-hexanol-SF_6. In supercritical water, significant hydrogen bonding is still present despite all the thermal energy and is highly pressure- and temperature-dependent. A fundamental description of pressure and temperature effects on hydrogen bonding is presented for a well-defined case, the formation of a complex between a donor and acceptor in an inert solvent, where no self-association is present. The partial molar enthalpy and volume change on complexation both become pronounced near the critical point, where the density is highly variable with temperature and pressure.

Introduction

Although molecular interactions in the supercritical fluid state have been characterized extensively based on studies of phase behavior, spectroscopy, and computer simulation (Johnston et al., 1989a,b; Ekart et al., 1991; Lee et al., 1991; Levelt Sengers, 1991; Christoforakos and Franck, 1986), the focus has been on nonspecific forces, with relatively few studies of hydrogen bonding. It has been demonstrated that the degree of hydrogen bonding can vary markedly from the gas phase to the liquid phase (Christian and Lane, 1975; Schneider, 1991), but unfortunately, only a few systems have been studied in both phases. Consequently, it is likely that hydrogen bonding will be sensitive to temperature and pressure in near-critical fluids where the density is highly variable.

The role of hydrogen bonding in supercritical fluid technology is important, yet poorly understood. Although supercritical water is of interest in hydrothermal (Antal et al., 1986), electrochemical (Flarsheim et al., 1989), and supercritical water oxidation processes (Thornton and Savage, 1990; Jin et al., 1990; Yang and Eckert, 1988; Webley and Tester, 1991), little is known about the degree of hydrogen bonding at these conditions. Hydrogen bonding has been studied to a somewhat greater extent in fluids with critical temperatures below 50°C. For example, solvatochromic experiments with phenol blue as a probe suggest that the hydrogen bond donor strength of fluoroform is comparable to that of chloroform (Kim and Johnston, 1987). Furthermore, the hydrogen bonds between fluoroform and phenol blue are well developed at 70 bar and do not change significantly with an increase in pressure. O'Shea et al. (1991) have compared the hydrogen bond donor-acceptor properties of three fluids with a similar critical temperature: CO_2, ethane, and fluoroform. While these fluids interact similarly with nonpolar solutes, they exhibit markedly different hydrogen bonding characteristics, as demonstrated by their influence on the tautomeric equilibria between the azo (hydrogen bond donor) and hydrazone (hydrogen bond acceptor) forms of 4-phenylazo-1-naphthol. Recently, Zagrobelny and Bright (1992), Debenedetti et al. (1991), and Sun et al. (1992) utilized photophysical techniques to probe local density augmentation in supercritical fluids, but hydrogen bonding was not considered.

Another interesting example of hydrogen bonding is the pronounced enhancement in the solubilities of certain solutes in a supercritical fluid with the addition of a cosolvent, for example, ethanol or tributyl phosphate (Dobbs et al., 1987; Walsh et al., 1989; Lemert and Johnston, 1991). Even greater solubility enhancement has been observed in organized molecular assemblies composed of surfactants. Randolph et al.

Correspondence concerning this article should be addressed to K. P. Johnston.

C. G. Panayiotou is on leave of absence from the Dept. of Chemical Engineering, University of Thessaloniki, 54006 Thessaloniki, Greece.

(1988) observed large changes in the degree of aggregation of cholesterol with pressure in CO_2, and others have observed pressure effects on aggregation for other hydrogen bonding substances such as nonionic surfactants containing ethoxy and hydroxyl moieties (Johnston et al., 1989; Fulton et al., 1990). The behavior of pressure effects on reverse micelles and microemulsions has been presented theoretically (Peck and Johnston, 1991). Additional examples where hydrogen bonding could be important in supercritical fluid technology include pressure effects on polymer morphology, protein conformation, and pressure effects on reversible and irreversible chemical reactions (Chateneuf et al., 1992; Combes et al., 1992).

Most theoretical treatments of hydrogen bonding postulate the existence of distinct molecular species in solution, resulting from chemical reactions described by equilibrium constants (Heidemann and Prausnitz, 1976; Ikonomou and Donohue, 1986; Anderko, 1991; Karachewski et al., 1991). Levin and Perram (1968) presented an alternative treatment based on statistical mechanics, in which the focus is on the counting of the number of arrangements of hydrogen bonds, not on the distribution of particular complexes. This philosophy is gaining attention (Luck, 1980; Veytsman, 1990). Panayiotou and Sanchez (1991) utilized this concept to derive a unified statistical thermodynamic lattice fluid theory for hydrogen-bonded fluids and their mixtures over a wide range in density. This equation will be referred to as the hydrogen bonding lattice fluid (LFHB) model. It was suggested that this model is appropriate for the supercritical region. A key advantage of this approach is that the existence of particular associates is not chosen. This advantage is also present in the statistical assocation fluid theory (SAFT), a perturbation model (Chapman et al., 1990; Huang and Radosz, 1991).

In this study, we examine the behavior of both macroscopic thermodynamic properties and the degree of hydrogen bonding for pure supercritical fluids as well as mixtures with the LFHB model. We consider two related objectives. The first objective is to treat complicated hydrogen-bonded networks in fluids with self-association. Examples include pure alkanols and water, and a binary mixture of 1-hexanol in SF_6. In a supercritical fluid, it is likely that the distribution of associated species of varying structure will be sensitive to the large changes in density. Thus, the LFHB model should be particularly well-suited to treat hydrogen bonding at these conditions (as is SAFT). The second objective is to obtain a fundamental understanding of density and temperature effects on hydrogen bonding, by examining a well-defined system in an inert solvent with cross-association without any self-association. In this case, an equilibrium constant can be defined for the formation of a hydrogen-bond donor-acceptor complex and used to investigate volume and enthalpy changes on complexation.

Theory

We begin with a summary of the statistical thermodynamic theory developed by Panayiotou and Sanchez (1991) for hydrogen-bonding fluids and their mixtures. The basic assumption is that the partition function may be separated into physical and chemical (hydrogen bonding) contributions. Each step in the derivation has clear physical meaning based on statistical mechanics. The physical part of the canonical partition function could be described by several available models; the lattice-fluid theory (Sanchez and Lacombe, 1976) was chosen, because of its well-defined derivation. Undoubtedly, more accurate, but more empirical, equations of state, such as modified Peng-Robinson equations of state (Stryjek and Vera, 1986), could be chosen. The chemical contribution of the partition function is derived by determining the number of ways of distributing the hydrogen bonds among the donor and acceptor groups in the system. The donor and acceptor must be in close spatial proximity as described by a mean field probability. The mean-field probability that a specific acceptor will be near a given donor depends on the system volume or total number of lattice sites and the entropy loss (intrinsically negative) associated with the formation of a hydrogen bond. The general formalism is valid for multicomponent systems of molecules having any number of hydrogen bond donor and acceptor groups, and is applicable over a wide range in density.

In the LFHB model, the canonical partition function is separated into physical and hydrogen bonding contributions:

$$Q = Q_P Q_H \tag{1}$$

Let d_i^k be the number of proton donor groups of type i in each molecule of type k, and a_j^k be the number of proton acceptor groups of type j in each molecule of type k. The total number of donor group of type i in the system is given by:

$$N_d^i = \sum_k d_i^k N_k \tag{2}$$

and similarly the total number of acceptor groups of type j is given by:

$$N_a^j = \sum_k a_j^k N_k \tag{3}$$

Let E_{ij}^0 be the energy change upon hydrogen bond formation between a donor group i and an acceptor group j. There are N_{ij} such bonds in the system and the total number of hydrogen bonds may be written:

$$N_H = \sum_i \sum_j N_{ij} \tag{4}$$

The number of donors of type i, N_{io}, and acceptors of type j, N_{jo}, that are not hydrogen bonded are given by

$$N_{io} = N_d^i - \sum_j N_{ij} \tag{5}$$

and

$$N_{jo} = N_a^i - \sum_i N_{ij} \tag{6}$$

The result for the partition function Q_H is:

$$Q_H(T, N_0, \{N_k\}, \{N_{ij}\}) = \left(\frac{\tilde{\rho}}{rN}\right)^{N_H} \prod_i^m \frac{N_d^i!}{N_{i0}!} \prod_j^n \frac{N_a^j!}{N_{0j}!} \prod_i^m \prod_j^n \frac{\exp(-N_{ij}F_{ij}^0/RT)}{N_{ij}!} \tag{7}$$

where rN is the total number of molecular segments in the system, N_o is the number of holes, and the Helmholtz free energy and Gibbs free energy of hydrogen bond formation are:

$$F_{ij}^0 = E_{ij}^0 - TS_{ij}^0 \tag{8a}$$

and

$$G_{ij}^0 = E_{ij}^0 - T\,S_{ij}^0 + PV_{ij}^0 \tag{8b}$$

The physical part of the Gibbs free energy is the well-known lattice fluid model (Sanchez and Lacombe, 1976) and the hydrogen-bonding part is given by:

$$\frac{G_H}{RT} = rN\left\{\sum_i^m \sum_j^n \nu_{ij}\left[1 + \frac{G_{ij}^0}{RT} + \ln\frac{\tilde{v}\nu_{ij}}{\nu_{io}\nu_{oj}}\right] + \sum_i^m \nu_d^i \ln\frac{\nu_{io}}{\nu_d^i} + \sum_j^n \nu_a^j \ln\frac{\nu_{oj}}{\nu_a^j}\right\} \tag{9}$$

where

$$\nu_{ij} \equiv \frac{N_{ij}}{rN},\ \nu_{io} \equiv \frac{N_{io}}{rN},\ \nu_d^i \equiv \frac{N_d^i}{rN};\ \text{etc.} \tag{10}$$

Minimizing the Gibbs free energy with respect to reduced volume $\tilde{v}$ yields the lattice fluid equation of state:

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}\left(1 - \frac{1}{\bar{r}}\right)\right] = 0 \tag{11}$$

where the reduced density, $\tilde{\rho} = 1/\tilde{v}$, represents the fraction of space occupied by all molecules in the system. The reduced pressure $\tilde{P}$ is defined by:

$$\tilde{P} = \frac{P}{P^*} = \frac{Pv^*}{\epsilon^*} \tag{12}$$

the reduced temperature $\tilde{T}$ by:

$$\tilde{T} = \frac{T}{T^*} = \frac{RT}{\epsilon^*} \tag{13}$$

and the modified average chain length $\bar{r}$ by:

$$\frac{1}{\bar{r}} = \sum_i \frac{\Phi_i}{r_i} - \sum_i^m \sum_j^n \nu_{ij} = \frac{1}{r} - \nu_H \tag{14}$$

where v^* is close-packed segment volume, ϵ^* is lattice-fluid energy, and P^* and T^* are the characteristic pressure and temperature, respectively. Equation 11 is identical in form to the original lattice-fluid equation of state (Sanchez and Lacombe, 1976) except that $1/\bar{r}$ term replaces usual $1/r$ term. The system volume is the sum of physical and chemical terms:

$$V = rN\tilde{v}v^* + \sum_i^m \sum_j^n N_{ij}\, V_{ij}^0 \tag{15}$$

Minimizing the Gibbs free energy with respect to N_{ij} gives the following equation:

$$\frac{\nu_{ij}}{\nu_{i0}\nu_{0j}} = \tilde{\rho}\exp\left(\frac{-G_{ij}^0}{RT}\right)\ \text{for all } (i, j) \tag{16}$$

or

$$\nu_{ij} = \left[\nu_d^i - \sum_k^n \nu_{ik}\right]\left[\nu_a^j - \sum_k^m \nu_{kj}\right]\tilde{\rho}\exp\left(\frac{-G_{ij}^0}{RT}\right) \tag{17}$$

The chemical potential of component k is given by:

$$\mu_k = \mu_{k,LF} + \mu_{k,H} \tag{18}$$

The LF contribution to the chemical potential is reported elsewhere (Panayiotou and Sanchez, 1991) and the hydrogen-bonding contribution is:

$$\frac{\mu_{k,\,H}}{RT} = r_k\nu_H - \sum_i^m d_i^k \ln\left(\frac{\nu_d^i}{\nu_{i0}}\right) - \sum_j^n a_j^k \ln\left(\frac{\nu_a^i}{\nu_{0j}}\right) \tag{19}$$

For each component, three LF scaling parameters (T^*, P^*, and ρ^*) and three hydrogen-bonding parameters (E^0, V^0, and S^0) for each type of hydrogen bond are required. The LF scaling parameters for many fluids and the hydrogen-bonding parameters for 1-alkanols (assumed to be the same for all alcohols) and for amines have been published (Panayiotou, 1990; Panayiotou and Sanchez, 1991).

It is instructive to discuss the LFHB model along with other well-defined theories, namely the chemical (Heidemann and Prausnitz, 1976) and perturbation theories (Chapman et al., 1990). In the highly useful chemical theories based on the model of Heidemann and Prausnitz (1976), somewhat arbitrary mixing rules are chosen to obtain a "closed-form" solution of the chemical equilibria and phase equilibria. Precautions must be taken so that the separation of the physical and chemical interactions does not lead to thermodynamic inconsistencies (Anderko, 1991; Donohue, 1992). In the LFHB model, the separation of these interactions does not present inconsistencies. The derivation of each term is well defined physically, so the model may be used to gain fundamental insight. For computer simulation data of a system of hydrogen-bonding sites on hard spheres, the LFHB model does not give good results for the compressibility factor due to the repulsive part of the physical term for hard spheres (Sanchez and Lacombe, 1976; Vimalchand and Donohue, 1989; Economou and Donohue, 1991), whereas the above chemical and perturbation theories are highly successful. Since the lattice fluid theory can represent PVT properties of nonbonding fluids with reasonable accuracy and since there is no coupling between the hydrogen bonding and nonbonding terms, as shown below, this is not a significant problem.

Specific Applications of the Hydrogen Bonding Lattice Fluid Model

Pure 1-alkanol

In the case of pure 1-alkanols there is only one hydrogen-bond donor and one acceptor site per molecule, hence only one type of hydrogen bond in the system and the minimization condition (Eq. 17) gives:

$$(N-N_{11})^2=N_{11}(rN\tilde{v})\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{20}$$

The physically meaningful solution of this quadratic equation is (Panayiotou and Sanchez, 1991)

$$r\nu_H\equiv\frac{N_{11}}{N}=1-\frac{\sqrt{A(A+4)}-A}{2} \tag{21}$$

where

$$A=r\tilde{v}\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{22}$$

The chemical potential of the 1-alkanol is given by:

$$\frac{\mu}{RT}=r\left\{\frac{-\tilde{\rho}+P\tilde{v}}{\tilde{T}}+(\tilde{v}-1)\ln(1-\tilde{\rho})+\frac{1}{r}\ln\tilde{\rho}\right\}+r\nu_H+2\ln(1-r\nu_H) \tag{23}$$

and the fraction of monomeric 1-alkanol is $(1-N_{11}/N)$.

Pure water

Pure water has two proton donor and two proton acceptor per molecule (Franks, 1972). We assume that only one type of hydrogen bond is present, hence the minimization condition equation becomes:

$$(2N-N_{11})^2=N_{11}(rN\tilde{v})\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{24}$$

The physically meaningful solution of the above quadratic equation is:

$$r\nu_H\equiv\frac{N_{11}}{N}=2-\frac{\sqrt{A(A+8)}-A}{2} \tag{25}$$

where the definition of A is same as in the case of 1-alkanols. The chemical potential of water is:

$$\frac{\mu}{RT}=r\left\{\frac{-\tilde{\rho}+P\tilde{v}}{\tilde{T}}+(\tilde{v}-1)\ln(1-\tilde{\rho})+\frac{1}{r}\ln\tilde{\rho}\right\}+r\nu_H+4\ln\left(\frac{2-r\nu_H}{2}\right) \tag{26}$$

and the fraction of monomeric water is $(1-N_{11}/2N)$.

Binary mixture of 1-alkanol(1) and an inert solvent(2)

The minimization condition equation becomes:

$$(N_1-N_{11})^2=N_{11}(rN\tilde{v})\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{27}$$

The useful solution of this quadratic is:

$$r\nu_{11}\equiv\frac{N_{11}}{N}=y_1-\frac{\sqrt{A(A+4)}-A}{2} \tag{28}$$

where y_1 is the mole fraction of the 1-alkanol.

Ternary mixture of an acceptor and a donor in an inert solvent

Here we create an example in which each molecule offers one-donor one-acceptor site. We intentionally allow only one type of hydrogen bond in this system without any self-association. The Gibbs free energy is to be minimized with respect to the number of donor-acceptor bonds N_{11}. The equations for this donor-acceptor example are:

$$(N_1-N_{11})(N_2-N_{11})=N_{11}(rN\tilde{v})\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{29}$$

or

$$r\nu_{11}=\frac{(y_1+y_2+A_{11})-\sqrt{(y_1+y_2+A_{11})-4y_1y_2}}{2} \tag{30}$$

where

$$A_{11}=r\tilde{v}\ \exp\left(\frac{G_{11}^0}{RT}\right) \tag{31}$$

Results and Discussion

Pure methanol and ethanol

Because the LFHB model treats hydrogen-bonded networks without the need to assume the existence of specific complexes, it is expected to be useful for modeling self-associated fluids such as alcohols. Indeed, Panayiotou and Sanchez (1991) predicted the vapor pressure and saturated liquid density of alkanols accurately with hydrogen bonding parameters E^o, S^o, and V^o from the literature, which were determined from excess properties. Our objective is to examine the degree of association of methanol and ethanol in the saturated liquid state.

The percentage of monomer for pure saturated liquid methanol and ethanol was predicted with Eq. 21 as shown in Figures 1 and 2, respectively. No adjustable parameters were fit to the data; the six parameters listed in Tables 1 and 2 were regressed previously from macroscopic thermodynamic properties (Panayiotou and Sanchez, 1991). The predictions are in reasonably good agreement with the data of Luck (1980), which were obtained with IR spectroscopy based on the free OH band. The greater curvature for the data compared with the theory is due in part to errors in the calculated density, especially near the critical point (Panayiotou, 1988). As shown in Eq. 20, the degree of association is influenced greatly by the density of the fluid. It will be seen below for water that the model underpredicts the change in the density of the expanded liquid near the critical point, a common weakness of most equations of state. Another reason for the discrepancy may be the uncertainty in the hydrogen-bonding parameters, particularly E^0. Despite these modest limitations, the LFHB model successfully

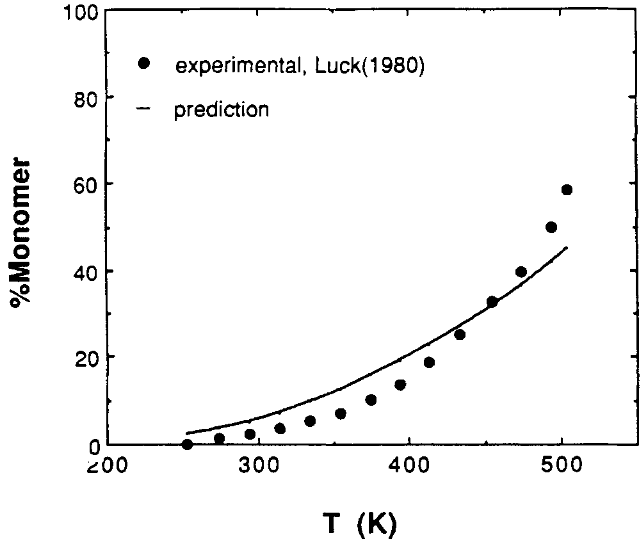

Figure 1. % Monomer in saturated liquid methanol.

predicts a microscopic property, the degree of hydrogen bonding, based on parameters obtained exclusively from macroscopic thermodynamic properties.

Pure water

Spectroscopic and computer simulation studies have been used to study association in water. Cochran et al. (1991) used molecular dynamics simulation to study water at ambient and supercritical conditions. They found that the number of hydrogen bonds per water molecule at supercritical conditions is about one third of the number of ambient conditions. Only a few conditions were studied due to the large amount of computer time required in the simulations. Franck (1973) reported the dielectric constant of water up to 500 MPa and 550°C, and also the IR and Raman spectra of HOD. At constant density, as the temperature is increased, the dielectric constant decreases due to the breakage of hydrogen bonds. The OD stretching vibration of HOD at 2,500 cm^{-1} at a constant density of about 1 g/mL in H_2O has been measured with infrared spectroscopy from 30°C to 400°C. The shift in maximum frequency and absorbance of the free OD stretch indicate a decrease in hydrogen bonding, upon increasing temperature. Based on Raman spectra of HOD at high temperature and pressure, it was suggested that there may be two distinguishable hydrogen-bonded and nonhydrogen-bonded states of the OD groups. Whereas these spectroscopic studies describe changes in hydrogen bonding with temperature qualitatively, a quantitative treatment is lacking.

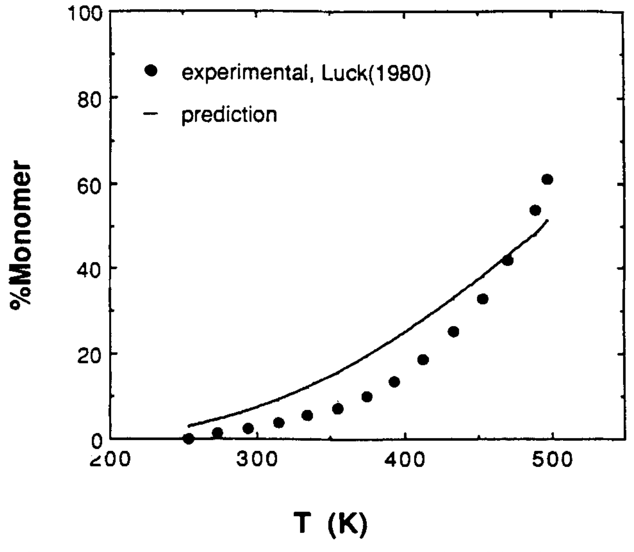

Figure 2. % Monomer in saturated liquid ethanol.

Table 1. LFHB Scaling Parameters for Pure Fluids

Fluid	T^* (K)	P^* (MPa)	ρ^* (kg/m^3)
Methanol	496	315	786
Ethanol	464	328	826
1-Hexanol	534	301	867
Water	518	475	853
Ethane	315	327	640
Sulfur Hexafluoride	288	396	2,665

Because of the complex nature of the hydrogen bonding in water, the calculation of both the macroscopic thermodynamic properties and the extent of hydrogen bonding is challenging. After studying several models for water-hydrocarbon mixtures, Michel et al. (1989) have recommended that a truly satisfactory approach must first focus on the equation of state for pure water, clearly separating the nonpolar interactions, polar interactions, and hydrogen bonding. Lee and Chao (1990) have reported an augmented Boublik-Alder-Chen-Kreglewski (BACK) equation of state for water, which has polar and nonpolar parts. It is a complex equation with 81 parameters, but it does not give information about the extent of hydrogen bonding. In the present study, our aim is to predict both the microscopic (hydrogen bonding) and macroscopic thermodynamic properties of pure water with a single set of physically meaningful parameters. The parameters will be obtained from properties of saturated water and used to predict the behavior of supercritical water.

Two of the LFHB parameters are available from the literature. The value of the hydrogen-bond energy, E^0, is −15.5 kJ/mol as suggested by Luck (1980), established by the overtone band of "free" OH groups at liquid conditions. The volume of hydrogen bonding, V^0, is calculated from the hard-core volume of water as suggested by Lee and Chao (1990):

$$V^0=\frac{1}{2}\left(v^{\infty}-\frac{MW}{\rho^*}\right) \tag{32}$$

where v^{∞} is the actual hard-core volume, 12.78 cm^3/mol, and MW is the molecular weight of water. The second term is only the physical part of the hard-core volume, whereas v^{∞} includes

Table 2. LFHB Parameters for Hydrogen Bonding

Type of Association	E^0 (kJ/mol)	S^0 (J/mol/K)	V^0 (cm^3/mol)
Methanol + Methanol	−25.1	−26.5	−5.6
Ethanol + Ethanol	−25.1	−26.5	−5.6
1-Hexanol + 1-Hexanol	−25.1	−26.5	−5.6
Water + Water	−15.5	−16.6	−4.2

both the physical and hydrogen-bonding volumes. The remaining four parameters, P^*, T^*, ρ^*, and S^0, are not available, hence they have been regressed from the vapor pressure, the saturated liquid and vapor densities, and the fraction of monomeric water, η_1 ($=r\nu_1$), in the saturated liquid by minimizing the following objective function:

$$O.F. = \sum_i \left|\frac{P^E_{\text{sat}} - P^C_{\text{sat}}}{P^E_{\text{sat}}}\right|_i + \left|\frac{\rho^E_l - \rho^C_l}{\rho^E_l}\right|_i + \left|\frac{\rho^E_v - \rho^C_v}{\rho^E_v}\right|_i + \left|\frac{\eta^E_1 - \eta^C_1}{\eta^E_1}\right|_i \tag{33}$$

Data points included in the regression are at least 25 K below the critical temperature. The resulting set of HBLF parameters for water are listed in Tables 1 and 2. This set of parameters is not unique, but the parameters appear to be physically meaningful.

The calculated saturated liquid density, vapor pressure and monomer fraction are presented in Figures 3-5, respectively. The calculated critical properties of water are, $T_c = 400°C$, $\rho_c = 15$ mol/L and $P_c = 26.25$ MPa. The T_c and P_c are somewhat larger than the experimental values, 374.2°C, and 22.05 MPa (Grigull et al., 1990). Classical equations of states have somewhat limited accuracy near the critical point. Note the vapor pressure is calculated over 5 orders of magnitude, thus some inaccuracy is to be expected. A better fit could be obtained with an objective function focusing more on the vapor pressure, but our goal is to treat both macroscopic and microscopic properties. The correlated values of T^* and ρ^* appear to be physically meaningful for the following reasons. The ratio T^*/T_c is considerably smaller for water than for hydrocarbons. This is expected since T^* only includes the physical part of the energy; water has a high T_c because of hydrogen bonding. Similarly, ρ^* is much lower than the actual hard-core density of water, because hydrogen bonding raises the density of water at elevated temperatures. The model is not applicable below 4°C where hydrogen bonding lowers the density as ice is formed.

Given the model parameters determined from subcritical water, the predicted densities of supercritical water from 0.1 to 100 MPa and 400°C to 800°C are shown in Figure 6. The results are in reasonably good agreement with the experimental data (Grigull et al., 1990), considering the pressures and temperatures in the supercritical region are well removed from the saturated region where the parameters were optimized. The calculated densities are also compared with the lattice-fluid equation of state without hydrogen bonding (Sanchez and Lacombe, 1976) in Table 3. At the lower temperatures where the fluid is the densest and most associated, the LFHB equation gives considerably better results. At high temperatures, where the fluid is close to ideal and hydrogen bonding is least prevalent, the models give comparable results as expected. Of course, empirical equations with a large number of adjustable constants may correlate densities even more accurately than the LFHB model, but they do not describe the extent of hydrogen bonding and cannot be extended to mixtures.

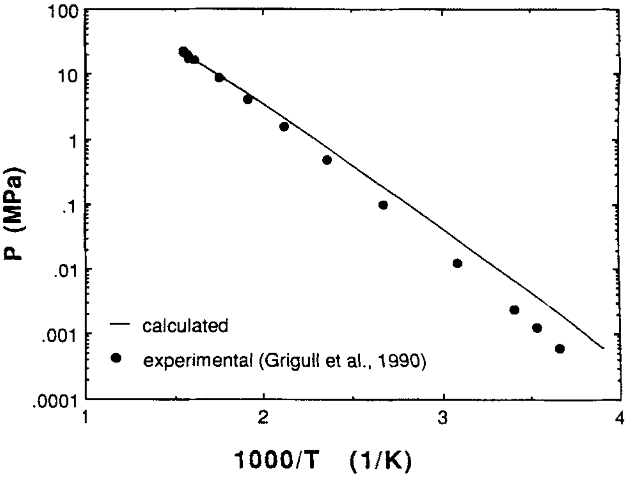

Figure 4. Vapor pressure of water.

A major strength of the LFHB model is the ability to determine the degree of hydrogen bonding in supercritical water. Very few theoretical and experimental studies have attempted to do this (Michel et al., 1989). The percentage of monomeric

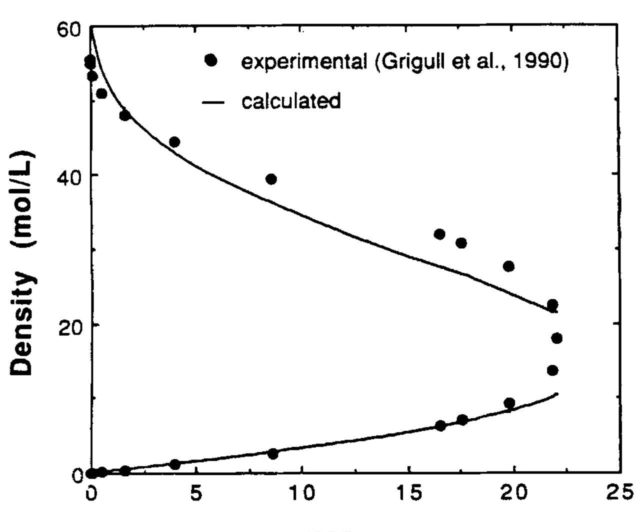

Figure 3. Density of saturated water.

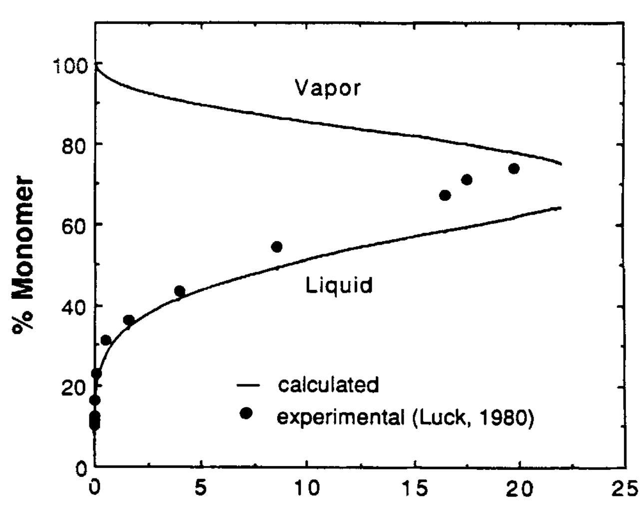

Figure 5. % Monomer in saturated water.

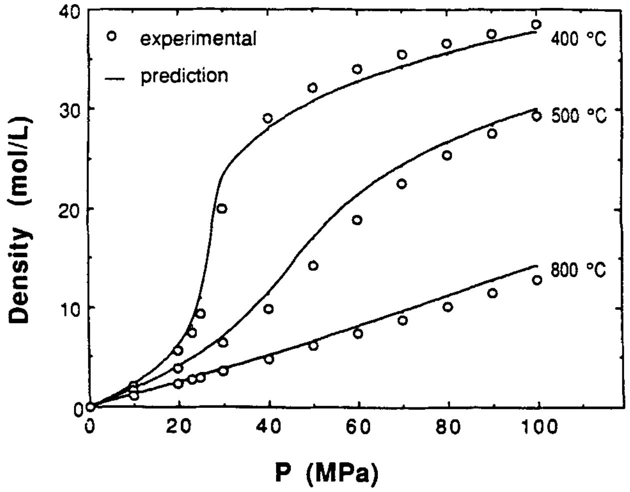

Figure 6. Density predictions for supercritical water.
Experimental data from Grigull et al., 1990.

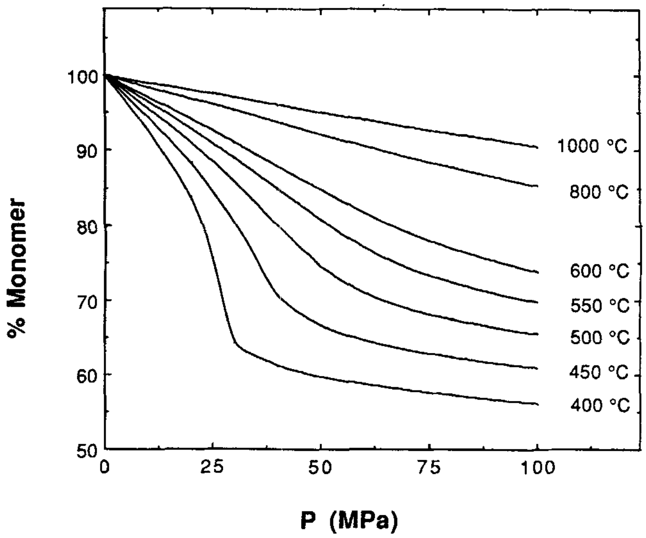

Figure 7. % Monomer vs. pressure in supercritical water.

water at supercritical conditions is presented in Figure 7 over a wide range of conditions. The interesting result is that association is prevalent in supercritical water, even with all the thermal energy and that the association is highly pressure- and temperature-dependent. Quantitative experimental data are not available and hence a comparison could not be made. Trends for the degree of association, however, are in good agreement with those reported by Franck (1973).

The complex behavior of the plot of monomer percentage vs. pressure may be greatly simplified with a density representation as shown in Figure 8. This results reflects the relationship between % monomer and density given in Eq. 24. The isotherms are nearly linear, but have a small positive curvature, which increases as the temperature is decreased toward the critical point. At a given density, particularly near the critical density, the change in % monomer with temperature is a much simpler function than the change at a constant pressure.

There is great interest in supercritical water oxidation of organic compounds with oxygen in water at pressures from 20 to 30 MPa and temperatures from 300 to 550°C. Note that water is not simply an ideal gas even at 550°C, but it is still associated, and the association is highly variable with pressure and temperature at the above conditions of interest. This association will influence solubility phenomena, reaction chemistry and corrosion, important issues in supercritical water oxidation and other important applications in supercritical water (Flarsheim et al., 1989; Shaw et al., 1991).

Table 3. Comparison of Calculated Densities of Supercritical Water: Pressure Range: 0.1 to 100 MPa

Temp. °C	Sanchez-Lacombe LF-EOS, % AAD (No Hydrogen Bonding)	Present Predictions % AAD	Data Points
400	10.66	5.72	13
450	8.95	4.93	11
500	8.81	7.30	11
550	7.97	8.50	11
600	6.27	7.99	13
800	4.64	5.70	13
Overall	7.82	5.64	72

1-hexanol-sulfur hexafluoride binary mixture

The vapor-liquid equilibria of this system were characterized in an innovative study by Nickel and Schneider (1989) with near-infrared spectroscopy at elevated pressures and temperatures. The total concentration of the alcohol in each phase was determined from the CH stretch and the concentration of the monomeric alcohol from the free OH stretch. These data afford a rare opportunity to test the ability of theory to calculate both the phase equilibria and the degree of hydrogen bonding in each phase. Recently, the statistical association fluid theory (SAFT) equation has been used to treat a similar system, the 1-hexanol-CO_2 system (Huang and Radosz, 1991). The results were in good agreement with experiment, and only one binary interaction parameter, k_{ij}, was used.

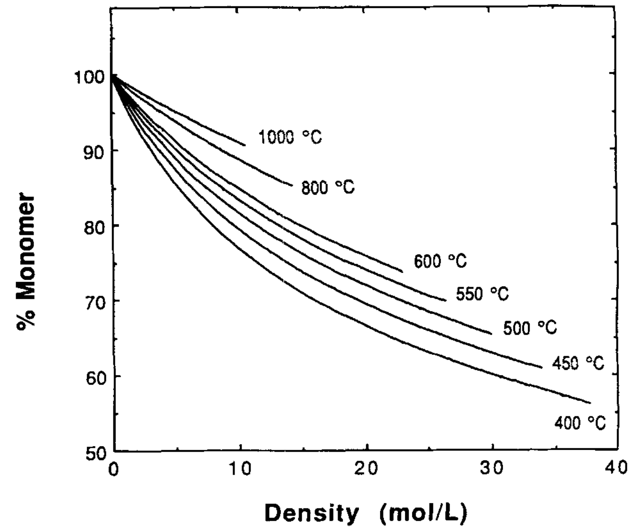

Figure 8. % Monomer vs. density in supercritical water.

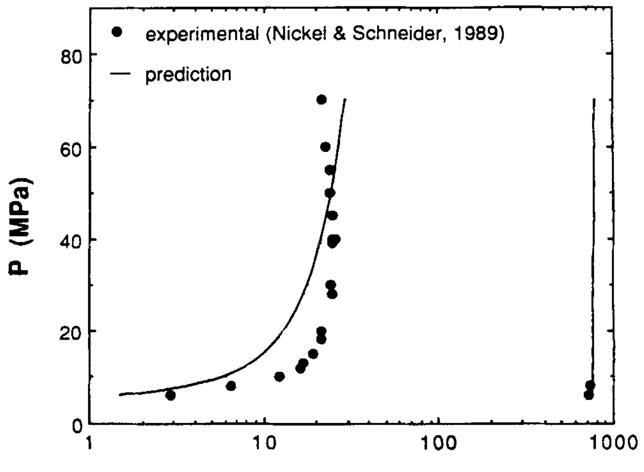

Figure 9. **Liquid-fluid phase equilibria of 1-hexanol and SF_6: total 1-hexanol. Concentration vs. pressure at 362.8 K.**

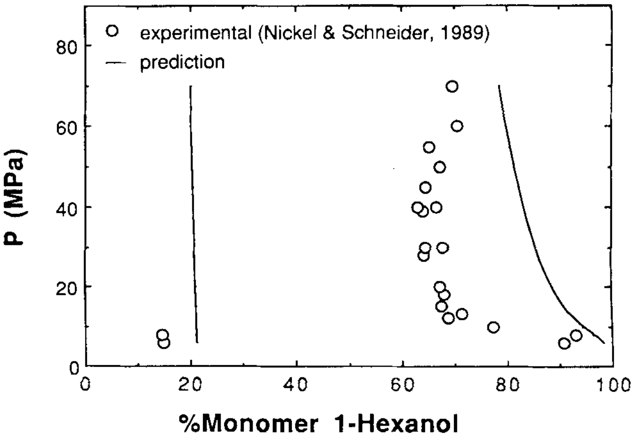

Figure 10. **Liquid-fluid phase equilibria of 1-hexanol and SF_6: % monomer 1-hexanol vs. pressure at 362.8 K.**

To apply the HBLF model, the lattice-fluid parameters (P^*, T^*, ρ^*) for SF_6 were regressed from the vapor pressure, and liquid and vapor density data, by minimizing the following objective function:

$$O.F. = \sum_i \left|\frac{P^E_{\text{sat}} - P^C_{\text{sat}}}{P^E_{\text{sat}}}\right|_i + \left|\frac{\rho^E_l - \rho^C_l}{\rho^E_l}\right|_i + \left|\frac{\rho^E_v - \rho^C_v}{\rho^E_v}\right|_i \qquad (34)$$

The size parameters for pure 1-hexanol and sulfur hexafluoride are obtained from the van der Waals surface area and volume parameters published by Daubert and Danner (1990). All of the energy and volume binary interaction parameters were set equal to unity in order to test the predictive behavior of the model without any adjustable mixture parameters.

The vapor-liquid equilibria of the binary 1-hexanol-SF_6 system is predicted in Figure 9 at 362.8 K. Above 10 MPa where the solvent becomes a dense fluid, the large increase in the 1-hexanol concentration in the fluid phase is captured with the model. The prediction of the percentage of the monomeric 1-hexanol in each phase, as shown in Figure 10, is in good agreement with experiment. In the liquid phase, very little of the 1-hexanol is in the monomeric form, whereas in the vapor, it is mostly monomer. This again illustrates the important effect of density on association as described in Eq. 27.

Hydrogen-bond donor and acceptor in an inert solvent

This section deals with the second major objective of the article to determine partial molar volume and enthalpy changes upon hydrogen bonding in supercritical fluids. It is not possible at present to do this for the examples discussed above, due to the complex nature of the self-association. Unfortunately, systems without self-association have not been studied experimentally in a supercritical fluid. Therefore, we consider a hypothetical system, in which a single hydrogen bond is formed between a donor and acceptor, without self-association. An example of such a system would be chloroform and acetone. The goal is to obtain an understanding of how this clearly-defined hydrogen bonding changes from gas-like densities through the critical region and up to high liquid-like densities. The physical lattice-fluid parameters for the donor and acceptor are taken to be the same as those of methanol, as are the association parameters. In this hypothetical system, however, self-association is not allowed. The acceptor only has one acceptor site and no donor sites, and *vice versa* for the donor.

In Figure 11, the monomer percentage of acceptor is plotted vs. reduced pressure at three different reduced temperatures. The mole fractions of acceptor and donor are kept constant, each at 0.01. At low pressures where gas-like conditions exist, nearly all of acceptors are in monomeric form. In this low-density region, there is only a slight probability that a donor molecule will be in proximity to an acceptor given their extremely low concentrations. At high pressures where solute concentrations are large (at constant mole fraction), association is prevalent. In the near-critical region, the degree of association is sensitive with respect to temperature and pressure. As the temperature is raised isobarically, hydrogen bonds

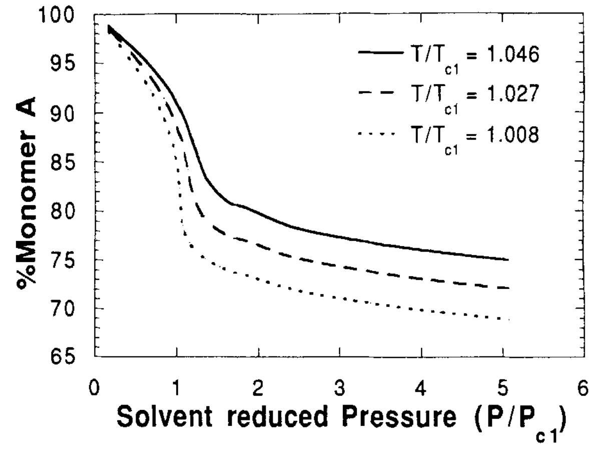

Figure 11. **% Monomer of the acceptor for the hypothetical case of donor-acceptor cross-association in 1 mol % donor and 1 mol % acceptor in supercritical ethane.**

are broken, because the energy of formation of the hydrogen bond is exothermic.

Because the formation of a hydrogen bond between acceptor and donor can only lead to an acceptor-donor complex, and no further associates, the hydrogen bonding is described by a single equilibrium constant. The number of moles of complex, acceptor and donor are $r\nu_{11}N$, $(y_1 - r\nu_{11})N$ and $(y_2 - r\nu_{11})N$, respectively. Based on true mole fractions K_y is then given by

$$K_y = \frac{r\nu_{11}(1 - r\nu_{11})}{(y_1 - r\nu_{11})(y_2 - r\nu_{11})} \tag{35}$$

The partial molar volume and enthalpy change upon hydrogen bonding, $\Delta\bar{v}$ and $\Delta\bar{h}$ are given by the following relationships:

$$\Delta\bar{v} = \bar{v}_{12} - \bar{v}_1 - \bar{v}_2 = -RT\left(\frac{\partial \ln K_y}{\partial P}\right)_{T,y} \tag{36}$$

and

$$\Delta\bar{h} = \bar{h}_{12} - \bar{h}_1 - \bar{h}_2 = RT^2\left(\frac{\partial \ln K_y}{\partial T}\right)_{P,y} \tag{37}$$

where $\bar{v}_{12}$ and $\bar{h}_{12}$ are the partial molar volume and enthalpy of the complex, respectively. Equation 29 may be rewritten in terms of apparent mole fractions y_1 and y_2:

$$(y_1 - r\nu_{11})(y_2 - r\nu_{11}) = r\nu_{11}(r\tilde{v}) \exp\left(\frac{G_{11}^0}{RT}\right) \tag{38}$$

Given this equation, K_y becomes:

$$K_y = \frac{(1 - r\nu_{11}) \exp\left(\frac{-G_{11}^0}{RT}\right)}{r\tilde{v}} \tag{39}$$

The calculated values for $\ln K_y$ are presented in Figure 12. In the low-pressure region, $\ln K_y$ is small due to the large $\tilde{v}$ or small probability the donor and acceptor will be near each other as expected from Eq. 39. As pressure and density increase, the number of encounters increases, thus raising $\ln K_y$. In the highly compressible near-critical region, the slope of $\ln K_y$ vs. pressure is extremely pronounced.

By using the equation of state (Eq. 11), along with Eqs. 38 and 39, one can derive:

$$\Delta\bar{v} = \frac{V_{11}^0 - v - rv^*\left(2 - \frac{\tilde{T}}{(1-\tilde{\rho})}\right)\left(\frac{\partial\tilde{\rho}}{\partial\tilde{P}}\right)_{\tilde{T}}}{(1 - r\nu_{11})} \tag{40}$$

For liquid-like conditions, this equation could be simplified due to very low isothermal compressibility. The calculated values of $\Delta\bar{v}$ are presented in Figure 13. At a reduced pressure above about 1.5, the fluid is liquid-like and $\Delta\bar{v}$ is a small negative number, as expected from Eq. 40. Near the critical point of the solvent, however, $\Delta\bar{v}$ becomes a large negative number on the order of thousands of cm^3/mol. Also, it changes markedly with temperature and pressure. The same type of behavior has been observed for the reversible redox reaction between I^- and I_2 in supercritical water (Flarsheim et al., 1989) and the tautomeric equilibrium between 2-hydroxypyridine and 2-pyridone (Peck et al., 1989).

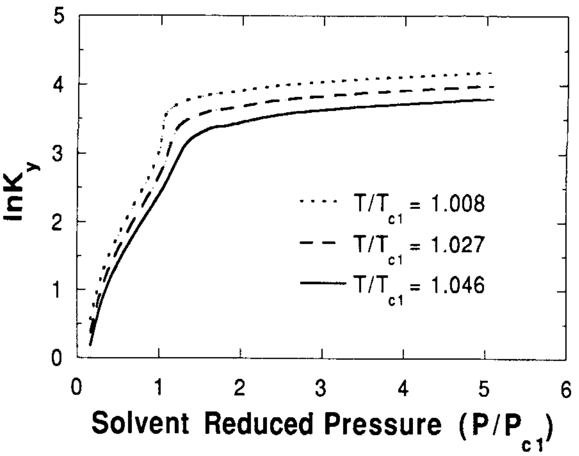

Figure 12. Equilibrium constant for the hypothetical case of donor-acceptor cross-association in supercritical ethane.

The unusual behavior of $\Delta\bar{v}$ may be explained by Eq. 40. Extremely large values of the isothermal compressibility (κ) leads to the pronounced volume changes on reaction. At each temperature, $\Delta\bar{v}$ is a minimum at the point where κ is a maximum, and this point shifts to higher reduced pressures as expected as T_r increases (Kim et al., 1985). Also the peak width increases with temperature as does that for κ. In essence, the behavior of K_y is directly analogous to that of density, again as shown in Eq. 39.

The $\Delta\bar{h}$ exhibits the same trends as $\Delta\bar{v}$ near the critical point of the solvent as shown in Figure 14. At temperatures well below critical, $\Delta\bar{h}$ is a small negative value as expected, but the exothermicity becomes magnified by the large κ and volume expansivity $1/v(\partial v/\partial T)_P$ near the critical point of the solvent. The similarity in the behavior of the partial molar volume and enthalpy has been explained previously (Chang et al., 1984;

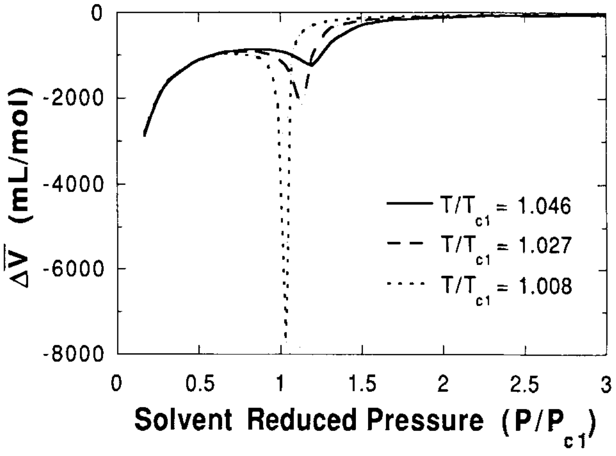

Figure 13. Partial molar volume change on association determined from the equilibrium constant in Figure 12.

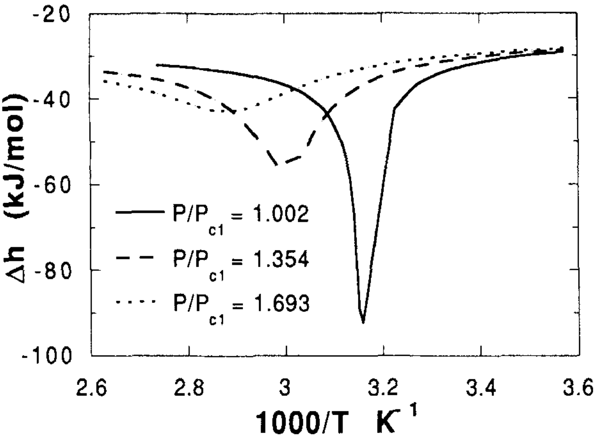

Figure 14. Partial molar enthalpy change on association determined from the equilibrium constant in Figure 12.

Debenedetti and Kumar, 1988). In conclusion, the small negative values of $\Delta\bar{v}$ and $\Delta\bar{h}$ for hydrogen bonding in liquids are magnified greatly by κ and the volume expansivity because of the large number of solvent molecules which are influenced by the solute near the critical point.

Conclusions

The LFHB model predicts the degree of hydrogen bonding and macroscopic thermodynamic properties of fluids over a wide range in density including the supercritical state, often in good agreement with experiment. At supercritical conditions, the degree of hydrogen bonding and K_y are highly pressure- and temperature-dependent at constant overall mole fraction, due to changes in density. Spectroscopic data are needed to confirm these predictions and further develop thermodynamic models to treat both microscopic and macroscopic behavior.

Acknowledgment

Acknowledgment is made to the Separation Research Program at the University of Texas, the State of Texas Energy Research in Applications Program, and the Camille and Henry Dreyfus Foundation for a Teacher-Scholar Grant (to KPJ). One of us (ICS) would like to acknowledge that financial support for this work has been provided by the Air Force Office of Scientific Research and National Science Foundation Division of Material Research.

Notation

a = acceptor group
d = donor group
V_{ij}^0 = volume of ij hydrogen bond formation
E_{ij}^0 = energy of ij hydrogen bond formation
F_{ij}^0 = Helmholtz free energy of ij hydrogen bond formation
G = Gibbs free energy
G_{ij}^0 = Gibbs free energy of ij hydrogen bond formation
$\bar{h}$ = partial molar enthalpy
K = equilibrium constant
MW = molecular weight
N_k = number of molecules of type k
$\tilde{P}$ = reduced pressure
Q = canonical partition function
r = segment length
$\bar{r}$ = modified average segment length
S_{ij}^0 = entropy of ij hydrogen bond formation
$\tilde{T}$ = reduced temperature
v = molar volume
v^* = closed pack volume per segment
$\tilde{v}$ = reduced volume
$\bar{v}$ = partial molar volume
v^∞ = hard-core volume
y = apparent mole fraction

Subscript and superscript

a, A = acceptor group
C = calculated
d, D = donor group
E = experimental
H = hydrogen bonding
k = type of molecule
LF = lattice-fluid
P = physical part
sat = saturation

Greek letters

ϵ^* = segment interaction energy
κ = isothermal compressibility
μ = chemical potential
ν = volume fraction of hydrogen bond
ρ = density
$\tilde{\rho}$ = reduced density

Literature Cited

Anderko, A., "Phase Equilibria in Aqueous Systems from an Equation of State based on the Chemical Approach," *Fluid Phase Equilib.*, **65**, 89 (1991).
Antal, M. J., A. Brittain, C. DeAlmeida, S. Ramayya, and J. C. Roy, "Heterolysis and Homolysis in Supercritical Water," *ACS Symp. Ser.*, No. 329, 77 (1986).
Bolander, R. W., J. L. Kassner, Jr., and J. T. Zung, "Semiempirical Determination of the Hydrogen Bond Energy for Water Clusters in the Vapor Phase: I. General Theory and Application to the Dimer," *J. Chem. Phys.*, **50**, 4402 (1969).
Chang, R. F., G. Morison, and J. M. H. J. Levelt Sengers, "The Critical Dilemma of Dilute Mixtures," *J. Phys. Chem.*, **88**, 3389 (1984).
Chapman, W. G., K. E. Gubbins, G. Jackson, and M. Radosz, "New Reference Equation of State for Associating Liquids," *Ind. Eng. Chem. Res.*, **29**, 1709 (1990).
Chateauneuf, J. E., C. B. Roberts, and J. F. Brennecke, *ACS Symp. Ser.*, No. 106 (1992).
Christian, S. D., and E. H. Lane, "Solvent Effects on Molecular Complex Equilibria," *Solutions and Solubilities*, M. R. J. Dack, ed., Chap. 6, John Wiley, New York (1975).
Cochran, H. D., P. T. Cummings, and S. Karabomi, "Solvation in Supercritical Water," p. 237, Int. Conf. Supercritical Fluids (1991).
Combes, J. R., K. P. Johnston, K. E. O'Shea, and M. A. Fox, "The Influence of Solvent-Solute and Solute-Solute Clustering on Chemical Reactions in Supercritical Fluids," *ACS Symp. Ser.*, No. 31 (1992).
Cristoforakos, M., and E. U. Franck, "An Equation-of-State for Binary Fluid Mixtures to High Temperature and High Pressures," *Ber Bunsenges Phys. Chem.*, **90**, 780 (1986).
Daubert, T. E., and R. P. Danner, "Data Compilation Table of Properties of Pure Compounds," *AIChE Symp. Ser.*, No. 203, Vol. 75 (1990).
Debenedetti, P. G., A. Chialvo, C. Eckert, and D. Tomasko, "Local Density Enhancements in Dilute Supercritical Mixtures: Comparison Between Theory and Experiment," Abstract from paper 204e, AIChE Meeting, Los Angeles (1991).
Debenedetti, P. G., and S. K. Kumar, "The Molecular Basis of Temperature Effects in Supercritical Fluid Extraction," *AIChE J.*, **34**(4), 645 (1988).
Dobbs, J. M., J. M. Wong, R. J. Lahiere, and K. P. Johnston,

"Modification of Supercritical Fluid Phase Behavior Using Polar Co-Solvents," *Ind. Eng. Chem. Res.*, **26**, 56 (1987).

Eckert, C. A., D. H. Ziger, K. P. Johnston, and S. Kim, "Solute Partial Molal Volumes in Supercritical Fluids," *J. Phys. Chem.*, **90**, 2738 (1986).

Economou, I. G., and M. D. Donohue, "Chemical, Quasi-Chemical and Perturbation Theories for Associating Fluids," *AIChE J.*, **37**(12), 1875 (1991).

Economou, I. G., and M. D. Donohue, "Thermodynamic Inconsistencies in and Accuracy of Chemical Equations of States for Associating Fluids," *Ind. Eng. Chem. Res.*, **31**, 1203 (1992).

Ekart, M. P., J. F. Brennecke, and C. A. Eckert, "Molecular Analysis of Phase Equilibria in Supercritical Fluids," *Supercritical Fluid Technology*, T. J. Bruno and J. F. Ely, eds., CRC Press, Boca Raton, FL (1991).

Flarsheim, W. M., A. J. Bard, and K. P. Johnston, "Pronounced Pressure Effects on Reaction Equilibria in Supercritical Fluids," *J. Phys. Chem.*, **93**, 4234 (1989).

Franks, F., "Water A Comprehensive Treatise," *The Physics and Physical Chemistry of Water*, Vol. 1, p. 372, Plenum Press, New York (1972).

Franck, E. U., "Concentrated Electrolyte Solutions at High Temperature and Pressures," *J. of Solution Chemistry*, **2** (2/3), 339 (1973).

Fulton, J. L., G. G. Yee, and R. D. Smith, "Inter- and Intra-Molecular Hydrogen-Bonding of Polyethylene Glycol Dodecyl Ethers in Supercritical Ethane," *J. Supercrit. Fluids*, **3**, 169 (1990).

Grigull, U., J. Straub, and P. Schiebener, eds., *Steam Tables in SI-Units*, Springer-Verlag, Heidelberg (1990).

Heidemann, R. A., and J. M. Prausnitz, "van der Waals-type Equation of State for Fluids with Associating Molecules," *Proc. Nat. Acad. Sci. USA*, **73**, 1773 (1976).

Huang, S. L., and M. Radosz, "Equation of State for Small, Large, Polydisperse, and Associating Molecules: Extension to Fluid Mixtures," *Ind. Eng. Chem. Res.*, **30**, 1994 (1991).

Ikonomou, G. D., and M. D. Donohue, "Thermodynamics of Hydrogen-Bonded Molecules: The Associated Perturbed Anisotropic Chain Theory," *AIChE J.*, **32**, 1716 (1986).

Jin, L., Y. T. Shah, and M. Abraham, "The Effect of Supercritical Water on the Catalytic Oxidation of 1,4-Dichlorobenzene," *J. Supercrit. Fluids*, **3**, 233 (1990).

Johnston, K. P., S. Kim, and J. Combes, "Spectroscopic Determination of Solvent Strength and Structure in Supercritical Fluid Mixtures," *Am. Chem. Soc. Symp. Ser.*, #406, 52 (1989).

Johnston, K. P., D. G. Peck, and S. Kim, "Modeling Supercritical Mixtures—How Predictive is It?" *Ind. Eng. Chem. Res.*, **28**, 1115 (1989).

Johnston, K. P., G. McFann, D. G. Peck, and R. M. Lemert, "Pressure Tunning of Reverse Micelles for Adjustable Solvation of Hydrophiles in Supercritical Fluids," *Amer. Chem. Soc. Symp. Ser.*, #406, 140 (1989).

Karachewski, A. M., W. J. Howell, and C. A. Eckert, "Development of the AVEC Model for Associating Mixtures Using NMR Spectroscopy," *AIChE J.*, **37**, 65 (1991).

Kim, S., J. M. Wong, and K. P. Johnston, "Theory of the Pressure Effect in Dense Gas Extraction," in "Supercritical Fluid Technology," J. Penninger, ed., Elsevier (1985).

Kim, S., and K. P. Johnston, "Clustering in Supercritical Fluid Mixtures," *AIChE J.*, **33**, 1603 (1987).

Lee, L. L., P. G. Debenedetti, and H. D. Cochran, "Fluctuation Theory of Supercritical Solutions," in "Supercritical Fluid Technology," T. J. Bruno and J. F. Ely, eds., CRC Press, Boca Raton, FL (1991).

Lee, M. L., and K. C. Chao, "Polar Pressure of Water and Simplified Augumented Back Equation of State," *Fluid Phase Equilib.*, **58**, 1 (1990).

Lemert, R. M., and K. P. Johnston, "Chemical Complexing Agents for Enhanced Solubilities in Supercritical Fluid Carbon Dioxide," *Ind. Eng. Chem. Res.*, **30**, 1222 (1991).

Levelt Sengers, J. M. H., "Thermodynamics of Solutions Near the Critical Point," *Supercritical Fluid Technology: Review in Modern Theory and Applications*, T. J. Bruno, and J. F. Ely, eds., CRC Press, Boca Raton, FL (1991).

Levine, S., and J. W. Perram, *Hydrogen-Bonded Solvent Systems*, A. K. Covington, and P. Jones, eds., Taylor and Francis, London (1968).

Luck, W. A. P., "A Model of Hydrogen-Bonded Liquid," *Angew. Chem. Int. Ed. Eng.*, **19**, 28 (1980).

Marsh, K., and F. Kohler, "Thermodynamic Properties of Associated Solutions," *J. Mol. Liquids*, **30**, 13 (1985).

Michel, S., H. H. Hooper, and J. M. Prausnitz, "Mutual Solubilities of Water and Hydrocarbon from Equation of State. Need for an Unconventional Mixing Rule," *Fluid Phase Equilib.*, **45**, 173 (1989).

Nickel, D., and G. M. Schneider, "Near-Infrared Spectroscopic Investigations on Phase Behaviour and Association of 1-Hexanol and 1-Decanol in Carbon Dioxide, Chlorotrifluoromethane, and Sulfur Hexafluoride," *J. Chem. Thermody.*, **21**, 293 (1989).

O'Shea, K. E., K. Kirmse, M. A. Fox, and K. P. Johnston, "Polar and Acid-Base Interaction in the Supercritical Fluid State," *J. Phys. Chem.*, **95**, 7863 (1992).

Peck, D. G., and K. P. Johnston, "Theory of the Pressure Effect on the Curvature and Phase Behavior of AOT Water-in-Oil Microemulsions in a Compressible Solvent," *J. Phys. Chem.*, **95**, 9549 (1991).

Panayiotou, C. G., "Thermodynamics of Alkanol-Alkane Mixtures," *J. Phys. Chem.*, **92**, 2960 (1988).

Panayiotou, C. G., "Thermodynamics of Associated Solutions. Mixtures of 1-Alkanols," *Fluid Phase Equilib.*, **56**, 171 (1990).

Panayiotou, C. G., "Thermodynamics of Mixtures of Amines and *n*-Alkanes and 1-Alkanols," *J. of Solution Chemistry*, **20**(1) (1990).

Panayiotou, C., and I. C. Sanchez, "Hydrogen Bonding in Fluid: an Equation-of-State Approach," *J. Phys. Chem.*, **95**, 10090 (1991).

Peck, D. G., A. J. Mehta, and K. P. Johnston, "Pressure Tuning of Chemical Reaction Equilibria in Supercritical Fluids," *J. Phys. Chem.*, **93**(10), 4297 (1989).

Randolph, T. W., D. S. Clark, H. W. Blanch, and J. M. Prausnitz, "Enzymatic Oxidation of Cholesterol Aggregates in Supercritical Carbon Dioxide," *Sci.*, **238**, 387 (1988).

Sanchez, I. C., and R. H. Lacombe, "An Elementary Molecular Theory of Classical Fluids. Pure Fluids," *J. Phys. Chem.*, **80**, 2352 (1976).

Shaw, R. W., T. B. Brill, A. A. Clifford, C. A. Eckert, and E. Ulrich Franck, "Supercritical Water, A medium for Chemistry," *C&EN*, 26 (Dec. 23, 1991).

Schneider, G. M., "High-Pressure Investigations on Fluid Systems—a Challenge to Experiment, Theory, and Application," *J. Chem. Thermody.*, **23**, 301 (1991).

Stryjek, R., and J. H. Vera, "Equation of State: Theories and Applications," K. C. Chao, and R. C. Robinson, Jr., ed., *ACS Symp. Ser.*, No. 300, p. 560, Amer. Chem. Soc., Washington, DC (1986).

Sun, Y.-P., M. A. Fox, and K. P. Johnston, "Spectroscopic Studies of *p*-(*N*,*N*-Dimethylamino) Benzonitrile and *p*-[(*N*,*N*-Dimethylamino) Ethyl]Benzoate in Supercritical Trifluoromethane, Carbon Dioxide, and Ethane," *J. Amer. Chem. Soc.*, **114**, 1187 (1992).

Thornton, T. D., and P. E. Savage, "Phenol Oxidation in Supercritical Water," *J. Supercrit. Fluids*, **3**, 240 (1990).

Veytsman, B. A., "Are Lattice Models Valid for Fluids with Hydrogen Bonds?" *J. Phys. Chem.*, **94**, 8499 (1990).

Vimalchand, P., and M. D. Donohue, "Comparison of Equations of State for Chain Molecules," *J. Phys. Chem.*, **93**, 4355 (1989).

Walsh, J. M., M. L. Greenfield, G. D. Ikonomou, and M. D. Donohue, "Hydrogen Bonding Competition in Entrainer Cosolvent Systems," *Chem. Eng. Comm.*, **86**, 124 (1989).

Webley, P., J. Tester, and H. Holgate, "Oxidation Kinetics of Ammonia and Ammonia-Methanol Mixtures in Supercritical Water in the Temperature Range 530-700°C at 246 bar," *Ind. Eng. Chem. Res.*, **30**, 1745 (1991).

Yang, H., and C. A. Eckert, "Homogeneous Catalysis in the Oxidation of p-Chlorophenol in Supercritical Water," *Ind. Eng. Chem. Res.*, **27**, 2009 (1988).

Zagrobelny, J. A., and F. V. Bright, "Investigation of Pyrene Excimer Formation in Supercritical CO_2," *ACS Symp. Ser.*, in press (1992).

Manuscript received Feb. 18, 1992, and revision received May 20, 1992.