Lattice-Fluid Equation of State with Hydrogen-Bond Cooperativity

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Hydrogen bonding plays an important role in thermodynamic properties of polar fluids. Existing equations of state that include h-bonding cannot accurately predict the phase behavior for polar fluids. In the theories for h-bond-chain forming molecules, h-bonding strength is considered a constant at a given temperature and pressure. Infrared spectroscopy and ab initio *calculations show that the h-bonding strength depends on whether or not the molecule was previously h-bonded at other sites. When an h-bond is formed between an already hydrogen-bonded species and a free species, the second h-bond has different energetic characteristics from the primary h-bond. In the case of* 1*-alkanol self-h-bonding, the equilibrium constant for the second h-bond is ten times that for the primary h-bond. This phenomenon called h-bond cooperativity was incorporated in a lattice-fluid-hydrogen-bonding equation of state. Calculations for pure* 1*-alkanols, show that the theory can be improved significantly by the incorporation of h-bond cooperativity. Agreement with the phase behavior and spectroscopic h-bonding data improves using cooperativity, without any additional adjustable parameters. Heat of mixing calculations agree well with the experimental data.*

Introduction

Hydrogen bonding (h-bonding) plays a vital role in determining the physical and thermodynamic properties of polar fluids. H-bond effects are usually stronger than any other nonionic intermolecular interactions (Prausnitz et al., 1986; Huyskens et al., 1991). Also, h-bonding influences the properties of polar polymer blends and mixtures (Coleman and Painter, 1995; Coleman et al., 1990; Walsh et al., 1989; Economou and Donohue, 1991; Koh et al., 1993). There have been several approaches to develop a unified h-bonding theory for accurate prediction of thermodynamic properties. In general, the models can be classified into two different approaches. The first one is the association theory that considers the chemical equilibrium mixtures of monomers and chain aggregates (Heidemann and Prausnitz, 1976; Huang and Radoz, 1990, 1991, 1993). The second approach is considering the equilibrium between formation and rupture of h-bonds using statistical thermodynamics, known as lattice fluid h-bonding theory (LFHB) (Veytsman, 1990; Panayiotou and Sanchez, 1991; Gupta et al., 1992; Gupta and Johnston, 1994; Gupta and Prausnitz, 1996). The second approach has several advantages over the first approach in modeling complex systems.

In all these theories, for h-bond-chain forming molecules, h-bonding strength is considered to be a constant at given temperature and pressure. However, spectroscopy and *ab initio* calculations have shown that the h-bonding strength depends on whether the molecule was previously h-bonded at other sites or not. When a h-bond is formed between previously *h*-bonded molecules and a free molecule, the second h-bond has different energetic characteristics than the first h-bond. For example, in the case of *l*-alkanol self-association, the equilibrium constant for the second h-bond is tenfold greater than that for the first h-bond (Gupta and Brinkley, 1998). This phenomenon is termed h-bond cooperativity.

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H-Bond cooperativity was postulated qualitatively by Frank and Wen (1957). From that time, various calculations have been presented in the literature to support the existence of the cooperative effects. A simple quantitative treatment of cooperativity was first given by Huyskens (1977) in which *h*-bond formation constants were measured for phenol with different proton acceptor groups. Cooperativity in water has been studied using several different approaches. Del Bene and Pople (1969) reported intermolecular energies of different water polymers using *ab initio* calculations. Kollman and Allen (1970) have studied dimer and polymer geometries and energies of water, HF, and ammonia using semi-empirical *ab initio* calculations. Following them, a sequence of theoretical calculations in the literature was able to verify the existence of cooperativity (Hankins et al., 1970; Kollman, 1977; Kurnig et al., 1986). Sciortino and Fornili (1989) have investigated the bond distribution, as well as geometric and energetic properties in water, using molecular dynamics calculations

In a different approach, several investigators have measured frequency shifts in their spectroscopic studies during h-bond formation. Gaw et al. (1984) used *ab initio* electronic structure theory to account for the frequency shifts. Infrared spectroscopic investigations of Kleeberg et al. (1987) have shown the cooperativity effects in 1,4-butanediol. Karachewski et al. (1989, 1991) have measured NMR chemical shifts and developed AVEC model to account for it in associating molecules. Kleeberg (1991) also explains the cooperativity effects in h-bond formation with various supporting results. Van Thiel et al. (1957) have studied *h*-bonding in methanol using infrared spectroscopy. Maes and Smets (1993) have used matrix-isolation FTIR spectroscopy to illustrate cooperativity in HF, HCl, and H_2O and provided a detailed case study of a trichlorophenol/water system. Recently, Gupta and Brinkley (1998) used FTIR spectroscopy to demonstrate the importance of cooperativity in self-association of *l*-alkanols.

Traditional h-bonding theories are not able to represent the phase behavior or spectroscopic results of polar species with a good accuracy. Incorporation of the cooperativity effect can perhaps improve these theories. Hence, the focus of this work is to examine the importance of cooperativity effects of h-bond formation on the phase behavior. Here, we have selected to work with pure *l*-alkanols since they have more than one h-bonding sites, and spectroscopic data are available. In this work, we first verify the extent of cooperativity using *ab initio* calculations for ethanol, then we test if the incorporation of cooperativity into the LFHB equation of state will improve the model. The performance is tested using vapor-liquid equilibria and spectroscopic data for *l*-alkanols and heat of mixing of alkanol/alkane mixtures.

Ab Initio Calculations

Cooperativity arises from the fact that the electrons in the molecule are rearranged upon formation of the h-bond. After the formation of the first h-bond, the formation of the second h-bond is easier or more difficult depending on the electronic charge reorientation in the species (Sear and Jackson, 1996). For example, in ethanol (Figure 1), the h-bonded hydrogen (a) is farther away from the oxygen (b) than in the non-h-bonded state. The increased OH bond length makes the oxygen a more effective acceptor. In a similar manner, the presence of the donor hydrogen (a) of the first bond near the oxygen acceptor loosens the un-h-bonded hydrogen (d) and increases its potential as a donor. As a result, subsequent bonds formed on (b) or (d) are stronger than those formed on a free ethanol molecule. *Ab initio* calculations are based on the electron wave functions of the atoms contained within a given domain. A system of these wave functions may be used to model a group of molecules and determine factors such as optimal bond lengths, strengths, angles, and vibrational frequencies. Due to their foundation in statistical mechanics, *ab initio* calculations are an excellent way to demonstrate the effects of cooperativity.

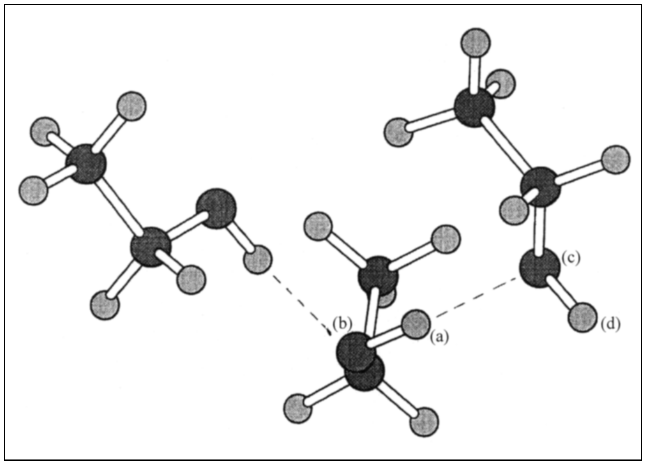

Figure 1. Structure of three ethanol molecules from the *ab initio* calculations.

Guassian-98 was used to model systems of one, two, and three ethanol molecules. The solver was instructed to use the Hartree-Fock method with a *6-31g(d)* basis set. In order to determine cooperativity, the ΔE of the two and three molecule systems from the noninteracting case was calculated by

$$\Delta E_d = E_2 - 2 \cdot E_1$$

$$\Delta E_t = E_3 - 3 \cdot E_1 \qquad (1)$$

where d is the h-bonded dimer, t is the h-bonded trimer, and E_i is the calculated energy of i ethanol molecules in the system. Table 1 shows the results of the three calculations corrected for BSSE using the point counterpoise method (Boys and Bernardi, 1970). In the case of two ethanol molecules, there is only one h-bond with h-bonding energy of -17.9 kJ/mol. For three ethanol molecules there are two h-bonds with a combined energy of -42.3 kJ/mol; this could also be represented as the first h-bond having -17.9 kJ/mol energy, while the second h-bond has an energy of -24.4 kJ/mol. The difference between the two energies clearly shows the cooperative effect. It is interesting to note that the energy difference of -6.5 kJ/mol yields the cooperativity factor (τ) of

Table 1. Results of *Ab Initio* Calculations for Ethanol Molecules

	One Molecule No *h*-Bonds	**Two Molecules** One *h*-Bond	**Three Molecules** Two *h*-bonds
Energy (Hartrees)	−154.0757446	−308.1607195	−462.2483411
BSSE Correction (H)	—	−0.0024324	−0.0050072
H-bonding Energy	—	−17.9 kJ/mol	−42.3 kJ/mol
Cooperativity Factor (at ambient T), τ	—	—	0.07
OH Bond Length (non-h-bonded H)	0.9466 Å	0.9473 Å	0.9474 Å
OH Bond Length (1st h-bonded H)	—	0.9511 Å	0.954 Å
OH Bond Length (2nd h-bonded H)	—	—	0.9533 Å

0.07 at ambient temperature. This is close to the value of 0.1 obtained from FTIR spectroscopy measurements by Gupta and Brinkley (1998). Now with the dual confirmation of the cooperativity factor, it can be incorporated in an equation of state for practical uses.

Lattice-Fluid Equation of State Including H-bond Cooperativity

The LFHB follows the work of Veytsman (1990), Panayiotou and Sanchez (1991), Gupta et al. (1992), and Gupta and Johnston (1994). The theoretical treatment for h-bond cooperativity has been introduced by Veytsman (1993) and Sear and Jackson (1996). Gupta and Brinkley (1998) demonstrated the cooperativity in *l*-alkanol-alkane mixtures using FTIR spectroscopy and lattice-fluid equilibria. Missopolinou and Panayiotou (1998) also combined cooperativity into a lattice fluid equation of state. This work follows from that of Veytsman (1993), Gupta and Brinkley (1998), and Missopolinou and Panayiotou (1998).

Pure Fluids

A system is considered of alkanol molecules with one h-bonding donor and one acceptor. Hence, in this self-associating system one molecule can have a maximum of two h-bonds. For simplicity, we consider only two kinds of h-bonds: dimer-like and polymer-like. Assuming that there is a total of N_{11} h-bonds out of which N_d are dimer-like h-bonds, these dimer-like bonds are considered weaker than any subsequent polymer-like bonds.

Now, let's follow the basic LFHB combinatorial approach. We calculate the number of ways of distributing the N_d dimer-like bonds and $N_{11} - N_d$ polymer-like bonds between adjacent donor and acceptor sites using mean-field approximation originally suggested by Veytsman (1991). There are $N\text{-}N_{11} = N_{10}$ free donors. The participating donor groups can be chosen in $N!/N_{10}!$ ways. There are $N - N_{11}$ weak acceptors and only N_d of them participate in h-bonding. The number of ways of choosing them is $(N\text{-}N_{11})!/(N\text{-}N_{11}\text{-}N_d)!$. The number of ways of choosing strong acceptors is $N_{11}!/N_d!$. Since N_d dimer-like h-bonds are indistinguishable and $N_{11}\text{-}N_d$ polymer-like bonds are indistinguishable, the result is divided by $N_d!(N_{11}\text{-}N_d)!$ to avoid over-counting. Finally, the number of ways of distributing the h-bonds is

$$\Omega = \frac{N!}{(N-N_{11})!}\,\frac{(N-N_{11})!}{(N-N_{11}-N_d)!}\,\frac{N_{11}!}{N_d!}\,\frac{1}{N_d!(N_{11}-N_d)!} \tag{2}$$

The partition function due to h-bonding (Q_H) is written as (Panayiotou and Sanchez, 1991)

$$\begin{aligned} Q_H &= \left(\frac{\tilde{\rho}}{rN}\right)^{N_{11}} \Omega \exp\left(\frac{-\Sigma N_{ij} G_{ij}^0}{kT}\right) \\ &= \left(\frac{\tilde{\rho}}{rN}\right)^{N_{11}} \frac{N!N_{11}!}{(N_{10}-N_d)!(N_{11}-N_d)!(N_d!)^2} \\ &\qquad \exp\left(\frac{-\left\{N_d G_d^0 + (N_{11}-N_d)G_p^0\right\}}{kT}\right) \end{aligned} \tag{3}$$

where $\tilde{\rho}$ is reduced density, r is segment length, and G_d^0 and G_p^0 are standard Gibbs free energy change upon dimer-like and polymer-like *h*-bond formation, respectively.

Gibbs free energy due to h-bonding is determined as

$$G_H = -kT \ln Q_H \tag{4}$$

Using the Sterling's approximation ($N! = N \ \ln \ N\text{-}N$) for a large N, Eqs. 3 and 4 yield

$$\begin{aligned} G_H/kT &= \frac{N_d G_d^0 + (N_{11}-N_d)G_p^0}{kT} - N_{11} \ln\left(\frac{\tilde{\rho}}{rN}\right) \\ &\quad - \left[\begin{aligned} &N \ln N - N + N_{11} \ln N_{11} - N_{11} - (N - N_{11} - N_d)\ln(N - N_{11} - N_d) + (N - N_{11} - N_d) \\ &- (N_{11} - N_d)\ln(N_{11} - N_d) + (N_{11} - N_d) - 2N_d \ln N_d + 2N_d \end{aligned}\right] \end{aligned} \tag{5}$$

Upon combining h-bonding contribution with the physical lattice fluid contribution (Sanchez and Lacombe, 1976) and minimizing the free energy with respect to each kind of h-bond results in the following coupled quadratic equations

$$\frac{(\nu_{11}-\nu_d)}{(1/r-\nu_{11}-\nu_d)\nu_{11}} = \tilde{\rho}\exp\left(\frac{-G_p^0}{kT}\right) \tag{6}$$

$$\frac{\nu_d}{(\nu_{11}-\nu_d)(1/r-\nu_{11}-\nu_d)} = \exp\left(\frac{-\left(G_d^0-G_p^0\right)}{kT}\right) = \tau \tag{7}$$

where

$$\nu_{11} = \frac{N_{11}}{rN}, \quad \text{and} \quad \nu_d = \frac{N_d}{rN} \tag{8}$$

Simultaneous Eqs. 6–7 are solved numerically to give the fractional h-bonding of each type. Minimizing the Gibbs free energy with respect to volume yields following equation of state

$$\tilde{\rho}^2 + \tilde{P} + \tilde{T}\left[\ln(1-\tilde{\rho}) + \tilde{\rho}(1-1/\bar{r})\right] = 0 \tag{9}$$

where

$$1/\bar{r} = 1/r - \nu_{11} \tag{10}$$

Equation 9 is similar as the original LFHB except that it has different equations for calculating the h-bonding. At the minimum, Gibbs free energy due to h-bonding is

$$G_H/kT = rN\left[\nu_{11} + \frac{1}{r}\ln(1 - r\nu_{11} - r\nu_d)\right] \tag{11}$$

and the chemical potential is given as

$$\frac{\mu}{kT} = r\left[-\frac{\tilde{\rho}}{\tilde{T}} + \frac{\tilde{P}}{\tilde{\rho}\tilde{T}} + \left(\frac{1}{\tilde{\rho}}-1\right)\ln(1-\tilde{\rho}) + \frac{\ln(\tilde{\rho})}{r}\right] + r\left(\nu_{11} + \frac{1}{r}\right)\ln(1-\nu_{11}-\nu_d) \tag{12}$$

where $\tilde{T} = T/T^*$ and $\tilde{P} = P/P^*$ are reduced temperature and reduced pressure, respectively.

Mixtures

Let's consider a mixture of N_2 alkanol molecules and N_1 alkane (or non-h-bonding) molecules. The physical part of the partition function takes a similar form as in the original lattice fluid theory by Lacombe and Sanchez (1976). The mixing rules used are as follows (Panayiotou, 1988)

$$\epsilon^* = \phi_1\epsilon_1^* + \phi_2\epsilon_2^* - 2\phi_1\phi_2\left[\epsilon_1^* + \epsilon_2^* - 2\xi_{12}(\epsilon_1^*\epsilon_2^*)^{1/2}\right] \tag{13}$$

and

$$v^* = \phi_1^2 v_1^* + \phi_2^2 v_2^* + 2\phi_1\phi_2\left(\frac{(v_1^*)^{1/3} + (v_2^*)^{1/3}}{2}\right)^3 \tag{14}$$

where

$$\phi_1 = \frac{r_1 N_1}{rN}; \qquad \phi_2 = \frac{r_2 N_2}{rN}$$

The h-bonding partition function is written using a similar combinatorial approach as we discussed for pure fluids

$$Q_H = \left(\frac{\tilde{\rho}}{rN}\right)^{N_{11}} \frac{N_2!N_{11}!}{(N_2-N_{11}-N_d)!(N_{11}-N_d)!(N_d!)^2} \exp\left(\frac{-\left\{N_d G_d^0 + (N_{11}-N_d)G_p^0\right\}}{kT}\right) \tag{15}$$

which leads to the following equations when minimizing the Gibbs free energy with respect to number of h-bonds

$$\frac{(\nu_{11}-\nu_d)}{(x_2/r-\nu_{11}-\nu_d)\nu_{11}} = \tilde{\rho}\exp\left(\frac{-G_p^0}{kT}\right) \tag{16}$$

$$\frac{\nu_d}{(\nu_{11}-\nu_d)(x_2/r-\nu_{11}-\nu_d)} = \exp\left(\frac{-\left(G_d^0-G_p^0\right)}{kT}\right) = \tau \tag{17}$$

The equation of state obtained by minimizing Gibbs free energy with respect to reduced density remains the same as in Eq. 9. The heat of mixing (H^E) is obtained from the energies of the mixtures and pure fluids

$$\frac{H^E}{rN} = -\tilde{\rho}\epsilon^* + \phi_1\tilde{\rho}_1\epsilon_1^* + \phi_2\tilde{\rho}_2\epsilon_2^* + E_p^0(\nu_{11}-\nu_d) + E_d^0\nu_d - \phi_2\left(E_p^0(\nu_{11}^{\text{pure}} - \nu_d^{\text{pure}}) + E_d^0\nu_d^{\text{pure}}\right) \tag{18}$$

where *pure* stands for pure alkanol h-bonding. In the right side, the first three terms and due to physical energy and later terms are due to h-bonding energy.

Results and Discussion

The theory was applied to a series of *l*-alkanols: methanol to *l*-octanol. The values for the polymer-like h-bonding parameters E^0, S^0, and V^0 were taken to be −25.1 kJ/mol, −26.5 J/(K·mol) and −5.6 cm³/mol respectively, same for all *l*-alkanols. These are the same values as previously used by Gupta et al. (1992) and Panayiotou and Sanchez (1991).

Table 2. Lattice-Fluid Physical Parameters for *l*-Alkanols

Alkanol	T^* (K)	P^* (MPa)	ρ^* (kg/m^3)	% Error*
Methanol	557.7	304.7	743.4	2.0
Ethanol	529.7	298.7	780.5	1.7
l-Propanol	542.9	304.3	814.2	2.3
l-Butanol	565.5	295.2	821.5	2.4
l-Pentanol	576.4	301.4	832.4	4.7
l-Hexanol	590.0	294.8	839.6	3.4
l-Heptanol	561.5	335.6	861.6	6.0
l-Octanol	576.0	322.8	862.1	5.2

*In saturated liquid density and vapor pressure.

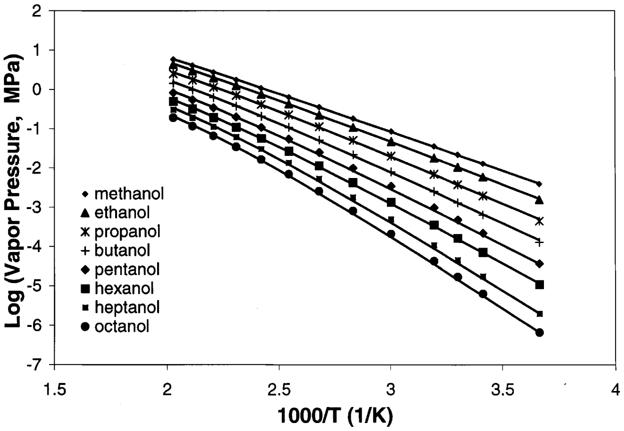

Figure 2. Vapor pressures of *l*-alkanols.

Lines are theory with cooperativity and points are data from Daubert and Danner (1990).

E^0 is also very close to the value (-24.4 kJ/mol) obtained from *ab initio* calculations. The h-bonding cooperativity factor τ was taken to be 0.1 for all *l*-alkanols as determined from spectroscopy (Gupta and Brinkley, 1998) and also *ab initio* calculations. Cooperativity factor τ is theoretically a temperature-dependent function. In practical cases, it does not vary significantly with temperature and hence can be used independent of temperature.

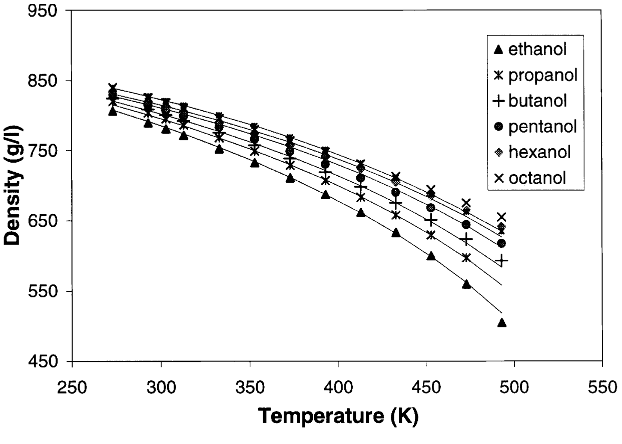

Figure 3. Saturated liquid densities of *l*-alkanols.

Lines are theory with cooperativity and points are data from Daubert and Danner (1990).

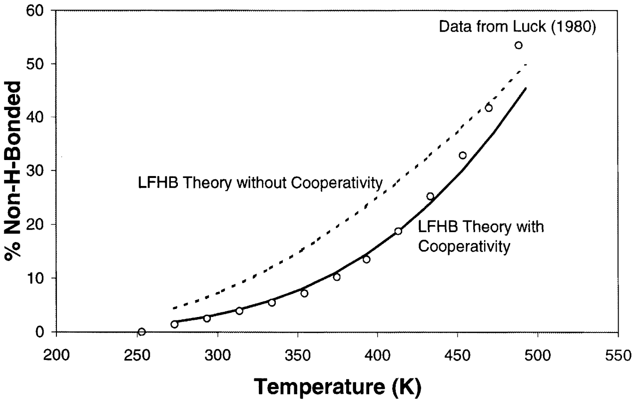

Figure 4. *H*-bonding in saturated-liquid ethanol.

Values for physical lattice-fluid parameters T^*, P^*, and ρ^* were estimated by fitting the equation of state to the saturated liquid density and vapor pressure data for pure *l*-alkanols (Daubert and Danner, 1990). Obtained parameters are listed in Table 2. Comparison of the correlation and the experimental data for vapor pressure is shown in Figure 2, and saturated liquid density is shown in Figure 3. Theory compares reasonably well with the data except for the density of a few higher *l*-alkanols at high temperatures.

The key feature of the improvement in the theory lies in the prediction of the degree of h-bonding. Fortunately, spectroscopic data are available for h-bonding in saturated liquid ethanol from Luck (1980). Theoretical predictions for % non-h-bonded ethanol compare very well with the experimental data (Figure 4), except near the critical region where it is well known that the lattice-fluid theories do not work well. Predictions are very much improved by the introduction of cooperativity in the LFHB model, without any adjustable parameters. The theory without cooperativity does not show enough of the curvature which is present in the data. With the inclusion of cooperativity, proper curvature in the prediction is achieved. This feature arises because dimer-like h-bonding increases with temperature at the expense of a decrease in the polymer-like h-bonding, as shown in Figure 5.

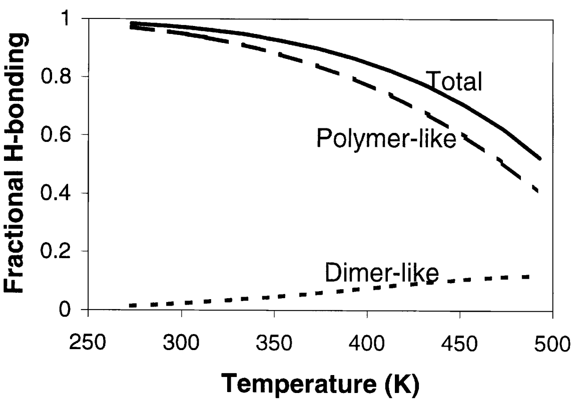

Figure 5. Calculated polymer-like and dimer-like h-bonding in saturated liquid ethanol.

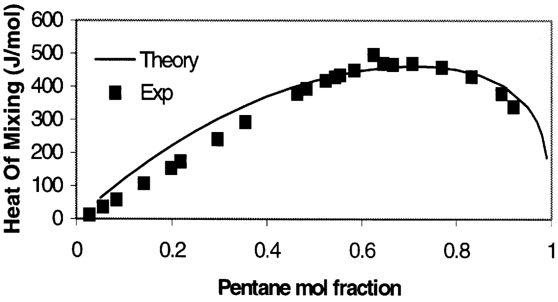

Figure 6. Heat of mixing of *n*-pentane with *l*-pentanol.

Experimental data taken from Christensen et al. (1982). $P = 170$ kPa, $T = 298.15$ K, $\xi_{12} = 0.990$.

Calculated heat of mixing is compared with the experimental data in Figures 6–7 for two *l*-alkanol/*n*-alkane mixtures. Binary energy interaction parameter ξ_{12} was adjusted to fit this data. Value of ξ_{12} is very close to unity. Calculations are in good agreement with data. It should be noted that the LFHB without cooperativity can also represent well H^E data with one adjustable parameter (Panayiotou, 1988). Hence, the two theories perform equally well for heat of mixing.

Calculations are made for self *h*-bonding of ethanol in supercritical carbon dioxide (Figures 8–9). Both dimer-like and polymer-like h-bonding increase with pressure due to the negative volume of h-bonding. With an increase in the ethanol mol fraction, polymer-like h-bonding increases faster than the dimer-like h-bonding. Ethanol is used as a cosolvent for the solubility enhancement in supercritical fluid technology. The h-bonding between the solute and ethanol is responsible in most cases for the enhancement. Hence, dimer-like h-bonded ethanol will be preferred over the polymer-like h-bonded ethanol chains, as the dimer-like ethanol will have more available h-bonding sites for the solute.

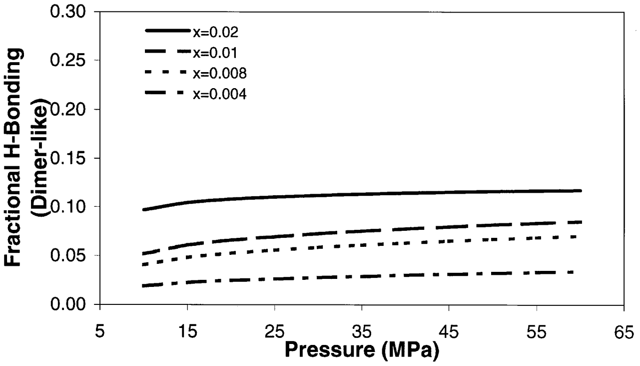

Figure 8. Dimer-like h-bonding in ethanol/CO$_2$ mixtures vs. pressure at 40°C, at different ethanol mol fractions (*x*).

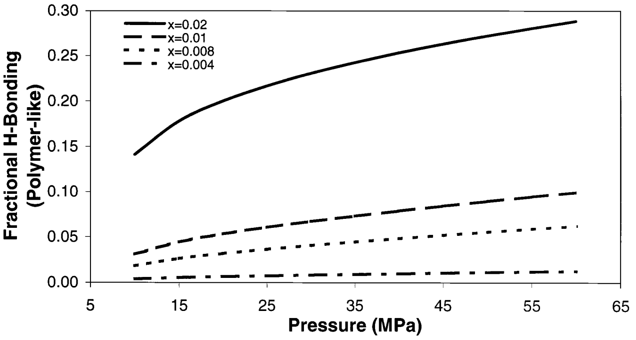

Figure 9. Polymer-like h-bonding in ethanol/CO$_2$ mixtures vs. pressure at 40°C, at different ethanol mol fractions (*x*).

Conclusion

Based on FTIR spectroscopy, *ab initio* calculations, and equation of state modeling, cooperativity plays an important role in the h-bonding of *l*-alkanols. The extent of cooperativity obtained from spectroscopy agrees well with the *ab initio* calculations: the equilibrium constant for the second h-bond is ten times that for the primary h-bond. Upon incorporation of cooperativity in lattice-fluid-hydrogen-bonding equation of state, the predictions for h-bonding are greatly improved. New lattice-fluid parameters are estimated for pure *l*-alkanols from vapor-liquid equilibria.

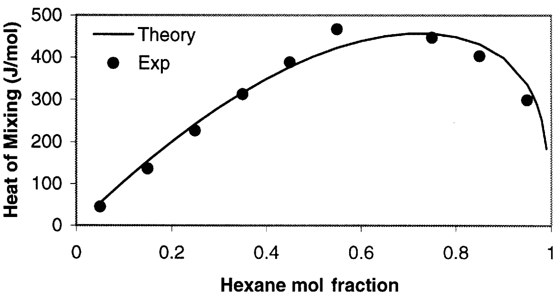

Figure 7. Heat of mixing of *n*-hexane with *l*-octanol.

Experimental data from Christensen et al. (1982). $P = 101.30$ kPa, $T = 298.15$ K, $\xi_{12} = 0.992$.

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