A Multi-Fluid Nonrandom Lattice Fluid Theory for Thermodynamic Properties of Hydrogen Bonding Fluids

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Abstract−A unified equation of state theory valid from pure fluids to multicomponent associated mixtures of molecules having any number of hydrogen (proton) donor and acceptor groups was formulated. Under the fundamental assumption that the intermolecular forces are divided into physical and chemical forces, generalized Veytsman's statistics for hydrogen bonding theory was combined with the nonrandom lattice-fluid theory. By the two-fluid approximation, configurational Helmholtz free energy was derived from the lattice of the Guggenheim combinatory. The Veytsman's statistics extended for dimers and n-mers was employed for the description of some associating systems including organic acid.

Key words: Hydrogen Bonding, Lattice Theory, Vapor-Liquid Equilibria, Alcohol, Acid

INTRODUCTION

Hydrogen bonding is stronger and has a much longer lifetime than the ordinary van der Waals interaction and it is often referred as chemical reaction. The hydrogen bonding interaction implies the formation of association complexes. The existence of this association has been invoked by the basis of the various theories of associated solution. Heidemann and Prausnitz [1976] assumed chemical equilibria between molecules to form new species and obtained the analytical solution for the chemical equilibria within an equation of state. Ikonomou and Donohue [1986, 1988] developed the APACT by applying this approach and combining with the perturbed-anisotropic-chain theory [Vimalchand and Donohue, 1985]. Panayitous and Sanchez [1991] proposed an equation of state based on Veytsman combinatorial expression [1990] for the number of ways of forming hydrogen bonds. They successfully described the thermodynamic behavior of systems of self-associated and cross-associated fluids. Some species like organic acids tend to form dimers, whereas some species like water and alcohols generally form n-mers. The Veytsman's statistics was originally proposed for n-mers and the equation of states incorporating the Veytsman's statistics do not generally give realistic results for organic acid system. Park et al. [2002] proposed an extension of Veytsman's statistics for hydrogen-bonding system with both dimers and n-mers which was named as NLF-HB EOS. Although the formulation of the NLF-HB EOS is self-consistent with a sound theoretical basis, a less complicated model would be convenient in engineering-oriented phase equilibrium calculations. In this work, a recently developed equation of state based on the two-liquid approximation of the lattice-hole theory [Shin et al., 1997; Yoo et al., 1997a, b, 1998] was extended for the phase equilibria of hydrogen bonding fluids. This

equation of state was able to extend to a complex system such as a polymer solution [Jung et al., 2002], solubility of dyes in supercritical carbon dioxide [Joung et al., 1998] and critical region [Shin et al., 2000].

A new version of hydrogen bonding contribution which extended Veytsman's statistics for hydrogen-bonding system with dimer and n-mers was employed. The main attention was placed on the demonstration of the resulting version of an equation of state named as MF-NLF-HB EOS for correlation of phase equilibria of hydrogen bonding fluids.

THERMODYNAMIC PROPERTIES

1. Helmholtz Energy

The configurational lattice-fluid partition function for systems with hydrogen bonding (HB) interactions can be approximated as a product of physical and chemical contributions. Omitting details in the derivation, the resulting expression for the configurational Helmholtz energy is written as

$$A^C = A^{C,P} + A^{C,HB} \tag{1}$$

The physical contribution, $A^{C,P}$, is given by Yoo et al. [1997a, b, 1998]:

$$\beta A^{C,P} = \sum_{i=1}^{c} N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \left(\frac{zN_q}{2}\right)\sum_{i=1}^{c} \theta_i \left[\ln\left(\sum_{j=0}^{c} \theta_j \tau_{ji}\right) + \beta\varepsilon_{ii}\right] \tag{2}$$

where $\theta_i = N_i q_i / N_q$, $q_M = \sum x_i q_i$, $zq_i = r_i(z-2) + 2$, $r_M = \sum x_i r_i$, $\rho_i = N_i r_i / N_r$, $\rho = \sum \rho_i$ and the nonrandomness factor τ_{ji} is defined as,

$$\tau_{ji} = \exp\{\beta(\varepsilon_{ji} - \varepsilon_{ii})\} \tag{3}$$

where ε_{ji} is the absolute value of the interaction energy between species j and i.

The expression for the Helmholtz energy due to hydrogen bonding can be readily derived as [Park et al., 2002],

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$$\beta A^{c,HB} = -\ln\Omega^c_{HB} = (N_{HB} - N_{HB0})\{\ln(N_r/r_H) + 1\}$$
$$+(N^D_{11} - N^{D0}_{11})\ln 2 - (N^D_{10}\ln N^D_{10} - N^D_{10}) + (N^{D0}_{10}\ln N^{D0}_{10} - N^{D0}_{10})$$
$$+\sum_m^M \{N^{HB}_{m0}\ln N^{HB}_{m0} - N^{HB0}_{m0}\ln N^{HB0}_{m0}\}$$
$$+\sum_n^N \{N^{HB}_{0n}\ln N^{HB}_{0n} - N^{HB0}_{0n}\ln N^{HB0}_{0n}\}$$
$$+\sum_m^M \sum_n^N \{\beta N^{HB}_{mn}A^{HB}_{mn} + (N^{HB}_{mn}\ln N^{HB}_{mn} - N^{HB}_{mn})$$
$$-(N^{HB0}_{mn}\ln N^{HB0}_{mn} - N^{HB0}_{mn})\} \tag{4}$$

where N^{HB}_{mn} is the number of hydrogen bonding of donor type m and acceptor type n, N^{HB}_{m0} is the number of unbonded donor of type m, N^{HB}_{0n} is the number of unbonded acceptor of type n. N^D_{11} is the number of pairs of dimerizing groups and N^D_{10} is that of unpaired dimerizing. The superscripts HBO and DO mean zero hydrogen bonding free energy and zero dimmer formation free energy properties, respectively. r_H is the segment number of donors or acceptors. The total number of hydrogen bonding at the finite hydrogen bonding free energy and at the limit of the zero hydrogen bonding free energy is defined by following equations, respectively.

$$N_{HB} = \sum_m \sum_n N^{HB}_{mn} \tag{5}$$

$$N_{HB0} = \sum_m \sum_n N^{HB0}_{mn} \tag{6}$$

Minimizing the Helmholtz energy with respect to N^{HB}_{mn} using $\partial(\beta A^{C,HB})/\partial N^{HB}_{mn} = 0$ gives the following equation for n-mers:

$$N^{HB}_{mn}N_r = N^{HB}_{m0}N^{HB}_{0n}r_H\exp(-\beta A^{HB}_{mn}) \tag{7}$$

and for dimers

$$(2N^D_{11})(N^1_d - 2N^D_{11})(N^1_a - 2N^D_{11})N_r = (N^{HB}_{m0}N^{HB}_{0n})^2 r_H\exp(-\beta A^{HB}_{mn}) \tag{8}$$

where N^1_d, N^1_a are the number of donor sites and acceptor sites of the type 1 of dimer formation.

2. EOS and Chemical Potential

Standard thermodynamic relations can be used to derive other thermodynamic functions such as the EOS and the chemical potential from Eq. (1). For example, the EOS for mixtures is given by

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho) - (\nu_{HB} - \nu_{HB0})\rho\right.$$

$$\left.+\frac{z}{2}\sum_{i=1}^c \theta_i\left(\frac{\tau_{0i}}{\sum_{k=0}^c \theta_k\tau_{0k}} - 1\right)\right\} \tag{9}$$

The chemical potential of component i in a mixture can be obtained by using the following equation,

$$\mu_i = \mu^P_i + \mu^{HB}_i \tag{10}$$

The chemical potential for species i is given by the sum of physical and chemical (i.e., hydrogen bonding) contributions. These contributions are expressed as follows.

$$\frac{\mu^P_i}{RT} = \lambda_i(T) - r_i\ln(1-\rho) + \ln\frac{\theta_i}{q_i} + r_i\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right]$$

$$+\frac{zq_i\theta}{2}\left\{1 - \frac{r_i}{q_i} - \frac{1}{\theta}\left[\ln\sum_{k=0}^c \theta_k\tau_{ki} + \beta\varepsilon_{ii} + \sum_{l=1}^c \frac{\theta_l(\tau_{il} - \tau_{0l}(r_i/q_i))}{\sum_{k=0}^c \theta_k\tau_{kl}}\right]\right\} \tag{11}$$

$$\frac{\mu^{HB}_i}{RT} = -\left(D_i\ln\frac{N^D_{10}}{N^{D0}_{10}} + \sum_m^M d^i_m\ln\frac{N^{HB0}_{m0}}{N^{HB}_{m0}} + \sum_n^N a^i_n\ln\frac{N^{HB0}_{0n}}{N^{HB}_{0n}}\right) \tag{12}$$

where, D_i is unit value only if molecule i has a dimerizing group, otherwise zero.

RESULTS AND DISCUSSION

We set coordination number z at 10 and the unit lattice volume V_H at 9.75 cm³mol⁻¹. The hydrogen bonding Helmholtz energy is defined by the following equation:

$$A^{HB}_{ii} = U^{HB}_{ii} - TS^{HB}_{ii} \tag{13}$$

Hydrogen bonding parameters (U^{HB}_{ii}, S^{HB}_{ii}) were given in the reference [Park et al., 2002]. Two molecular energy and size parameters were fitted to the saturated liquid density and vapor pressure data. They were correlated by the following equation of states as functions of temperature.

$$\varepsilon_{11}/k = E_a + E_b(T - T_0) + E_c[T\ln(T/T_0) + T - T_0] \tag{14}$$

$$r_1 = R_a + R_b(T - T_0) + R_c[T\ln(T/T_0) + T - T_0] \tag{15}$$

where $T_0 = 298.15$ K is a reference temperature. The estimated values of coefficients for Eq. (14) and (15) are summarized in Table 1

Table 1. Temperature coefficients of Eq. (14) and (15) for hydrogen bonding components

Chemicals	E_a	E_b	E_c	R_a	R_b	R_c
Methanol	84.1198	0.22939	0.35062	3.25856	0.003292	−0.0019
Ethanol	86.2273	0.15103	0.15712	4.72326	0.003214	−0.00234
Propanol	89.9716	0.11388	0.08600	6.25494	0.002864	−0.00204
Butanol	94.4333	0.09110	0.03817	7.78540	0.002875	−0.00008
Pentanol	94.2575	0.12735	0.14017	5.52668	0.063549	0.144511
Hexanol	102.4904	0.12227	0.11774	9.75133	−0.00135	−0.01539
Heptanol	105.6287	0.09335	0.02734	11.4754	−0.00834	−0.03454
Acetic acid	100.7946	0.15607	0.20233	6.29542	−0.00155	−0.00942
Propionic acid	99.8893	0.05936	−0.02382	8.62261	−0.00036	−0.00325
Water	360.2713	−0.37257	0.09315	1.85793	−0.00023	−0.00361

Table 2. Binary interaction parameters (λ_{12}) and absolute average deviation (AAD) for vapor liquid equilibrium calculation

System	T(K)	Binary parameter		AADP[a]		AADY[b]	
		MF-NLF-HB	MF-NLF	MF-NLF-HB	MF-NLF	MF-NLF-HB	MF-NLF
n-Butane+methanol	323.15	0.05978	0.05706	1.106	13.172	0.007	16.010
n-Pentane+1-pentanol	303.15	0.01394	0.03184	1.592	7.747	0.001	6.071
1-Propanol+n-decane	368.15	0.00143	0.06500	8.775	11.479	0.021	14.868
n-Heptane+ethanol	343.15	0.03190	0.06400	1.925	22.765	0.023	44.860
n-Heptane+butanol	348.15	0.02230	0.06345	2.023	9.467	0.010	15.080
n-Hexane+methanol	333.15	0.05336	0.09502	2.621	15.570	0.044	21.868
Benzene+1-butanol	318.15	−0.00493	0.05528	3.927	4.600	0.008	6.928
Toluene+1-butanol	333.15	−0.00685	0.04955	3.333	3.433	0.024	6.203
Ethanol+1-propanol	343.15	0.03862	0.01737	0.882	3.039	0.018	5.338
Methanol+ethanol	298.15	0.03251	0.00114	1.332	1.485	0.016	4.700
Methanol+1-propanol	333.17	0.03459	0.00342	0.779	0.364	0.130	0.950
n-Heptane+acetic acid	303.15	0.06711	0.05275	1.586	8.573	0.014	17.657
Benzene+acetic acid	293.15	0.02958	0.03166	0.711	3.772	0.006	11.658
Toluene+acetic acid	353.15	0.03941	0.04470	1.414	1.272	0.014	14.571
acetic acid+propionic acid	313.15	0.00688	−0.00567	0.402	2.404	0.011	20.632
Average error				2.161	7.276	0.023	13.83

[a]$\mathrm{AADP} = (100/\mathrm{n}_T) \sum_i^N |P_i^{calc} - P_i^{exp}| / P_i^{exp}$. [b]$\mathrm{AADY} = (1/\mathrm{n}_T) \sum_i^N |y_i^{calc} - y_i^{exp}| / y_i^{exp}$

for 10 selected hydrogen bonding substances. The present EOS has one binary energy parameter λ_{12} for a binary system which is defined by

$$\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{12})^{1/2}(1-\lambda_{12}) \qquad (16)$$

The MF-NLF-HB EOS was applied to the vapor liquid equilibrium data of 15 binary systems [Gmehling et al., 1980] and the correlation results are summarized in Table 2. The calculation results of the present MF-NLF-HB EOS were compared with MF-NLF model [Yoo et al., 1997a, b, 1998]. Average error percents for 15 binary systems of MF-NLF-HB model (AADP=2.161, AADY=0.023) were lower than those of MF-NLF EOS (AADP=7.276, AADY=

13.83). The calculated results by MF-NLF-HB are similar to NLF-HB model [Park et al., 2002].

In Fig. 1, calculation results of vapor pressures for water, ethanol and acetic acid were compared with experimental data of Reid et al. [1986]. Acetic acid was considered to form dimers. Calculation results of the present EOS agreed well with experimental vapor pressure data for various types of associated pure fluids. Fig. 2 shows the comparison of the present model with experimental VLE data for heptane+butanol system. Calculation results of MF-NLF-HB EOS (AADP=2.023, AADY=0.010) for heptane+butanol system agreed well with the experimental data compared with calculation
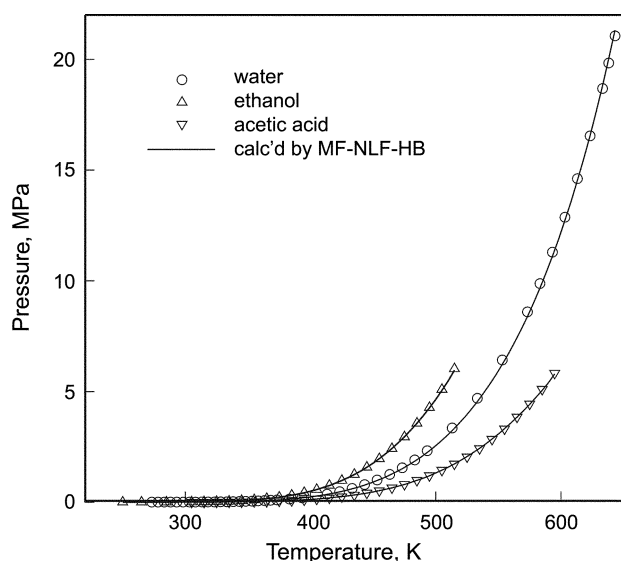
Fig. 1. Comparison of experimental vapor pressures with calculated results.
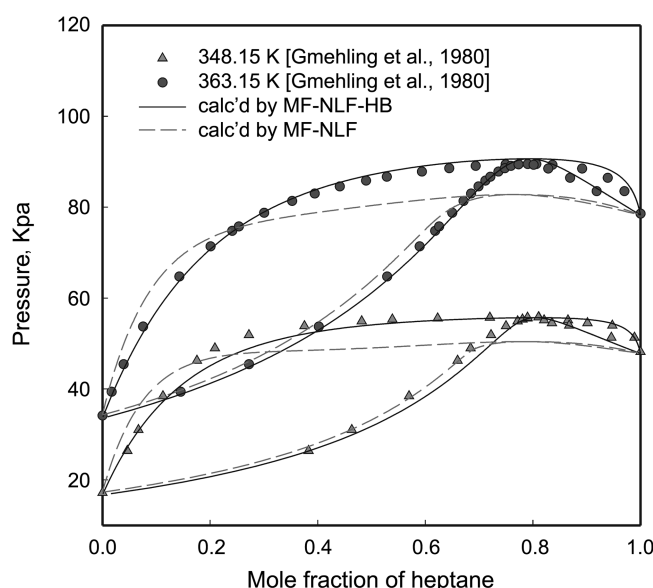
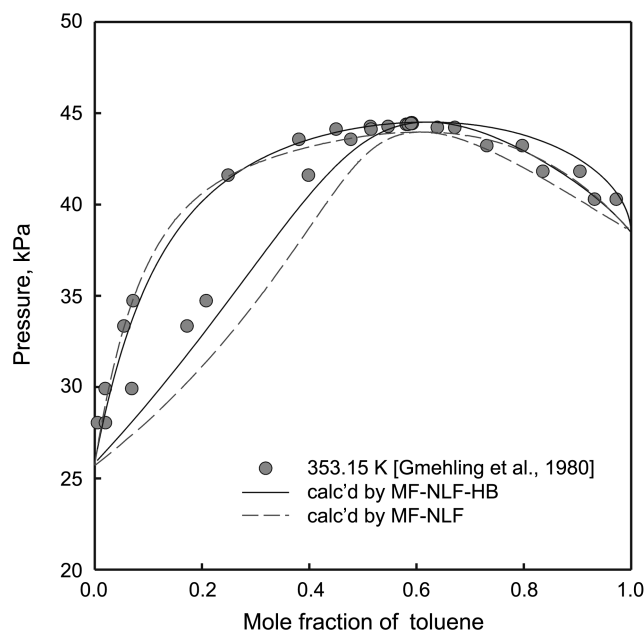**Fig. 2. Vapor-liquid equilibria of heptane and butanol system at 348.15 K and 363.15 K.**

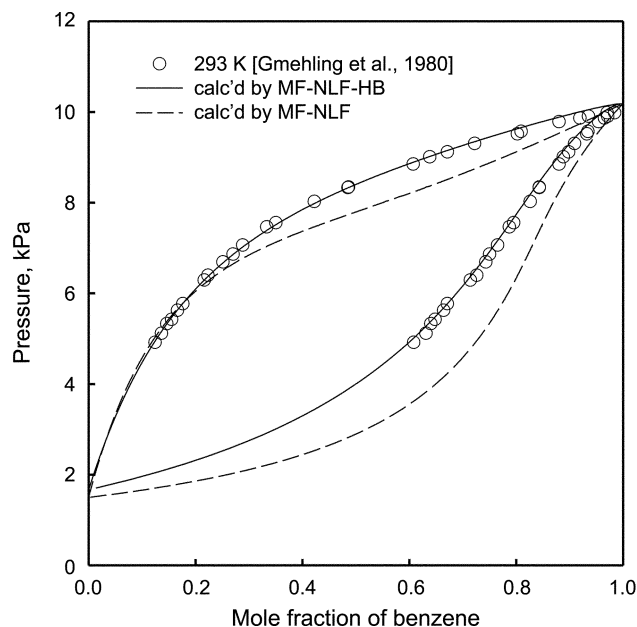**Fig. 3. Vapor-liquid equilibria of toluene and acetic acid system at 353.15 K.**

Fig. 4. Vapor-liquid equilibria of benzene and acetic acid system at 293.15 K.

results of MF-NLF EOS (AADP=9.467, AADY=15.080) which did not have hydrogen bonding contribution term. A comparison of the calculation result with experimental vapor liquid equilibria of toluene+acetic acid and benzene+acetic acid systems is shown in Figs. 3 and 4, respectively. Considerable improvements of present MF-NLF-HB EOS were obtained for the system containing organic acid compared with MF-NLF EOS.

CONCLUSION

The modified Veytsman's statistics extended for both dimmers and n-mers was adopted as hydrogen bonding contribution term. The MF-NLF-HB EOS was tested for the calculation of vapor pressure of various associated fluids and their mixtures (i.e., alcohol-alkane, alcohol-alcohol, acid-alkane, acid-acid mixture). With one binary interaction parameter fitted to data, good calculation results were obtained for most systems compared with experimental data. Especially, MF-NLF-HB EOS showed good agreement with highly non-ideal mixtures of azeotropic systems and binary systems containing organic acid.

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NOMENCLATURE

A^C : configurational Helmholtz energy [J·mol^{-1}]
a_n^j, d_m^i : numbers of acceptor type n in species j and donor type m in species i
λ_{ij} : binary interaction parameter for i-j contacts
n_T : number of total molecules
N_a^n, N_d^m : total number of acceptor groups of type n and donor group of type m
N_0 : number of vacant sites or holes
N_r : defined by $N_r = N_0 + \sum_{i=1}^{c} N_i r_i$
N_q : defined by $N_q = N_0 + \sum_{i=1}^{c} N_i q_i$
P : pressure [Pa]
q_i : surface area parameter
r_H : segment number of associative site
r_i : segment number of molecule i
R : universal gas constant [J·mol^{-1}·K^{-1}]
T : temperature [K]
V_H : volume of unit cell, 9.75 [cm^3·mol^{-1}]
y : mole fraction of vapor phase
z : lattice coordination number [z=10]

Greek Letters

β : 1/kT [J^{-1}]
ε_{ij} : interaction energy for i-j segment contacts [J]
λ_i : part of chemical potential due to internal degrees of freedom of component i
μ_i : chemical potential for component i [J·mol^{-1}]
θ : surface area fraction
ρ : reduced density defined by $\rho = \sum_{i=1}^{c} N_i r_i / N_r$
τ_{ij} : nonrandomness factor defined by Eq. (3)

Superscripts

c : number of components
HB : hydrogen bonding contribution
HB0 : zero hydrogen bonding free energy

P   : physical contribution

Subscripts

a, d   : acceptor and donor
i, j, k, l : components i, j, k and l
ij, mn : interaction pairs, i-j and m-n
M   : property of mixture
m, n   : donor group and acceptor group
mo, on : unbonded donor and unbonded acceptor

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