수소 결합을 고려한 다유체 격자 상태방정식에 의한 상평형 계산

오병철, 신헌용*, 김화용
서울대학교 응용화학부-화학공정신기술연구소, 서울산업대학교 화학공학과*

Multi-fluid nonrandom lattice theory for phase equilibria of hydrogen bonding substances

Byung Chul Oh, Hun Yong Shin*, Hwayong Kim
School of Chemical Engineering and Institute of Chemical Processes, Seoul National University
Department of Chemical Engineering, Seoul National University of Technology*

Introduction

New lattice equation-of-state theory was formulated by the nonrandom two-fluid approximation of the lattice-hole theory. Present model was valid from pure fluids to multicomponent associated mixtures of molecules having any number of hydrogen (proton) donor and acceptor groups. Under a fundamental assumption that the intermolecular forces are divided into physical and chemical forces, the further generalized Veytsman statistics for hydrogen bonding contributon 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 was extended for dimers and n-mers for the description of some associating systems including organic acid as well as alcohol.

Theory

Molecular systems which have strong intermolecular forces, such as hydrogen bonding, deviate remarkably from ideal solution behavior. Recently an extensive treatment of equation of state thermodynamics of systems which have the hydrogen bonding contribution was reported by Panayitous and Sanchez [1]. Panayitous and Sanchez proposed an equation of state based on Veytsman combinatorial expression [2] for the number of ways of forming hydrogen bonds. They have proved successful in describing 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-mer. The Veytsman' s statistics was originally proposed for n-mers and equation of states incorporating the Veytsman' s statistics do not generally gives realistic result for organic acid system. Park et al. [3] proposed an extension of Veytsman' s statistics for hydrogen-bonding systems with both dimers and n-mer. Although the formulation of the 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, an equation of state recently developed based on the two-liquid approximation of the lattice-hole theory[4] was extended. Main attention was placed on the demonstration of the resulting version of MF-NLF-HB EOS for correlation of phase equilibria of hydrogen bonding fluids.

Thermodynamic Properties

Thermodynamic properties derived from the Helmholtz's free energy. The configurational lattice-fluid partition function for systems with hydrogen bonding interactions is approximated as a product of physical and chemical contribution. Omitting derivational details, the resulting expression for the configurational Helmholtz free energy is written as

$$A^c = A^c_P + A^c_{HB} \tag{1}$$

where the physical contribution, A^c_P , is based on the general nonrandom lattice-fluid combinatory after Guggenheim [5]. The physical contribution was given by Yoo et al.[4] and chemical contribution was given by Park et al.[3].

Equation of state was obtained from the Helmholtz eneregy.

$$P = \frac{1}{\beta V_H}\left\{ \frac{z}{2} \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho) - (\upsilon_{HB} - \upsilon_{HB0})\rho + \frac{z}{2} \sum_{i=1}^{c} \theta_i \left(\frac{\tau_{0i}}{\sum_{k=0}^{c} \theta_k \tau_{ki}} - 1 \right) \right\} \tag{2}$$

where $q_M = \sum x_i q_i$, $r_M = \sum x_i r_i$, $\rho = \sum \rho_i$, $\rho_i = V^*_i / V$, $V^*_i = N_a r_i V_H$ and $\tau_{ji} = \exp[\beta(\varepsilon_{ji} - \varepsilon_{ii})]$. z is coordination number and x_i is the mole fraction of species i in a mixture. The fraction of hydrogen bonds in the system (υ_{HB}) is given by the summed fraction of (k, l) pairs of hydrogen bonds, ν_{kl} as

$$\nu_{HB} = \sum_{k=1}^{K} \sum_{l=1}^{L} N^{HB}_{kl} / \sum_{i=1}^{c} N_i r_i = \sum_k^K \sum_l^L \nu_{kl} \tag{3}$$

Subscript and superscript HB means hydrogen bonding properties and HB0 means zero hydrogen bonding properties. N^{HB}_{kl} is number of hydrogen bonding between donor type k and acceptor type l . The chemical potential of hydrogen bonding term is

$$\mu^{HB}_i / kT = -D_i \ln \frac{N^D_{10}}{N^{D0}_{10}} - \sum_k d^i_{k=1} \ln \frac{N^{HB0}_{k0}}{N^{HB}_{ko}} - \sum_l a^i_{l=1} \ln \frac{N^{HB0}_{0l}}{N^{HB}_{0l}} \tag{4}$$

where d^i_k is the number of donor type k in molecular i and a^i_l is the number of acceptor type l in molecular i . D_i is unit value only if molecular i has dimerizing group otherwise zero. N^{HB}_{k0} is the number of unbonded donors of type k and N^{HB}_{0l} is the number of unbonded acceptors of type l defined by

$$N^{HB}_{k0} = N^k_d - \sum_l^L N^{HB}_{kl} \ , \ N^{HB}_{0l} = N^l_a - \sum_k^K N^{HB}_{kl} \tag{5}$$

And the total number of donor groups of type l, N^l_d , and that of acceptor groups of types k, N^k_a , are given by

$$N^k_d = \sum_{i=1}^{C} d^i_k N_i \ , \ N^l_a = \sum_{j=1}^{C} a^j_l N_j \tag{6}$$

Results and Discussions

For this model, coordination number z is constant value 10 and lattice volume V_H is 9.75 cm3mol-1. And the hydrogen bonding parameters for each type of donor-acceptor pairs were given by Park et al.[3]. Two molecular energy and size parameters for physical interactions are the segment interaction energy, ε_{ii} , and the segment number, r_i , which were fiited to the saturated liquid density and vapor pressure data. These parameters were made as functions of temperature by following equation.

$$\varepsilon_{11}/k = E_a + E_b(T - T_0) + E_c[Tln(T_0/T) + T - T_0] \tag{7}$$

$$r_1 = R_a + R_b(T - T_0) + R_c[T\ln(T_0/T) + T - T_0] \tag{8}$$

where $T_0 = 298.15K$ was a reference temperature. The estimated values of coefficients for Eq. 6 and 7 were summarized in Table 1 for some hydrogen bonding substances. The present EOS has one binary energy parameter λ_{12} for binary mixture, which was defined by $\varepsilon_{12} = (\varepsilon_{11}\varepsilon_{22})^{1/2}(1-\lambda_{12})$.

In Fig. 1, calculation results of vapor pressures for water, methanol and acetic acid were compared with experimental data of Reid et al [6]. Acetic acid was considered to form dimers. Fig. 2 showed the comparison of the presenting model with experimental VLE data for heptane-butanol. Benzene-acetic acid systems and acetic acid-propionic acid mixture were well correlated by present model in Fig. 3 and 4. Vapor-liquid equilibria for binary mixtures of organic acid, alcohol and alkane were calculated using the model. Satisfactory agreements were obtained for most systems compared with experimental data.

Table 1. Temperature coefficients of Eq. 7 and 8 for hydrogen bonding components.

chmicals	Ea	Eb	Ec	Ra	Rb	Rc
methanol	84.1198	0.22939	0.35062	3.25856	0.003292	-0.00190
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	0.14451
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
formic acid	137.1014	0.04988	0.01889	5.72919	-0.00882	-0.08893
acetic acid	100.7946	0.15607	0.20233	6.29542	-0.00155	-0.00942
propionic acid	99.8893	0.05936	-0.02383	8.62261	-0.00036	-0.00325
water	360.2713	-0.37257	0.09315	1.85793	-0.00023	-0.00361

References

[1] C. Panayiotou and I.C. Sanchez, J. Phys. Chem., 95, 10090 (1991).
[2] B.A. Veytsman, J. Phys. Chem., 94, 8499 (1990).
[3] B.H. Park, J.W. Kang, K.-P. Yoo and C.S. Lee, Fluid Phase Equilibira, 4883, 1 (2001).
[4] K.-P. Yoo, H.Y. Shin, S.Y. Hwang and C.S. Lee, Fluid Phase Equilibria, 150-151, 191 (1998).
[5] E.A. Guggenheim, “Mixture” , Clarendon Press, Inc., New York (1952).

[6] R.C. Reid, J.M. Prausnitz, B.E. Poling, “The Properties of Gases and Liquids”, 4th Ed., McGraw-Hill, New York (1986).

[7] J. Gmehling, U. Onken and W. Arlt, “Vapor-Liquid Equilibrium Data Collection”, DECHEMA (Chemistry Data Series), Vol. I (1980).

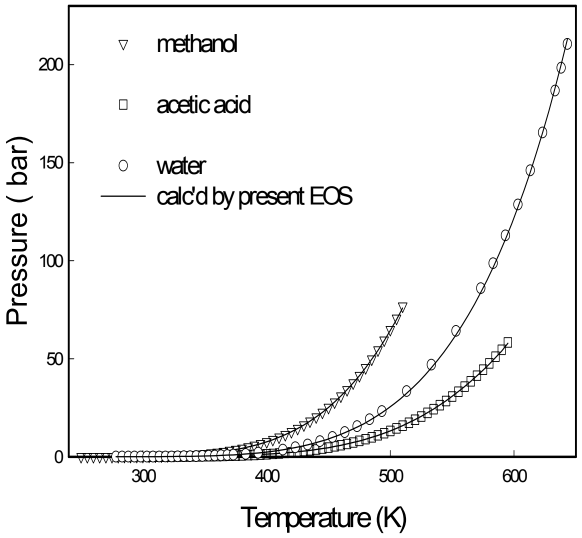

Fig.1. Comparison of experimental vapor pressure with calculated results.

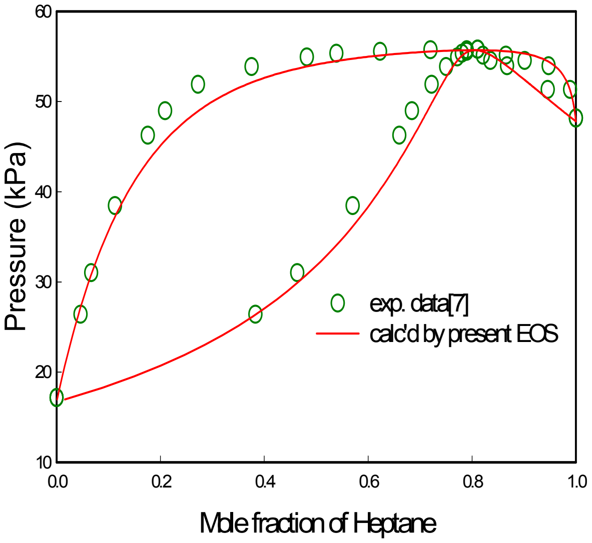

Fig. 2. VLE of heptane and butanol system at 348.15K ($\lambda_{12}=0.0223$).

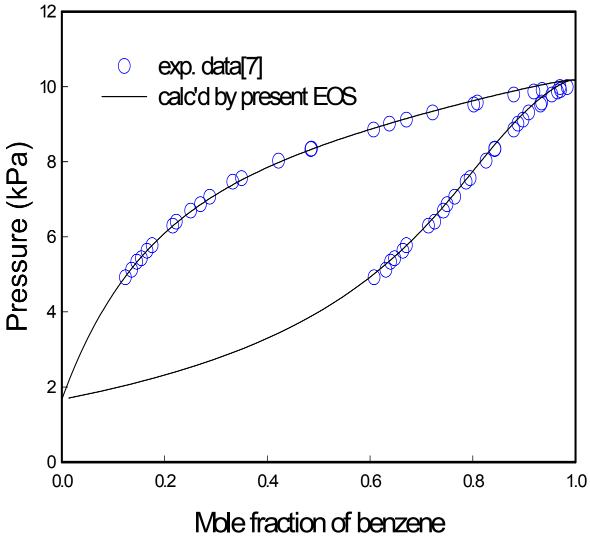

Fig. 3. VLE of benzene and acetic acid system at 294.15K ($\lambda_{12}=0.02958$).

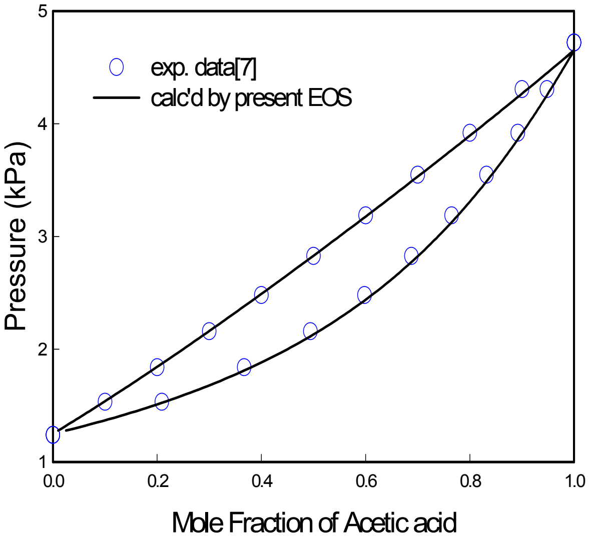

Fig. 4. VLE of acitic acid and propionic acid system at 313.15K ($\lambda_{12}=0.00688$).