

A multi-fluid nonrandom lattice fluid model: Mixtures

Moon Sam Shin, Ki-Pung Yoo*, Chul Soo Lee** and Hwayong Kim†

School of Chemical and Biological Engineering and Institute of Chemical Processes,
Seoul National University, Seoul 151-744, Korea

*Department of Chemical and Biomolecular Engineering, Sogang University, Seoul 121-742, Korea

**Department of Chemical and Biological Engineering, Korea University, Seoul 136-701, Korea

(Received 18 November 2005 • accepted 23 December 2005)

Abstract—A multi-fluid nonrandom lattice fluid model with no temperature dependence of close packed volumes of a mer, segment numbers and energy parameters of pure systems and its consistent method for phase equilibrium calculation were presented in the previous paper. In this work, the model was extended to mixtures by using consistent method for phase equilibrium calculation with fugacity coefficients derived from the present equation of state and it was applied to vapor-liquid equilibrium. We consistently tested the present model on 17 phase equilibrium data sets of vapor-liquid equilibria and compared it with the MF-NLF model and the SAFT model. The present model (3 pure parameters for pure component and one binary interaction parameter) showed better results for most systems than the MF-NLF model (6 adjustable pure parameters and one binary interaction parameter) and the SAFT model (3 pure parameters and one binary interaction parameter).

Key words: Multi-fluid, Nonrandom, Lattice, Local Composition, Equation of State

INTRODUCTION

In the previous paper [Shin et al., 2005], we briefly reviewed the existing lattice fluid theories stemming from the full Guggenheim's combinatorial and the local composition theories and presented a general derivation of a quasi-chemical nonrandom lattice fluid model and this model to pure fluids and discussed the results. The local composition theory [Wilson, 1964] and rigid lattice description without vacant sites (or holes) of fluid systems [Guggenheim, 1952] have been widely utilized to formulate various excess Gibbs free energy expressions such as NRTL [Renon and Prausnitz, 1968] and UNIQUAC [Abrams and Prausnitz, 1975]. However, they can be applied only to liquid mixtures at low pressure. To overcome this limitation, various equation-of-state theories have also been proposed by imbedding holes into the rigid lattice description of fluids. One of the well known examples is the EOS after Sanchez and Lacombe [Sanchez and Lacombe, 1976; Lacombe and Sanchez, 1976].

The present authors also recently proposed the multi-fluid nonrandom lattice fluid (MF-NLF) equation of state [Shin et al., 1995; Yoo et al., 1995, 1997] and the MF-NLF model was capable of describing properties for complex systems. However, the MF-NLF model has strong temperature dependence of energy parameters and segment numbers of pure systems; thus empirical correlations as functions of temperature were adopted for reliable and convenient use in engineering practices. If the MF-NLF model neglects the temperature dependence of these parameters, this model cannot predict thermodynamic properties accurately.

In addition, Neau [Neau, 2002] represented a consistent method for phase equilibrium calculation using the fugacity coefficients derived from Sanchez-Lacombe equation of state. It was pointed out

that configurational chemical potential derived from configurational partition function does not verify phase equilibrium property.

A multi-fluid lattice fluid model with no temperature dependence of close packed volumes of a mer, segment numbers and energy parameters of pure systems and its consistent method for phase equilibrium calculation were presented in the previous paper [Shin et al., 2005]. We found that the present model with 3 parameters describes quantitatively the vapor pressure and the saturated density for each pure fluid. In this work, we extend the structure of the formalism for pure fluids to mixtures using a consistent method for phase equilibrium calculation with fugacity coefficients derived from this model, and discuss the quantitative applicability of the model to the calculation of vapor-liquid phase equilibria.

THE MODEL AND THERMODYNAMIC PROPERTIES

The canonical partition function may be written in the classical approximation of statistical thermodynamics [Prausnitz et al., 1999],

$$Q(N, T, V) = Q^{int}(N, T) Q^{kin}(N, T) Z_N(N, T, V) \quad (1)$$

where Q^{int} , Q^{kin} are the internal and kinetic part of the canonical partition function and Z_N is the configurational partition function.

The expression for the canonical Helmholtz free energy may be obtained from the internal and kinetic part of the Helmholtz free energy and the configurational Helmholtz free energy.

$$\beta A(N, T, V) = \beta A^{int}(N, T) + \beta A^{kin}(N, T) + \beta A^c(N, T, V) \quad (2)$$

The configurational Helmholtz free energy A^c is obtained from the athermal part which is equivalent to a combinatorial contribution in the random array and the residual part which is due to the residual nonrandom interaction energy.

†To whom correspondence should be addressed.

E-mail: hwayongk@snu.ac.kr

$$\beta A^c = \sum_{i=1}^c N_i \ln \tilde{\rho}_i + N_0 \ln(1 - \tilde{\rho}) - \frac{Z}{2} N_q \ln \left[1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right] - \left(\frac{Z N_q}{2} \right) \sum_{i=1}^c \theta_i \left[\ln \left(\sum_{j=0}^c \theta_j \tau_{ji} \right) + \beta \varepsilon_{ii} \right] \quad (3)$$

The EOS (equation of state) is obtained from the equation of configurational Helmholtz free energy,

$$P = P^c = - \left(\frac{\partial A}{\partial V} \right)_{T, N} = - \left(\frac{\partial A^c}{\partial V} \right)_{T, N} \quad (4)$$

Obviously, the configurational pressure obtained in this way is the absolute pressure: $P = P^c$.

The canonical and configurational chemical potentials are expressed from the canonical and configurational Helmholtz free energy, respectively,

$$\mu_i = \left(\frac{\partial A(N, T, V)}{\partial N_i} \right)_{T, V, N_j} = \left[\left(\frac{\partial A^{int}(N, T)}{\partial N_i} \right)_{T, N_j} + \left(\frac{\partial A^{kin}(N, T)}{\partial N_i} \right)_{T, N_j} + \left(\frac{\partial A^c(N, T, V)}{\partial N_i} \right)_{T, V, N_j} \right] \quad (5)$$

$$\mu_i^c = \left(\frac{\partial A^c(N, T, V)}{\partial N_i} \right)_{T, V, N_j} \quad (6)$$

The canonical chemical potentials are not equal to the configurational chemical potentials since A^{int} , A^{kin} are functions of both temperature and number of molecules. The configurational chemical potentials can be used for phase equilibrium conditions in the classical lattice fluid model; thus the Sanchez-Lacombe model leads to an erroneous method for phase equilibrium calculations.

To overcome this problem, phase equilibrium conditions should be calculated by using fugacity coefficients which can be derived directly from the equation of state because the configurational pressure is equal to the absolute pressure. Fugacity coefficients were calculated by derivation of the residual Helmholtz free energy $A^r(T, V, N)$ obtained by integration of the lattice fluid equation of state.

$$\ln \phi_i = \left(\frac{\partial A^r(T, V, N)}{\partial N_i} \right)_{T, V, N_j} - \ln Z \quad (7)$$

$$A^r(T, V, N) = - \int_{\infty}^V \left(P - \frac{NkT}{V} \right) dV \quad (8)$$

EOS AND FUGACITY COEFFICIENT FOR MIXTURES

A multi-fluid nonrandom lattice fluid model (MLF) with no temperature dependence of close packed volumes of a mer, segment numbers and energy parameters of pure systems was presented in the previous paper [Shin et al., 2005]. In this work, we extend the structure of the formalism for pure fluids to mixtures using a consistent method for phase equilibrium calculation with fugacity coefficients derived from this model

The volume of the mixture is

$$v = v^* N_r = v^* (N_0 + \sum_i r_i N_i) \quad (9)$$

$$r = \sum x_i r_i, \quad q = \sum x_i q_i, \quad x_i = \frac{N_i}{N}, \quad N = \sum N_i \quad (10)$$

$$N_r = N_0 + \sum N_i r_i, \quad N_q = N_0 + \sum N_i q_i \quad (11)$$

$$z q_i = r_i (z - 2) + 2 \quad (12)$$

N_0 and N_i denote the number of holes and molecular species i , respectively, and ε_{ij} is the absolute value of the interaction energy between a segment of species i and that of species j , which is assumed as follows,

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii} \varepsilon_{jj}} (1 - k_{ij}) \quad (13)$$

For the mixture, and in the one-fluid approach, the following combining and mixing rules of v^* are assumed.

$$v^* = \sum \phi_i v_i^* \quad (14)$$

where the segment fraction ϕ_i is defined by

$$\phi_i = \frac{r_i N_i}{\sum r_i N_i} = \frac{x_i r_i}{r} \quad (15)$$

From Eq. (4), we obtain the expression for equation of state for the mixtures.

$$\frac{\tilde{P}}{\tilde{T}} = - \ln(1 - \tilde{\rho}) + \frac{Z}{2} \ln \left[1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right] - \frac{\theta^2}{\tilde{T}} \quad (16)$$

Here, all the quantities with the tilde ($\sim$) denote the reduced variables defined by

$$\tilde{P} = \frac{P}{P^*}, \quad \tilde{T} = \frac{T}{T^*}, \quad \tilde{\rho} = \frac{\rho}{\rho^*} = \frac{\sum r_i N_i}{N_r}, \quad \rho^* = \frac{1}{r v^*} \quad (17)$$

where the reducing parameters are defined by

$$P^* v^* = k T^* = \frac{Z}{2} \varepsilon_M \quad (18)$$

and ε_M , θ , θ_i , and the nonrandomness factor τ_{ji} are defined by

$$\varepsilon_M = \frac{1}{\beta \theta^2} \left[\sum_{i=1}^c \theta_i \left(1 - \frac{\tau_{0i}}{\sum_{k=0}^c \theta_k \tau_{ki}} \right) \right] \quad (19)$$

$$\theta = \frac{\sum N_i q_i}{N_q} = \frac{(q/r) \tilde{\rho}}{1 + (q/r - 1) \tilde{\rho}} = 1 - \theta_0 \quad (20)$$

$$\theta_i = \frac{N_i q_i}{N_q} \quad (21)$$

$$\tau_{ji} = \exp[\beta(\varepsilon_{ji} - \beta \varepsilon_{ii})] \quad (22)$$

The Residual Helmholtz energy, $A^r(T, V, N)$ and fugacity coefficients were calculated given by Eq. (7) and Eq. (8).

$$\frac{A^r}{kT} = N_r \left[\left(\frac{1}{\tilde{\rho}} - 1 \right) \ln(1 - \tilde{\rho}) \right] - \left[\frac{Z N_r}{2 \tilde{\rho}} + N(1 - r) \right] \ln \left(1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right) + N - \frac{N q \theta}{\tilde{T}} \quad (23)$$

$$\ln \phi_i = (Z - 1) \frac{r_i}{r} \left(\frac{v_i^*}{v^*} - 1 \right) + r_i \frac{\tilde{P}}{\tilde{T}} - \frac{Z q_i}{2} \ln \left(1 + \left(\frac{q}{r} - 1 \right) \tilde{\rho} \right) - \ln Z + \frac{r_i \theta^2}{\tilde{T}} + (1 - r_i) \theta - \frac{Z q_i}{2} \left[\ln \sum_{k=0}^c \theta_k \tau_{ki} + \beta \varepsilon_{ii} + \sum_{l=1}^c \frac{\theta_l (\tau_{li} - \tau_{0l}(r_l/q_l))}{\sum_{m=0}^c \theta_m \tau_{ml}} \right] \quad (24)$$

Table 1. Binary interaction parameters, k_{ij} of the present model, the MF-NLF model, the SAFT model regressed from the experimental phase-equilibrium data and their average fitting error percent

System	T range, °C	Models	k_{ij}	AADP (%)	AADY (%)
1. Acetone-c Hexane	45, 55, 65	MF-NLF	0.07564	3.627	5.586
		MLF	0.07874	0.930	1.150
		SAFT	0.10836	4.161	5.100
2. Acetone-Hexane	45, 55, 65	MF-NLF	0.07134	2.791	6.187
		MLF	0.08401	0.755	2.237
		SAFT	0.08729	3.033	4.330
3. Acetone-Benzene	30, 40, 50	MF-NLF	0.02034	0.690	2.039
		MLF	0.01782	0.856	1.387
		SAFT	0.03991	1.857	2.949
4. Heptane-3 pentanone	65, 80	MF-NLF	0.03622	1.406	5.223
		MLF	0.04504	0.804	3.317
		SAFT	0.03425	1.932	4.403
5. 2 Butanone-c Hexane	50	MF-NLF	0.05368	1.277	3.856
		MLF	0.05666	0.578	1.456
		SAFT	0.07355	2.303	3.863
6. Ethylacetate-c Hexane	20, 30, 45	MF-NLF	0.04720	1.041	3.359
		MLF	0.04679	0.896	2.974
		SAFT	0.08616	2.104	3.150
7. Methylacetate-c Hexane	35, 40	MF-NLF	0.06772	0.910	3.883
		MLF	0.06548	0.964	2.353
		SAFT	0.10933	3.336	5.642
8. Ethylacetate-Heptane	50	MF-NLF	0.04316	1.330	3.434
		MLF	0.04956	1.613	2.861
		SAFT	0.06476	2.342	4.160
9. Heptane-Butylacetate	74.7, 100	MF-NLF	0.02916	1.532	4.622
		MLF	0.03345	1.421	3.556
		SAFT	0.04172	2.105	3.882
10. Diethylether-Acetone	0, 20, 30	MF-NLF	0.02428	1.804	6.275
		MLF	0.03199	1.169	4.880
		SAFT	0.02847	2.766	4.612
11. Benzene-Heptane	55	MF-NLF	0.02258	1.100	2.993
		MLF	0.02845	0.828	2.108
		SAFT	0.01788	1.847	4.196
12. Hexane-Benzene	55, 70	MF-NLF	0.01826	0.994	1.029
		MLF	0.02573	0.743	1.269
		SAFT	0.01483	1.915	2.232
13. Benzene-Toluene	61	MF-NLF	0.00151	0.385	1.274
		MLF	0.00088	0.206	1.290
		SAFT	0.00046	1.235	2.959
14. c Hexane-Toluene	50, 60, 70	MF-NLF	0.01409	1.027	3.016
		MLF	0.01700	1.303	2.612
		SAFT	0.01483	2.036	3.884
15. Pentane-Hexane	25	MF-NLF	-0.00187	0.490	1.114
		MLF	-0.00292	0.550	0.897
		SAFT	-0.00307	1.919	2.948
16. Hexane-Methylcyclopentane	60	MF-NLF	0.00131	0.167	0.371
		MLF	0.00093	0.374	0.881
		SAFT	0.00122	2.882	1.100
17. Dimethyl Ether-Butane	39.83	MF-NLF	0.03470	0.154	3.610
		MLF	0.03813	0.548	3.885
		SAFT	0.03971	3.443	3.206

RESULTS AND DISCUSSION

There are apparently 3 molecular parameters for pure fluids: v_i^* , r_i , ε_{i1} and the binary interaction parameter k_{ij} for mixtures in the present model. We set $z=10$ as used in lattice fluid theories of the same genre [Panayiotou and Vera, 1982]. In the previous paper [Shin et al., 2005], we listed values of v_i^* , r_i , ε_{i1} for 80 pure components. We needed to determine k_{ij} from binary data for the binary mixtures. We randomly selected 17 representative binary mixtures for vapor-liquid equilibrium calculation. Using the pure molecular parameters, the binary interaction parameters were fitted to mixture data.

Isothermal vapor-liquid equilibrium properties can be calculated by imposing the following conditions, not using configurational chemical potentials but using fugacity coefficients.

$$P^L = P^V \quad (25)$$

$$x_i \phi_i(T, P, x) = y_i \phi_i(T, P, y), \quad i=1, 2, \dots, c \quad (26)$$

where x_i and y_i denote sets of mole fraction of all components in liquid and vapor phase, respectively.

Assuming pressure and initial sets the vapor composition y_i for isothermal bubble-point pressure calculation, we can calculate densities and fugacity coefficients of liquid and vapor phases. If fugacities of each species in each phase are sufficiently close, the calculation is terminated. Otherwise, we modify y_i using the relation for each component and update pressure, respectively,

$$y_i^{new} = y_i^{old} \frac{f_i^L}{f_i^V} \quad (27)$$

$$P^{new} = P^{old} \sum y_i \quad (28)$$

And calculation is repeated until convergence is obtained. Similarly, the isobaric bubble-point temperature can be calculated by specifying pressure, and replacing $P^{new} = P^{old} \sum y_i$ by

$$T^{new} = T^{old} / \sum y_i \quad (29)$$

The binary interaction parameter k_{ij} is determined in this calcu-

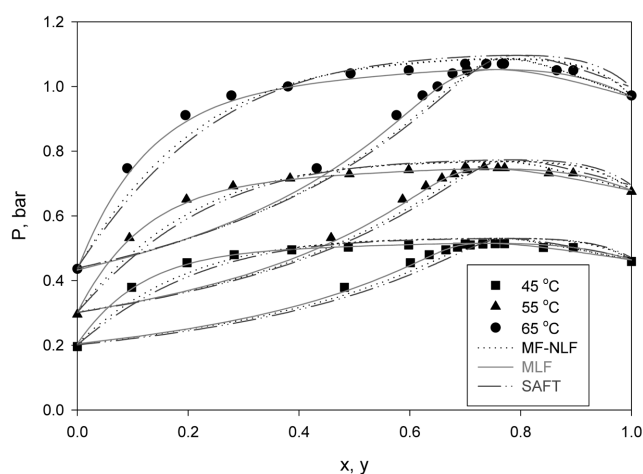


Fig. 1. Isothermal vapor-liquid P-x equilibria for acetone-cyclohexane system at 45, 55, 65 °C.

lation such that the deviation of calculated values from experimental data is minimal. Experiment data of vapor-liquid equilibrium are from KDB [Kang et al., 2001]. The present model (MLF) is compared with the MF-NLF model, the SAFT [Huang and Radosz] model, and the binary interaction parameter k_{ij} values for binary vapor-liquid systems are summarized in Table 1 together with percent average absolute deviation (AAD %) in pressure and vapor compositions.

The present model correlates the experimental data well within a 3.5 error percentile as shown Table 1 for most systems. In Fig. 1 and Fig. 2, the calculated P-x equilibria of the present model, the MF-NLF model, and the SAFT model for acetone-cyclohexane system and acetone-hexane system at 45, 55 and 65 °C are compared with experimental data. The present model shows better calculated results than the MF-NLF model and the SAFT model in both systems.

The P-x equilibria for the heptane-3 Pentanone system at 45, 80 °C in Fig. 3 and 2 butanone-cyclohexane system at 50 °C in Fig. 4 show the agreement of the present model is better than that of the MF-NLF model and the SAFT model.

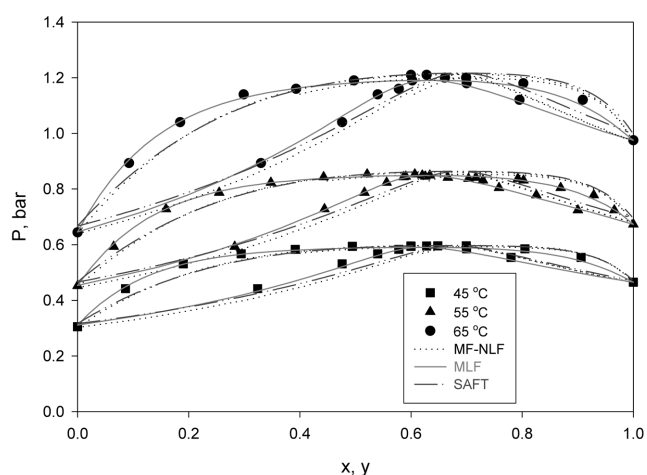


Fig. 2. Isothermal vapor-liquid P-x equilibria for acetone-hexane system at 45, 55, 65 °C.

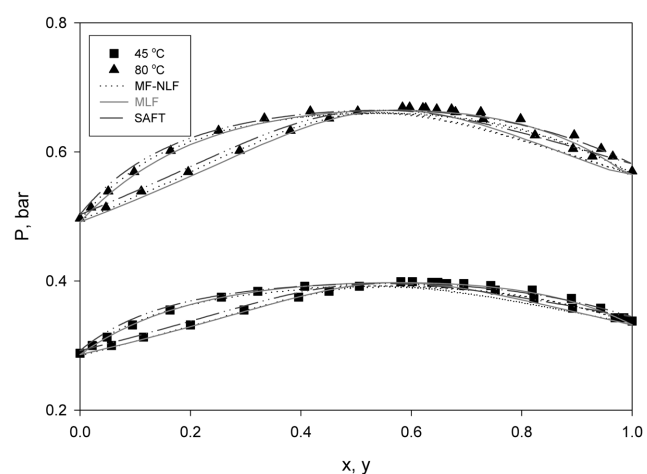


Fig. 3. Isothermal vapor-liquid P-x equilibria for heptane-3 pentanone system at 45, 80 °C.

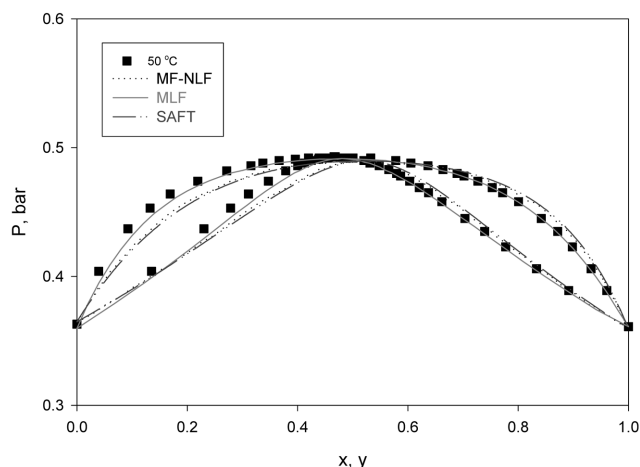


Fig. 4. Isothermal vapor-liquid P-x equilibria for 2 butanone-cyclohexane system at 50 °C.

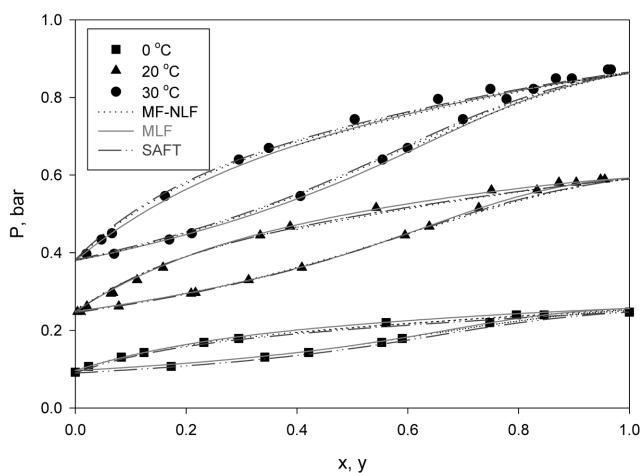


Fig. 5. Isothermal vapor-liquid P-x equilibria for diethylether-acetone system at 0, 20, 30 °C.

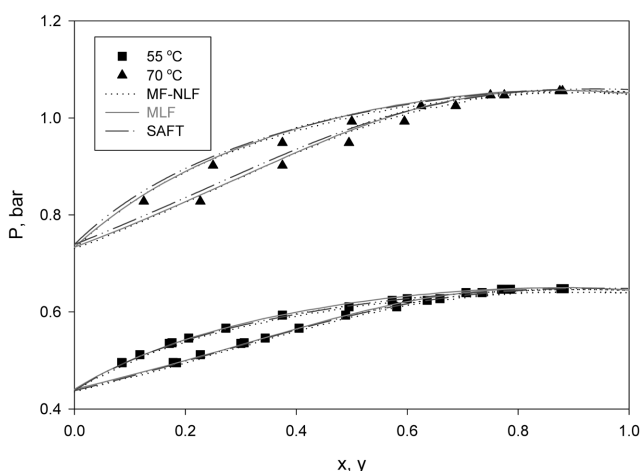


Fig. 6. Isothermal vapor-liquid P-x equilibria for hexane-benzene system at 55, 70 °C.

In Fig. 5 and Fig. 6, the calculated P-x equilibria of the present model, the MF-NLF model and the SAFT model for diethylether -

acetone system 0, 20, 30 °C and hexane-benzene system at 55, 70 °C are compared with experimental data. The present model has slightly better calculated results than the MF-NLF model and the SAFT model in both systems.

CONSLUSIONS

We have extended the structure of the formalism for pure fluids with 3 molecular parameters to mixtures by using a consistent method for phase equilibrium calculation with fugacity coefficients derived from the present model (MLF).

We have consistently tested the present model on 17 phase equilibrium data sets of vapor-liquid equilibria and compared it with the MF-NLF model and the SAFT model. The present model (3 pure parameters for pure component and one binary interaction parameter) showed better results for most systems than the MF-NLF model (6 adjustable pure parameters and one binary interaction parameter) and the SAFT model (3 pure parameters and one binary interaction parameter).

ACKNOWLEDGMENT

This work was supported by the BK21 project of Ministry of Education of Korea.

NOMENCLATURE

- A : Helmholtz free energy
- $A^{(i)}$: regression constants in Eq. (26), (28), (29)
- c : number of the component
- f : fugacity
- k : Boltzmann's constant
- N : number of molecules
- N_r : defined by Eq. (8)
- N_q : defined by Eq. (5)
- m : effective number of segments with the molecule for SAFT model
- MM : molar mass
- P : pressure
- P^c : configurational pressure
- Q : canonical partition function
- q : surface area parameter
- r : number of segments per molecule
- T : temperature
- u^0 : dispersion energy of interaction between segments for SAFT model
- V : volume
- v : molar volume
- v_l^* : close packed volume of a mer
- v^{00} : segment volume for SAFT model
- z : lattice coordination number
- Z : compressibility factor
- Z_N : configuration partition function

Greek Letters

- β : reciprocal temperature (1/kT)
- Γ_{ij} : quasi-chemical nonrandomness factor

ε_{ij}	: molecular interaction energy
ε_M	: defined by Eq. (17)
ϕ	: fugacity coefficient
ρ	: molar density
ρ^*	: close packed molar density
μ	: chemical potential
τ_{ij}	: nonrandomness factor
θ	: surface area fraction

Superscripts

a	: athermal solution properties
c	: configurational properties
r	: residual properties
~	: reduced properties
*	: characteristic properties

Subscripts

i	: component i
0	: vacant sites or holes
int	: internal part
kin	: kinetic part

REFERENCES

- Abrams, D. S. and Prausnitz, J. M., "Statistical thermodynamics of liquid mixtures: A new expression for the excess Gibbs energy of partly or completely miscible systems," *AIChE J.*, **21**, 116 (1975).
- Guggenheim, E. A., *Mixtures*, Clarendon Press, Oxford, 215 (1952).
- Huang, S. H. and Radosz, M., "Equation of state for small, large, poly-disperse and associating molecules," *Ind. Eng. Chem. Res.*, **29**, 2284 (1990).
- Kang, J., Yoo, K., Kim, H., Lee, J., Yang, D. and Lee, C. S., "Development and current status of the Korea thermophysical properties database (KDB)," *Int. J. Thermophys.*, **22**, 487 (2001).
- Lacombe, R. H. and Sanchez, I. C., "Statistical thermodynamics of fluid mixtures," *J. Phys. Chem.*, **80**, 2368 (1976).
- Neau, E., "A consistent method for phase equilibrium calculation using the Sanchez-Lacombe lattice-fluid equation-of-state," *Fluid Phase Equilibria*, **203**, 133 (2002).
- Panayiotou, C. and Vera, J. H., "Statistical thermodynamics of r-mer fluids and their mixtures," *Polymer J.*, **14**, 681 (1982).
- Prausnitz, J. M., Lichtenhalter, R. N. and de Azevedo, E. G., *Molecular thermodynamics of fluid-phase equilibria*, Prentice-Hall, Englewood Cliffs, NJ (1999).
- Renon, H. and Prausnitz, J. M., "Local compositions in thermodynamic excess functions for liquid mixtures," *AIChE J.*, **14**, 135 (1968).
- Sanchez, I. C. and Lacombe, R. H., "An elementary molecular theory of classical fluids. pure fluids," *J. Phys. Chem.*, **80**, 2352 (1976).
- Shin, M. S., Yoo, K. P., Lee, C. S. and Kim, H., "A Multi-fluid nonrandom lattice fluid model. I. General derivation and application to pure fluids," *Submitted to Korean J. Chem. Eng.* (2005).
- Shin, M. S., Yoo, K. P., You, S. S. and Lee, C. S., "A new nonrandom lattice fluid model and its simplification by two-liquid theory for phase equilibria of complex mixtures," *Int. J. Thermophysics*, **16**, 723 (1995).
- Wilson, G. M., "Vapor-liquid equilibrium. XI. A new expression for the excess free energy of mixing," *J. Am. Chem. Soc.*, **86**, 127 (1964).
- Yoo, K. P., Kim, H. and Lee, C. S., "Unified equation of state based on the lattice fluid theory for phase equilibria of complex mixtures. Part I. Molecular thermodynamic framework," *Korean J. Chem. Eng.*, **12**, 277 (1995).
- Yoo, K. P., Kim, H. and Lee, C. S., "Unified equation of state based on the lattice fluid theory for phase equilibria of complex mixtures. Part II. Application to complex mixtures," *Korean J. Chem. Eng.*, **12**, 289 (1995).
- Yoo, K. P., Shin, H. Y. and Lee, C. S., "Approximate nonrandom two-fluid lattice-hole theory. General derivation and description of pure fluids," *Bull. Korean Chem. Soc.*, **18**, 965 (1997).
- Yoo, K. P., Shin, H. Y. and Lee, C. S., "Approximate nonrandom two-fluid lattice-hole theory. Thermodynamic properties of real mixtures," *Bull. Korean Chem. Soc.*, **18**, 841 (1997).
- Yoo, K. P., Shin, M. S., Yoo, S. J., You, S. S. and Lee, C. S., "A new equation of state based on nonrandom two-fluid lattice theory for complex mixtures," *Fluid Phase Equilibria*, **111**, 175 (1995).