

Calculation of Complex Phase Equilibria in the Critical Region of Fluid Mixture Based on Multi-Fluid Lattice Equation of State

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Abstract—Quantitative correlation of critical loci and multiphase behaviors has received considerable attention because the increased industrial importance of processes operating within the high-pressure region such as supercritical fluid extraction. However, in the critical region, classical thermodynamic models such as equations of state (EOS) frequently fail to correlate phase equilibrium properties. Recently, the present authors proposed a new lattice-hole EOS based on the multi-fluid approximation of the nonrandom lattice theory. The model requires only two molecular parameters reflecting size and interaction energy for a pure fluid and one additional interaction parameters for a binary mixture. In this work, the reliable applicability of the EOS was demonstrated to various phase equilibria of complex mixtures in the critical region. Demonstration of the EOS was made to calculate multiphase behaviors such as solid-liquid-vapor (SLV) equilibria and critical loci of binary complex mixtures at high pressure. For P-T, P-x, and T-p phase diagrams tested, the model agrees well with experimental data.

Key words: Lattice Theory, Equation of State, Multi-Fluid Approximation, High-Pressure VLE, Critical Loci, Multi-Phase Equilibria

INTRODUCTION

Various formulations of thermodynamic theories of solutions can be developed from the framework of the generalized Guggenheim combinatorial of lattice statistical mechanics [1952]. The excess function models, such as Flory-Huggins [1941, 1942], UNIQUAC [Abrams and Prausnitz, 1975], and various extended versions of these models are based on the rigid lattice description. However, they can be applied only to liquid mixtures at low pressure. To overcome this limitation, various equation-of-state theories also have been proposed by imbedding holes into the rigid lattice description of fluids. One of well-known examples is the EOS after Sanchez and Lacombe [1976].

The present authors also recently proposed an elementary EOS based on the nonrandom lattice-hole theory [Yoo et al., 1993, 1994]. Although the formulations of the previous rigorous EOSs are self-consistent with a sound theoretical basis, a less complicated model would be more convenient in engineering-oriented equilibrium calculations. In this work we present our efforts of applying the new semi-theoretical EOS model [MF-NLF EOS, Yoo et al., 1997a, b] to various phase equilibria of mixtures as well as pure fluids with emphasis in the critical region.

HELMHOLTZ FREE ENERGY AND OTHER THERMODYNAMIC FUNCTIONS

Omitting derivational details [Yoo et al., 1997a, b], the final expression of the configurational Helmholtz free energy for a general mixture is written as

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

where, $q_M = \sum_i x_i q_i$, $r_M = \sum_i x_i r_i$, $\rho_i = N_i r_i / N$, and ρ is the mole fraction of species i . The summation covers all molecular species. From the Helmholtz free energy given by Eq. (1), expressions of other thermodynamic properties can be obtained in a straight manner. Since the volume V is represented by $V = V_H(N_0 + \sum_i N_i r_i)$, the EOS is obtained by

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

The chemical potential of component i , μ_i , is

$$\frac{\mu_i}{RT} = \lambda_i(T) - r_i \ln(1 - \rho) + \ln \frac{\theta_i}{q_i} + r_i \ln \left[1 + \left(\frac{q_M}{r_M} - 1 \right) \rho \right] + \frac{z q_i \theta}{2} \left\{ 1 - \frac{r_i}{q_i} - \frac{1}{\theta} \times \left[\ln \sum_{k=0}^c \theta_k \tau_{ki} + \beta \epsilon_{ii} + \sum_{j=1}^c \frac{\theta_j (\tau_{ij} - \tau_{0i}(r_j/q_j))}{\sum_{k=0}^c \theta_k \tau_{ki}} \right] \right\} \quad (3)$$

If we set the subscripts $i=1$ and $j=0$, the Eq. (1)-(3) reduce to the expressions for pure fluids.

DETERMINATION OF MOLECULAR PARAMETERS

By setting the coordination number, z equals to 10 and the unit

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lattice cell volume, V_H is $9.75 \text{ cm}^3 \text{ mol}^{-1}$, there are two molecular parameters in the EOS for pure fluids; V_1^* and ϵ_{11} . Based on experimental information, these parameters for various pure fluids were regressed at each isotherm and made them functions of temperature for convenient use in practice. They are

$$\epsilon_{11}/k = E_a + E_b(T - T_0) + E_c(T \ln T_0/T + T - T_0) \quad (4)$$

$$V_1^* = V_a + V_b(T - T_0) + V_c(T \ln T_0/T + T - T_0) \quad (5)$$

where the reference temperature, $T_0 = 298.15 \text{ K}$.

For a 1-2 binary mixture, we have one additional binary interaction energy parameter, λ_{12} , which is defined by

$$\epsilon_{12} = (\epsilon_{11}\epsilon_{22})^{0.5}(1 - \lambda_{12}) \quad (6)$$

CRITICAL LOCI AND MULTIPHASE BEHAVIORS

The general and quantitative applicability of the EOS to various phase equilibria behaviors of mixtures in the subcritical region is demonstrated elsewhere [Yoo et al., 1997a, b]. In this work, attention is limited to the application of this model to critical phase behaviors of mixtures. To calculate the critical loci and multiphase behaviors of binary mixtures, the critical and stability condition for a mixture in terms of Helmholtz free energy [You et al., 1994b] are given by

$$\left(\frac{\partial^2 A}{\partial x^2}\right)_{T,V} + \left(\frac{\partial P}{\partial x}\right)_{T,V} Q = 0 \quad (7)$$

$$\left(\frac{\partial^3 A}{\partial x^3}\right) - 3\left(\frac{\partial^2 P}{\partial x^2}\right)Q - 3\left(\frac{\partial^2 P}{\partial x \partial V}\right)_T Q^2 + \left(\frac{\partial^2 P}{\partial V^2}\right)_{T,x} Q^3 = 0 \quad (8)$$

where

$$Q = \frac{(\partial P / \partial x)_{T,V}}{(\partial P / \partial V)_{T,x}} \quad (9)$$

By using numerical method, the critical loci of mixtures can be determined with the thermodynamic variables T , P and V which simultaneously satisfy the EOS [Eq. (2)] and the critical condition of mixture [Eq. (7) and (8)].

The explicit expressions for these equations obtained by the present EOS are given elsewhere [Yoo et al., 1997a]. Three phase equilibria are determined by the relation,

$$\mu_i^\alpha(T, P, x_i^\alpha) = \mu_i^\beta(T, P, x_i^\beta) = \mu_i^\gamma(T, P, x_i^\gamma) \quad (10)$$

where α , β and γ denote different phases. The expression for the chemical potential of fluids is given by Eq. (3). For a pure solid the chemical potential is written

$$\mu_{i,\text{pure}}^{\text{solid}}(T, P) = \Delta\mu_i(T, P) + \mu_{i,\text{pure}}^{\text{liquid}}(T, P) \quad (11)$$

where $\Delta\mu_i$ represents the departure from solid to hypothetical liquid at the same temperature and pressure. This term is discussed elsewhere [You et al., 1993]. Various types of multiphase equilibria including the binodal and spinodal stabilities can be calculated by using these equations. They include LLVE, SLVE as well as two phase equilibria such as VLE, LLE and VSE including UCST and LCST in liquid mixtures.

The three phase equilibrium locus ends at a critical end point where it is intersected by a mixture critical locus. Since the degree

of freedom for a three phase binary mixture is one, the existing phase equilibria are expressed by a locus. When one variable is fixed, one can readily calculate three phase equilibria.

While complicated (multi) phase behaviors such as critical locus of fluid mixtures can be described by an EOS, quantitative agreements are seldom reported even for simple solutions. Thus, we illustrated here the calculated critical T -critical P loci of carbon dioxide-n-heptane system. Because we use only one binary parameter for wide range of temperature and pressure region, the binary parameter for critical loci can be obtained from binary vapor-liquid equilibrium calculation, solid-vapor equilibrium calculation, etc. In Fig. 1, we can find experimental VLE data of carbon dioxide-n-heptane system and calculated results. We obtained the parameter which is best fit to the experimental data. We calculated the critical loci of carbon dioxide-n-heptane system with the same parameter as VLE calculation (Fig. 2). Also, we illustrated here the

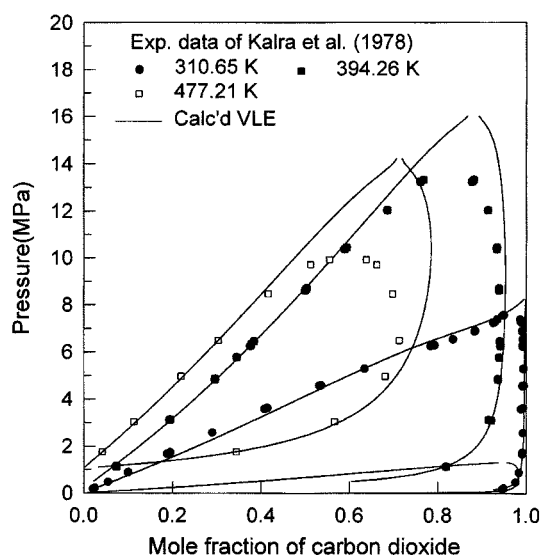


Fig. 1. Calculated high pressure VLE for the CO_2 /heptane system at 310.65, 352.59, 394.26 and 477.21 K ($\lambda_{12} = 0.0932$).

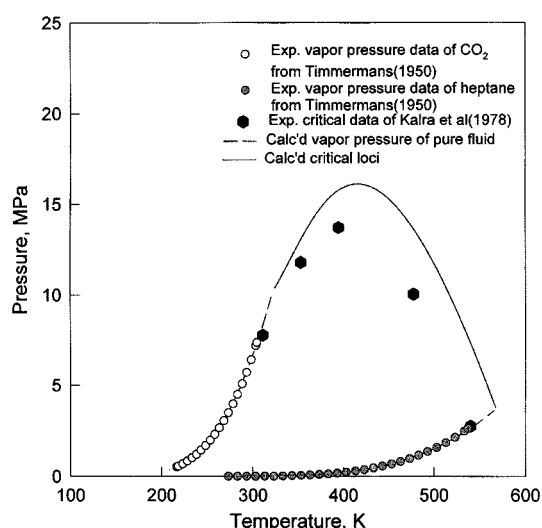


Fig. 2. Calculated and experimental critical temperature and pressure of carbon dioxide-n-heptane system ($\lambda_{12} = 0.0932$).

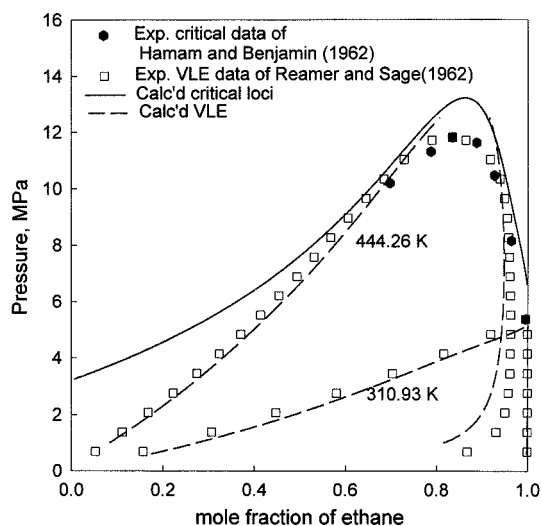


Fig. 3. Calculated and experimental VLE of ethane-decane system and critical P-x ($\lambda_{12}=0.00097$).

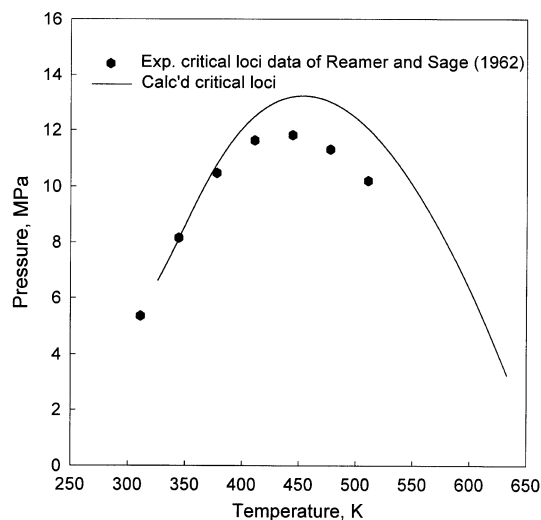


Fig. 4. Calculated and experimental critical temperature and pressure of ethane-decane system ($\lambda_{12}=0.00097$).

calculated P-x projected loci of critical behaviors for ethane/decane system (Fig. 3). Here we used the same value of λ_{12} without any readjustment which was used already in VLE calculation. We used isothermal experimental data (310.93, 344.26, 377.59, 410.93, 444.26 K) [Reamer and Sage, 1962]. From Fig. 3, We can find the calculated results fit well with experimental VLE and critical P-x data with only one binary adjustable parameter. In Fig. 4 and 5, calculated T_c - P_c loci and T_c - V_c loci by the present EOS for ethane/decane system was shown. The present EOS quantitatively fit the critical volume and fit reasonably well the critical T-P loci of the mixture.

In Fig. 6, the critical loci calculated by the present EOS for CO_2 /benzene system is shown. The binary parameter of CO_2 /benzene system was obtained from experimental isothermal P-x-y data (313.40-310.93 K) [Nagahama et al., 1974]. The present EOS quantitatively fits the critical loci of the mixture. The P-T projection of the three phase SLV equilibria behavior, UCEP and critical loci for

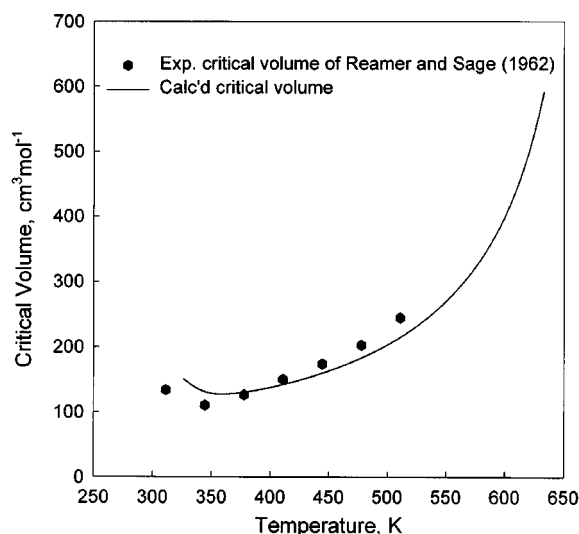


Fig. 5. Calculated and experimental T_c - V_c of ethane-decane system ($\lambda_{12}=0.00097$).

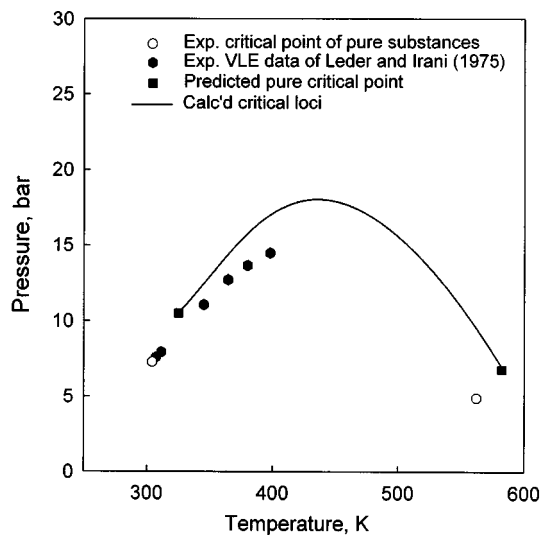


Fig. 6. Calculated and experimental critical loci of CO_2 -benzene system ($\lambda_{12}=0.0893$).

CO_2 /naphthalene system [Cheong et al., 1986] is shown in Fig. 7. Also in this system, we obtained the binary parameter from CO_2 /naphthalene SVE experimental data (308.15-328.15 K) [Johnston et al., 1981]. In this system the results of P-T locus for SLV below UCEP by the present EOS agree well with the data, and UCEP is decided as the point which SLV line meet critical loci. Due to the limited space of this paper, we omit further demonstration. However, we can conclude that the present EOS fit such difficult critical loci and multiphase behaviors of complex mixtures correlates quantitatively well.

CONCLUSION

The EOS stemmed from the nonrandom two-fluid approximation of the lattice-hole theory has been applied to the calculation of high-pressure phase equilibria. The MF-NLF EOS was also applied well to the calculation of multiphase behavior and critical loci

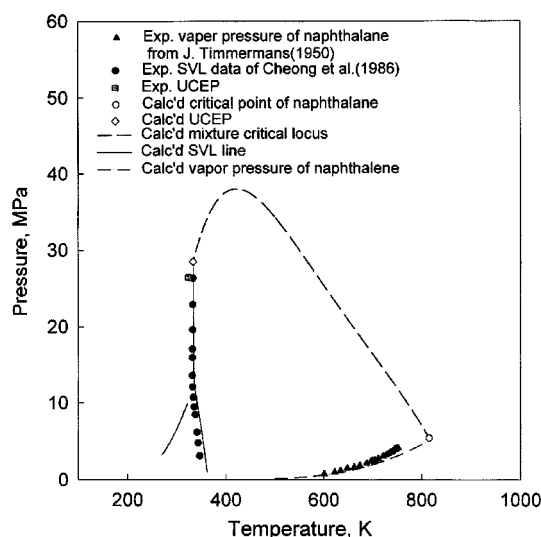


Fig. 7. Calculated SLV equilibria and critical P-T locus of CO₂/naphthalene system ($\lambda_{12}=0.07534$).

of mixtures whose molecules differ greatly in size. It is shown that this model gives satisfactory predictions of multiphase behavior using the binary parameter fixed already in the calculation of common VLE calculation. Thus, it is also true that if we adjust the new binary parameter for critical loci, the accuracy of the present EOS can be further improved. Necessary computer program used in this work will be released to the readers upon request (e-mail: kpyoo@ccs.aogang.ac.kr).

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REFERENCES

- Abrams, D. and Prausnitz, J. M., "Statistical Thermodynamics of Liquid Mixture: A New Expression for the Excess Gibbs Energy of Partly or Completely Miscible System," *AIChE J.*, **21**, 116 (1975).
- Cheong, P. L., Zhang, D., Ohgaki, K. and Fu, B. C.-Y., "High Pressure Equilibria for Binary Systems Involving a Solid Phase," *Fluid Phase Equilibria*, **29**, 555 (1986).
- Guggenheim, A., "Mixture," Clarendon Press, Oxford, Ch. IX, 1952.
- Johnston, K. P. and Eckert, C. A., "An Analytical Carnahan Starling - van der Waals Model for Solubility of Hydrocarbon Solids in Supercritical Fluids," *AIChE J.*, **27**, 773 (1981).
- Kalra, H., Kubota, H., Robinson, D. B. and Ng, H.-J., "Equilibrium Phase Properties of the Carbon Dioxide-n-Heptane System," *J. of Chem. Eng. Data*, **23**, 317 (1978).
- Leder, F. and Irani, C. J., "Upper Critical Solution Temperatures in Carbon Dioxide-Hydrocarbon Systems," *J. Chem. Eng. Data*, **20**, 323 (1973).
- Nagahama, K., Konishi, H., Hoshino, D. and Hirata, M., "Binary Vapor-liquid Equilibria of Carbon Dioxide," *J. Chem. Eng. Jpn.*, **7**, 323 (1974).
- Reamer, H. H. and Sage, B. H., "Phase Equilibria in Hydrocarbon System; Volumetric & Phase Behavior of the Ethane-n-decane System," *J. Chem. Eng. Data*, **7**, 161 (1962).
- Sanchez, I. C. and Lacombe, R. H., "Theory of Liquid-liquid and Liquid-vapor Equilibria," *Nature*, **252**, 381 (1974).
- Timmermans, J., "Physico-Chemical Constants of Pure Organic Compounds," Vol. 1 and Vol. 2, Elsevier. Scientific Publishing Company, New York (1950).
- 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 (1997a).
- 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 (1997b).
- You, S. S., Lee, C. S. and Yoo, K.-P., "Modeling of Supercritical Fluid-phase Equilibria using a New Nonrandom Lattice-fluid Theory," *J. Supercrit. Fluids*, **6**, 69 (1993).
- You, S. S., Yoo, K.-P. and Lee, C. S., "An Approximate Nonrandom Lattice Theory of Fluids. General Derivation and Application to Pure Fluids," *Fluid Phase Equilibria*, **93**, 193 (1994a).
- You, S. S., Yoo, K.-P. and Lee, C. S., "An Approximate Nonrandom Lattice Theory of Fluids. Mixture," *Fluid Phase Equilibria*, **93**, 215 (1994b).