UNIFIED EQUATION OF STATE BASED ON THE LATTICE FLUID THEORY FOR PHASE EQUILIBRIA OF COMPLEX MIXTURES
PART II. APPLICATION TO COMPLEX MIXTURES

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Abstract—In part I of the present article [Yoo et al., 1995], new rigorous and simplified lattice-fluid equations of state (EOS) were derived and their characteristic features of the molecular thermodynamic foundation were discussed by applying to pure fluids. In this part II, both EOSs were extended to various phase equilibrium properties of mixtures. Comparison of the models with experimental mixture data ranges from density, to equilibria of vapor-liquid, vapor-solid and liquid-liquid phases for nonpolar/nonpolar, nonpolar/polar, polar/polar mixtures. Both models were also applied to supercritical fluid phase equilibria and activities of solvents in polymer solutions. With two temperature dependent parameters for pure compounds and one temperature-independent binary interaction energy parameter for a binary mixtures, results obtained to date illustrated that both EOSs are quantitatively applicable to versatile phase equilibria of mixtures over a wide range of temperatures, pressures and compositions.

Key words: Theory, Equation of State, Nonrandom Lattice Fluid Theory, Fluid-phase Equilibria, Complex Mixtures

INTRODUCTION

In part I, we briefly reviewed the existing thermodynamic models stemmed from the lattice fluid theories and also cited extensively the related literatures in this fields [Yoo et al., 1995]. We also presented a general derivation of a new formulation and its simplified version for Helmholtz free energy, EOS, chemical potential, and derived properties for pure fluids and fluid mixtures from a nonrandom lattice fluid theory. The rigorous but explicit formulation of the configurational Helmholtz free energy was derived based on an expansion of the full Guggenheim combinatory [Guggenheim, 1952] of nonrandom lattice fluid theory around the reference athermal solution. From which various equations relevant to phase equilibria such as EOS and chemical potential were obtained. The self-consistency of the rigorous EOS and its capacity to phase equilibria were fully demonstrated in part I and in articles appeared elsewhere by the present authors [You et al., 1993, 1994a, b, c; Shin et al., 1994a, b; 1995a, b; Yoo et al., 1994, 1995]. However, we had a notion that the expression of the rigorous EOS is somewhat complicated for easy engineering practice. Thus, we placed our efforts to make the rigorous EOS less complicated while preserving inherent nature of the original derivation and comparable accuracy. As a result, we formulated very recently a simplified version for easy and versatile engineering purposes. Thus, in part II, major attention is placed to the extension of the simplified EOS for phase equilibrium calculation of mixtures.

In part II, we presented our efforts of application of both EOSs to complex mixtures, and discuss the consequences of application of the models to the calculation of vapor-liquid, liquid-liquid with UCST, activities of polymer solutions, vapor-solid phase equilibria of mixtures containing complex and/or macromolecular species up to high pressure.

THE MODEL EOS AND THERMODYNAMIC PROPERTIES

1. Rigorous Formulations of Helmholtz Free Energy, EOS and Chemical Potential
1-1. Helmholtz Free Energy

As discussed in part I [Yoo et al., 1995], in a three dimensional lattice of coordination number z and of unit cell volume, V_H, the rigorous expression of Helmholtz free energy is derived by utilizing the series expansion to the full Guggenheim combinatory of the nonrandom lattice model and it is written,

$$\beta A^c = \Sigma N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]$$

$$-\left(\frac{zN_q}{2}\right)\beta[\Sigma\Sigma\theta_i\theta_j\varepsilon_{ij}+\left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}$$

$$(\varepsilon_{ij}+\varepsilon_{kl}+\varepsilon_{ik}-\varepsilon_{jk})] \qquad (1)$$

where $\beta=1/kT$; N_o, the overall number of vacant sites; N_i the number of sites occupied by component i and

$$N_q = N_o + \Sigma\ N_i q_i \qquad (2)$$

$$N_r = N_o + \Sigma\ N_i r_i \qquad (3)$$

$$\theta_i = N_i q_i / N_q, \quad \theta_o = 1 - \Sigma\ \theta_i \qquad (4)$$

$$\tilde{\theta}_i = \theta_i/\theta \text{ for hole free basis} \qquad (5)$$

$$\theta = \frac{\Sigma N_i q_i}{N_o + \Sigma N_i q_i} \qquad (6)$$

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$$\rho = \Sigma \frac{V_i^*}{V} = \frac{\Sigma N_i r_i}{N_o + \Sigma N_i r_i} \tag{7}$$

$$V = V_H(N_o + \Sigma N_i r_i) \tag{8}$$

$$\phi_i = N_i r_i / N_r, \quad \phi_o = 1 - \Sigma \phi_i \tag{9}$$

$$q_M = \Sigma \ x_i q_i \tag{10}$$

$$r_M = \Sigma \ x_i r_i \tag{11}$$

x_i is the mole fraction of species i. The lattice interaction energy 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,

$$\varepsilon_{ij} = (\varepsilon_{ii}\varepsilon_{jj})^{0.5} \ (1 - \lambda_{ij}) \tag{12}$$

where the λ_{ij} is the binary interaction parameter. ε_{ij} between holes and molecular species is set to zero. Thus, from Eq. (1) all other configurational thermodynamic functions relevant to phase equilibrium calculation can be formulated.

1-2. EOS and Chemical Potential

Since the system volume V is represented by Eq. (7), the pressure explicit rigorous EOS is obtained from A^c [Eq. (1)],

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] - \ln(1-\rho)\right\} - \left(\frac{z}{2}\right)\theta^2\frac{\varepsilon_M^{(R)}}{V_H} \tag{13}$$

where $\varepsilon_M^{(R)}$ is defined as,

$$\varepsilon_M^{(R)} = \frac{1}{\theta^2}\left[\Sigma\Sigma\theta_i\theta_j\varepsilon_{ij} + \left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}(\varepsilon_{ij}+3\varepsilon_{kl}-2\varepsilon_{ik}-2\varepsilon_{jk})\right] \tag{14}$$

Summations are over all molecular species unless otherwise specified.

The chemical potential for mixture is also written as

$$\frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(R)}}{RT} \tag{15}$$

where

$$\frac{\mu_i^{(A)}}{RT} = \gamma_i(T) - r_i\ln(1-\rho) + \ln\left(\frac{\theta_i}{q_i}\right) + r_i\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right] \tag{16}$$

$$\frac{\mu_i^{(R)}}{RT} = -\frac{zq_i\beta\varepsilon_M\theta^2}{2}\left[1-\frac{r_i}{q_i} - \frac{2\Sigma\theta_j\varepsilon_{ij}+\beta\Sigma\Sigma\Sigma\theta_k\theta_l\theta_m\varepsilon_{ik}(\varepsilon_{ik}+2\varepsilon_{lm}-2\varepsilon_{kl}-\varepsilon_{il})}{\theta^2\varepsilon_M}\right] \tag{17}$$

1-3. Activity and Activity Coefficient

If necessary, the difference of chemical potential of component i in the mixture and the chemical potential of pure component i at the same temperature and pressure, $\Delta\mu_i/RT$ can readily be derived. Then, the activity coefficient can be obtained by the expression

$$\frac{\Delta\mu_i}{RT} = \frac{\mu_i - \mu_{i, \ pure}}{RT} = \ln a_i = \ln(x_i \ \gamma_i) \tag{18}$$

The Flory-Huggins χ_{ij} interaction parameter [Yoo et al., 1995] may be directly obtained by the equation

$$\frac{\Delta\mu_i}{RT} = \ln \ \phi_i + \left[1-\frac{r_i}{r_j}\right]\phi_j + \chi_{ij}\phi_j^2 \tag{19}$$

One of the advantages inherent to the lattice fluid theory is that the Guggenheim combinatory can readily be extended to r-mers

and thus the EOS proposed here can be applied to polymer solutions. Comparison of the present EOS to experimental data for polymer solutions are discussed in part II of the present article.

1-4. Molar Configurational Internal Energy

It also can be obtained from Eq. (1),

$$\frac{\beta U^c}{N} = -\left(\frac{T}{N}\right)\left(\frac{\partial\beta A^c}{\partial T}\right)_{N_0,N_i}$$

$$= \frac{zq_M}{2}\ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]$$

$$+ \frac{z\beta q_M}{2}\left[\Sigma\Sigma\theta_i\varepsilon_{ij}\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}-\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-1\right)\right.$$

$$+ \left(\frac{\beta}{2}\right)\Sigma\Sigma\Sigma\Sigma\theta_i\theta_j\theta_k\theta_l\varepsilon_{ij}\left\{(\varepsilon_{ij}+\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})\right.$$

$$\times\left(\frac{q_i'}{q_i}+\frac{q_j'}{q_j}-\frac{q_M'}{q_M}\theta+\frac{\varepsilon_{ij}'}{\varepsilon_{ij}}-2\right)$$

$$-\frac{q_M'}{q_M}\theta(2\varepsilon_{ij}+4\varepsilon_{kl}-3\varepsilon_{ik}-3\varepsilon_{jk})+\varepsilon_{ij}'+\varepsilon_{kl}'-\varepsilon_{ik}'-\varepsilon_{jk}'$$

$$\left.\left.+\frac{q_k'}{q_k}(\varepsilon_{kl}-\varepsilon_{ik}-\varepsilon_{jk})+\frac{q_l'}{q_l}\varepsilon_{kl}\right\}\right] \tag{20}$$

where primed quantities denote derivatives with respect to lnT and N is the total number of molecules. In particular, $\varepsilon_{ij}'(i \neq j)$ is given by

$$\varepsilon_{ij}' = \left(\frac{\varepsilon_{ij}}{2}\right)\left[\frac{\varepsilon_{ii}'}{\varepsilon_{ii}}+\frac{\varepsilon_{jj}'}{\varepsilon_{jj}}-\frac{\lambda_{ij}'}{(1-\lambda_{ij})}\right] \tag{21}$$

and

$$q_i' = r_i'\frac{(z-2)}{z} = (V_i^*)'\frac{(z-2)}{zN_aV_H} \tag{22}$$

where the characteristic volume V_i^* is defined as,

$$V_i^* = r_iN_aV_H \tag{23}$$

Equations for other thermodynamic properties may be obtained from Helmholtz free energy.

1-4. Excess Functions of Mixing

Since the reduced volume pure component i is denoted by V_i ($= V_i^*/\rho_i$), the excess volume of mixing $\underline{V}^E$ can be expressed in terms of mole fraction x_i as,

$$\underline{V}^E = r_MV_H\underline{V} - x_ir_iV_HV_i - x_jr_jV_HV_j \tag{24}$$

With the ideal volume V_o of the mixture given by assuming the additivity of the pure component volumes, Eq. (24) is written as,

$$\frac{V^E}{V_o} = \frac{V}{\Sigma\phi_iV_i} - 1 \tag{25}$$

where ϕ_i is the segment fraction of component i as given by Eq. (9).

The excess heat or the excess enthalpy of mixing, $\underline{H}^E$ is,

$$\underline{H}^E = (\underline{U}+P\underline{V})_{mixture} - \Sigma x_i(\underline{U}_i+P\underline{V}_i)_{pure,i} \tag{26}$$

where $\underline{U}$ and $\underline{U}_i$ are molar internal energies of a mixture and a pure liquid of component i, respectively. Here, we omit the resultant expressions derived by the EOS presented.

2. Simplified Versions of Helmholtz Free Energy, EOS and Chemical Potential

2-1. Helmholtz Free Energy

As discussed in part I [Yoo et al., 1995], the final expression of the simplified Helmholtz free energy is given as the sum of

three contribution; 'athermal', 'ideal solution', and 'excess' solution terms,

$$\beta A^c = \beta A^{c(A)} + \beta A^{c(IS)} + \beta A^{c(E)} \tag{27}$$

where

$$\beta A^{c(A)} = \Sigma N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q \ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] \tag{28}$$

$$-\beta A^{c(IS)} = \frac{zN_q}{2} \theta \Sigma N_i q_i \varepsilon_{ii} \tag{29}$$

$$-\beta A^{c(E)} = \frac{zN_q}{2} \Sigma \theta_i \ln[\Sigma \overline{\theta}_j \tau_{ji}] \tag{30}$$

2-2. EOS and Chemical Potential

The simplified EOS can be obtained from Eq. (27). The apparent form is identical to the case of rigorous EOS [Eq. (13)]. However, ε_M is differently given by

$$P = \frac{1}{\beta V_H}\left\{\frac{z}{2}\ln\left[1 + \left(\frac{q_M}{r_M} - 1\right)\rho\right] - \ln(1-\rho)\right\} - \left(\frac{z}{2}\right)\theta^2 \frac{\varepsilon_M^{(S)}}{V_H} \tag{31}$$

$$\varepsilon_M^{(S)} = \Sigma\overline{\theta}_i \varepsilon_{ij} + \Sigma\overline{\theta}_j \frac{\Sigma\overline{\theta}_k \tau_{kj}(\varepsilon_{kj} - \varepsilon_{jj})}{\Sigma\overline{\theta}_k \tau_{kj}} \tag{32}$$

Also, the chemical potential for simplified case is obtained from Eq. (27) as,

$$\frac{\mu_i}{RT} = \frac{\mu_i^{(A)}}{RT} + \frac{\mu_i^{(S)}}{RT} \tag{33}$$

where $\mu_i^{(A)}/RT$ is given by Eq. (16) and

$$\frac{\mu_i^{(S)}}{RT} = -\frac{zq_i\beta\varepsilon_M\theta^2}{2}\left[1 - \frac{r_i}{q_i} - \frac{1}{\theta}\frac{(1+\varepsilon_{ii})}{\varepsilon_M}\right] + \frac{zq_i}{2}\left[1 - \ln(\Sigma\overline{\theta}_j\tau_{ji}) - \Sigma\frac{\overline{\theta}_j\tau_{ij}}{\Sigma\overline{\theta}_k\tau_{kj}}\right] \tag{34}$$

These general equations for multicomponent mixtures easily reduce to their pure forms since all ε_M become ε_{ii} and τ_{ij} become 1 for pure fluids [Yoo et al., 1995]. Since other thermodynamic functions such as excess properties and activities of solvent in polymer solutions can be derived in a same manner as the case of the rigorous EOS and we omit them here for the simplified EOS case.

MOLECULAR PARAMETERS

In part I of this article and in references published by the authors [You et al., 1994a; Shin, 1995b], we presented values of V_i^* and ε_{ii} about 200 pure components for both EOSs as functions of temperature and discussed the results. Thus we omit the pure molecular parameter tables in part II. As far as we could, the various types of pure fluids such as nonpolar, weak polar, strong polar components, supercritical substances, low vapor pressure compounds and common polymers were included for the determination of pure parameters. $z=10$ and $V_H=9.75$ cm³/mol were found to be satisfactory values. Therefore, for their binary mixture we need to determine λ_{ij} from various phase equilibria data of mixtures.

We randomly selected various representative mixtures, especially, mixtures in which one or both components are complex and/or of polar nature and calculated various possible types of phase equilibrium behaviors. Then, using the pure molecular parameters, the binary interaction parameters, λ_{ij}, were fitted to

mixture data. The values of λ_{ij}, and their consequences are presented in the next application sections for both EOSs.

PHASE EQUILIBRIUM COMPUTATIONS OF MIXTURES

Practical methods used to calculate phase equilibria can be roughly divided into two groups [Yoo et al., 1995]; the so-called gamma-phi and EOS methods. The first group employs separate methods for the calculation of liquid phase activity coefficients (γ) and vapor phase fugacity coefficients (ϕ). Moreover, it requires separate techniques to calculate the pure component properties that are relevant to phase equilibrium computations. On the other hand, the EOS method uses a homogeneous model for all fluid phases and is equally applicable to pure component and mixture properties. Modeling of both models (i.e., γ-models and EOS) is now an active area on research and equally important, however, more emphasis on EOS than γ-models being placed mainly due to the homogeneous nature inherent in EOSs [Flory, 1942; Huggins, 1942]. To arrive at practical solutions by a new EOS to real phase equilibrium problems, it is almost always necessary to develop relatively large and complex computer programs. To elaborate such programs, the knowledge of both thermodynamic background and models of equilibria is essential.

No matter what type of an excellent EOS is on hand, the specific computation technique for solving specific phase equilibrium problem is equivalently important and cumbersome process in modeling a new thermodynamic model for engineering practice in mind. It is the authors' intention to provide here a comprehensive background for phase equilibrium computations using the new EOSs (they are somewhat more complicated than the cases of cubic EOSs). Thus, we present in this section on the algorithmic aspects for various types of phase equilibrium calculations of mixtures based on both EOSs presented here. The algorithms and related computer program can be obtained from the authors upon request.

1. Vapor-Liquid Equilibria

Isothermal vapor-liquid equilibrium properties can be calculated by imposing the following conditions,

$$P^V = P^L \tag{35}$$

$$\mu_i^V(T, P, \{y\}) = \mu_i^L(T, P, \{x\}) \tag{36}$$

where $\{y\}$ and $\{x\}$ denote sets of mole fractions of all components in vapor and liquid phases, respectively. Assuming an initial set of the partition coefficient $\{K\}$, we can calculate $\{y\}$ and $\{x\}$ at constant temperature and pressure, from which densities of liquid and vapor phases are calculated by Eq. (13) for the rigorous case and by Eq. (31) for simplified case. Then we calculate μ_i^L and μ_i^V by Eq. (15) for rigorous case and by Eq. (33) for the simplified case. If chemical potentials of both phases are sufficiently close, the calculation is terminated. Otherwise we modify $\{K\}$ using the relation for each component,

$$K_{i,new} = K_{i,old} \exp\left[\frac{(\mu_i^L - \mu_i^V)}{RT}\right] \tag{37}$$

and the calculation is repeated until the convergence is obtained. λ_{ij} is determined in this calculation such that the deviation of calculated values from experimental data be minimum. λ_{ij} values with fitting errors for binary vapor-liquid systems for both EOSs are summarized in the next section.

2. Liquid-Liquid Equilibria

The calculation of liquid-liquid equilibria can readily be carried out with the phase equilibrium criterion,

$$\mu_i^{L'}(T, P, \{x'\}) = \mu_i^{L''}(T, P, \{x''\}) \tag{38}$$

where superscripts L' and L'' represent the coexisting liquid phases. At the upper critical solution temperatures (UCST) of partially miscible mixtures compositions of coexisting phases become identical. The UCST behavior is one of the interesting characteristics of binary liquid mixtures and is a good candidate for testing the theoretical consistency of the present model.

3. Solid-Vapor Equilibria

In the solid-vapor equilibrium calculation, solid phase is assumed pure. The equilibrium condition then becomes,

$$\mu_i^V(T, P, \{y\}) = \mu_{i,pure}^S(T, P) \tag{39}$$

The chemical potential in the solid phase causes difficulty in practice since it cannot be evaluated using Eqs. (15) or (33). If both sides of Eq. (39) are subtracted by the chemical potential of a pure supercooled liquid, we have

$$\mu_i^V(T, P, \{y\}) = \Delta\mu_{i,pure}(T, P) + \mu_{i,pure}^L(T, P) \tag{40}$$

$$\Delta\mu_{i,pure}(T, P) = \mu_{i,pure}^S(T, P) - \mu_{i,pure}^L(T, P) = RT \ln\left(\frac{f_i^S}{f_i^L}\right)_{pure}$$
$$= \underline{V}_i^{sat,S}(P - P_i^{sat,S}) \ln (P_i^{sat,S}\phi_i^{sat,V})$$
$$- RT \ln (P\phi_{i,pure}^L) \tag{41}$$

where $\underline{V}_i^{sat,S}$ is the molar volume of a solid at its vapor pressure, $P_i^{sat,S}$. The fugacity equation for a pure component is needed for the evaluation of Eq. (40) and was derived as given in part I.

For high molecular weight species of which the vapor pressure is not well known and negligible, we use the following relation instead of Eq. (40)

$$\Delta\mu_{i,pure}(T, P) = \Delta\mu_{i,pure}(T, P_i^{sat}) + P\Delta \underline{V}^f \tag{42}$$

where $\Delta \underline{V}^f$ is the molar volume change on fusion and $\Delta\mu_{i,pure}$ (T, P_i^{sat}) is evaluated along the path (saturated solid→triple point →saturated liquid) as presented by Prausnitz et al. [1986]. The result is,

$$\Delta\mu_{i,pure}(T, P_i^{sat}) = \Delta\underline{H}^f(T_f)\left(1 - \frac{T}{T_f}\right) + \int_{T_t}^{T}\Delta\underline{C}_p dT - T\int_{T_t}^{T}\frac{\Delta\underline{C}_p}{T}dT \tag{43}$$

where $\Delta\underline{H}^f$ is the molar heat of fusion and $\Delta\underline{C}_p$ is $\underline{C}_p^s - \underline{C}_p^l$. Triple point properties may be replaced by properties at normal melting points. Bondi [1967] provides group contribution methods for estimating $\Delta\underline{V}^f$, $\Delta\underline{H}^f$ and $\Delta\underline{C}_p$.

With $\Delta\mu_{i,pure}(T, P)$ obtained using Eqs. (41) or (42), Eq. (40) is now readily solved by iteration to give the composition and the density of the vapor phase.

4. Multiphase Behavior and Critical Loci

Three phase equilibria are determined by the relation,

$$\mu_i^a = \mu_i^b = \mu_i^c \tag{44}$$

where a, b and c denote different phases. Solution of this equation is obtained by simultaneous solution of the two independent relations. The evaluation of chemical potential for each phase is discussed previously. Various types of multiphase equilibrium behaviors can be calculated using this relation. They include liquid-liquid-vapor (LLV) equilibria and solid-liquid-vapor (SLV) equilibria. A three phase equilibrium locus ends at a critical end point where it is intersected by a mixture critical locus. The well-known

mixture critical conditions are also expressed in terms of Helmholtz free energy [Rowlinson and Swinton, 1982].

$$\left(\frac{\partial^2\underline{A}}{\partial x^2}\right)_{V,T} + \left(\frac{\partial P}{\partial x}\right)_{V,T}Q = 0 \tag{45}$$

$$\left(\frac{\partial^3\underline{A}}{\partial x^3}\right)_{V,T} + 3\left(\frac{\partial^2 P}{\partial x^2}\right)_{V,T}Q - \left(\frac{\partial^2 P}{\partial x\partial\underline{V}}\right)_T Q^2 + \left(\frac{\partial^2 P}{\partial\underline{V}^2}\right)_{x,T}Q^3 = 0 \tag{46}$$

where

$$Q = \left(\frac{\partial P}{\partial x}\right)_{V,T}\Big/\left(\frac{\partial P}{\partial\underline{V}}\right)_{x,T} \tag{47}$$

and quantities underlined denote molar properties.

Since the degree of freedom for a three-phase binary mixture is one, the coexisting phase equilibria is expressed by a locus. With one variable fixed one can readily calculate three-phase equilibria. To calculate LLV equilibria for fixed pressure, for example, the total number of variables to be calculated becomes seven (i.e., T, x_1^a, x_2^a, x_1^b, x_2^b, y_1, y_2) and there are seven corresponding relations (i.e., 4 phase equilibrium criteria and 3 mass balance constraints).

In the calculation of SLV equilibria the solid phase is assumed pure. Again we have one degree of freedom. If pressure is fixed, for example, we have five unknowns (i.e., T, x_1, x_2, y_1, y_2) and five relations (i.e. 3 equilibrium relations and 2 mass balance relations). In both cases a critical locus can be calculated using Eqs. (45) and (46). The intersection of the multiphase equilibrium locus with the critical locus determines the critical end point.

5. Activities of Solvents in Polymer Solutions

For polymeric species, vapor pressure is frequently not well known and is usually negligible. The activities of solvents can be determined from the simplified equation of vapor-liquid equilibria of solvents as,

$$\mu_{i,pure}^V(T, P) = \mu_i^L(T, P, x) \text{ for solvents} \tag{48}$$

where the right hand side of Eq. (48) can be calculated by Eq. (18).

COMPARISON OF THE MODELS TO EXPERIMENTAL MIXTURE DATA

1. Rigorous EOS Case

1-1. Phase Equilibria of Complex Mixtures

To evaluate the utility of the new rigorous EOS, we tested the model on various types of phase equilibria of mixtures. So far we randomly selected 26 representative binary mixtures wherein one or both components were of complex and or of polar nature and calculated various possible types of phase equilibrium behaviors such as VLE, LLE, VSE and excess enthalpy. The best fits of binary interaction energy parameter, λ_{ij} for 26 tested systems and 12 polymer systems are reported elsewhere [You et al., 1993, 1994a]. As far as concern the case of rigorous EOS, much of the fitting results already appeared elsewhere [You et al., 1994b, c]. Thus we intend to illustrate here only a few graphical comparisons.

The azeotropic T-{x} equilibria for chloroform(1)-diisopropyl ether(2) [Chevalier, 1969] in Fig. 1 show the agreement is quite good with $\lambda_{12} = -.0490$. When compared with the calculated results by the well known γ-model UNIQUAC [Abrams and Prausnitz, 1975] which used two binary parameters, the present results are seen to be similar. High pressure VSE of ethane(1)-naphtha-
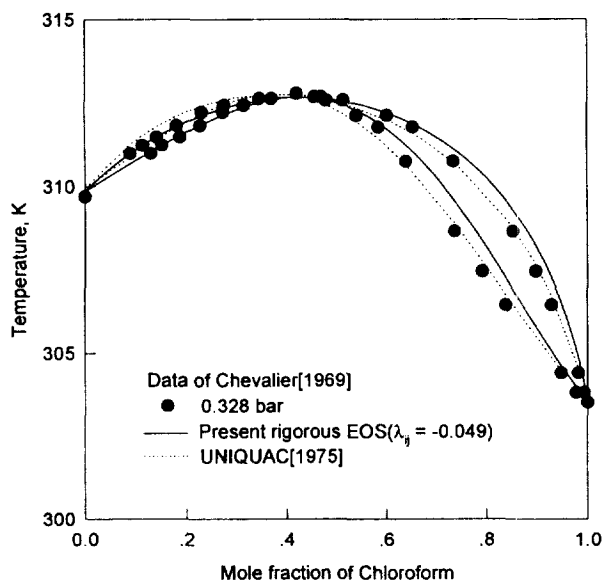
Fig. 1. Isobaric vapor-liquid azeotropic T-x equilibria by the rigorous EOS for chloroform(1)-diisopropyl ether(2) system at 0.328 bar.
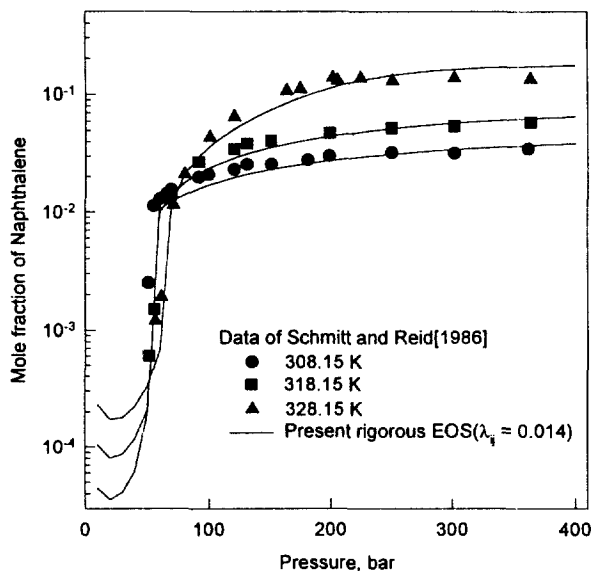

Fig. 3. Isothermal excess enthalpy H^E-x for chloroform(1)-acetic acid (2)[λ_{12}= −.0604] and methanol(1)-formic acid(2)[λ_{12}= −.05 42] systems at 298.15 K by the rigorous EOS.

Fig. 2. Isothermal vapor-solid P-y equilibria by the rigorous EOS for methane(1)-naphthalene(2) system at 308.15, 318.15 and 328. 15 K.

Fig. 4. P-T projection of three phase SLV and UCEP for CO_2(1)-naphthalene(2) system by the rigorous EOS.

lene(2) with λ_{12}=.0140 [Smitt and Reid, 1986] is shown in Fig. 2. The present EOS quantitatively describes the high pressure P-{y} equilibria over a wide range of pressure and temperature. The calculated heats of mixing for the system which show negative deviation are compared with data for chloroform(1)-acetic acid (2) [Abramov et al., 1991] and methanol(1)-formic acid(2) system [Zhao et al., 1991] in Fig. 3. For the former system agreements are excellent, while the latter system shows some deviations. The error for the calculations lies within an average value of 8%.

In Fig. 4, the calculated SLV phase diagram for CO_2-naphthalene is compared with experimental data [McHugh, 1981; McHugh and Yogan, 1984; Lemert and Johnston, 1989]. It is seen

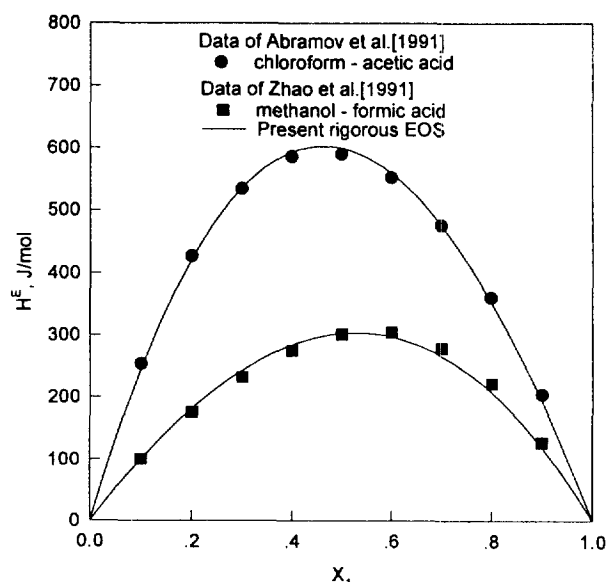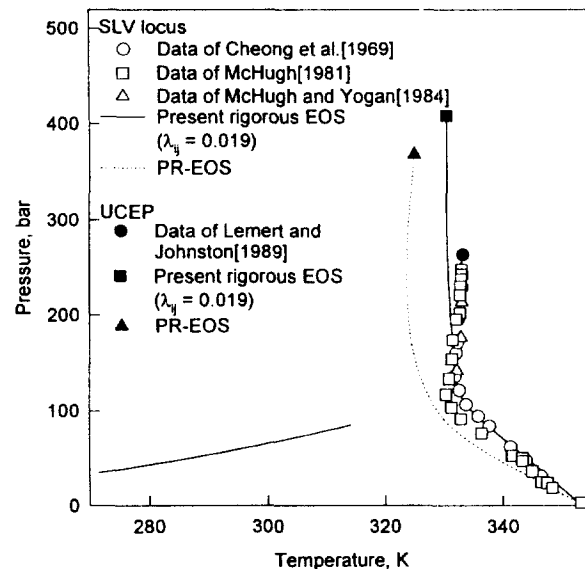that SLV locus is quantitatively calculated. The agreement is some what better than that of the Peng-Robinson EOS [Peng and Robinson, 1976]. But errors in the critical end point are large. As discussed in detail elsewhere by the present authors [You et al., 1993, 1994c], the model fits erroneously the critical solution temperatures of binary solutions.

1-2. Activities of Solvents in Polymer Solutions

Since the range of mixtures which this EOS would be applicable is very wide, the EOS is extended to the calculation of activities in polymer solutions. The best fitted λ_{12} for 16 binary systems are summarized in Table 1. We arbitrarily chose 4 other well-known EOSs (new Flory [Flory, 1970], Kumar et al. [1978], Panayiotou and Vera [1982], Sanchez-Lacombe [1978], and Random

Table 1. Binary interaction energy parameters between solvents and polymers for the rigorous EOS

System	T range (K)	λ_{ij}	AAD [%][a]	References
Polystyrene				
-Cyclohexane	307-317	.0256	4.39	47
-Benzene	288-333	.0105	1.68	48
-m Xylene	293.15	-.0015	13.28	57
-Chloroform	298-323	.0029	5.15	58
-Carbon tetrachlodide	293.15	.0102	0.91	57
-n Propyl acetate	298-343	.0166	1.44	58
-n Butyl acetate	293.15	.0188	1.68	57
Polyisobutylene				
-n Hexane	298-338	.0011	2.83	46
-Cyclohexane	298-338	.0119	2.19	32, 46, 58
-Benzene	298-338	.0321	3.08	32, 58
-Ethyl benzene	338.15	.0134	7.01	32
Polyvinylacetate				
-Benzene	303.15	.0140	4.89	59
-Vinyl acetate	303.15	.0063	3.03	59
Polydimethylsiloxane				
-n Heptane	298-313	.0119	1.72	27
Polypropylene oxide				
-Chloroform[b]	278.68	-.1429	8.30	54
-Carbon tetrachloride[b]	278.68	-.1251	4.53	54

a: AAD%=$\Sigma[\rho_{cal,i}-\rho_{exp,i}]/\rho_{exp,i}/$(number of data point)$\times$100

b: binary parameters determined by experimental heat of mixing data and
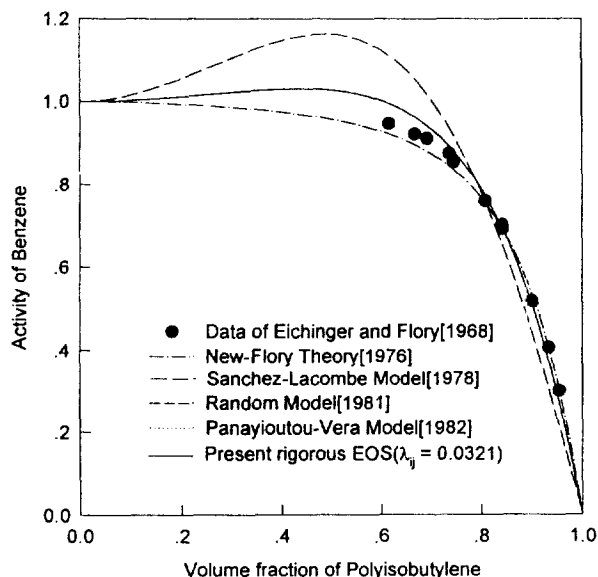
Fig. 5. Calculated activities by several theories for benzene(1)-polyisobutylene(2) system at 298.15 K.

model [Okada and Nose, 1981a, b]) for the comparison. In Fig. 5, the calculated activities of benzene in polyisobutylene with λ_{12} =.0321 is compared with experiment [Eichinger and Flory, 1968] and other models. As discussed in part I of the present article, the present EOS is the most recent and rigorous one and at the same time less adaptable for empirical fitting to experiment. Moreover, most of the other models contain more parameters except the Sanchez-Lacombe which use temperature independent pure
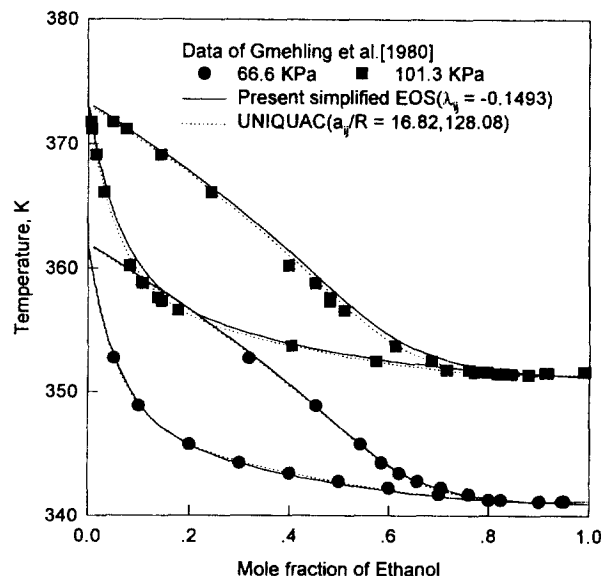
Fig. 6. Calculated T-x equilibria by the simplified EOS for ethanol(1)-water(2) system at 66.6 and 101.3 KPa.

molecular parameters. Thus one would expect that the fitted results by the Sanchez-Lacombe would be worse than others. As one can see in Fig. 5, the Flory's model with 3-pure and 2-mixing parameters is the best one than others, however, we believe that the present EOS is reasonably comparable with others despite the most rigorous nature of the present model. We omit further discussion here. Instead, we recommend to further interested readers an article presented elsewhere by the present authors [Yoo et al., 1994].

2. Simplified EOS Case

2-1. Low Vapor Pressure VLE

For 32 arbitrarily chosen binary VLE systems, the λ_{ij} and fitted errors are summarized in references 9 and 10. All experimental data are from the DECHEMA Chemical Data Series [Gmehling et al., 1980]. For each type of systems as defined by DIPPR [Gess et al., 1991]. The VLE systems tested here are classified as Nonpolar(NP)/NP, NP/Weak Polar(WP), NP/Strong polar(SP), WP/WP and WP/SP nonpolar(NP) and they are fitted by the present simplified EOS. As an example, calculated T-{x}-{y} of ethanol(1)-water(2) mixture with λ_{12}=-0.149 is shown in Fig. 6 at 66.6 and 101.3 kPa. While the UNIQUAC [Abrams and Prausnitz, 1975] uses two mixing parameters, the simplified EOS requires only one λ_{12} when the pure parameters, ε_{ii} and V_i^* are available as presented in part I. We omit further graphical illustration to save pages, however, the simplified EOS fits surprisingly well the experiments with single temperature independent λ_{ij}'s regardless of the different complexities of the candidate mixtures.

2-2. High Pressure VLE

High pressure VLE and bubble point P-T calculations require an initial estimate of pressure for the conditions above the critical point since in this region an additional flash calculation is necessary. Other procedures are basically identical to the case of low pressure VLE. For 23 randomly chosen systems [3 supercritical solvents (CO_2, ethane, and ethylene) and 23 solutes such as alkanes, alkenes, aromatics and alcohols], high pressure VLE computations are carried out and their λ_{ij} with fitting errors are summarized in references 9 and 10. In all correlations, we used single
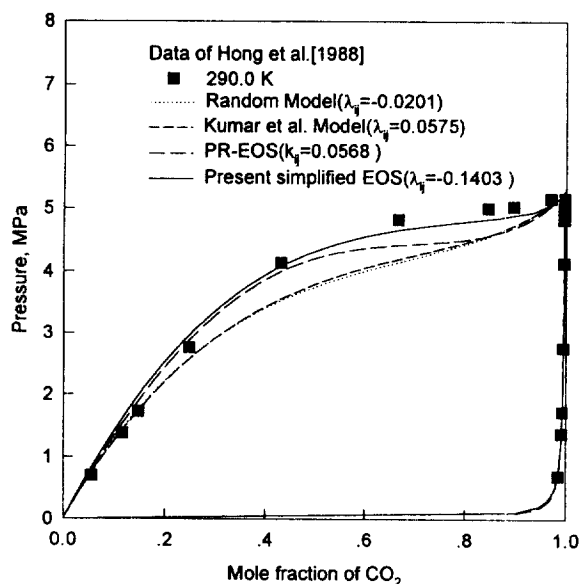
Fig. 7. Isothermal P-x-y equilibria by several models for $CO_2(1)$-methanol(2) system at 290.0 K.
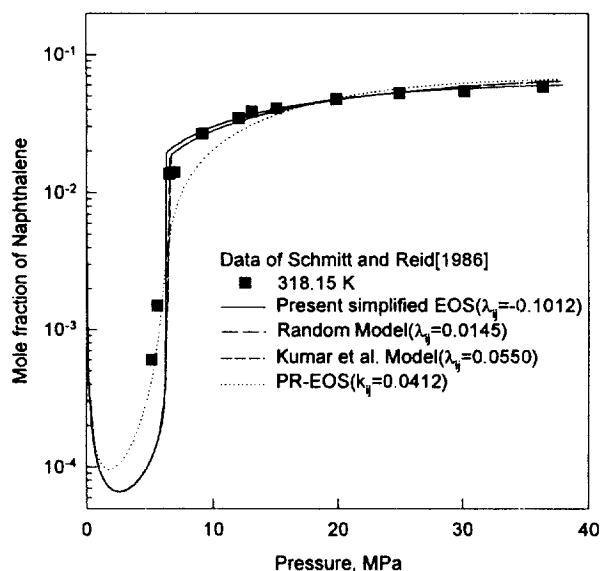

Fig. 8. Isothermal supercritical P-y equilibria for naphthalene(1)-ethane(2) system at 318.15 K.

Fig. 9. Calculated ternary supercritical P-y equilibria by the simplified EOS for phenanthrene-pentane(1)-CO_2(2) system at 318.15 K.

Table 2. Binary interaction energy parameters between solvents and polymers for the simplified EOS

System	T range [K]	λ_{ij}	AAD [%]	Reference
Polyisobutylene				
-Benzene	283.15-353.15	−.0322	3.47	46, 32
-Butane	298.15-319.65	−.0330	1.80	32
-Cyclohexane	298.15-338.15	−.0146	1.71	46, 32
-Isobutane	298.15-319.65	−.0346	1.81	47
-Neopentane	298.15-319.65	−.0339	1.57	47
-Pentane	298.15-308.15	−.0245	4.42	47
Polystyrene				
-Acetone	298.15-323.15	−.0467	4.88	37
-Benzene	288.15-333.15	−.0151	8.65	47
-Cyclohexane	303.15-338.15	−.0260	0.49	46, 49
-Chloroform	298.15-323.15	−.0086	3.55	37
-Ethylbenzene	283.15-303.15	−.0126	0.08	50
-2 Butanone	298.15-343.15	−.0315	2.77	51, 52
-Propylacetate	298.15-343.15	−.0216	1.28	37
-Toluene	298.15-353.15	−.0011	1.15	46, 49, 52
Polyvinylacetate				
-Acetone	303.15	−.0191	5.08	39
-Benzene	303.15	−.0136	5.72	53
-Vinylacetate	303.15	−.0081	3.34	53
Polypropylene oxide				
-Benzene	318.15-347.85	−.0035	1.01	38, 39
-Chloroform	278.68	.1069	15.58	54
-Carbontetrachloride	278.68	.0028	0.70	54

temperature independent, λ_{ij} for each system. We found that the simplified EOS again correlates data extremely well to such high pressure systems where existing γ-models (i.e., UNIQUAC) frequently fail without adopting so-called 'g^E-EOS mixing rules' as discussed in part I. As a graphical illustration, calculated CO_2(1)-methanol(2) P-{y} results with λ_{12}= −0.1403 are compared with experimental data [Hong and Kobayashi, 1988] at 290.0 K in Fig. 7. We conclude that the calculated results by the simplified EOS are better than those by other EOSs (P-R EOS [Peng and Robinson, 1976], Kumar et al. [1987], random EOS [Okada and Nose, 1981a, b]. Although we do not claim yet the generality of our conclusions, the practical usefulness of the simplified EOS is evident upon the authors' judgement.
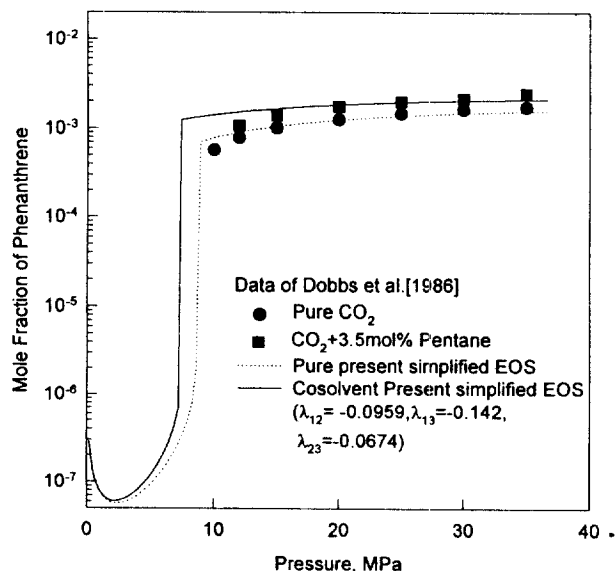
2-3. Solid-Vapor Equilibria

In references 9 and 10, the fitted λ_{ij} and their respective errors are summarized for 15 candidate SVE mixtures. As discussed in part I , in the previous section and elsewhere by the present authors [You et al., 1993, 1994c], a caution must be placed on the calculation of vapor pressure and densities at subcooled state for pure solutes before mixing [i.e., Eq. (41)-(43)].

In general, PR-EOS fits experiment better than the present EOS. It probably due to the better agreement of the PR-EOS
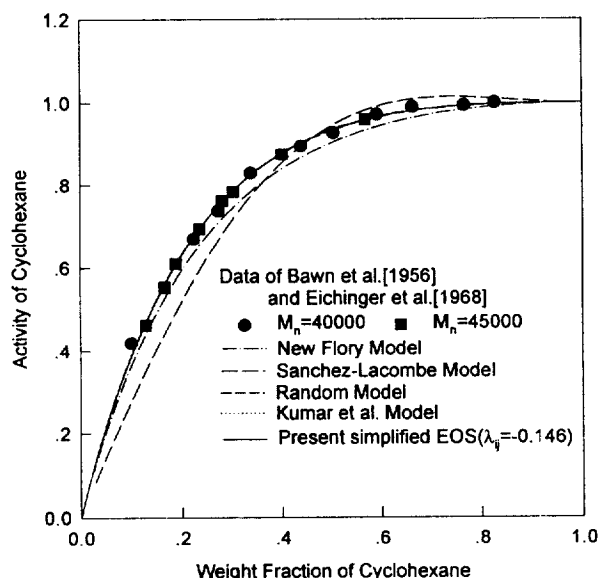
Fig. 10. Calculated activities of solvents by the simplified EOS (λ_{12} = -0.146) and by others for cyclohexane(1)-polyisobutylene (2) system at 298.15 K.
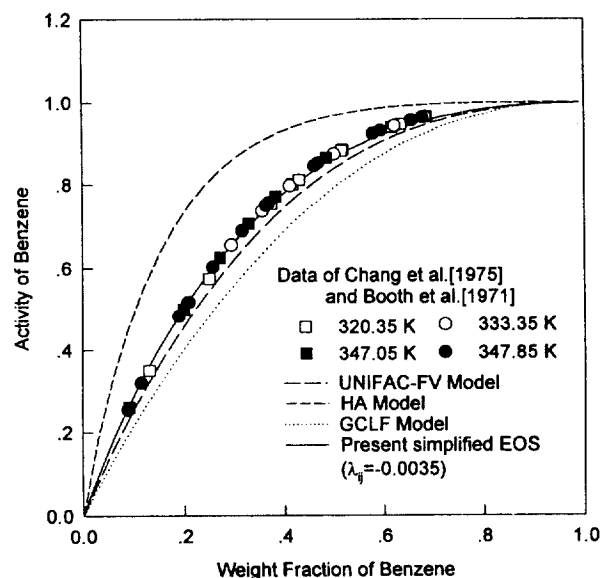

Fig. 11. Activities of solvent by the simplified EOS (λ_{12} = -0.0035) and by group contribution models for benzene(1)-polypropylene oxide(2) system.

in the near critical region than ours as shown in Fig. 8. However, at very high pressure, the results by the simplified EOS are quantitatively comparable or sometimes better than the PR-EOS and the other EOSs in the same genre. Also, as shown in Fig. 9, experimental data on the effect of cosolvent penthane (3.5 mol %) to the supercritical solubility of phenanthrene(1) in CO_2(2) [Hong and Kobayashi, 1988] are fitted by the simplified EOS and we found that the present model correlate quantitatively well even the ternary systems. Again we omit further graphical demonstrations here.

2-4. VLE of Polymer Solutions

For 20 arbitrarily chosen organic solvent-common polymer solute systems, regressed λ_{ij} with fitting errors are summarized in reference 10 and in Table 2. For every tested systems, the densities of coexisting phases are calculated by pure state simplified EOS [Eq. (31)]. Except for the system of polypropylene oxide(1)-chloroform(2), the absolute average errors are within 5% for all the systems.

As an example, the calculated solubilities of cyclohexane(1) in polyisobutylene(2) solution at 298.15 K [Eichinger and Flory, 1968; Bawn and Wajid, 1956] are shown in Fig. 10. When compared with the values calculated by other models in the same genre [Flory, 1970; Kumar et al., 1987; Panayiotou and Vera, 1982; Okada and Nose, 1982a, b; Sanchez and Lacombe, 1978] and by the PR-EOS [Peng and Robinson, 1976], the simplified EOS can be a practical tool for phase equilibrium calculations of macromolecular solutions. Finally, to speculate a possibility of extending the simplified EOS as a group contribution form in the future, we presented a comparison of results by the simplified EOS with existing group contribution methods in Fig. 11 for experimental benzene-polypropylene solution data [Chang and Bonner, 1975; Booth and Devoy, 1971]. The group contribution models compared here are the UNIFAC-FV [Oishi and Prausnitz, 1978], Flory-HA [Holten-Anderson et al., 1987], and GCLF [High and Danner, 1990]. Since there exists a polarity difference, the results by the group contribution methods are not so satisfactory
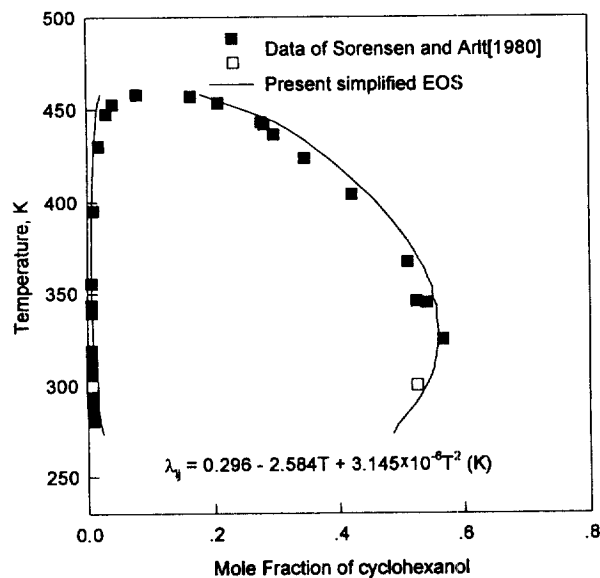
Fig. 12. Calculated LLE for cyclohexane(1)-water(2) solution by the simplified EOS.

but the simplified EOS is seen to be quite quantitative. The extension work of the simplified EOS as a group contribution EOS is now in progress by the present authors and it will appear in this journal soon.

2-5. Liquid-Liquid Equilibria

As discussed previously in this article and in part I, the EOS method uses a single homogeneous model for all fluid phase equilibrium calculations and is equally applicable to pure components and mixture properties. However, almost all of existing EOSs are frequently inferior to solution models and sometimes inapplicable to LLE calculations. The reason is obviously the difficulty of modeling properties at condensed state by the volumetric EOSs. Thus, application of the simplified EOS to LLE calculation is clearly

a crucial test for the usefulness of the present model. It is, also, a situation that most of other EOSs in the same genre [Kumar et al., 1987; Panayiotou and Vera, 1982; Okada and Nose, 1982a, b; Sanchez and Lacombe, 1978] were not yet tried exclusively on the LLE problem.

Currently, we are placing our efforts on the extension of the simplified EOS with temperature-dependent binary energy parameters to the LLE of complex mixtures. Here we present some limited results obtained to date. To correlate LLE, we first make λ_{ij}, as a simple function of temperature based on authors' empiricism as,

$$\lambda_{ij} = \lambda_{ij}^{(0)} + \lambda_{ij}^{(1)}T + \lambda_{ij}^{(2)}T^2 \tag{49}$$

One of illustrations of LLE for cyclohexanol(1)-water(2) solution(2) [Sorenson and Arlt, 1980] and in Fig. 12. We intendedly illustrate in the figure for one of the systems could fit relatively well to date with Eq. (49), however as expected, we are experiencing some uncertain errors for other systems. We feel a need of further refinement and accordingly such work is in progress by the present authors.

CONCLUSION

We discussed very briefly in part II the results obtained to date for modeling various phase equilibria of complex mixtures utilizing the new EOSs recently formulated by the present authors. We found that both the rigorous EOS and the simplified EOS correlate various phase equilibria properties of mixtures surprisingly well. Further refinements such as application to LLE and the group contribution application are in progress by the present authors' laboratories.

We sincerely welcome any criticism and encouragement by the interested readers. The necessary computer programs for phase equilibrium calculations with the EOSs can be obtained from the authors upon request.

ACKNOWLEDGEMENT

NOMENCLATURE

A^c : configurational Helmholtz free energy
$A^{c(R)}$: random contribution to A^c
$A^{c(IS)}$: 'ideal solution' contribution to A^c
$A^{c(E)}$: 'excess' contribution to A^c
N_a : Avogadro's number
N_i : number of molecular species i
N_{ij} : number of i-j segment contacts for the nonrandom distribution
N_0 : number of vacant sites or holes
N_r : defined by $N_r = N_0 + \Sigma N_i r_i$
N_q : defined by $N_q = N_0 + \Sigma N_i q_i$
P : pressure [bar]
q_i : surface area parameter
q_M : mole fraction average of q_i
r_i : segment number
r_M : mole fraction average of r_i
R : universal gas constant [J mol^{-1}K^{-1}]

T : temperature [K]
U^c : configurational internal energy
V : molar volume [cm^{3}mol^{-1}]
V_i^* : characteristic volume of component i [cm^{3}mol^{-1}]
V_H : volume of a unit cell [cm^3]
x_i : (liquid) mole fraction of component i
y_i : vapor mole fraction of component i
z : lattice coordination number

Greek Letters

β : reciprocal temperature [1/kT]
τ_{ij} : nonrandomness factor defined by Eq. (26)
ε_{ij} : interaction energy for i-j segment contacts (J)
ϕ_i : fugacity coefficient for component i
ρ : total segment fraction
ρ_i : segment fraction of component i
μ_i : chemical potential for component i
λ_{ij} : binary interaction parameter for i-j contacts
θ : total surface area fraction
θ_i : surface area fraction of component i
$\overline{\theta}_i$: surface area fraction of component i on the hole free basis

Superscripts

L : liquid phase
sat : saturation state
S : solid phase
V : vapor phase
$'$: derivative with respect to ln T

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