A Simple Two-Liquid Approximation of Lattice Theory for Modeling Thermodynamic Properties of Complex Fluids

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Abstract

A simple equation of state(EOS) applicable to complex fluids was formulated based on the nonrandom two-liquid approximation of the lattice-hole theory. The EOS requires two molecular parameters representing molecular size and interaction energy for a pure fluid, and one additional interaction parameter for a binary mixture. The model quantitatively describes configurational properties of pure fluids and phase equilibria behaviors of mixtures. It gives a good phase equilibria description even to liquid-liquid equilibria of systems containing simple, complex or macromolecular species. To our knowledge, no other approximate molecular theory originating from the classical lattice theories has been presented which describes the entire range of configurational properties of fluids from a practical point of view, although the formulation EOS was based on a phenomenological argument in a sense.

Key words: Statistical mechanics, lattice-hole theory, two-liquid theory, equation of state, configurational properties, phase equilibria

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1. Introduction

The two-liquid theory provides a useful point of departure for deriving semi-empirical equations to represent thermodynamic excess functions for highly nonideal

mixtures[1]. The two-liquid approximation of the rigid lattice description of fluids[2] has been widely utilized to formulate various excess Gibbs free energy expressions such as NRTL[3] and UNIQUAC[4]. Although, these excess function models cannot be applied to the configurational properties of pure fluids, they can be applied to a limited extent to liquid mixtures at low pressure.

To overcome this limitation and to formulate an equation of state(EOS) rather than an excess function model, one can imbed vacant sites(holes) to the rigid lattice description of fluid systems, and the underlying concept of the two-liquid approximation can be applied.

The present authors recently attempted to introduce the two-liquid approximation to the nonrandom lattice-hole theory to obtain an elementary EOS[5]. However, they applied to a limited extent, the two-liquid approximation only to the mixed state of the nonrandom lattice description of fluids. This article is an obvious extention of the previous work with a general two-liquid approximation of the nonrandom lattice-hole theory from pure state to mixed state of fluid systems[6]. We present here the application of the new EOS to both the configurational properties of pure fluids over a wide range of pressures and temperatures, and vapor-liquid, vapor-solid and liquid-liquid equilibria of various mixed systems of complex fluids.

2. Helmholtz Free Energy and Other Thermodynamic Functions

As we presented elsewhere [6], the configurational Helmholtz free energy for a general mixture, including pure fluids, is written as

$$\beta A^c = \sum_{i=1}^{c} N_i \ln \rho_i + N_0 \ln(1-\rho) - \frac{z}{2} N_q$$

$$\times \ln\left[1+\left(\frac{q_M}{r_M}-1\right)\rho\right]-\left(\frac{zN_q}{2}\right)\sum_{i=1}^{c}\theta_i\left[\ln\left(\sum_{j=0}^{c}\theta_j\tau_{ji}\right)+\beta\varepsilon_{ii}\right] \tag{1}$$

where, $q_M=\Sigma x_i q_i$, $r_M=\Sigma x_i r_i$, $\rho_i=N_i r_i/N_r$, $\rho=\Sigma\rho_i$ and x_i 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 $V=V_H\left(N_0+\Sigma_i N_i r_i\right)$, the EOS is obtained by

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

The chemical potential of component i, μ_i is

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

$$+\frac{zq_i\theta}{2}\left\{1-\frac{r_i}{q_i}-\frac{1}{\theta}\left[\ln\sum_{k=0}^{c}\theta_k\tau_{ki}+\beta\varepsilon_{ii}+\sum_{l=1}^{c}\frac{\theta_l\left(\tau_{il}-\tau_{0l}\left(r_i/q_i\right)\right)}{\Sigma_{k=0}^{c}\theta_k\tau_{kl}}\right]\right\} \tag{3}$$

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

3. Determination of Molecular Parameters

By setting the coordination number(z) at 10 and the unit lattice cell volume(V_H) at 9.75 cm^3mol^{-1}, there are two molecular parameters in the EOS for pure fluids, namely V_1^* and ε_{11}, to be determined. However, these parameters are intrinsically temperature dependent. Thus, whenever the necessary, and experimental information is available, the regressed parameters at each isotherm can be fitted by an empirical function of

temperature for convenient use in engineering practice. In this work, the formulas proposed by Kehiaian[7] were employed. The two formulas are;

$$\epsilon_{11} / k = E_a + E_b\left(T - T_0\right) + E_c\left(T \ln \frac{T}{T_0} + T - T_0\right), \text{ and} \tag{4}$$

$$V_1^* = V_a + V_b\left(T - T_0\right) + V_c\left(T \ln \frac{T}{T_0} + T - T_0\right); \tag{5}$$

where the reference temperature, T_0 is 273.15 K.

Estimated values of coefficients in Eqs. (4) and (5), calculated from data sources[8] are summarized in Table 1 for hydrocarbons, and in Table 2 for common polymer systems.

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

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

The best fitted λ_{12} for some systems are shown in the Figs. 1~6 in the next section.

4. Phase Equilibria Calculations

Pure PVT Properties. Although omitted lengthy discussion here due to limited space, the EOS can predict configurational properties such as sub- and super-critical PVT behaviors of pure hydrocarbons quantitatively well. A comparison of experimental[9] and calculated specific volumes of polystyrene, as functions of temperature and pressure are illustrated in Fig. 1. For the entire range of the T-P plane, the present model correlates the data quantitatively well.

Phase Equilibria of Mixtures. Calculation of various types of (multi)phase

equilibria(i.e., VLE, LLE, VSE and critical locus, etc.) utilizing a relatively complex model require special care. However, this matter is discussed in further detail elsewhere[6]. Instead, we briefly present here some calculated results of phase equilibria of mixtures using the present EOS.

A comparison of calculated and experimental[10] high pressure P-x-y equilibria for the decane/CO_2 system at 377.59, 410.93 and 442.26 K are shown in Fig. 2. By a single value of l_{12} = 0.1259, the EOS was shown to fit the data quantitatively well. In Fig. 3, the calculated results of a P-x equilibria of the nonadecane/CO_2 system with l_{12} = 0.1513 at 313.15 and 433.15 K, were compared with experimental values[11]. For high carbon number systems with gaseous compounds, the EOS correlated quantitatively well.

To evaluate the prediction capability of the model for critical phase equilibria behavior of binary systems, a comparison of experimental[12] and calculated P-T loci for the decane/CO_2 system was conducted, and is shown in Fig. 4. By the same value of l_{12} = 0.1259 used in the subcritical VLE of this system(Fig. 1), the present EOS correlated the type I of near critical phase diagram[13] relatively well. Furthermore, the calculated results of vapor pressures of pure components, UCEP, SVE, SLVE and critical P-T loci of the naphthalene/CO_2 system(l_{12} = 0.0753) were compared with experimental values[14], and are illustrated in Fig. 5. For the entire range of P-T plane, the EOS predicts correctly these critical mixture critical phenomena.

As a final illustration, calculated weight-fraction activities of cyclohexane in a cyclohexane/polystyrene system at 298.15 K were shown with experimental values[15, 16]. Over the entire range of weight fractions of cyclohexane, the EOS predicted accurately the sorption equilibria of the polymer solutions. Although not illustrated this

here, the EOS fit quantitatively well the activities of solvents in other polymer systems which were made from systems listed in Table 2. Based on preliminary experience, the temperature dependence of EOS parameters, V_1^* and ε_{11} are insignificant for polymers. Thus in the case of polymers, we used a temperature-independent V_1^* as shown in Table 2.

5. Conclusion

The EOS presented here is a further elaborated version of a previous article the authors published in FPE [5]. In the previous model, we introduced the concept of nonrandom two-liquid approximation to the lattice-hole theory from binary systems, with an assumption of hole-free basis. However, in this work, we have eliminated the assumption of hole-free basis and further applied the two-liquid approximation from pure fluids to mixtures. Thus, in a single expression in general mixtures including pure fluids, the present EOS can be applied to phase equilibrium calculations. Results obtained to date demonstrate that the present EOS can be quantitatively applied to the configurational properties of pure fluids and various (multi)phase equilibrium problems of complex mixtures whose molecules differ greatly in size.

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Table 1. Coefficients of energy and volume parameters for some pure substances†

	Ea	Eb	Ec	Va	Vb	Vc
Ethane	75.30597	-0.00782	-0.10958	50.00875	0.00851	0.02579
Butane	90.14383	0.00191	-0.05541	79.00241	0.00213	0.03805
Pentane	93.98580	0.00956	-0.04549	93.68969	0.00072	0.03863
1-Hexene	97.03353	0.02559	0.00999	103.88880	-0.00908	-0.00321
Cyclohexane	108.34441	0.01904	-0.01258	93.51527	-0.00549	0.00465
Hexane	96.84253	0.01474	-0.03550	108.00225	-0.00166	0.03810
Heptane	98.55286	0.02003	-0.02929	123.21581	-0.00436	0.04477
Octane	100.19321	0.02377	-0.02461	137.49850	-0.00564	0.04830
Nonane	100.40065	0.04356	0.01821	152.59733	-0.01640	0.02908
Decane	101.40404	0.02477	-0.03543	151.85464	-0.00270	0.06698
Nonadecane	105.03467	0.04300	-0.01428	297.84004	-0.00797	0.10198
Eisosane	106.34487	0.03995	-0.01365	310.35896	0.02765	0.17023
Methanol	193.87737	-0.35382	-0.27502	37.79108	0.02889	-0.00421
Ethanol	163.58386	-0.27274	-0.28516	53.04182	0.03362	0.02603
Butanol	141.53014	-0.17221	-0.26086	82.55258	0.02879	0.06712
Carbon dioxide	85.91302	-0.10298	-0.36562	34.28608	0.01428	-0.01304
Water	411.30305	-0.68966	-0.31798	17.79060	0.00152	-0.02890
Naphthalene	133.60559	0.05528	0.03019	114.96641	-0.03665	-0.07748

† For most systems, the values of coefficients are reliable in the temperature range of 253-513K

Table 2. Coefficients of energy and volume parameters for several common polymers†

Polymer	E_a K	E_b -	E_c	V_1^* cm^3/g
Polyisobutylene	129.80899	.09884	0.	1.00534
Poly(methyl methacrylate)	186.54804	-.26584	0.	.78493
Poly(n buthyl methacrylate)	130.38981	.05275	0.	.87539
Polyethylene(branched)	125.90716	.07050	0.	1.09120
Polyethylene(HMW,linear)	126.19111	.07192	0.	1.10371
Polyethylene(linear)	128.03908	.05796	0.	1.08934
Polystyrene	153.98175	-.01782	0.	.87741
Poly(vinyl acetate)	132.63399	.08225	0.	.78125
poly(dimethyl siloxane)	99.67046	.07505	0.	.89121

† V_1^* represents the temperature independent specific volumes

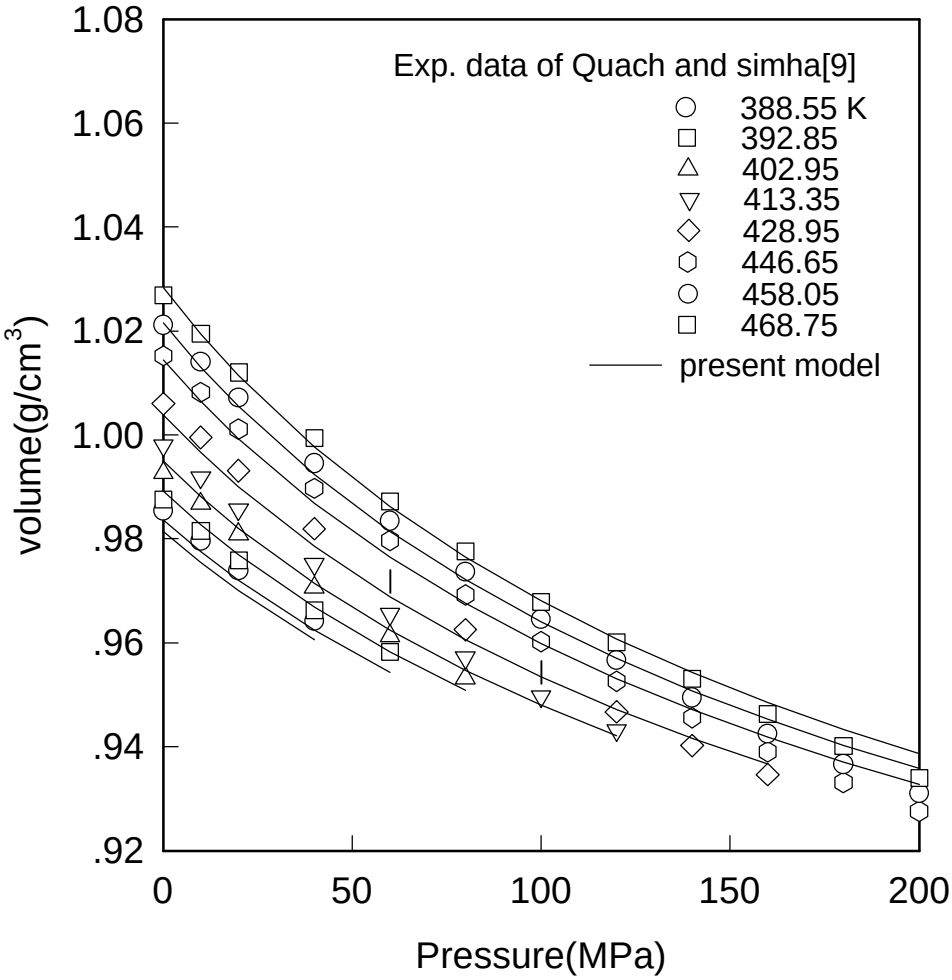

Fig. 1. Calculated specific volumes of poly(styrene, PS)

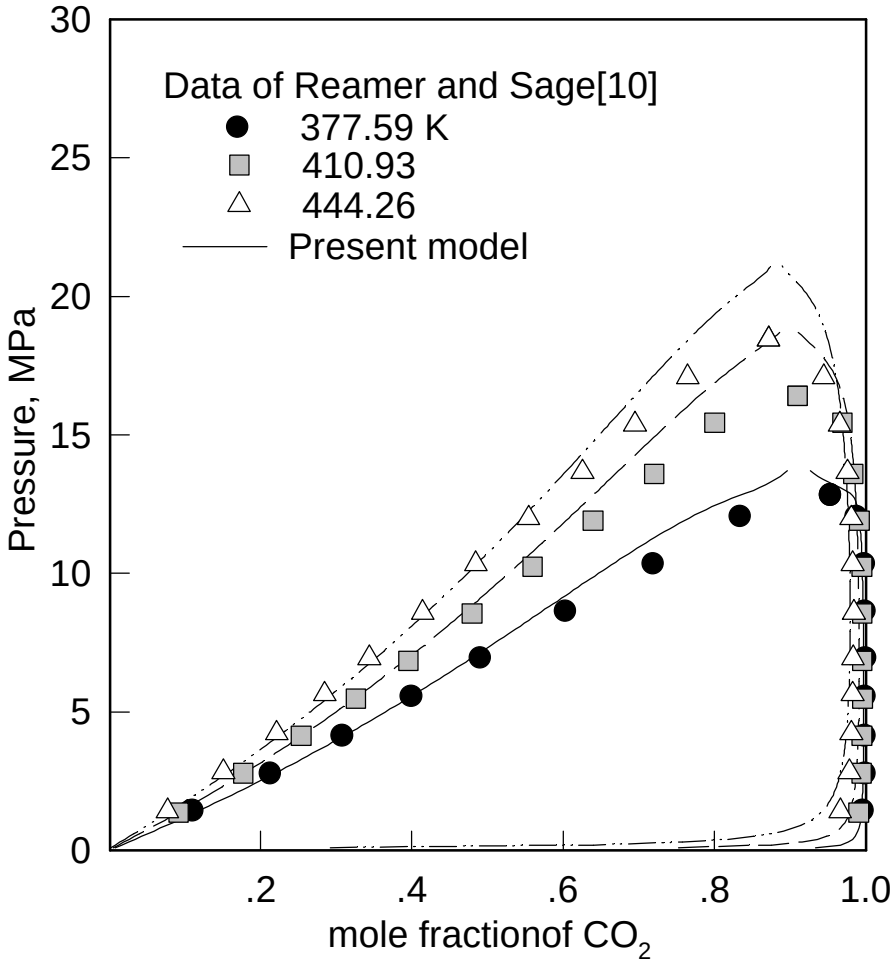

Fig. 2. Calculated high pressure P-x data for the CO_2/decane system with

λ_{12} = 0.12595 for all the isotherms

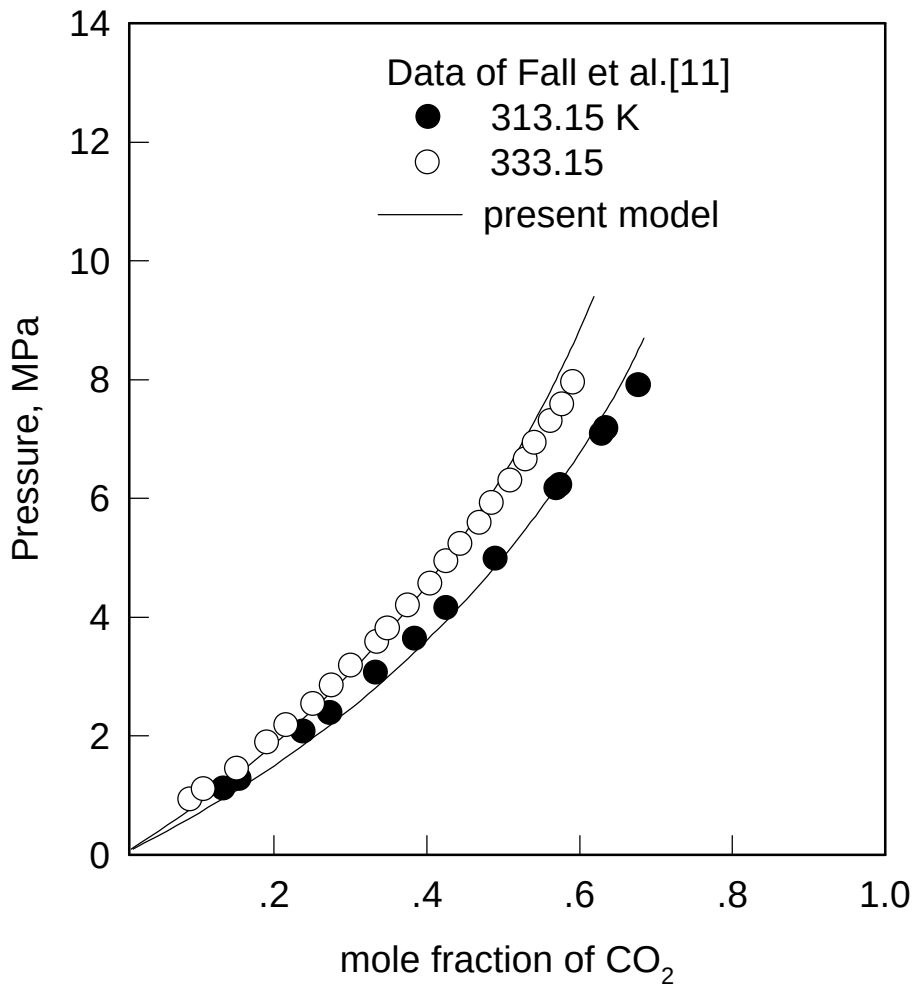

Fig. 3. Calculated P-x data for the CO_2/nonadecane system at two isotherms

(λ_{12} = 0.15134)

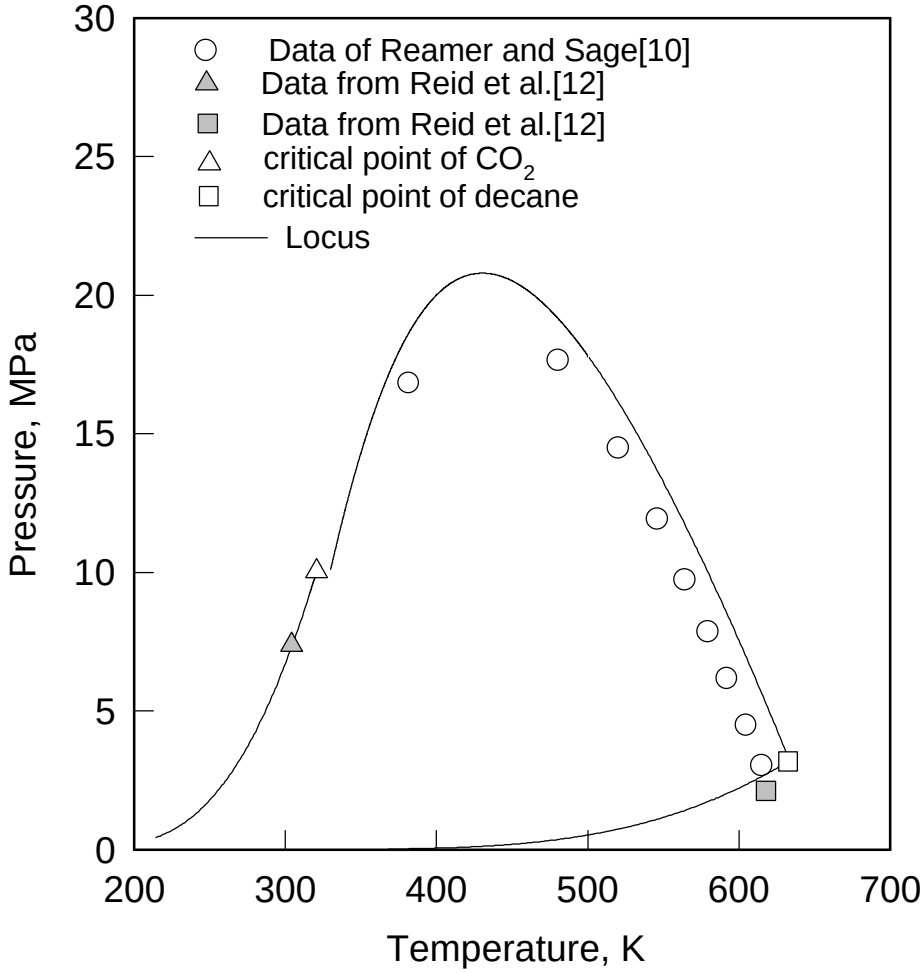

Fig. 4. Calculated critical P-T locus for CO_2/decane system(λ_{12} =.12595).

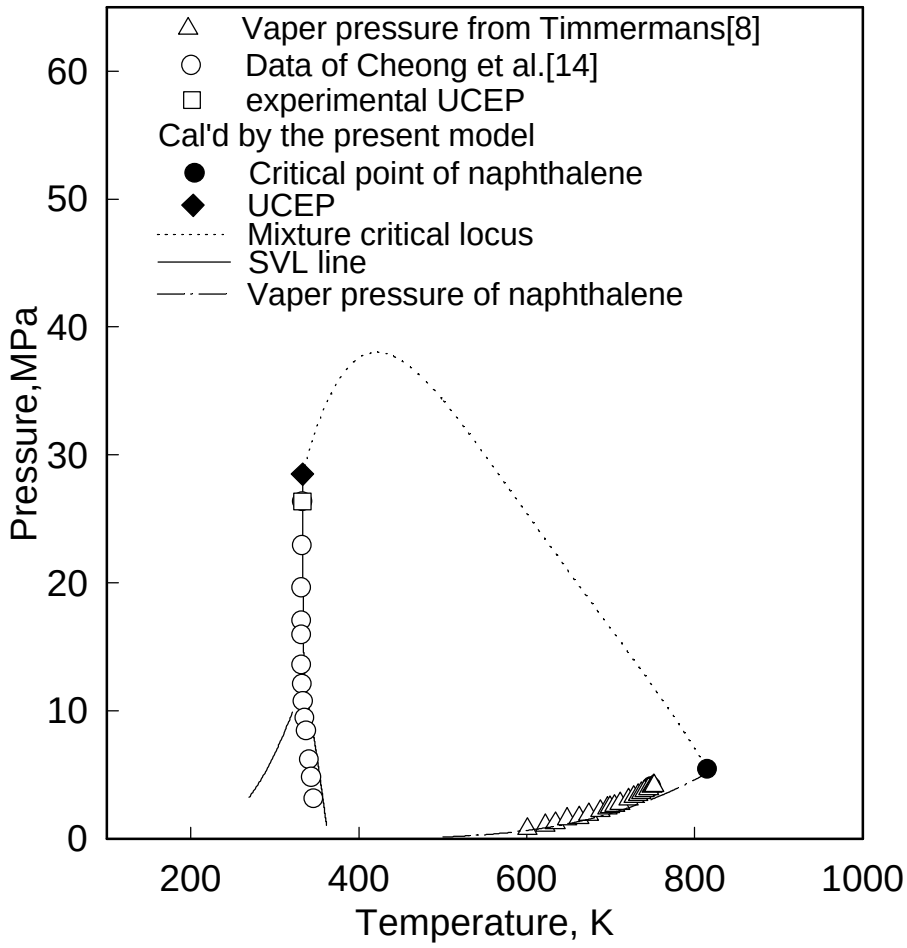

Fig. 5. Calculated SLV equilibria and critical P-T locus of CO_2/naphthalene system

(λ_{12} = 0.07534 is used which was obtained from SVE calculation).

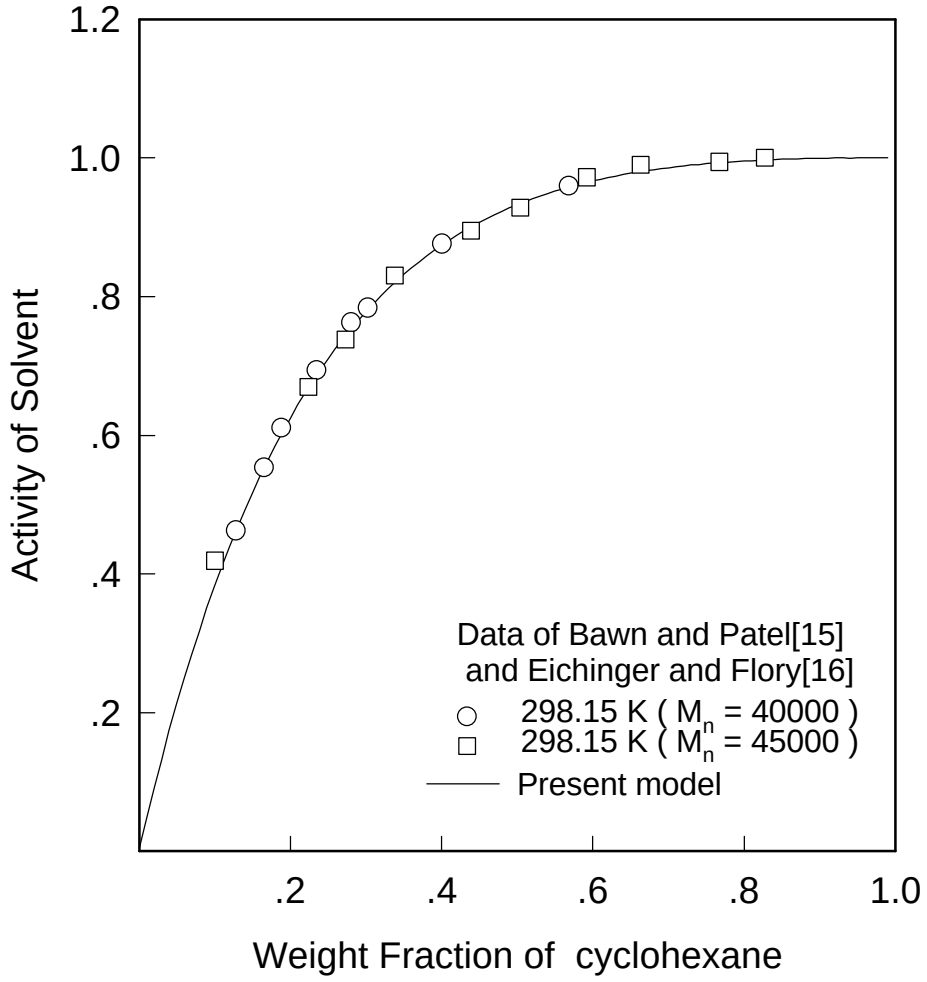

Fig. 6. Calculated activities of cyclohexane in cyclohexane/poly(isobutylene) system at 298.15 K