ELSEVIER

Fluid Phase Equilibria 129 (1997) 21–35

FLUID PHASE EQUILIBRIA

VLE calculations by applying a modified perturbed hard sphere EOS

Min-Lon Yu, Yan-Ping Chen *

Department of Chemical Engineering, National Taiwan University, Taipei, Taiwan.

Received 22 November 1995; accepted 22 August 1996

Abstract

An equation of state (EOS), developed by using an improved expression of the coordination number model of square-well fluids, was applied in vapor–liquid equilibrium (VLE) calculations of real fluids and their mixtures. The EOS was written in a perturbed hard sphere form which had three parameters for each pure fluid. In this work, the EOS parameters for pure nonpolar and polar fluids were determined. It is demonstrated that the pure fluid properties were satisfactorily correlated and the EOS parameters showed reasonable physical significance. In the VLE calculations of fluid mixtures, the results were again satisfactory and were superior to those from commonly used cubic-type EOS. It is indicated that this modified perturbed hard sphere (MPHS) EOS yielded significantly better VLE calculation results on asymmetric systems of nonpolar + polar binary mixtures. The scattering of the binary interaction parameters of this MPHS-EOS was less than that from other EOSs. Ternary calculations by directly applying the binary parameters were also successful. © 1997 Elsevier Science B.V.

Keywords: Theory; Equation of state; Vapor–liquid equilibria; Mixture

1. Introduction

The square-well (SW) potential function has been widely used in developing equations of state (EOS) from statistical thermodynamics. This potential function is simple and reasonable to model the real fluid behavior and many computer simulation data are available in applying this potential function. Thermodynamic properties of SW fluids are dependent on the molecular interactions, the well depth, and the microscopic structure which is usually expressed by the coordination number model. By incorporating the coordination number model and the generalized van der Waals partition function (Sandler, 1985), a theoretically-based EOS can then be developed. Lee et al. (1985, Lee et al., 1986, Lee and Sandler, 1987, Lee et al., 1989) have proposed a coordination number model and

---

* Corresponding author.

0378-3812/97/$17.00 © 1997 Elsevier Science B.V. All rights reserved.

PII S0378-3812(96)03176-7

the corresponding EOS in their respective works. Lee and Chao (1987) and Guo et al. (1990a,Guo et al., 1990b) have also presented their coordination number models and Guo et al. (1990b) have derived their EOS. Some of these EOS cannot be employed in fluid mixture calculations owing to the complexity of the coordination number models and this has limited their applications in engineering computations.

A new coordination number model for SW fluids was proposed in our previous study (Yu and Chen, 1995). This new coordination number model, which included a density-dependent correction term to the low density expression, satisfied the low density and the close-packed limiting requirements, and agreed well with the molecular simulation results at intermediate densities. This new model has been tested with the molecular simulation data on both pure and mixture SW fluids, and better results have been obtained in comparison with those from other coordination number models. A new EOS, written in a modified perturbed hard sphere (MPHS) form, was developed from our coordination number model. In our previous work, the MPHS-EOS showed good results for the compressibility factor calculations of SW fluids and their mixtures. This EOS was also used for real *n*-paraffins as a preliminary study in our previous work and satisfactory correlations on vapor pressures and liquid densities were observed. In this study, we extended our calculations to other nonpolar and polar pure fluids and applied the MPHS-EOS for vapor–liquid equilibrium (VLE) calculations on binary and ternary mixtures. We compared the VLE calculation results from the MPHS-EOS with those from the commonly used cubic-type EOS of Peng and Robinson (1976) and Patel and Teja (1982) to test the applicability of the MPHS-EOS in phase equilibrium computations.

2. The MPHS equation of state and pure component parameters

A new coordination number model has been proposed in our previous work (Yu and Chen, 1995) where the coordination number at any density is written as a product of the low density limit expression and a correction term. The correction term was correlated in our previous work using molecular simulation data of SW fluids. For a mixture of unlike fluids i and j, the coordination number N_{ij} is written as

$$N_{ij}=\frac{4\pi}{3}(\lambda^3-1)x_i\rho\sigma_{ij}^3\exp\left(\frac{\epsilon_{ij}}{kT}\right)\left\{1+\left[1.45\exp\left(\frac{-\epsilon_{ij}}{kT}\right)-1\right]\left[1-\exp(1-\phi_{ij})\right]\right\} \tag{1}$$

where

$$\phi_{ij}=\frac{\sqrt{2}+\rho\sigma_{ij}^3}{\sqrt{2}-\rho\sigma_{ij}^3} \tag{2}$$

and the cross terms of the SW potential function parameters are

$$\sigma_{ij}=\frac{1}{2}(\sigma_{ii}+\sigma_{jj}) \tag{3}$$

$$\epsilon_{ij}=(\epsilon_{ii}\epsilon_{jj})^{0.5} \tag{4}$$

The coordination numbers of the SW fluids calculated from this model have been compared with those from the molecular simulation data and satisfactory agreements have been observed (Yu and Chen, 1995). Applying this coordination number model, an EOS was then derived using the generalized van der Waals theory and the canonical partition function (Sandler, 1985).

Using the Carnahan–Starling EOS (Carnahan and Starling, 1969) for the repulsive term, a modified perturbed hard sphere (MPHS) EOS was developed for a pure fluid (Yu and Chen, 1995)

$$Z=\frac{1+\zeta+\zeta^2-\zeta^3}{(1-\zeta)^3}-\frac{4.75}{3}\pi\rho\sigma^3\left[\frac{1.45\epsilon}{kT}-\exp(1-\phi)\left[\frac{1.45\epsilon}{kT}+1-\exp\left(\frac{\epsilon}{kT}\right)\right]\right.$$
$$\left.\times\left[\frac{2\sqrt{2}-\rho\sigma^3-\sqrt{2}\,\phi}{\sqrt{2}-\rho\sigma^3}\right]\right] \qquad (5)$$

where ζ $(=\pi\rho\sigma^3/6)$ and ϕ are two dimensionless functions of the reduced density. In the MPHS-EOS, ρ is the number density, and σ and ϵ/k are the molecular diameter and the interaction energy between molecules, respectively. A temperature-dependent function was introduced into the energy parameter for real fluid calculations and it is expressed as

$$\frac{\epsilon}{k}=\left(\frac{\epsilon}{k}\right)_0\left[1+m\left(1-T_r^{0.5}\right)\right]^2 \qquad (6)$$

where $(\epsilon/k)_0$ is the value of (ϵ/k) at the critical temperature and T_r is the reduced temperature. Parameter m characterizesd the temperature dependence of (ϵ/k). For each pure fluid, there are three parameters σ, $(\epsilon/k)_0$ and m in the MPHS-EOS. These parameters were evaluated by fitting the saturated properties of pure fluids. The following objective function was minimized in this work to obtain the optimal pure fluid parameters

$$Q=\Sigma\left[\left(\frac{P^{\mathrm{vp,cal}}-P^{\mathrm{vp,exp}}}{P^{\mathrm{vp,exp}}}\right)^2+\left(\frac{V^{\mathrm{L,cal}}-V^{\mathrm{L,exp}}}{V^{\mathrm{L,exp}}}\right)^2\right] \qquad (7)$$

where the summation is over all data points on the saturation curve. Table 1 lists the MPHS-EOS parameters for typical pure fluids. Table 1 also shows the deviations in vapor pressure and saturated liquid molar volume calculated by the MPHS-EOS on these typical pure fluids. Generally, this EOS gave satisfactory results. More data have been tested in this study where the grand absolute average deviations of 0.66% in vapor pressure and 1.60% in saturated liquid molar volume over 2199 data points were obtained. For nonpolar and weakly polar components, it was observed that the pure component parameters in the MPHS-EOS showed regular correlations with their characteristic properties. Fig. 1 presents a plot of $(\epsilon/k)_0$ against the critical temperatures for nonpolar and weakly polar pure fluids which exhibited a nearly linear relationship with a constant slope of 0.832. This value is in agreement with the theoretical values determined from other coordination number models or molecular dynamics simulation data (as shown by Guo et al., 1990b) showing that the slope is between 0.775 and 0.84 for a pure SW fluid. Fig. 2 shows a plot of the effective hard core volumes (equal to $\pi\sigma^3/6$) against the van der Waals volumes for nonpolar and weakly polar pure fluids, and this plot also has a linear relationship. The van der Waals volumes were determined from a group

Table 1
Pure component parameters of the MPHS-EOS

Component	No. of data pts.	Temp. range/K	$(\epsilon/\kappa)_0$	σ	m	AAD%		Data sources
						V^L	P	
Methane	44	91 ~ 187	152.68	3.49	−0.041	0.94	0.97	1
Butane	27	223 ~ 392	344.61	4.77	0.140	0.67	0.20	1
Octane	30	320 ~ 552	466.86	5.92	0.310	1.27	0.43	1
Hexadecane	41	422 ~ 594	608.88	7.49	0.548	1.77	0.19	2
2-Methylpentane	23	289 ~ 480	404.24	5.39	0.214	0.52	0.51	1
Cyclopropane	34	197 ~ 386	322.12	4.11	0.074	0.99	0.35	1
Ethene	36	136 ~ 277	226.75	3.82	0.042	0.93	0.57	1
1-Hexene	33	283 ~ 334	412.91	5.29	0.203	0.82	0.15	1
Ethanol	25	279 ~ 471	431.18	4.14	0.470	2.71	2.90	1
1-Propanol	23	305 ~ 492	436.91	4.53	0.542	1.46	0.81	1
1-Butanol	25	320 ~ 523	453.12	4.87	0.556	1.39	1.56	1
Benzene	42	284 ~ 550	455.39	4.78	0.158	1.23	0.36	1
Toluene	26	301 ~ 537	484.68	5.11	0.184	1.64	0.49	1
Carbon dioxide	37	217 ~ 297	244.94	3.42	0.186	0.83	0.29	3
Fluorine	18	95 ~ 140	114.61	3.05	0.033	0.90	0.49	3
Water	17	313 ~ 473	567.70	2.80	0.134	3.28	1.82	3
Hydrogen chloride	10	159 ~ 230	270.32	3.28	0.021	1.97	0.43	3
Acetone	27	275 ~ 471	426.57	4.48	0.190	1.87	0.79	1
Grand average						1.31	0.68	

$\mathrm{AAD\%} = \dfrac{100}{\mathrm{NP}} \Sigma_i \left(\dfrac{X^{\mathrm{cal}} - X^{\mathrm{exp}}}{X^{\mathrm{exp}}} \right)$; $X = V^V, V^L$, or P; NP = number of data points.

Experimental data sources: 1. Smith and Srivastava (1986); 2. Rossini et al. (1952); 3. Vargaftik (1975).

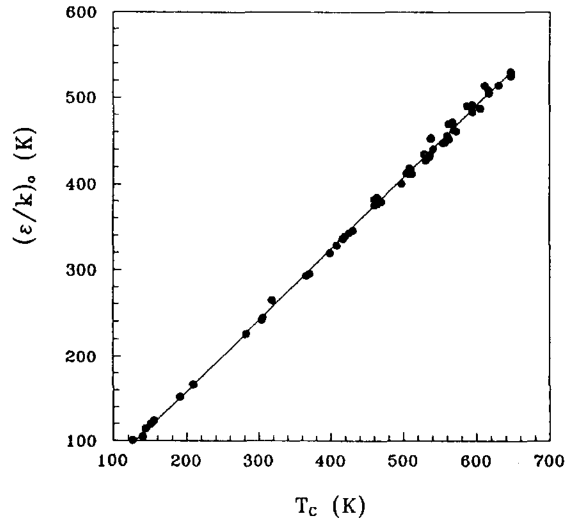

Fig. 1. Plot of $(\varepsilon/k)_0$ against the critical temperatures for nonpolar and weakly polar components including alkanes, cycloalkanes, alkenes, aromatics, alkanones, small molecules and halogenated alkanes.

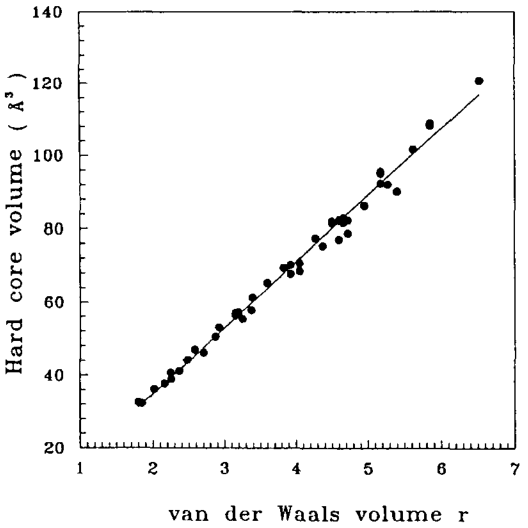

Fig. 2. Plot of the hard core volumes ($\pi\sigma^3/6$) against the Van der Waals volumes for nonpolar and weakly polar components including alkanes, cycloalkanes, alkenes, aromatics, alkanones and halogenated alkanes.

contribution method described by the UNIFAC model (Larsen et al., 1987). This indicated that σ has a good physical significance as a molecular diameter parameter. The parameter m, which was used to correct the temperature-dependence of (ϵ/k), also increased linearly with the acentric factors for nonpolar and weakly polar pure fluids, as shown in Fig. 3. From the above observations, generalized

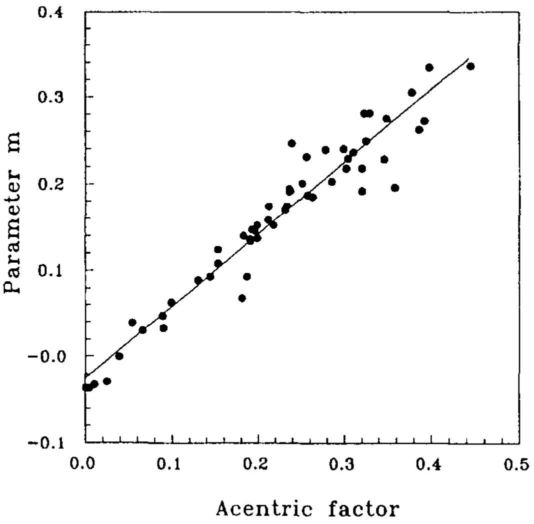

Fig. 3. Plot of parameter m against the acentric factors for nonpolar and weakly polar components including alkanes, cycloalkanes, alkenes, aromatics, alkanones, small molecules and halogenated alkanes.

correlations for pure component parameters of nonpolar and weakly polar fluids are proposed for the MPHS-EOS

$$\left(\frac{\epsilon}{k}\right)_0 = \frac{T_c}{1.25 - 0.07\omega} \tag{8}$$

$$\sigma = \left(\frac{6r}{0.055\pi}\right)^{1/3} \tag{9}$$

and

$$m = 0.9377\omega - 0.0477 \tag{10}$$

where T_c, ω and r are the critical temperature, acentric factor and van der Waals volume, respectively. For nonpolar and weakly polar components, these generalized correlations gave satisfactory results in correlating the pure fluid properties. These correlation equations are useful in further predictive phase equilibrium calculations.

3. Extension of the MPHS-EOS to fluid mixtures and VLE calculations

The MPHS-EOS was extended to fluid mixtures in this work and the mixture EOS was written as

$$Z = \frac{1+\zeta+\zeta^2-\zeta^3}{(1-\zeta)^3} - \frac{4.75}{3}\pi\sum_i\sum_j x_i x_j \rho_{ij}^* \times\left[\frac{1.45}{T_{ij}^*} - \exp(1-\phi_{ij})\left(\frac{1.45}{T_{ij}^*}+1-\Omega_{ij}\right)\left(\frac{2\sqrt{2}-\rho_{ij}^*-\sqrt{2}\,\phi_{ij}}{\sqrt{2}-\rho_{ij}^*}\right)\right] \tag{11}$$

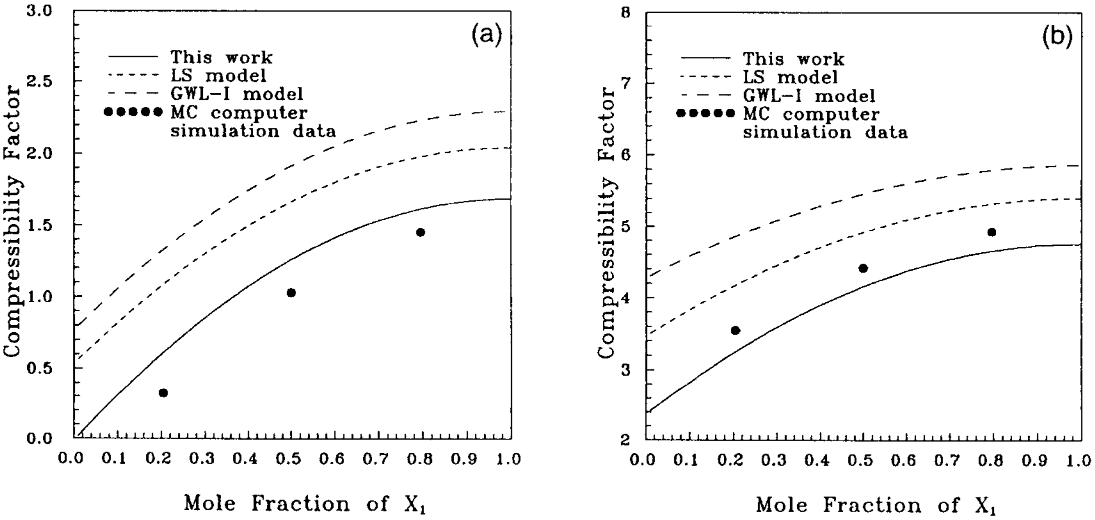

Fig. 4. Comparison of the calculated compressibility factors of SW fluid by various models (a) ($\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT = 1.0$, $\varepsilon_{12}/kT = 0.5$, $\rho\sigma^3 = 0.55$, $\sigma_{22}/\sigma_{11} = 1$) and (b) ($\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT = 1.0$, $\varepsilon_{12}/kT = 0.5$, $\rho\sigma^3 = 0.80$, $\sigma_{22}/\sigma_{11} = 1$). MC computer simulation data source: Lee and Chao, 1987.

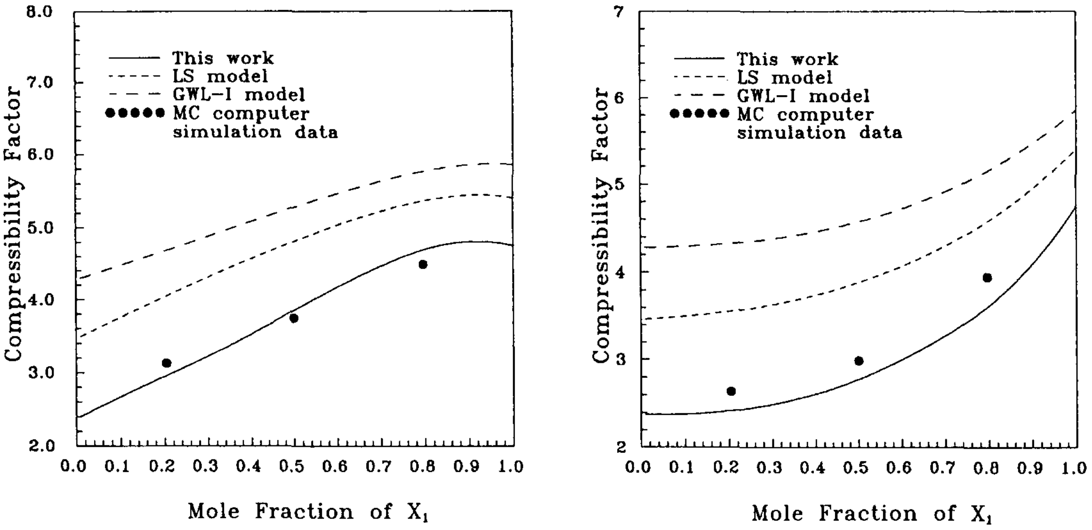

Fig. 5. Comparison of the calculated compressibility factors of SW fluid by various models (a) ($\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT = 1.0$, $\varepsilon_{12}/kT = 0.5$, $\rho\sigma^3 = 0.80$, $\sigma_{22}/\sigma_{11} = 1.50$) and (b) ($\varepsilon_{11}/kT = 0.5$, $\varepsilon_{22}/kT = 1.0$, $\varepsilon_{12}/kT = 1.0$, $\rho\sigma^3 = 0.80$, $\sigma_{22}/\sigma_{11} = 1.25$). MC computer simulation data source: Lee and Chao, 1987.

where $\rho_{ij}^* = \rho\sigma_{ij}^3$, $T_{ij}^* = (kT)/(\epsilon_{ij})$, $\Omega_{ij} = \exp((\epsilon_{ij})/(kT))$, $\zeta = (\pi\rho)/(6)\sum_i x_i\sigma_{ii}^3$ and $\phi_{ij} = (\sqrt{2} + \rho_{ij}^*)/(\sqrt{2} - \rho_{ij}^*)$. In contrast to the conventional cubic-type EOS, there was no need to introduce additional mixing rules in mixture property calculations. Using this EOS, we have calculated the compressibility factors for binary SW fluid mixtures and the results are presented in Figs. 4 and 5. In these figures, the calculated compressibility factors were plotted against the compositions for various reduced densities and potential energy parameters. We also compared the results from other methods: those determined from the coordination number models of Lee and Sandler, 1987 (LS model) and of Guo et al., 1990a, Guo et al., 1990b (GWL-1 model). It is demonstrated that our calculated results have better agreement with the molecular simulation data than those from the other two EOS models. Yu and Chen (1995) have shown more comparisions of the calculated coordination numbers and compressibility factors of SW fluid mixtures from this MPHS-EOS with the molecular simulation data and those from other EOS models. The MPHS-EOS showed good ability in calculating the properties of the SW fluids. The extension of our calculations to real fluid mixtures on nonpolar and polar systems is presented in this study. In the real fluid mixture calculations, the cross-interaction properties were defined as

$$\epsilon_{ij} = \sqrt{\epsilon_{ii}\epsilon_{jj}}\,(1 - k_{ij}) \tag{12}$$

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{13}$$

where k_{ij} is a binary interaction parameter and was determined using experimental data. In this work,

k_{ij} was treated as a temperature-independent constant for a specific binary system. The expression of the fugacity coefficient from the MPHS-EOS is

$$\begin{aligned}\ln\hat{\Phi}_i = {} & 4.9742\sum_j x_j \rho_{ij}^*\left[\exp(1-\phi_{ij})\left(1-\Omega_{ij}+\frac{1.45}{T_{ij}^*}\right)-\frac{1.45}{T_{ij}^*}\right] \\ & + 4.9742\sum_j x_j \rho_{ji}^*\left[\exp(1-\phi_{ji})\left(1-\Omega_{ji}+\frac{1.45}{T_{ji}^*}\right)-\frac{1.45}{T_{ji}^*}\right] \\ & + 4.9742\sum_i\sum_j x_i x_j \rho_{ij}^*\left[\exp(1-\phi_{ij})\left(1-\Omega_{ij}+\frac{1.45}{T_{ij}^*}\right)(1-\phi_{ij})\frac{\sqrt{2}}{\sqrt{2}-\rho_{ij}^*}\right] \\ & - \frac{\zeta(3\zeta-4)}{(1-\zeta)^2} - \frac{2\zeta-4}{(1-\zeta)^3}\left(\frac{\pi N_{AV}}{6V}\sigma_{ii}^3\right) - \ln Z \end{aligned} \tag{14}$$

In the VLE calculations, the equal fugacity criterion was employed. We calculated the bubble point pressures and compositions of binary and ternary mixtures in this work, and compared our VLE calculation results using the MPHS-EOS with those from commonly used cubic-type Peng–Robinson (PR) EOS (Peng and Robinson, 1976) and the Patel–Teja (PT) EOS (Patel and Teja, 1982). For the cubic-type EOS, van der Waals mixing rules were used for mixture property calculations. One temperature-independent binary interaction parameter l_{ij} was employed in evaluating the energy parameter of the cubic EOS

$$a = \sum_i \sum_j x_i x_j \sqrt{a_i a_j}\,(1-l_{ij}) \tag{15}$$

4. VLE calculation results and discussion

In this work, we calculated the VLE of 116 binary systems with similar to significantly different polarities. Three EOSs of PR, PT and MPHS were employed in this study and binary interaction parameters were empirically fitted for each EOS using experimental data. Table 2 presents typical calculation results for systems with similar polarities. It is observed that with the optimal binary interaction parameters, the MPHS-EOS yielded good results on bubble point pressures as well as on vapor phase compositions. The MPHS-EOS showed comparable results to those from the commonly used PR and PT cubic EOS. Table 3 shows typical VLE calculation results on binary mixtures with large differences in polarities. For the mixtures of components with large differences in polarities, it is demonstrated that the MPHS-EOS gave obviously better results. Taking the alcohol–paraffin binary mixtures for example, the PR- and PT-EOS methods have relatively larger absolute average deviations of more than 10% in bubble point pressure and vapor composition, even with their best-fitted binary parameters. The MPHS-EOS gave much smaller deviations in these systems which exhibited significant differences in polarity. The MPHS-EOS also yielded better results on other binary families as shown in Table 3. The binary VLE calculation results are also shown graphically in this work. Fig. 6 shows the calculated *Pxy* curve for the binary mixture of ethanol and cyclohexane at

Table 2

Comparison of the VLE calculation results for typical nonpolar and weakly polar binary mixtures by various equations of state with their optimal binary parameters

Component 1	Component 2	No. of data pts.	Temp. range/K	Optimal k_{ij} or l_{ij}			AAD% in P			AAD% in y_1		
				PR	PT	MPHS	PR	PT	MPHS	PR	PTM	PHS
2-Methylpentane	*n*-Hexane	9	298	0.001	0.004	0.004	0.39	0.34	0.31	1.55	0.81	0.64
1-Heptene	*n*-Heptane	14	328	0.015	0.018	0.005	2.35	2.45	0.40	3.23	3.57	0.40
Benzene	Cyclohexane	38	298 ~ 343	0.022	0.023	0.020	1.58	1.33	0.35	1.30	1.12	1.06
Chloroform	Benzene	24	308 ~ 323	−0.015	−0.014	−0.014	1.25	1.25	0.96	2.24	2.07	1.47
Acetone	Toluene	15	318	0.035	0.036	0.019	1.98	1.50	0.71	1.06	0.93	0.54
n-Heptane	Pyridine	13	353	0.035	0.038	0.050	1.08	1.43	0.68	3.84	4.05	1.01
n-Pentane	Acetone	32	238 ~ 298	0.091	0.091	0.082	4.38	4.78	2.69	2.78	2.74	2.33
Acetone	*n*-Hexane	56	253 ~ 328	0.087	0.089	0.079	3.81	3.69	2.50	5.30	5.27	2.04
Acetone	*n*-Heptane	7	323	0.099	0.100	0.073	5.38	5.19	1.51	3.68	3.52	1.03
Diethyl ether	Acetone	11	303	0.034	0.033	0.026	1.57	2.0	0.86	2.94	2.80	2.01
Ethanol	1-Propanol	36	323 ~ 353	0.003	0.014	0.005	2.31	1.02	1.13	4.53	0.82	0.89
Ethanol	1-Pentanol	10	353 ~ 406	0.005	0.012	0.002	3.71	4.32	2.56	5.01	4.62	3.57
Grand average							2.64	2.48	1.42	3.34	2.77	1.49

Data sources: Gmehling et al., 1978 and subsequent equilibrium data collections.

Table 3

Comparison of the VLE calculation results for typical polar mixtures by various equations of state with their optimal binary parameters

Component 1	Component 2	No. of data pts.	Temp. range/K	Optimal k_{ij} or l_{ij}			AAD% in P			AAD% in y_1		
				PR	PT	MPHS	PR	PT	MPHS	PR	PT	MPHS
1-Pentene	Methanol	13	300 ~ 322	0.016	0.017	0.072	15.12	15.38	6.16	6.50	6.82	3.77
n-Pentane	Methanol	22	303 ~ 335	0.017	0.019	0.095	9.83	10.16	9.07	12.34	12.36	10.03
Methanol	Cyclohexane	25	318 ~ 328	0.079	0.082	0.105	12.27	12.66	5.31	15.29	15.54	6.23
n-Hexane	Methanol	12	318	0.023	0.026	0.095	10.54	10.82	9.19	14.46	14.71	10.58
Methanol	*n*-Heptane	7	332 ~ 334	0.025	0.033	0.089	14.16	14.23	4.03	10.67	10.57	5.68
Ethanol	Isooctane	35	273 ~ 323	0.003	0.006	0.080	15.39	16.25	7.82	23.85	23.73	14.15
1-Propanol	*n*-Decane	12	368	0.053	0.058	0.059	13.71	11.22	5.83	4.65	4.25	1.58
Methanol	Toluene	14	337 ~ 363	0.111	0.116	0.085	15.51	15.42	2.76	9.54	9.79	4.07
Ethanol	*p*-Xylene	15	352 ~ 389	0.087	0.092	0.079	11.62	10.19	3.02	7.22	7.21	5.16
Methanol	CCl_4	18	308 ~ 328	0.082	0.085	0.083	10.82	11.20	5.36	25.45	25.68	12.86
Methanol	Ethyl acetate	53	313 ~ 333	0.010	0.015	0.030	4.13	4.30	1.77	7.90	7.72	3.43
Ethyl formate	Ethanol	12	318	0.055	0.055	0.047	2.46	2.85	0.76	2.68	2.53	1.05
Ethanol	2-Butanone	14	328	0.025	0.028	0.033	1.70	1.90	0.84	2.60	2.54	2.31
Diethyl ether	Ethanol	19	298	−0.013	−0.013	0.034	6.58	6.42	1.94	2.73	3.11	0.81
Grand average							10.69	9.31	4.23	11.50	11.52	6.33

Data sources: Gmehling et al. (1978) and subsequent equilibrium data collections.

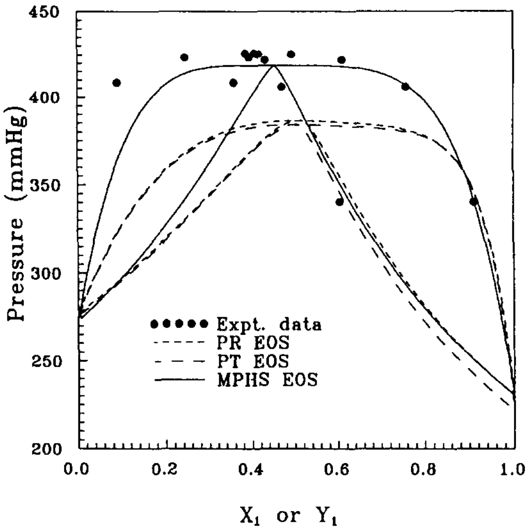

Fig. 6. Comparison of VLE calculation results by various EOS for the binary mixture of ethanol (1) and cyclohexane (2) at 323 K.

323 K. This mixture is strongly nonideal with an azeotrope. It is shown that the PR- and PT-EOS gave appreciable calculated errors even with their optimally fitted binary parameters. The MPHS-EOS yielded reasonably good agreement with the experimental data. Similar results are shown in Fig. 7 where the MPHS-EOS gave better VLE calculation results than those from the cubic EOS for the binary mixture of methanol and benzene at 318 K. Table 4 presents a comparison of the optimally fitted binary parameters of the three EOSs in our VLE calculations. For each family of binary

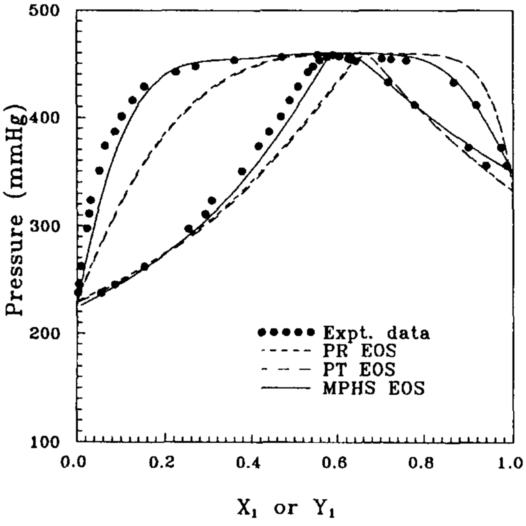

Fig. 7. Comparison of VLE calculation reults by various EOS for the binary mixture of methanol (1) and benzene (2) at 318 K.

Table 4
Comparison of the scattering of binary parameters of various EOS methods

Family of binary mixtures	No. of data pts.	Temp. range/K	$100(\text{Max } k_{ij} - \text{Min } k_{ij})/\text{Max } k_{ij}$		
			PR	PT	MPHS
Alkane + benzene	136	298 ~ 353	119	122	15
Alkane + toluene	67	298 ~ 398	125	113	75
Alkane + pyridine	64	353 ~ 370	69	71	12
Alkane + acetone	155	238 ~ 328	21	20	11
Alkane + methanol	85	297 ~ 335	83	82	32
Alkane + ethanol	201	263 ~ 433	98	96	22
Alkane + 1-propanol	80	318 ~ 368	50	57	29
Aromatic + methanol	66	308 ~ 363	25	27	5
Aromatic + ethanol	69	308 ~ 389	17	13	13
Aromatic + 1-propanol	98	303 ~ 377	50	45	27
Alkanone + methanol	81	308 ~ 351	157	109	52
Alkanone + ethanol	67	305 ~ 361	27	28	14
Ester + methanol	132	293 ~ 333	81	70	36
Ester + ethanol	115	298 ~ 353	70	70	57
Ester + 1-propanol	61	313 ~ 371	72	60	51

Max k_{ij} or min k_{ij}: maximum or minimum binary parameters used on VLE calculations for each EOS.

mixtures, the scattering of the binary parameters were evaluated and are shown in Table 4. It is observed that the scattering of the binary parameters of the MPHS-EOS is less than that of other EOSs. This advantage makes it promising either to extend the MPHS-EOS on predictive VLE calculations where estimated binary parameters of a specific family of mixture may be used, or to apply the MPHS-EOS to multicomponent VLE computations.

Table 5
Typical ternary systems studied in this research

No.	Component 1	Component 2	Component 3	No. of data pts.	Temperature range/K	Pressure range/mm Hg
1	Acetone	$CHCl_3$	Methanol	36	329 ~ 335	760
2	$CHCl_3$	Methanol	Benzene	35	329 ~ 335	760
3	Methanol	Ethanol	Methyl acetate	6	331 ~ 338	760
4	Acetone	Methanol	Cyclohexane	63	308 ~ 328	358 ~ 868
5	Methanol	Benzene	Cyclohexane	19	312 ~ 328	334 ~ 763
6	CCl_4	Ethanol	Benzene	36	323	355 ~ 426
7	Ethanol	$CHCl_3$	*n*-Hexane	108	308 ~ 328	240 ~ 701
8	Ethanol	$CHCl_3$	*n*-Hexane	36	331 ~ 337	760
9	Acetone	Ethanol	*n*-Hexane	21	328	636 ~ 884
10	Acetone	Ethanol	*n*-Hexane	21	324 ~ 334	760
11	Benzene	Ethanol	*n*-Hexane	7	333 ~ 339	760
12	Ethanol	Benzene	*n*-Heptane	148	306 ~ 352	180 ~ 760
13	Toluene	Cyclohexane	Ethanol	19	323	249 ~ 408
14	Benzene	*n*-Heptane	1-Propanol	77	348	450 ~ 713

Data sources: Gmehling et al. (1978) and subsequent equilibrium data collections.

Table 6
Comparison of the VLE calculation results for ternary systems from various equation of state

No.	AAD% in P			AAD% in y_1			AAD% in y_2		
	PR	PT	MPHS	PR	PT	MPHS	PR	PT	MPHS
1	2.62	2.64	4.61	11.64	11.62	14.01	10.98	10.58	8.95
2	7.57	7.91	3.18	12.13	11.89	9.74	14.82	14.82	9.53
3	2.84	2.61	7.83	8.54	8.90	7.36	8.22	7.12	5.14
4	5.13	5.44	0.94	7.46	7.41	4.59	13.16	13.46	6.33
5	17.61	17.91	3.51	18.67	18.85	5.31	19.92	20.18	6.52
6	7.63	8.92	3.77	8.77	8.69	4.47	15.96	15.66	8.46
7	13.62	14.87	6.04	25.65	25.04	14.73	11.82	13.05	6.13
8	14.18	15.34	5.16	26.51	26.30	16.07	12.22	13.42	6.56
9	11.09	12.05	1.58	17.82	19.11	4.97	15.34	15.33	5.00
10	10.83	11.81	2.01	17.92	19.23	5.46	17.70	17.77	8.23
11	17.45	18.30	9.05	20.08	21.32	7.17	37.87	38.67	21.07
12	9.54	9.29	4.97	22.15	21.80	12.72	18.38	17.90	10.89
13	12.05	12.25	4.33	12.04	10.89	4.93	14.66	14.24	6.22
14	7.95	10.10	5.86	9.24	9.18	5.57	10.95	10.40	7.23
Grand avg.	9.69	10.39	4.48	17.20	17.04	9.94	14.66	14.74	8.11

Table 5 presents typical ternary systems where VLE calculations were made in this study. In the ternary calculations, binary parameters determined from binary VLE computations were used directly. Table 6 shows typical ternary calculated results and the comparisons among three EOS methods. It is demonstrated that the MPHS-EOS gave better results in bubble point pressures and vapor phase compositions for most of the ternary systems. It is again shown that the MPHS-EOS yielded significant improvement on the mixtures where constituents have large differences in polarities.

5. Conclusion

A new MPHS-EOS was used in this study on VLE calculations of binary and ternary fluid mixtures. EOS parameters of pure fluids were evaluated and generalized correlations for these parameters were obtained for nonpolar and weakly polar fluids. The MPHS-EOS presented satisfactory VLE calculation results on binary and ternary systems. The MPHS-EOS showed significant improvement on the VLE calculations for fluid mixtures having large differences in polarities. The MPHS-EOS showed better VLE calculation results than those from the commonly used PR and PT cubic EOS. The MPHS-EOS also had less scattering of the optimally fitted binary parameters for a specific family of mixtures than the other cubic EOSs.

6. Nomenclature

a	cubic-type EOS energy parameters
f	fugacity

k	Boltzmann's constant
k_{ij}, l_{ij}	binary interaction parameter
m	temperature-dependent parameter in Eq. (6)
N	number of molecules
N_{AV}	Avogadro's number
P	pressure
Q	object function
r	van der Waals volume parameter
T	absolute temperature
T_{c}	critical temperature
T^*	dimensionless parameter of kT/ϵ
V	volume
x, y	mole fraction
Z	compressibility factor

6.1. Greek letters

ϵ	depth parameter of the SW potential
Φ	fugacity coefficient
ϕ	density function defined in Eq. (2)
λ	width parameter of the SW potential
ρ	number density
ρ^*	reduced density, $\rho\sigma^3$
σ	molecular diameter
Ω	dimensionless parameter in Eq. (11)
ζ	dimensionless parameter of $(\pi\rho/6)\Sigma x_i\sigma_i^3$
ω	acentric factor

6.2. Subscripts

c	critical properties
i, j	component i or j
1,2	component 1 or 2

6.3. Superscripts

cal	calculated
exp	experimental
L	liquid phase
V	vapor phase
VP	vapor pressure
*	dimensionless properties

Acknowledgements

The authors are grateful to the National Science Council of the Republic of China for supporting this research.

References

Carnahan, N.F. and Starling, K.E., 1969. Equation of state for non-attracting spheres. J. Chem. Phys., 51: 635–636.

Gmehling, J., Onken, U., Arlt, W., Grenzheuser, P., Weidlich, U., Kolbe, B. and Rarey-Nies, J., 1978–1988. Vapor–Liquid Equilibrium Data Collection. DECHEMA, Frankfurt, Germany.

Guo, M.-X., Wang, W.-C. and Lu, H.-Z., 1990(a). Equations of state for pure and mixture square-well fluids. I. Coordination number models. Fluid Phase Equilibria, 60: 37–45.

Guo, M.-X., Wang, W.-C. and Lu, H.-Z., 1990(b). Equations of state for pure and mixture square-well fluids. II. Equations of state. Fluid Phase Equilibria, 60: 221–237.

Larsen, B.L., Rasmussen, P. and Fredenslund, A., 1987. A modified UNIFAC group-contribution model for prediction of phase equilibria and heats of mixing. Ind. Eng. Chem. Res., 26: 2274–2286.

Lee, K.-H., Lombardo, M. and Sandler, S.I., 1985. The generalized van der Waals partition function. II. Application to the square-well fluid. Fluid Phase Equilibria, 21: 177–196.

Lee, K.-H., Sandler, S.I. and Patel, N.C., 1986. The generalized van der Waals partition function. III. Local composition models for a mixture of equal size square-well fluid. Fluid Phase Equilibria, 25: 31–49.

Lee, K.-H. and Sandler, S.I., 1987. The generalized van der Waals partition function. IV. Local composition models for mixtures of unequal-size molecules. Fluid Phase Equilibria, 34: 113–147.

Lee, K.-H., Dodd L.R. and Sandler, S.I., 1989. The generalized van der Waals partition function. V. Mixtures of square-well fluids of different sizes and energies. Fluid Phase Equilibria, 50: 53–77.

Lee, R.J. and Chao, K.C., 1987. Coordination number and thermodynamics of square-well fluid mixtures. Molecular Phys. 61: 1431–1442.

Patel, N.C. and Teja, A.S., 1982. A new cubic equation of state for fluid and fluids mixtures. Chem. Eng. Sci., 37:463–473.

Peng, D.-Y. and Robinson, D.B., 1976. A new two-constant equation of state. Ind. Eng. Chem., Fundam., 15: 59–64.

Rossini, F.D., Pitzer, K.S., Arnett, R.L., Braun, R.M. and Pimental, G.C., 1952. Selected values of properties of hydrocarbons and related compounds. API Project 44, Canegie, Pittsburgh.

Sandler, S.I., 1985. The generalized van der Waals partition function. I. Basic theory. Fluid Phase Equilibria, 19: 233–257.

Smith, B.D. and Srivastava, R., 1986. Thermodynamic Data for Pure Compounds. Elsevier, Amsterdam.

Vargaftik, N.B., 1975. Tables on the Thermodynamic Properties of Liquids and Gases. 2nd. edn., Hemisphere Publishing Corp. Washington, D.C.

Yu, M.-L. and Chen, Y.-P., 1995. An equation of state from a new coordination number model. Fluid Phase Equilibria, 111: 37–51.