

Prediction of phase equilibria for mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures by cubic equation of state with G^E type mixing rule based on COSMO-RS

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Abstract

The phase equilibria for the mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures were predicted by a cubic equation of state with an excess Gibbs free energy (G^E) type mixing rule using information from the conductor–like screening model for real solvents (COSMO-RS) method. The systems predicted were water + hydrocarbon, water + alcohol, hydrocarbon + alcohol binary systems and water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems. COSMO-RS method was used to calculate activity coefficients of the mixtures. UNIQUAC equation was adopted as an activity coefficient model in G^E type mixing rule. The interaction parameters in UNIQUAC equation were determined with the activity coefficients calculated by COSMO-RS method. The modified Huron–Vidal mixing rule (MHV1) and a modified Soave–Redlich–Kwong (MSRK) equation of state were chosen as the G^E type mixing rule and the cubic equation of state, respectively. Further, the MHV1 mixing rule was modified to apply in high temperature regions.

It was found that the prediction method proposed here can represent the phase behavior of the mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures. The predicted results are compared with those calculated by a predictive Soave–Redlich–Kwong (PSRK) equation of state. The predicted results in this work are more accurate than those calculated by PSRK equation of state.

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1. Introduction

Chemical processes utilizing water near the critical point have been considered in various fields. Cracking processes of waste plastics, polyethylene and polypropylene, and heavy hydrocarbons have received much attention in the framework of the recycling of resources and environmental conservation [1–4]. Hydration processes of olefin in sub- and supercritical water have been also reported recently [5]. In these processes, low molecular weight hydrocarbons, such as alkanes, alkenes and alcohols are produced as products. Therefore, it is required for process design to elucidate the phase behavior

of the mixtures consisting of water and these compounds at high temperatures and pressures near the critical point of water.

In previous works, the phase equilibria for water + hydrocarbon [6,7], water + alcohol [8], water + hydrocarbon + hydrocarbon [9] and water + hydrocarbon + alcohol [10] systems at high temperatures and pressures were correlated using a modified Soave–Redlich–Kwong (MSRK) equation of state [11] with an exponent type mixing rule [12]. In the calculation model, the binary parameters were optimized by using the phase equilibrium data. However, there are few experimental data at high temperatures and pressures, and therefore the application of the model is confined to the systems of which phase equilibrium data are available.

Group contribution methods, such as ASOG [13] and UNIFAC [14] activity coefficient models, a predictive SRK (PSRK)

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[15] and Peng–Robinson ASOG (PRASOG) [16] equation of states, are capable of solving the problem. Because it is considered that a molecule consists of several groups, and these methods can reduce the number of parameters needed to calculate the thermodynamic properties for the mixtures. Although group contribution methods are applicable to a large variety of the mixtures, the group parameters interested are not necessarily given. Klamt and Eckert [17–19] have proposed the conductor-like screening model for real solvents (COSMO-RS) method based on quantum calculations, without data fitting. It was confirmed from the recent publications that COSMO-RS method can be very useful tool to predict the thermodynamic properties of fluids and their mixtures [20–23]. However, the method cannot be applied in high pressure region, because the vapor phase is assumed as ideal gas. A method has been newly considered for phase equilibrium calculations at high pressure by Constantinescu et al. [24]. In the method, infinite dilution activity coefficients at low pressure calculated by COSMO-RS method were adopted to Huron–Vidal mixing rule [25], excess Gibbs free energy (G^E) type mixing rule, with UNIFAC equation and the mixing rule was applied to the attractive term in SRK equation of state. This calculation method seems to be possible to predict the vapor–liquid equilibria for the mixtures containing polar compounds, such as water, alcohol and acetone at high pressures without data fitting.

In this work, a calculation method is constructed for the prediction of phase equilibria of the asymmetric mixtures, which consisting of water, hydrocarbons and alcohols at high temperatures and pressures. COSMO-RS method was applied for calculations of activity coefficients for the mixtures. UNIQUAC equation [26] was used to describe the activity coefficients. The interaction parameters in UNIQUAC equation were determined from the activity coefficients calculated by COSMO-RS method. A modified Huron–Vidal (MHV1) mixing rule [27,28] with UNIQUAC equation was adopted as a mixing rule of the attractive term in a modified Soave–Redlich–Kwong (MSRK) equation of state proposed by Sandarushi et al. [11]. In MHV1 mixing rule, one parameter was redetermined in order to extend the mixing rule to high temperature regions. The predicted systems are water + hydrocarbon, water + alcohol, hydrocarbon + alcohol binary systems and water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems. It is shown that the phase behavior for the asymmetric mixtures containing water, hydrocarbons and alcohols at high temperatures and pressures can be represented by the method proposed in this work. The results predicted by the present method are compared with those by PSRK equation of state.

2. Calculation procedure

The calculation of the phase equilibria was carried out based on the following three steps.

- (1) Activity coefficients were calculated for the binary systems, water + hydrocarbon, water + alcohol, hydrocarbon + alcohol and hydrocarbon + hydrocarbon systems in variety compositions at 423–623 K by COSMO-RS method.

COSMO-RS calculations were performed based on COSMOtherm Version C2.1 program [29].

- (2) The interaction parameters in UNIQUAC equation were determined from the activity coefficients calculated in step 1 by Marquart method [30].
- (3) The phase equilibria were calculated by MSRK equation of state with MHV1 mixing using the UNIQUAC interaction parameters determined in step 2. The phase equilibrium calculations were performed with the thermodynamic relations given by the following equations.

$$py_i\varphi_i^V = px_i\varphi_i^L \quad \text{for vapor–liquid equilibria (VLE)} \quad (1)$$

$$px_i^I\varphi_i^I = px_i^{II}\varphi_i^{II} \quad \text{for liquid–liquid equilibria (LLE)} \quad (2)$$

and

$$\ln \varphi_i = \frac{1}{RT} \int_V^\infty \left\{ \left(\frac{\partial p}{\partial n_i} \right)_{T,V,n_{i \neq j}} - \frac{RT}{V} \right\} dV - \ln Z \quad (3)$$

where x and y denotes the mole fraction in liquid and vapor phases. n , φ and Z are the amount of substance, the fugacity coefficient and the compressibility factor, respectively. Superscripts I, II, V and L mean the phases I and II, vapor and liquid phases, respectively. Subscript i denotes the component i .

3. Calculation method

3.1. COSMO-RS method

COSMO-RS method [17–19] has capabilities to predict thermodynamic properties of fluids from a statistical approach by quantum calculations, based on conductor-like screening model (COSMO) [31]. In these calculations, a charge density σ of a segment on the molecular surface is calculated in a virtual conductor. The distribution function $P_i(\sigma)$ of the obtained σ , which is called σ -profile, for each molecule can give the σ -profile of the mixture $P(\sigma)$ by using $P_i(\sigma)$ and the mole fraction x_i of component i in the mixture.

$$P(\sigma) = \sum_i x_i P_i(\sigma) \quad (4)$$

Molecular interaction energies E_{int} are described as the summation of the three contribution terms, electrostatics E_{misfit} , which means the interactions by a difference between molecular surface charges, van der Waals interaction E_{vdW} and hydrogen bonding E_{HB} .

$$E_{\text{int}} = E_{\text{misfit}} + E_{\text{vdW}} + E_{\text{HB}} \quad (5)$$

The chemical potential of the contact surface segment $\mu_S(\sigma)$ on the molecular surface are derived using Eqs. (4) and (5) as follows.

$$\exp \left(-\frac{\mu_S(\sigma)}{kT} \right) = \int P(\sigma') \exp \left[-\frac{E_{\text{int}}(\sigma, \sigma') - \mu_S(\sigma')}{kT} \right] d\sigma' \quad (6)$$

where k and T are the Boltzmann constant and the temperature, respectively. $E_{\text{int}}(\sigma, \sigma')$ means the interaction energies

Table 1

Volume and surface area parameters in UNIQUAC equation, critical properties and MSRK parameters m_a and m_b of pure compounds

Compound	r_i^a	q_i^a	T_c [K] ^b	p_c [MPa] ^b	m_a^b	m_b^b
Water	0.9200	1.400	647.1	22.1	0.9499	0.1633
Methane	1.1292	1.124	190.5	4.60	0.4631	0.0698
Ethane	1.8000	1.700	305.4	4.88	0.5558	0.1208
Propane	2.4800	2.240	369.8	4.25	0.6038	0.1563
Butane	3.1510	2.776	425.1	3.80	0.6601	0.1789
Pentane	3.8254	3.316	469.6	3.37	0.6215	0.1818
Hexane	4.4998	3.856	507.4	3.01	0.7446	0.2476
Heptane	5.1742	4.396	540.2	2.74	0.7841	0.2828
Decane	7.9197	6.016	617.6	2.10	0.8905	0.3863
Dodecane	8.5500	7.100	658.2	1.83	0.9604	0.4479
Hexadecane	11.2400	8.260	720.5	1.42	1.1274	0.5506
Benzene	3.1878	2.400	562.1	4.90	0.6043	0.2285
Toluene	3.9228	2.968	591.8	4.11	0.7117	0.2242
Ethylbenzene	4.5972	3.508	617.1	3.61	0.7458	0.2512
Methanol	1.4311	1.432	512.6	8.09	1.3013	0.2005
Ethanol	2.1055	1.972	513.9	6.14	1.1545	0.4047
2-Propanol	2.7791	2.508	508.3	4.76	0.6434	0.7854
2-Butanol	3.4535	3.048	536.0	4.20	0.3404 ^c	0.8829 ^c
2-Pentanol	3.0480	4.208	560.3	3.68	0.7940 ^c	0.6071 ^c

^a Cited from reference [33].^b Cited from reference [11].^c Cited from reference [10].

of a segment pair σ – σ' between molecular surface. $\mu_S(\sigma)$ are obtained by iterative calculation of Eq. (6). The integral range corresponds to the number of molecular surface segment. The chemical potential of the component i , μ_i , in the mixture is calculated by integration of Eq. (6) over the surface of the component i .

$$\mu_i = \mu_i^C + \int P_i(\sigma) \mu_S(\sigma) d\sigma \quad (7)$$

The first term in the right hand of Eq. (7) means the combinatorial contribution of molecular size and shape to the chemical potential. The chemical potential obtained by Eq. (7) is used to calculate the activity coefficient of component i , γ_i .

$$\gamma_i = \exp \left[-\frac{\mu_i - \mu_i^0}{kT} \right] \quad (8)$$

where superscript “0” denotes the property of pure component i .

3.2. Equation of state

The modified Soave–Redlich–Kwong (MSRK) equation of state proposed by Sandarushi et al. [11] were applied for the calculations of the phase equilibria. This equation of state was modified in the attractive term of the original SRK equation of state [32] to calculate the vapor pressures of polar substances with more accurate than the original equation. MSRK equation of state is given as follows.

$$p = \frac{RT}{v-b} - \frac{a}{v(v+b)} \quad (9)$$

where p is the pressure, R the gas constant, T the temperature and v is the molar volume. The energy parameter a and the size

parameter b are, respectively, given as.

$$a = \frac{0.42724R^2T_c}{p_c} \alpha, \quad \alpha = 1 + (1 - T_r) \left(m_a + \frac{m_b}{T_r} \right) \quad (10)$$

$$b = \frac{0.08664RT_c}{p_c} \quad (11)$$

The subscripts c and r mean the critical and reduced properties, respectively, and parameters m_a and m_b are obtained from a fit to the vapor pressures of pure substances. The critical properties and the parameters m_a and m_b for the substances treated in this work are listed in Table 1.

3.3. Mixing rules

MHV1 [27,28], which is a G^E type mixing rule, and conventional mixing rules are applied for the energy and size parameters of the equation of state. The excess Gibbs free energy G^E at zero pressure ($p \rightarrow 0$) can be derived from SRK equation of state [32] and is given by the following equation.

$$\frac{G_0^E}{RT} + \sum_i x_i \ln \left(\frac{b}{b_i} \right) = h(\pi) - \sum_i x_i h_i(\pi_i),$$

$$\pi = \frac{a}{bRT}, \quad \pi_i = \frac{a_i}{b_iRT} \quad (12)$$

The $h(\pi)$ or $h_i(\pi_i)$ is approximated by a linear function of π or π_i by Michelsen [27,28].

$$h(\pi) = \lambda_a + \lambda_b \pi, \quad h_i(\pi_i) = \lambda_a + \lambda_b \pi_i \quad (13)$$

Table 2
Values of parameter π in Eq. (12) at $T_r = 0.85$ and 0.90

Compound	T_r	π
Water	0.85	6.80
	0.90	6.10
Butane	0.85	6.98
	0.90	6.21
Hexane	0.85	6.71
	0.90	6.04
Decane	0.85	6.56
	0.90	5.95
Methanol	0.85	7.14
	0.90	6.32
2-Propanol	0.85	7.17
	0.90	6.31
2-Butanol	0.85	7.01
	0.90	6.21

The energy parameter in SRK equation of state can be given from Eqs. (12) and (13) as follows.

$$\frac{a}{b} = \sum_i x_i \frac{a_i}{b_i} + \frac{1}{\lambda_b} \left[G_0^E + RT \sum_i x_i \ln \left(\frac{b}{b_i} \right) \right] \quad (14)$$

In the original MHV1 mixing rule, the parameter λ_b was fitted in the range of $10.0 < \pi < 13.0$ which means near the room temperature, and the value was -0.593 . The parameter was modified here in order to apply to the high temperature regions because the phase equilibria at high temperatures and pressures were focused in this work. The parameters π_i for pure substances at the reduced temperature $T_r = 0.85$ and 0.90 were calculated by Eq. (12) and the values are listed in Table 2. As listed in Table 2, these values are ranging in about 6.0–7.0. Fig. 1 shows the relationship between the parameters π_i and $h_i(\pi_i)$. The parameter λ_b was determined from the slope in the range $6.0 < \pi_i < 7.0$ at higher temperatures. The value determined in this work was -0.456 , and was used to calculate the phase equilibria at high temperatures and pressures.

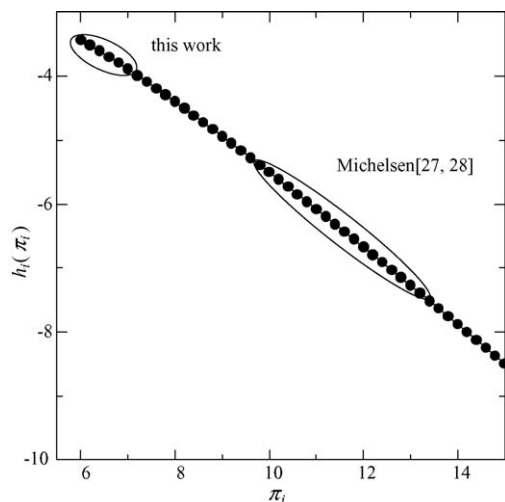


Fig. 1. Extrapolation method in this work and Michelsen [27,28].

Table 3
UNIQUAC interaction parameters for water(1) + hydrocarbon(2) systems

Hydrocarbon(2)	c_{12}	d_{12} [K]	c_{21}	d_{21} [K]
Methane	-0.9136	-326.06	2.8085	-1693.3
Ethane	-0.4590	-577.02	2.3827	-1341.6
Propane	0.1445	-827.98	1.9794	-1108.9
Butane	0.5388	-991.06	1.7376	-969.85
Hexane	0.9499	-1133.6	1.4162	-837.47
Heptane	1.0541	-1172.7	1.3096	-796.52
Decane	1.5589	-1233.0	0.6774	-512.59
Dodecane	1.2902	-1254.6	0.9455	-674.28
Hexadecane	1.8046	-1388.2	0.6270	-485.99
Benzene	1.4325	-1178.5	1.1320	-465.26
Toluene	1.6200	-1217.7	0.8676	-410.47
Ethylbenzene	1.6336	-1212.4	0.7274	-383.92

The activity coefficients by COSMO-RS method were utilized to calculate the excess Gibbs free energy in G^E type mixing rule for the energy parameter of the equation of state. UNIQUAC equation [26] was applied to express the activity coefficients calculated by COSMO-RS method. The UNIQUAC equation composes of the two contribution terms as follows.

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \quad (15)$$

The superscripts C and R denote the combinatorial and residual contributions due to molecular size and shape, and molecular interactions, respectively. The combinatorial contribution is calculated with the van der Waals volume and surface area parameters r_i and q_i . The residual contribution in UNIQUAC equation is given as.

$$\ln \gamma_i^R = q_i \left\{ 1 - \ln \left(\sum_j \theta_j \tau_{ji} \right) - \sum_j \frac{\theta_j \tau_{ij}}{\sum_k \theta_k \tau_{kj}} \right\}, \quad (16)$$

$$\theta_i = \frac{q_i x_i}{\sum_j q_j x_j}$$

$$\tau_{ij} = \exp \left(c_{ij} + \frac{d_{ij}}{T} \right) \quad (17)$$

The values of r_i and q_i are listed in Table 1. The interaction parameters c_{ij} and d_{ij} in Eq. (17) were determined from the activity coefficients calculated by COSMO-RS method for water + hydrocarbon, water + alcohol, hydrocarbon + alcohol and hydrocarbon + hydrocarbon systems in variety compositions at 423–623 K. The values of c_{ij} and d_{ij} determined in this work are listed in Tables 3–6.

Table 4
UNIQUAC interaction parameters for water(1) + alcohol(2) systems

Alcohol(2)	c_{12}	d_{12} [K]	c_{21}	d_{21} [K]
Methanol	-1.2994	-68.25	1.0338	-106.10
Ethanol	0.7477	-763.99	0.08687	187.52
2-Propanol	0.8512	-740.64	-0.04941	165.45
2-Butanol	0.8245	-748.54	0.07312	40.039
2-Pentanol	0.6339	-636.61	0.01131	-38.647

Table 5
UNIQUAC interaction parameters for hydrocarbon(1) + alcohol(2) systems

Hydrocarbon(1)	Alcohol(2)	c_{12}	d_{12} [K]	c_{21}	d_{21} [K]
Pentane	Ethanol	0.4734	−378.42	0.00634	−93.359
Hexane	2-Propanol	0.3143	−245.05	0.0236	−70.066
Heptane	2-Propanol	0.2347	−201.21	0.0783	−106.21
Decane	2-Propanol	0.1806	−178.06	0.1194	−124.36
Decane	2-Buatanol	0.0992	−86.095	0.1309	−114.20

A conventional mixing rule was used to the size parameter in MSRK equation of state. The mixing rule is given in the following equation.

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (18)$$

A combining rule of the size parameter was expressed as an arithmetic average of $b_i^{1/3}$ and $b_j^{1/3}$.

$$b_{ij}^{1/3} = \frac{1}{2}(b_i^{1/3} + b_j^{1/3}) \quad (19)$$

The combining rule has been applied to polymer + solvent systems by Louli and Tassios [34]. It is expected that the expression is effective to the system of which molecular size differences are large, such as water + decane, water + dodecane and water + hexane + hexadecane systems.

4. Results and discussion

The phase equilibria for water + hydrocarbon, water + alcohol, hydrocarbon + alcohol binary systems, water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems at high temperatures and pressures were predicted by the above mentioned calculation method. The predicted results are listed in Tables 7–11. The deviations between the predicted and experimental results are evaluated using Eqs. (20)–(24). The predicted results by the present method are also compared with those by PSRK equation of state.

(a) water(1) + hydrocarbon(2) systems,

$$\delta = \frac{1}{2N} \left(\sum_{k=1}^N |y_{1,\text{calc}}^k - y_{1,\text{exp}}^k| + \sum_{k=1}^N |x_{1,\text{calc}}^k - x_{1,\text{exp}}^k| \right) \times 100 \quad \text{for VLE } (T-p \text{ fixed}) \quad (20)$$

Table 7
Predicted results of phase equilibria for water(1) + hydrocarbon(2) systems

Hydrocarbon(2)	T [K]	N	δ^a	δ^b	Ref.
Methane	423.2	5	0.52	n.p. ^c	[35]
	523.2	5	2.98	n.p. ^c	[35]
	603.2	5	1.96	n.p. ^c	[35]
Ethane	473.2	8	2.70	10.3	[36]
	523.2	8	4.57	9.68	[36]
	573.2	15	12.9	8.30	[36]
Propane	618.0	8	0.38	1.17	[37]
Butane	443.0	20	36.5	40.0	[38]
	477.0	19	29.7	34.3	[38]
	511.0	17	21.7	30.4	[38]
Decane	573.2	22	2.12	18.0	[6,39]
	593.2	19	2.50	16.4	[6,39]
	613.2	10	0.99	3.02	[6,39]
Dodecane	603.0	18	2.51	37.5	[40]
	633.0	18	3.29	27.3	[40]
Benzene	498.2	8	4.58	17.3	[41]
	553.2	9	0.50	1.54	[41]
	573.2	9	6.24	7.12	[41]
	603.2	9	0.18	1.02	[41]
Toluene	553.2	4	2.12	13.9	[7]
	573.2	9	1.03	20.0	[7]
	583.2	9	2.17	6.06	[7]
Ethylbenzene	553.2	6	2.25	18.4	[7]
	573.2	6	2.33	15.6	[7]

^a This work.

^b PSRK.

^c n.p., parameters are not available.

$$\delta = \frac{1}{2N} \left(\sum_{k=1}^N |x_{1,\text{calc}}^{I,k} - x_{1,\text{exp}}^{I,k}| + \sum_{k=1}^N |x_{1,\text{calc}}^{II,k} - x_{1,\text{exp}}^{II,k}| \right) \times 100 \quad \text{for LLE } (T-p \text{ fixed}) \quad (21)$$

(b) water(1) + alcohol(2) and hydrocarbon(1) + alcohol(2) systems,

$$\delta = \frac{1}{2N} \left(\sum_{k=1}^N |y_{1,\text{calc}}^k - y_{1,\text{exp}}^k| + \sum_{k=1}^N \frac{|p_{\text{calc}}^k - p_{\text{exp}}^k|}{p_{\text{exp}}^k} \right) \times 100 \quad \text{for VLE } (T-x_1 \text{ fixed}) \quad (22)$$

Table 6
UNIQUAC interaction parameters for hydrocarbon(1) + hydrocarbon(2) systems

Hydrocarbon(1)	Hydrocarbon(2)	c_{12}	d_{12} [K]	c_{21}	d_{21} [K]
Hexane	Hexadecane	0.00698	0.0000	−0.00095	−0.5642
Toluene	Decane	0.0085	−36.486	−0.0018	−33.795
Toluene	Ethylbenzene	−0.00135	−65.724	0.000014	−93.957
Benzene	Heptane	0.0511	−51.596	0.0432	−54.559

Table 8
Predicted results of phase equilibria for water(1) + alcohol(2) systems

Alcohol(2)	<i>T</i> [K]	<i>N</i>	δ^a	δ^b	Ref.
Methanol	423.2	14	2.53	1.11	[42]
	473.2	15	1.75	1.21	[42]
	523.2	6	5.89	0.91	[42]
Ethanol	423.2	17	3.91	5.02	[43]
	473.2	17	3.38	5.92	[43]
	523.2	16	5.83	5.22	[43]
	573.2	7	1.43	0.97	[43]
	598.2	7	1.33	1.09	[43]
2-Propanol	473.2	18	5.36	0.91	[43]
	523.2	12	7.68	4.86	[43]
	548.2	20	4.51	2.66	[8,43]
	573.2	11	3.10	3.01	[8,43]
2-Butanol	523	6	15.8	11.0	[8]
	548	7	7.49	34.3	[8]
	573	6	4.72	41.9	[8]
2-Pentanol	523	6	5.87	4.81	[8]

^a This work.

^b PSRK.

Table 9
Predicted results of phase equilibria for hydrocarbon(1) + alcohol(2) systems

Hydrocarbon(1)	Alcohol(2)	<i>T</i> [K]	<i>N</i>	δ^a	δ^b	Ref.
Pentane	Ethanol	422.6	9	3.59	5.04	[44]
		465.4	13	1.40	36.9	[44]
		500.0	5	0.30	2.98	[44]
Hexane	2-Propanol	483.15	14	2.17	21.5	[45]
		493.15	18	1.34	14.9	[45]
		503.15	9	0.48	4.06	[45]
Heptane	2-Propanol	483.15	11	3.39	37.8	[46]
		498.15	11	2.43	24.9	[46]
		508.15	7	2.40	43.3	[46]
		523.15	7	0.82	n.c. ^c	[46]

^a This work.

^b PSRK.

^c n.c., calculated result of two phase region is so small.

Table 10
Predicted results of phase equilibria for water(1) + hydrocarbon(2) + hydrocarbon(3) systems

Hydrocarbon(2)	Hydrocarbon(3)	<i>T</i> [K]	<i>p</i> [MPa]	<i>N</i>	δ^a	δ^b	Ref.
Hexane	Hexadecane	573	20.0	10	5.73	45.7	[47]
Toluene	Decane	553	20.0	5	3.19	38.9	[9]
		573	20.0	8	6.48	52.6	[9]
Toluene	Ethylbenzene	553	20.0	6	7.68	45.9	[9]
Benzene	Heptane	561.0	24.82	7	6.95	24.2	[9]
		566.5	24.82	6	6.32	26.2	[9]
		572.1	24.82	6	8.31	34.6	[9]
		583.2	24.82	7	5.99	36.1	[9]
		605.4	24.82	4	3.40	5.60	[9]

^a This work.

^b PSRK.

Table 11
Predicted results of phase equilibria for water(1) + hydrocarbon(2) + alcohol(3) systems

Hydrocarbon(2)	Alcohol(3)	<i>T</i> [K]	<i>p</i> [MPa]	<i>N</i>	δ^a	Ref.
Hexane	2-Propanol	573	20.0	8	3.65	[10]
Decane	2-Propanol	573	20.0	7	3.39	[10]
		593	20.0	5	5.82	[10]
		573	15.0	5	4.29	[10]
Decane	2-Butanol	553	20.0	5	1.81	[10]

^a This work.

(c) water(1) + hydrocarbon(2) + hydrocarbon(3) systems,

$$\delta = \left[\frac{1}{3N} \sum_{k=1}^N \sum_{i=1}^3 |x_{i,\text{calc}}^{I,k} - x_{i,\text{exp}}^{I,k}| + \frac{1}{N} \sum_{k=1}^N \sum_{i=1}^2 |x_{i,\text{calc}}^{I,k} - x_{i,\text{exp}}^{I,k}| \right] \times 100 \quad \text{for LLE } (T-p-x_3^{\text{II}} \text{ fixed}) \quad (23)$$

(d) water(1) + hydrocarbon(2) + alcohol(3) systems,

$$\delta = \left[\frac{1}{3N} \sum_{k=1}^N \sum_{i=1}^3 |x_{i,\text{calc}}^{I,k} - x_{i,\text{exp}}^{I,k}| + \frac{1}{N} \sum_{k=1}^N |x_{1,\text{calc}}^{\text{II},k} - x_{1,\text{exp}}^{\text{II},k}| + |x_{3,\text{calc}}^{\text{II},k} - x_{3,\text{exp}}^{\text{II},k}| \right] \times 100 \quad \text{for LLE } (T-p-x_2^{\text{II}} \text{ fixed}) \quad (24)$$

where *k* means the phase equilibrium data point. *N* is the number of data points for each system at constant temperature for the binary systems, or temperature and pressure for the ternary systems.

The calculations for water + hydrocarbon system were performed with the fixed temperature and pressure. Figs. 2 and 3 show the predicted results for water + decane and water + benzene systems. These systems show the vapor–liquid and the liquid–liquid equilibria at low and high pressure regions at constant temperature, respectively. The predicted results are in good agreement with the experimental data for both the vapor–liquid and the liquid–liquid equilibria. As shown in Table 7, the predicted results in this work for the other systems

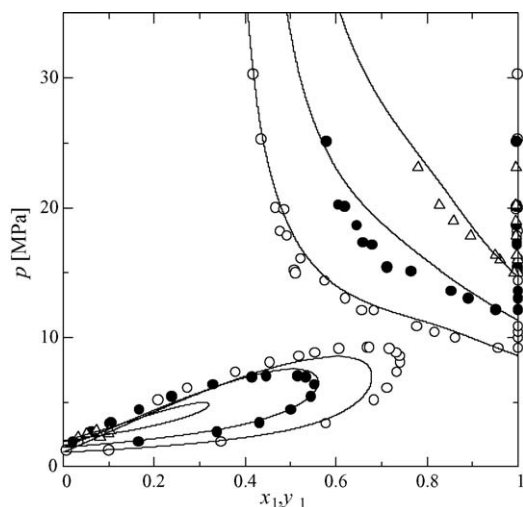


Fig. 2. Phase equilibria for water(1)+decane(2) system. Experimental data [6,39]: (○) 573 K, (●) 593 K and (△) 613 K. Predicted results in this work: (—).

show also good agreement with the experimental data. It is noted that the present method is better than PSRK equation of state.

The temperature and the mole fraction of water in liquid phase are fixed in the phase equilibrium calculation for water + alcohol systems. The results for water + ethanol and water + 2-propanol systems are shown in Figs. 4 and 5. The good predicted results are obtained in wide range of temperature, 423–598 K, as shown in Figs. 4 and 5. It is found that the results for the other water + alcohol systems are also in good agreement with the experimental data as well as those by PSRK equation of state as listed in Table 8.

For hydrocarbon + alcohol systems, the phase equilibria were calculated with the fixed temperature and mole fraction of hydrocarbon in liquid phase. The predicted results for pentane + ethanol system are given in Fig. 6. As shown in Fig. 6, the

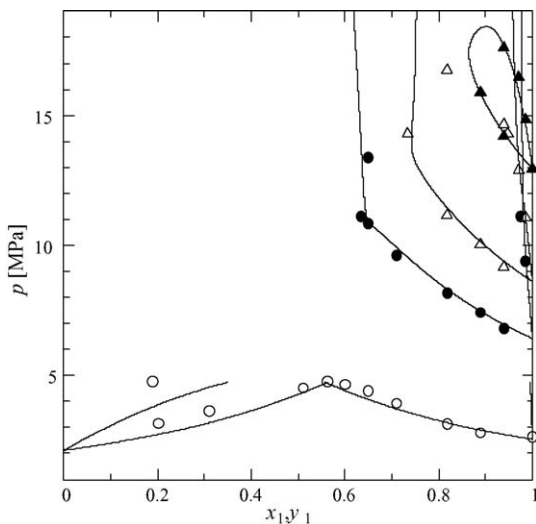


Fig. 3. Phase equilibria for water(1)+benzene(2) system. Experimental data [41]: (○) 498.2 K, (●) 553.2 K, (△) 573.2 K and (▲) 603.2 K. Predicted results in this work: (—).

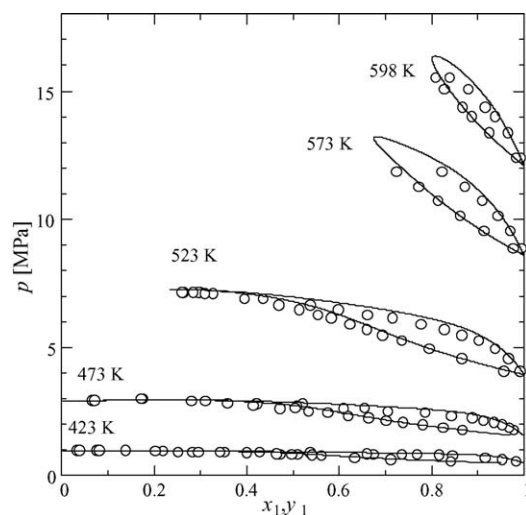


Fig. 4. Phase equilibria for water(1)+ethanol(2) system. Experimental data [43]: (○). Predicted results in this work: (—).

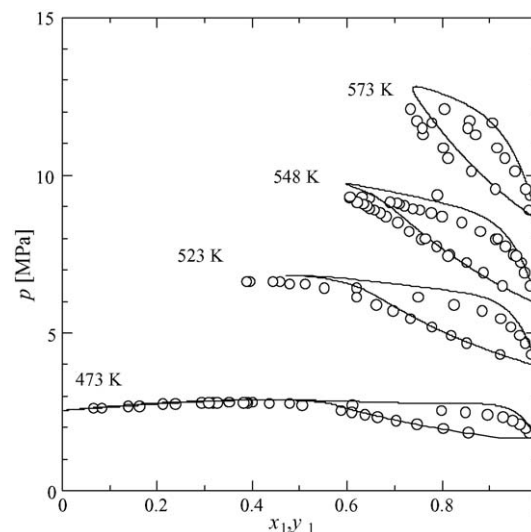


Fig. 5. Phase equilibria for water(1)+2-propanol(2) system. Experimental data [8,43]: (○). Predicted results in this work: (—).

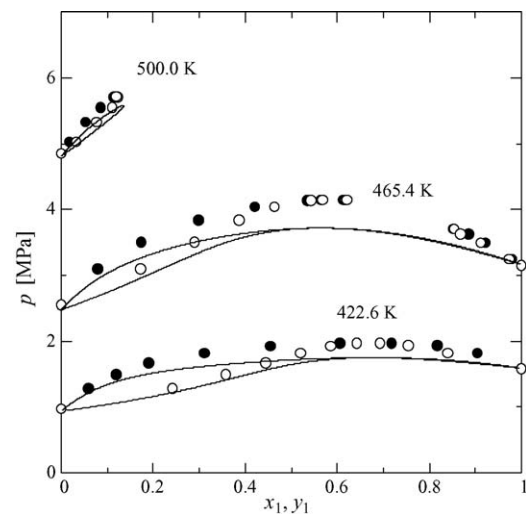


Fig. 6. Phase equilibria for pentane(1)+ethanol(2) system. Experimental data [44]: (○) vapor phase, (●) liquid phase. Predicted results in this work: (—).

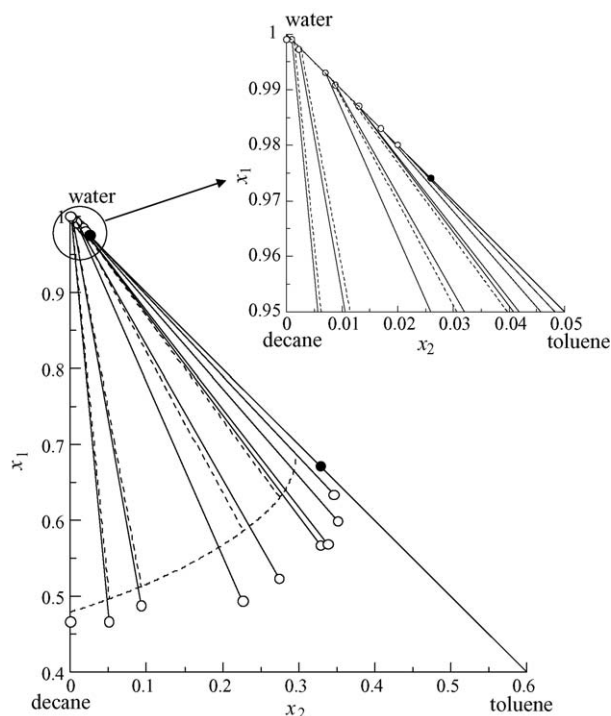


Fig. 7. Phase equilibria for water(1) + toluene(2) + decane(3) system at 573 K and 20.0 MPa. Experimental data: (○—○) ternary data [9], (●) binary data for water + toluene system [7]. Predicted results in this work: (---).

mixture shows the phase behavior with azeotropic points at 422.6 and 465.4 K. Although the deviations with the experimental data are slightly large near the azeotropic points, the predicted results represent the phase behavior qualitatively. Table 9 shows that the predicted performance of the present method is better than those by PSRK equation of state for the hydrocarbon + alcohol systems.

The calculations were executed for water + hydrocarbon + hydrocarbon ternary systems in which the temperature, pressure and one of the mol fractions of hydrocarbon in hydrocarbon rich phase were fixed. The predicted results for water + toluene + decane system at 573 K and 20.0 MPa are shown in Fig. 7. The solubility lines predicted by the present method are slightly different from the experimental data. It is found that the good results in the slopes of tie lines are obtained. Table 10 describes that the deviations by the present method for the experimental data for water + hydrocarbon + hydrocarbon ternary systems are smaller than those by PSRK.

The phase equilibria for water + hydrocarbon + alcohol ternary systems were also calculated with the fixed temperature, pressure and mole fraction of hydrocarbon in hydrocarbon rich phase. Fig. 8 gives the results for water + decane + 2-butanol system at 573 K and 20.0 MPa. The results of the solubility line in hydrocarbon rich phase show good agreement with the experimental data. In Table 11, the predicted results for water + hydrocarbon + alcohol ternary systems in this work are listed. PSRK predicts have given so small two liquid phase region, in which no experimental data are reported, for water + hydrocarbon + alcohol ternary systems at high temperatures and pressures. The results of PSRK can-

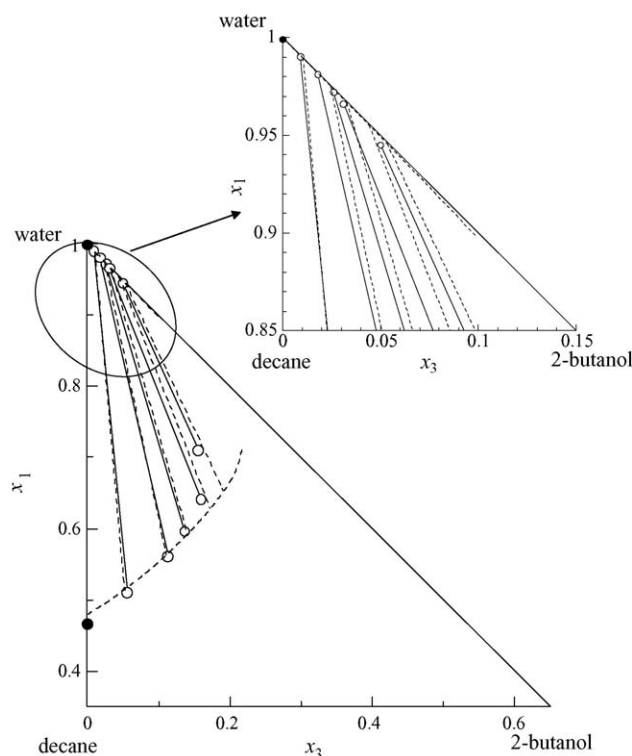


Fig. 8. Phase equilibria for water(1) + decane(2) + 2-butanol(3) system at 573 K and 20.0 MPa. Experimental data [10]: (○—○) ternary data, (●) binary data for water + decane system. Predicted results in this work: (---).

not be compared with the experimental data. Table 11 shows good predicted results are obtained by the present method for water + hydrocarbon + alcohol systems.

The predicted results by new method are better than those by PSRK for all systems focused in this work at high temperatures and pressures. The parameter in MHV1 mixing rule was redetermined at high temperatures. The interaction parameters in UNIQUAC for MHV1 mixing rule were determined using the activity coefficients calculated by COSMO-RS method. This calculation method without data fitting enables to represent the phase equilibria for asymmetric systems at high temperatures and pressures.

5. Conclusion

A phase equilibrium calculation method without data fitting was proposed based on a cubic equation of state with G^E type mixing rule, which was coupled with UNIQUAC equation. COSMO-RS method was adopted to calculate the activity coefficients in the mixture. The interaction parameters in UNIQUAC equation were determined using the activity coefficients by COSMO-RS method. MHV1 mixing rule was used as a G^E type mixing rule. The mixing rule was modified to extend to high temperature conditions. The phase equilibria of the asymmetric systems consisting of water, hydrocarbons, and alcohols at high temperatures and pressures were predicted by MSRK equation of state with the MHV1 mixing rule. The systems predicted in this work were water + hydrocarbon, water + alcohol, hydrocarbon + alcohol

binary systems, water + hydrocarbon + hydrocarbon and water + hydrocarbon + alcohol ternary systems. It is shown that the predicted results by the present method can represent the phase behavior for these several systems though somewhat large deviations are occasionally given. It is noted that the present method is more accurate than those by PSRK equation of state.

List of symbols

a	energy parameter in MSRK ($\text{m}^6 \text{Pa mol}^{-2}$)
b	size parameter in MSRK ($\text{m}^3 \text{mol}^{-1}$)
c	interaction parameter in UNIQUAC
d	interaction parameter in UNIQUAC (K)
E	interaction energy (J)
G	molar Gibbs free energy (J mol^{-1})
k	Boltzmann constant (J K^{-1})
m_a, m_b	substance parameters in MSRK
N	number of data points
n	amount of substance (mol)
P	σ -profile
p	pressure (Pa)
q	surface area parameter in UNIQUAC
R	gas constant ($\text{J mol}^{-1} \text{K}^{-1}$)
r	volume parameter in UNIQUAC
T	temperature (K)
V	volume (m^3)
v	molar volume ($\text{m}^3 \text{mol}^{-1}$)
x	mole fraction in liquid phase
y	mole fraction in vapor phase

Greek letters

γ	activity coefficient
δ	deviation between calculated and experimental results
θ	surface area fraction in UNIQUAC
λ_a, λ_b	parameters in MHV1 mixing rule
μ	chemical potential (J)
σ	charge density on molecular surface ($\text{e } \text{\AA}^{-2}$)
φ	fugacity coefficient

Subscripts

c	critical property
HB	hydrogen bonding contribution to interaction energy
i, j, k	components i – k
int	interaction energy
misfit	electrostatic misfit contribution to interaction energy
r	reduced property
S	surface contact segment on molecular surface
vdW	van der Waals interaction contribution to interaction energy
0	zero pressure
1, 2, 3	components 1–3

Superscripts

C	combinatorial contribution
E	excess property
k	data point
L	liquid phase
R	residual contribution

V	vapor phase
I, II	phases I and II
o	pure compound property

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