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Correlation of Phase Equilibria for Water + Hydrocarbon Systems at High Temperatures and Pressures by Cubic Equation of State

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A modified-Soave-Redlich-Kwong (MSRK) equation of state with an exponent-type mixing rule for the energy parameter and a conventional mixing rule for the size parameter is applied to correlate the phase equilibria for four binary mixtures of water + hydrocarbon (benzene, hexane, decane, and dodecane) systems at high temperatures and pressures. It is noted that good correlation results are obtained by using the mixing rules with interaction parameters between unlike molecules.

Introduction

Recently, many kinds of new chemical processes using supercritical water as a reaction solvent have been studied. The processes, in which waste plastics and biomasses are decomposed rapidly in supercritical water and chemical raw materials are recovered, are the focus of much attention from the stand points of recycling of resources and environmental conservation. In such processes, low molecular weight hydrocarbons such as aromatic compounds and paraffins are produced as decomposed products. Therefore, it is very important to understand phase equilibria for water + hydrocarbon systems at high temperatures and pressures for process design.

Among many methods reported for calculation of phase equilibria, a cubic equation of state seems to be useful because of its simplicity and it can provide successful phase equilibria by selecting suitable mixing rules. The SRK equation of state is one of the most popular cubic equations of state used in process design. In this work, therefore, a modified-SRK (MSRK) equation of state (Sandarusi *et al.*, 1986) was adopted to correlate the phase equilibria. An MSRK equation of state is proposed by modifying the attractive term of the SRK equation of state in order to calculate the saturated vapor pressures of many organic and inorganic compounds accurately. The phase equilibria of

four binary mixtures of water + hydrocarbon (benzene, hexane, decane, and dodecane) systems at high temperatures and pressures were correlated by the MSRK equation of state with an exponent-type mixing rule previously proposed (Higashi *et al.*, 1994) for the mixtures containing polar substances.

1. MSRK Equation of State

The MSRK equation of state (Sandarusi *et al.*, 1986) is given as follows.

$$p = \frac{RT}{(v-b)} - \frac{a(T)}{v(v+b)} \quad (1)$$

where

$$a(T) = \frac{0.42747\alpha(T)R^2T_C^2}{P_C} \quad (2)$$

$$b = \frac{0.08664RT_C}{P_C} \quad (3)$$

and

$$\alpha(T) = 1 + (1 - T_r) \left(m + \frac{n}{T_r} \right) \quad (4)$$

The critical properties required and the parameters m and n for water and four hydrocarbons used in the present work are listed in **Table 1**.

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Table 1 Critical properties and parameters m and n (Sandarusi *et al.*, 1986)

Substance	T_c [K]	p_c [MPa]	m	n
Water	647.3	22.1	0.9500	0.1630
Benzene	562.1	4.90	0.6043	0.2285
Hexane	507.4	3.01	0.7446	0.2476
Decane	617.6	2.11	0.8905	0.3863
Dodecane	658.2	1.82	0.9604	0.4479

2. Exponent-Type Mixing Rules

In this work, an exponent-type mixing rule proposed in the previous study (Higashi *et al.*, 1994) is adopted for the energy parameter a . Namely, the parameter a is given by

$$a = \sum_i \sum_j x_i^{\beta_{ij}} x_j^{\beta_{ji}} a_{ij} \quad (5)$$

The mixing rule is characterized by the empirical exponent parameters β which represent a deviation from random mixing. In this work, the following expressions are assumed for simplicity.

$$\beta_{11} = \beta_{22} = \beta_{21} = 1 \quad (6)$$

Furthermore, the following combining rule is adopted.

$$a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j} \quad (7)$$

where k_{ij} is the interaction energy parameter between unlike molecules. The following mixing and combining rules are used for the size parameter b .

$$b = \sum_i \sum_j x_i x_j b_{ij} \quad (8)$$

and

$$b_{ij} = (1 - l_{ij}) \frac{b_i + b_j}{2} \quad (9)$$

where l_{ij} is the interaction size parameter between unlike molecules. The fugacity required to calculate phase equilibria can be readily derived from Eq. (1) and the mixing rules.

3. Results and Discussion

The phase equilibria for water + decane, + benzene, + dodecane, and + hexane systems, which are typical water + paraffin and water + aromatic compound binary systems, are correlated. The values of

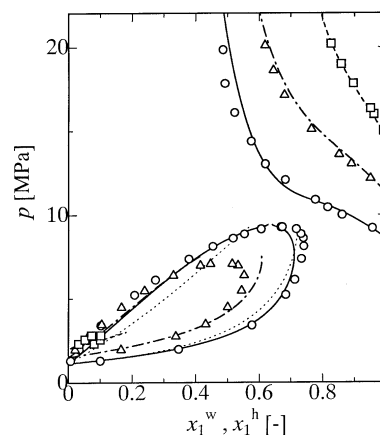


Fig. 1 Phase equilibria for water (1) + decane (2) system: Experimental data of Wang and Chao (1990), (○) 573.2 K, (△) 593.2 K, (□) 613.2 K; Calculated results of present mixing rules, (—) 573.2 K, (- - -) 593.2 K, (- · -) 613.2 K; Calculated results of modified conventional mixing rule, (· · ·) 573.2 K

k_{12} , l_{12} , and β_{12} are adjusted to give precise fits to the experimental data.

3.1 Water + decane system

Phase equilibria for a water + decane system at 573.2, 593.2, and 613.2 K are correlated. At these temperatures, two different phase equilibrium regions, which are regarded as vapor-liquid equilibria (VLE) and liquid-liquid equilibria (LLE), exist depending on composition and pressure (Wang and Chao, 1990). The authors evaluated the parameters k_{12} , l_{12} , and β_{12} . The phase equilibria at the three temperatures can be correlated using the constant parameter values in the LLE region. The values are listed in **Table 2**. On the other hand, in the VLE region, the parameter k_{12} should be expressed by the following equation;

$$k_{12} = -0.78 + \frac{700}{T} \quad (10)$$

though l_{12} and β_{12} are constants as listed in Table 2.

Figure 1 shows the phase equilibria for the water + decane system. As illustrated in Fig. 1, both VLE and LLE calculated are in good agreement with the experimental data though VLE at 593.2 K show slight deviations. As shown in Table 2, the value of the parameter β_{12} is equal to unity for the LLE region, namely, conventional mixing rules give good results in this region. However, contribution of the parameter β_{12} is important in the VLE region. In other words, the distribution of molecules in the VLE region seems to be much different from random distribution.

Furthermore, the modified conventional mixing rules which have two adjustable parameters proposed by Adachi and Sugie (1986) are compared with the present mixing rules. The modified conventional mixing rules are shown as follows.

Table 2 Correlation results for water(1) + hydrocarbon (2) systems

System	Temp. [K]	k_{12}	l_{12}	β_{12}	N^*	Dev. $^{**} \times 10^2$	Ref.
Water(1) + Decane(2)	573.2 (VLE)	0.44	0.40	2.1	22	2.5	a
	(LLE)	0.36	0.10	1.0	20	0.9	a
	593.2 (VLE)	0.40	0.40	2.1	16	3.0	a
	(LLE)	0.36	0.10	1.0	10	0.8	a
	613.2 (VLE)	0.36	0.40	2.1	6	1.8	a
	(LLE)	0.36	0.10	1.0	14	0.6	a
Water(1) + Benzene(2)	498.2	0.20	0.12	1.35	12	3.4	b
	553.2	0.21	0.12	1.35	10	1.7	b
	573.2	0.21	0.12	1.35	10	1.3	b
	579.6	0.22	0.12	1.35	10	2.7	b
	603.2	0.22	0.12	1.35	7	0.9	b
Water(1) + Dodecane(2)	603.6 (VLE)	0.49	0.33	2.02	18	1.5	c
	(LLE)	0.27	0.07	0.55	14	0.2	c
	633.0 (VLE)	0.44	0.14	1.78	14	1.2	c
Water(1) + Hexane(2)	628.0	0.06	-0.89	3.42	14	0.9	d

*Number of data points

$$^{**} \text{Dev.} = \frac{1}{N} \left(\sum |x_{1,\text{calc}}^{\text{h}} - x_{1,\text{exp}}^{\text{h}}| + \sum |x_{1,\text{calc}}^{\text{w}} - x_{1,\text{exp}}^{\text{w}}| \right)$$

a; Data of Wang and Chao (1990), b; Rebert and Kay (1959), c; Stevenson *et al.* (1994), d; De Loos *et al.* (1982)

$$a = \sum_i \sum_j x_i x_j a_{ij} \quad (11)$$

where

$$a_{ij} = \left[1 - \left\{ s_{ij} + u_{ij} (x_i - x_j) \right\} \right] \sqrt{a_i a_j} \quad (12)$$

$$b = \sum_i x_i b_i \quad (13)$$

The calculated results are illustrated in Fig. 1. As shown in Fig. 1, it seems difficult to correlate the VLE at 573.2 K by the modified conventional mixing rules proposed by Adachi and Sugie. The present mixing rules can give a particularly good correlation for the VLE in the decane rich phase.

3.2 Water + benzene system

In the water + benzene system, correlations are carried out at 498.2, 553.2, 573.2, 579.6, and 603.2 K. In this system, a heteroazeotropic point exists at 498.2 K. Because 553.2 K is above the three-phase critical end point temperature, a heteroazeotropic point does not exist, and the phase diagram consists of both VLE and LLE regions. VLE changes to LLE with increasing pressure. In water rich regions, the vapor phase changes to a liquid phase without a volume change at the transition point. The phase behaviors mentioned

above appear from 541.5 to 579.6 K. The critical solution temperature is reported as 579.6 K (Rebert and Kay, 1959).

The values of l_{12} and β_{12} are determined as constants, and k_{12} are expressed as a function of temperature as follow.

$$k_{12} = 0.30 - \frac{49}{T} \quad (14)$$

The parameters determined and the correlation performance are listed in Table 2 and illustrated in Fig. 2. In this system, good correlation results are obtained for all temperatures. The vapor phase compositions calculated in the benzene rich phase show slight deviations from the experimental data at 498.2 K.

The performance of the present mixing rules is compared with that of an unsymmetrical mixing rule (Kabadi and Danner, 1985). The unsymmetrical mixing rule was proposed to improve the energy parameter a for the calculation of water + hydrocarbon systems. As shown in Eq. (15), Kabadi and Danner (1985) divided the water + hydrocarbon interaction term a_{wi} into two terms: a'_{wi} as a measurement of molecule-molecule attraction between water and hydrocarbon and a concentration-dependent term $a''_{wi} x_w$ as a measurement of the structural effect of the hydrocarbon on water. The unsymmetrical mixing rule is shown as follows.

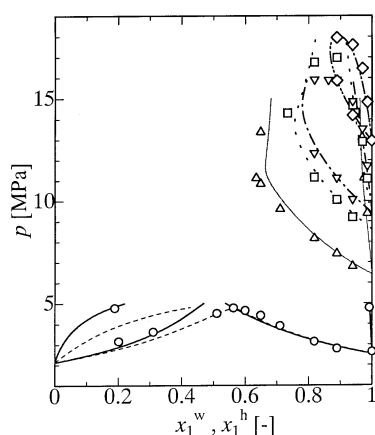


Fig. 2 Phase equilibria for water(1) + benzene(2) system: Experimental data of Rebert and Kay (1959), (○) 498.2 K, (△) 553.2 K, (□) 573.2 K, (▽) 579.6 K, (◇) 603.2 K: Calculated results of present mixing rules, (—) 498.2 K, (---) 553.2 K, (- · - ·) 573.2 K, (- · - ·) 579.6 K, (- · - ·) 603.2 K: Calculated results of unsymmetrical mixing rule, (- - -) 498.2 K

$$a_{wi} = a'_{wi} + a''_{wi} x_w \quad (15)$$

therefore,

$$a = \sum_{i=1}^n \sum_{j=1}^n x_i x_j a_{ij} + \sum_{i=1}^n a''_{wi} x_w^2 x_i \quad (16)$$

where $a_{ij} = a_{ji}$; $a_{ij} = (a_i a_j)^{1/2}$ if i and j are both hydrocarbons; and $a_{ij} = (1/2)a'_{wj}$ if i is water and j is hydrocarbon. The mixing rule for size parameter b is the same as Eq. (13). Since the unsymmetrical mixing rule can be applied only up to 533.2 K, the calculated results of water + benzene system at 498.2 K are compared. The calculated results using the unsymmetrical mixing rule are also shown in Fig. 2. The present mixing rules give particularly good correlated results compared with the unsymmetrical mixing rule proposed by Kabadi and Danner (1985) in the benzene rich region.

Since the unsymmetrical mixing rule is based on a group contribution method, it has the advantage that it is possible to calculate phase equilibria without fitting parameters. However, the unsymmetrical mixing rule can be applied only up to 533.2 K and therefore it cannot be applied near the critical region.

3.3 Water + dodecane and water + hexane systems

The calculations of water + dodecane (Stevenson *et al.*, 1994) and water + hexane (De Loos *et al.*, 1982) systems were carried out at 603.6–633.0 K and 628.0 K, respectively. The calculated deviations and the parameters in the present mixing rules are listed in Table 2. In the case of water + dodecane system, the values of the parameter β_{12} in the VLE region are close to those of the water + decane system. The deviations in

the VLE correlation of water + dodecane and water + hexane systems are small.

Conclusion

Phase equilibria of four binary systems, namely water + decane, + benzene, + dodecane, and + hexane systems at high temperatures and pressures are correlated by using the MSRK equation of state with an exponent-type mixing rule previously proposed. The calculated results are in good agreement with the experimental data for all systems.

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Nomenclature

a	=	parameter of EOS	[Pa·m ⁶ ·mol ⁻²]
a'_{wi}	=	parameter indicate water-hydrocarbon interaction in Eq. (15)	[Pa·m ⁶ ·mol ⁻²]
a''_{wi}	=	parameter indicate structural effect of hydrocarbon interaction in Eq. (15)	[Pa·m ⁶ ·mol ⁻²]
b	=	parameter of EOS	[m ³ ·mol ⁻¹]
k	=	interaction energy parameter	[—]
l	=	interaction size parameter	[—]
m, n	=	parameters in Eq. (4)	[—]
p	=	pressure	[Pa]
R	=	gas constant	[m ³ ·Pa·mol ⁻¹ ·K ⁻¹]
s	=	interaction energy parameter	[—]
T	=	temperature	[K]
u	=	interaction energy parameter	[—]
v	=	molar volume	[m ³ ·mol ⁻¹]
x	=	mole fraction	[—]
β	=	exponent in Eq. (5)	[—]

<Subscript>

C	=	critical property
i, j	=	components i and j
r	=	reduced property
1	=	component 1 (water)
2	=	component 2 (hydrocarbon)

<Superscript>

h	=	hydrocarbon rich phase
w	=	water rich phase

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