

## Calculation of phase equilibrium for water+carbon dioxide system using nonrandom lattice fluid equation of state

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**Abstract**—For the geological sequestration of carbon dioxide to prevent global warming, the phase equilibrium data for water and carbon dioxide mixture play an important role in process design and operation. In this work, the non-random lattice fluid equation of state with hydrogen bonding (NLF-HB EOS) was applied for the prediction of phase equilibrium of mixtures containing water and carbon dioxide. A new set of pure component parameters for carbon dioxide above critical condition was found and optimum binary interaction parameters were reported to correlate mutual solubility of mixtures. The calculated results were compared with the Peng-Robinson Equation of State with the conventional mixing rule (PR-EOS) and the Wong-Sandler mixing rule (PR-WS-EOS). The calculation results show that NLF-HB EOS can correlate mutual solubility of water+carbon dioxide mixtures with reasonable accuracy within a single theoretical framework.

Key words: Mutual Solubility, Carbon Dioxide, Water, Equation of State

### INTRODUCTION

The properties of mixtures containing water and carbon dioxide have significant importance in geological sciences and many industrial processes. Particularly, the phase equilibrium for CO<sub>2</sub>-H<sub>2</sub>O mixture is the most important information for geological sequestration processes. Water and methane are the most common impurities involved in carbon dioxide sequestration processes [1-3]. Modeling the phase equilibrium for a carbon dioxide+water mixture is a difficult task owing to the complex nature of components involved. Water is a hydrogen-bonding species whereas carbon dioxide cannot form hydrogen bond. Carbon dioxide is weakly polar species at low temperatures and behaves as nonpolar component at high temperature limit. Slight presence of water in the carbon-dioxide rich phase significantly influences the overall properties of condensed phase mixture at high pressure.

In 1964, Takenouch and Kennedy [4] reported that CO<sub>2</sub>-rich phase and H<sub>2</sub>O-rich phase are immiscible over a wide range of temperature and pressure. Some researchers [5,6] tried to predict the phase equilibrium using virial coefficients to account for the deviation from ideal condition. This type of research cannot be extended to high pressure range owing to the nature of the virial equation. Panagiotopoulos and Reid [7] applied composition-dependent mixing rule using cubic EOS, which is thermodynamically inconsistent [8]. Bamberger [9] studied the phase equilibrium for the high pressure region using the similar composition-dependent mixing rule. Wong and Sandler [10] proposed a consistent mixing rule, and Shyu and

coworkers [11] applied the Wong-Sandler mixing rule using Peng-Robinson EOS for the calculation of phase equilibrium for the water-carbon dioxide mixture. Two temperature-dependent binary interaction parameters were used in study. King and coworkers [12] correlated mutual solubility of supercritical and liquid carbon dioxide in water using the Kritcherskii-Kasanovskii equation [13]. However, this equation was identified as a limited model and cannot be applicable to high temperature ranges [14]. Although some previous results show reasonable correlation of experimental data, models are a combination of two models (excess Helmholtz energy model+excess Gibb energy model) with two or more adjustable binary interaction parameters.

Nonrandom lattice fluid equation of state (NLF EOS) was originally developed for the mixtures with large difference in molecular sizes [15,16]; this theory was extended to polar mixtures using hydrogen bond lattice statistics (NLF-HB EOS) [17]. This model has been tested for various types of systems [18]. In this work, NLF-HB EOS was applied for the calculation of phase equilibrium containing water and carbon dioxide. The main purpose of this work is to provide a reliable correlation with single theoretical framework and minimum number of binary interaction parameters.

### THEORY

#### 1. PR EOS (Peng-Robinson Equation of State)

The Peng-Robinson equation of state [19] is one of the most widely-used engineering EOS:

$$P = \frac{RT}{v-b} - \frac{a(T)}{v(v+b) + (v-b)^2} \quad (1)$$

For a pure fluid, constant  $b$  is given by

$$b = 0.007780 \left( \frac{RT_c}{P_c} \right) \quad (2)$$

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<sup>\*</sup>This paper is dedicated to Professor Jae Chun Hyun for celebrating his retirement from Department of Chemical and Biological Engineering of Korea University.

**Table 1. Pure component parameters used for the correlation of experimental data with the PR and PR-WS equation of state**

Comp.	M.W.	T <sub>c</sub> (K)	P <sub>c</sub> (MPa)	ω	C <sub>1</sub>	C <sub>2</sub>	C <sub>3</sub>	Ref.
Water	18.02	647.14	22.060	0.344	0.6697	2.6135	-6.8237	[21]
CO <sub>2</sub>	44.01	304.14	7.375	0.239	0.6035	2.5178	-13.6530	[21]
Hexane	86.18	507.60	3.025	0.299	0.8708	-0.7041	1.8596	[21]

While  $a(T)$ , a function of temperature, is given by

$$a(T)=a(T_c)\alpha(T_r,\omega) \quad (3)$$

$$a(T_c)=0.45724\frac{R^2T_c^2}{P_c} \quad (4)$$

$$\alpha(T_r,\omega)=\sqrt{1+m(1-T_r^{1/2})} \quad (5)$$

$$m=0.37464+1.54226\omega-0.26992\omega^2 \quad (6)$$

A simple classical mixing rule with one binary interaction parameter ( $k_{ij}$ ) was used to calculate mutual solubility of CO<sub>2</sub> and H<sub>2</sub>O systems:

$$a_{mix}=\sum_i\sum_j\sqrt{a_{ij}a_{ji}}x_ix_j(1-k_{ij}) \quad (7)$$

Mathias and Copeman [20] suggested the component-specific  $\alpha(T)$  equation as the following equation with three parameters for each component.

$$\alpha(T)=[1+C_1(1-T_r^{0.5})+C_2(1-T_r^{0.5})^2+C_3(1-T_r^{0.5})^3] \quad (8)$$

Three parameters ( $C_1$ ,  $C_2$  and  $C_3$ ) for the PR EOS were obtained from vapor pressure data provided in KDB (Korean Thermophysical Properties Data Bank) [21]. Pure component parameters and Mathias-Copeman parameters for the correlation of experimental data with PR-WS EOS are summarized in Table 1.

## 2. PR-WS EOS (Peng-Robinson Equation of State with the Wong and Sandler Mixing Rules)

Wong and Sandler [22,23] proposed a mixing rule which is applicable to associating mixtures at high pressure. This model also became one of the most popular methods for process design due to its simplicity and the ability to utilize the collection of activity coefficient model database. The Wong-Sandler mixing rule is based on the following assumption:

$$G^E(T, P=1 \text{ bar}, x_i) \approx A^E(T, P=1 \text{ bar}, x_i) \approx A^E(T, \text{high } P, x_i) \quad (9)$$

**Table 2. Pure component parameters (volume and surface fraction) for UNIQUAC model used in PR-WS mixing rule**

Component	r <sub>i</sub>	q <sub>i</sub>	Ref.
Water	0.92	1.40	[21]
CO <sub>2</sub>	1.32	1.28	[21]
Hexane	4.50	3.86	[21]

**Table 3. Pure parameters (energy parameters and size parameters) for the NLF-HB equation of state**

Comp.	ε <sub>a</sub>	ε <sub>b</sub>	ε <sub>c</sub>	r <sub>a</sub>	r <sub>b</sub>	r <sub>c</sub>
Water	154.9086	-0.3952	-0.3994	1.2890	0	0
CO <sub>2</sub>	93.2000	-0.1370	-0.1946	2.7277	0.0100	0.0880
Hexane	113.2402	-0.0220	-0.0380	8.2836	0	0

An excess Gibbs energy model is required for the PR-WS EOS. The UNIQUAC model [24] is used for  $G^E$  in this study. This activity model introduces two additional pure component parameters ( $r_i$ ,  $q_i$ ) which are shown in Table 2. Thus, the PR-WS EoS model uses eight parameters for pure species composed of three critical constants ( $T_c$ ,  $P_c$ , acentric factor), three Mathias-Copeman parameters ( $C_1$ ,  $C_2$  and  $C_3$ ) and two UNIQUAC parameters ( $r_i$ ,  $q_i$ ).

## 3. NLF-HB EOS (Nonrandom Lattice Fluid with Hydrogen-Bonding Equation of State)

The NLF EoS was proposed by You [15,16] and extended to the associating system, the NLF-HB EoS model [17,18].

The expression of chemical potential of the NLF-HB EoS is given as,

$$\begin{aligned} \mu_i/RT = & (r_i + l_i) \ln \left[ 1 + \left( \frac{q_M}{r_M} - 1 \right) \rho \right] - r_i \ln(1 - \rho) + \ln \left( \frac{\theta}{q_i} \right) + \left( \frac{z\beta}{2} \right) q_i \varepsilon_M \theta^2 \\ & \times \left[ 1 - \frac{r_i}{q_i} - \frac{2 \sum_k \theta_k \varepsilon_{ik} + \beta \sum_k \sum_l \theta_k \theta_l \varepsilon_{ij} (\varepsilon_{ij} + 2\varepsilon_{kl} - 2\varepsilon_{jk} - \varepsilon_{ik})}{\varepsilon_M \theta^2} \right] \\ & - \sum_k d_k' \ln \frac{N_d^k}{N_{k0}} - \sum_l a_l' \ln \frac{N_a^l}{N_{l0}} \end{aligned} \quad (10)$$

If associating components are present in the mixture, the following nonlinear equations have to be solved.

$$N_{kl}^{HB} N_r = N_{k0} N_{l0} \exp(-\beta A_{kl}) \quad (11)$$

The size and energy parameters can be determined using the properties of pure components (vapor pressure and saturation liquid density). The pure component size and energy parameters were assumed as the following temperature-dependent function:

$$r_i = r_a + r_b(T - T_0) + r_c [T \ln(T/T_0) + T - T_0] \quad (12)$$

$$\varepsilon_{ij}/k = \varepsilon_a + \varepsilon_b(T - T_0) + \varepsilon_c [T \ln(T/T_0) + T - T_0] \quad (13)$$

where the reference temperature  $T_0$  is 298.15 K. Pure parameters (energy parameters and size parameters) of CO<sub>2</sub> and H<sub>2</sub>O for NLF-HB EoS are given in Table 3.

In this study, two component-specific parameters ( $r_i$  and  $\varepsilon_i$ ) of carbon dioxide were re-estimated to get better results for the mutual solubility calculation by the NLF-HB EoS model. Because vapor pressure and saturation liquid densities are no longer available beyond the critical point, size and energy parameters were fitted to get a fair result of the pressure-volume-temperature (PVT) relation and phase equilibrium calculation.

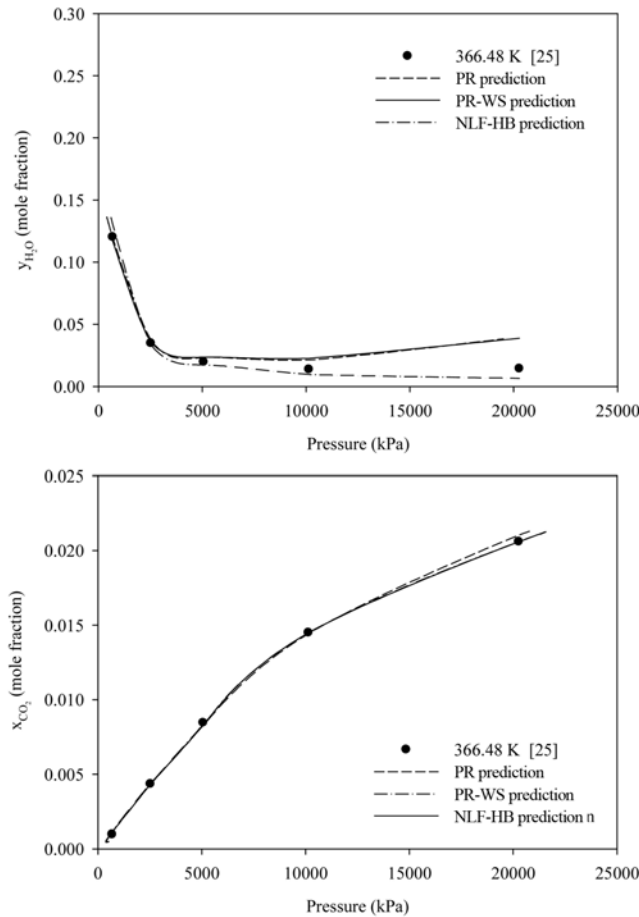
The interaction energy for i-j segment contacts is represented as

$$\varepsilon_{ij} = (\varepsilon_i \varepsilon_j)^{1/2} (1 - k_{ij}) \quad (14)$$

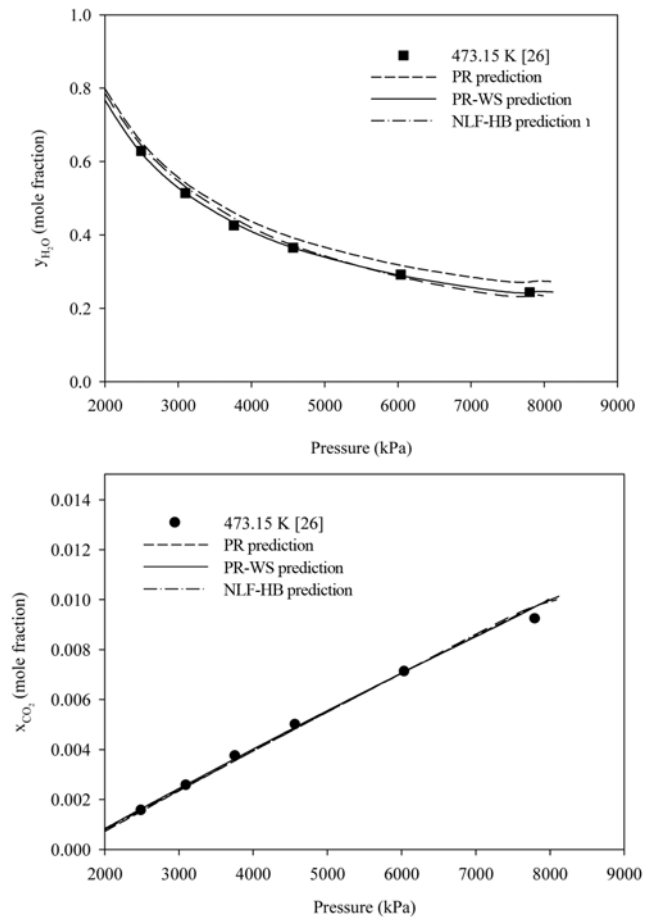
A single temperature-dependent binary interaction parameter ( $k_{ij}$ ) has been used to fit the data sets for this calculation.

# RESULTS AND DISCUSSION

To correlate mutual solubility of CO<sub>2</sub> and H<sub>2</sub>O systems, three EOS models were compared with published experimental data [25, 26] within the ranges of pressure (1-10,000 kPa) and temperature



**Fig. 1. Mutual solubility of H<sub>2</sub>O and CO<sub>2</sub> at 366.48 K.** Experimental data [25] are shown as symbols and correlations are shown as lines by three EOS: PR, PR-WS and NLF-HB. H<sub>2</sub>O mole fraction in the CO<sub>2</sub> rich-phase (upper figure) and CO<sub>2</sub> mole fraction in the H<sub>2</sub>O rich-phase (lower figure).



**Fig. 2. Mutual solubility of H<sub>2</sub>O and CO<sub>2</sub> at 473.15 K.** Experimental data [25] are shown as symbols and correlations are shown as lines by three EOS: PR, PR-WS and NLF-HB. H<sub>2</sub>O mole fraction in the CO<sub>2</sub> rich-phase (upper figure) and CO<sub>2</sub> mole fraction in the H<sub>2</sub>O rich-phase (lower figure).

**Table 4. Comparison of mutual solubility calculation results of carbon dioxide and water at 366.48 K [25] and 473.15 K [26]**

T (K)	PR			$k_{ij}$ $a_{ij}$ $a_{ji}$	PR-WS		NLF-HB		
	$k_{ij}$	AADP (%)	AADy (%)		AADP (%)	AADy (%)	$k_{ij}$	AADP (%)	AADy (%)
366.48	-0.0476	3.95	0.96	-2.98E-01 1.40E+03 1.22E+03	3.16	0.80	0.0177	2.89	0.62
473.15	0.0299	1.87	2.56	3.76E-01 2.50E+03 1.06E+02	2.04	0.64	0.3630	1.69	0.79

$$AADP = \frac{1}{N_{data}} \sum_i \left| \frac{P_i^{exp} - P_i^{cal}}{P_i^{exp}} \right| \times 100, \quad AADy = \frac{1}{N_{data}} \sum_i |y_i^{exp} - y_i^{cal}| \times 100$$

(348.15–473.15 K).

Fig. 1 shows a comparison of the calculation result at 366.48 K [25]. The H<sub>2</sub>O mole fraction in the CO<sub>2</sub> rich-phase and the CO<sub>2</sub> mole fraction in the H<sub>2</sub>O rich-phase are calculated and represented in this Fig. 1. Mutual solubility of the carbon dioxide and water system at 473.15 K [26] is also calculated and shown in Fig. 2. The numeri-

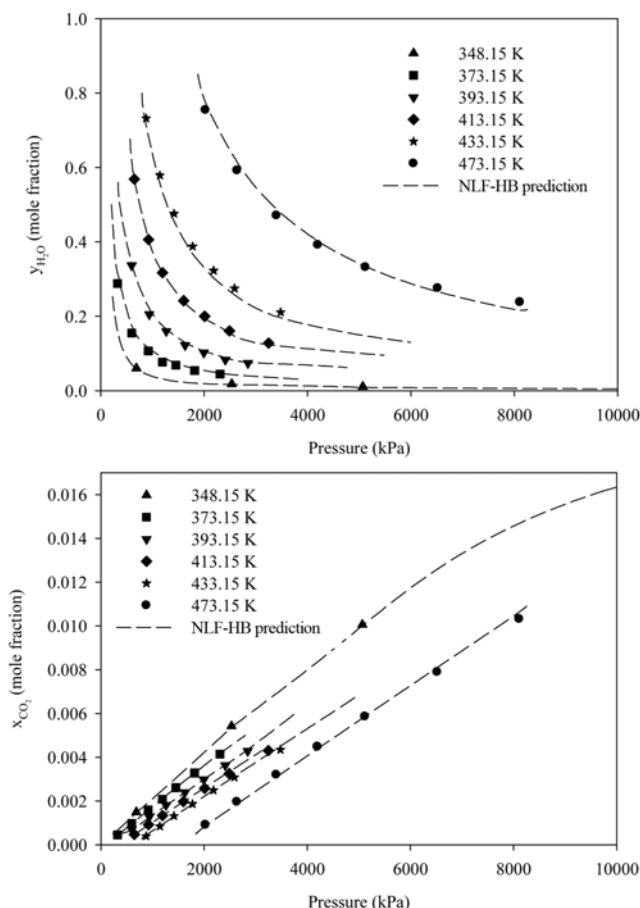


Fig. 3. Mutual solubility of H<sub>2</sub>O and CO<sub>2</sub> along with changes of temperature. Experimental data [26] are shown as symbols and correlations are shown as line by NLF-HB EOS. H<sub>2</sub>O mole fraction in the CO<sub>2</sub> rich-phase (upper figure) and CO<sub>2</sub> mole fraction in the H<sub>2</sub>O rich-phase (lower figure).

Table 5. Mutual solubility prediction results of H<sub>2</sub>O and CO<sub>2</sub> along with changes to temperature using the NLF-HB EOS

T (K)	NLF-HB		
	$k_{ij}$	AADP (%)	AADy (%)
348.15	-0.0044	1.46	0.31
373.15	0.0114	0.65	1.12
393.15	0.0517	1.01	0.58
413.15	0.1089	1.16	0.25
433.15	0.2021	1.33	1.56
473.15	0.3418	1.69	0.79

$$\text{AADP} = \frac{1}{N_{\text{data}}} \sum_i \left| \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right| \times 100, \quad \text{AADy} = \frac{1}{N_{\text{data}}} \sum_i |y_i^{\text{exp}} - y_i^{\text{cal}}| \times 100$$

cal results at 366.48 K and 473.15 K are summarized in Table 4. The calculated results of mutual solubility in H<sub>2</sub>O and CO<sub>2</sub> systems along with changes to temperature by the NLF-HB model are shown in Fig. 3 and Table 5, respectively.

### 1. Comparison of Calculation Results

As shown in Figs. 1-2 and Table 4, NLF-HB EOS shows best results among three models - PR EOS, PR-WS EOS and NLF-HB EOS. PR EOS has larger differences in pressure ranging from 1.87 to 3.95% and mole fraction error ranging from 0.96 to 2.56%, but NLF-HB EOS and PR-WS EOS have smaller differences in pressure and mole fraction.

Especially at low temperature and CO<sub>2</sub>-rich phase, NLF-HB shows superior results among the three models. A possible reason for such behavior is that the correct consideration of hydrogen bonding of water is reflected in NLF-HB EOS. Fig. 3 shows the calculation result along with changes with temperature. We can identify that the NLF-HB EOS has smaller differences in pressure ranging from 1.01 to 1.69% and mole fraction error ranging from 0.25 to 1.56%. Numerical values of binary interaction parameters are summarized in Table 5.

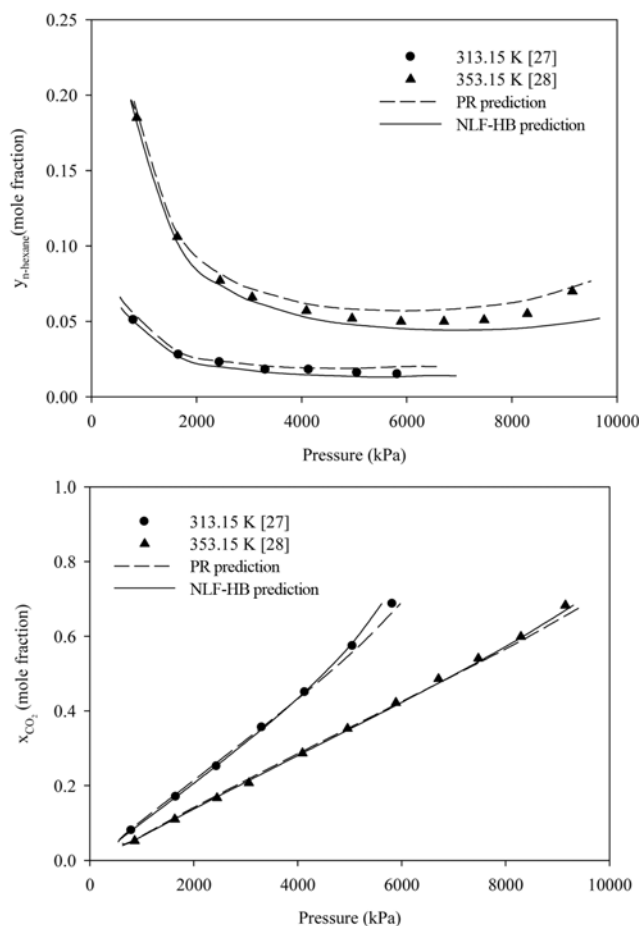


Fig. 4. VLE calculation result for n-hexane and CO<sub>2</sub> at 313.15 K and 353.15 K. Experimental data [27,28] are shown as symbols and correlations are shown as lines by two EOS: PR and NLF-HB. N-Hexane mole fraction in the CO<sub>2</sub> rich-phase (upper figure) and CO<sub>2</sub> mole fraction in the n-hexane rich-phase (lower figure).

**Table 6. Comparison of VLE calculation results of the n-hexane and carbon dioxide system**

T(K)	PR			NLF-HB		
	$k_{ij}$	AADP (%)	AADy (%)	$k_{ij}$	AADP (%)	AADy (%)
313.15	0.1246	2.58	0.31	0.1189	1.02	0.21
353.15	0.1243	2.86	0.70	0.1121	1.60	0.62

$$\text{AADP} = \frac{1}{N_{\text{data } i}} \sum_i \left| \frac{P_i^{\text{exp}} - P_i^{\text{cal}}}{P_i^{\text{exp}}} \right| \times 100, \quad \text{AADy} = \frac{1}{N_{\text{data } i}} \sum_i |y_i^{\text{exp}} - y_i^{\text{cal}}| \times 100$$

## 2. Application to Carbon Dioxide+n-Hexane System

To test the validity of the NLF-HB model and new carbon dioxide parameters, reference data [27,28] of VLE for the binary n-hexane and carbon dioxide systems at 313.15 K and 353.15 K were also compared with PR EOS. N-hexane is a nonpolar component and can be a good candidate to verify the validity of new parameters at supercritical condition of carbon dioxide. As shown in Table 5, pressure and mole fraction differences are smaller for NLF-HB EOS compared with PR-EOS.

## CONCLUSION

The mutual solubility of CO<sub>2</sub> and H<sub>2</sub>O systems was correlated by three EOS models: the Peng-Robinson Equation of State (PR EOS), the Peng-Robinson equation of state with the Wong and Sandler mixing rules (PR-WS EOS), and the nonrandom lattice fluid equation of state with hydrogen binding (NLF-HB EOS). Published experimental data within the ranges of pressure (1–10,000 kPa) and temperature (up to 473.15 K) were examined. For the NLF-HB calculation, two component-specific parameters ( $r_i$  and  $\varepsilon_i$ ) of carbon dioxide were re-estimated to give better results at the supercritical condition. NLF-HB EOS gives better results with fewer binary interaction parameters (1 temperature dependent parameter) compared with PR-WS EOS (3 temperature dependent parameters).

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## NOMENCLATURE

- a, d : number of acceptor or donor groups, respectively
- R : gas constant [=8.314 J/mol K]
- P : pressure [MPa]
- T : absolute temperature [K]
- T<sub>0</sub> : reference temperature, 298.15 K
- R : gas law constant
- N<sub>i</sub> : the number of molecules of the species i
- k : binary interaction parameter for i-j contacts
- l<sub>i</sub> : bulkiness factor
- q<sub>i</sub> : surface area parameter
- q<sub>M</sub> : mole fraction average of q<sub>i</sub>

- r<sub>i</sub> : segment number
- r<sub>M</sub> : mole fraction average of r<sub>i</sub>
- z : lattice coordination number

## Greek Letters

- β : kT where k is the Boltzmann constant
- ε : interaction energy parameter between components
- μ : chemical potential
- θ : surface area fraction of a component
- ρ : reduced density

## Subscripts

- i : component i
- ij : interactions between components i and j
- M : mixture

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