Determination of Mutual Solubility between CO_2 and Water by Using the Peng−Robinson Equation of State with Modified Alpha Function and Binary Interaction Parameter

Xiaoli Li and Daoyong Yang*

Petroleum Systems Engineering, Faculty of Engineering and Applied Science, University of Regina, Regina, Saskatchewan, Canada, S4S 0A2

ABSTRACT: Techniques have been developed to determine mutual solubility between CO_2 and water by using the Peng−Robinson equation of state (PR EOS) with a modified alpha function and a new binary interaction parameter (BIP) correlation in the presence and absence of hydrocarbons. More specifically, the alpha function for the water compound is modified by improving its prediction for water vapor pressure in the full temperature range of 273.16 to 647.10 K with an overall absolute average relative deviation (AARD) of 0.07%. Also, the polynomial temperature-dependent BIP correlation for the CO_2−water pair in the aqueous phase is proposed by matching CO_2 solubility in water at temperatures from 273.15 to 448.15 K and pressures up to 100 MPa. It is found that the newly modified alpha function together with the proposed BIP correlation provides more accurate prediction of the CO_2 solubility in water with an overall AARD of 6.12%, compared with 8.67% from the previous exponential BIP correlation. As for the nonaqueous phase of the binary CO_2−water system, it is found that a constant BIP for the CO_2−water pair generally results in a good agreement between the reported and predicted compositions of the CO_2-rich phase. Furthermore, the accurate solubility prediction of either CH_4 or CO_2 in the water-rich phase of the ternary CH_4−CO_2−water systems has been achieved with an overall AARD of 6.15% at a temperature of 344.15 K and pressures of 10, 20, 50, and 75 MPa, respectively.

1. INTRODUCTION

The phase behavior of the CO_2−water system has attracted great interest for industry operations, especially in the area of CO_2 geological sequestration and petroleum development.[1,2] It is a global and challenging task to mitigate CO_2 emissions into the atmosphere since such potential climate change may lead to a rising temperature in the near future.[3] As for a depleted oil reservoir containing a large amount of water after waterflooding and/or coexisting with an aquifer, it is recommended to be a good candidate for geologically storing CO_2 since there exists abundant porous spaces together with generally good caprock.[4] In addition, the solvent-assisted methods, e.g., gas flooding, vapor extraction (VAPEX), and cyclic solvent injection (CSI), have seen certain successful applications for enhancing oil recovery from hydrocarbon reservoirs,[5−7] among which CO_2 is found to be one of the most prevailing agents mainly due to its superior capability of viscosity reduction, swelling effect, and interfacial tension reduction.[8,9] Physically, water inevitably exists in the formation in a form of either initial connate water or injected water, resulting in a range of 5−50% water saturation.[10,11] Thus, it is of fundamental and practical importance to accurately determine the composition of each equilibrium phase of the CO_2−water systems under reservoir conditions in the presence and absence of hydrocarbons.

Several attempts have been made to quantify the phase compositions of gas−water systems.[2,12−15] Henry's law constant is commonly used to compute CO_2 solubility in the aqueous phase, whereas the cubic equation of state (EOS) was used to characterize the nonaqueous phase of CO_2−water systems.[11,12] As such, two different theories are respectively introduced to model the aqueous and nonaqueous phases,

resulting in an unfavorable and inconsistent algorithm associated with phase equilibrium calculation. Also, the statistical associating fluid theory (SAFT)[16,17] has been employed to model the phase behavior of water-involved systems. The corresponding fluid mixtures may be involved with monomeric molecules as well as clusters of like and unlike molecules.[16] Then, various modifications for the SAFT have been developed, e.g., SAFT-VR (variable range)[18,19] and perturbed-chain SAFT.[20] In general, the complicated SAFT theory requires microscopic knowledge of the molecular structures,[21] which might not be applicable in many industry applications.

The Peng−Robinson EOS (PR EOS)[22] has been extensively used to characterize the phase behavior of reservoir hydrocarbon fluids,[9,23−26] while it has been utilized to determine two- or three-phase equilibria for hydrocarbon−water systems (e.g., CH_4−water or C_2H_6−water system).[27] A good reproducibility of compositions in both nonaqueous liquid and nonaqueous vapor phases have been achieved, but the predicted composition for the aqueous phase is inconsistent with the experimental data in several orders of magnitude due to the extremely small hydrocarbon solubility in water.[27] As such, Peng and Robinson suggested the following two modifications for the systems containing water:[28] (a) parameter a in the EOS should incorporate an exclusive alpha function for water compound since the initial one was developed based on a

water-free database and (b) the binary interaction parameters (BIPs) for the aqueous and nonaqueous phases should be treated separately. Consequently, Peng and Robinson developed an alpha function for water in the PR EOS from predicting the vapor pressure of water in a limited temperature range of 284.8 to 466.1 K.[28] Subsequently, Søreide and Whitson proposed a modified alpha function for predicting water vapor pressure within an accuracy of 0.2% at temperatures from 288.2 to 598.15 K.[29] As for the second suggested modification for the PR EOS, limited CO_2 solubility data has been collected to generate a BIP correlation for a CO_2−water pair in the aqueous phase.[29]

In this study, techniques have been developed to determine mutual solubility between CO_2 and water by using the PR EOS with a modified alpha function and a new BIP correlation in the presence and absence of hydrocarbons. More specifically, on the basis of the International Association for the Properties of Water and Steam Formulation 1995 (IAPWS-95),[30] the new alpha function for water compound is correlated by more extensively predicting the water vapor pressure in the full temperature range of 273.16−647.10 K. In addition, 193 experimental data points of CO_2 solubility in water available in the literature at temperatures from 273.15 to 448.15 K have been collected and included in the database to generate the temperature-dependent BIP correlation for CO_2−water pair in the aqueous phase. The newly developed alpha function for water can also be used to accurately compute the nonaqueous phase compositions of CO_2−water systems. Then, the ternary CH_4−CO_2−water systems are introduced to further examine the newly developed alpha function together with the BIP correlations by respectively predicting the mole fractions of CO_2 and CH_4 in the aqueous phase at 344.15 K.

2. MATHEMATICAL FORMULATION

2.1. PR EOS. Due to its wide application in the petroleum and chemical industries, the PR EOS is chosen as the primary EOS for this study. The methodology discussed here will also be applicable to the Soave−Redlich−Kwong EOS (SRK EOS).[31] After being originated from the Redlich−Kwong EOS (RK EOS 1949)[32] and SRK EOS (1972),[31] the PR EOS (1976)[22] is expressed as follows

$$p = \frac{RT}{V_M - b} - \frac{a}{V_M(V_M + b) + b(V_M - b)} \tag{1a}$$

$$a = a_c \alpha \tag{1b}$$

$$a_c = 0.457235 \frac{R^2 T_c^2}{p_c} \tag{1c}$$

$$b = 0.0777969 \frac{RT_c}{p_c} \tag{1d}$$

where p is pressure in megapascals (MPa), T is temperature in kelvin (K), V_M is molar volume in cubic meters per kilomole (m³/kmol), R is the universal gas constant, α is the alpha function which can be formulated in various expressions discussed later, and T_c and p_c are critical temperature in kelvin and pressure in megapascals, respectively.

Mixing Rule. For a mixture system, the following van der Waals' mixing rule is used to calculate the parameters a and b in eq 1a,[33]

$$a = \sum_i \sum_j x_i x_j (a_i a_j)^{0.5} (1 - \delta_{ij}) \tag{2}$$

$$b = \sum_j x_j b_j \tag{3}$$

where x_i and x_j are the compositions of the ith and jth substance, respectively, and δ_{ij} is the BIP between the ith and jth components.

Universal Alpha Function. The initial alpha function in eq 1b for predicting the vapor pressure of a pure substance is given by Peng and Robinson,[22]

$$\alpha_{PR} = [1 + (0.37464 + 1.54226\omega - 0.26992\omega^2)(1 - T_r^{0.5})]^2 \tag{4}$$

where ω is acentric factor, T_r is reduced temperature, the subscript "PR" of α indicates the initials who developed the alpha function. It is worthwhile noting that the water compound is not included in the database to develop eq 4. Recently, a modified alpha function has been proposed by Li and Yang to more accurately predict the vapor pressures of 59 pure substances, e.g., water, CO_2, Ar, CH_4, C_2H_6, and pure heavy alkanes up to *n*-tritetracontane (n-$C_{43}H_{88}$),[34]

$$\begin{aligned} \alpha_{LY} = \exp\{&(0.13280 - 0.05052\omega + 0.25948\omega^2)(1 - T_r) \\ &+ 0.81769\ln[1 + (0.31355 + 1.86745\omega - 0.52604\omega^2) \\ &(1 - \sqrt{T_r})]^2\} \end{aligned} \tag{5}$$

In this study, eq 5 is utilized to determine the parameter a of the nonwater compounds (i.e., CO_2 and CH_4) due to its capability for accurately modeling and predicting the reservoir fluids phase behavior at high pressures and elevated temperatures.[25,26]

Alpha Function for Water. As recommended by Peng and Robinson, a modified alpha function which can accurately reproduce the water vapor pressure, could substantially improve the phase equilibrium calculation for aqueous phase.[28] In this study, on the basis of the IAPWS-95,[30] an exclusive alpha function for water compound is developed to improve its vapor pressure prediction in a wide temperature range.

According to the IAPWS-95, the equation for computing water vapor pressure is updated by Wagner and Pruß as follows,[30]

$$\begin{aligned} p_b = p_c \exp\Bigg\{ \frac{T_c}{T}\Bigg[&d_1\left(1 - \frac{T}{T_c}\right) + d_2\left(1 - \frac{T}{T_c}\right)^{1.5} \\ &+ d_3\left(1 - \frac{T}{T_c}\right)^3 + d_4\left(1 - \frac{T}{T_c}\right)^{3.5} + d_5\left(1 - \frac{T}{T_c}\right)^4 \\ &+ d_6\left(1 - \frac{T}{T_c}\right)^{7.5} \Bigg]\Bigg\} \end{aligned} \tag{6}$$

where p_b is the vapor pressure of water in megapascals, T is temperature in kelvin, p_c = 22.064 MPa, T_c = 647.096 K, d_1 = −7.85951783, d_2 = 1.84408259, d_3 = −11.7866497, d_4 = 22.6807411, d_5 = −15.9618719, and d_6 = 1.80122502. In this work, the vapor pressure of water calculated from eq 6 is used as the benchmark to evaluate the prediction accuracies of various alpha functions incorporated in the PR EOS therein-

Table 1. Database for Developing the BIP Correlation for CO_2–Water Pair in the Aqueous Phase

data points	solubility	unit	T, K	p, MPa	ref
29	5.365–38.500	cm^3/g H_2O	323.15–373.15	2.53–70.93	35
42	11.62–41.07	cm^3/g H_2O	285.15–313.15	2.53–50.66	36
1	39.74	cm^3/g H_2O	298.15	50.66	37
26	0.0038–0.0300	mole fraction	374.15–393.15	2.33–70.32	38
12	2.102–6.614	g/100g H_2O	273.15–298.15	1.01–4.56	39
7	0.0166–0.0317	mole fraction	344.15	10.00–100.00	40
29	0.0080–0.0217	mole fraction	323.20–353.10	4.05–14.11	41
6	0.0156–0.0234	mole fraction	278.05–283.15	2.00–3.70	42
41	0.00063–0.02944	mole fraction	298.15–448.15	1.09–17.55	43

after. It is feasible mainly due to the fact that extensive experimental results can be accurately reproduced by eq 6 on the basis of the current international temperature scale of 1990 (ITS-90), which is the best approximation of the thermodynamic temperature within the present experimental uncertainties.[30] The detailed information of eq 6 can be found elsewhere.[30]

In terms of eq 6, a more comprehensive alpha function for water is correlated by fitting the water vapor pressure (i.e., p_b in eq 6) with the PR EOS in this study. It should be noted that the vapor pressure line in the p–T phase diagram of pure water is confined by the triple point where T_t = 273.16 K and the critical point where T_c = 647.10 K.[30] In our programming generated by using Matlab software (version: R2012a), the temperature step size is set to 1.0 K along such a vapor pressure line. Consequently, the following alpha function, which is not only a function of the reduced temperature of water, but also respectively corresponding to the triple point and critical point, is rigorously proposed in the full temperature range of 273.16–647.10 K,

$$\alpha_{H_2O,modified}$$
$$= [c_1 + c_2(1 - T_{rw}) - c_3(1 - T_{rw}^{-1}) + c_4(1 - T_{rw}^{-2})]^2 \tag{7}$$

where T_{rw} is the reduced temperature of water, c_1 = 1.00095, c_2 = 0.39222, c_3 = 0.07294, and c_4 = 0.00706 with the standard errors of 0.00002, 0.00085, 0.00109, and 0.00023, respectively. The correlated eq 7 coupled with the PR EOS for predicting the water vapor pressure yields an R^2 value of 1.0000, indicating that the regression curve perfectly fits the data. The coefficients c_1–c_4 are regressed by using SigmaPlot software (version 11.0).

In comparison, three alpha functions respectively developed by Peng and Robinson (1980),[28] Søreide and Whitson (1992),[29] and Li and Yang (2010)[34] are also applied to reproduce the water vapor pressure in the full temperature range. The Peng–Robinson correlation is provided as follows[28]

$$\alpha_{H_2O,PR} = [1.0085677 + 0.82154(1 - T_{rw}^{0.5})]^2 \tag{8}$$

It is previously found that eq 8 provides an improved prediction of water vapor pressure in the temperature range of 284.81–466.06 K.[29] Søreide and Whitson then further modified the alpha function for pure water in the following expression:[29]

$$\alpha_{H_2O,SW} = [1 + 0.4530(1 - T_{rw}) + 0.0034(T_{rw}^{-3} - 1)]^2 \tag{9}$$

It is claimed that eq 9 could predict the water vapor pressure within an accuracy of 0.2% at temperatures ranging from 288.15 to 598.15 K.[29] Note that water compound contributes to

develop the Li–Yang alpha function (see eq 5),[34] which is also considered in this study as another candidate alpha function used for predicting the vapor pressure of water here after.

2.2. BIP Correlation. *2.2.1. Aqueous Phase.* As mentioned previously, two sets of BIPs are required in the PR EOS for modeling the aqueous phase and nonaqueous phase compositions, respectively. Compared with hydrocarbons, numerous efforts have been made to determine the CO_2 solubility in water due to its wide industry applications. Herein, it is necessary to clarify that the terminology "solubility" used in this work is defined as the mole fraction of the aqueous compound (i.e., water) in the nonaqueous phase, or the mole fraction of the nonaqueous compound (e.g., CO_2 or CH_4) in the aqueous phase.

As tabulated in Table 1, 193 experimental data points of CO_2 solubility in water are reported in the literature from 1939 to 2013[35−43] at temperatures from 273.15 to 448.15 K and pressures up to 100 MPa have been collected to generate a database. On the basis of this extensive database, a new BIP correlation for the CO_2–water pair in the aqueous phase can be developed and utilized in the PR EOS to accurately determine the aqueous phase composition. Consequently, 193 BIP values can be optimized in the PR EOS to perfectly match the 193 solubility data points. The programming of PR EOS calculation is also developed by using the Matlab software. Finally, the following polynomial BIP correlation which is a function of the reduced temperature is proposed to best fit the optimized BIP values with an R^2 value of 0.9959,

$$\delta_{CO_2,modified}^{AQ} = -1.104324 + 2.040527T_r - 1.417707T_r^2$$
$$+ 0.379003T_r^3 \tag{10}$$

where $\delta_{CO_2,modified}^{AQ}$ is the BIP for the CO_2–water pair in the aqueous phase and T_r is the reduced temperature of CO_2. The coefficients in eq 10 are regressed by using the SigmaPlot software. In comparison, the exponential BIP correlation on the basis of limited database developed by Søreide and Whitson is also used to calculate CO_2 solubility in pure water, i.e.,[29]

$$\delta_{CO_2,SW}^{AQ} = -0.31092 + 0.23580T_r$$
$$- 21.2566\exp(-6.7222T_r) \tag{11}$$

Both eqs 10 and 11 are evaluated in terms of their accuracy for predicting CO_2 solubility in water hereafter.

The ternary CH_4–CO_2–water systems are used to further validate the proposed alpha function for water and the polynomial BIP correlation for the CO_2–water pair in the aqueous phase. It is previously found that the BIP for hydrocarbon–water pair in the aqueous phase is dependent on both temperature and the acentric factor of the hydro-

carbon.[29] Accordingly, the following BIP correlation is used for the CH$_4$−water pair,[29]

$$\delta_{CH_4, SW}^{AQ} = 1.1120 - 1.7369\omega^{-0.1} + (1.1001 + 0.8360\omega)T_r$$
$$- (0.15742 + 1.0988\omega)T_r^2 \tag{12}$$

where $\delta_{CH_4, SW}^{AQ}$ is the BIP for the CH$_4$−water pair in the aqueous phase and T_r is the reduced temperature of CH$_4$.

2.2.2. Nonaqueous Phase. The PR EOS could maintain its high prediction accuracy without performing modification to quantify the compositions of nonaqueous liquid/vapor phase of the systems containing water.[27] As such, the solubility of water in the CO$_2$-rich phase or hydrocarbon-rich phase can be determined with a good agreement between the experimental measurements and the predicted data. In addition, a constant BIP value for either the CO$_2$−water pair or CH$_4$−water pair is found to be sufficient to perform the composition calculation for nonaqueous phase in the CO$_2$/hydrocarbon−water systems.[29] In this study, the BIP constants of 0.1896[29] and 0.5000[27] are assigned to the CO$_2$−water pair and CH$_4$−water pair, respectively. It should also be noted that the BIP for CO$_2$−CH$_4$ pair is set to be 0.1300[40] for either the nonaqueous or aqueous phase.

Regarding the predicted water vapor pressure and the equilibrium phase compositions of the CO$_2$−water systems, the newly developed alpha function and BIP correlation are respectively compared with the previous methods. The absolute average relative deviation (AARD) is used as the objective function to evaluate the prediction accuracy of each method,

$$AARD = \frac{1}{n} \sum_{i=1}^{n} \left| \frac{X_i^{cal} - X_i^{exp}}{X_i^{exp}} \right| \tag{13}$$

where n is the number of data points, X_i^{cal} is the calculated vapor pressure of water or the CO$_2$/CH$_4$ solubility in water, and X_i^{exp} is the measured data collected from the literature.

3. RESULTS AND DISCUSSION

3.1. Alpha Function. The physical and critical properties of CH$_4$, CO$_2$, and water used in this study are tabulated in Table 2.[30,44] As can be seen, water containing the hydrogen bond

Table 2. Physical and Critical Properties of CH$_4$, CO$_2$, and Water

compound	molecular weight	critical temperature, K	critical pressure, MPa	acentric factor	ref
CH$_4$	16.04	190.58	4.604	0.011	44
CO$_2$	44.01	304.19	7.382	0.228	44
water	18.02	647.10	22.064	0.344	30

exhibits the distinctive property with a large critical temperature and pressure. Hence, it is necessary to modify the attraction term (i.e., the parameter a) in the PR EOS to improve the phase equilibrium prediction for water. Figure 1 plots the vapor pressure of water at the full temperatures from 273.16 to 647.10 K. The empty circular symbol is calculated from eq 6 for the water vapor pressure based on the IAPWS-95, whereas the solid line is calculated from the PR EOS with the newly developed alpha function (see eq 7). As can be seen, there exists an excellent agreement between these two curves, indicating that the vapor pressure of water can be exactly reproduced by the newly proposed alpha function.
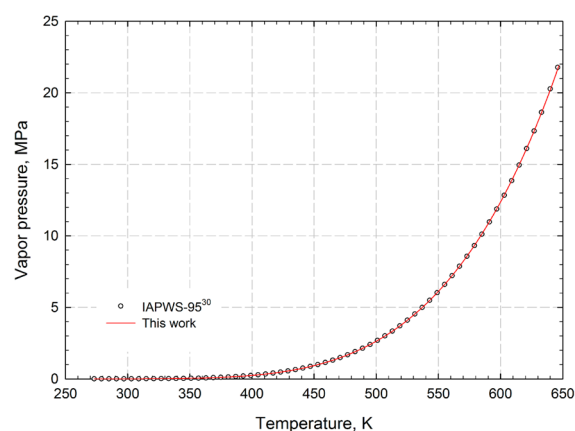

Figure 1. Vapor pressure of water calculated based on both the IAPWS-95 and PR EOS with the modified alpha function for water (i.e., eq 7) in this work in the full temperature range of 273.16−647.10 K.

The newly proposed alpha function and the three other existing alpha functions, i.e., the correlations proposed by Peng and Robinson (see eq 8),[28] Søreide and Whitson (see eq 9),[29] and Li and Yang (see eq 5)[34] are evaluated and compared in this study. These four alpha functions are initially developed on the basis of various reduced temperature ranges as listed in Table 3. In order to more conveniently analyze the results

Table 3. Reduced Temperature Ranges Used in Developing Each Alpha Function and the Corresponding AARDs for Predicting the Vapor Pressure of Water in the Full Reduced Temperature of 0.422−1.000

α-function	range of T_{rw}	AARD in full T_{rw}, %
Peng and Robinson[28]	0.422−0.723	1.50
Søreide and Whitson[29]	0.422−0.924	1.41
Li and Yang[34]	0.422−1.000	3.41
this work	0.422−1.000	0.07

obtained from different alpha functions, the zoom-in diagrams at the low and high temperatures are respectively depicted in Figure 2.

As can be seen in Figure 2a and b, the correlation developed in this work yields the best match to the curve obtained from the IAPWS-95. The Peng−Robinson correlation also has a generally good prediction accuracy with the slightly under-estimated vapor pressure at a low temperature range of 300−320 K (see Figure 2a), though it is far below the IAPWS-95 curve at a high temperature from 620 to 640 K (see Figure 2b). This is attributed to the fact that this alpha function is formulated at the limited reduced temperature only up to 0.723 (see Table 3).[28] Although the alpha function proposed by Søreide and Whitson[29] can generate a good prediction in a higher temperature range of 620−640 K, it yields a relative larger deviation compared with this work in a low temperature range. This is attributed to the fact that the water vapor pressure data used in the Søreide−Whitson correlation[29] is slightly inconsistent with the IAPWS-95.[30] Finally, the recently developed alpha function[34] underestimates the water vapor pressure to a large extent at a low temperature since hydrocarbons account for the major weight in its regression procedure.[34]
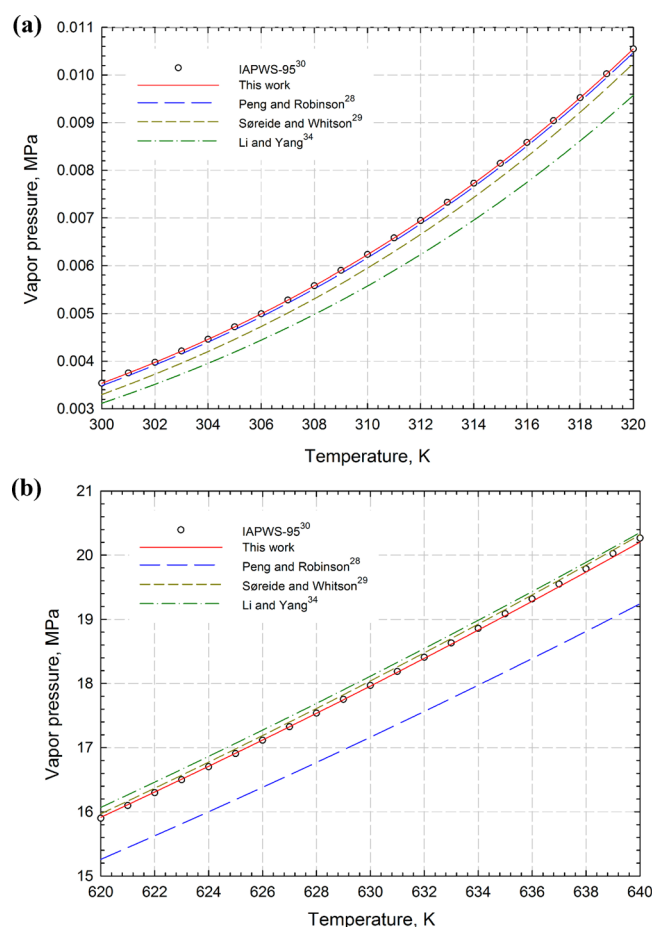
(a)

(b)

Figure 2. Comparison of the calculated vapor pressure of water from different correlations in a temperature range of (a) 300−320 and (b) 620−640 K, respectively.

For quantitatively comparing the prediction accuracy, the AARD is calculated for 375 temperature points with an increased step of 1.0 K from 273.16 to 647.10 K. As such, the AARDs of the previously mentioned four alpha functions for predicting water vapor pressure in the full reduced temperature range of 0.422−1.000 can be found in Table 3. Although the alpha function developed by Li and Yang[34] covers the full temperature range, the largest AARD of 3.41% is produced compared with 1.50% from the Peng−Robinson correlation, 1.41% from the Søreide−Whitson correlation,[29] and 0.07% from this work, respectively.

3.2. BIP Correlation. As can be seen in Table 1, the original CO_2 solubility data of CO_2−water systems, covering the wide ranges of temperature and pressure, are included in the database to develop the BIP correlation for the CO_2−water pair in the aqueous phase. Since the collected data from different literatures are not consistent in unit, it is necessary to convert the unit to mole fraction of CO_2 in the aqueous phase. As such, in terms of the $p−x$ diagram, the distribution of the 193 data points of CO_2 solubility in water at various isothermal conditions is presented in Figure 3, where p is pressure and x is the CO_2 mole fraction in the aqueous phase. First, it can be concluded that the mole fraction of CO_2 in the aqueous phase increases with the pressure at a given temperature, though such an increment in solubility is in a small range. Take the data points at 344.15 K as an example, the solubility only increases from 0.0166 to 0.0317 when pressure is rapidly increased from
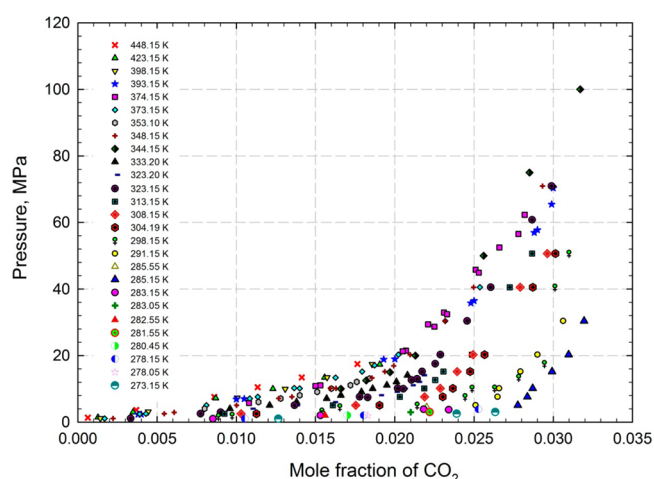

Figure 3. CO_2 mole fractions in the aqueous phase of the binary CO_2−water systems at the different temperatures.[35−43]

10.0 to 100.0 MPa. To account for such a limited increment, most of the experiments are conducted at a low-pressure region (see Figure 3). Second, at the isobaric condition, the CO_2 mole fraction generally increases with a decrease in temperature. At a given pressure of 30.4 MPa, the solubility increases from 0.0232 to 0.0319 when temperature decreases from 373.15 to 285.15 K.

Compared with pressure, the solubility is found to have a much stronger dependence on temperature as can be seen in Figure 4. To more clearly explain this statement, some of the
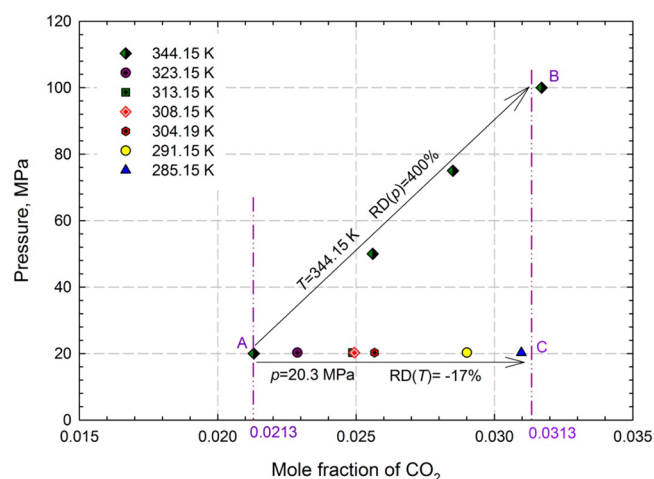

Figure 4. Relative deviations (RDs) of T (p is fixed) and p (T is fixed) at the same solubility change from 0.0213 to 0.0313.[35,36,40] RD(p) = $(p_B − p_A)/p_A$ and RD(T) = $(T_C − T_A)/T_A$.

experimental data points shown in Figure 3 are selected and more clearly represented in Figure 4 as an example. If the CO_2 solubility is supposed to increase from 0.0213 (point A) to approximate 0.0313 (points B and C), two simple approaches can be implemented. One path is from point A to B corresponding to an isothermal process. The pressure increases from 20.0 to 100.0 MPa at a fixed temperature 344.15 K, yielding a relative deviation of pressure, RD(p), of 400%. Another path is from point A to C corresponding to an isobaric process. The temperature decreases from 344.15 to 285.15 K at a fixed pressure 20.3 MPa, yielding a relative deviation of

temperature, $RD(T)$, of only −17%. Therefore, the CO_2 solubility is much more sensitive to temperature, compared with pressure. Consequently, the developed BIP is considered to be a temperature-dependent correlation.

By means of the PR EOS coupled with the newly proposed alpha function for water, an accurate BIP value can be rigorously optimized corresponding to each experimental solubility data. As shown in Figure 5, the 193 empty circles
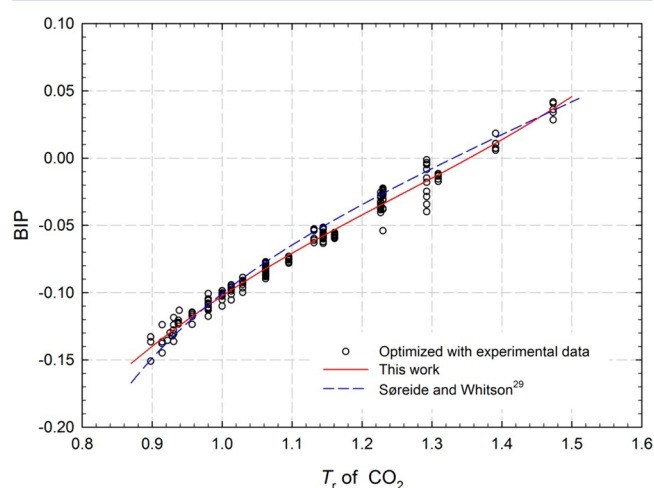

Figure 5. Comparison of the BIP obtained from the experimental solubility, this work, and Søreide−Whitson correlation, respectively.

are obtained by respectively best fitting the 193 solubility data points. The multiple BIPs are found to be highly concentrated at a single reduced temperature, e.g., there are 10 optimized BIP values in a limited range of −0.0785 to −0.0818 at the single reduced temperature of 1.063, implying that pressure imposes an extremely weak impact on CO_2 solubility in water, compared with the temperature. Accordingly, the temperature-dependent BIP correlation (i.e., eq 10) is developed to continuously fit such scattered BIPs (see the solid line in Figure 5). In addition, the dashed line resulting from the Søreide−Whitson correlation (i.e., eq 11) is also presented for

the purpose of comparison. Generally, the calculated BIPs are overestimated in a wide range of moderate reduced temperature ($1.0 < T_r < 1.4$) and underestimated in a low reduced temperature ($T_r < 1.0$), respectively.

3.3. Mutual Solubility. 3.3.1. Aqueous Phase. Both the alpha function for water and the BIP correlation for the CO_2−water pair in the aqueous phase proposed in this work have been incorporated in the PR EOS to predict the CO_2 solubility in water-rich phase of the CO_2−water system. Also, the BIP correlation from Søreide and Whitson[29] (see eq 11) is coupled with the newly developed alpha function for water for comparison purpose. As listed in Table 4, CO_2 solubility data at 27 temperatures ranging from 273.15 to 448.15 K together with the corresponding AARDs for predicting the CO_2 solubility from different BIP correlations are presented. As the multiple solubility data points can be measured at the same temperature from the literature, the AARD is calculated according to eq 13 corresponding to each temperature. It is found that a better accuracy can be obtained from the BIP correlation developed in this work at most of the experimental temperatures. For instance, the predicted CO_2 solubilities obtained from the Søreide−Whitson BIP correlation at 273.15, 281.55, 333.20, 353.10, and 398.15 K yield large AARDs of 26.93%, 10.42%, 12.39%, 13.40%, and 8.29%, respectively, whereas the corresponding AARDs obtained from this work are found to be 15.14%, 0.31%, 4.68%, 5.19%, and 2.28%, respectively. The Søreide−Whitson correlation shows its slightly improved AARDs at some temperatures, e.g., 280.45, 282.55, and 374.15 K. Overall, as for the 193 solubility data points, the new alpha function together with the BIP correlation developed in this work has a better reproducibility with an overall AARD of 6.12% in comparison with 8.67% from the Søreide−Whitson BIP correlation.

The typical results are graphed in Figure 6 to compare the measured and predicted CO_2 solubility obtained from the proposed BIP correlation and the Søreide and Whitson BIP correlation at temperatures of 285.15, 273.15, 278.15, 323.2, 333.2, 374.15, 423.15, and 448.15 K, respectively. As can be seen in Figure 6a, CO_2 solubility in water slightly increases with the rapidly increased pressure at the 285.15 K. The model

Table 4. AARDs for Predicting CO_2 Solubility in the Aqueous Phase with the Different BIP Correlations on the Basis of the Modified Alpha Function (i.e., Equation 7)

|		AARD, %				AARD, %	
T, K	solubility data points	BIP (Søreide and Whitson)[29]	BIP (this work)	T, K	solubility data points	BIP (Søreide and Whitson)[29]	BIP (this work)
273.15	3	26.93	15.14	313.15	9	5.74	4.24
278.05	1	6.30	6.71	323.15	17	7.82	5.21
278.15	3	19.84	15.45	323.20	10	11.10	4.35
280.45	1	2.48	7.91	333.20	10	12.39	4.68
281.55	1	10.42	0.31	344.15	7	5.69	6.63
282.55	1	1.96	6.64	348.15	15	8.27	4.41
283.05	1	9.26	0.01	353.10	9	13.40	5.19
283.15	4	14.66	11.73	373.15	15	7.20	3.96
285.15	6	14.74	6.06	374.15	14	6.02	10.52
285.55	1	34.68	25.26	393.15	12	10.20	12.14
291.15	7	7.42	4.83	398.15	6	8.29	2.28
298.15	12	6.30	6.25	423.15	6	5.15	2.86
304.19	8	4.43	4.98	448.15	6	3.40	3.15
308.15	8	4.82	5.12				
				overall	193	8.67	6.12
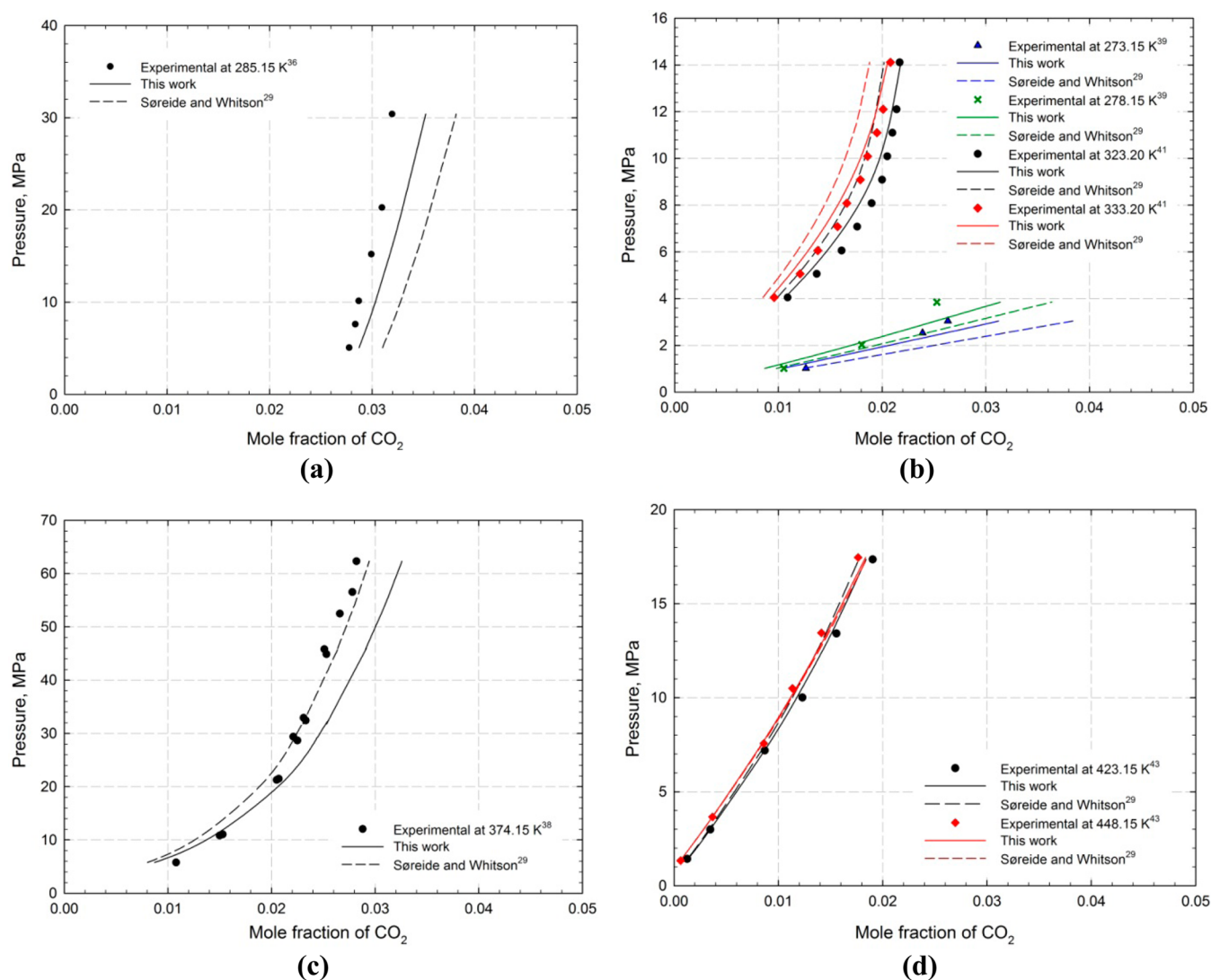
Figure 6. Comparison of the measured and predicted CO_2 solubility in water-rich phase of the binary CO_2−water systems with the BIP correlation developed in this work and developed by Søreide and Whitson at (a) 285.15 K; (b) 273.15, 278.15, 323.2, and 333.2 K; (c) 374.15 K; and (d) 423.15 and 448.15 K, respectively.

developed in this work can be used to more accurately predict the 6 data points with an overall AARD of 6.06%, which is far smaller than an AARD of 14.74% obtained from the Søreide−Whitson correlation. As can be found from the four isothermal lines presented in Figure 6b, it is difficult to achieve a higher CO_2 solubility at a higher temperature. In addition, the techniques developed in this study have achieved a better agreement between the experimentally measured and the theoretically predicted solubility. Despite of the satisfying overall performance of the technique developed in this work as seen in Table 4, it is possible that the developed correlation might provide the poor prediction for some individual cases. For instance, as shown in Figure 6c, CO_2 solubility data are measured at pressures up to 62.3 MPa. With regard to the 14 data points, there exists a larger AARD of 10.52% for the predicted solubility at 374.15 K with the techniques developed in this study, compared with an AARD of 6.02% from the Søreide−Whitson BIP correlation. A larger deviation in this work occurs at high pressures due to the fact that the solubility data at low pressures account for a larger proportion in the database to generate the BIP correlation. Furthermore, a fair

performance of the developed technique is also presented in Figure 6d, indicating both correlations can achieve a relatively accurate prediction at temperatures of 423.15 and 448.15 K. Finally, it is worthwhile nothing that the overall performance is far more important than individual performance from the viewpoint of predictive reliability.

3.3.2. Nonaqueous Phase. Although the newly proposed alpha function for water has been successfully applied to predict the aqueous phase composition, it is necessary to validate its application in the nonaqueous phase of the binary CO_2−water systems. As mentioned previously, a constant BIP is sufficient to model the phase behavior of the nonaqueous phase.[27] In this study, the BIP for CO_2−water pair is set to 0.1896 as recommended by Whitson and Brule.[10] Hou et al. provided the experimental compositions of the CO_2-rich phase of the CO_2−water systems from 298.15 to 448.15 K,[43] which are plotted in Figure 7 together with the predicted results by using the proposed model in this study. The mole fraction of water in the CO_2-rich phase is found to increase with either a decrease in pressure or an increase in temperature. There exists an excellent agreement between the measured and predicted nonaqueous
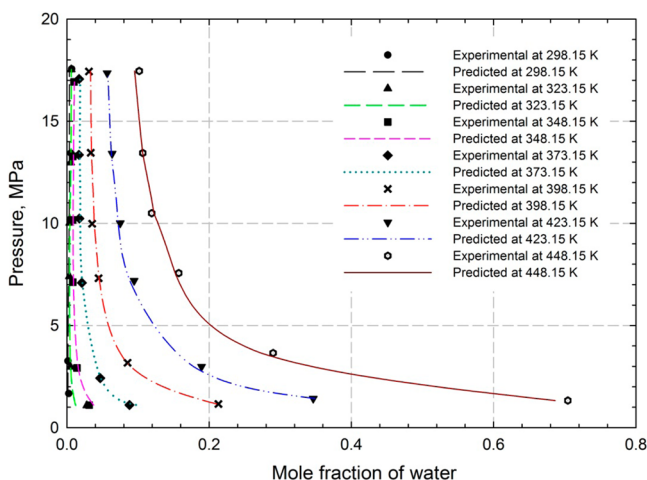
Figure 7. Measured[43] and predicted nonaqueous phase compositions of the binary CO_2-water systems at 298.15, 323.15, 348.15, 373.15, 398.15, 423.15, and 448.15 K, respectively.

phase compositions. Therefore, the PR EOS with the proposed alpha function for water can be used to accurately predict both aqueous phase and nonaqueous phase compositions for binary CO_2–water systems.

3.4. Ternary CH_4–CO_2–Water Systems. The solubility of CO_2 in the water-rich phase in the presence of CH_4 is further examined by introducing the ternary CH_4–CO_2–water systems. The experimental data are collected from the work of Dhima et al.,[40] in which different feeds of CH_4–CO_2 mixtures are designed to respectively determine the CH_4 and CO_2 solubilities in water. As listed in Table 5, different feeds of

Table 5. Feeds of the CH_4–CO_2 Mixtures Prepared for the Ternary CH_4–CO_2–Water Systems[40]

	CH_4 mole fraction in CH_4–CO_2 mixture	
pressure, MPa	mixture no. 1	mixture no. 2
10	0.5670	0.8045
20	0.5700	0.8102
50	0.5850	0.8205
75	0.5870	0.8260

CH_4–CO_2 gaseous mixtures are charged in the presence of water at temperature of 344.15 K and pressures of 10, 20, 50, and 75 MPa, respectively. Although the CH_4 mole fractions in the gaseous mixtures are various under laboratory conditions, they can be reasonably divided into two categories. The CH_4 mole fractions of 0.5670, 0.5700, 0.5850, and 0.5870 in gaseous mixtures are designated as mixture no. 1; whereas, the CH_4 mole fractions of 0.8045, 0.8102, 0.8205, and 0.8260 are designated as mixture no. 2.

Figure 8 presents the experimentally measured and the theoretically predicted CH_4 and CO_2 solubilities in water-rich phase of the ternary CH_4–CO_2–water systems at 344.15 K. Note that the solubility of the nonpolar compound CH_4 in the polar compound of water is scarce, compared with that of CO_2. For both CH_4 and CO_2, the solubility increases with an increase in pressure at 344.15 K. In addition, it is found that the more CH_4 is in the dry gaseous mixture (see mixture no. 2 in Table 5), the greater the amount of CH_4 is dissolved in water. Similarly, CO_2 solubility in the aqueous phase is increased if the CO_2 mole fraction in the dry gaseous mixture is increased. It is also demonstrated that the PR EOS together with the proposed alpha function for water and the BIP correlation for the CO_2–water pair developed in this work is able to accurately predict the CO_2 mole fraction in the water-rich phase of not only the binary CO_2–water system but also the ternary CH_4–CO_2–water system.

4. CONCLUSIONS

Techniques have been developed to determine mutual solubility between CO_2 and water by using the PR EOS with a modified alpha function and a new binary interaction parameter in the presence or absence of hydrocarbons. Compared with the existing alpha functions, the modified alpha function with a corrected attraction term in the PR EOS is able to more accurately reproduce the water vapor pressure in the full temperature range of 273.15 to 647.10 K. On the basis of the collected 193 reported solubility data available in the literature, it is found that the CO_2 solubility in water-rich phase has a stronger dependence on temperature, but a weak dependence on pressure. The proposed temperature-dependent BIP correlation coupled with the modified alpha function for
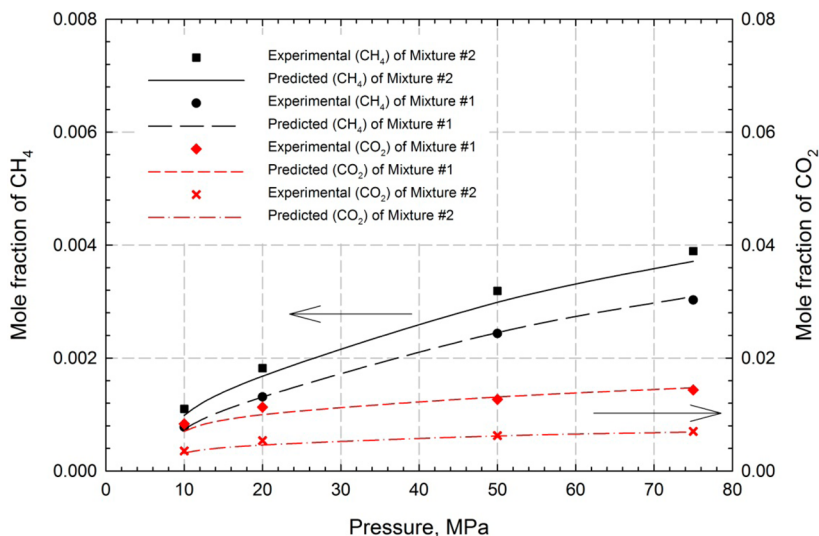

Figure 8. Measured[40] and predicted aqueous phase compositions of the ternary CH_4–CO_2–water systems at 344.15 K.

the PR EOS results in a good prediction of CO_2 solubility in water-rich phase with an overall AARD of 6.12% at temperatures up to 448.15 K and pressures up to 100 MPa. It is also found that the proposed polynomial BIP correlation provides the more accurate prediction in the low pressure range since most of the collected solubilities in the database used to generate BIP correlation are measured at low pressures. As for the water solubility in CO_2-rich phase, a constant BIP value for CO_2–water pair is found to be sufficient to determine the composition of the nonaqueous phase. An increased water mole fraction in the CO_2-rich phase is predicted with the increased temperature or the decreased pressure. Finally, it is demonstrated that the model is able to accurately predict the CO_2 mole fraction in aqueous phase in the presence of CH_4 at 344.15 K.

■ AUTHOR INFORMATION

Corresponding Author
*Phone: 1-306-337-2660. Fax: 1-306-585-4855. E-mail: tony. yang@uregina.ca.

Notes
The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

■ NOMENCLATURE

Roman Symbols
a = attraction parameter in PR-EOS
a_c = PR EOS constant
b = van der Waals volume, m³/kmol
c_1, c_2, c_3, and c_4 = coefficients defined in eq 7
d_1, d_2, d_3, d_4, d_5, and d_6 = coefficients defined in eq 6
n = number of data points
p = pressure, MPa
p_b = vapor pressure of water, MPa
p_c = critical pressure, kPa
R = universal gas constant
T = temperature, K
T_c = critical temperature, K
T_r = reduced temperature
T_{rw} = reduced temperature of water
T_t = temperature at the triple point, K
V_M = molar volume, m³/kmol
x = phase composition vector
X_i^{cal} = calculated objective parameter
X_i^{exp} = measured objective parameter

Greek Symbols
α = α function in PR EOS
α_{LY} = universal alpha function developed by Li and Yang[34]
$\alpha_{H_2O, modified}$ = alpha function for water modified in this work
$\alpha_{H_2O, PR}$ = alpha function for water developed by Peng and Robinson[2]
$\alpha_{H_2O, SW}$ = alpha function for water developed by Søreide and Whitson[29]
α_{PR} = universal alpha function developed by Peng and Robinson[22]
$\delta_{CH_4, SW}^{AQ}$ = BIP for CH_4–water pair in the aqueous phase developed by Søreide and Whitson[29]

$\delta_{CO_2, modified}^{AQ}$ = BIP for CO_2–water pair in the aqueous phase modified in this work
$\delta_{CO_2, SW}^{AQ}$ = BIP for CO_2–water pair in the aqueous phase developed by Søreide and Whitson[29]
δ_{ij} = BIP between component ith and jth
ω = acentric factor

Abbreviations
AARD = absolute average relative deviation
BIP = binary interaction parameter
CSI = cyclic solvent injection
IAPWS-95 = international association for the properties of water and steam formulation 1995
ITS-90 = international temperature scale of 1990
PR EOS = Peng–Robinson equation of state
RD = relative deviation
SAFT = statistical associating fluid theory
VAPEX = vapor extraction

■ REFERENCES

(1) Gaspar Ravagnani, A. T. F. S.; Ligero, E. L.; Suslick, S. B. CO_2 sequestration through enhanced oil recovery in a mature oil field. *J. Petr. Sci. Eng.* **2009**, *65* (3–4), 129–138.

(2) Michel, S.; Hooper, H. H.; Prausnitz, J. M. Mutual solubilities of water and hydrocarbons from an equation of state. Need for an unconventional mixing rule. *Fluid Phase Equilib.* **1989**, *45* (2–3), 173–189.

(3) IPDD. *Climate change 2007: The physical science basis. Contribution of working group I to the fourth assessment report of the intergovernmental panel on climate change*; Cambridge University Press: Cambrige, UK, 2007, pp 996.

(4) Zendehboudi, S.; Leonenko, Y.; Shafiei, A.; Soltani, M.; Chatzis, I. Modeling of CO_2 droplets shrinkage in *ex situ* dissolution approach with application to geological sequestration: Analytical solutions and feasibility study. *Chem. Eng. J.* **2012**, *197*, 448–458.

(5) Zheng, S.; Yang, D. Pressure maintenance and improving oil recovery in terms of water-alternating-CO_2 processes in thin heavy oil reservoirs. *SPE Reserv. Eval. Eng.* **2013**, *16* (1), 60–71.

(6) Upreti, S. R.; Lohi, A.; Kapadia, R. A.; El-haj, R. Vapor extraction of heavy oil and bitumen: A review. *Energy Fuels* **2007**, *21* (3), 1562–1574.

(7) Ivory, J.; Chang, J.; Coates, R.; Forshner, K. Investigation of cyclic solvent injection process for heavy oil recovery. *J. Can. Pet. Technol.* **2010**, *49* (9), 22–23.

(8) Godec, M. L.; Kuuskraa, V. A.; Dipietro, P. Opportunities for using anthropogenic CO_2 for enhanced oil recovery and CO_2 storage. *Energy fuels* **2013**, *27*, 4183–4189.

(9) Li, H.; Zheng, S.; Yang, D. Enhanced swelling effect and viscosity reduction of solvents-CO_2-heavy oil systems. *SPE J.* **2013**, *18* (4), 695–707.

(10) Whitson, C. H.; Brule, M. R. *Phase behavior*; Monograph Series; SPE: Richardson, TX, 2000.

(11) Li, Y. K.; Nghiem, L. X. Phase Equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry's law. *Can. J. Chem. Eng.* **1986**, *64* (3), 486–496.

(12) Nghiem, L. X.; Heidemann, R. A. General acceleration procedure for multiphase flash calculation with application to oil-gas-water systems. *Proceedings of the Second European symposium on enhanced oil recovery*; Paris, November 8–10, 1982; Editions Technip: Paris; pp 303–316.

(13) Heidemann, R. A. Three-phase equilibria using equations of state. *AIChE J.* **1974**, *20* (5), 847–855.

(14) Luks, K. D.; Fitzgibbon, P. D.; Banchero, J. T. Correlations of the equilibrium moisture content of air and of mixtures of oxygen and nitrogen for temperatures in the range of 230 to 600 K at pressures up to 100 Atm. *Ind. Eng. Chem. Process Des. Dev.* **1976**, *15* (2), 326–332.

(15) Mehra, R. K.; Heidemann, R. A.; Aziz, K. Computation of multiphase equilibrium for compositional simulation. *Soc. Petr. Eng. J.* **1982**, *22* (1), 61−68.

(16) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. SAFT: equation-of-state solution model for associating fluids. *Fluid Phase Equilib.* **1989**, *52*, 31−38.

(17) Chapman, W. G.; Gubbins, K. E.; Jackson, G.; Radosz, M. New reference equation of state for associating liquids. *Ind. Eng. Chem. Res.* **1990**, *29* (8), 1709−1721.

(18) Gil-Villegas, A.; Galindo, A.; Whitehead, P. J.; Mills, S. J.; Jackson, G.; Burgess, A. N. *J. Chem. Phys.* **1997**, *106*, 4168−4186.

(19) Galindo, A.; Davies, L. A.; Gil-Villegas, A.; Jackson, G. The thermodynamics of mixtures and the corresponding mixing rules in the SAFT-VR approach for potentials of variable range. *Mol. Phys.* **1998**, *93* (2), 241−252.

(20) Gross, J.; Sadowski, G. Application of perturbation theory to a hard-chain reference fluid: an equation of state for square-well chains. *Fluid Phase Equilib.* **2000**, *168* (2), 183−199.

(21) Forte, E.; Galindo, A.; Trusler, J. P. M. Experimental and molecular modeling study of the three-phase behavior of (*n*-decane +carbon dioxide+water) at reservoir conditions. *J. Phys. Chem. B* **2011**, *115* (49), 14591−14609.

(22) Peng, D. Y.; Robinson, D. B. A new two-constant equation of state. *Ind. Eng. Chem. Fundam.* **1976**, *15* (1), 59−64.

(23) Li, H.; Yang, D. Phase behaviour of C_3H_8-*n*-C_4H_{10}-heavy oil systems at high pressures and elevated temperatures. *J. Can. Pet. Technol.* **2013**, *52* (1), 30−40.

(24) Jia, N.; Memon, A.; Gao, J.; Zuo, J.; Zhao, H.; Ng, H.-J. Three-phase equilibrium study for heavy-oil/solvent/steam system at high temperatures. *J. Can. Petrol. Technol.* **2011**, *50* (6), 68−79.

(25) Li, H.; Yang, D.; Li, X. Determination of three-phase boundaries of solvent(s)-CO_2-heavy oil systems under reservoir conditions. *Energy Fuels* **2013**, *27* (1), 145−153.

(26) Li, X.; Li, H.; Yang, D. Determination of multiphase boundaries and swelling factors of solvent(s)-CO_2-heavy oil systems at high pressures and elevated temperatures. *Energy Fuels* **2013**, *27* (3), 1293−1306.

(27) Peng, D.-Y.; Robinson, D. B. Two and three phase equilibrium calculations for systems containing water. *Can. J. Chem. Eng.* **1976**, *54* (5), 595−599.

(28) Peng, D.-Y.; Robinson, D. B. Two- and three-phase equilibrium calculations for coal gasification and related processes. *Thermodynamics of aqueous systems with industrial applications*; Newman, S.A., Ed.; ACS Symposium Series; American Chemical Society: Washington, D.C., 1980; Vol. *393*, pp 393−414.

(29) Søreide, I.; Whitson, C. H. Peng-Robinson prediction for hydrocarbons, CO_2, N_2, and H_2S with pure water and NaCl brine. *Fluid Phase Equilib.* **1992**, *77*, 217−240.

(30) Wagner, W.; Pruß, A. The IAPWS formulation 1995 for the thermodynamic properties of ordinary water substance for general and scientific use. *J. Phys. Chem. Ref. Data* **2002**, *31* (2), 387−535.

(31) Soave, G. Equilibrium constants from a modified Redlich-Kwong equation of state. *Chem. Eng. Sci.* **1972**, *27* (6), 1197−1203.

(32) Redlich, O.; Kwong, J. N. S. On the thermodynamics of solutions. V. an equation of state. Fugacities of gaseous solutions. *Chem. Rev.* **1949**, *44* (1), 233−244.

(33) Edmister, W. C.; Lee, B. I. *Applied Hydrocarbon Thermodynamics*, 2nd ed.; Gulf Publishing Co.: Houston, 1984; Vol. *I*.

(34) Li, H.; Yang, D. Modified α function for the Peng-Robinson equation of state to improve the vapor pressure prediction of non-hydrocarbon and hydrocarbon compounds. *Energy Fuels* **2011**, *25* (1), 215−223.

(35) Wiebe, R.; Gaddy, V. L. The solubility in water of carbon dioxide at 50, 75 and 100°C, at pressures to 700 atm. *J. Am. Chem. Soc.* **1939**, *61* (2), 315−318.

(36) Wiebe, R.; Gaddy, V. L. The solubility of carbon dioxide in water at various temperatures from 12 to 40° and at pressures to 500 atm. Critical Phenomena. *J. Am. Chem. Soc.* **1940**, *62* (4), 815−817.

(37) Wiebe, R. The binary system carbon dioxide-water under pressure. *Chem. Rev.* **1941**, *29* (3), 475−481.

(38) Prutton, C. F.; Savage, R. L. The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100, 120° and high pressures. *J. Am. Chem. Soc.* **1945**, *67* (9), 1550−1554.

(39) Stewart, P. B.; Munjal, P. Solubility of carbon dioxide in pure water, synthetic sea water, and synthetic sea water concentrates at −5° to 25°C, 10- to 45-atm. Pressure. *J. Chem. Eng. Data* **1970**, *15* (1), 67−71.

(40) Dhima, A.; Hemptinne, J.-C. de; Jose, J. Solubility of hydrocarbons and CO2 mixtures in water under high pressure. *Ind. Eng. Chem. Res.* **1999**, *38* (8), 3144−3161.

(41) Bamberger, A.; Sieder, G.; Maurer, G. High-pressure (vapor +liquid) equilibrium in binary mixtures of (carbon dioxide+water or acetic acid) at temperatures from 313 to 353 K. *J. Supercrit. Fluids* **2000**, *17* (2), 97−110.

(42) Servio, P.; Englezos, P. Effect of temperature and pressure on the solubility of carbon dioxide in water in the presence of gas hydrate. *Fluid Phase Equilib.* **2001**, *190* (1−2), 127−134.

(43) Hou, S.-X.; Maitland, G. C.; Trusler, J. P. M. Measurement and modeling of the phase behavior of the (carbon dioxide+water) mixture at temperatures from 298.15 to 448.15 K. *J. Supercrit. Fluids* **2013**, *73*, 87−96.

(44) Yaws, C. L. *Yaw's handbook of thermodynamic and physical properties of chemical compounds*; Knovel: New York, 2003.