



Prediction of CO₂-CH₄-H₂S-N₂ gas mixtures solubility in brine using a non-iterative fugacity-activity model relevant to CO₂-MEOR



Babak Shabani, Javier Vilcáez*

Boone Pickens School of Geology, Oklahoma State University, Stillwater, OK 74078, USA

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ABSTRACT

Numerical simulations of carbon dioxide-microbial enhanced oil recovery (CO₂-MEOR) would require computationally rigorous iterative methods to solve resulting system of flow, transport and kinetic reaction equations. This includes additional iterative procedures to account for the solubility of gas mixtures in the aqueous phase. This work proposes a new non-iterative fugacity-activity thermodynamic model to predict the solubility of CO₂-CH₄-H₂S-N₂ gas mixtures in brine. This model can readily be implemented in MEOR simulation programs to account for mass transfer and kinetics of microbial reactions in CO₂-MEOR operations. Fugacity coefficients (ϕ_i) in the proposed model were calculated using Predictive Peng-Robinson 78 (PPR78) and Peng-Robinson (PR) equation of state (EOS). The proposed model was successful in predicting CO₂ solubility in the aqueous phase with ϕ_i calculated either using PPR78 EOS or PR EOS. Comparison showed that at temperature and pressure conditions relevant to MEOR, using calibrated binary interaction parameters (PR EOS) leads to more accurate predictions than binary interaction parameters estimated from the group contribution expression (PPR78 EOS). Comparison of predicted CO₂-CH₄-H₂S gas mixtures solubility in the aqueous phase obtained with the proposed non-iterative fugacity-activity model and an iterative fugacity-activity model, confirmed that proposed model with ϕ_i calculated using PR EOS can be used as substitute for iterative fugacity-activity models that relies on the solution of Rachford-Rice equation.

1. Introduction

Carbon dioxide capture and storage (CCS) operations involves capturing CO₂ produced from large power generation plants, compressing it for transportation and injecting into deep geological formations such as saline aquifers and depleted oil reservoirs. CCS is regarded as a potential effective method for reducing CO₂ emissions into the atmosphere. However, CCS is yet to become a standard of practice (Benson et al., 2012). One reason hindering the application of CCS to reduce the emissions of CO₂ into the atmosphere is the cost of CCS projects. Coupling CCS with enhanced oil recovery (EOR) projects has emerged as a promising method to reduce or compensate for the cost of CCS projects. CO₂ due to its low minimum miscibility pressure compared to other gases such as methane and nitrogen, has a swelling effect on oil enhancing its mobility. Another method to reduce or compensate for the cost of CCS projects is to couple it with microbial enhanced oil recovery (MEOR) projects. MEOR consists of injecting selected microbial nutrients into depleted oil reservoirs to stimulate the activity of indigenous microbes whose metabolic products enhance the oil recovery. A new method (CO₂-MEOR), which combines the injection of CO₂

and stimulating nutrients has been proposed to biogenically convert CO₂ and oil to CH₄ in depleted oil reservoirs (Vilcáez, 2015a, 2015b). The formed CH₄ in depleted oil reservoirs can be recovered more easily than oil, and its commercialization as energy source might reduce or compensate for the cost of CCS projects. Preliminary experimental and numerical simulation studies have shown that a CO₂-MEOR method is possible in principle. However, this method would not be of general application because it depends on hydrogeological, geochemical, and microbiological conditions that are different in each depleted oil reservoir. One way to screen potential of depleted oil reservoirs to implement CO₂-MEOR is to perform numerical simulation studies.

Most numerical simulation studies on MEOR have focused on the microbiological formation of biopolymers, biosurfactants, biomass (microbial cells), and fatty acids which enhance the mobility of oil by reducing the viscosity and interfacial tension of oil against water (Azadpour et al., 1996; Giangiacomo and Dennis, 1997; Nemati et al., 2001), and/or by increasing or reducing the porosity/permeability of target zones containing oil (Brown et al., 2000; Vilcáez et al., 2013). The biogenic formation of CO₂-CH₄-H₂S-N₂ gases mixtures, which can happen in depleted oil reservoirs inhabited by fermentative,

* Corresponding author.

E-mail address: vilcaez@okstate.edu (J. Vilcáez).

sulfate reducing, methanogenic, and denitrifying microbes is usually neglected in numerical simulation studies of MEOR. Including the biogenic formation of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-N}_2$ gas mixtures is particularly important in simulations of $\text{CO}_2\text{-MEOR}$ to determine how much, how fast, and where valuable hydrocarbon gases (CH_4), and souring gases (H_2S) will accumulate in the reservoir (Hitzman et al., 2004). This is because the dissolution of the injected and the biogenically formed gases can significantly change the chemical composition and pH of the aqueous phase, which in turn can have a large impact on the activity of the targeted microbial species. MEOR methods that rely on biogenic formation of N_2 gas to restore pressure in depleted oil reservoirs have been proposed before (Nuryadi et al., 2011). Accounting for the solubility of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-N}_2$ gas mixtures in brine will also allow to determine to which degree the biogenically formed gases can restore pressure.

Two thermodynamic models are widely employed to predict the solubility of gas mixtures in water and brine. They differ in the thermodynamic properties used to represent the equilibrium condition of each compound in the gas and aqueous phase. In the first model, called fugacity-activity model, the equilibrium condition of each compound is expressed in terms of gas phase fugacity coefficients and liquid phase activity coefficients. In this case, the fugacity coefficients are calculated using an equation of state (EOS), whereas activity coefficients are calculated using an activity model. In the second method, called fugacity-fugacity method, the equilibrium condition of each compound in the gas and aqueous phase is expressed in terms of gas and liquid fugacity coefficients. In this case, both fugacity coefficients are calculated using an EOS that needs iterative estimation of K-value at each time step and at each grid. Because the fugacity-activity model can be solved using a non-iterative method, this thermodynamic model is preferred over the fugacity-fugacity model that requires an iterative method for its solution.

Numerous non-iterative fugacity-activity models have been proposed to predict the solubility of pure CO_2 in water and brine (Duan and Sun, 2003; Duan et al., 2006; Hou et al., 2013; Mao et al., 2013; Spycher and Pruess, 2005; Spycher et al., 2003; Yan et al., 2011; Zhao et al., 2015). This is not the case of $\text{CO}_2\text{-H}_2\text{S-CH}_4\text{-N}_2$ gas mixtures, for which very few non-iterative fugacity-activity models have been proposed. Zirrahi et al. (2010) developed a non-iterative fugacity-activity model to predict the phase equilibrium behavior of acid gas mixtures ($\text{CO}_2\text{-H}_2\text{S-CH}_4$), and water and brine. However, the method is not accurate in predicting CO_2 and H_2S solubility in the aqueous phase. Most proposed models to predict the solubility of gas mixtures are iterative models that requires solving Rachford-Rice equation (Eq. (A1)). For instance, Ziabakhsh-Ganji and Kooi (2012) developed an iterative fugacity-activity model to predict $\text{CO}_2\text{-N}_2\text{-H}_2\text{S-CH}_4\text{-SO}_2$ gas mixtures solubility in brine. In this model, fugacity coefficients in the gas phase are calculated using Peng-Robinson (PR) EOS, whereas activity coefficients in the aqueous phase are reproduced based on Pitzer formalism and Henry's law. Similarly, Li et al. (2015) presented an iterative fugacity-fugacity model to calculate the mutual solubility of a gas mixtures ($\text{CO}_2\text{-SO}_2\text{-H}_2\text{S-CH}_4\text{-N}_2$) in brine for a wide range of pressures, temperatures, and salinity conditions. These two models use Rachford-Rice equation whose iterative solution requires information on the initial feed of each compound including H_2O (z_i in Eq. (A1)) in the mixture. The use of Rachford-Rice equation makes models inefficient for implementation in reactive transport simulation programs because additional iterations would be required for its solution. Li et al. (2014) compared the performance of the fugacity-fugacity and fugacity-activity models in predicting the solubility of $\text{CO}_2\text{-H}_2\text{S-CH}_4$ gas mixtures in brine. They confirmed that fugacity-activity models are more time efficient than fugacity-fugacity models.

Typical temperatures of conventional sandstone and carbonate oil reservoirs at depths shorter than 3000 m are within 50–95 °C (Millikan, 1941). Taking into account that successful field scale MEOR operations have been reported for reservoirs of temperatures

as high as 92.2 °C (Strappa et al., 2004), and that methanogenic microbes are capable of growing at temperatures ranging from 0 °C to 110 °C (Goodchild et al., 2004; Huber et al., 1989), the temperature range considered relevant to $\text{CO}_2\text{-MEOR}$ in this work is within 0–100 °C.

Possible concentration ranges for individual gases in $\text{CO}_2\text{-CH}_4\text{-N}_2\text{-H}_2\text{S}$ gas mixtures in depleted oil reservoirs subjected to $\text{CO}_2\text{-MEOR}$ are expected to be highly variable depending on the geological, geochemical and microbiological condition of the depleted oil reservoir. Under appropriate conditions, CO_2 is expected to have the highest concentration, followed by CH_4 and H_2S . Therefore, the proposed non-iterative method in this work will be tested using experimental data of gas mixtures containing highest concentrations of CO_2 .

This work introduces a new non-iterative fugacity-activity model to predict the solubility of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-N}_2$ gas mixtures in water and brine that does not require solving Rachford-Rice equation. This model is simple enough to be readily incorporated into multiphase and multicomponent reactive transport programs that account for kinetic microbial reactions taking place in the aqueous phase. The proposed model is solved using the Predictive-Peng-Robinson 1978 (PPR78) EOS and Peng-Robinson (PR) EOS to calculate fugacity coefficients in the gas phase. The use of the PPR78 EOS in an iterative fugacity-fugacity model resulted in accurate predictions of $\text{CO}_2\text{-CH}_4\text{-N}_2\text{-H}_2\text{S}$ gas mixture solubilities in brine (Privat and Jaubert, 2014). This is attributed to the property that binary interaction parameters in PPR78 EOS is a function of temperature and can be estimated for any mixture containing alkanes, aromatics and naphthalenes using critical temperatures, critical pressures, and acentric factors of pure compounds (Vitu et al., 2008). This approach greatly reduces the need for experimental data. The PPR78 EOS has not been used before in a non-iterative fugacity-activity model to predict the solubility of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-N}_2$ gas mixtures in brine at temperatures, pressures and composition conditions relevant to MEOR.

For simplicity and comparison purposes, in this work the proposed non-iterative model solved using PPR78 EOS will be referred to as model 1 whereas the same model solved using PR EOS will be referred to as model 2. In both models activity coefficients of aqueous species are calculated based on Henry's law and Pitzer correlation.

In the following sections, first the proposed non-iterative fugacity-activity model for predicting the solubility of $\text{CO}_2\text{-CH}_4\text{-H}_2\text{S-N}_2$ gas mixtures in brine will be introduced. Then, the performance of the proposed model is evaluated using experimental data of solubility of pure CO_2 and $\text{CO}_2\text{-H}_2\text{S-CH}_4$, $\text{CO}_2\text{-H}_2\text{S}$, $\text{CO}_2\text{-CH}_4$, and $\text{CO}_2\text{-N}_2$ gas mixtures in water and brine. The performance of the proposed models will also be evaluated in comparison with the performance of an iterative fugacity-activity model that uses Rachford-Rice equation. This later model will be referred to as model 3.

2. Thermodynamic model

In a system with gas and liquid phases at equilibrium, the fugacity of each compound in the gas phase (f_i^g) is equal to the fugacity of that compound in the liquid phase (f_i^l):

$$f_i^g = f_i^l \quad (1)$$

For the gas phase, f_i^g can be expressed as:

$$f_i^g = P\phi_i y_i \quad (2)$$

where P is the total pressure in the system, and ϕ_i and y_i are the fugacity coefficient and molar fraction of each compound in the gas phase, respectively. For the liquid phase (because of the relatively low solubility of $\text{CO}_2, \text{H}_2\text{S}, \text{CH}_4$ and N_2 gases and its nonionic character in the aqueous phase and considering the effect of salinity in the solubility of gases) f_i^l can be expressed as (Spycher and Pruess, 2005):

Table 1
Second order interaction parameters (Ziabakhsh-Ganji and Kooi, 2012).

Constant	$\lambda_{\text{CO}_2\text{-Na}}$	$\lambda_{\text{H}_2\text{S-Na}}$	$\lambda_{\text{N}_2\text{-Na}}$	$\lambda_{\text{CH}_4\text{-Na}}$
c_1	-0.0652869	1.03658689	-2.0939363	-5.7066455E-01
c_2	1.6790636E-04	-1.1784797E-03	3.1445269E-03	7.2997588E-04
c_3	40.838951	-1.7754826E+02	3.91E+02	1.52E+02
c_4	0	-4.5313285E-04	-2.9973977E-07	3.1927112E-05
c_5	0	0	0	0
c_6	-3.9266518E-02	0	-1.5918098E-05	-1.6426510E-05
c_7	0	0	0	0
c_8	2.1157167E-02	0	0	0
c_9	6.5486487E-06	0	0	0
c_{10}	0	0.47751650E+02	0	0

$$f_i^l = h_i \gamma_i x_i \quad (3)$$

where h_i is Henry's constant, γ_i is the activity coefficient, and x_i is the molar fraction of each compound in the liquid phase. Equating fugacities gives:

$$h_i \gamma_i x_i = P \phi_i y_i \quad (4)$$

which can be rearranged to obtain K_i as follows:

$$K_i = \frac{y_i}{x_i} = \frac{h_i \gamma_i}{P \phi_i} \quad (5)$$

where K_i is the phase equilibrium constant of compound i in Rachford-Rice equation. In the proposed model, except for H_2O , K_i values of CO_2 , H_2S , CH_4 and N_2 in the system are calculated using Eq. (5). K_i for H_2O is calculated using the relation proposed by Spycher et al. (2003):

$$K_{\text{H}_2\text{O}} = \frac{y_{\text{H}_2\text{O}}}{x_{\text{H}_2\text{O}}} = \frac{K_{\text{H}_2\text{O}}^0}{f_{\text{H}_2\text{O}} P} \exp \left[\frac{(P-1) \times 18.18}{RT} \right] \quad (6)$$

where $K_{\text{H}_2\text{O}}^0$ is the equilibrium constant of H_2O at the reference pressure of 1 bar, R is gas constant, and T is temperature in Kelvin. The approach of Spycher et al. (2003) is used to calculate $K_{\text{H}_2\text{O}}^0$:

$$\log(K_{\text{H}_2\text{O}}^0) = -2.209 + 3.097 \times 10^{-2}\theta - 1.098 \times 10^{-4}\theta^2 + 2.048 \times 10^{-7}\theta^3 \quad (7)$$

where θ is temperature in Celsius.

In the proposed model, the molar fraction of H_2O in the gas phase ($y_{\text{H}_2\text{O}}$) is calculated using the following equation:

$$y_{\text{H}_2\text{O}} = \frac{1 - \sum \frac{y_i}{K_i}}{\frac{1}{K_{\text{H}_2\text{O}}} - \sum \frac{y_i}{K_i}} \quad (8)$$

This equation is similar to that proposed by Spycher et al. (2003) to predict the solubility of pure CO_2 in brine:

$$y_{\text{H}_2\text{O}} = \frac{1 - \frac{1}{K_{\text{CO}_2}}}{\frac{1}{K_{\text{H}_2\text{O}}} - \frac{1}{K_{\text{CO}_2}}} \quad (9)$$

Note that the application of Eq. (8) to a pure CO_2 -brine system produces Eq. (9) of Spycher et al. (2003). In the proposed equation in this work (Eq. (8)), y_i is the initial molar fraction of CO_2 , H_2S , CH_4 and N_2 in the gas phase. The calculated $y_{\text{H}_2\text{O}}$ (Eq. (8)) is used to correct the molar fractions of CO_2 , H_2S , CH_4 and N_2 in the gas phase using the following normalization equation:

$$y_i^n = \frac{y_i}{1 + y_{\text{H}_2\text{O}}} \quad (10)$$

where y_i^n is the normalized molar fractions of CO_2 , H_2S , CH_4 , and N_2 in the gas phase. This simplification has not been used before and might result in loss of accuracy due to the lack of inclusion of the binary interactions parameters for H_2O - CO_2 , H_2O - H_2S , H_2O - CH_4 and H_2O - N_2 . However, because temperature and pressure conditions relevant to

MEOR do not result in high H_2O solubility in the gas phase, it is safe to assume that the omission of the effect of H_2O in the calculation of gas fugacity coefficients will not result in a significant loss of accuracy in predicting the solubility of CO_2 - H_2S - CH_4 - N_2 gas mixtures in brine. Following this procedure, the equilibrium molar fractions of all compounds including H_2O in brine can be directly calculated from the equation:

$$x_i = \frac{y_i^n}{K_i} \quad (11)$$

where x_i is the molar fraction of dissolved compounds in the aqueous phase, and y_i^n calculated from Eq. (10) is the molar fraction of each compound in the existing or injected mixture of gases. Activity coefficients of dissolved gases in the aqueous phase are calculated following the approach of Ziabakhsh-Ganji and Kooi (2012) who proposed to use the correlation of Pitzer (1973):

$$\ln \gamma_i = \sum_c 2m_c \lambda_{i-\text{Na}} + \sum_a 2m_a \lambda_{i-\text{Cl}} + \sum_c \sum_a 2m_a m_c \xi_{i-\text{Na-Cl}} \quad (12)$$

where m_c and m_a are anion and cation molalities, respectively, $\lambda_{i-\text{Na}}$ and $\xi_{i-\text{Na-Cl}}$ are second and third order interaction parameters that depend on pressure and temperature, $\lambda_{i-\text{Cl}}$ is assumed to equal zero in most previous studies (Duan and Sun, 2003; Li et al., 2014; Ziabakhsh-Ganji and Kooi, 2012), and $\lambda_{i-\text{Na}}$ and $\xi_{i-\text{Na-Cl}}$ are calculated using the following equation:

$$\text{Par}(T, P) = c_1 + c_2 T + \frac{c_3}{T} + c_4 P + \frac{c_5}{P} + c_6 \frac{P}{T} + c_7 \frac{T}{P^2} + \frac{c_8 P}{630 - T} + c_9 T \ln(P) + c_{10} \frac{P}{T^2} \quad (13)$$

where $\text{Par}(T, P)$ is either $\lambda_{i-\text{Na}}$ or $\xi_{i-\text{Na-Cl}}$, T is temperature in Kelvin, and P is pressure in bar. Values of c_1 through c_{10} for $\lambda_{i-\text{Na}}$ and or $\xi_{i-\text{Na-Cl}}$ are presented in Tables 1, 2, respectively.

Henry's constant (h_i) of dissolved gases in the aqueous phase are calculated using the correlation of Akinfiev and Diamond (2003) which was subsequently employed by Ziabakhsh-Ganji and Kooi (2012). It is noteworthy that this correlation is valid for infinite dilution as expressed by:

$$\ln h_i = (1 - \eta) \ln f_{\text{H}_2\text{O}}^0 + \eta \ln \left(\frac{RT}{M_{\text{wH}_2\text{O}}} \rho_{\text{H}_2\text{O}}^0 \right) + 2 \rho_{\text{H}_2\text{O}}^0 \Delta B \quad (14)$$

where T is temperature in Kelvin, η is a constant for each gas dissolved in water, $M_{\text{wH}_2\text{O}}$ is molecular mass of water, $f_{\text{H}_2\text{O}}^0$ is the fugacity, and $\rho_{\text{H}_2\text{O}}^0$ is the density of pure water which are calculated using Fine and Millero (1973) correlation (Eq. (A4–A8)), and ΔB represents the difference in interaction between dissimilar molecules and that between identical solvent molecules. ΔB is determined from the following equation:

$$\Delta B = \tau + \beta \left(\frac{10^3}{T} \right)^{0.5} \quad (15)$$

Table 2

Third order interaction parameters (Ziabakhsh-Ganji and Kooi, 2012).

Constant	$\xi_{\text{CO}_2\text{-Na-Cl}}$	$\xi_{\text{H}_2\text{S-Na-Cl}}$	$\xi_{\text{N}_2\text{-Na-Cl}}$	$\xi_{\text{CH}_4\text{-Na-Cl}}$
c_1	-1.144624E-02	-0.010274152	-6.3981858E-03	-2.9990084E-03
c_2	2.8274958E-05	0	0	0
c_3	0	0	0	0
c_4	0	0	0	0
c_5	0	0	0	0
c_6	1.3980876E-02	0	0	0
c_7	0	0	0	0
c_8	-1.4349005E-02	0	0	0
c_9	0	0	0	0
c_{10}	0	0	0	0

Table 3

Parameters for Henry's constant (Ziabakhsh-Ganji and Kooi, 2012).

Gas	H	τ	β
CO_2	-0.114535	-5.279063	6.187967
H_2S	0.77357854	0.270494	0.275434
CH_4	-0.092248	-5.779280	7.26273
N_2	-0.008194	-5.175337	6.906469

Table 4

Group interaction parameters for PPR78 EOS in bar ($A_{ij}=A_{ji}$, and $B_{ij}=B_{ji}$) (Privat and Jaubert, 2014).

Gas	CO_2	H_2S	N_2	CH_4	H_2O
CO_2	0	-	-	-	-
H_2S	A=1349 B=2014	0	-	-	-
N_2	A=984.2 B=2214	A=3195 B=5501	0	-	-
CH_4	A=1373 B=1942	A=1812 B=2889	A=379 B=372	0	-
H_2O	A=5593 B=2779	A=6039 B=5991	A=25740 B=54900	A=22650 B=47220	0

Table 5

Binary interaction parameters for PR EOS ($k_{ij}=k_{ji}$).

Gas	CO_2	H_2S	N_2	CH_4	H_2O
CO_2	0	-	-	-	-
H_2S	0.099 ^a	0	-	-	-
N_2	-0.007 ^a	0	0	-	-
CH_4	0.1 ^a	0.084 ^b	0	0	-
H_2O	0.19014 ^c	0.105 ^c	0.32547 ^c	0.47893 ^c	0

^a extracted from Li and Yan (2009).^b extracted from Kontogeorgis et al. (2006).^c extracted from Ziabakhsh-Ganji and Kooi (2012).

where τ (cm^3g^{-1}) and β ($\text{cm}^3\text{K}^{0.5}\text{g}^{-1}$) are adjustable parameters. The values of η , τ and β are listed in Table 3.

Fugacity coefficients (ϕ_i) in both PPR78 EOS and PR EOS are calculated from the following fugacity equation:

$$\ln \phi_i = \frac{b_i}{b} (Z - 1) - \ln(Z - B) - \frac{A}{B(\delta_2 - \delta_1)} \left(\frac{2 \sum_{j=1}^N y_j a_{ij}}{a} - \frac{b_i}{b} \right) \ln \left(\frac{Z + \delta_2 B}{Z + \delta_1 B} \right) \quad (16)$$

where δ_1 is $1 + \sqrt{2}$, δ_2 is $1 - \sqrt{2}$. The a_i , b_i and m_i parameters of pure components in the mixture are calculated from:

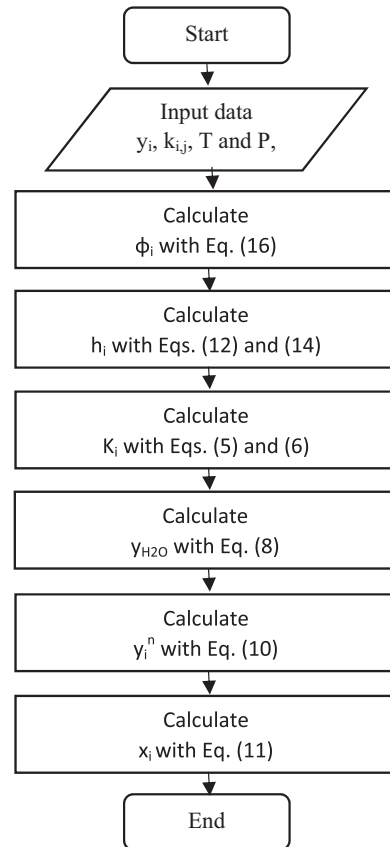


Fig. 1. Flow chart of calculation procedure.

$$\begin{cases} a_i(T) = 0.457236 \frac{R^2 T_{c,i}^2}{P_{c,i}} \left[1 + m_i \left(1 - \sqrt{\frac{T}{T_{c,i}}} \right) \right]^2 \\ b_i = 0.077796 \frac{R T_{c,i}}{P_{c,i}} \\ m_i = 0.37464 + 1.54226 \omega_i - 0.26992 \omega_i^2 \end{cases} \quad (17)$$

here P_c , T_c and ω_i are the critical pressure, critical temperature and acentric factor of pure compounds, respectively.

The a and b parameters of the mixture gas are obtained by applying classic mixing rules widely employed in oil reservoir simulation software:

$$\begin{cases} a = \sum_{i=1}^N \sum_{j=1}^N y_i y_j a_{ij} \\ b = \sum_{i=1}^N y_i b_i \\ a_{ij} = \sqrt{a_i a_j} (1 - k_{ij}) \end{cases} \quad k_{ij}=0 \quad (18)$$

where N denotes the number of compounds in the mixture, and k_{ij} the binary interaction parameter between binary pairs in the mixture. The

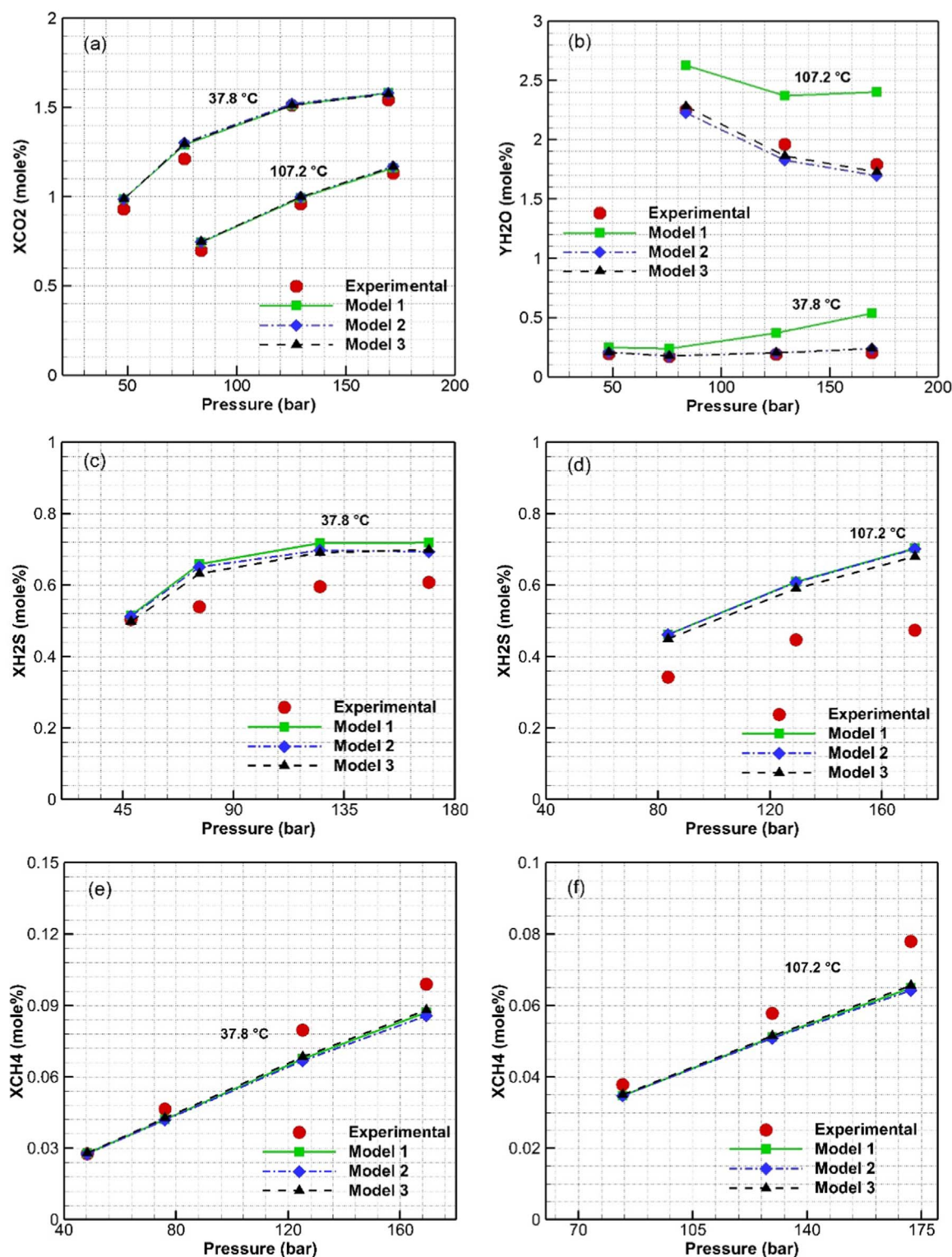


Fig. 2. Comparison between experimental (Huang et al., 1985) and predicted $\text{CO}_2\text{-H}_2\text{S-CH}_4$ gas mixture solubility in water. (a) CO_2 solubility in the aqueous phase at 37.8 °C and 107.2 °C; (b) H_2O solubility in the gas phase at 37.8 °C and 107.2 °C; (c) H_2S solubility in the aqueous phase at 37.8 °C; (d) H_2S solubility in the aqueous phase at 107.2 °C; (e) CH_4 solubility in aqueous phase at 37.8 °C; (f) CH_4 solubility in aqueous phase at 107.2 °C.

difference between PPR78 EOS and PR EOS is in the way the binary interaction parameters (k_{ij}) between the binary pairs i and j is calculated. Binary interaction parameters are the single most important parameter in both PPR78 EOS and PR EOS that affects phase equilibrium predictions of multicomponent systems.

In PPR78 EOS, k_{ij} is temperature dependent through the application of the following group contribution expression:

$$k_{ij}(T) = \frac{A_{ij} \left(\frac{298.15}{T} \right)^{\left(\frac{B_{ij}}{A_{ij}} - 1 \right)} - \left(\frac{\sqrt{a_i(T)}}{b_i} - \frac{\sqrt{a_j(T)}}{b_j} \right)^2}{2 \left(\frac{\sqrt{a_i(T) \cdot a_j(T)}}{b_i \cdot b_j} \right)} \quad (19)$$

where T is temperature in Kelvin. A_{ij} and B_{ij} are group interaction parameters. Their estimated values for mixed CO_2 , CH_4 , H_2S , N_2 and

Table 6

Absolute Average Relative Deviation (AARD %) between experimental and calculated solubilities in the aqueous phase.

Reference	Component	AARD%		
		Model 2	Model 1	Model 3
Huang et al. (1985)	CO ₂	4.17	3.94	4.18
	H ₂ S	26.60	27.89	24.04
	CH ₄	11.35	10.80	10.12
	H ₂ O	15.54	57.71	6.77
Dhima et al. (1999)	CO ₂	6.28	7.50	–
	CH ₄	4.70	4.49	–
	CO ₂	6.48	6.40	–
Al Ghafri et al. (2014)	CH ₄	34.79	34.81	–
	H ₂ O	33.06	32.72	–
	H ₂ O	11.40	161.14	–
Foltran et al. (2015)	H ₂ O	11.40	161.14	–
Savary et al. (2012)	H ₂ S	6.36	6.50	–

H₂O gases are listed in Table 4.

In PR EOS, k_{ij} are constant values determined directly by minimizing the difference between predicted and experimental data. k_{ij} values for mixed CO₂, CH₄, H₂S, N₂ and H₂O gases are listed in Table 5.

Finally, Z in Eq. (16) is the compressibility factor calculated from the following cubic equation:

$$Z^3 - (1 - B)Z^2 + (A - 2B - 3B^2)Z - (AB - B^2 - B^3) = 0 \quad (20)$$

which is derived from the general form of Peng-Robinson EOS for mixtures:

$$P(T, v) = \frac{RT}{v - b_i} - \frac{a_i(T)}{v(v + b_i) + b_i(v - b_i)} \quad (21)$$

where the dimensionless parameters A and B are defined as:

$$A = \frac{aP}{(RT)^2} \quad (22)$$

$$B = \frac{bP}{RT} \quad (23)$$

Z can be easily determined from Eq. (20) either analytically or numerically. It may have three roots, in which case the intermediate root is ignored and the one that gives the lowest Gibbs energy difference is selected as the correct root. The Gibbs energy difference at two roots Z_g and Z_l is determined from (Danesh, 1998):

$$\frac{(G_g - G_l)}{RT} = \left[Z_g - Z_l + \ln \left(\frac{Z_l - B}{Z_g - B} \right) - \frac{A}{B(\delta - \delta_l)} \right] \ln \left(\frac{Z_l + \delta_l B}{Z_l + \delta_g B} \right) \left(\frac{Z_g + \delta_g B}{Z_g + \delta_l B} \right) \quad (24)$$

where Z_g and Z_l are the maximum and minimum roots, respectively. If Gibbs energy difference is positive, Z_l is selected, otherwise, Z_g is considered the correct root that should be used in Eq. (16).

The calculation of gas fugacity coefficients using PPR78 EOS and PR EOS is accomplished assuming that the mole fraction of H₂O in the gas phase (y_{H_2O}) is zero. This assumption yields a non-iterative procedure which is time efficient compared with iterative procedures that rely on Rachford-Rice equation (Spycher and Pruess, 2005; Spycher et al., 2003). The proposed calculation procedure is outlined in Fig. 1.

3. Results and discussion

Experimental data used to test the performance of models 1 and 2 correspond to temperatures from 35 to 120 °C and pressures from 30 and 300 bar. These temperature and pressure ranges correspond to oil

reservoir conditions where microbial activity can be used to enhance the recovery of oil.

Deviations between calculated and measured values are expressed in terms of the absolute relative deviation percentage (ARD%):

$$ARD\% = \left(\frac{|x_{exp} - x_{cal}|}{x_{exp}} \right) \times 100 \quad (25)$$

and in terms of the average absolute relative deviation percentage (AARD%):

$$AARD\% = \frac{1}{N^{exp}} \sum \left(\frac{|x_{exp} - x_{cal}|}{x_{exp}} \right) \times 100 \quad (26)$$

where x_{exp} and x_{cal} are the experimental and calculated molar fractions of the gas, respectively, and N^{exp} is the number of data points.

3.1. Pure CO₂

Table A-2 contains ARD% between experimental and predicted solubility values of CO₂ in water. Experimental solubility values were collected from 29 references and correspond to CO₂-poor gas phase in equilibrium with pure water. The AARD% between experimental and predicted solubility values for models 1 and 2 are 4.08 and 3.98, respectively. These were calculated using 306 data points. These values indicate that both models 1 and 2 achieve good predictions for the solubility of a CO₂-poor gas phase in water at temperature and pressure ranges relevant to MEOR.

Table A-3 contains ARD% between experimental and predicted solubility values of H₂O in CO₂-rich gas phase. Experimental data were collected from 12 references and correspond to pure CO₂ gas phase in equilibrium with pure water. It is found that model 2 is capable of reproducing experimental data of H₂O solubility in pure CO₂ with good precision as indicated by the AARD% of 6.14. Model 1 was successful in the regeneration of experimental data of H₂O solubility in pure CO₂ for pressures lower than 50 bar. However, this model overestimated H₂O solubility in the gas phase for higher pressures. The AARD% of H₂O solubility in the gas phase for model 1 is 137.09.

Table A-4 contains ARD% between experimental and predicted solubility values of CO₂ in brine with NaCl molality of 0.0172–6 m. Predicted solubility values with models 1 and 2 are in good agreement with experimental data for temperature and pressure conditions relevant to MEOR. For instance, for a NaCl molality of 0.0172, the AARD% for models 1 and 2 are 4.47 and 5.56, respectively, and for a higher NaCl molality of 0.172 the AARD% for models 1 and 2 are 3.86 and 4.49, respectively. The AARD% for both models increases with increasing temperature. For instance, for a NaCl molality of 0.0172, the ARD% between experimental and predicted solubility values at 60 °C and 80 °C for model 1 increases from 0.42 to 1.45, whereas for model 2 it increases from 6.93 and 8.0. At higher NaCl molalities, ARD% between experimental and predicted solubility values generally decreases with increasing temperature.

Models 1 and 2 have been proven to have acceptable accuracy in reproducing experimental solubility values of CO₂ in water and brine. Subsequently, this work tests the validity of the proposed model in predicting the solubility of CO₂-CH₄-H₂S-N₂ gas mixtures in water and brine. For this, the solubility predictions obtained with models 1 and 2 are compared against experimental data on the solubility CO₂-H₂S-CH₄, CO₂-H₂S, CO₂-CH₄, and CO₂-N₂ gas mixtures in water and brine. It is also compared with solubility predictions obtained with the model proposed by Ziabakhsh-Ganji and Kooi (2012) which is referred to as model 3 in this work. Model 3 uses the Rachford-Rice equation that requires an iterative approach to be solved.

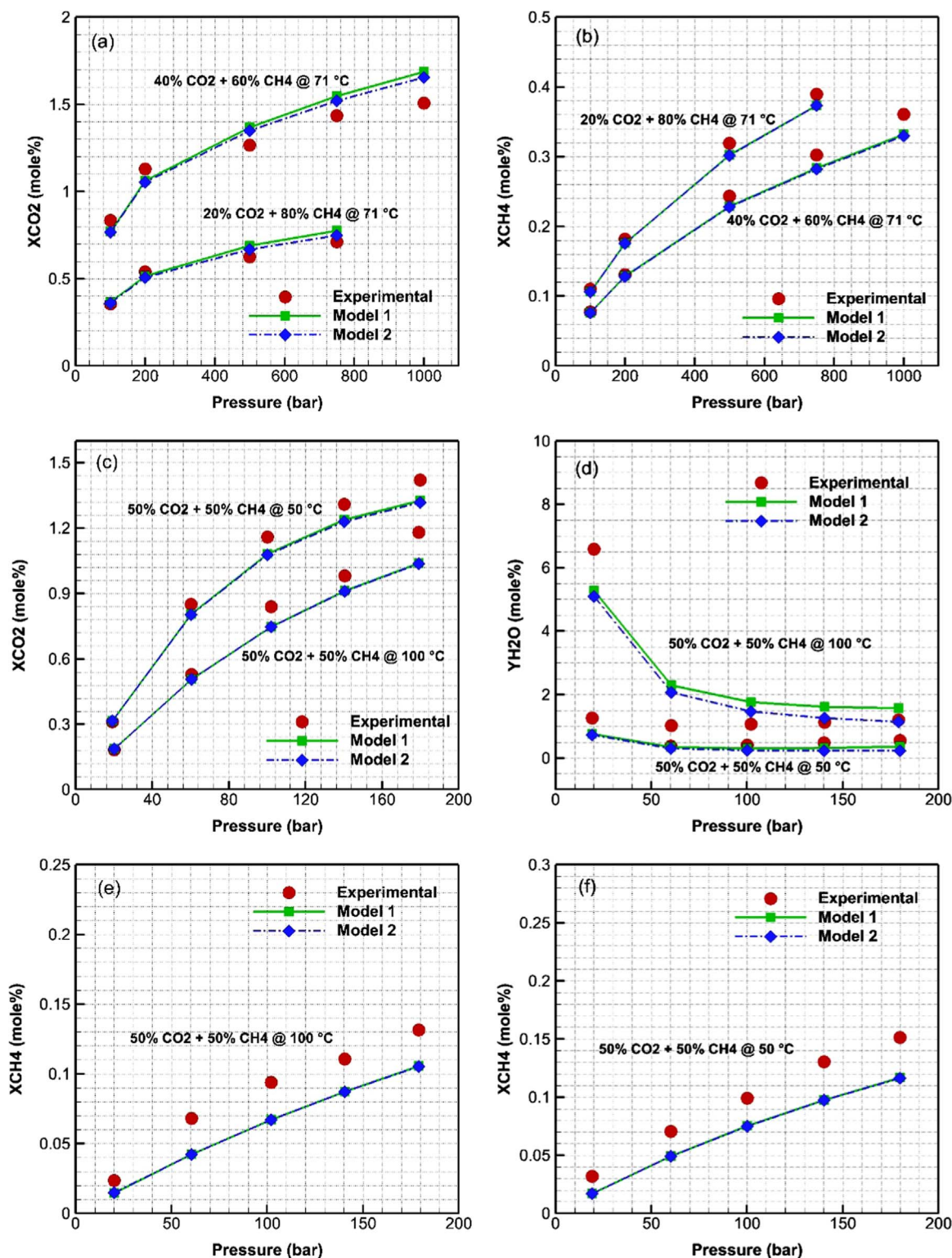


Fig. 3. Comparison between experimental and predicted CO_2 - CH_4 gas mixtures solubility in water. (a) and (c) CO_2 solubility in aqueous phase; (d) H_2O Solubility in the gas phase; (b), (e) and (f) CH_4 solubility in water. Experimental data for (a) and (b) are from [Dhima et al. \(1999\)](#), other experimental data are from [Al Ghafrí et al. \(2014\)](#).

3.2. CO_2 - CH_4 - H_2S

Published experimental data of CO_2 - CH_4 - H_2S - N_2 gas mixtures solubility in brine is scarce. Hence, experimental data of CO_2 - CH_4 - H_2S gas mixtures solubility in water reported by [Huang et al. \(1985\)](#) is used to test models 1, 2 and 3. This experimental data includes information on the initial feed of each compound, including H_2O in

the mixture, which is needed to solve Rachford-Rice equation used by model 3. [Fig. 2](#) compares experimental and predicted solubility values of CO_2 , H_2S and CH_4 in water at 37.8–107 °C and 40–180 bar. The AARD% between experimental and predicted solubility values for models 1, 2 and 3 are summarized in [Table 6](#). All three models predicted similar solubility values for CO_2 , H_2S and CH_4 in water, confirming the feasibility of using a non-iterative approach instead of

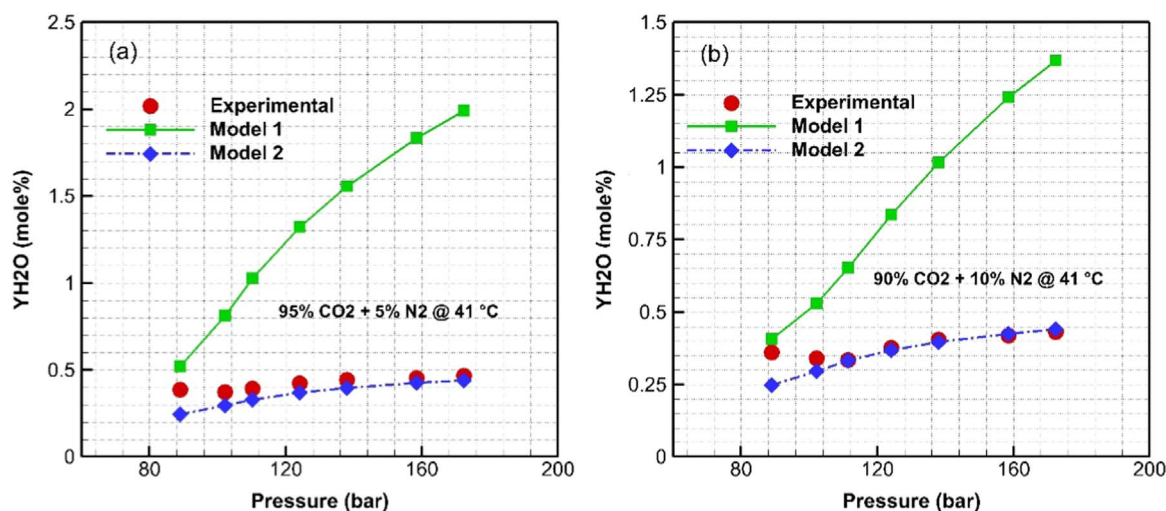


Fig. 4. Comparison between experimental (Foltran et al., 2015) and predicted H₂O solubility in a CO₂-N₂ gas mixture phase.

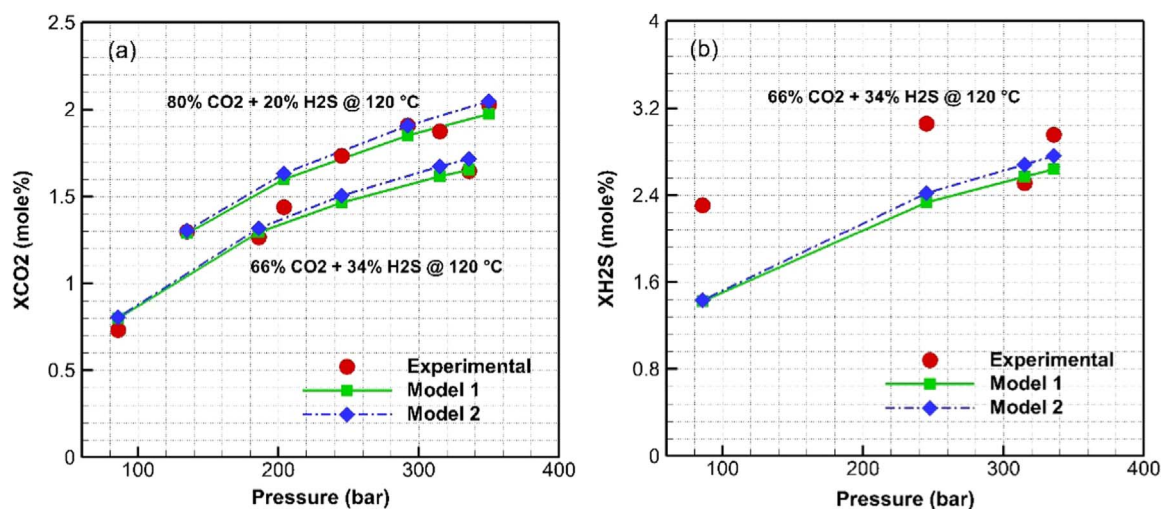


Fig. 5. Comparison between experimental (Savary et al., 2012) and predicted CO₂-H₂S gas mixtures solubility in water. (a) CO₂ solubility in aqueous phase; (b) H₂S solubility in aqueous phase.

an iterative approach to predict the solubility of gas mixtures in water at temperature and pressure conditions relevant to MEOR. Because it uses iterative approach, model 3 gives slightly better results than models 1 and 2, which use a non-iterative approach. However, the difference is insignificant given the exhausting computational requirement of model 3.

A comparison between the performance of model 1 and 2 shows that model 1 better predicts the solubility of gas mixtures in water than model 2. The AARD% of CH₄ and H₂S in water for model 1 are 9.45 and 15.79 at 37.8 °C, and 12.15 and 39.98 at 107.2 °C, respectively. Differently, the AARD% of CH₄ and H₂S in water with model 2 are 10.04 and 13.36 at 37.8 °C, and 12.67 and 39.84 at 107.2 °C, respectively. Both models underestimated the solubility of CH₄ and overestimated the solubility of H₂S in pure water. Comparisons show that as temperature increases, the accuracy of both models in predicting CH₄ and H₂S solubility in pure water decreases.

3.3. CO₂-CH₄

The experimental solubility values of CO₂-CH₄ gas mixtures in water at 71 °C and 100–1000 bar reported by Dhima et al. (1999), and at 50–100 °C and 19–180 bar reported by Al Ghafri et al. (2014) are compared with solubility values of CO₂-CH₄ gas mixtures predicted with models 1 and 2.

Fig. 3a and b compare experimental and predicted solubility values of CO₂ and CH₄ in water at 71 °C and 100–1000 bar. Within this high pressure range, predicted solubility values obtained with models 1 and 2 are almost identical and showed high accuracy. Model 1 predicted the solubility of CO₂ and CH₄ in water with an AARD% of 7.50 and 4.49, respectively, and model 2 predicted the solubility of CO₂ and CH₄ in water with an AARD% of 6.28 and 4.70, respectively.

Fig. 3c–f compare experimental and predicted solubility values of CO₂-CH₄ gas mixtures in water at 50–100 °C and 19–180 bar. A comparison between experimental and predicted solubility values of CO₂ in water obtained with models 1 and 2 within this low pressure range, shows a high accuracy of both models to predict the solubility of CO₂ in water. Models 1 and 2 predicted CO₂ solubility in water with an AARD% of 6.19 and 6.43, respectively. However, the accuracy of both models to predict the solubility of CH₄ in water decreased for this low pressure range. Both model 1 and 2 predicted CH₄ solubility in water with an AARD% of 29.3. The AARD% for H₂O solubility in the gas phase for models 1 and 2 within this low pressure range are 42.49 and 32.64, respectively.

Because pressure conditions in depleted oil reservoirs fall within the high pressure range (up to 1000 bar), it is expected that the proposed model will be suitable to predict the solubility of CO₂-CH₄-H₂S-N₂ gas mixtures in brine in reactive transport simulations of MEOR.

3.4. CO₂-N₂

Experimental data of H₂O solubility in CO₂-N₂ gas mixtures at 41 °C and 80–190 bar was reported by Foltran et al. (2015). Fig. 4 compares experimental and predicted H₂O solubility values at two different CO₂-N₂ gas mixture compositions. Model 2 reproduced H₂O solubility data with an AARD% between the calculated and experimental solubilities of 11.40. Model 1 overestimated the solubility of H₂O in the gas phase. These results confirm that the proposed model solved using PPR78 EOS to calculate fugacity coefficients in the gas phase (model 1) is not suitable to predict the solubility of H₂O in CO₂-CH₄-H₂S-N₂ gas mixtures.

3.5. CO₂-H₂S

Experimental solubility values of CO₂-H₂S gas mixtures in water at 120 °C, 86–350 bar, were reported by Savary et al. (2012). These experimental solubility values are compared with solubility values predicted with models 1 and 2 (Fig. 5). A very good agreement between experimental and predicted solubility values of CO₂ in water were obtained with both models. The AARD% between experimental and calculated solubility values for both models is 6.4% (Table 6). Both models predicted the solubility of H₂S in water with an AARD% of around 30. This indicates the lack of accuracy of both models to predict the solubility of H₂S in water at high H₂S concentration conditions.

4. Conclusions

A new non-iterative fugacity-activity thermodynamic model to predict the solubility of CO₂-CH₄-H₂S-N₂ gas mixtures in water and brine has been proposed. Gas phase fugacity coefficients (ϕ_i) in the proposed model were calculated using PPR78 EOS (model 1) and PR EOS (model 2). Comparisons between experimental and predicted solubility values at temperature and pressure conditions relevant to MEOR have shown that:

- The proposed model predicts the solubility of pure CO₂ in water and brine of salinity up to 2.5 m NaCl. Up to this salinity level, predictions of CO₂ solubility with the proposed model are accurate using either PPR78 EOS or PR EOS to calculate ϕ_i . The proposed

model using PR EOS to calculate ϕ_i accurately predicts H₂O solubility in CO₂-rich phases. However, the proposed model using PPR78 EOS to calculate ϕ_i leads to inaccurate predictions of H₂O solubility in CO₂-rich phases. Inaccuracy increases with increasing temperature, pressure and salinity.

- The proposed model's predictions of CO₂-CH₄-H₂S gas mixtures solubility in water are good and are almost identical using either PPR78 EOS or PR EOS to calculate ϕ_i . However, similar to the predictions of pure CO₂ solubility in water, the proposed model using PPR78 EOS to calculate ϕ_i (model 1) overestimates H₂O solubility in CO₂-CH₄-H₂S gas mixtures.
- Comparisons of the proposed model's predictions of CO₂-CH₄-H₂S gas mixtures solubility in water against predictions obtained with an iterative fugacity-activity model have shown that the proposed non-iterative model using PR EOS to calculate ϕ_i can be used as substitute for iterative fugacity-activity models that relies on the solution of Rachford-Rice equation.
- PR EOS that uses calibrated constant binary interaction parameters to calculate ϕ_i in the proposed model leads to better predictions of CO₂-CH₄-H₂S, CO₂-CH₄, CO₂-N₂, and CO₂-H₂S gas mixtures solubility in water than PPR78 EOS that used temperature and composition dependent binary interaction parameters to calculate ϕ_i . As such, it is recommended that the proposed model be used with ϕ_i calculated using PR EOS.
- Most experimental data used in this work are for pure gas and gas mixtures solubility in water. Nonetheless, it is expected that the proposed model will be equally suitable in reproducing experimental data of CO₂-CH₄-H₂S-N₂ gas mixtures solubility in brine. This is because the activity correlations used in the proposed model include the effect of salinity, and binary interaction parameters of PR EOS can always be recalibrated using new experimental data if necessary.
- The injected and biogenically formed gases in depleted oil reservoirs can dissolve in both the aqueous and oil phases. The partitioning of gases between the aqueous and oil phases can be included in a simulation program by including one additional experimental or empirical correlation describing the solubility of each individual gas in the oil phase. However, this correlation would need to be solved simultaneously with the thermodynamic model describing the solubility of gases in the aqueous phase.

Appendix A

Flash calculations using PR EOS are performed to predict gas-liquid equilibrium conditions. These calculations relies on the solution of Rachford-Rice equation (Eq. (A1)) where the total mole fraction (z_i) of each compound must be known beforehand:

$$\sum_{i=1}^N \frac{z_i(K_i - 1)}{1 + (K_i - 1)n^V} = 0 \quad (\text{A1})$$

The solution of Rachford-Rice equation yields the mole fraction of the gas phase (n^V) in equilibrium with the liquid phase. Equilibrium constant of compound i in Rachford-Rice equation are calculated from Eqs. (5) and (6) at given temperature and pressure conditions. Then, the mole fraction of each compound in the liquid and gas phases is determined using following equations:

$$x_i = \frac{z_i}{1 + (K_i - 1)n^V} \quad (\text{A2})$$

$$y_i = \frac{K_i z_i}{1 + (K_i - 1)n^V} \quad (\text{A3})$$

Table A-1
Constants for Eq. (A10).

Constant	a_1	a_2	a_3	a_4	a_5	a_6
	-7.8595178	1.8440825	-11.786649	22.680741	-15.9618719	1.8012250

Table A-2Experimental data of CO₂ solubility in pure water and calculated ARD% values.

Temp °C	Pressure (bar)	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	Reference
35.00	50.70	1.754	0.582	0.498	Wiebe and Gaddy (1940)
35.00	76.00	2.189	0.511	0.766	Wiebe and Gaddy (1940)
35.00	101.30	2.288	0.072	1.352	Wiebe and Gaddy (1940)
35.00	152.00	2.394	0.849	1.445	Wiebe and Gaddy (1940)
35.00	202.70	2.495	0.714	2.125	Wiebe and Gaddy (1940)
35.00	39.20	1.083	36.418	36.332	Sander (1912)
35.00	39.20	1.306	13.124	13.054	Sander (1912)
35.00	49.00	1.381	24.960	24.860	Sander (1912)
35.00	49.00	1.604	7.587	7.501	Sander (1912)
35.00	58.80	1.663	16.031	15.907	Sander (1912)
35.00	58.80	1.430	34.936	34.793	Sander (1912)
35.00	68.60	1.968	6.159	5.992	Sander (1912)
35.00	68.60	1.824	14.540	14.360	Sander (1912)
35.00	78.50	2.127	3.426	3.065	Sander (1912)
35.00	40.90	1.574	3.201	3.264	Liu et al. (2011)
35.00	60.80	2.035	3.409	3.520	Liu et al. (2011)
35.00	80.90	2.240	1.082	1.642	Liu et al. (2011)
35.00	100.80	2.314	1.112	2.507	Liu et al. (2011)
35.00	120.50	2.375	1.400	3.187	Liu et al. (2011)
35.00	140.10	2.454	2.677	4.737	Liu et al. (2011)
35.00	158.30	2.494	2.648	4.937	Liu et al. (2011)
35.01	35.46	0.810	69.182	69.084	Vilcu and Gainar (1967)
35.01	40.53	0.990	52.876	52.777	Vilcu and Gainar (1967)
35.01	45.60	1.120	46.816	46.709	Vilcu and Gainar (1967)
35.01	50.66	1.310	34.581	34.469	Vilcu and Gainar (1967)
35.01	55.73	1.480	26.359	26.237	Vilcu and Gainar (1967)
35.01	60.80	1.630	20.582	20.444	Vilcu and Gainar (1967)
35.01	65.86	1.810	13.195	13.038	Vilcu and Gainar (1967)
35.01	70.93	1.960	8.164	7.971	Vilcu and Gainar (1967)
35.01	75.99	2.140	1.748	1.487	Vilcu and Gainar (1967)
35.05	30.29	1.259	3.845	3.895	Valtz et al. (2004)
35.05	40.05	1.563	4.075	4.136	Valtz et al. (2004)
35.05	49.85	1.837	5.088	5.165	Valtz et al. (2004)
35.05	59.49	2.033	4.543	4.647	Valtz et al. (2004)
35.05	60.77	2.066	4.956	5.064	Valtz et al. (2004)
35.05	69.72	2.229	5.659	5.816	Valtz et al. (2004)
35.05	69.86	2.152	2.196	2.360	Valtz et al. (2004)
35.05	70.29	2.221	4.979	5.142	Valtz et al. (2004)
35.05	79.63	2.304	4.229	4.637	Valtz et al. (2004)
37.71	73.09	2.017	2.232	2.031	Chapoy et al. (2004)
40.00	50.70	1.609	0.575	0.478	Wiebe and Gaddy (1940)
40.00	76.00	2.032	0.120	0.344	Wiebe and Gaddy (1940)
40.00	101.30	2.186	0.290	0.840	Wiebe and Gaddy (1940)
40.00	126.70	2.256	0.610	1.131	Wiebe and Gaddy (1940)
40.00	152.00	2.308	1.048	1.113	Wiebe and Gaddy (1940)
40.00	202.70	2.488	2.044	4.724	Wiebe and Gaddy (1940)
40.00	100.00	2.070	5.680	4.535	Bando et al. (2003)
40.00	150.00	2.230	4.375	2.173	Bando et al. (2003)
40.00	200.00	2.340	3.932	1.117	Bando et al. (2003)
40.05	46.67	1.639	6.735	6.817	Kiepe et al. (2002)
40.05	56.64	1.902	8.753	8.856	Kiepe et al. (2002)
40.05	66.44	2.123	10.427	10.564	Kiepe et al. (2002)
40.05	92.32	2.481	13.138	13.804	Kiepe et al. (2002)
40.21	41.19	1.420	1.812	1.889	Chapoy et al. (2004)
45.00	41.00	1.305	1.703	1.793	Liu et al. (2011)
45.00	60.90	1.711	1.722	1.862	Liu et al. (2011)
45.00	81.10	2.022	3.356	3.623	Liu et al. (2011)
45.00	100.80	2.170	3.380	4.155	Liu et al. (2011)
45.00	120.60	2.231	2.648	4.008	Liu et al. (2011)
45.00	141.10	2.266	1.512	3.299	Liu et al. (2011)
45.00	158.60	2.296	0.897	2.974	Liu et al. (2011)
45.08	30.01	1.018	1.570	1.644	Valtz et al. (2004)
45.08	39.69	1.293	3.287	3.374	Valtz et al. (2004)
45.08	39.77	1.259	0.524	0.613	Valtz et al. (2004)
45.08	49.52	1.508	2.619	2.726	Valtz et al. (2004)
45.08	49.82	1.532	3.745	3.851	Valtz et al. (2004)
45.08	59.78	1.720	3.428	3.563	Valtz et al. (2004)
45.08	59.92	1.726	3.626	3.760	Valtz et al. (2004)
45.08	69.23	1.895	4.590	4.763	Valtz et al. (2004)
45.08	69.84	1.905	4.644	4.820	Valtz et al. (2004)
45.08	79.33	2.031	4.791	5.035	Valtz et al. (2004)
48.82	52.16	1.420	1.399	1.268	Chapoy et al. (2004)
48.99	93.33	2.017	2.165	2.605	Chapoy et al. (2004)

(continued on next page)

Table A-2 (continued)

Temp °C	Pressure (bar)	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	Reference
49.95	51.00	1.420	1.754	1.882	Koschel et al. (2006)
49.95	105.30	2.000	1.514	0.761	Koschel et al. (2006)
49.95	142.00	2.140	1.278	0.411	Koschel et al. (2006)
49.95	202.00	2.270	1.973	0.632	Koschel et al. (2006)
50.00	50.70	1.367	1.563	1.432	Wiebe and Gaddy (1939)
50.00	76.00	1.779	0.183	0.055	Wiebe and Gaddy (1939)
50.00	101.30	2.018	0.538	1.160	Wiebe and Gaddy (1939)
50.00	126.70	2.106	0.582	0.763	Wiebe and Gaddy (1939)
50.00	152.00	2.174	0.966	0.902	Wiebe and Gaddy (1939)
50.00	202.70	2.289	1.169	1.422	Wiebe and Gaddy (1939)
50.00	200.00	2.300	0.434	2.107	Tödheide and Franck (1963)
50.00	68.20	1.651	1.738	1.542	Briones et al. (1987)
50.00	75.30	1.750	1.355	1.119	Briones et al. (1987)
50.00	87.20	1.768	7.550	7.179	Briones et al. (1987)
50.00	101.30	2.081	3.549	4.152	Briones et al. (1987)
50.00	122.10	2.096	0.283	0.944	Briones et al. (1987)
50.00	147.50	2.215	1.466	3.210	Briones et al. (1987)
50.00	147.50	2.207	1.109	2.859	Briones et al. (1987)
50.00	176.80	2.262	0.188	2.417	Briones et al. (1987)
50.00	101.33	1.980	1.380	0.745	D'souza et al. (1988)
50.00	152.00	2.100	4.523	2.590	D'souza et al. (1988)
50.00	101.00	2.075	3.357	3.953	Dohrn et al. (1993)
50.00	201.00	2.347	1.486	3.989	Dohrn et al. (1993)
50.00	100.00	1.970	1.486	0.887	Bando et al. (2003)
50.00	150.00	2.090	4.761	2.860	Bando et al. (2003)
50.00	200.00	2.290	0.872	1.679	Bando et al. (2003)
50.00	80.00	1.601	14.233	13.926	Portier and Rochelle (2005)
50.00	80.00	1.658	10.270	9.974	Portier and Rochelle (2005)
50.00	100.00	1.693	18.083	17.386	Portier and Rochelle (2005)
50.00	120.00	1.952	7.290	6.036	Portier and Rochelle (2005)
50.00	120.00	1.917	9.229	7.952	Portier and Rochelle (2005)
50.00	100.00	1.999	0.013	0.577	Shagiakhmetov and Tarzimanov (1981)
50.00	200.00	2.293	0.740	1.808	Shagiakhmetov and Tarzimanov (1981)
50.00	35.00	1.029	2.024	1.926	Oleinik (cited in Namiot and Bondareva (1991))
50.00	50.00	1.357	1.318	1.189	Oleinik (cited in Namiot and Bondareva (1991))
50.00	75.00	1.773	0.140	0.371	Oleinik (cited in Namiot and Bondareva (1991))
50.00	100.00	2.014	0.732	1.317	Oleinik (cited in Namiot and Bondareva (1991))
50.00	130.00	2.130	0.047	1.462	Oleinik (cited in Namiot and Bondareva (1991))
50.00	160.00	2.216	0.028	1.955	Oleinik (cited in Namiot and Bondareva (1991))
50.00	33.00	0.996	0.516	0.422	Zel'vinskii (1937)
50.00	33.01	0.977	2.506	2.410	Zel'vinskii (1937)
50.00	33.21	1.016	0.944	1.037	Zel'vinskii (1937)
50.00	33.23	0.986	2.141	2.045	Zel'vinskii (1937)
50.00	47.42	1.273	4.000	3.873	Zel'vinskii (1937)
50.00	47.50	1.282	3.419	3.294	Zel'vinskii (1937)
50.00	47.50	1.326	0.021	0.142	Zel'vinskii (1937)
50.00	57.76	1.523	0.455	0.605	Zel'vinskii (1937)
50.00	61.10	1.597	1.570	1.729	Zel'vinskii (1937)
50.00	61.73	1.617	2.137	2.298	Zel'vinskii (1937)
50.00	61.91	1.624	2.382	2.543	Zel'vinskii (1937)
50.00	62.82	1.634	2.111	2.276	Zel'vinskii (1937)
50.00	74.19	1.796	1.994	2.215	Zel'vinskii (1937)
50.00	74.80	1.849	4.390	4.610	Zel'vinskii (1937)
50.00	75.49	1.828	2.826	3.054	Zel'vinskii (1937)
50.00	90.79	2.061	6.221	6.592	Zel'vinskii (1937)
50.00	92.71	2.036	4.318	4.729	Zel'vinskii (1937)
50.00	93.22	2.050	4.779	5.196	Zel'vinskii (1937)
50.00	49.55	1.366	0.005	0.131	Malinin and Saveleva (1972)
50.00	49.55	1.372	0.406	0.532	Malinin and Saveleva (1972)
50.00	49.55	1.372	0.420	0.546	Malinin and Saveleva (1972)
50.00	49.55	1.373	0.529	0.655	Malinin and Saveleva (1972)
50.00	39.01	1.210	5.457	5.555	Matouš et al. (1969)
50.00	33.32	1.003	0.610	0.515	Al Ghafri et al. (2014)
50.00	44.15	1.269	0.991	1.104	Al Ghafri et al. (2014)
50.00	55.85	1.561	4.986	5.123	Al Ghafri et al. (2014)
50.00	69.53	1.758	3.394	3.586	Al Ghafri et al. (2014)
50.00	90.62	2.004	3.619	3.999	Al Ghafri et al. (2014)
50.00	135.21	2.173	1.236	2.747	Al Ghafri et al. (2014)
50.00	186.83	2.280	0.042	2.326	Al Ghafri et al. (2014)
50.00	74.06	1.829	3.867	4.084	Hou et al. (2013)
50.00	100.21	2.054	2.602	3.182	Hou et al. (2013)
50.00	129.73	2.141	0.584	1.985	Hou et al. (2013)
50.00	175.33	2.255	0.033	2.245	Hou et al. (2013)
50.00	41.10	1.170	1.782	1.673	Liu et al. (2011)

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Table A-2 (continued)

Temp °C	Pressure (bar)	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	Reference
50.00	61.20	1.570	0.237	0.075	Liu et al. (2011)
50.00	81.00	1.815	1.368	1.087	Liu et al. (2011)
50.00	101.00	2.001	0.242	0.377	Liu et al. (2011)
50.00	120.40	2.087	0.400	0.784	Liu et al. (2011)
50.00	159.90	2.161	2.534	0.502	Liu et al. (2011)
50.05	40.50	1.090	7.921	7.806	Bamberger et al. (2000)
50.05	50.60	1.370	1.129	0.998	Bamberger et al. (2000)
50.05	60.60	1.610	2.934	3.090	Bamberger et al. (2000)
50.05	70.80	1.760	2.579	2.780	Bamberger et al. (2000)
50.05	80.80	1.900	3.354	3.621	Bamberger et al. (2000)
50.05	90.90	2.000	3.361	3.745	Bamberger et al. (2000)
50.05	100.90	2.050	2.252	2.851	Bamberger et al. (2000)
50.05	111.00	2.100	2.082	2.974	Bamberger et al. (2000)
50.05	121.00	2.140	2.003	3.172	Bamberger et al. (2000)
50.05	141.10	2.170	0.303	1.946	Bamberger et al. (2000)
50.05	50.00	1.473	6.727	6.847	Yan et al. (2011)
50.05	100.00	2.137	6.489	7.039	Yan et al. (2011)
50.05	150.00	2.206	0.776	2.575	Yan et al. (2011)
50.05	200.00	2.285	1.070	1.486	Yan et al. (2011)
50.05	300.00	2.492	0.175	3.280	Yan et al. (2011)
55.00	43.70	1.187	2.017	2.146	Liu et al. (2011)
55.00	61.10	1.501	1.813	1.992	Liu et al. (2011)
55.00	84.80	1.797	1.000	1.320	Liu et al. (2011)
55.00	99.90	1.918	0.445	0.963	Liu et al. (2011)
55.00	122.00	2.057	1.245	2.277	Liu et al. (2011)
55.00	131.90	2.105	1.626	2.892	Liu et al. (2011)
55.00	152.30	2.131	0.324	1.394	Liu et al. (2011)
60.00	100.00	1.850	1.135	1.632	Bando et al. (2003)
60.00	150.00	2.040	1.821	0.258	Bando et al. (2003)
60.00	200.00	2.250	1.409	3.723	Bando et al. (2003)
60.00	41.00	1.020	1.699	1.551	Mohammadian et al. (2015)
60.00	83.00	1.646	1.621	1.291	Mohammadian et al. (2015)
60.00	103.00	1.839	0.670	0.120	Mohammadian et al. (2015)
60.00	138.00	2.019	0.731	0.564	Mohammadian et al. (2015)
60.00	158.00	2.071	1.543	0.172	Mohammadian et al. (2015)
60.00	172.00	2.104	1.942	0.029	Mohammadian et al. (2015)
60.00	193.00	2.152	2.258	0.045	Mohammadian et al. (2015)
60.05	40.50	0.960	6.944	6.789	Bamberger et al. (2000)
60.05	50.60	1.210	0.541	0.369	Bamberger et al. (2000)
60.05	60.60	1.380	0.079	0.126	Bamberger et al. (2000)
60.05	70.80	1.570	2.783	3.025	Bamberger et al. (2000)
60.05	80.80	1.660	0.733	1.040	Bamberger et al. (2000)
60.05	90.90	1.790	2.181	2.567	Bamberger et al. (2000)
60.05	100.90	1.860	1.337	1.846	Bamberger et al. (2000)
60.05	111.00	1.950	2.356	3.026	Bamberger et al. (2000)
60.05	121.00	2.010	2.519	3.395	Bamberger et al. (2000)
60.05	141.10	2.080	1.672	3.000	Bamberger et al. (2000)
70.00	35.00	0.773	4.933	4.746	Oleinik (cited in Namiot and Bondareva (1991))
70.00	50.00	1.037	4.199	3.970	Oleinik (cited in Namiot and Bondareva (1991))
70.00	75.00	1.404	2.245	1.911	Oleinik (cited in Namiot and Bondareva (1991))
70.00	100.00	1.673	0.995	0.469	Oleinik (cited in Namiot and Bondareva (1991))
70.00	130.00	1.885	0.318	0.642	Oleinik (cited in Namiot and Bondareva (1991))
70.00	160.00	2.014	0.389	1.141	Oleinik (cited in Namiot and Bondareva (1991))
71.00	100.00	1.660	1.067	0.536	Dhima et al. (1999)
71.00	125.00	1.820	1.811	0.932	Dhima et al. (1999)
71.00	150.00	1.970	0.231	1.093	Dhima et al. (1999)
71.00	200.00	2.130	0.611	1.567	Dhima et al. (1999)
75.00	50.70	1.002	3.839	3.578	Wiebe and Gaddy (1939)
75.00	76.00	1.351	2.756	2.382	Wiebe and Gaddy (1939)
75.00	101.30	1.630	0.775	0.214	Wiebe and Gaddy (1939)
75.00	152.00	1.937	0.708	0.613	Wiebe and Gaddy (1939)
75.00	202.70	2.098	1.474	0.706	Wiebe and Gaddy (1939)
75.00	101.33	1.560	5.313	4.727	D'souza et al. (1988)
75.00	152.00	1.880	3.761	2.400	D'souza et al. (1988)
75.00	35.91	0.760	3.543	3.329	Zawisza and Malesinska (1981)
75.00	50.70	1.013	2.762	2.504	Gillespie et al. (1982)
75.00	101.40	1.626	1.056	0.493	Gillespie et al. (1982)
75.00	202.70	2.104	1.184	0.989	Gillespie et al. (1982)
75.00	32.63	0.717	1.171	0.971	Zel'vinskii (1937)
75.00	32.71	0.723	0.487	0.288	Zel'vinskii (1937)
75.00	33.11	0.727	0.984	0.783	Zel'vinskii (1937)
75.00	47.22	0.985	0.066	0.305	Zel'vinskii (1937)
75.00	47.24	0.971	1.409	1.166	Zel'vinskii (1937)
75.00	61.07	1.219	1.894	2.180	Zel'vinskii (1937)

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Table A-2 (continued)

Temp °C	Pressure (bar)	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	Reference
75.00	61.73	1.204	0.031	0.262	Zel'vinskii (1937)
75.00	61.84	1.208	0.173	0.466	Zel'vinskii (1937)
75.00	62.03	1.219	0.856	1.148	Zel'vinskii (1937)
75.00	76.70	1.406	0.694	1.059	Zel'vinskii (1937)
75.00	76.94	1.436	2.560	2.920	Zel'vinskii (1937)
75.00	77.36	1.423	1.306	1.673	Zel'vinskii (1937)
75.00	93.27	1.606	2.208	2.681	Zel'vinskii (1937)
75.00	94.46	1.611	1.803	2.288	Zel'vinskii (1937)
75.00	49.55	0.988	3.489	3.233	Malinin and Saveleva (1972)
75.00	49.55	0.994	2.874	2.620	Malinin and Saveleva (1972)
75.00	49.55	0.996	2.616	2.362	Malinin and Saveleva (1972)
75.00	49.55	0.997	2.523	2.270	Malinin and Saveleva (1972)
75.00	71.23	1.267	4.999	4.644	Hou et al. (2013)
75.00	101.67	1.593	3.312	2.733	Hou et al. (2013)
75.00	132.82	1.856	0.094	0.884	Hou et al. (2013)
75.00	169.18	1.993	1.315	0.322	Hou et al. (2013)
75.15	153.10	1.920	1.787	0.434	Sako et al. (1991)
79.70	101.80	1.660	3.719	4.285	Nighswander et al. (1989)
79.95	40.50	0.800	3.811	3.553	Bamberger et al. (2000)
79.95	60.60	1.140	0.025	0.296	Bamberger et al. (2000)
79.95	70.80	1.280	0.472	0.841	Bamberger et al. (2000)
79.95	80.80	1.400	0.646	1.071	Bamberger et al. (2000)
79.95	90.90	1.510	0.926	1.419	Bamberger et al. (2000)
79.95	100.90	1.600	0.745	1.321	Bamberger et al. (2000)
79.95	111.00	1.720	2.903	3.566	Bamberger et al. (2000)
79.95	121.00	1.760	1.052	1.846	Bamberger et al. (2000)
79.95	131.00	1.840	1.934	2.857	Bamberger et al. (2000)
79.96	49.39	1.111	12.207	12.451	Kiepe et al. (2002)
79.96	67.00	1.437	14.698	14.997	Kiepe et al. (2002)
79.96	85.50	1.734	16.877	17.258	Kiepe et al. (2002)
80.00	100.00	1.323	19.444	18.759	Portier and Rochelle (2005)
80.00	100.00	1.445	9.308	8.681	Portier and Rochelle (2005)
80.00	38.81	0.799	0.259	0.015	Matouš et al. (1969)
80.00	41.00	0.813	3.147	2.889	Mohammadian et al. (2015)
80.00	62.00	1.122	3.283	2.944	Mohammadian et al. (2015)
80.00	83.00	1.333	6.098	5.630	Mohammadian et al. (2015)
80.00	103.00	1.568	2.420	1.805	Mohammadian et al. (2015)
80.00	138.00	1.782	3.471	2.389	Mohammadian et al. (2015)
80.00	158.00	1.903	1.986	0.585	Mohammadian et al. (2015)
80.00	172.00	1.938	3.134	1.476	Mohammadian et al. (2015)
80.00	193.00	2.012	3.054	1.052	Mohammadian et al. (2015)
80.00	213.00	2.064	3.506	1.194	Mohammadian et al. (2015)
80.20	43.10	0.850	2.625	2.360	Nighswander et al. (1989)
80.30	101.60	1.640	3.004	3.577	Nighswander et al. (1989)
80.50	61.10	1.120	1.979	1.645	Nighswander et al. (1989)
80.50	77.60	1.370	1.490	1.895	Nighswander et al. (1989)
80.50	78.40	1.380	1.543	1.953	Nighswander et al. (1989)
80.60	43.40	0.840	4.072	3.800	Nighswander et al. (1989)
93.30	50.70	0.851	5.710	5.310	Gillespie et al. (1982)
93.30	101.40	1.459	1.559	0.865	Gillespie et al. (1982)
93.30	202.70	2.074	0.749	2.718	Gillespie et al. (1982)
99.95	50.50	0.790	8.852	8.383	Koschel et al. (2006)
99.95	100.80	1.360	5.440	4.664	Koschel et al. (2006)
99.95	194.70	2.010	0.008	1.845	Koschel et al. (2006)
100.00	50.70	0.812	6.218	5.759	Wiebe and Gaddy (1939)
100.00	76.00	1.135	4.180	3.594	Wiebe and Gaddy (1939)
100.00	101.30	1.400	2.729	1.967	Wiebe and Gaddy (1939)
100.00	152.00	1.794	0.504	0.780	Wiebe and Gaddy (1939)
100.00	202.70	2.023	0.962	1.018	Wiebe and Gaddy (1939)
100.00	200.00	2.000	1.585	0.371	Tödheide and Franck (1963)
100.00	45.60	0.760	3.842	3.416	Zawisza and Malesinska (1981)
100.00	100.00	1.444	1.216	1.937	Shagiakhmetov and Tarzimanov (1981)
100.00	200.00	2.030	0.084	1.843	Shagiakhmetov and Tarzimanov (1981)
100.00	32.49	0.574	2.123	1.756	Zel'vinskii (1937)
100.00	33.01	0.590	0.791	0.427	Zel'vinskii (1937)
100.00	33.10	0.583	2.287	1.918	Zel'vinskii (1937)
100.00	33.13	0.581	2.653	2.282	Zel'vinskii (1937)
100.00	33.21	0.578	3.447	3.073	Zel'vinskii (1937)
100.00	46.71	0.801	0.514	0.097	Zel'vinskii (1937)
100.00	47.36	0.812	0.388	0.032	Zel'vinskii (1937)
100.00	47.39	0.815	0.047	0.372	Zel'vinskii (1937)
100.00	47.51	0.794	2.873	2.442	Zel'vinskii (1937)
100.00	61.71	1.083	6.734	7.185	Zel'vinskii (1937)
100.00	61.76	0.981	3.058	2.558	Zel'vinskii (1937)

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Table A-2 (continued)

Temp °C	Pressure (bar)	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	Reference
100.00	61.81	1.046	3.285	3.754	Zel'vinskii (1937)
100.00	62.11	1.083	6.192	6.649	Zel'vinskii (1937)
100.00	75.99	1.240	4.651	5.187	Zel'vinskii (1937)
100.00	91.19	1.448	7.253	7.868	Zel'vinskii (1937)
100.00	49.55	0.801	5.621	5.170	Malinin and Saveleva (1972)
100.00	49.55	0.805	5.175	4.726	Malinin and Saveleva (1972)
100.00	49.55	0.805	5.123	4.674	Malinin and Saveleva (1972)
100.00	70.88	1.085	3.525	2.973	Hou et al. (2013)
100.00	102.35	1.365	6.051	5.256	Hou et al. (2013)
100.00	133.52	1.626	3.869	2.773	Hou et al. (2013)
100.00	170.70	1.872	1.594	0.046	Hou et al. (2013)

Table A-3

Experimental data of H₂O solubility in CO₂-rich phase and calculated AARD% values.

Temp °C	Pressure bar	Y _{H2O} Mole%	AAD % Model-2	ARD % Model-1	Reference
35.00	91.20	0.384	9.199	284.703	King et al. (1992)
35.00	101.30	0.407	6.788	340.803	King et al. (1992)
35.00	111.50	0.414	3.333	391.785	King et al. (1992)
35.00	126.70	0.435	2.840	434.700	King et al. (1992)
35.00	136.80	0.440	1.306	465.885	King et al. (1992)
35.00	152.00	0.457	1.845	492.501	King et al. (1992)
35.00	202.70	0.498	3.465	558.673	King et al. (1992)
35.06	30.29	0.230	8.791	31.231	Valtz et al. (2004)
35.06	40.05	0.200	5.675	37.510	Valtz et al. (2004)
35.06	49.85	0.170	13.025	60.789	Valtz et al. (2004)
35.06	59.49	0.160	15.879	83.740	Valtz et al. (2004)
35.06	70.56	0.170	13.613	115.602	Valtz et al. (2004)
35.06	79.30	0.230	4.147	175.917	Valtz et al. (2004)
35.06	79.63	0.250	2.078	166.815	Valtz et al. (2004)
40.00	101.30	0.428	7.464	254.119	King et al. (1992)
40.00	111.50	0.440	2.371	315.955	King et al. (1992)
40.00	126.70	0.467	1.012	367.090	King et al. (1992)
40.00	152.00	0.507	1.879	416.954	King et al. (1992)
40.00	177.30	0.543	4.006	446.203	King et al. (1992)
40.00	202.70	0.580	7.096	461.219	King et al. (1992)
40.00	89.00	0.392	19.211	132.493	Foltran et al. (2015)
40.00	102.10	0.445	10.274	247.000	Foltran et al. (2015)
40.00	111.40	0.454	5.441	302.539	Foltran et al. (2015)
40.00	124.10	0.481	4.874	342.332	Foltran et al. (2015)
40.00	91.19	0.320	5.204	227.307	Springer et al. (2012)
45.07	30.01	0.440	4.993	11.924	Valtz et al. (2004)
45.07	39.80	0.380	8.450	15.033	Valtz et al. (2004)
45.07	49.56	0.350	11.212	19.938	Valtz et al. (2004)
45.07	59.92	0.330	11.713	30.406	Valtz et al. (2004)
45.07	69.30	0.290	1.101	61.062	Valtz et al. (2004)
50.00	50.70	0.383	0.539	34.192	Wiebe and Gaddy (1941)
50.00	60.80	0.357	0.810	45.628	Wiebe and Gaddy (1941)
50.00	76.00	0.350	0.414	68.018	Wiebe and Gaddy (1941)
50.00	101.30	0.449	5.519	132.811	Wiebe and Gaddy (1941)
50.00	152.00	0.610	1.138	299.754	Wiebe and Gaddy (1941)
50.00	202.70	0.677	1.140	374.029	Wiebe and Gaddy (1941)
50.00	200.00	1.000	33.325	217.534	Tödheide and Franck (1963)
50.00	101.33	0.550	22.840	90.236	D'souza et al. (1988)
50.00	152.00	0.790	23.664	208.671	D'souza et al. (1988)
50.00	101.00	0.547	22.741	89.317	Dohrn et al. (1993)
50.00	201.00	0.682	2.097	367.441	Dohrn et al. (1993)
50.00	36.38	0.466	0.438	20.709	King Jr and Coan (1971)
50.00	36.38	0.463	0.207	21.491	King Jr and Coan (1971)
50.00	46.31	0.396	1.639	31.492	King Jr and Coan (1971)
50.00	74.06	0.350	0.206	64.141	Hou et al. (2013)
50.00	100.21	0.403	3.826	150.701	Hou et al. (2013)
50.00	129.73	0.533	3.275	265.658	Hou et al. (2013)
50.00	175.33	0.614	4.127	361.564	Hou et al. (2013)
50.05	40.50	0.460	5.461	17.634	Bamberger et al. (2000)
50.05	50.60	0.360	7.299	43.081	Bamberger et al. (2000)
50.05	60.60	0.370	2.432	40.666	Bamberger et al. (2000)
50.05	70.80	0.340	3.356	63.597	Bamberger et al. (2000)
50.05	80.80	0.340	4.804	85.498	Bamberger et al. (2000)
50.05	90.90	0.410	7.664	88.744	Bamberger et al. (2000)
50.05	100.90	0.450	6.127	129.223	Bamberger et al. (2000)

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Table A-3 (continued)

Temp °C	Pressure bar	Y _{H₂O} Mole%	AAD % Model-2	ARD % Model-1	Reference
50.05	111.00	0.500	4.610	176.388	Bamberger et al. (2000)
50.05	121.00	0.550	5.228	210.199	Bamberger et al. (2000)
50.05	141.10	0.610	4.769	263.271	Bamberger et al. (2000)
60.05	40.50	0.660	2.742	24.560	Bamberger et al. (2000)
60.05	50.60	0.550	8.261	39.161	Bamberger et al. (2000)
60.05	60.60	0.550	0.318	36.583	Bamberger et al. (2000)
60.05	70.80	0.510	2.470	51.000	Bamberger et al. (2000)
60.05	80.80	0.500	2.785	64.208	Bamberger et al. (2000)
60.05	90.90	0.470	10.577	93.945	Bamberger et al. (2000)
60.05	100.90	0.490	10.119	114.627	Bamberger et al. (2000)
60.05	111.00	0.530	8.102	136.684	Bamberger et al. (2000)
60.05	121.00	0.580	5.848	159.532	Bamberger et al. (2000)
60.05	141.10	0.780	11.361	160.307	Bamberger et al. (2000)
75.00	101.30	0.829	2.955	69.456	Wiebe and Gaddy (1941)
75.00	126.70	0.855	4.772	106.590	Wiebe and Gaddy (1941)
75.00	152.00	0.956	1.812	137.522	Wiebe and Gaddy (1941)
75.00	202.70	1.130	2.408	185.347	Wiebe and Gaddy (1941)
75.00	50.70	1.087	0.880	21.977	Gillespie et al. (1982)
75.00	101.40	0.727	17.405	93.370	Gillespie et al. (1982)
75.00	202.70	0.938	17.568	243.755	Gillespie et al. (1982)
75.00	101.33	0.740	15.339	89.877	D'souza et al. (1988)
75.00	152.00	0.900	8.147	152.301	D'souza et al. (1988)
75.00	37.39	1.250	5.271	21.886	King Jr and Coan (1971)
75.00	37.49	1.260	4.235	20.740	King Jr and Coan (1971)
75.00	51.27	1.040	2.919	26.998	King Jr and Coan (1971)
75.00	51.47	1.020	4.695	29.315	King Jr and Coan (1971)
75.00	91.19	0.850	0.787	55.184	Springer et al. (2012)
75.00	71.23	0.845	7.844	47.468	Hou et al. (2013)
75.00	101.67	0.805	6.042	74.976	Hou et al. (2013)
75.00	132.82	0.836	9.238	124.946	Hou et al. (2013)
75.00	169.18	0.996	2.849	163.135	Hou et al. (2013)
79.95	40.50	1.430	4.906	22.012	Bamberger et al. (2000)
79.95	60.60	1.090	7.321	36.475	Bamberger et al. (2000)
79.95	70.80	1.040	4.559	39.730	Bamberger et al. (2000)
79.95	80.80	0.970	6.877	50.430	Bamberger et al. (2000)
79.95	90.90	0.920	9.486	62.936	Bamberger et al. (2000)
79.95	100.90	0.930	6.969	68.772	Bamberger et al. (2000)
79.95	111.00	0.900	10.644	85.718	Bamberger et al. (2000)
79.95	121.00	0.960	4.960	87.660	Bamberger et al. (2000)
79.95	131.00	1.000	2.767	95.767	Bamberger et al. (2000)
93.30	50.70	1.970	4.523	23.324	Gillespie et al. (1982)
93.30	101.40	1.374	8.097	57.071	Gillespie et al. (1982)
93.30	202.70	1.432	10.450	146.630	Gillespie et al. (1982)
100.00	36.78	3.280	1.841	9.230	King Jr and Coan (1971)
100.00	37.19	3.230	1.142	10.150	King Jr and Coan (1971)
100.00	44.79	2.770	0.612	14.897	King Jr and Coan (1971)
100.00	44.79	2.740	1.714	16.155	King Jr and Coan (1971)
100.00	51.47	2.480	2.137	19.263	King Jr and Coan (1971)
100.00	51.47	2.510	0.916	17.837	King Jr and Coan (1971)
100.00	91.19	1.610	15.842	56.247	Springer et al. (2012)
100.00	70.88	2.102	0.565	24.263	Hou et al. (2013)
100.00	102.35	1.747	2.840	44.948	Hou et al. (2013)
100.00	133.52	1.675	2.845	64.666	Hou et al. (2013)
100.00	170.70	1.712	2.336	89.733	Hou et al. (2013)

In the proposed model, Fine and Millero (1973) correlation is used to determine the fugacity and density of pure water:

$$\frac{1}{\rho} = V^0 - \frac{V^0 P}{B + A_1 P + A_2 P^2} \quad (\text{A4})$$

$$V^0 = \frac{1 + 18.1597 \times 10^{-3} \theta}{0.9998 + 18.2249 \times 10^{-3} \theta - 7.9222 \times 10^{-6} \theta^2 - 55.4485 \times 10^{-9} \theta^3 + 149.7562 \times 10^{-12} \theta^4 - 393.2952 \times 10^{-15} \theta^5} \quad (\text{A5})$$

$$B = 19654.32 + 147.037 \theta - 2.2155 \theta^2 + 1.0478 \times 10^{-2} \theta^3 - 2.2789 \times 10^{-5} \theta^4 \quad (\text{A6})$$

$$A_1 = 3.2891 - 2.391 \times 10^{-3} \theta + 2.8446 \times 10^{-4} \theta^2 - 2.82 \times 10^{-6} \theta^3 + 8.477 \times 10^{-9} \theta^4 \quad (\text{A7})$$

$$A_2 = 6.245 \times 10^{-5} - 3.913 \times 10^{-6} \theta - 3.499 \times 10^{-8} \theta^2 + 7.942 \times 10^{-10} \theta^3 - 3.299 \times 10^{-12} \theta^4 \quad (\text{A8})$$

where θ is temperature in Celsius, and ρ is the density of pure water in $\text{cm}^3 \text{g}^{-1}$. The fugacity of H_2O is calculated using the approach proposed by King et al. (1992):

Table A-4

Experimental data of CO₂ solubility in NaCl brine and calculated AARD% values.

Temp °C	Pressure bar	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	NaCl Molality mole/kg _{H2O}	Reference
60.00	83.00	1.637	1.775	1.445	0.0172	Mohammadian et al. (2015)
60.00	103.00	1.833	0.576	0.026	0.0172	Mohammadian et al. (2015)
60.00	138.00	2.012	0.700	0.594	0.0172	Mohammadian et al. (2015)
60.00	172.00	2.096	1.899	0.070	0.0172	Mohammadian et al. (2015)
60.00	193.00	2.143	2.292	0.011	0.0172	Mohammadian et al. (2015)
80.00	41.00	0.719	16.203	15.912	0.0172	Mohammadian et al. (2015)
80.00	83.00	1.263	11.580	11.088	0.0172	Mohammadian et al. (2015)
80.00	103.00	1.475	8.447	7.795	0.0172	Mohammadian et al. (2015)
80.00	138.00	1.722	6.628	5.512	0.0172	Mohammadian et al. (2015)
80.00	158.00	1.839	5.158	3.713	0.0172	Mohammadian et al. (2015)
80.00	172.00	1.872	6.371	4.661	0.0172	Mohammadian et al. (2015)
80.00	213.00	2.024	5.156	2.806	0.0172	Mohammadian et al. (2015)
80.00	94.90	1.410	4.496	3.942	0.171	Nighswander et al. (1989)
80.10	99.40	1.540	1.841	2.399	0.171	Nighswander et al. (1989)
80.20	41.30	0.760	6.456	6.188	0.171	Nighswander et al. (1989)
80.20	60.20	1.010	7.707	7.361	0.171	Nighswander et al. (1989)
80.20	60.70	1.080	1.342	1.014	0.171	Nighswander et al. (1989)
80.30	40.40	0.740	7.257	6.988	0.171	Nighswander et al. (1989)
80.30	80.40	1.350	1.584	2.004	0.171	Nighswander et al. (1989)
80.50	80.50	1.340	0.909	1.335	0.171	Nighswander et al. (1989)
60.00	41.00	0.976	1.972	1.823	0.172	Mohammadian et al. (2015)
60.00	83.00	1.531	4.850	4.509	0.172	Mohammadian et al. (2015)
60.00	138.00	1.944	0.485	0.807	0.172	Mohammadian et al. (2015)
60.00	158.00	1.956	3.278	1.532	0.172	Mohammadian et al. (2015)
60.00	172.00	2.025	1.754	0.215	0.172	Mohammadian et al. (2015)
60.00	193.00	2.065	2.435	0.127	0.172	Mohammadian et al. (2015)
80.00	41.00	0.703	14.658	14.371	0.172	Mohammadian et al. (2015)
80.00	83.00	1.231	10.372	9.884	0.172	Mohammadian et al. (2015)
80.00	138.00	1.697	4.415	3.322	0.172	Mohammadian et al. (2015)
80.00	172.00	1.835	4.670	2.986	0.172	Mohammadian et al. (2015)
80.00	213.00	1.958	4.916	2.570	0.172	Mohammadian et al. (2015)
100.00	48.00	0.635	3.286	2.850	1	Zhao et al. (2015)
49.95	51.00	1.110	1.086	1.215	1	Koschel et al. (2006)
49.95	100.30	1.640	3.687	4.267	1	Koschel et al. (2006)
49.95	143.80	1.770	2.848	4.509	1	Koschel et al. (2006)
50.05	50.00	1.167	7.363	7.482	1	Yan et al. (2011)
50.05	100.00	1.672	5.725	6.283	1	Yan et al. (2011)
50.00	150.00	1.766	1.832	3.622	1	Zhao et al. (2015)
50.05	150.00	1.772	2.161	3.943	1	Yan et al. (2011)
50.05	200.00	1.909	3.808	6.252	1	Yan et al. (2011)
50.05	300.00	2.011	0.353	3.806	1	Yan et al. (2011)
99.95	50.70	0.600	14.394	13.899	1	Koschel et al. (2006)
99.95	104.00	1.120	3.871	3.076	1	Koschel et al. (2006)
99.95	191.40	1.610	1.108	2.902	1	Koschel et al. (2006)
100.05	50.00	0.753	9.889	10.277	1	Yan et al. (2011)
100.05	100.00	1.195	5.050	5.746	1	Yan et al. (2011)
100.05	150.00	1.444	1.230	2.471	1	Yan et al. (2011)
100.00	150.00	1.458	2.132	3.362	1	Zhao et al. (2015)
100.05	200.00	1.682	3.649	5.510	1	Yan et al. (2011)
100.05	300.00	1.864	1.083	2.057	1	Yan et al. (2011)
40.16	38.44	0.861	15.357	15.420	2.5	Kiepe et al. (2002)
40.16	51.37	1.089	17.734	17.816	2.5	Kiepe et al. (2002)
40.16	63.73	1.272	19.581	19.694	2.5	Kiepe et al. (2002)
40.16	77.89	1.431	21.049	21.246	2.5	Kiepe et al. (2002)
40.16	91.29	1.517	21.628	22.187	2.5	Kiepe et al. (2002)
50.00	57.39	0.875	4.228	4.372	2.5	Hou et al. (2013)
50.00	87.30	1.146	7.499	7.821	2.5	Hou et al. (2013)
50.00	117.73	1.238	5.622	6.676	2.5	Hou et al. (2013)
50.00	150.20	1.293	4.466	6.219	2.5	Hou et al. (2013)
50.00	182.11	1.335	3.409	5.657	2.5	Hou et al. (2013)
79.92	40.82	0.532	11.277	11.499	2.5	Kiepe et al. (2002)
79.92	52.21	0.660	12.848	13.100	2.5	Kiepe et al. (2002)
79.92	64.70	0.789	14.376	14.669	2.5	Kiepe et al. (2002)
79.92	76.79	0.902	15.632	15.974	2.5	Kiepe et al. (2002)
79.92	100.61	1.091	17.578	18.058	2.5	Kiepe et al. (2002)
100.00	57.42	0.545	0.459	0.922	2.5	Hou et al. (2013)
100.00	87.89	0.745	0.125	0.519	2.5	Hou et al. (2013)
100.00	118.67	0.911	0.747	1.644	2.5	Hou et al. (2013)
100.00	149.21	1.039	1.320	2.554	2.5	Hou et al. (2013)
100.00	180.13	1.139	1.476	3.117	2.5	Hou et al. (2013)
40.23	40.27	0.657	18.607	18.670	4	Kiepe et al. (2002)
40.23	59.78	0.898	22.111	22.208	4	Kiepe et al. (2002)
40.23	73.78	1.029	23.823	23.980	4	Kiepe et al. (2002)

(continued on next page)

Table A-4 (continued)

Temp °C	Pressure bar	X _{CO2} Mole%	ARD% Model-2	ARD% Model-1	NaCl Molality mole/kg _{H2O}	Reference
40.23	81.22	1.080	24.365	24.596	4	Kiepe et al. (2002)
40.23	90.61	1.120	24.545	25.054	4	Kiepe et al. (2002)
50.00	150.00	1.036	14.019	15.599	4	Zhao et al. (2015)
50.00	59.54	0.697	12.175	12.313	4	Hou et al. (2013)
50.00	89.53	0.875	12.393	12.727	4	Hou et al. (2013)
50.00	120.17	0.956	11.777	12.825	4	Hou et al. (2013)
50.00	149.59	0.997	10.710	12.344	4	Hou et al. (2013)
50.00	179.54	1.025	9.130	11.220	4	Hou et al. (2013)
100.00	150.00	0.878	14.214	15.299	4	Zhao et al. (2015)
100.00	60.68	0.466	12.272	12.695	4	Hou et al. (2013)
100.00	89.16	0.620	11.995	12.570	4	Hou et al. (2013)
100.00	120.03	0.752	11.846	12.656	4	Hou et al. (2013)
100.00	149.24	0.857	12.370	13.470	4	Hou et al. (2013)
100.00	181.62	0.924	10.130	11.650	4	Hou et al. (2013)
50.00	150.00	0.902	20.033	21.505	5	Zhao et al. (2015)
50.05	50.00	0.553	21.098	21.200	5	Yan et al. (2011)
50.05	100.00	0.804	19.883	20.361	5	Yan et al. (2011)
50.05	150.00	0.906	20.384	21.848	5	Yan et al. (2011)
50.05	200.00	0.915	14.775	16.961	5	Yan et al. (2011)
50.05	300.00	0.989	10.110	13.257	5	Yan et al. (2011)
100.00	150.00	0.769	19.710	20.727	5	Zhao et al. (2015)
100.05	50.00	0.351	19.838	20.184	5	Yan et al. (2011)
100.05	100.00	0.598	19.841	20.433	5	Yan et al. (2011)
100.05	150.00	0.789	21.697	22.689	5	Yan et al. (2011)
100.05	200.00	0.947	23.968	25.450	5	Yan et al. (2011)
100.05	300.00	1.047	15.594	18.239	5	Yan et al. (2011)
50.00	150.00	0.803	26.802	28.151	6	Zhao et al. (2015)
100.00	150.00	0.689	26.006	26.944	6	Zhao et al. (2015)

$$f_{\text{H}_2\text{O}}^0 = P_s \exp \left[\frac{18.0152 \times (P - P_s)}{\rho RT} \right] \quad (\text{A9})$$

where P_s is obtained using the correlation of Shibue (2003):

$$\ln \left(\frac{P}{P_c} \right) = \frac{T_c}{T} \left[a_1 \left(1 - \frac{T}{T_c} \right) + a_2 \left(1 - \frac{T}{T_c} \right)^{1.5} + a_3 \left(1 - \frac{T}{T_c} \right)^3 + a_4 \left(1 - \frac{T}{T_c} \right)^{3.5} + a_5 \left(1 - \frac{T}{T_c} \right)^4 + a_6 \left(1 - \frac{T}{T_c} \right)^{7.5} \right] \quad (\text{A10})$$

Values of a_1 to a_6 is reported in Table A-1.

See Table A-2–A-4.

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