Research Article

Modelling of the Phase-Partitioning Behaviors for CO₂-Brine System at Geological Conditions

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An improved phase-partitioning model is proposed for the prediction of the mutual solubility in the CO₂-brine system containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻. The correlations are computationally efficient and reliable, and they are primarily designed for incorporation into a multiphase flow simulator for geology- and energy-related applications including CO₂ sequestration, CO₂-enhanced geothermal systems, and CO₂-enhanced oil recovery. The model relies on the fugacity coefficient in the CO₂-rich phase and the activity coefficient in the aqueous phase to estimate the phase-partitioning properties. In the model, (i) the fugacity coefficients are simulated by a modified Peng-Robinson equation of state which incorporates a new alpha function and binary interaction parameter (BIP) correlation; (ii) the activity coefficient is estimated by a unified equilibrium constant model and a modified Margules expression; and (iii) the simultaneous effects of salting-out on the compositions of the CO₂-rich phase and the aqueous phase are corrected by a Pitzer interaction model. Validation of the model calculations against literature experimental data and traditional models indicates that the proposed model is capable of predicting the phase-partitioning behaviors in the CO₂-brine system with a higher accuracy at temperatures of up to 623.15 K and pressures of up to 350 MPa. Using the proposed model, the phase diagram of the CO₂+H₂O system is generated. An abrupt change in phase compositions is revealed during the transfer of the CO₂-rich phase from vapor to liquid or supercritical. Furthermore, the preliminary simulation shows that the salting-out effect can considerably decrease the water content in the CO₂-rich phase, which has not been well experimentally studied so far.

1. Introduction

CO₂-water/brine is one of the most important and commonly encountered systems [1–3] in CO₂ sequestration [4–11], CO₂-enhanced oil recovery (EOR) [2, 12, 13], CO₂-enhanced geothermal systems (EGS) [14, 15], global CO₂-tracing [16–19], and so on. In these chemical-, petroleum-, and environment-related technological applications, accurate prediction of the phase-partitioning properties over a wide pressure-temperature-salt composition (P-T-x) range is essential for the understanding of the CO₂ flow and trapping mechanism in subsurface formations [7, 11, 20, 21] and the potential rock-fluid chemical interactions [4, 14].

By now, CO₂ solubility in water/brine has attracted great interest. The injected CO₂ can dissolve into formation water, form carbonic acid, and react with reservoir rocks, altering the porosity and permeability of the porous media [22–24]. This complicated geochemical process related to CO₂ dissolution has a long-term positive or adverse influence on the performance of subsurface systems. Firstly, the preliminary simulation revealed that the heat exploitation efficiency was decreased by 27% in a CO₂ geothermal system due to CO₂ dissolution and mineral precipitation [25]. Borgia et al. [26] indicated that the geothermal reservoir could even be dead in 1 year. Secondly, Enick and Klara [27] and Chang et al. [28] indicated that the geothermal reservoir could even be dead in 1 year. Secondly, Enick and Klara [27] and Chang et al. [28] demonstrated that the ultimate CO₂ recovery was significantly decreased owing to a large proportion of CO₂ trapping in the formation water in the CO₂ EOR process. Thirdly, CO₂ dissolution is a controlling factor for long-term environmental safe storage [11, 20, 21, 29, 30], given...
the fact that the solubility trapping accounts for 90% of the total storage capacity in CO$_2$ sequestration in saline aquifers [7, 20, 21]. Compared to CO$_2$ solubility, the water content in the CO$_2$-rich phase has been largely ignored [4, 31]. However, it is of same importance because the amount of water in the CO$_2$-rich phase determines the capability of injected CO$_2$ to dry subsurface rocks [14, 32, 33] and affects the type of chemical fluid-rock interactions [14, 34, 35]. Furthermore, water vaporization can lead to salinity concentrating and then decrease the CO$_2$ solubility in the aqueous phase. Therefore, it is of fundamental and practical importance to build an accurate model of the mutual solubility in the CO$_2$-brine system.

Regarding the CO$_2$+H$_2$O system, a large abundance of experimental studies have been carried out to obtain straightforward knowledge of the phase-partitioning behaviors [1, 36–42], which can facilitate the development of an accurate phase equilibrium model. The modelling approaches can be generally divided into two categories: $q$-$q$ models and $q$-$y$ models. The $q$-$q$ model relies on a homogeneous equation of state (EOS) to estimate the fugacity coefficient of different components in the CO$_2$-rich phase and the aqueous phase. However, the classic cubic EOS is not capable of accurately characterizing the phase behaviors in a strongly nonideal system [2, 43], in which the water and CO$_2$ molecules can form a hydrogen bond and can associate [44]. A feasible approach is the incorporation of the excess Gibbs energy model into a cubic EOS or statistical associated fluid theory (SAFT) [21, 43]. The main advantages of $q$-$q$ models are their capacities for reproducing volumetric properties and estimating the phase properties near the critical point. However, they are commonly much more computationally complicated compared to the $q$-$y$ models [4]. Furthermore, the microscopic knowledge of molecular structures is necessary but not applicable in some industry applications [2]. The $q$-$y$ model relies on the activity coefficient in the aqueous phase and the fugacity coefficient in the CO$_2$-rich phase. Although these type of models are not physically rigorous and accurate enough near the critical point [43], they could be much more amenable to integration with chemical equilibrium simulation [4, 45]. Considering its good extensibility and computational efficiency, the $q$-$y$ approach was most commonly used in the large-scale multiphase flow simulations [8, 14, 46]. From this concern, this study focuses on developing a new $q$-$y$ type model.

Based on Peng-Robinson’s EOS and Henry’s law, Li and Ngheim [47] developed a model to predict the CO$_2$ solubility below 473 K, in which a scaled-particle theory was incorporated to account for the effect of NaCl concentration. However, it was indicated that the model calculations were generally not accurate enough [17], Hu et al. [48] demonstrated that the cubic and virial EOS were capable of predicting CO$_2$ solubility up to 50 MPa, but the simulation error at high pressure was found to be unacceptable. Assembled from 21 literature experimental studies, a databank of CO$_2$ solubility containing 508 pieces of data was developed by Akinfeev and Diamond [42]. They proposed an accurate $q$-$y$ model with a valid range of 0-100 MPa and below 100°C, but the model is not accurate enough for estimating the water content in the CO$_2$-rich phase. Sorensen et al. [49] developed a model of CO$_2$ solubility in pure water (348-623 K and 1.6-140 MPa) and in NaCl solutions (298-523 K and 0.1-138.2 MPa). However, the corresponding simulation errors can reach 37% and 20.3%, respectively. Mao et al. [50] built an accurate model for CO$_2$ solubility in NaCl solution, but it cannot be used for estimating CO$_2$ solubility in other brines or water content in the CO$_2$-rich phase. Dubessy et al. [51] proposed an unsymmetric $q$-$y$ model to simulate the compositions of different phases in 40°C-270°C. However, it is only valid below 30 MPa. Similarly, Portier and Rochelle [52] developed a model of CO$_2$ solubility in pure water and brine with a valid thermodynamic range of 0-300°C and 0-30 MPa.

Using the unsymmetric $q$-$y$ approach, Duan and Sun [17] and Spycher and Pruess [14] developed the most commonly used and cited models in the geological scientific community [3, 11, 30]. Combining a virial EOS for pure CO$_2$ and a semiempirical Pitzer interaction equation, the model of Duan and Sun [17] can be used to simulate the CO$_2$ solubility in pure water and brines up to 533 K and 200 MPa. It is in general computationally accurate and efficient. However, Hou et al. [45] claimed that the model calculations of Duan and Sun [17] disagreed significantly with their experimental measurements at 448.15 K. Similarly, Guo et al. [9] demonstrated that the model calculation substantially deviates from the measurements above 523.15 K. Affected by the scope of the experimental database used in model development, the model calculations in other brines were not as accurate as those in NaCl solutions [45]. Furthermore, this model cannot be used for accurately estimating the water content in the CO$_2$-rich phase. The models of Spycher et al. [8] and Spycher and Pruess [14] rely on the Redlich–Kwong EOS for calculating the fugacity coefficient in the CO$_2$-rich phase, whereas the activity coefficient in the aqueous phase is treated by the correlations of an equilibrium constant for pure water and a Pitzer interaction expression for brines. Compared to the model of Duan and Sun [17], it includes two more experimental studies for parameter determination [30] and is suitable for both CO$_2$ solubility in the aqueous phase and water content in the CO$_2$-rich phase. However, the valid pressure range was limited to 0-60 MPa [1, 11]. In order to accurately estimate the phase compositions, different model parameter sets were utilized according to the temperature ranges and phase transition of CO$_2$. This discontinuity may affect the smoothness of derivatives and damage the Jacobian-based numerical formulation in large-scale multiphase flow simulation. Furthermore, the effect of salting out on the water content in the CO$_2$-rich phase was neglected in their model. Owing to the improvement of experimental approaches, more available literature data used as fitting constraints can help to increase the accuracy of new thermodynamic formulations [2, 14, 42, 45, 53].

Based on the pioneering experimental and modelling studies, a unified model is developed in this study to characterize the phase-partitioning behaviors in the CO$_2$-water/brine system. There are three major improvements compared to the traditional models. Firstly, both the CO$_2$ solubility in the aqueous phase and water content in the CO$_2$-rich phase can be accurately estimated at temperatures
up to 623.15 K and pressures up to 350 MPa. Secondly, an updated phase equilibrium databank assembled from 114 literature experimental studies was developed for model calibration. Thirdly, the salting-out effect of Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻ on the composition of both the aqueous phase and the CO₂-rich phase is considered.

2. Thermodynamic Modelling of CO₂-H₂O System

2.1. Thermodynamic Framework for Vapor-Liquid Phase Equilibrium

According to the thermodynamic principle, the necessary criterion for multiphase equilibrium is equality of the fugacity of each fluid component in the aqueous phase and the CO₂-rich phase. The fugacity of component \( i \) in the CO₂-rich phase is as follows:

\[
 f_i^{G} = f_i^{Aq},
\]

where \( f \) is the fugacity (in Pa), \( i \) is the component, G and Aq represent the CO₂-rich phase and the aqueous phase, respectively. The fugacity of component \( i \) in the CO₂-rich phase is as follows:

\[
 f_i^{G} = p \phi_i \gamma_i, \tag{2}
\]

where \( p \) is the pressure (in Pa); \( \gamma_i \) is the mole fraction of component \( i \) in the CO₂-rich phase, \( \gamma_{H2O} + \gamma_{CO2} = 1 \); \( \phi_i \) is the fugacity coefficient of component \( i \), dimensionless. Regarding the strongly nonideal system composed of CO₂ and H₂O, an accurate binary interaction correlation is necessary for estimation of the effect of asymmetric interaction between molecules.

In equation (1), the fugacity of component \( i \) in the aqueous phase can be estimated by Jager et al. [54]:

\[
 f_i^{Aq} = f_{i0} \exp \left[ \frac{\mu_{i0} - g_{i0}}{RT} \right], \tag{3}
\]

where \( f_{i0} \) is the fugacity of component \( i \) in the ideal gas state (in Pa); \( g_{i0} \) is the Gibbs free energy of component \( i \) in the ideal gas state (in Pa); \( \mu_{i0} \) is the chemical potential of component \( i \) in the aqueous phase (in Pa); \( R \) is the gas constant, \( R = 8.314472 \text{ Pa}\cdot\text{m}^2\cdot\text{mol}^{-1}\cdot\text{K}^{-1} \); and \( T \) is temperature (in K).

Substituting the expressions of Gibbs free energy and chemical potential (as shown in Appendix A) into equation (3), the following equation can be obtained:

\[
 f_i^{Aq} = K_i a_i \exp \left[ \frac{\phi \gamma_i}{p_0} \frac{v_{iA}}{RT} \right], \tag{4}
\]

where \( K_i \) is the equilibrium constant of component \( i \), which is a function of temperature and pressure; \( a_i \) is the activity of component \( i \) in the aqueous phase; \( v_{iA} \) is the partial molar volume of component \( i \) (in m³/mol); \( p_0 \) is the reference pressure (in Pa), which is set as the saturated vapor pressure of water.

2.1.1. Water. In equation (4), the activity of component \( i \) in the aqueous phase is as follows:

\[
 a_{i,H2O} = x_{i,H2O} \gamma_{H2O}^*, \tag{5}
\]

\[
 \gamma_{H2O}^* = \frac{\gamma_{H2O}^{\text{Re f}}}{\gamma_{H2O}^{\text{ref}}} = \frac{y_{H2O}^{\text{Re f}}}{y_{H2O}^{\text{Ref}}} = \frac{y_{H2O}^*}{y_{H2O}^{\text{sol}}}, \tag{6}
\]

where \( x_i \) is the mole fraction of component \( i \) in the aqueous phase (in mol/mol); \( y_{i,H2O}^{\text{ref}} \) is the activity coefficient of water at the reference state, dimensionless. Following the symmetric convention, it is equal to one for pure water. \( y_{H2O}^* \) is the relative activity coefficient of water that includes two parts: (i) \( \gamma_{H2O}^* \) represents the relative activity coefficient of water in the CO₂+H₂O system. It approaches one when the CO₂ solubility is negligible at low pressure and temperature. (ii) \( y_{H2O}^{\text{sol}} \) represents the effect of electrolytes on the activity of water, which is generated by the long-range and short-range interactions between the cations, anions, and water molecules. It is equal to one for pure water and generally decreases with increasing salt concentration.

When the gas solubility in the aqueous phase is low without salts, the proposed model can be simplified as Raoult’s law, i.e., the water activity is equal to its mole fraction in the aqueous phase (\( x_{H2O} = x_{i,H2O} \)).

2.1.2. CO₂. In equation (4), the activity coefficient of CO₂ can be estimated by

\[
 a_{CO2} = m_{CO2} \gamma_{CO2}, \tag{7}
\]

where \( m_{CO2} \) is the molality of CO₂ in the aqueous phase (in mol/kg), and \( \gamma_{CO2}^{\text{Re f}} \mid_{m_{CO2}=0} = y_{CO2}^* \) is the activity coefficient of CO₂ at the reference state:

\[
 \gamma_{CO2}^{\text{Re f}} \mid_{m_{CO2}=0} = \frac{1}{1 + m_{CO2} M_{H2O}} = 1 - x_{CO2}, \tag{8}
\]

where \( M_{H2O} \) is the molality of water, \( M_{H2O} = 0.01802 \text{ kg/mol} \). The calculation of CO₂ activity in the aqueous phase corresponds to the unsymmetric convention. Namely, the CO₂ activity coefficient is equal to unity as the concentration of dissolved CO₂ is 0 mol/kg. Equation (8) is used to generate a molality to mole fraction correction [55].

With the substitution of equation (8) into equation (7), the following expression can be obtained:

\[
 a_{CO2} = \frac{x_{CO2} y_{CO2}^*}{M_{H2O}}, \quad y_{CO2}^* = \frac{y_{CO2}^{\text{sol}}}{y_{CO2}^{\text{ref}}}, \tag{9}
\]

where \( y_{CO2}^* \) is the relative activity coefficient of CO₂ in the aqueous phase that contains two parts: (i) \( y_{CO2}^{\text{sol}} \) represents the relative activity coefficient in the CO₂+H₂O system. It
approaches one if the solubility of CO₂ is negligible. It was 
revealed that the simulation error of CO₂ solubility 
approaches 7% if the activity coefficient γₓ,∅ is simplified as 
unity [6]. (ii) γₓ,solute CO₂ represents the effect of electrolytes on 
the relative activity coefficient of CO₂, which is equal to unity 
for pure water and increases with salt content increasing 
in brine.

2.2. Fugacity Modelling of the CO₂-Rich Phase. The fugacity 
and thermodynamic properties of the CO₂-rich phase are 
commonly estimated by EOS. Owing to its advantages of 
computational efficiency and accuracy, cubic EOS is the most 
commonly used type of EOS models in numerical simula-
tions of multiphase flow [56].

It has been indicated that the Peng-Robinson EOS is 
suitable for predicting thermodynamic properties and phase 
equilibrium of the fluid system containing sour gas and water 
[57]. In this study, we present a modified Peng-Robinson 
EOS, which incorporates a new alpha model and binary 
interaction correlation. The expression of the Peng-
Robinson EOS is as follows [58]:

\[
p = \frac{RT}{v - b} - \frac{a(T)}{v(v + b) + b(v - b)},
\]

where \(v\) is specific volume (in m³/mol), \(a\) is intermolecular 
atraction parameter, and \(b\) is the intermolecular repulsion 
parameter.

Using the Peng-Robinson EOS, the fugacity coefficient of 
component \(i\) can be written as follows:

\[
\ln φ_i = \frac{1}{RT} \int_V^\infty \left[ \frac{\partial p}{\partial n_i} \right]_{T,V,n_{ji}} - \frac{RT}{V} \right] dV - \ln Z
\]

\[
= \frac{b_i}{b} (Z - 1) - \ln |Z - B|
\]

\[
- \frac{A}{\delta_1 - \delta_2} \left[ \sum_{j=1}^{N} x_{ij} a_{ij} \right] - \frac{b_i}{b} \ln \left[ \frac{Z + \delta_1 B}{Z + \delta_2 B} \right],
\]

where \(n_i\) is the mole of component \(i\)(in mol); \(V\) is volume (in 
m³); \(Z\) is the gas compression factor; \(\delta_1\) and \(\delta_2\) are \(1 + \sqrt{2}\) 
and \(1 - \sqrt{2}\), respectively; \(A = ap/(RT)\); and \(B = bp/(RT)\).

2.2.1. Alpha Model. The accuracy of the phase equilibrium of 
a pure material mainly relies on the cohesion factor, which is 
the basis for multiphase equilibrium simulation [2, 59]. The 
cohesion factor popularly known as the alpha function repre-
sents the effect of mutual attraction between molecules. It is 
in general a function of temperature and acentric factor, as 
indicated by previous models [58, 59]. An alpha function 
should fulfill the following criteria: (1) As the temperature 
increases and tends to infinity, it should approach zero. (2) 
Embodying the attraction forces between molecules, it must 
always be positive. (3) It should be equal to unity at the critical 
point.

In this study, a modified alpha equation is proposed to 
increase the accuracy of simulated saturation pressure of 
CO₂ and water:

\[
a_i = \left[ 1 + \kappa_i (1 - T_r^{1/2}) \right]^2 \exp \left[ a_i (1 - T_r^b) \right], \tag{12}
\]

where \(\alpha\) is the cohesion factor; \(T_r\) is the reduced temperature; 
\(\kappa_i\), \(a_i\), and \(b_i\) are the model parameters, which can be 
estimated by the experimental data of saturation pressure of 
CO₂ and H₂O. If \(b_i\) and \(b_i\) are set as zero, equation (12) 
can be simplified as the original expression in the Peng-
Robinson EOS.

2.2.2. Mixing Rule. The mixing rule is primarily intended for 
characterizing the interaction force between different mole-
cules. Using the Van der Waals mixing rule, the expression 
for \(a\) and \(b\) in the Peng-Robinson EOS can be written as 
follows [58]:

\[
a = \sum_i \sum_j x_i x_j a_{ij}, \tag{13}
\]

\[
b = \sum_i x_i b_i, \tag{14}
\]

where

\[
a_{ij} = (1 - k_{ij}) \sqrt{a_i a_j}, \tag{15}
\]

where \(k_{ij}\) is the parameter of binary interaction between the 
components \(i\) and \(j\), which has a significant influence on 
the accuracy of phase equilibrium simulation.

The previous analysis indicated that the traditional Van 
der Waals mixing rule has a good applicability for hydrocar-
bon mixtures. However, it is not accurate enough for the 
strongly nonideal system containing CO₂ and water, owing 
to the existence of asymmetric intermolecular forces. Here, 
a correlation of temperature is proposed to describe the 
binary interaction parameter between CO₂ and water.

\[
k = k_0 + k_1 \left( \frac{T}{T_{C,CO2}} \right) + k_2 \left( \frac{T}{T_{C,CO2}} \right)^2, \tag{16}
\]

where \(k_0\)-\(k_2\) are constants, \(T_{C,CO2}\) is the critical temperature 
of CO₂(in K).

2.3. Fugacity Modelling of the Aqueous Phase. Substituting 
equation (5), equation (6), and equation (9) into equation 
(2) and equation (4), the fugacity model of CO₂ and water 
in the aqueous phase can be obtained:

\[
f_{H₂O}^{AQ} = K_{H₂O} x_{H₂O} y_{H₂O}^{0,solute} \exp \left( \frac{V_{H₂O}}{RT} \right), \tag{17}
\]

\[
f_{CO₂}^{AQ} = \frac{1}{M_{H₂O}} K_{CO₂} x_{CO₂} y_{CO₂}^{0,solute} \exp \left( \frac{V_{CO₂}}{RT} \right). \tag{18}
\]
It can be found that the fugacity coefficient of gas in the aqueous phase is controlled by three parameters: (1) the equilibrium constant of CO$_2$ in the aqueous phase ($K_{CO2}$), which can be simplified as Henry’s constant at low pressure; (2) the relative activity coefficient including the effect of temperature and pressure for pure water, and the effect of electrolytes; and (3) specific volume which accounts for the effect of pressure.

2.3.1. Equilibrium Constant. The CO$_2$-rich phase has significant variations in thermodynamic properties, as it transfers from vapor to liquid or supercritical. In order to accurately describe the effect of CO$_2$ phase transition, a common approach is to select different equilibrium constant models according to the CO$_2$ phase states [14, 60, 61]. This piecewise parameter group may lead to an unsmooth functional form and a discontinuity of its derivative, which is crucial for the Jacobian-based numerical formulation in a functional form and a discontinuity of its derivative, which can be generated in the traditional models, especially at a high pressure, since a constant value of CO$_2$-specific volume is employed. This is because pressure may have a considerable influence on the CO$_2$-specific volume [1]. In this study, a correlation of the specific volume item as a function of temperature and pressure is proposed:

$$V_{CO2} = \int_{P_0}^{P} v_{CO2} dp = \frac{c_1 + c_2 T + c_3 p}{T + c_4 p} \ln T (p - p_0), \tag{21}$$

where $c_1$-$c_4$ are fitted parameters and $p_0$ is the reference pressure (in Pa).

The relative coefficients $y_{CO2}^0$ and $y_{H2O}^0$ at different temperature and pressure conditions can be estimated using the modified Margules model developed by Carlson and Colburn [62]:

$$\ln \left( y_{CO2}^0 \right) = 2A_M x_{CO2} x_{H2O}, \tag{22}$$

$$\ln \left( y_{H2O}^0 \right) = (A_M - 2A_{Mf}) x_{CO2}. \tag{23}$$

Incorporating equation (22) and equation (23) into the developed mutual solubility model will not influence the symmetric and unsymmetrical conventions for the fugacity models of CO$_2$ and water in the aqueous phase. Namely, the activity coefficients of CO$_2$ and water are equal to one in infinite dilution solution.

$$A_M = A_{Mf} T^2 + A_{Mb} T + A_{Mc}, \tag{24}$$

where $A_{Mf}$, $A_{Mb}$, and $A_{Mc}$ are fitted parameters.

2.4. Simulation Method. Substituting equation (17) and equation (18) into equation (2), the equations for water content in the CO$_2$-rich phase and CO$_2$ solubility in the aqueous phase can be obtained:

$$y_{H2O} = \frac{K_{H2O} y_{H2O}^0 x_{H2O} \exp \left( \frac{V_{H2O} (RT)}{p \gamma_{H2O}} \right)}{p \gamma_{H2O} x_{H2O}}, \tag{25}$$

$$y_{CO2} = \frac{K_{CO2} y_{CO2}^0 x_{CO2} \exp \left( \frac{V_{CO2} (RT)}{M_{H2O} \gamma_{CO2}} \right)}{M_{H2O} \gamma_{CO2} x_{CO2}}. \tag{26}$$

The sum of mole fractions of CO$_2$ and water in the CO$_2$-rich phase is equal to one. Therefore, the following expression can be obtained combining equation (25) and equation (26):

$$\frac{K_{H2O} y_{H2O}^0 x_{H2O} \exp \left( \frac{V_{H2O} (RT)}{p \gamma_{H2O}} \right)}{p \gamma_{H2O} x_{H2O}} + \frac{K_{CO2} y_{CO2}^0 x_{CO2} \exp \left( \frac{V_{CO2} (RT)}{M_{H2O} \gamma_{CO2}} \right)}{M_{H2O} \gamma_{CO2} x_{CO2}} - 1 = 0. \tag{27}$$
| No. | Acronym | Author                          | Time  | Exp. | Temperature (°C) | Pressure (MPa) |
|-----|---------|--------------------------------|-------|------|-----------------|----------------|
| 1   | W1      | Wiebe and Gaddy [39]           | 1939  | 29   | 50-100          | 2.5-70.9       |
| 2   | W2      | Wiebe [65]                      | 1941  | 73   | 0-100           | 2.5-70.9       |
| 3   | P1      | Prutton and Savage [78]         | 1945  | 26   | 101-120         | 2.3-70.3       |
| 4   | H1      | Houghton et al. [79]            | 1957  | 171  | 0-100           | 0.1-3.6        |
| 5   | E1      | Ellis [80]                      | 1959  | 36   | 114-348         | 0.5-16.4       |
| 6   | M1      | Malinin [75]                    | 1959  | 36   | 200-300         | 9.7-49.0       |
| 7   | T1      | Todheide and Franck [73]        | 1963  | 104  | 50-350          | 20.0-350.0     |
| 8   | T2      | Takenouchi and Kennedy [72]     | 1964  | 116  | 110-350         | 10.0-150.0     |
| 9   | T3      | Takenouchi and Kennedy [81]     | 1965  | 21   | 150-300         | 10.0-60.0      |
| 10  | G1      | Greenwood et al. [82]           | 1966  | 16   | 11.85-24.85     | 5.0-40.0       |
| 11  | S1      | Stewart and Munjal [83]         | 1970  | 12   | 0-25            | 1.0-4.6        |
| 12  | M2      | Malinin and Kurovskaya [84]     | 1975  | 2    | 100-150         | 4.8-4.9        |
| 13  | D1      | Drummond [85]                   | 1981  | 2    | 300-300         | 19.1-19.6      |
| 14  | S2      | Shagakhmetov and Tarzimanov [70]| 1981  | 6    | 100-150         | 10.1-60.1      |
| 15  | Z1      | Zawisza and Malesinska [86]     | 1981  | 33   | 50-200          | 0.2-5.4        |
| 16  | G2      | Gillepsie and Wilson [67]       | 1982  | 33   | 15.6-260        | 0.7-20.3       |
| 17  | B1      | Briones et al. [87]             | 1987  | 8    | 50-50           | 6.8-17.7       |
| 18  | N1      | Nakayama et al. [63]            | 1987  | 6    | 25.05-25.05     | 3.6-11.0       |
| 19  | D2      | D’Souza et al. [56]             | 1988  | 4    | 50-75           | 10.1-15.2      |
| 20  | M3      | Müller et al. [88]              | 1988  | 20   | 100-200         | 0.3-8.0        |
| 21  | N2      | Nighswander et al. [40]         | 1989  | 33   | 79.7-198.1      | 2.0-10.2       |
| 22  | S3      | Sako et al. [69]                | 1991  | 7    | 75.15-148.25    | 10.2-19.7      |
| 23  | K1      | King et al. [89]                | 1992  | 27   | 15-25           | 6.1-24.3       |
| 24  | D3      | Dohrn et al. [90]               | 1993  | 5    | 50-50           | 10.1-30.4      |
| 25  | R1      | Rumpf et al. [36]               | 1994  | 7    | 50.01-50.03     | 1.1-5.8        |
| 26  | T4      | Teng et al. [66]                | 1997  | 40   | 4.85-24.85      | 5.0-40.0       |
| 27  | D4      | Dhima et al. [91]               | 1999  | 7    | 71-71           | 10.0-100.0     |
| 28  | B2      | Bamberger et al. [92]           | 2000  | 29   | 50.05-79.95     | 4.1-14.1       |
| 29  | B3      | Blencoe et al. [71]             | 2001  | 8    | 300-300         | 27.6-56.7      |
| 30  | K2      | Kiepe et al. [38]               | 2002  | 43   | 40.05-120.02    | 0.9-9.3        |
| 31  | B4      | Bando et al. [93]               | 2003  | 12   | 30-60           | 10.0-20.0      |
| 32  | C1      | Chapoy et al. [94]              | 2004  | 27   | 0.99-78.16      | 0.2-9.3        |
| 33  | V1      | Valtz et al. [95]               | 2004  | 47   | 5.07-45.08      | 0.5-8.0        |
| 34  | B5      | Bermejo et al. [37]             | 2005  | 26   | 23.58-96.5      | 1.6-8.3        |
| 35  | K3      | Koschel et al. [96]             | 2006  | 8    | 49.95-99.95     | 2.1-20.2       |
| 36  | Q1      | Qin et al. [68]                 | 2008  | 7    | 50.45-102.65    | 10.6-49.9      |
| 37  | H2      | Han et al. [97]                 | 2009  | 28   | 40.05-70.05     | 4.3-18.3       |
| 38  | F1      | Ferrentino et al. [98]          | 2010  | 18   | 35-50           | 7.6-13.1       |
| 39  | L1      | Liu et al. [41]                 | 2011  | 31   | 35-55           | 2.1-16.0       |
| 40  | Y1      | Yan et al. [30]                 | 2011  | 18   | 50.05-140.05    | 5.0-40.0       |
| 41  | L2      | Lucile et al. [99]              | 2012  | 30   | 25-120          | 0.5-5.1        |
| 42  | S4      | Savary et al. [100]             | 2012  | 3    | 150-150         | 11.3-33.7      |
| 43  | H3      | Hou et al. [45]                 | 2013  | 42   | 25-175          | 1.1-17.6       |
| 44  | T5      | Tong et al. [20]                | 2013  | 18   | 101-101.84      | 7.2-27.3       |
| 45  | A1      | Al Ghaffri et al. [101]         | 2014  | 8    | 50-50           | 2.1-18.7       |
| 46  | B6      | Bastami et al. [102]            | 2014  | 10   | 55-102          | 6.9-20.7       |
| 47  | G3      | Guo et al. [9]                  | 2014  | 131  | 0-300           | 10.0-120.0     |
| 48  | C2      | Carvalho et al. [10]            | 2015  | 66   | 10.09-90.27     | 0.3-12.1       |
The flow chart for model simulation includes the following steps:

1. Based on prediction of the water saturation pressure, the water content in the CO₂-rich phase can be roughly estimated using the law of partial pressure, \( y_{H_2O,0} = \frac{P_{H_2O}}{P} \). With the estimated CO₂ phase composition, the fugacity of water in the CO₂-rich phase can be calculated using the modified Peng-Robinson EOS. Then, the water content \( y_{H_2O,1} \) can be corrected by equation (25) assuming \( x_{H_2O} = 1 \).

2. Using a Newton-Raphson algorithm, \( x_{CO_2} \) can be estimated by equation (27). Then, the mole fraction of water \( x_{H_2O} \) in aqueous phase can be calculated based on mass conservation.

3. According to the estimated composition of the aqueous phase, the mole fractions of CO₂ and water in the CO₂-rich phase can be recalculated using equation (25) and equation (26).

4. Repeat steps (2) and (3) until the convergence criterion of maximum permissible error is satisfied.

3. Parameterization

3.1. Experimental Database in CO₂+H₂O System. An extensive experimental databank is developed for the CO₂+H₂O and CO₂+brine systems, which includes the data of compositions of the CO₂-rich phase and the aqueous phase assembled from 114 literature studies, as shown in Tables 1–3 of Appendix B. The measurements in the databank are obtained at

| No. | Acronym | Author | Time | Exp. | Temperature (°C) | Pressure (MPa) |
|-----|---------|--------|------|------|-----------------|---------------|
| 49  | M4      | Mohammadian et al. [29] | 2015 | 20   | 60-80           | 0.1-21.3      |
| 50  | C3      | Caumon et al. [18]      | 2016 | 22   | 65-65           | 0.3-19.5      |
| 51  | J1      | Jacob and Saylor [11]   | 2016 | 50   | 23.85-23.85     | 1.4-12.4      |
| 52  | T6      | Truche et al. [19]      | 2016 | 7    | 200-280         | 3.1-13.2      |
| 53  | M5      | Mousavi [77]            | 2017 | 8    | 50-100          | 7.9-52.4      |
| Sum |         |                     | 1597 | 0-350| 0.1-350.0       |               |

| No. | Acronym | Author | Time | Exp. | Temperature (°C) | Pressure (MPa) |
|-----|---------|--------|------|------|-----------------|---------------|
| 1   | W1      | Wiebe and Gaddy [74] | 1941 | 39   | 25-75           | 0.1-70.9      |
| 2   | M1      | Malinin [75]         | 1959 | 26   | 200-300         | 19.5-58.8     |
| 3   | T1      | Todheide and Franck [73] | 1963 | 104  | 50-350          | 20.0-350.0    |
| 4   | T2      | Takenouchi and Kennedy [72] | 1964 | 116  | 110-350         | 10.0-150.0    |
| 5   | K1      | King Jr and Coan [103] | 1971 | 22   | 25-100          | 1.7-5.1       |
| 6   | G1      | Gillespie and Wilson [67] | 1982 | 33   | 15.6-260        | 0.7-20.3      |
| 7   | B1      | Briones et al. [87]   | 1987 | 8    | 50-50           | 6.8-17.7      |
| 8   | N1      | Nakayama et al. [63]  | 1987 | 1    | 25.05-25.05     | 3.6-3.6       |
| 9   | S1      | Song and Kobayashi [104] | 1987 | 19   | 12-31.06        | 0.7-13.8      |
| 10  | D1      | D’Souza et al. [56]   | 1988 | 4    | 50-75           | 10.1-15.2     |
| 11  | M2      | Müller et al. [88]    | 1988 | 20   | 100-200         | 0.3-8.1       |
| 12  | S2      | Sako et al. [69]      | 1991 | 8    | 75.15-148.25    | 10.2-20.9     |
| 13  | K2      | King et al. [89]      | 1992 | 41   | 15-40           | 5.2-20.3      |
| 14  | D2      | Dohrn et al. [90]     | 1993 | 5    | 50-50           | 10.1-30.4     |
| 15  | J1      | Jackson et al. [105]  | 1995 | 2    | 50-75           | 34.5-34.5     |
| 16  | B2      | Bamberger et al. [92] | 2000 | 29   | 50.05-79.95     | 4.1-14.1      |
| 17  | V1      | Valtz et al. [95]     | 2004 | 30   | 5.07-45.07      | 0.5-8.0       |
| 18  | Q1      | Qin et al. [68]       | 2008 | 7    | 50.45-102.65    | 10.6-49.9     |
| 19  | K3      | Kim et al. [44]       | 2012 | 26   | 10.05-38.85     | 8.1-20.1      |
| 20  | H1      | Hou et al. [45]       | 2013 | 39   | 25-175          | 1.1-17.5      |
| 21  | M3      | Meyer and Harvey [106] | 2015 | 58   | 10-80           | 0.5-5.0       |
| 22  | C1      | Caumon et al. [18]    | 2016 | 21   | 100-100         | 0.5-20.1      |
| 23  | M4      | Mousavi [77]          | 2017 | 14   | 100-150         | 1.6-55.2      |
| Sum |         |                     | 672  | 5.07-350| 0.1-350.0       |               |
temperatures up to 623.15 K and pressures up to 350 MPa, which cover the potential thermodynamic conditions in common geological applications, such as petroleum engineering, geothermal development, and CO2 sequestration.

3.2. Parameter Determination. The proposed model contains a variety of parameters. Overall, the sensitivity of model parameters to different types of experimental data is different. For example, the water content in the CO2-rich phase is mainly controlled by the binary interaction parameters between different components in the fugacity model of the gas phase [1], although it may be not very accurate at high temperature (higher than 150°C). In this study, the different types of model parameters are firstly determined by their closely related experimental data. Then, using the determined parameters as initial values, all the model parameters are corrected simultaneously based on the developed experimental databank.

### Table 3: The experimental databanks of CO2 solubility in brines.

| No. | Author                  | Temperature (°C) | Pressure (MPa) | Exe. | Salt  |
|-----|-------------------------|------------------|----------------|------|-------|
| 1   | Bando et al. [93]       | 30-60            | 10-20          | 36   | NaCl  |
| 2   | Carvalho et al. [10]    | 19.93-80.08      | 1.02-14.29     | 44   | NaCl  |
| 3   | Guo et al. [3]          | 5-200            | 10-40          | 142  | NaCl  |
| 4   | Hou et al. [107]        | 50-150           | 2.61-18.21     | 36   | NaCl  |
| 5   | Jacob and Saylor [11]   | 23.85-23.85      | 1.72-10.69     | 28   | NaCl  |
| 6   | Kiepe et al. [38]       | 40.23-79.93      | 0.19-10.1      | 63   | NaCl  |
| 7   | Koschel et al. [96]     | 49.95-99.95      | 5-20.24        | 14   | NaCl  |
| 8   | Liu et al. [41]         | 45-45            | 2.1-15.83      | 8    | NaCl  |
| 9   | Messabe et al. [108]    | 50-150           | 4.99-20.23     | 40   | NaCl  |
| 10  | Mohamadian et al. [29]  | 60-80            | 2.1-21.3       | 42   | NaCl  |
| 11  | Nighswander et al. [40] | 80-200.5         | 2.11-10.03     | 32   | NaCl  |
| 12  | Rumpf et al. [36]       | 39.99-159.93     | 0.47-9.64      | 63   | NaCl  |
| 13  | Savary et al. [100]     | 120-120          | 12.5-30.5      | 6    | NaCl  |
| 14  | Yan et al. [30]         | 50.05-140.05     | 5-40           | 35   | KCl   |
| 15  | Mousavi et al. [77]     | 5-150            | 0.90-57.24     | 85   | NaCl  |
| 16  | Takenouchi and Kennedy  | 150-300          | 10-60          | 29   | NaCl  |
| 17  | Hou et al. [107]        | 50-100           | 2.92-18.22     | 24   | KCl   |
| 18  | Jacob and Saylor [11]   | 23.85-23.85      | 2.1-9.65       | 20   | KCl   |
| 19  | Perez-Salado Kamps et al. [109] | 39.95-159.95 | 0.41-9.40     | 93   | KCl   |
| 20  | Kiepe et al. [38]       | 40.01-80.25      | 0.09-10.51     | 88   | KCl   |
| 21  | Liu et al. [41]         | 45-45            | 2.09-15.81     | 8    | KCl   |
| 22  | Mousavi et al. [77]     | 50-150           | 8.21-54.83     | 19   | KCl   |
| 23  | Bastami et al. [102]    | 55-102           | 6.89-20.68     | 22   | CaCl2 |
| 24  | Liu et al. [41]         | 45-45            | 2.09-15.86     | 8    | CaCl2 |
| 25  | Prutton and Savage [78] | 75.5-121         | 1.52-71.23     | 116  | CaCl2 |
| 26  | Tong et al. [20]        | 34.85-151.49     | 1.53-37.99     | 36   | CaCl2 |
| 27  | Mousavi et al. [77]     | 50-150           | 6.52-59.59     | 43   | CaCl2 |
| 28  | Tong et al. [20]        | 36.37-151.53     | 1.25-34.93     | 39   | MgCl2 |
| 29  | Mousavi et al. [77]     | 50-150           | 8.23-54.48     | 35   | MgCl2 |
| 30  | Mousavi et al. [77]     | 50-150           | 10.02-57.10    | 18   | NaKCaMg|
| 31  | Bermejo et al. [37]     | 13.82-95.66      | 1.98-13.11     | 113  | Na2SO4|
| 32  | Rumpf and Maurer [110]  | 39.96-160.01     | 0.42-9.71      | 102  | Na2SO4|
| 33  | Liu et al. [41]         | 45-45            | 2.48-15.99     | 8    | NaK   |
| 34  | Tong et al. [20]        | 35.75-151.52     | 1.07-17.16     | 14   | NaK   |
| 35  | Liu et al. [41]         | 45-45            | 2.46-16.02     | 8    | NaCa  |
| 36  | Poulain et al. [53]     | 49.85-149.85     | 1.01-19.93     | 24   | NaCa  |
| 37  | Liu et al. [41]         | 35-55            | 1.34-15.87     | 83   | NaKCa |
| 38  | Poulain et al. [53]     | 49.85-149.85     | 1-19.97        | 24   | NaKCa |
|     | Sum                     |                  | 1648           |      |       |
The algorithm is used to determine the model parameters as follows [14]:

1. The parameters in alpha model are determined by the experimental data of the saturation pressure of CO$_2$ and water.
2. The binary interaction parameters between CO$_2$ and water in the gas phase is determined by the experimental data of water content in the CO$_2$-rich phase. While in this step of parameter determination, the necessary data of CO$_2$ solubility is referred to measured data of mutual solubility or the simulated results of the traditional model.
3. The model parameters in the fugacity model of the aqueous phase are determined by the experimental data of CO$_2$ solubility in the aqueous phase. Similarly, the other phase composition data that are necessary in this parameter determination procedure can be referred to measured data or simulated results of the traditional model.
4. The parameters in the Pitzer interaction models are determined by the measurements of CO$_2$ solubility in brines.
5. Using the determined results in steps (1)-(4) as initial values, all the model parameters are corrected simultaneously by the developed experimental databank.

The determined model parameters in this study are listed in Table 4.

### 4. Model Performance in CO$_2$-Water System

#### 4.1. Model Verification

4.1.1. CO$_2$ Solubility. Figure 1 represents the comparison between the simulated and measured data of CO$_2$ solubility below 100°C. As seen, the solubility of CO$_2$ generally increases with temperature increasing. There is an abrupt change in the variation trend of the curves at around 10 MPa, which is mainly caused by the variations of thermodynamic properties during the CO$_2$-rich phase transferring from vapor to liquid or supercritical.

A large quality of studies have been carried out to measure the CO$_2$ solubility below 100°C. Overall, the literature experimental data is in close agreement with the calculations of the proposed model, Sypcher and Pruess [14], and Duan and Sun [17]. By comparison, a significant deviation is found using the model of Li and Yang [2].

However, there is considerable consistency between the experimental datasets of different literature studies. At $T = 25^\circ$C, the experimental data of Hou et al. [45] and Nakayama et al. [63] deviates obviously from those of other studies. Its deviation approaches to 15% at $P = 18$ MPa. When the pressure is larger than 20 MPa, the experimental data of Greenwood and Barnes [64] agrees well with those of Wiebe.
Figure 1: Comparison between the simulated and measured data of CO₂ solubility below 100°C. LY2013 represents the model of Li and Yang [2]; DS2003 represents the model of Duan and Sun [17]; SP2010 represents the model of Spycher and Pruess [14]. The indexes of experiment datasets are listed in Table 1.
[65], but it has a significant deviation from those of Teng et al. [66] and Gillespie and Wilson [67]. At $T = 50^\circ$C, 75$^\circ$C, or 100$^\circ$C, the experimental data adopted from different literature studies are generally consistent, except for the data of Qin et al. [68] at 50$^\circ$C, and the data of Sako et al. [69] and Kiepe et al. [38] at 100$^\circ$C.

It can be seen that the simulated results of Spycher and Pruess [14] deviate significantly from the experimental data at $T = 100^\circ$C and $P > 60$ MPa. Similarly, the simulation error of Duan and Sun [17] tends to significantly increase at pressures larger than 150 MPa. By comparison, the proposed model is in good agreement with the experimental datasets at 0-350 MPa.

Figure 2 represents the comparison between the simulated and measured data of CO$_2$ solubility between 100$^\circ$C and 300$^\circ$C. LY2013 represents the model of Li and Yang [2]; DS2003 represents the model of Duan and Sun [17]; SP2010 represents the model of Spycher and Pruess [14]. The indexes of experiment datasets are listed in Table 1.

[11Lithosphere](http://pubs.geoscienceworld.org/gsa/lithosphere/article-pdf/doi/10.2113/2021/3474828/5358619/3474828.pdf)
models, the model of Duan and Sun [17] is more accurate than those of Spycher and Pruess [14] and Li and Yang [2].

(iv) Compared to other models, the proposed model has a better accuracy over a wide temperature and pressure range.

As shown in Figure 3, the CO₂ solubility in the aqueous phase and H₂O content in the CO₂-rich phase significantly increase with temperature above 300°C. The inconsistency is obvious as the fluid system approaches to be miscible.

The experimental measurements of different studies agree well at \( T = 300°C \) and \( P < 50 \text{ MPa} \). At \( T = 300°C \), the data of Blencoe [71] is consistent with that of Takenouchi and Kennedy [72], but shows a significant deviation with that of Todheide and Franck [73]. As already indicated by Spycher and Pruess [14], a complete mixing is necessary to reach a fully miscible state. However, this appears to be not sufficient in experiments of Takenouchi and Kennedy [72]. By comparison, the model appears in much better agreement with the data determined by Todheide and Franck [73].

Above 300°C, the proposed model and Spycher and Pruess [14] have a better agreement with the scattered literature data, but the model of Duan and Sun [17] tends to be invalid.

4.1.2. H₂O Content. A comparison between the simulated and measured data of H₂O content in the CO₂-rich phase is shown in Figure 4. As seen, the H₂O content decreases rapidly with pressure increasing, and approaches to constant at high pressure.

Similar to that of CO₂ solubility, there is an abrupt change in H₂O content as the CO₂-rich phase transfers from vapor to liquid or supercritical. This variation appears to be obvious at low temperature and tends to decrease with temperature increasing. Although the identical model parameters are used for different CO₂ phases, the proposed model can accurately reproduce the phase-partitioning behaviors over a wide temperature and pressure range. This approach is the derivative, continuous and smooth, which facilitates its incorporation into Jacobian-based numerical formulation in a multiphase flow simulator.

There exists a considerable inconsistency between different experimental datasets. At 50°C, the data of Todheide and Franck [73] differs slightly from those of other studies. For example, the simulation error between Todheide and Franck [73] and Wiebe and Gaddy [74] approaches 28% at 20 MPa. At 200°C, the measured data of Takenouchi and Kennedy [72] and Malinin [75] obviously deviate from those of Todheide and Franck [73]. The possible reason for inconsistency between these experimental studies has been widely analyzed, which is beyond the scope of this work. The simulated results of the proposed model appear to be closer to the measurements of Todheide and Franck [73].

There are obvious differences in the calculation results of water content by different models: (i) In the model of Duan and Sun [17], the water content in the gas phase is equal to the ratio of water vapor pressure to the total pressure. Although this simplification is valid at low pressure, it can generate a significant deviation at high pressure. (ii) The model of Li and Yang [2] can accurately reproduce the composition of the CO₂-rich phase. However, successful convergence is difficult in many thermodynamic conditions, dependent on the valid temperature and pressure range of this model and limitations of the \( \varphi-\varphi \) type approach. (iii) Although both the proposed model and Spycher and Pruess [14] can accurately reproduce the water content, our model shows a better accuracy at temperatures up to 300°C and pressures larger than 200 MPa.

Figure 3: Comparison between the simulated and measured data of CO₂ solubility above 300°C. DS2003 represents the model of Duan and Sun [17]; SP2010 represents the model of Spycher and Pruess [14]. The indexes of experiment datasets are listed in Table 1.
4.1.3. Error Analysis. Figure 5 shows the comparison in calculation errors of the proposed model and the traditional models. Both the models of Duan and Sun [17] and Spycher and Pruess [14] rely on the fugacity coefficient in the CO\(_2\)-rich phase and the activity coefficient in the aqueous phase, which are the two most commonly used models in the geological field [1–3]. By comparison, the overall simulation error of Spycher and Pruess [14] is slightly larger than that of Duan and Sun [17], owing to a valid pressure range of 0-60 MPa. However, the model of Duan and Sun [17] can only produce a rough estimate of water content in the CO\(_2\)-rich phase with an overall simulation error larger than 50%.

Compared to Duan and Sun [17] and Spycher and Pruess [14], the simulation error of Li and Yang [2] is considerably larger. The possible reasons are analyzed as follows: (i) The cubic EOS is not perfectly suitable for characterizing the fugacity of the aqueous phase in a strongly nonideal system containing water, although it can be improved via the incorporation of a modified alpha equation and a binary interaction model. (ii) The quality of experimental data determines the calculation accuracy of the model to a large extent. It may be the main factor that affects the model accuracy given the fact that a limited experimental databank containing 109 pieces of data is used by Li and Yang [2].

Regarding the proposed model, the average simulation errors for CO\(_2\) solubility and H\(_2\)O content are 4.765% and 8.182%, respectively, which are better than other models over a wide temperature and pressure range. We cannot find a
further improvement of model performance by increasing the number of parameters and altering the forms of equations. The increase of calculation accuracy needs more high-precision experimental data at high temperature and pressure conditions.

The aforementioned analysis indicates that all the models have good accuracy for experimental data at low temperatures and pressures, which accounts for the majority of the databank. This suggested that the difference in average simulation errors of different models is mainly generated by the simulation error at high temperatures and pressures.

4.2. Phase Diagram

4.2.1. CO₂ Solubility. Figure 6 shows the phase diagram of CO₂ solubility at different temperatures and pressures. The color region represents the gas-liquid state. The gray area on the bottom represents the single CO₂-rich phase, in which the system pressure is lower than the water saturation pressure. The gray area on the top is the single aqueous phase. The fluid system tends to be completely miscible as temperature and pressure increases [14].

The distribution of contours and variations of colors indicate that the CO₂ solubility increases with pressure increasing. Furthermore, the CO₂ solubility firstly increases and then decreases with temperature [20]. A more rapid change in CO₂ solubility can be found above 150°C compared to that at a low temperature region [53].

4.2.2. Water Content. Figure 7 shows the phase diagram of water content at different temperatures and pressures. Similar to Figure 6, the color area represents the immiscible region, while the gray area represents the miscible region.

As shown, the water content in the CO₂-rich phase increases with temperature increasing. It is more sensitive to changes in temperature above 100°C. Furthermore, the water content rapidly decreases with pressure increasing, showing a complicated variation trend.

5. Extension of the Model to Brines

5.1. Modelling. One advantage of the φ-γ model is the good extensibility to complicated systems containing multiple ions [4, 45]. Commonly, the salting-out effect is widely indicated to considerably decrease gas solubility [76]. However, its effect on composition of the CO₂-rich phase is generally neglected in previous studies [4, 14]. In this study, a modified Pitzer interaction model is incorporated into the developed model to demonstrate the effect of multiple solutes on the phase-partitioning behaviors of the CO₂-brine system.

Considering the interaction between different components in the aqueous phase, the excess Gibbs free energy of an aqueous phase can be estimated as follows [76]:

\[
\frac{G^E}{RTn_{H_2O}M_{H_2O}} = f_1(l) + \sum_{i,j} m_i m_j \lambda_{ij}(l) + \sum_{i,j,k} m_i m_j m_k \mu_{ijk},
\]

where \(G^E\) is the excess Gibbs free energy of an aqueous phase (in J/mol); \(m_i\) is the molality of component in the aqueous phase (in mol/kg); \(\lambda_{ij}\) is the binary interaction parameter; \(\mu_{ijk}\) is the ternary interaction parameter; \(l\) is the ion strength, where \(l = 0.5 \sum z_i^2\); \(z_i\) is the charge number of ion \(i\); and \(f_1(l)\) is the Debye-Hückel item.

Using the expansion form of equation (28), the activity coefficient of CO₂ and water can be obtained:

\[
\begin{align*}
\ln y^s_{\text{solute}} &= 2 \sum_{s} m_{s} \lambda_{Gs} + 6 \sum_{n} m_{n} \left( \sum_{s} m_{s} \mu_{Gns} \right) \\
&\quad + 3 \sum_{c,a} m_{c} m_{a} \chi_{Ga},
\end{align*}
\]

\[
\ln a_{\text{solute}} = M_{H_2O} \left[ 2A^\phi \frac{n^{1.5}}{1 + b n^{0.5}} - 2 \sum_{c,a} m_{c} m_{a} \\
- \left( \lambda_{ca} + \sum_{i=a,c} m_{i} z_{i} \right) \frac{C_{ca}^{\phi}}{2 \left( z_{c} z_{a} \right)} - 2 \sum_{n} m_{n} \sum_{s} m_{s} \lambda_{mn} \\
- 6 \sum_{n} m_{n} \sum_{c,a} m_{c} m_{a} \chi_{nca} - \sum_{c,a} m_{c} \right],
\]

where \(\lambda_{Gs}\) is the parameter of binary interaction between gas and salt; \(m_{s}\) is the molality of salt (in mol/kg); \(\chi_{Ga}\) and \(\mu_{Gns}\) are the parameters of ternary interaction between ions and CO₂; \(\mu_{Gns}\) is set to zero in this study. The subscript \(a\) represents anion, while \(c\) represents cation; \(A^\phi\) is Debye-Hückel parameter for the osmotic coefficient; and \(C_{ca}^{\phi}\) is the third osmotic virial coefficient in Pitzer’s equation.
Table 5: Simulation errors of CO₂ solubility in different brines.

| Salt         | Temperature (°C) | Pressure (MPa) | Exe. | DS2003  | SP2010  | This model |
|--------------|------------------|----------------|------|----------|----------|------------|
| NaCl         | 5-300            | 0.19-60        | 703  | 5.20%    | 9.37%    | 5.78%      |
| KCl          | 23.85-159.95     | 0.09-54.83     | 252  | 14.88%   | 9.84%    | 5.98%      |
| CaCl₂        | 34.85-151.49     | 1.52-71.23     | 225  | 4.90%    | 11.43%   | 4.37%      |
| MgCl₂        | 36.37-151.53     | 1.25-54.48     | 74   | 6.92%    | 9.22%    | 4.11%      |
| NaKCaMg      | 50-150           | 10.02-57.10    | 18   | 7.87%    | 12.82%   | 9.99%      |
| Na₂SO₄       | 13.82-160.01     | 0.42-13.11     | 215  | 27.33%   | 33.58%   | 4.33%      |
| NaK          | 35.75-151.52     | 1.07-17.16     | 22   | 4.39%    | 6.28%    | 3.48%      |
| NaCa         | 49.85-149.85     | 1.01-19.93     | 32   | 3.73%    | 6.28%    | 5.06%      |
| NaKCa        | 35-149.85        | 1-19.97        | 107  | 3.73%    | 3.31%    | 2.56%      |
| Sum          |                  |                |      | 9.56%    | 12.42%   | 5.15%      |

Note: DS2003 represents the model of Duan and Sun [17]; SP2010 represents the model of Spycher and Pruess [14]. NaK represents NaCl+KCl; NaCa represents NaCl+CaCl₂; NaKCaMg represents NaCl+KCl+CaCl₂+MgCl₂; and NaKCa represents NaCl+KCl+CaCl₂. “Exe” represents the number of experimental data. The details of the experimental database are presented in Appendix B.
Considering the effect of temperature variation, the parameter of binary interaction between CO₂ and salt is estimated using the following correlation:

\[ \lambda_{GS} = B_0 + B_1 T + B_2 T^2, \]  

where \( B_0, B_1, \) and \( B_2 \) are the fitted parameters; and \( S \) represents salt. Using the literature experimental data of phase-partitioning properties in the CO₂-brine system, the ternary and binary interaction parameters in the developed model are determined, as shown in Table 4.

Substituting equation (29) and equation (30) into equation (25), equation (26), and equation (27), the mutual solubility in the CO₂-brine system can be estimated.

5.2. Comparison to the Experimental Data. The most commonly encountered ions in the geological field include Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, and SO₄²⁻. An extensive databank of experimental measurements in such a brine of single salt or mixed salts are developed, covering a wide temperature and pressure range. Using the collected data, the binary and ternary interaction parameters between CO₂ and salt are determined and listed in Table 3.

Validation of the model simulation against the literature experimental data and other models is shown in Table 5.
The average simulation error of CO₂ solubility in different brines is 5.15%, which has a better accuracy over the models of Spycher and Pruess [14] and Duan and Sun [17].

5.3. Phase-Partitioning Behaviors in CO₂-Brine System. Figure 8 shows the CO₂ solubility in a mixed brine of NaCl, KCl, and CaCl₂. The comparison indicates that the proposed model can accurately reproduce the CO₂ solubility in a complicated brine system. Similar to that in a single salt solution, the CO₂ solubility in a mixed brine decreases with ion concentration.

In traditional models, the salting-out effect on water content in the CO₂-rich phase is commonly neglected. However, it has been widely indicated that the binary interaction between electrolytes and water can decrease the water activity in the aqueous phase. This suggested that the composition of the gas phase could be altered by the dissolved solutes in water.

A comparison of water content in the CO₂-rich phase considering the salting-out effect or not is shown in Figure 9. As seen, the salting-out effect can decrease the water content in the gas phase which has been preliminary verified by the experimental data of Mousavi [77]. The inset in Figure 9 shows that the water fraction in the gas phase with salt is 21% lower than that without salt. Furthermore, it has been found that the increase of temperature can enhance the effect of salting out on water content.

To the best of our knowledge, the experimental studies on water content in the CO₂-rich phase for the CO₂-brine system are still very few. However, the solubility of water in CO₂ is crucial to the capacity of injected CO₂ to dry the formations [14, 32, 33] and the potential fluid-rock reactivity [14, 34, 35]. More experimental data on this topic is still necessary to help obtain a comprehensive understanding of the phase-partitioning behaviors in the CO₂-brine system.

6. Conclusions

In this study, a unified ϕ-γ-type thermodynamic model developed to estimate the phase-partitioning behaviors of the CO₂-brine system containing Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, or SO₄²⁻ at temperatures up to 623.15 K and pressures up to 350 MPa. In the model, the fugacity coefficient in the CO₂-rich phase is treated using a modified Peng-Robinson EOS which incorporates a new alpha equation and binary interaction parameter correlation. The activity coefficient in the aqueous phase relies on a unified model of a gas equilibrium constant, the Margules expression, and a Pitzer interaction model.

An extensive experimental database is developed to calibrate the proposed model. The simulation errors for CO₂ solubility and water content in the CO₂+H₂O system are 4.765% and 8.182%, respectively. Regarding the brine containing multiple ions, the simulation deviation of CO₂ solubility is less than 5.1%. A detailed comparison indicates that the proposed model has a better accuracy and a wider valid temperature-pressure range compared to the traditional models. Furthermore, the effect of salting out on the composition of the CO₂-rich phase can be accurately evaluated.

Using the proposed model, the phase diagrams of mutual solubility in the CO₂+H₂O system are generated. More sensitivity of phase compositions to temperature is revealed above 100°C. There exist the abrupt changes in CO₂ solubility and water content as the CO₂-rich phase transfers from vapor to liquid or supercritical.

Appendix

A. Fugacity Model of the Aqueous Phase

The fugacity equation of a fluid component in the aqueous phase is as follows [54]:

\[
f_i^{eq} = f_{io} \exp \left( \frac{\mu_{iA} - g_{io}}{RT} \right), \tag{A.1}\]

where \( g_{io} \) is the Gibbs free energy at the ideal gas state, which can be estimated as follows:

\[
g_{io} = \mu_{i0}^{(0)} + RT \ln (f_{io}) = T \frac{g_{io0}}{T_0} - T \frac{h_{io}}{T_0^2} dT, \tag{A.2}\]

where \( \mu_{i0}^{(0)} \) is the chemical potential of component \( i \) at the ideal gas state (in J/mol).

The chemical potential of component \( i \) in the aqueous phase is as follows:

\[
\mu_{iA} = \mu_{i0}^{(0)} + RT \ln a_i, \tag{A.3}\]

\[
\mu_{iA}^{(0)} = T \frac{g_{iA0}}{T_0} - T \frac{h_{iA}}{T_0^2} dT + \int_{P_a}^P v_{iA} dP, \tag{A.4}\]

where \( \mu_{iA}^{(0)} \) is the chemical potential of component \( i \) in the aqueous phase (in J/mol).

Substituting equation (A.2) and equation (A.3) into equation (A.1), we obtain

\[
f_i^{eq} = \exp \left( \frac{\mu_{iA}^{(0)} - \mu_{iA}^{(0)} + \ln (a_i)}{RT} \right). \tag{A.5}\]

The difference between chemical potentials of component \( i \) in the gas and aqueous phases at the reference state is as follows:

\[
\mu_{iA}^{(0)} - \mu_{iA}^{(0)} = \Delta \mu_{iA} = \int_{P_a}^P v_{iA} dP, \tag{A.6}\]

\[
\Delta \mu_{iA}^{(0)} = T \frac{g_{iA0}}{T_0} - T \frac{h_{iA}}{T_0^2} dT + RT \ln (f_{io}) - T \frac{g_{iA0}}{T_0} + T \frac{h_{iA}}{T_0^2} dT. \tag{A.7}\]
Substituting equation (A.6) into equation (A.5), the expression for the fugacity of component $i$ in the aqueous phase is as follows:

$$f_i^{Aq} = \exp \left( \frac{\Delta H^{(0)}_{iAg}}{RT} + \ln (a_i) \right) \exp \left( \int_{P_i}^{P} \frac{v_{\text{ia}}}{RT} dp \right). \quad (A.8)$$

Equation (A.8) can be rewritten as a function of the equilibrium constant:

$$f_i^{Aq} = K_i a_i \exp \left( \frac{V_i}{RT} \right), \quad (A.9)$$

where

$$K_i = \exp \left( \frac{\Delta H^{(0)}_{iAg}}{RT} \right), \quad (A.10)$$

$$V_i = \int_{P_i}^{P} v_{\text{ia}} dp.$$  

**B. Experimental Database**

The experimental databases for CO$_2$ solubility in the aqueous phase and brines are presented in Table 1 and Table 3, respectively, while those for the H$_2$O content in the CO$_2$-rich phase are listed in Table 2.

**Data Availability**

All data, models, and code generated or used during the study appear in the submitted article.

**Conflicts of Interest**

The authors declare that they have no conflicts of interest. Parts of this work were carried out in 2018-2019 by the senior author (Xiaohui Sun) while he was a visiting scholar at Lawrence Berkeley National Laboratory.

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**References**

[1] H. Zhao, M. Fedkin, R. Dilmore, and S. N. Lvov, “Carbon dioxide solubility in aqueous solutions of sodium chloride at geological conditions: Experimental results at 323.15, 373.15, and 423.15 K and 150 bar and modeling up to 573.15 K and 2000 bar,” *Geochimica et Cosmochimica Acta*, vol. 149, pp. 165–189, 2015.

[2] X. Li and D. Yang, “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,” *Industrial & Engineering Chemistry Research*, vol. 52, no. 38, pp. 13829–13838, 2013.

[3] H. Guo, Y. Huang, Y. Chen, and Q. Zhou, “Quantitative Raman spectroscopic measurements of CO$_2$ solubility in NaCl solution from (273.15 to 473.15) K at $p = (10, 20, 30, \text{ and } 40.0) \text{ MPa}$,” *Journal of Chemical & Engineering Data*, vol. 61, no. 1, pp. 466–474, 2016.

[4] R. D. Springer, Z. Wang, A. Anderko, P. Wang, and A. R. Felmy, “A thermodynamic model for predicting mineral reactivity in supercritical carbon dioxide: I. Phase behavior of carbon dioxide-water-chloride salt systems across the H$_2$O-rich to the CO$_2$-rich regions,” *Chemical Geology*, vol. 322-323, pp. 151–171, 2012.

[5] X. H. Sun, Z. Y. Wang, H. Y. Li, H. K. He, and B. J. Sun, “A simple model for the prediction of mutual solubility in CO$_2$-brine system at geological conditions,” *Desalination*, vol. 504, article 114972, pp. 1–18, 2021.

[6] L. W. Diamond and N. N. Akin, “Solubility of CO$_2$ in water from ~1.5 to 100 °C and from 0.1 to 100 MPa: Evaluation of literature data and thermodynamic modelling,” *Fluid Phase Equilibria*, vol. 208, no. 1-2, pp. 265–290, 2003.

[7] R. Shukla, P. G. Ranjith, A. Haque, and X. Choi, “A review of studies on CO$_2$ sequestration and caprock integrity,” *Fuel*, vol. 89, no. 10, pp. 2651–2664, 2010.

[8] N. Spycher, K. Pruess, J. Ennis-King et al., “CO$_2$–H$_2$O mixtures in the geological sequestration of CO$_2$. I. Assessment and calculation of mutual solubilities from 12 to 100°C and up to 600 bar,” *Geochimica et Cosmochimica Acta*, vol. 67, no. 16, pp. 3015–3031, 2003.

[9] H. Guo, Y. Chen, Q. Hu, W. Lu, W. Ou, and L. Geng, “Quantitative Raman spectroscopic investigation of geo-fluids high-pressure phase equilibria: part I. Accurate calibration and determination of CO$_2$ solubility in water from 273.15 to 573.15 K and from 10 to 120 MPa,” *Fluid Phase Equilibria*, vol. 382, pp. 70–79, 2014.

[10] P. J. Carvalho, L. M. Pereira, N. P. Gonçalves, A. J. Queimada, and J. A. Coutinho, “Carbon dioxide solubility in aqueous solutions of NaCl: measurements and modeling with electrolyte equations of state,” *Fluid Phase Equilibria*, vol. 388, pp. 100–106, 2015.

[11] R. Jacob and B. Z. Saylor, “CO$_2$ solubility in multi-component brines containing NaCl, KCl, CaCl$_2$ and MgCl$_2$ at 297 K and 1–14 MPa,” *Chemical Geology*, vol. 424, pp. 86–95, 2016.

[12] H. Li, S. Zheng, and D. Yang, “Enhanced swelling effect and viscosity reduction of solvent(s)/CO$_2$/heavy-oil systems,” *SPE Journal*, vol. 18, no. 4, pp. 695–707, 2013.

[13] G. Cui, L. Yang, Z. Qiu, Y. Wang, and S. Ren, “Geochemical reactions and their influence on petrophysical properties of ultra-low permeability oil reservoirs during water and CO$_2$ flooding,” *Journal of Petroleum Science and Engineering*, vol. 203, p. 108672, 2021.

[14] N. Spycher and K. Pruess, “A phase-partitioning model for CO$_2$–brine mixtures at elevated temperatures and pressures: application to CO$_2$-enhanced geothermal systems,” *Transport in Porous Media*, vol. 82, no. 1, pp. 173–196, 2010.
generation from a depleted high-temperature gas reservoir by recycling CO$_2$,” Energy, vol. 217, article 119340, 2021.

[16] F. J. Millero, “Thermodynamics of the carbon dioxide system in the oceans,” Geochemica et Cosmochimica Acta, vol. 59, no. 4, pp. 661–677, 1995.

[17] Z. Duan and R. Sun, “An improved model calculating CO$_2$ solubility in pure water and aqueous NaCl solutions from 273 to 533 K and from 0 to 2000 bar,” Chemical Geology, vol. 193, no. 3-4, pp. 257–271, 2003.

[18] M. Caumon, J. Sterpenich, A. Randi, and J. Pirounon, “Measuring mutual solubility in the H$_2$O-CO$_2$ system up to 200 bar and 100 °C by in situ Raman spectroscopy,” International Journal of Greenhouse Gas Control, vol. 47, pp. 63–70, 2016.

[19] L. Truche, E. F. Bazarkina, G. Berger, M. C. Caumon, G. Bessaque, and J. Dubessy, “Direct measurement of CO$_2$ solubility and pH in NaCl hydrothermal solutions by combining in-situ potentiometry and Raman spectroscopy up to 280°C and 150 bar,” Geochemica et Cosmochimica Acta, vol. 177, pp. 238–253, 2016.

[20] D. Tong, J. M. Trusler, and D. Vega-Maza, “Solubility of CO2 in Aqueous Solutions of CaCl2 or MgCl2 and in a Synthetic Formation Brine at Temperatures up to 423 K and Pressures up to 2124 bar,” Journal of Chemical & Engineering Data, vol. 58, no. 7, pp. 2116–2124, 2013.

[21] A. Hassanpouryouzband, M. V. Farahani, J. Yang et al., “Solubility of flue gas or carbon dioxide-nitrogen gas mixtures in water and aqueous solutions of salts: experimental measurement and thermodynamic modeling,” Industrial & Engineering Chemistry Research, vol. 58, no. 8, pp. 3377–3394, 2019.

[22] T. Xu, G. Feng, Y. Shi et al., “On fluid-rock chemical interaction in CO$_2$-based geothermal systems,” Journal of Geochemical Exploration, vol. 144, pp. 179–193, 2014.

[23] S. Zhang, H. H. Liu, M. I. J. Van Dijke, S. Geiger, and S. M. Agar, “Constitutive relations for reactive transport modeling: effects of chemical reactions on multi-phase flow properties,” Transport in Porous Media, vol. 114, no. 3, pp. 795–814, 2016.

[24] L. André, P. Audigane, M. Azaroual, and A. Menjouz, “Numerical modeling of fluid–rock chemical interactions at the supercritical CO$_2$–liquid interface during CO$_2$ injection into a carbonate reservoir: the Dogger aquifer (Paris Basin, France),” Energy Conversion and Management, vol. 48, no. 6, pp. 1782–1797, 2007.

[25] L. Zhang, G. Cui, Y. Zhang, B. Ren, S. Ren, and X. Wang, “Influence of pore water on the heat mining performance of supercritical CO$_2$ injected for geothermal development,” Journal of CO2 Utilization, vol. 16, pp. 287–300, 2016.

[26] A. Borgia, K. Pruess, T. J. Kneafsey, C. M. Oldenburg, and L. Pan, “Numerical simulation of salt precipitation in the fractures of a CO$_2$-enhanced geothermal system,” Geothermics, vol. 44, pp. 13–22, 2012.

[27] R. M. Enick and S. M. Klara, “Effects of CO$_2$ solubility in brine on the compositional simulation of CO$_2$ floods,” SPE Reservoir Engineering, vol. 7, no. 2, pp. 253–258, 1992.

[28] Y. Chang, B. K. Coats, J. S. Nolen et al., “A compositional model for CO$_2$ floods including CO$_2$ solubility in water,” SPE Reservoir Evaluation & Engineering, vol. 1, no. 2, pp. 153–160, 1998.

[29] E. Mohammadian, H. Hamidi, M. Asadullah, A. Azerpour, S. Motamedi, and R. Junin, “Measurement of CO$_2$ solubility in NaCl brine solutions at different temperatures and pressures using the potentiometric titration method,” Journal of Chemical & Engineering Data, vol. 60, no. 7, pp. 2042–2049, 2015.

[30] W. Yan, S. Huang, E. H. Stenby et al., “Measurement and modeling of CO$_2$ solubility in NaCl brine and CO$_2$-saturated NaCl brine density,” International Journal of Greenhouse Gas Control, vol. 5, no. 6, pp. 1460–1477, 2011.

[31] J. H. Kwak, J. Z. Hu, R. V. F. Turcu et al., “The role of H$_2$O in the carbonation of forsterite in supercritical CO$_2$,” International Journal of Greenhouse Gas Control, vol. 5, no. 4, pp. 1081–1092, 2011.

[32] T. Giorgis, M. Carpita, A. Battistelli et al., “2D modeling of salt precipitation during the injection of dry CO$_2$ in a depleted gas reservoir,” Energy Conversion and Management, vol. 48, no. 6, pp. 1816–1826, 2007.

[33] S. Hurter, D. Labregere, and J. Berge, “Simulations of dry-out and halite precipitation due to CO$_2$ injection,” Geochemistry, Geophysy, Geosystems, vol. 71, pp. A426–A426, 2007.

[34] J. Moore, M. Adams, R. Allis, S. Lutz, and S. Rauzi, “Mineralogical and geochemical consequences of the long-term presence of CO$_2$ in natural reservoirs: an example from the Springerville-St. Johns Field, Arizona, and New Mexico, USA,” Chemical Geology, vol. 217, no. 3–4, pp. 365–385, 2005.

[35] J. L. Palandri, R. J. Rosenbauer, and Y. K. Kharaika, “Ferric iron in sediments as a novel CO$_2$ mineral trap: CO$_2$–SO$_2$ reaction with hematite,” Applied Geochemistry, vol. 20, no. 11, pp. 2038–2048, 2005.

[36] B. Rumpf, H. Nicolaïsen, C. Ócal, and G. Maurer, “Solubility of carbon dioxide in aqueous solutions of sodium chloride: experimental results and correlation,” Journal of Solution Chemistry, vol. 23, no. 3, pp. 431–448, 1994.

[37] M. D. Bermejo, A. Martin, L. J. Florusse, C. J. Peters, and M. J. Cocero, “The influence of Na$_2$SO$_4$ on the CO$_2$ solubility in water at high pressure,” Fluid Phase Equilibria, vol. 238, no. 2, pp. 220–228, 2005.

[38] J. Kiepe, S. Horstmann, K. Fischer, and J. Gmehling, “Experimental determination and prediction of gas solubility data for CO$_2$+H$_2$O mixtures containing NaCl or KCl at temperatures between 313 and 393 K and pressures up to 10 MPa,” Industrial & Engineering Chemistry Research, vol. 41, no. 17, pp. 4393–4398, 2002.

[39] R. Wiebe and V. L. Gaddy, “The solubility in water of carbon dioxide at 50, 75, and 100, at pressures to 700 atmospheres,” Journal of the American Chemical Society, vol. 61, no. 2, pp. 315–318, 1939.

[40] J. A. Nighswander, N. Kalogerakis, and A. K. Mehrotra, “Solubilities of carbon dioxide in water and 1 wt.% sodium chloride solution at pressures up to 10 MPa and temperatures from 80 to 200 degree C,” Journal of Chemical & Engineering Data, vol. 34, no. 3, pp. 355–360, 1989.

[41] Y. Liu, M. Hou, G. Yang, and B. Han, “Solubility of CO$_2$ in aqueous solutions of NaCl, KCl, CaCl$_2$ and their mixed salts at different temperatures and pressures,” Journal of Supercritical Fluids, vol. 56, no. 2, pp. 125–129, 2011.

[42] N. N. Akinfeev and L. W. Diamond, “Thermodynamic model of aqueous CO$_2$–H$_2$O–NaCl solutions from -22 to 100°C and from 0.1 to 100 MPa,” Fluid Phase Equilibria, vol. 295, no. 1, pp. 104–124, 2010.

[43] H. Zhao and S. N. Lvov, “Phase behavior of the CO$_2$–H$_2$O system at temperatures of 273–623 K and pressures of 0.1–200 MPa using Peng- Robinson-Struyk-Vera equation of state with a modified Wong-Sandler mixing rule: An
extension to the CO₂–CH₄–H₂O system,” *Fluid Phase Equilibria*, vol. 417, pp. 96–108, 2016.

[44] S. Kim, Y. Kim, B. H. Park, J. H. Lee, and J. W. Kang, “Measurement and correlation of solubility of water in carbon dioxide-rich phase,” *Fluid Phase Equilibria*, vol. 328, pp. 9–12, 2012.

[45] S. X. Hou, G. C. Maitland, and J. M. Trusler, “Measurement and modeling of the phase behavior of the (carbon dioxide + water) mixture at temperatures from 298.15 K to 448.15 K,” *The Journal of Supercritical Fluids*, vol. 73, pp. 87–96, 2013.

[46] M. T. Reagan, G. J. Moridis, K. S. Seim et al., “Application to CO₂ solubility in aqueous NaCl solutions and the measurement and correlation of solubility of water in carbon dioxide-rich phase,” *Chemical Geology*, vol. 103, pp. 191–203, 2002.

[47] Y. Li and L. X. Nghiem, “Phase equilibria of oil, gas and water/brine mixtures from a cubic equation of state and Henry’s law,” *The Canadian Journal of Chemical Engineering*, vol. 64, no. 3, pp. 486–496, 1986.

[48] J. Hu, Z. Duan, C. Zhu, and I. M. Chou, “PVTx properties of the CO₂–H₂O and CO₂–H₂O–NaCl systems below 647 K: assessment of experimental data and thermodynamic models,” *Chemical Geology*, vol. 238, no. 3–4, pp. 249–267, 2007.

[49] H. Sorensen, K. S. Pedersen, and P. L. Christensen, “Modeling of gas solubility in brine,” *Organic Geochemistry*, vol. 33, no. 6, pp. 635–642, 2002.

[50] S. Mao, D. Zhang, Y. Li, and N. Liu, “An improved model for calculating CO₂ solubility in aqueous NaCl solutions and the application to CO₂–H₂O–NaCl fluid inclusions,” *Chemical Geology*, vol. 347, pp. 43–58, 2013.

[51] J. Dubessy, A. Tarantola, and J. Sterpenich, “Modelling of liquid-vapour equilibria in the H₂O–CO₂–NaCl and H₂O–H₂S–NaCl systems at 270°C,” *Oil & Gas Science and Technology*, vol. 60, no. 2, pp. 339–355, 2005.

[52] S. Portier and C. Rochelle, “Modelling CO₂ solubility in pure water and NaCl-type waters from 0 to 300°C and from 1 to 300 bar: application to the Utsira Formation at Sleipner,” *Chemical Geology*, vol. 217, no. 3–4, pp. 187–199, 2005.

[53] M. Poulain, H. Messabeb, A. Lach et al., “Experimental measurements of carbon dioxide solubility in Na–Ca–K–Cl solutions at high temperatures and pressures up to 20 MPa,” *Journal of Chemical & Engineering Data*, vol. 64, no. 6, pp. 2497–2503, 2019.

[54] M. D. Jager, A. L. Ballard, E. D. Sloan et al., “The next generation of hydride prediction: II. Dedicated aqueous phase fugacity model for hydride prediction,” *Fluid Phase Equilibria*, vol. 211, no. 1, pp. 85–107, 2003.

[55] H. C. Helgeson, D. H. Kirkham, and G. C. Flowers, “Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 600°C and 5 kb,” *American Journal of Science*, vol. 281, pp. 1249–1516, 1981.

[56] R. D’ouza, J. R. Patrick, and A. S. Teja, “High pressure phase equilibria in the carbon dioxide-n-hexadecane and carbon dioxide-water systems,” *The Canadian Journal of Chemical Engineering*, vol. 66, no. 2, pp. 319–323, 1988.

[57] T. A. Al-Sahaf, A. J. Kidnay, and E. D. Sloan, “Liquid + vapor equilibria in the nitrogen + carbon dioxide + methane system,” *Industrial & Engineering Chemistry Fundamentals*, vol. 22, no. 4, pp. 372–380, 1983.

[58] D. Y. Peng and D. B. Robinson, “A new two-constant equation of state,” *Industrial & Engineering Chemistry Fundamentals*, vol. 15, no. 1, pp. 59–64, 1976.

[59] K. A. M. Gasem, W. Gao, Z. Pan, and R. L. Robinson Jr., “A modified temperature dependence for the Peng–Robinson equation of state,” *Fluid Phase Equilibria*, vol. 181, no. 1–2, pp. 113–125, 2001.

[60] M. Zirrahi, R. Aziz, H. Hassanzadeh, and M. Moshefghian, “Prediction of water content of sour and acid gases,” *Fluid Phase Equilibria*, vol. 299, no. 2, pp. 171–179, 2010.

[61] M. Zirrahi, R. Aziz, H. Hassanzadeh, and M. Moshefghian, “Mutual solubility of CH₄, CO₂, H₂S, and their mixtures in brine under subsurface disposal conditions,” *Fluid Phase Equilibria*, vol. 324, pp. 80–93, 2012.

[62] H. Carlson and A. P. Colburn, “Vapor-liquid equilibria of nonideal solutions: utilization of theoretical methods to extend data,” *Industrial and Engineering Chemistry*, vol. 34, no. 5, pp. 581–589, 1942.

[63] T. Nakayama, H. Sagara, K. Arai, and S. Saito, “High pressure liquid liquid equilibria for the system of water, ethanol and 1,1-difluoroethane at 323.2 K,” *Fluid Phase Equilibria*, vol. 38, no. 1–2, pp. 109–127, 1987.

[64] H. J. Greenwood, Ed.H. L. Barnes, “Section 17: Binary mixtures of volatile components,” in *Handbook of Physical Constants*, H. J. Greenwood and , Eds., p. 97, The Geological Society of America Memoir, 1966.

[65] R. Wiebe, “The binary system carbon dioxide-water under pressure,” *Chemical Reviews*, vol. 29, no. 3, pp. 475–481, 1941.

[66] H. Teng, A. Yamasaki, M. K. Chun, and H. Lee, “Solubility of liquid CO₂ in water at temperatures from 278 K to 293 K and pressures from 6.44 MPa to 29.49 MPa and densities of the corresponding aqueous solutions,” *The Journal of Chemical Thermodynamics*, vol. 29, no. 11, pp. 1301–1310, 1997.

[67] P. C. Gillespie and G. M. Wilson, *Vapor-Liquid and Liquid-Liquid Equilibria: Water-Methane, Water-Carbon Dioxide, Water-Hydrogen Sulphide, Water-Npentane, Water-Methane-Npentane*, Research report RR-48, Gas Processors Association, Tulsa Okla, 1982.

[68] J. Qin, R. J. Rosenbauer, and Z. Duan, “Experimental measurements of vapor-liquid equilibria of the H₂O+CO₂+CH₄ ternary system,” *Journal of Chemical & Engineering Data*, vol. 53, no. 6, pp. 1246–1249, 2008.

[69] T. Sako, T. Sugeta, N. Nakazawa et al., “Phase equilbrium study of extraction and concentration of furfural produced in reactor using supercritical carbon dioxide,” *Journal of Chemical Engineering of Japan*, vol. 24, no. 4, pp. 449–455, 1991.

[70] R. A. Shagiaikmetov and A. A. Tarzimanov, *Deposited document SPSTL 200 khp-D81-1982 (1981).* Summarized in: Sharlin, P.: *Carbon Dioxide in Water and Aqueous Electrolyte Solutions*. *Solubility Data Series*, vol. 62, International Union of Pure and Applied Chemistry, Oxford University Press, 1996.

[71] J. G. Blencoe, M. T. Naney, and L. Anovitz, “The CO₂–H₂O system: III. A new experimental method for determining liquid-vapor equilibria at high supercritical temperatures,” *American Mineralogist*, vol. 86, no. 9, pp. 1100–1111, 2001.

[72] S. Takenouchi and G. C. Kennedy, “The binary system H₂O–CO₂ at high temperatures and pressures,” *American Journal of Science*, vol. 262, no. 9, pp. 1055–1074, 1964.
K. Tödheide and E. U. Frank, "Das zweiphasengebiet und die kritische kurve im system kohlendioxid–wasser bis zu drucken von 3500 bar," Ztschrift Für Physikalische Chemie, vol. 37, no. 5-6, pp. 387–401, 1963.

R. Wiebe and V. L. Gaddy, "Vapor phase composition of carbon dioxide-water mixtures at various temperatures and at pressures to 700 atmospheres," Journal of the American Chemical Society, vol. 63, no. 2, pp. 475–477, 1941.

S. D. Malinin, "The system water-carbon dioxide at high temperatures and pressures," Geokhimiya, vol. 3, pp. 235–245, 1959.

K. S. Pitzer and G. Mayorga, "Thermodynamics of electrolytes. II. Activity and osmotic coefficients for strong electrolytes with one or both ions univalent," The Journal of Physical Chemistry, vol. 77, no. 19, pp. 2300–2308, 1973.

S. R. Mousavi Belfeh Teymouri, Phase Equilibria Measurements and Modelling of CO2-Rich Fluids/Brine Systems, Heriot-Watt University, Edinburgh, 2017.

C. F. Prutton and R. L. Savage, "The solubility of carbon dioxide in calcium chloride-water solutions at 75, 100, 120 and high pressures," Journal of the American Chemical Society, vol. 67, no. 9, pp. 1550–1554, 1945.

G. Houghton, A. M. McLean, and P. D. Ritchie, "Compressibility, fugacity, and water-solubility of carbon dioxide in the region 0–36 atm and 0–100°C," Chemical Engineering Science, vol. 6, no. 3, pp. 132–137, 1957.

A. J. Ellis, "The solubility of carbon dioxide in water at high temperatures," American Journal of Science, vol. 257, no. 3, pp. 217–234, 1959.

S. Takenouchi and G. C. Kennedy, "The solubility of carbon dioxide in NaCl solutions at high temperatures and pressures," American Journal of Science, vol. 263, no. 5, pp. 445–454, 1965.

S. P. Clark, Handbook of Physical Constants, Geological Society of America, New Haven, 1966.

P. B. Stewart and P. K. Munjral, "Solubility of carbon dioxide in pure water, synthetic sea water, and synthetic sea water concentrates at -5.deg. to 25.deg. and 10- to 45-atm. pressure," Journal of Chemical and Engineering Data, vol. 15, no. 1, pp. 67–71, 1970.

S. D. Malinin and N. A. Kurovskaya, "Investigations of CO2 solubility in a solution of chlorides at elevated temperatures and pressures of CO2," Geokhimiya, vol. 4, pp. 547–551, 1975.

S. E. Drummond, "Boiling and mixing of hydrothermal fluids: chemical effects on mineral precipitation," Ph.D. Thesis, Pennsylvania State University, 1981.

A. Zawisza and B. Malesinska, "Solubility of carbon dioxide in liquid water and of water in gaseous carbon dioxide in the range 0.2–5 MPa and at temperatures up to 473 K," Journal of Chemical and Engineering Data, vol. 26, no. 4, pp. 388–391, 1981.

J. A. Briones, J. C. Mullins, M. C. Thies, and B. U. Kim, "Ternary phase equilibria for acetic acid-water mixtures with supercritical carbon dioxide," Fluid Phase Equilibria, vol. 36, pp. 235–246, 1987.

G. Müller, E. Bender, and G. Maurer, "Das dampffluggleichgewicht des ternären systems ammoniak-kohlendioxid-wasser bei hohen wasser gehalten im bereich zwischen 373 und 473 Kelvin," Berichte der Bunsengesellschaft für Physikalische Chemie, vol. 92, no. 2, pp. 148–160, 1988.

M. B. King, A. Mubarak, J. D. Kim, and T. R. Bott, "The mutual solubilities of water with supercritical and liquid carbon dioxides," The Journal of Supercritical Fluids, vol. 5, no. 4, pp. 296–302, 1992.

R. Dohrn, A. P. Bünz, F. Devlieghere, and D. Thelen, "Experimental measurements of phase equilibria for ternary and quaternary systems of glucose, water, CO2 and ethanol with a novel apparatus," Fluid Phase Equilibria, vol. 83, pp. 149–158, 1993.

A. Dhim, J. C. de Hemptinne, and J. Jose, "Solubility of hydrocarbons and CO2 mixtures in water under high pressure," Industrial & Engineering Chemistry Research, vol. 38, no. 8, pp. 3144–3161, 1999.

A. Bamberger, G. Sieder, and G. Maurer, "High-pressure (vapor + liquid) equilibrium in binary mixtures of (carbon dioxide + water or acetic acid) at temperatures from 313 to 353 K," The Journal of Supercritical Fluids, vol. 17, no. 2, pp. 97–110, 2000.

S. Bando, F. Takemura, M. Nishio, E. Hihara, and M. Akai, "Solubility of CO2 in aqueous solutions of NaCl at (30 to 60) °C and (10 to 20) MPa," Journal of Chemical & Engineering Data, vol. 48, no. 3, pp. 576–579, 2003.

A. Chapoy, A. H. Mohammadi, A. Chareton, B. Tohidi, and D. Richon, "Measurement and modeling of gas solubility and literature review of the properties for the carbon dioxide—water system," Industrial & Engineering Chemistry Research, vol. 43, no. 7, pp. 1794–1802, 2004.

A. Valtz, A. Chapoy, C. Coquelet, P. Paricaud, and D. Richon, "Vapour–liquid equilibria in the carbon dioxide–water system, measurement and modelling from 278.2 to 318.2 K," Fluid Phase Equilibria, vol. 226, pp. 333–344, 2004.

D. Koschel, J. Y. Coxam, L. Rodier, and V. Majer, "Enthalpy and solubility data of CO2 in water and NaCl (aq) at conditions of interest for geological sequestration," Fluid Phase Equilibria, vol. 247, no. 1-2, pp. 107–120, 2006.

J. M. Han, H. Y. Shin, B. M. Min, K. H. Han, and A. Cho, "Measurement and correlation of high pressure phase behavior of carbon dioxide+water system," Journal of Industrial and Engineering Chemistry, vol. 15, no. 2, pp. 212–216, 2009.

G. Ferrentino, D. Barletta, M. O. Balaban, G. Ferrari, and M. Poletto, "Measurement and prediction of CO2 solubility in sodium phosphate monobasic solutions for food treatment with high pressure carbon dioxide," The Journal of Supercritical Fluids, vol. 52, no. 1, pp. 142–150, 2010.

F. Lucile, P. Cézac, F. Contamine, J. P. Serin, D. Houssin, and P. Arpentinier, "Solubility of carbon dioxide in water and aqueous solution containing sodium hydroxide at temperatures from (293.15 to 393.15) K and pressure up to 5 MPa: experimental measurements," Journal of Chemical & Engineering Data, vol. 57, no. 3, pp. 784–789, 2012.

V. Savary, G. Berger, M. Dubois et al., "The solubility of CO2 +H2S mixtures in water and 2 M NaCl at 120 °C and pressures up to 35 MPa," International Journal of Greenhouse Gas Control, vol. 10, pp. 123–133, 2012.

S. Z. Al Ghafri, E. Forte, G. C. Maitland, J. J. Rodriguez-Henriquez, and J. M. Trusler, "Experimental and modeling study of the phase behavior of (methane+CO2+water) mixtures," The Journal of Physical Chemistry B, vol. 118, no. 49, pp. 14461–14478, 2014.

A. Bastami, M. Allahgholi, and P. Pourafshary, "Experimental and modelling study of the solubility of CO2 in various..."
CaCl₂ solutions at different temperatures and pressures,” *Petroleum Science*, vol. 11, no. 4, pp. 569–577, 2014.

[103] A. D. King Jr. and C. R. Coan, "Solubility of water in compressed carbon dioxide, nitrous oxide, and ethane. Evidence for hydration of carbon dioxide and nitrous oxide in the gas phase," *Journal of the American Chemical Society*, vol. 93, no. 8, pp. 1857–1862, 1971.

[104] K. Y. Song and R. Kobayashi, "Water content of CO₂ in equilibrium with liquid water and/or hydrates," *SPE Formation Evaluation*, vol. 2, no. 4, pp. 500–508, 1987.

[105] K. Jackson, L. E. Bowman, and J. L. Fulton, "Water solubility measurements in supercritical fluids and high-pressure liquids using near-infrared spectroscopy," *Analytical Chemistry*, vol. 67, no. 14, pp. 2368–2372, 1995.

[106] C. W. Meyer and A. H. Harvey, "Dew-point measurements for water in compressed carbon dioxide," *AICHE Journal*, vol. 61, no. 9, pp. 2913–2925, 2015.

[107] S. X. Hou, G. C. Maitland, and J. M. Trusler, "Phase equilibria of (CO₂+H₂O+NaCl) and (CO₂+H₂O+KCl): measurements and modeling," *The Journal of Supercritical Fluids*, vol. 78, pp. 78–88, 2013.

[108] H. Messabebe, F. Contamine, P. Cézac, J. P. Serin, and E. C. Gaucher, "Experimental measurement of CO₂ solubility in aqueous NaCl solution at temperature from 323.15 to 423.15 K and pressure of up to 20 MPa," *Journal of Chemical & Engineering Data*, vol. 61, no. 10, pp. 3573–3584, 2016.

[109] Á. Pérez-Salado Kamps, E. Meyer, B. Rumpf, and G. Maurer, "Solubility of CO₂ in aqueous solutions of KCl and in aqueous solutions of K₂CO₃," *Journal of Chemical & Engineering Data*, vol. 52, no. 3, pp. 817–832, 2007.

[110] B. Rumpf and G. Maurer, "An experimental and theoretical investigation on the solubility of carbon dioxide in aqueous solutions of strong electrolytes," *Berichte der Bunsengesellschaft fuer physikalische chemie*, vol. 97, no. 1, pp. 85–97, 1993.