

Thermodynamic Properties of a Gas–Liquid–Solid System

Subjects: Environmental Sciences

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Emission reduction in the main greenhouse gas, CO₂, can be achieved efficiently via CO₂ geological storage and utilization (CCUS) methods such as the CO₂ enhanced oil/water/gas recovery technique, which is considered to be an important strategic technology for the low-carbon development of China's coal-based energy system. During the CCUS, the thermodynamic properties of the CO₂–water–rock system, such as the interfacial tension (IFT) and wettability of the caprock, determine the injectability, sealing capacity, and safety of this scheme. Thus, researchers have been conducting laboratory experiments and modeling work on the interfacial tension between CO₂ and the water/brine, wettability of caprocks, the solubility of gas–liquid binary systems, and the pH of CO₂-saturated brine under reservoir temperature and pressure conditions.

Keywords: CO₂ geological storage and utilization ; thermodynamic properties ; CO₂ trapping mechanisms

1. Interfacial Tension between CO₂ and Water/Brine

The threshold capillary pressure that determines the efficiency of residual trapping is a function of the wettability and the interfacial tension (IFT) between the CO₂ and reservoir brines, as described by the standard Young–Laplace equation, as shown in Equation (1) [1][2]. This threshold capillary pressure characterizes the penetration ability of the non-wetting phase (CO₂) into the macropores and throats of the reservoir rock that were originally water saturated. Research findings suggest that lower IFT leads to enhanced CO₂ capillary trapping, as it reduces the capillary pressure required for CO₂ capture within pore spaces, thereby improving storage efficiency. Due to the complexity of the actual reservoir, the wettability of the sealing site can be represented by measuring the contact angles (CAs) of the CO₂-brine-rock system. Thus, the laboratory and modelling work of CO₂–brine IFTs and rock CAs have been reviewed, and the key findings are highlighted in this section.

$$P_c^{\text{th}} = \frac{2\gamma_{\text{w/b,CO}_2} \cos \theta}{R} \quad (1)$$

where P_c^{th} is the threshold capillary pressure of brine/water-saturated caprock $\gamma_{\text{w/b,CO}_2}$ (mN·m⁻¹) is the IFT between water/brine and CO₂, θ is the CA between the brine/water and rocks in a CO₂ atmosphere, and R is the maximum radius of cylindrical caprocks.

Different methods exist for measuring the IFT between gases and liquids. Among these, the pendent drop method, which is based on the axisymmetric drop shape analysis (ADSA) technique, is widely used because of its high accuracy and efficiency. Pictures of the pendent drop of the desired solution were captured using a CCD camera at a high resolution under the evaluated temperature and pressure conditions. However, the accuracy of the calculated IFTs based on this method strongly depends on the density difference between the gas and liquid, as illustrated in Equation (2).

$$\gamma = \frac{g\Delta\rho D_e^2}{H} \quad (2)$$

where g is the gravity constant; γ is the IFT; $\Delta\rho$ is the density difference; H is the shape factor, which is related to the drop shape parameters; and D_e is the horizontal diameter of the drop. Therefore, the accuracy of the obtained density difference determines the integrity of the IFT values measured using the pendent drop method.

Numerous experimental studies have been conducted on the IFT between CO₂ and reservoir fluids using the pendent drop method based on the ADSA technique [2][3][4][5]. Initially, most laboratory studies were conducted on CO₂ + water binary systems under reservoir conditions. Then, considering the effects of actual reservoir brine's ionic strengths and types on the IFT between the CO₂-brine system, the IFTs of the CO₂ + brine binary system consistent with the reservoir conditions were measured, where temperatures and pressures ranged from 278 to 423 K and 0.1–70 MPa, respectively [2][3][4][6][7][8]. However, owing to the differences in the experimental procedures and methods, disparities and contradictions exist in the experimental results, which has led to doubts regarding the accuracy and reliability of the IFT data in the literature [9]. Accurate determination of the density difference between CO₂ and water/brine is critical to the IFT measurement results based on ADSA, as shown in Equation (1) [1]. Due to the mutual dissolution of CO₂ and water/brine, the density of the two-phase equilibrium must be considered when measuring the two-phase IFT [10]. Thus, the difference between density difference determination methods also leads to a disparity in the IFTs reported in the literature. It is found that the IFT of the CO₂ + brine system increases with molalities, and those with divalent ion is twice larger than the monovalent ions at the same temperature, pressure, and molality conditions [11]. The measurement time also influenced the accuracy of the measured IFT data [9]. Larger errors were observed in the obtained data when waiting too long for the measurement, where the drop shape presented less integrity. The poor results (excessively small IFT) in Chun's [6] work resulted from waiting for days for the system to reach phase equilibrium, as observed in previous literature [9].

To supplement the IFT database between CO₂ and water/brines, the research scope was extended to higher temperatures and pressures via modelling methods. The molecular dynamics (MD) method was developed to better understand the relationship between the surface strength and IFT for the CO₂ + H₂O binary system; however, a relatively high deviation between the predicted and experimental values was found [12][13][14]. In recent years, an artificial neural network (ANN) method was presented to estimate the IFTs for a CO₂ + water/brine binary system [15][16][17][18][19]. The ANN method exhibited a high level of accuracy with respect to different systems, while it was strongly dependent on the experimental data; thus, the estimation is restricted to the experimental conditions and cannot be extended to predictions beyond the experimental temperature and pressure ranges with high integrity. In previous work conducted by Chow [20], a theoretical model uses of square gradient theory (SGT) applied to the 'statistical associating fluid-theory variable-range Mie' (SAFT-VR-Mie) Equation of State (EoS) was developed for the IFTs of the CO₂ + H₂O/CO₂ binary system and the CO₂ + N₂/Ar + H₂O ternary system. The model exhibited a high level of integrity for the CO₂ + H₂O/brine binary system. The SAFT theory proposed by Chapman et al. [21][22] is one of the most successful models for modern algebraic descriptions of chain fluids and has been applied to estimate the thermodynamic and phase equilibrium properties of complex fluid mixtures in recent years [23][24][25][26][27]. However, the SAFT EoS is too complicated and requires too many factors and parameters. Most recently, Jerauld et al. [28] proposed a revised correlation method for the accurate estimation of the CO₂-brine IFT based on over 1600 data points from the literature and concluded that the Kashafi [29] method has better qualitative behavior and improves predictions with an AARE of approximately 5%. Neural network- and machine learning-based models have high computing speeds, strong adaptability, and a fault-tolerant ability; however, the normalization method lacks thermodynamic meaning. Moreover, the thermodynamic relationships between the main CO₂ trapping mechanisms in terms of solubility and IFT for the CO₂ + H₂O/brine binary system need to be elaborated in detail [30].

It was concluded that the interfacial characteristics of rock–fluid systems have a significant influence on the efficiency of CO₂ capillary trapping during saline aquifer sequestration [31]. Thus, in previous studies, the IFT between CO₂ and brine of different concentrations under reservoir pressure and temperature conditions has been investigated systematically. The results indicate that the IFT of the CO₂-brine binary system depends on the temperature, pressure, and molality [1][10][32]. According to previous research, the CO₂-brine IFT has a very limited pressure dependence tendency after the pseudo-plateau is reached. As for the salt concentrations, a linear relationship exists between the average increase in the CO₂-brine IFT and the brine molality [2][10]. According to previous research, this can be expressed using the following equations [33].

$$\gamma = A_{\gamma}[m^{+}] + B_{\gamma} \quad (3)$$

$$m^{+} = \sum_{i=1}^n z_i m_i \quad (4)$$

$$A_{\gamma} = a_1 + a_2 p_r + a_3 T_r \quad (5)$$

$$B_{\gamma} = b_1 + b_2 p_r + b_3 T_r + b_4 p_r^2 + b_5 p_r T_r + b_6 T_r^2 \quad (6)$$

Then, a modified empirical correlation based on experimental data was presented, where $\Delta\gamma$ is the deviation between the experimental and estimated values for the CO₂-brine IFT. The modified empirical correlation uses only a few regression coefficients with a relatively low error for most of the experimental data with around 600 data points. The prediction results reached good agreement with the experiment. Thus, IFTs between CO₂-brine can be estimated via the modified empirical correlation based on the linear relations of $\Delta\gamma$ and salinity, covering a wide range of temperatures (373–423 K), pressures (3–30 MPa), and ionic strengths (0–4.9 mol·kg⁻¹) for brines containing Na⁺, K⁺, Ca²⁺, and Mg²⁺.

However, to predict the IFTs when the isotherms reached a plateau, the empirical correlations based on the linear relation method yielded larger deviations ($\Delta\gamma$ larger than ± 4 mN·m⁻¹) than expected. Moreover, a large discontinuity in the slope for the IFTs against temperature at a constant pressure when passing from the liquid/vapor to the super-critical/liquid region was observed. Therefore, a model that is smooth and continuous in slope and successfully fits the IFT data corresponding to the CO₂ geological storage conditions, especially those covering the CO₂ phase-change region with thermodynamic significance, needs to be developed in future work. The following conclusions are relevant based on the results discussed above:

- Different methods exist to measure the IFT between gases and liquids. Among these, the pendant drop method, which is based on the axisymmetric drop shape analysis (ADSA) technique, is widely used because of its high accuracy and efficiency.
- An accurate measurement of the IFT in CO₂ reservoir brines at the evaluated high-temperature and pressure ranges corresponding to actual reservoir conditions relies on the integrity of the experimental apparatus and approach.
- Because of the temperature and pressure limitations of the desired experimental apparatus, a prediction model for the IFT between CO₂ and reservoir brines in accordance with the actual reservoir conditions covering a wide range of temperatures, pressures, ionic types, and strengths is essential.
- The results indicate that the IFT of the CO₂-brine binary system depends on the temperature, pressure, and molality. However, the pressure has a limited influence on the CO₂-brine IFT after the pseudo-plateau has been reached.

A simplified IFT prediction model with thermodynamic significance and high integrity for predicting IFTs when a pseudo-plateau is reached needs to be developed. And the model needs to cover a wide range of temperatures and pressures corresponding to the CO₂ geological storage conditions in future work.

2. Wettability of the CO₂-Water/Brine-Rock System

Multiphase flows in porous media are of great importance in many industrial processes in terms of geological CO₂ sequestration and utilization, including enhanced oil/gas/water recovery [34][35]. The effects of fluid properties and flow conditions have been widely studied in previous research, whereas less emphasis has been given to the wettability of the CO₂-water/brine-rock system, which is a key parameter influencing the storage capacity and security of the CO₂ geological storage scheme [36].

The seepage characteristics of reservoir fluids are a function of wettability because the fluid distribution in the pore space of reservoir rocks is governed by rock wettability [34]. Therefore, it is important to accurately measure the rock wettability under CO₂ geological storage conditions. The wettability of the CO₂-water/brine-rock system was estimated by measuring the contact angles of individual rock sample surfaces under reservoir conditions using conventional methods, including the ADSA [31][37]. However, conventional contact angle and tomographic imaging methods have serious limitations [36].

The wettability alteration of caprocks as a function of the temperature and pressure in the presence of supercritical CO₂ has been systematically investigated in previous studies. The wettability of the CO₂-brine-mica/quartz system barely changes and remains wet, regardless of the conditions observed [38]. The substrates remained hydrophilic in most of the experimental temperature, pressure, and salinity ranges, whereas a sudden increase in the CAs (5–13°) was observed when CO₂ was converted from the subcritical to the supercritical region for different rock samples in previous work [2]. Alterations in the wettability of the caprock in the presence of supercritical CO₂ have also been reported in other studies [37][38][39][40]. Based on previous research, wettability alternations of the caprock should be taken into consideration for accurate estimation of the CO₂ storage capacity of a potential sequestration site. The wettability of rock/CO₂/brine and rock/oil/CO₂-enriched brine systems has been analyzed critically, and a future outlook was proposed in previous literature

[41]. Until very recently, only limited investigations have been conducted regarding the CAs between reservoir rocks and water or brine, although wettability has a profound influence on fluid–fluid interactions in the presence of a solid surface under CO₂ storage conditions [35].

Traditional contact angle measurements overlook the 3D pore geometry, surface roughness, and chemical heterogeneity, making them more prone to error. Hence, a micro-computed tomography (CT) scanner method was used to measure the local CAs of a CO₂–brine–glass beads system at the pore scale [42][43]. However, there are obvious limitations and disadvantages associated with using the CT method. It is expensive, time-consuming, and the medical CT resolution is too low, resulting in only averaged saturations being measured, and this curvature measurement may be biased owing to its voxelized nature [35]. To overcome some of the abovementioned limitations and to deepen the fundamental understanding of the flow processes of supercritical CO₂ via brine-saturated porous media, Nuclear Magnetic Resonance (NMR) with molecular resolution has recently been used to measure CO₂–rock wettability in recent work [36]. Despite recent advances in ability to accurately measure the wettability under reservoir conditions and engineer wettability in the subsurface, the complex physics of wetting continues to challenge microscopic and macroscopic descriptions [35], owing to measurement disparities, variation in the sample type, roughness, contamination, and cleaning procedures [31][40][44][45]. Stefan et al. [46] proposed that the broad spread of CA data in the literature was caused by surface contamination. Thus, establishing a practical cleaning procedure for the surfaces of sample substrates is of vital importance for the accurate measurement of rock wettability [2][37][45][46][47].

Overall, the data on CO₂–brine IFTs and rock CAs from laboratory studies are inadequate and contain discrepancies. Most of the experimental studies discussed above used the pendent drop method based on the ADSA method. Thus, experimental errors, inconsistent measurement procedures, and errors in the subsequent analytical techniques could explain these disparities. Therefore, to obtain adequate data with high integrity for CO₂–brine IFTs and rock CAs corresponding to reservoir conditions, further laboratory and modelling research in terms of molecular dynamics and simplified equations of state is required, and the thermodynamic relations between interphase properties need to be elaborated in particular.

Based on the results discussed above, the following conclusions are relevant:

- Conventional methods in terms of the contact angle and tomographic imaging measurements have serious limitations.
- The disparity in the CA results in the reported data can be attributed to the differences in the experimental procedures, substrates, roughness, and cleaning procedures used for the substrate surfaces.
- The effects of the ionic strength and ionic type on the CAs of different substrates need to be further investigated to verify the effects of salinity on CAs.
- Alternation in the wettability of the caprock in the presence of supercritical CO₂ has been observed, and a molecular dynamics method should be implemented to simulate this phenomenon at the molecular level.

3. The Mutual Solubility between CO₂ and Water/Brine

Solubility capture is one of the main long-term carbon capture mechanisms, accounting for approximately 20% of the total capture amount at the initial stage of injection. It can capture up to 90% of the CO₂ injection amount [48][49]. Thus, the mutual solubility between CO₂ and reservoir fluids is one of the key thermodynamic properties that determines the flexibility of the CO₂ saline aquifer sequestration scheme. Over the years, solubility data for CO₂ + H₂O systems have been reviewed and analyzed [50]. Laboratory solubility data for a CO₂ + H₂O system covering a wide range of temperatures and pressures are available in the previously published literature [51][52][53]. Recently, empirical equations and estimation models for water-saturated CO₂ were developed based on experimental data available in the literature [54][55]. Then, modeling for the estimation of mutual solubility in the CO₂ + H₂O binary system was conducted [56][57][58][59][60]. In addition, estimation methods of the *p*–*T*–*x* properties of the CO₂ + H₂O binary system were proposed by others [61][62].

Considering the effects of salinity on solubility, solubility estimation models based on the hybrid G^E equation of state (EoS) [63], Anderko–Pitzer EOS [64], Pitzer EoS [65][66], PC-SAFT EoS [67], mixed solvent electrolyte (MSE) model, and Soave–Redlich–Kwong (SRK) EoS [68] were developed by previous researchers. Mutual solubility research on the CO₂ + brine/complex brine binary system containing ions such as Na⁺, K⁺, Mg²⁺, and Ca²⁺ as well as Cl^{1–}, SO₄^{2–} for a temperature (*T*) of 273 K < *T* < 469 K, a molality (*m*) of 0 mol·kg^{–1} < *m* < 5.0 mol·kg^{–1}, and pressure (*p*) of up to 104 MPa has been carried out over the years and is presented. Hou et al. [69] performed mutual solubility measurements on the

CO₂ + H₂O binary system, and considering the effects of the dissolved salts, vapor–liquid equilibria were measured for the CO₂ + H₂O + NaCl/KCl system using the same analytical apparatus [69]. Duan's model [70] was found to be broadly satisfactory for measuring the solubility of CO₂ in NaCl (aq) but performed poorly for assessing the solubility of CO₂ in KCl (aq). Ratnakar et al. [71] developed a method that uses an ionic strength-based mixing rule and extended the well-known Setschenow relation to capture the impact of a mixture of salts containing mono- or multivalent ions to predict the gas solubility in brine solutions with single or mixed salts. Then, Zhao et al. [72] used the Setschenow coefficient of ions to calculate the solubility of CO₂ in mixed salt solutions. Most recently, Sun et al. [53] proposed a simple model for the prediction of mutual solubility in CO₂ + H₂O and CO₂ + brine systems.

In the meantime, a well-developed model was proposed by Spycher and Pruess [73] to calculate the composition of the compressed CO₂ and liquid H₂O phases at equilibrium based on a noniterative procedure to evaluate the feasibility of CO₂ geologic sequestration for temperatures between 285 K and 383 K and pressures of up to 60 MPa (i.e., 285 K ≤ *T* ≤ 383 K; *p* ≤ 60 MPa) by equating chemical potentials and using the Redlich–Kwong EoS. Because the equilibrium constant *K* (i.e., directly related to the standard Gibbs free energy of the reaction as $\Delta G^0 = -RT \ln K$) is a more fundamental thermodynamic property than Henry's law constant *H*, and because the formulation can be more easily extended to a non-ideal aqueous phase (i.e., resulting from the addition of salts) than formulations involving Henry's law constant, *K* instead of *H* was used in their solubility model. In 2005, their [74] solubility model was extended to include the effect of chloride salts in the aqueous phase by combining the activity coefficient formulations of Duan and Sun [66] and Rumpf et al. [75] with their solubility correlations with an accuracy within the experimental uncertainty for solutions of up to 6 mol·kg⁻¹ NaCl and 4 mol·kg⁻¹ CaCl₂. Then, Spycher and Pruess extended the temperature range of their solubility model up to 573 K (285 K ≤ *T* ≤ 573 K; *p* ≤ 60 MPa) in 2010 [76]. The Redlich and Wong equation [77] was used in the Spycher and Pruess [76] solubility model. Nevertheless, the basic Redlich–Kwong [78] equation can only be applied to a few rather simple fluids. This is because the parameters of the equation are based entirely on the two critical constants, namely the critical temperature (*T_c*) and the critical pressure (*p_c*), and do not involve the acentric factor. The equation of Peng and Robinson [79] is structurally similar to the Redlich and Kwong [77] equation, but it contains an acentric factor for its application to a pure fluid. The content related to the equation of state can be found in the literature [80][81].

Therefore, to better estimate the phase equilibrium properties of mixtures composed of interacting molecules, the interaction parameter *K_{ij}* based on the EoS and mixing rules can be correlated with the modified Peng–Robinson [79] EoS and the mixing rules of Panagiotopoulos and Reid [82]. Furthermore, in the Spycher and Pruess [76] model, different coefficients and parameters were developed for temperatures of above 373 K and below 373 K, such as the Margules expression and the equilibrium constant *K*. The activity coefficients used for the effects of different chloride salts in the brine system were the same, although it has been proven that the ion type has a significant influence on the mutual solubility of the CO₂ + brine binary system. Thus, to develop a more reliable and simplified solubility model covering the *P–T* range of interest for applications to geologic CO₂ sequestration, the original solubility model of Spycher and Pruess needs to be further modified by replacing the Redlich–Kwong [77] EoS with the Peng–Robinson [79], and the calculation methods of the mole fraction, equilibrium constant, and fugacity coefficient also needed to be optimized.

Based on the results discussed above, the following conclusions are relevant:

- Empirical equations and estimation models for CO₂ + H₂O systems have been widely implemented to calculate the solubility of water-saturated CO₂; however, they have limitations in estimating the solubility of H₂O in compressed CO₂.
- There are still too many parameters in the Duan et al. model, and most importantly, it is not intended to compute the solubility of H₂O in a compressed CO₂ gas phase and does not distinguish between ions of the same charge.
- Although the Krichevsky–Kasarnovsky (KK) approach provides a reasonably good representation of the data, it either fails to fit the data or yields an unphysically negative slope at higher temperatures.
- The well-developed Spycher and Pruess model is widely used to develop a more reliable and simplified model for determining the mutual solubility between CO₂ and brines containing different ionic species and of different strengths.
- In the Spycher and Pruess model, different coefficients and parameters have been developed for temperatures above 373 K and below 373 K, such as the Margules expression and equilibrium constant *K*, which have no thermodynamic meaning. Furthermore, the activity coefficients used to determine the effects of different chloride salts in the brine system were the same. The interaction parameter *K_{ij}*, based on the EoS and mixing rules, can still be correlated with the modified Peng–Robinson and the mixing rules of Panagiotopoulos and Reid.

The main methods used for modelling the solubility of liquid or gas phases include an EoS that is usually based on ϕ - ϕ or γ - ϕ equations. Previous solubility models were either limited to a certain range of temperatures or pressures, or were too complex. Most importantly, until very recently, limited research has been available for the simultaneous calculation of the mutual solubility of the CO₂-rich phase and the H₂O-rich phase with high integrity for the application of the CO₂ saline aquifer storage scheme. Furthermore, the interaction mechanism coupling with multiple factors of the gas–liquid–solid interface properties and the dissolution and acidification process needs to be explored in future work.

4. pH of CO₂-Saturated Brine

Modeling and experimental research have been carried out over the years to estimate the pH of the CO₂-saturated brine system. In general, electrometric or optical methods are used to measure the pH of CO₂-saturated brine or water, where the former is based on the electrode system [83], and the latter is based on UV–vis spectrophotometry [84][85][86]. Careful calibration of the measurement system is essential for both measurement approaches.

Previous studies on the pH of CO₂-saturated aqueous solutions have mainly focused on water [87][88][89][90][91], seawater [92], and NaCl brines [93][94][95][96][97][98][99][100][101]. However, reservoir brines contain Na⁺, Cl[−], K⁺, Ca²⁺, Mg²⁺, SO₄^{2−}, HCO₃[−], and CO₃^{2−}, which are expected to significantly influence the fluid properties [102][103][104]. Measurements of brines containing salts other than, or in addition to, NaCl were performed by Stefansson et al. [105], who studied complex systems containing Na₂CO₃, NaHCO₃, NaOH, HCl, and NaCl, and by Li et al. [101], who studied both NaCl and NaHCO₃ brines. An updated literature review on the pH measurement of CO₂-saturated aqueous solutions is presented in previous work [106]. According to a review of the previous literature [87][90][91][92][93][94][96][99][101][106][107], it can be concluded that the electrometric method is often used to measure the pH of CO₂-saturated aqueous solutions covering a wide range of temperatures and pressures (pressures up to 35 MPa), due to its reliability and stability under reservoir conditions. While Toews et al. [88] and Parton et al. [89] measured the pH of the CO₂-H₂O system for the temperatures and pressures ranging from 298 to 343 K and from 7 to 20 MPa, respectively, via optical methods. Then, Shao et al. [98] used an optical method to measure the pH of a CO₂-NaCl system for temperatures and pressures ranging from 298 to 366 K and from 0 to 20 MPa, respectively, while the pressure was 0.1 MPa for the same measurement system in Millero et al.'s work [97]. Also, in Stefansson et al.'s [105] work, the optical method was used to measure the pH of a CO₂-saturated complex brine system at a low pressure range (pressures ranging from 1 to 2 MPa).

Typically, geochemical simulators such as PHREEQC [108] and EQ3NR [109] have been used to model the pH of gas-saturated aqueous solutions. These models implement the Pitzer model to calculate the activity coefficients of solutes in the aqueous phase, the correlations of Henry's constant and an equation of state for gaseous components, and the correlations of standard equilibrium constants for aqueous-phase chemical reactions [110][111][112]. In a previous study on NaCl and NaHCO₃, as well as KCl brines, the Pitzer model accounted well for the measured pH over a wide range of temperatures, pressures, and ionic strengths [101][106]. This type of model offers a convenient route for predicting the pH of complex brines with dissolved CO₂; however, additional validation is required for brines other than NaCl (aq). Prior to estimating the pH, the solubility of gas-saturated aqueous solutions is calculated first in the PHREEQC; thus, the two important thermodynamic properties (pH and solubility) of gas-saturated aqueous solutions can be evaluated via geochemical simulators such as PHREEQC. However, there are limited studies available in the literature to investigate the thermodynamic relations between the pH and solubility of gas-saturated aqueous solutions.

Given the lack of experimental data, it is important to measure the pH of CO₂-saturated brines other than NaCl (aq) over wide ranges of temperatures, pressures, and molalities. The range of investigated conditions should include those relevant to CO₂ storage in deep-saline aquifers. In previous work, the pH of CO₂-saturated aqueous KCl solutions was measured over wide ranges of temperature and pressure and at salt molalities of 2 mol·kg^{−1} and 4 mol·kg^{−1} [106]. It was observed that the influence of KCl on the pH under conditions of a constant temperature and CO₂ partial pressure was different from that of NaCl, with the pH in the former being slightly higher. However, this difference in behavior is probably only significant in brines with high K⁺ molalities [106]. The Pitzer model combined with the MacInnes convention [113], as implemented in PHREEQC version 3.5.0, provides a generally good prediction of the pH of the CO₂-saturated aqueous KCl solutions [106]. Hence, previous work served to validate a geochemical simulator based on the Pitzer model for the prediction of pH in systems involving CO₂ dissolved in water, NaCl (aq), NaHCO₃ (aq), and KCl (aq) [91][101][106]. The influence of divalent cations on the pH of CO₂-saturated aqueous solutions might be different from that of monovalent cations; thus, the model requires further validation for systems involving CO₂ dissolved in brine containing other types of ionic ions, such as Ca²⁺ and Mg²⁺. There are no publications on the pH of a saturated CO₂-CaCl₂ solution and a saturated CO₂-MgCl₂ solution under high-temperature and high-pressure conditions. Therefore, the aim of future research on the pH of saturated CO₂-brine is to validate the integrity of geochemical simulators based on the Pitzer model.

Based on the results discussed above, the following conclusions are relevant:

- Very limited research is available for the pH of gas-saturated aqueous solutions under CO₂ saline aquifer storage conditions, although it is considered to be one of the most important parameters of reservoir fluids.
- In general, electrometric or optical methods are used to measure the pH of CO₂-saturated brine or water. On the basis of the literature review, it can be concluded that the electrometric method is often used to measure the pH of CO₂-saturated aqueous solutions covering a wide range of temperatures and pressures (pressures of up to 35 MPa) due to its reliability and stability under reservoir conditions.
- Geochemical simulators based on the Pitzer model offer a convenient route for predicting the pH of complex brines with dissolved CO₂. However, additional validation is required for brines other than NaCl (aq).
- The pH and solubility of gas-saturated aqueous solutions can be evaluated via geochemical simulators such as PHREEQC. However, there are limited studies available in the literature to investigate the thermodynamic relations between the pH and solubility of gas-saturated aqueous. The mechanisms of dissolution and acidizing during the CO₂ saline aquifer storage process need to be studied systematically, and thermodynamics relations between the pH and solubility of gas-saturated aqueous solutions need to be clarified.
- Given the lack of experimental data, it is important to measure the pH of CO₂-saturated brines other than NaCl (aq) over wide ranges of temperatures, pressures, and molality. The range of investigated conditions should include those relevant to CO₂ storage in deep-saline aquifers. The results of these experiments were compared with calculations based on the Pitzer model to validate the geochemical simulators based on the Pitzer model.

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