

Experimental and modelling study of the solubility of CO₂ in various CaCl₂ solutions at different temperatures and pressures

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Abstract: Study of the thermodynamic behaviour of CaCl₂-H₂O-CO₂ systems is important in different scientific areas in the chemical and petroleum engineering fields. For example, a system including salt-H₂O-CO₂ is a common system in CO₂ geological storage. During carbonate matrix acidizing, this mixture also appears as the spent acid. Hence, study of the behaviour of this system and the solubility of CO₂ in CaCl₂ brine in different thermodynamic conditions is critical.

In this study, CO₂ solubility in 0, 1.90 and 4.80 mol/L CaCl₂ solutions at 328.15 to 375.15 K and 68.9 to 206.8 bar were measured. These values are normal for oil reservoirs. A popular thermodynamic model is available in the literature for estimating the CO₂ solubility in pure water and NaCl solutions. In this paper, the available model was modified by experimental work to be applicable for CaCl₂ as well. Based on the measured data, the component interaction parameters in the base model were adjusted for a CaCl₂-H₂O-CO₂ system. The developed model could predict CO₂ solubility in different conditions with remarkable accuracy, particularly for high concentration solutions and at high pressures. This improvement is up to 65% better than in the base model. This model can be used in Darcy scale models for predicting wormhole propagation during carbonate matrix acidizing.

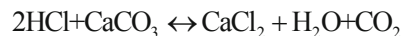
Key words: Solubility of CO₂-CaCl₂, carbonate acidizing, spent acid, wormhole propagation modelling, solubility measurement

1 Introduction

In recent years some researchers have been paying attention to environmental issues such as CO₂ capture and geological storage in deep saline aquifers or depleted hydrocarbon reservoirs. Consequently, CO₂ solubility in pure water and brine has been widely studied. A variety of experimental and modelling investigations into the solubility of CO₂ in brine, especially with NaCl, has been accomplished. Since the major salt in aquifers is NaCl, the CO₂-H₂O-NaCl system has been studied extensively. In addition, there are a limited number of studies of the solubility of CO₂ in other electrolyte solutions. A detailed description of the available experimental data on the solubility of CO₂ in different electrolyte solutions is presented by Springer et al (2012). The main purpose of these studies is the estimation of the soluble CO₂ mole fraction in pure or saline water.

The CaCl₂-H₂O-CO₂ system is a common compositional system in carbonate matrix acidizing. Hydrochloric acid

(HCl) is one of the most common acids used during carbonate matrix acidizing. CO₂, water and CaCl₂ are produced from the reaction of HCl and calcite.



Hence, the solubility of CO₂ in CaCl₂ solutions is important during matrix acidizing and acid fracturing in carbonate formations. The produced CO₂ may remain in the solution in a specific range of temperatures and pressures or may release and form a separate phase which affects the wormhole propagation in matrix acidizing and also etching patterns in acid fracturing jobs (Pournik et al, 2013). Traditionally, during acid fracturing and matrix acidizing experiments, the pressure is controlled to be above 68.9 bar, to prevent two phase flow. The released CO₂ can have some effects on the performance of wormholing during carbonate matrix acidizing. It can change the chemistry of the HCl and calcite reaction and retard the reaction between acid and carbonate (Pournik et al, 2013). Thus, it can be considered as a retarding agent. On the other hand, the formation of a separate CO₂ phase can prevent the movement of the acid

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front into some pores or make it harder to move because of the relative permeability effect between fresh/spent acid and CO₂ phases. Hence, formation of a separate CO₂ phase can change wormholing performance and also the depth of penetration.

There are several methods on different scales for modelling the movement of the acid front during matrix acidizing (Golfier et al, 2002). The main objective is to study the mechanism of wormholing and the effect of different parameters on this complicated phenomenon. A comprehensive model is one which properly estimates the time of breakthrough and depth of penetration and also predicts the wormholing regime. Darcy models can be used to study the matrix acidizing on a core scale. These models work on the basis of gridding the medium and solving the equations of continuity, velocity, concentration and porosity simultaneously. They facilitate the design of an acid job. Nevertheless, the previous Darcy scale models proposed for carbonate matrix acidizing do not consider the chemical and physical effects of carbon dioxide on the performance of the stimulation job (Golfier et al, 2002; Panga et al, 2005; Kalia and Balakotaiah, 2007). The model introduced in this study can be applied together with the above-mentioned equations to capture the physical and chemical effects of carbon dioxide in acid jobs. Thus, it can be used to improve the accuracy of estimations in wormhole breakthrough time and other important parameters of Darcy scale models.

The systems containing CaCl₂ have not been experimentally studied as widely as NaCl-containing solutions. To calculate

the solubility of CO₂ for this case, the models resulting from NaCl-based systems are simply extended for CaCl₂ with some correction factors. The results of a study of CO₂ solubility in different ranges of pressure and temperature was reported by Shaughnessy and Kunza (1981). This shows that the amount of CO₂ production during acidizing with 15% HCl is much greater than the solubility of CO₂ in spent acid in the operational ranges of temperature and pressure.

In contrast to the attention paid to NaCl solutions, the number of publications on the CaCl₂-H₂O-CO₂ system is very limited. This is readily apparent in Table 1, where the experimental studies of CO₂ solubility in CaCl₂ solutions by different authors are shown.

Scharlin and Cargill (1996) and Springer et al (2012) reviewed the few published studies of the CaCl₂-H₂O-CO₂ system. The experimental conditions studied by Mackenzie (1877), Setchenow (1892), Kobe and Williams (1935), Malinin (1959), Onda et al (1970), Malinin and Savelyeva (1972), Malinin and Kurovskaya (1975), Yasunishi and Yoshida (1979), Eremina et al (1989), and He and Morse (1993) are not particularly relevant as regards the reservoir conditions owing to low pressure and temperature values. The most significant paper published on CO₂ solubility in CaCl₂ solutions is that of Prutton and Savage (1945), since the range of temperatures, pressures and salt concentrations of their experimental studies were consistent with reservoir conditions. They measured the CO₂ solubility in CaCl₂ solutions at 348.65, 374.15, 394.15 K and pressures from 15.2 to 709.28 bar.

Table 1 Experimental studies of CaCl₂-H₂O-CO₂ system (after Scharlin and Cargill, 1996; Springer et al, 2012)

Reference	Temperature range, K	Pressure range, bar	CaCl ₂ concentration, mol·kg ⁻¹
Mackenzie (1877)	281.15-303.15	1.01	0.4-1.7
Setchenow (1892)	288.35	1.01	0.15-5
Kobe and Williams (1935)	298.15	1.01	6
Prutton and Savage (1945)	348.65-394.15	15.2-709.28	1-3.9
Malinin (1959)	473.15-623.15	101.33-395.17	1
Onda et al (1970)	298.15	1.01	0.2-2.3
Malinin and Savelyeva (1972)	298.15-348.15	47.62	0.2-4.4
Malinin and Kurovskaya (1975)	373.15-423.15	47.62	0.9-8.8
Yasunishi and Yoshida (1979)	298.15-308.15	1.01	0.2-5.3
Eremina et al (1989)	298.15-313.15	1.01	0.0025-0.025
He and Morse (1993)	273.15-363.15	0.3-1.01	0.1-5

In this paper, the CaCl₂-H₂O-CO₂ system at different ranges of pressure, temperature and CaCl₂ molality, which are consistent with reservoir conditions, is studied to measure and model the solubility of CO₂ during carbonate acidizing. The developed model can be used to improve the acidizing models in Darcy scale.

2 Experiments

The purpose of these experiments is to measure the CO₂ solubility in different CaCl₂ solutions. The temperature and pressure ranges considered for these experiments are the same

as the normal conditions of spent acid during acidizing jobs.

2.1 Materials

The purity of CO₂ was 99.99%. The anhydrous CaCl₂ provided by Merck KGaA was of analytical grade. In addition, distilled water was used throughout the experiments.

2.2 Apparatus and procedures

Fig. 1 shows a schematic of apparatus used in this study to estimate the solubility of CO₂ in CaCl₂ solutions. This

apparatus is similar to the one used by Bando et al (2003) and Yan et al (2011). It consisted of a DBR pump for the 0.1-2000 cm^3/h in constant pressure mode, a high pressure cylinder with a volume of 500 cm^3 and a maximum bearable pressure of 689 bar, a stainless steel pycnometer, high pressure transfer lines, an oven with the maximum temperature of 493.15 K and 0.1 K precision, a pressure transducer for the 1-620 bar

range with 0.007 bar precision, a densitometer, and a vacuum pump.

An agitating pump system as shown in Fig. 2 was designed to agitate the high pressure cylinder in the oven. The system included a motor, a gearbox, a shaft, a pulley, a drive belt and two bearings. The motor and gearbox were out of the oven during the experiments.

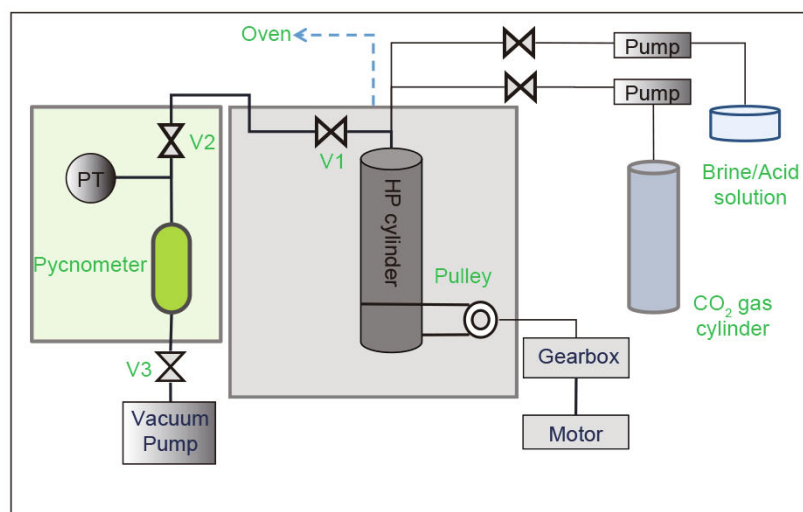


Fig. 1 Schematic of a set-up for solubility measurement

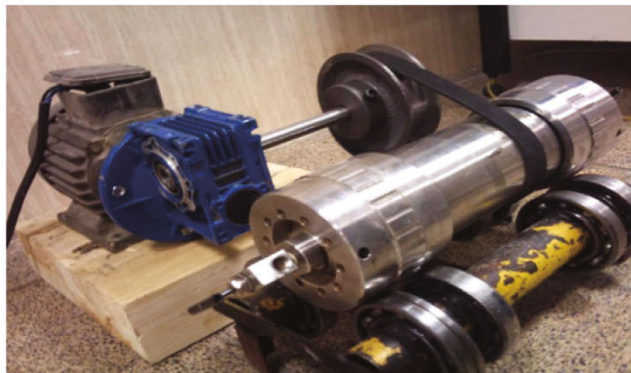


Fig. 2 Agitating pump system

First of all, the high pressure cylinder was opened and washed with distilled water and evacuated by a vacuum pump. CaCl_2 solution and CO_2 were then pumped into the high pressure cylinder and pressurized to the final experimental pressure. Then the high pressure cylinder was agitated at the desired temperature for 3 hours. The effects of agitating time were investigated for 1.9 mol/L CaCl_2 solution at 137.9 bar and 351.65 K (Fig. 3). In this study, the soluble CO_2 mole fraction changed negligibly for data acquired in experiments for longer than 3 hours of agitation. In order to ensure equilibrium, the samples were agitated for 3 hours. As the pressure changed during the agitating period, the pressure was adjusted again.

The concentration of the injected CO_2 was more than its saturation concentration to ensure reaching the saturation concentration of CO_2 in solution. Thus, there was a separate

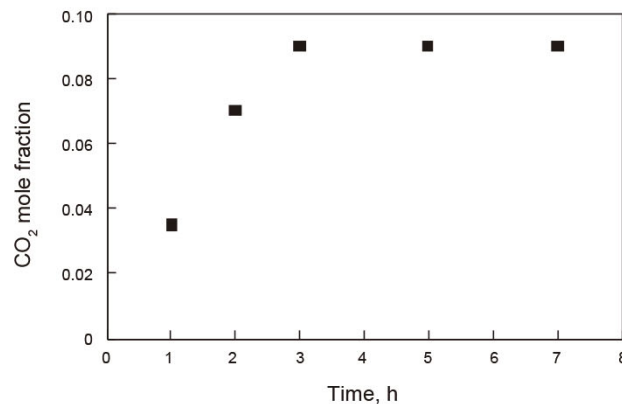


Fig. 3 The effect of agitating time on the mole fraction of soluble CO_2 (a set of experiments for 1.9 mol/L CaCl_2 solution at 351.65 K and 137.9 bar)

supercritical CO_2 phase in the high pressure cylinder after reaching equilibrium. Since the high pressure cylinder had just one exhaust, the cylinder should be inverted for sampling to ensure the exiting of only saturated solution. The solution was transferred gradually through lines to a pycnometer. The pycnometer filled with solution was weighed (W_1) at the final temperature and pressure. Knowing the weight of the evacuated pycnometer (W_0) and its volume means that we can determine the solution density. To determine the amount of CO_2 dissolved in this solution, the pycnometer must be aged for 1 hour under room conditions to reach room temperature. Then, the pycnometer valve was opened and the gas was released slowly from the top of the pycnometer until no more gas was released and the weight of the cylinder did not

change. Immediately, the pycnometer valve was closed to maintain the gas phase equilibrium. Finally, the pycnometer with the remaining solution was weighed (W_2). All of the experiments were repeated.

The total volume of soluble CO_2 consisted of the CO_2 released in the gas phase when the temperature and pressure were reduced to atmospheric conditions ($V_{CO_2}^{(1)}$), CO_2 remaining in the gas phase in the pycnometer after its valve was opened ($V_{CO_2}^{(2)}$), and CO_2 remaining in the liquid phase at atmospheric pressure and room temperature ($V_{CO_2}^{(3)}$).

The difference between W_1 and W_2 is the amount of CO_2 in the gas phase which is released while the valve of the pycnometer is being opened. Hence,

$$V_{CO_2}^{(1)} = 22414 \times (W_1 - W_2) / 44.0095 \tag{1}$$

where $22,414 \text{ cm}^3$ is the volume of one mole of any gas at standard temperature and pressure (273.15 K and 1.01 bar (1 bar = 0.1 MPa)) and 44.0095 is the molecular weight of CO_2 .

The CO_2 in the gas phase which remained in the pycnometer after opening of the valve can be calculated through Eqs. (2)-(4).

$$\begin{aligned} W_2 - W_0 &= \rho_{CO_2} V_{CO_2, T_{room}}^{(2)} + W_{brine} \\ \Rightarrow W_{brine} &= [(W_2 - W_0) - \rho_{CO_2} V_{cylinder}] / (1 - (\rho_{CO_2} / \rho_{brine})) \end{aligned} \tag{2}$$

$$V_{CO_2, T_{room}}^{(2)} = V_{cylinder} - (W_{brine} / \rho_{brine}) \tag{3}$$

$$V_{CO_2}^{(2)} = V_{CO_2, T_{room}}^{(2)} \times (273.15 / T_{room}) \tag{4}$$

where ρ_{CO_2} is the CO_2 density, g/cm^3 ; ρ_{brine} is the $CaCl_2$ brine density, g/cm^3 ; $V_{cylinder}$ is the volume of the pycnometer, cm^3 .

To estimate the CO_2 solubility, it is required to estimate the amount of soluble CO_2 in $CaCl_2$ solutions at atmospheric pressure and room temperature. With reference to the method published by Yasunishi and Yoshida (1979), the solubility of CO_2 in aqueous electrolyte solutions can be estimated by the Ostwald coefficient through Eqs. (5)-(7).

$$\log(L_0/L) = AC_s / (1 + BC_s) \tag{5}$$

$$L = V_G / V_L \tag{6}$$

$$V_{CO_2}^{(3)} = V_L = L \times ((W_2 - W_0) / \rho_{brine}) \tag{7}$$

where L is the Ostwald coefficient; L_0 is the Ostwald coefficient of the gas in pure water; C_s is the molar concentration of electrolyte, mol/L; V_G is the volume of gas absorbed at the observed temperature and pressure; V_L is the volume of the absorbing liquid; and A and B are empirical constants dependent upon the particular solute present, as shown in Table 2, L/mol. These constants were experimentally obtained by Yasunishi and Yoshida (1979) for different electrolyte solutions such as $CaCl_2-H_2O$ using the method of least squares.

The absolute value of soluble CO_2 volume in solution is then calculated from Eq. (8).

$$V_{CO_2} = V_{CO_2}^{(1)} + V_{CO_2}^{(2)} + V_{CO_2}^{(3)} \tag{8}$$

The CO_2 solubility in terms of molality is then given by $V_{CO_2} / 22.414 W_{water}$, in which W_{water} can be calculated by Eq. (9) (Yan et al, 2011).

$$\begin{aligned} W_{water} &= W_{brine} / \left(1 + (1/1000) (44.0095 m_{CO_2} + 110.9840 m_{CaCl_2}) \right) \end{aligned} \tag{9}$$

Moreover, the mole fraction of CO_2 soluble in the solution can be calculated by Eq. (10):

$$x_{CO_2} = m_{CO_2} / (m_{CO_2} + 55.508) \tag{10}$$

where x_{CO_2} is the total mole fraction of CO_2 soluble in liquid; m_{CO_2} is the molality of CO_2 in the liquid phase, mol/L.

Table 2 Parameters of Eq. (5) for solubility of CO_2 (Yasunishi and Yoshida, 1979)

Temperature, K	A, L/mol	B, L/mol
298.15	0.211	0.0572
308.15	0.19	0.0529

2.3 Experimental results

The results of the experiments conducted in this study for pure water are listed in Table 3 and also depicted in Fig. 4. Dashed lines are the experiments conducted by Koschel et al (2006) and the solid lines represent the experiments of this study at different temperatures. Koschel et al (2006) measured the CO_2 solubility in pure water at 323.15 K and 373.15 K and 20.6-202 bar. Although the experimental conditions are not the same, this comparison confirms the accuracy of the experimental technique used in this study.

Table 3 Experimentally determined mole fractions of CO_2 in pure water

Temperature, K	Pressure, bar	CO_2 mole fraction in water
	68.9	0.0161
328.15	137.9	0.0206
	206.8	0.0234
348.15	68.9	0.0142
	137.9	0.0183
351.65	68.9	0.0131
	206.8	0.0211
368.15	68.9	0.0119
	206.8	0.0206
375.15	137.9	0.0170

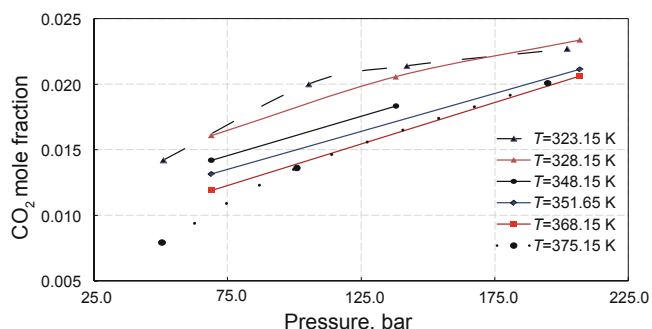


Fig. 4 Experimentally determined mole fractions of CO₂ versus temperature in pure water

The other results of the experiments conducted in this study are listed in Tables 4 and 5. These data show the trend of changes in CO₂ solubility in solution with changing pressure and temperature.

Table 4 Experimentally determined mole fractions of CO₂ in 1.9 mol/L CaCl₂ solution

Temperature, K	Pressure, bar	CO ₂ mole fraction in water
328.15	68.9	0.0070
	137.9	0.0095
	206.8	0.0103
348.15	68.9	0.0063
	137.9	0.0088
	206.8	0.0099
351.65	137.9	0.0088
	137.9	0.0083
368.15	137.9	0.0083
	206.8	0.0096
375.15	68.9	0.0058
	206.8	0.0096

Table 5 Experimentally determined mole fractions of CO₂ in 4.8 mol/L CaCl₂ solution

Temperature, K	Pressure, bar	CO ₂ mole fraction in water
328.15	68.9	0.0032
	137.9	0.0049
	206.8	0.0050
348.15	137.9	0.0041
	206.8	0.0046
351.65	68.9	0.0030
	206.8	0.0045
368.15	68.9	0.0026
	137.9	0.0039
	206.8	0.0045
375.15	137.9	0.0038

These data indicate that at low pressures the solubility of CO₂ in CaCl₂ solutions increased directly with pressure. At high pressures, however, the effect of pressure on CO₂ solubility faded and the rate of increase in CO₂ solubility reduced with an increase in pressure. This observation was previously reported (Hangx, 2005; Liu et al, 2011; Savary et al, 2012). On the other hand, the temperature and CaCl₂ concentrations had inverse effects on CO₂ solubility.

3 Model development

The solubility of CO₂ in pure water and brine at reservoir conditions have been studied by Akinfiev and Diamond (2010) for conditions up to 373.15 K and 1,000 bar, by Duan and Sun (2003) for conditions up to 533.15 K and 2,000 bar and by Spycher et al (2003; 2005) for conditions up to 373.15 K and 600 bar. Duan and Sun (2003) presented a popular thermodynamic model for the estimation of CO₂ solubility in pure water and aqueous NaCl solutions. They stated, however, that as the model is based on a specific interaction approach it is possible to use it to predict CO₂ solubility in other systems as well.

The method of CO₂ solubility estimation proposed by Duan and Sun (2003) is based on the balance between chemical potentials between CO₂ in liquid and gas phases. This balance results in Eq. (11).

$$\ln m_{CO_2} = \ln y_{CO_2} \phi_{CO_2} P - \mu_{CO_2}^{(0)} / RT - 2\lambda_{CO_2-Na} (m_{Na} + m_K + 2m_{Ca} + 2m_{Mg}) - \zeta_{CO_2-Na-Cl} m_{Cl} (m_{Na} + m_K + m_{Mg} + m_{Ca}) + 0.07m_{SO_4^{2-}}$$

where y_{CO_2} is the mole fraction of CO₂ in the vapor phase; P is the total pressure, bar; ϕ is the fugacity coefficient; ζ and λ are the interaction parameters; R is the universal gas constant, 0.08314 bar·L·mol⁻¹·K⁻¹; T is the absolute temperature, K; μ is the chemical potential and $m_{SO_4^{2-}}$ is the molality of SO₄²⁻ in the liquid phase (if any), mol/L.

Due to the lack of vapor composition data for the CO₂-H₂O-NaCl system in the conditions of the study, it is assumed that the water vapor pressure of H₂O-NaCl mixture is equal to the pure water saturation pressure. Based on the study of Duan and Sun (2003), this assumption may lead to errors (up to 5%) for $\mu_{CO_2}^{(0)} / RT$. They stated that these errors have a negligible effect on the calculation of CO₂ solubility. Thus, y_{CO_2} can be calculated by $y_{CO_2} = (P - P_{H_2O}) / P$. Duan and Sun suggested an empirical equation for calculating P_{H_2O} as:

$$P = (P_c T / T_c) \left[1 + c_1 (-t)^{1.9} + c_2 t + c_3 t^2 + c_4 t^3 + c_5 t^4 \right] \quad (12)$$

where P_c is the critical pressure of water, $P_c=220.85$ bar; T_c is the critical temperature of water, $T_c=647.29$ K; P_{H_2O} is the pure water pressure, bar; $t = (T - T_c) / T_c$ and the parameters of Eq. (12), c_1 - c_5 , are listed in Table 6.

Table 6 Parameters for Eq. (12) (after Duan and Sun, 2003)

Constant	Value
c_1	-38.640844
c_2	5.894842
c_3	59.876516
c_4	26.654627
c_5	10.637097

Duan et al (1992) also developed an equation of state for supercritical CO₂, as in Eq. (13).

$$\begin{aligned}
 Z &= P_r V_r / T_r \\
 &= 1 + \left[(a_1 + a_2 / T_r^2 + a_3 / T_r^3) / V_r \right] \\
 &+ \left[(a_4 + a_5 / T_r^2 + a_6 / T_r^3) / V_r^2 \right] \\
 &+ \left[(a_7 + a_8 / T_r^2 + a_9 / T_r^3) / V_r^4 \right] \\
 &+ \left[(a_{10} + a_{11} / T_r^2 + a_{12} / T_r^3) / V_r^5 \right] \\
 &+ \left[a_{13} / (T_r^3 V_r^2) \right] \times \left[a_{14} + (a_{15} / V_r^2) \right] \times \exp(-a_{15} / V_r^2)
 \end{aligned} \quad (13)$$

To calculate V_r , the reduced temperature and pressure should be calculated and substituted in the EOS developed by Duan et al (1992) as in Eq. (13). The parameters of Eq. (13) are listed in Table 7.

Table 7 Parameters for Eq. (13) (after Duan and Sun, 2003)

Constant	Value	Constant	Value
a_1	8.99288497E-02	a_9	-1.77265112E-03
a_2	-4.94783127E-01	a_{10}	-2.51101973E-05
a_3	4.77922245E-02	a_{11}	8.93353441E-05
a_4	1.03808883E-02	a_{12}	7.88998563E-05
a_5	-2.82516861E-02	a_{13}	-1.66727022E-02
a_6	9.49887563E-02	a_{14}	1.39800000E+00
a_7	5.20600880E-04	a_{15}	2.96000000E-02
a_8	-2.93540971E-04		

They also deduced the formula to calculate the fugacity coefficient of CO₂, referring to this as EOS. The only unknown variables are interaction parameters. These interaction parameters are estimated by Eq. (14), with the constants listed in Table 8.

$$\begin{aligned}
 Par(T, P) &= c_1 + c_2 T + c_3 / T + c_4 T^2 + c_5 / (630 - T) + \\
 &c_6 P + c_7 P \ln T + c_8 P / T + c_9 P / (630 - T) + \\
 &c_{10} P^2 / (630 - T)^2 + c_{11} T \ln P
 \end{aligned} \quad (14)$$

where Par is the interaction parameters.

Interaction parameters are proposed for NaCl solutions. However, Duan and Sun (2003) extended their model in predicting the CO₂ solubility in CaCl₂-H₂O system. They concluded that the model developed by the interaction parameters for NaCl solutions, can be applied for CaCl₂ solutions as well. The parameters λ 's and ζ 's for Na⁺ and Cl⁻ and also the standard chemical potential of CO₂ in the liquid phase are essential to calculate the CO₂ solubility as a function of temperature, pressure and salinity. On the other hand, measurements can only be made in electrically neutral solutions; thus, one of the parameters must be assigned arbitrarily. λ_{CO_2-Cl} is assumed to be zero and other parameters are found through fitting available experimental data with the model.

Table 8 Interaction parameters (after Duan and Sun, 2003)

Parameter	$\mu_{CO_2}^{(0)} / RT$	λ_{CO_2-Na}	$\zeta_{CO_2-Na-Cl}$
c_1	28.9447706	-0.411370585	0.00033639
c_2	-0.035458177	0.000607632	-1.98299E-05
c_3	-4770.67077	97.5347708	—
c_4	1.02783E-05	—	—
c_5	33.8126098	—	—
c_6	0.009040371	—	—
c_7	-0.00114934	—	—
c_8	-0.307405726	-0.023762247	0.002122208
c_9	-0.090730149	0.017065624	-0.005248733
c_{10}	0.000932713	—	—
c_{11}	—	1.41336E-05	—

Regarding the experimental data measured in this study and the data reported by Prutton and Savage (1945), the interaction parameters of Duan and Sun's solubility model are modified for CaCl₂ solutions. The constants of Eq. (14) listed in Table 8 are modified with the 'GRG nonlinear' optimization method. The optimized interaction parameters λ_{CO_2-Ca} and $\zeta_{CO_2-Ca-Cl}$, in comparison with the ones presented by Duan and Sun (2003) for NaCl solutions, are shown in Table 9. As can be seen from the table, $\mu_{CO_2}^{(0)} / RT$ is not changed, because it is independent of the solvent in the solution.

In order to determine the optimized constants, RMS error between experimental measurements and model estimations has been minimized. As Eq. (15) shows, the error formulation used in this study is root mean square error (RMSE).

$$RMSE = \sqrt{\frac{\sum_{t=1}^n (x_{1,t} - x_{2,t})^2}{n}} \quad (15)$$

Table 9 Interaction parameters for NaCl and CaCl₂ solutions

Parameter	$\mu_{\text{CO}_2}^{(0)}/RT$	$\lambda_{\text{CO}_2\text{-Na}}$	$\lambda_{\text{CO}_2\text{-Ca}}$	$\zeta_{\text{CO}_2\text{-Na-Cl}}$	$\zeta_{\text{CO}_2\text{-Ca-Cl}}$
c_1	28.9447706	-0.411370585	-0.410242812	0.00033639	-0.001974592
c_2	-0.035458177	0.000607632	0.000607209	-1.98299E-05	-1.98299E-05
c_3	-4770.67077	97.5347708	97.49964043	—	—
c_4	1.02783E-05	—	—	—	—
c_5	33.8126098	—	—	—	—
c_6	0.009040371	—	—	—	—
c_7	-0.00114934	—	—	—	—
c_8	-0.307405726	-0.023762247	-0.027105563	0.002122208	0.000218708
c_9	-0.090730149	0.017065624	0.020284659	-0.005248733	-0.001804966
c_{10}	0.000932713	—	—	—	—
c_{11}	—	1.41336E-05	1.41336E-05	—	—

4 Results and discussion

The model proposed by Duan and Sun (2003) overestimates the CO₂ solubility in high molality solutions and also at high pressures as well. This observation was previously reported in the literature (Hangx, 2005; Darwish and Hilal, 2010). A comparison between the CO₂ solubility estimation by the base and modified models has been conducted. RMSE is reduced for both 1.90 and 4.80 mol/L CaCl₂ solutions. The model is more accurate for higher concentration of CaCl₂ and higher pressures as well. Furthermore, the total RMSE, considering all available experimental data including pure water, 1.90 and 4.80 mol/L solutions is reduced. Hence, the developed model is more accurate. The comparison between CO₂ mole fractions estimated by the Duan model and the modified Duan model is illustrated in Fig. 5.

CO₂ solubility estimations for the 1.90 mol/L CaCl₂ solution show negligible change. A significant change can be seen in Fig. 5 for 4.80 mol/L CaCl₂ solutions, however. This indicates that this improvement has more meaning for high concentrations of CaCl₂ solutions.

Similar study of the experimental data reported by Prutton and Savage (1945) proves that predictions of the new model are in better agreement with their experimental data as well. Fig. 6 shows a comparison between data estimated by the Duan model, modified Duan models and Prutton and Savage's (1945) experiments.

All plots of Fig. 6 show this improvement for different values of temperature, pressure and CaCl₂ concentrations.

RMS errors are plotted in Figs. 7 and 8 for the experiments of this study and Prutton and Savage's (1945) article, respectively. RMSE of CO₂ solubility estimations are reduced by about 14%, 53% and 65% on the basis of the Prutton and Savage (1945) results for 1.01, 2.28 and 3.90 mol/L CaCl₂ solutions, respectively. Moreover, estimations have been improved about 25% for 4.80 mol/L CaCl₂ solutions as regards the experiments of this study. It can be concluded that the modified model shows a significant

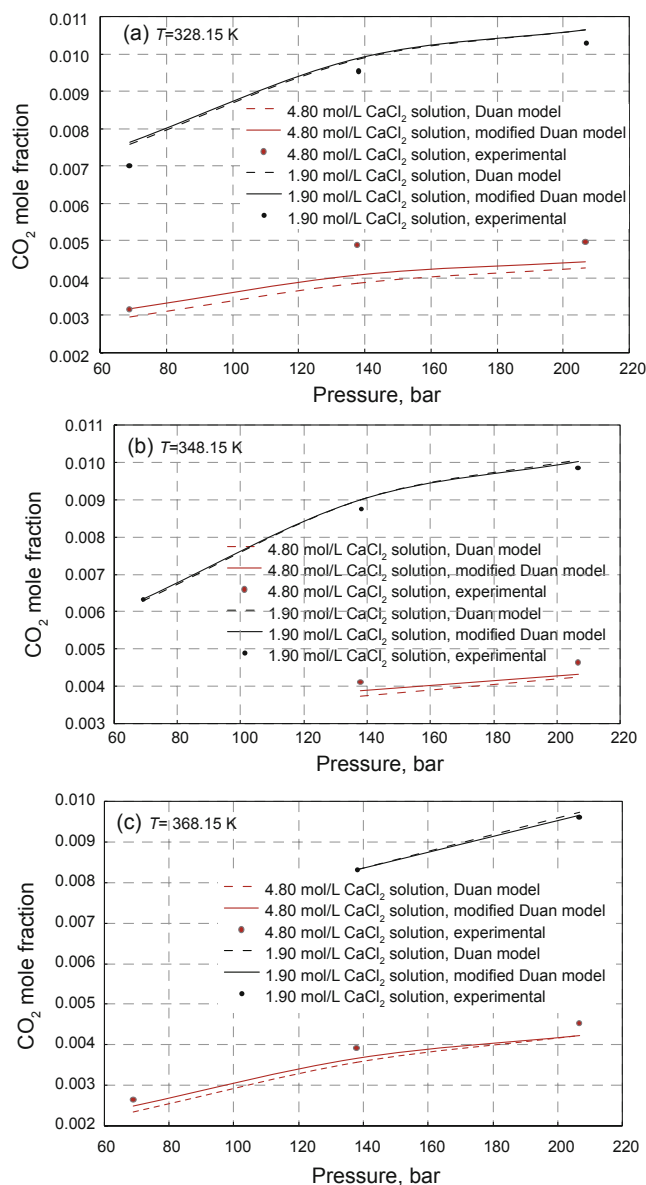


Fig. 5 A comparison of the Duan and modified Duan models in estimating the CO₂ solubility in CaCl₂ solutions at (a) 328.15 K, (b) 348.15 K, and (c) 368.15 K

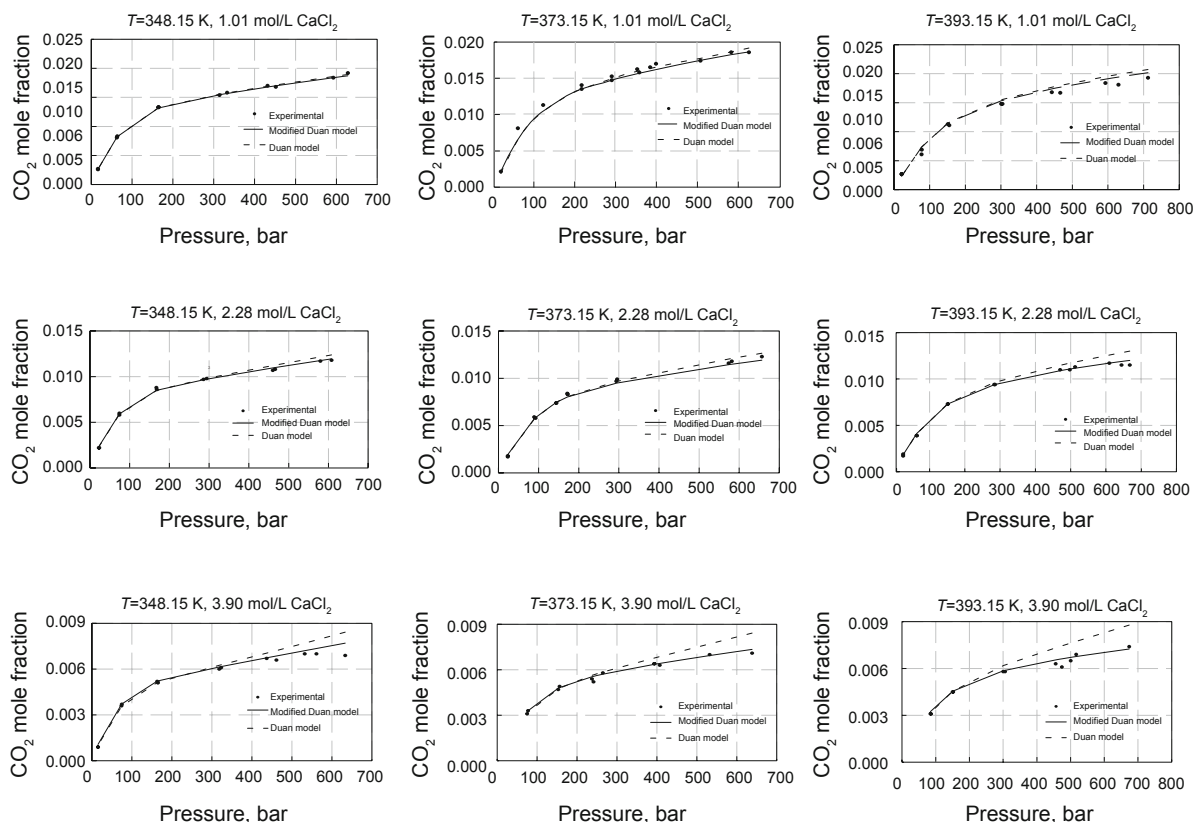


Fig. 6 A comparison of the Duan and modified Duan models in estimating the CO_2 solubility based on data from Prutton and Savage (1945)

improvement in CO_2 mole fraction estimations. The model presents better results for high concentration solutions. The RMSE of the 4.80 mol/L solution shows a significant reduction, but that for the 1.90 mol/L solution is almost unchanged.

Hence, the modified model can be used to estimate soluble CO_2 mole fraction in CaCl_2 solutions in better agreement with experiments in comparison with the base model.

Differences between experiments and model estimates increase with pressure, temperature and CaCl_2 molality. Adding more CaCl_2 to the solution results in decreasing CO_2 solubility within the system. The base model cannot match

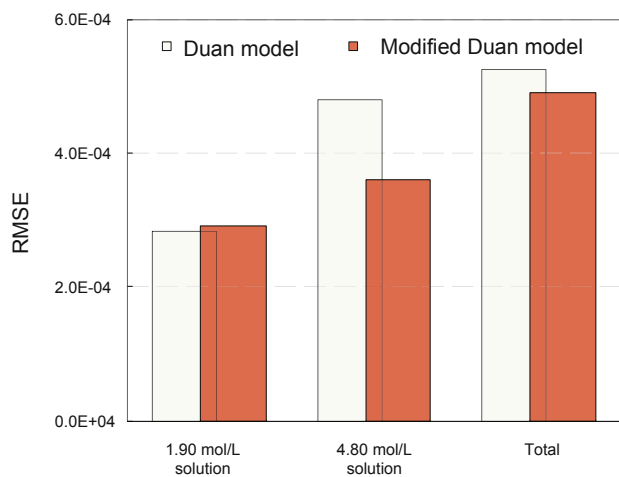


Fig. 7 Plot of RMSE for the modified Duan versus the Duan model for the experiments in this study

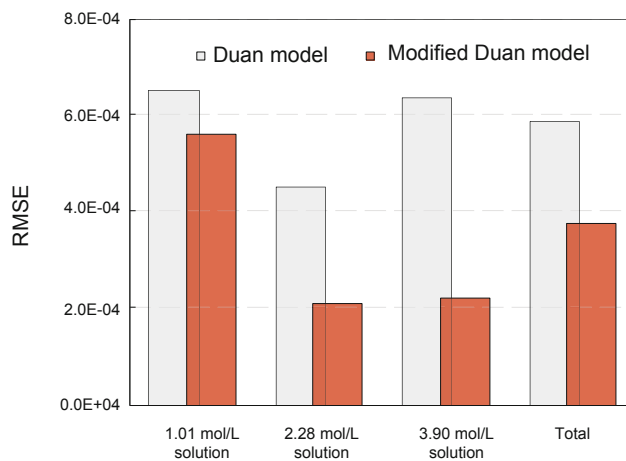


Fig. 8 Plot of RMSE for the modified Duan versus the Duan model for the experiments in Prutton and Savage's (1945) study

this behaviour, but the new developed model can predict the behaviour of the system more precisely. This comparison shows a significant reduction in CO_2 solubility prediction in 3.90 mol/L CaCl_2 solutions compared with the Duan model, as shown in Fig. 6.

Since the range of CaCl_2 concentrations in this study is consistent with the carbonate matrix acidizing conditions, this improvement in estimating the soluble CO_2 mole fraction is noteworthy in wormhole propagation models. The original form of the Duan model overestimates CO_2 solubility in spent acid and consequently minimizes the effect of released CO_2 during matrix acidizing. Nevertheless, the modified model

presented in this study gives more reasonable estimates of CO₂ solubility in spent acid. This solubility model can be used in an integrated study on wormhole propagation during matrix acidizing.

5 Conclusions

1) The solubility of CO₂ in saline water is of particular importance regarding environmental issues such as CO₂ capture and geological storage. Hence, the thermodynamic behavior of CO₂-H₂O-NaCl has been studied extensively. In contrast, CO₂-H₂O-CaCl₂ has only been studied to a limited extent. Since this system regularly forms during carbonate acidizing with HCl, this study investigates the solubility of CO₂ in CaCl₂ solutions.

2) An experimental apparatus for solubility measurement was prepared and the solubility of CO₂ in 0, 1.90 and 4.80 mol/L CaCl₂ solutions at 328.15 to 375.15 K and 68.9 to 206.8 bar was measured. The results of the experiments demonstrate that CO₂ solubility decreases with increasing concentration, increasing temperature and decreasing pressure. The effect of pressure, however, diminishes at higher pressures.

3) A modified model was developed by refitting the interaction parameters to predict the CO₂ solubility in CaCl₂ solutions. The modified model can predict solubility better than the available Duan and Sun thermodynamic model. This improvement is up to 65% better than the Duan and Sun model. In addition, the modified model estimates the CO₂ solubility in high concentration solutions and also high pressures with noticeable accuracy. Prediction by this model is also in agreement with the experimental measurements of this study.

4) Darcy models on the basis of core scale predict wormholing in carbonate formations during matrix acidizing. In the course of reactions between acid and carbonates CO₂ is produced. Since carbon dioxide can chemically and physically affect the performance of an acid job, it is of great importance to know the conditions in which CO₂ is not soluble in the solution (spent acid) and can form a separate phase. The modified thermodynamic model presented in this study can be applied in Darcy scale wormhole propagation models to improve the accuracy of their predictions.

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