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Densities for Ternary System of $CaCl_2$–H_2O–CO_2 at Elevated P-T: An Experimental and Modeling Approach

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Received: 6 September 2018; Accepted: 8 October 2018; Published: 20 October 2018

Abstract: Very few thermodynamic models exist for estimation of density alteration due to solution of CO_2 in a pure H_2O and $CaCl_2$–H_2O system. All of these models require density of $CaCl_2$ solution to estimate density of $CaCl_2$–H_2O–CO_2 system. Similarly, models presented to calculate $CaCl_2$ solution density need pure H_2O density in advance. The main approach to model density of $CaCl_2$–H_2O–CO_2 system is based on estimation of density alteration of $CaCl_2$–H_2O system due to the solution of CO_2 mole fraction. Hence, to estimate CO_2–$CaCl_2$–H_2O system density, density of $CaCl_2$ solution is necessary, and to estimate density of $CaCl_2$–H_2O system, density of pure H_2O is required in advance. Firstly in this paper, density of 0, 1.91, and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2 at 328.15 to 375.15 °K and 68.9 to 206.8 Bar were measured through laboratory experiments. Then, a new model is developed to estimate the density of $CaCl_2$ solutions containing CO_2 based on the experiments conducted in this study. The average and maximum absolute deviations of the new model from the experimental data are 0.0047 and 0.0177, respectively. Hence, the new model combined with other existing models to separately calculate density of the $CaCl_2$ solution can be used to accurately predict density of the $CaCl_2$–H_2O–CO_2 system in a wide range of P-T applicable for subsurface reservoirs.

Keywords: $CaCl_2$–H_2O–CO_2 system; chloride solution density; density measurement; density estimation; well stimulation; matrix acidizing; limestone reservoirs

1. Introduction

Thermodynamic behavior of $CaCl_2$–H_2O–CO_2 system is important in different scientific and engineering areas, such as well stimulation (i.e., matrix acidizing and acid fracturing) in both limestone and sandstone reservoirs; geological CO_2 sequestration, especially in sandstone reservoirs; and enhanced oil recovery (EOR) using CO_2 injection. Changes in thermodynamic behavior of pure H_2O and $CaCl_2$ solution with addition of CO_2 is of great importance for accurate evaluation of capacity of saline aquifer for CO_2 sequestration. In recent years, researchers have been paying attention to environmental issues such as CO_2 capture and geological storage in deep saline aquifers or depleted hydrocarbon reservoirs. However, the target depleted hydrocarbon reservoirs are mostly sandstone reservoirs [1–6]. Nevertheless, understanding thermodynamic behavior of this mixture is also important in flow enhancement, and well stimulation in petroleum production operations (i.e., matrix acidizing and acid fracturing) commonly used in carbonate reservoirs (i.e., limestone) are also a subject of great interest.

Different thermodynamic models have been proposed in the literature to simulate parameters affecting subsurface CO_2 storage [7–11]. The $CaCl_2$–H_2O–CO_2 system also appears in limestone matrix

acidizing, where hydrochloric acid (HCl) is the most common acid used for limestone matrix acidizing. A mixture of $CaCl_2$–H_2O–CO_2 is produced, while HCl and calcite react as follows:

$$2HCl + CaCO_3 \leftrightarrow CaCl_2 + H_2O + CO_2$$

Hence, density of CO_2–$CaCl_2$–H_2O system should be accurately estimated during matrix acidizing and acid fracturing in limestone formations. It should be noted that in spite of extensive studies on matrix acidizing, chemical and physical behavior of spent acid solutions is not yet properly addressed. Different experimental investigations on measurements of density of CO_2–$CaCl_2$–H_2O at different temperatures and pressures are reported in the literature, as shown in Table 1 [12–22].

Table 1. Experimental studies to measure density of the CO_2–$CaCl_2$–H_2O system.

Reference	Temperature Range (°K)	Pressure Range (Bar)
Nighswander [13]	353.15–471.15	20.4–102.1
King et al. [14]	288.15–298.15	60.8–243.2
Fenghour et al. [15]	415–700	60–300
Teng et al. [16]	278–293	64–295
Yaginuma et al. [17]	304.1	10–100
Tegetmeier et al. [18]	374.15	0–300
Song et al. [19]	273.15–284.15	50–125
Li et al. [20]	332.15	Up to 290
Hebach et al. [21]	284–332	10–300
Song et al. [22]	274–333	100–180

Very few models have been developed to calculate density of saline solutions during CO_2 sequestration at reservoir conditions. As the major salt in aquifers is NaCl, thermodynamic behavior of CO_2–H_2O–NaCl system has been widely investigated to estimate the density. In spite of the attention paid to NaCl solutions, experimental data concerning CO_2–$CaCl_2$–H_2O system remain scarce.

Teng et al. [16] and Song et al. [19] proposed simple correlations based on available experimental data. Bando et al. [23] further developed the model proposed by Teng et al. [16] for NaCl solutions. Bachu and Adams [24] introduced a thermodynamic model based on apparent molar volume estimation using a correlation presented by Garcia [25]. As mentioned, for all of these models, density of the base fluids should be estimated in advance. Then, by considering the amount of CO_2 dissolved in the solution, the new density is updated.

In this paper, first $CaCl_2$–H_2O–CO_2 system at different ranges of pressure, temperature, and $CaCl_2$ molality, similar to reservoir conditions, is investigated in a laboratory to measure density of $CaCl_2$–H_2O–CO_2. The main approach to model density of $CaCl_2$–H_2O–CO_2 system is based on the estimation of density alteration of $CaCl_2$–H_2O system because of the solution of CO_2 mole fraction. Hence, to estimate CO_2–$CaCl_2$–H_2O system density, density of $CaCl_2$ solution is necessary and to estimate density of $CaCl_2$–H_2O system, density of pure water is required in advance. In this paper, experimental studies have been carried out and based on the available data for CO_2–$CaCl_2$–H_2O system. Then, a new model is developed to calculate the density of $CaCl_2$–H_2O system. The new model, combined with other existing models to separately calculate density of $CaCl_2$ solution, can be used to accurately predict density of $CaCl_2$–H_2O–CO_2 system in a wide range of P-T applicable for subsurface reservoirs.

2. Experimental Work

The purpose of these experiments was to measure density of different $CaCl_2$ solutions saturated with CO_2. The experiments are similar to the ones previously reported by Bastami et al. [26] to measure CO_2 solubility at different $CaCl_2$ solutions at temperatures ranging from 328.15 to 375.15 °K

and pressures from 68.9 to 206.8 Bar. The temperature and pressure ranges considered for these experiments are similar to typical P-T condition of subsurface reservoirs.

2.1. Materials

The purity of CO_2 is 99.99%. The anhydrous $CaCl_2$ provided by Merck KGaA (Darmstadt, Germany) is of analytical grade. In addition, distilled water was used throughout the experiments.

2.2. Apparatus and Procedures

Figure 1 shows a schematic of the apparatus used in this study to estimate density of $CaCl_2$ solutions saturated with CO_2 and solubility of CO_2 in $CaCl_2$ solutions. The apparatus consisted of a DBR pump for 0.1–2000 cm^3/h range with 0.07 Bar precision at pressure constant mode, a high pressure cylinder with a volume of 500 cm^3 and maximum bearable pressure of 689 Bar, a pycnometer made of St–Cr alloy, high pressure transfer lines, an oven with maximum temperature of 493.15 °K with 0.1 °K precision, a pressure transducer for 1–620 Bar range with 0.007 Bar precision, a densitometer, and a vacuum pump. An agitating pump system, as shown in Figure 2, was also 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 bull bearings. The motor and gearbox were out of the oven during the experiments.

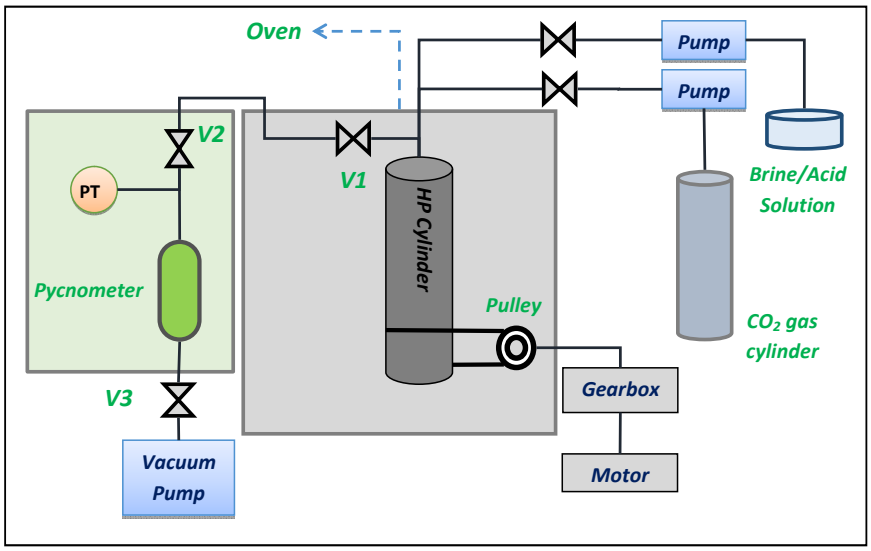


Figure 1. Schematic of the set-up used for the experiments. PT: Pressure Transducer; HP: High Pressure.

Figure 2. Agitating pump system designed to agitate the high-pressure cylinder in the oven.

First, the high pressure cylinder was opened and washed with distilled water to ensure that no $CaCl_2$ solution remained in the high pressure cylinder, and evacuated by a vacuum pump. $CaCl_2$ solution and CO_2 were then pumped into the high pressure cylinder and pressurized up to the final experimental pressure. Then, the high pressure cylinder was agitated at the desired temperature for 3 h. The effects of agitating time were then investigated for 1.91 mol/kg-$CaCl_2$ solution at 137.9 Bar and 351.65 °K (Figure 3). In this study, the soluble CO_2 mole fraction changed negligibly for data acquired in experiments after 3 h of agitation. Hence, to ensure equilibrium, the samples were agitated for 3 h. Pressure was adjusted to remain constant during the agitating time.

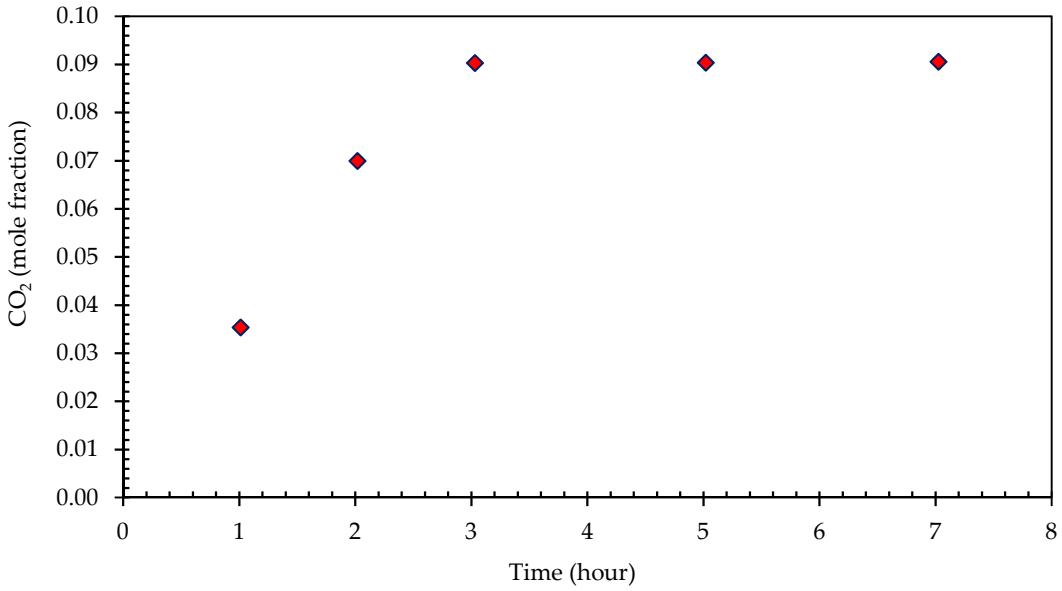


Figure 3. Effect of agitating time on mole fraction of soluble CO_2 (a set of experiments for 1.91 mol/kg-$CaCl_2$ solution at 351.65 °K and 137.9 Bar).

Concentration of the injected CO_2 was set to be more than its saturation concentration to guarantee achieving saturation concentration of CO_2 in the solution. Thus, there was a separate supercritical CO_2 phase in the high pressure cylinder after reaching equilibrium. As the high pressure cylinder had just one exhaust, the cylinder should be reversed for sampling to ensure that only saturated solution was produced. The solution was transferred gradually through lines to a pycnometer. The pycnometer, filled with solution, was weighed at the final temperature and pressure. Knowing the weight of the vacuumed pycnometer and its volume means that we can determine the solution density. The procedure used for determining CO_2 solubility has been published previously by Bastami et al. [26].

3. Model Development

As mentioned earlier in this text, addition of CO_2 to pure water or $CaCl_2$–H_2O solution causes density alteration. Different models exist for estimation of density of CO_2–$CaCl_2$–H_2O. In all models, to estimate density of the CO_2 bearing solution, it is necessary to have a good prediction of solution density of either pure H_2O or $CaCl_2$ solution. Hence, estimation of pure H_2O and $CaCl_2$ solution density is the first step to compare the ability of different models to estimate density of a complex system such as $CaCl_2$–H_2O–CO_2. For model development, we investigated density of CO_2–H_2O and CO_2–$CaCl_2$–H_2O systems in a laboratory and used different available models to find the best model in terms of accuracy in prediction of density of these two systems. Nevertheless, all of these models examined need densities of pure H_2O and $CaCl_2$ solution in advance.

3.1. Pure Water Density

Density of pure water increases with a decrease in temperature and increase in pressure. However, because of the incompressibility of water, changes in water density with pressure are negligible. The best model to estimate water density is the model presented as IAPWS97. However, because of a large number of parameters and the required considerable computation efforts, simpler equations with insignificant deviations proposed to reduce the number of parameters and consequently increase efficiency of the computations. Batzle and Wang [27] proposed a correlation (Equation (1)) to calculate pure H_2O density as a function of temperature and pressure. They recommended this equation for the P-T range of 293–623 °K and 50–1000 Bar, respectively.

$$\begin{array}{l}\rho_w = 1 + 1 \times 10^{-6}\left(-80T - 3.3T^2 + 0.00175T^3 + 489P - 2TP + 0.016T^2P\right. \\ \left.-1.3 \times 10^{-5}T^3P - 0.333P^2 - 0.002TP^2\right)\end{array} \quad (1)$$

where T is temperature (°C), P is pressure (MPa), and ρ_w is pure H_2O density in (g/cm^3).

Islam and Carlson [28] proposed another simple correlation (Equation (2)), the deviation of which from IAPWS97 within the P-T range of current study is insignificant.

$$\rho_w = a_0 + \sum_{i=1}^{3} b_i 10^{c_i T} + \sum_{i=0}^{2} d_i P^i \quad (2)$$

where T is temperature (°K), P is pressure (MPa), and the constants of the equation are listed in Islam and Carlson [28]. These two models are used in this study to achieve an accurate model for estimation of density of CO_2–H_2O and CO_2–$CaCl_2$–H_2O systems.

3.2. $CaCl_2$ Solution Density

A number of experimental studies are reported for estimation of density of different electrolyte solutions. Mao and Duan [29] presented a detailed study of available experimental data. Al Ghafri et al. [30] reported density of various electrolyte solutions with molalities up to 6 mol/kg at P-T ranges of 283–472 °K and 10–685 Bar, respectively. Their measurements are of great importance in this study because of the fact that P-T conditions in their study are consistent with typical reservoir P-T.

Kemp et al. [31] proposed a model to calculate density of solutions containing single salts and various salt mixtures. Although they developed a model for estimation of density of brines for drilling fluid systems, it can be used for estimation of density of other electrolyte solutions at high P-T conditions. Their model is based on Equation (3).

$$\rho_b = \left(1.0 + \sum_i m_i M_i\right) / \left[(1.0/\rho_w) + \sum_i m_i \nu_i\right] \quad (3)$$

where m_i is molality of the ith salt (mol/kg); M_i is the molecular weight of the ith salt; ρ_b, ρ_w are density of brine and pure H_2O, respectively (g/cm^3); and ν_i is the apparent molal volume of the ith salt. To find the value of apparent molal volume, they used the "specific interaction model", which is an extension of the Debye-Hückel model. The complete procedure for calculations can be found in Kemp et al. [31].

Furthermore, Mao and Duan [29] developed a PVTX model for aqueous chloride solutions of binary systems such as $CaCl_2$–H_2O. They attempted to obtain a universal model for all binary solutions. They showed that their model (Equation (4)) can accurately estimate density of different aqueous chloride solutions.

$$\begin{array}{l}\frac{1000+mM_s}{m\rho_b} = \frac{V(m_r)}{m_r} + \frac{1000}{\rho_w}\left(\frac{1}{m} - \frac{1}{m_r}\right) + \nu|z_+z_-|A_v[h(I_m) - h(I_{m_r})] + \\ 2\nu_+\nu_- RT\left[B_v(m - m_r) + \nu_+ z_+ C_v\left(m^2 - m_r^2\right)\right]\end{array} \quad (4)$$

where T is temperature (°K); m is molality of brine; m_r is reference molality, which is determined by Mao and Duan [29]; I is ionic strength; M_s is molar mass of calcium chloride (g/mol); z and ν are ion charges and number of charges, respectively; A_v is the volumetric Debye-Hückel limiting law slope; and $V(m_r)$, B_v, and C_v are pressure and temperature dependent parameters, which can be calculated using the correlations introduced by Mao and Duan [29]. As can be observed from these two thermodynamic models, both of them require density of pure H_2O at the desired P-T.

3.3. CO_2–H_2O Density

Teng et al. [16] presented a model to estimate density of water by adding CO_2 (Equation (5)):

$$\rho_c = \rho_W + 1.96 \times 10^{-1} x_{CO_2} + 1.54 \times 10 x_{CO_2}^2 \quad (5)$$

where x_{CO_2} is mole fraction of CO_2 in liquid phase and ρ_c is solution density with CO_2 (g/cm^3).

Song et al. [19] also proposed a density model for dilute solution of CO_2 (Equation (6)):

$$\rho_c = \rho_w[1 + 0.275 wt(CO_2)] \quad (6)$$

where ρ_w and $wt(CO_2)$ are water density and mass fraction of CO_2, respectively.

Bachu and Adams [24] proposed a thermodynamic model based on apparent partial molar volume (Equation (7)) to estimate density of aqueous solutions with addition of CO_2:

$$\rho_{aq} = \frac{\rho_w}{1 - X_{sol}\left(1 - \frac{V_\phi}{M}\rho_w\right)} \quad (7)$$

where M is the molecular weight of solute (44.01 g/mol for CO_2), X_{sol} is the mass fraction of solute (CO_2), and V_ϕ is the apparent partial molar volume. Garcia [25] proposed Equation (8) for calculating the apparent molar volume of CO_2:

$$V_\phi = 37.51 - 9.585 \times 10^{-2} T + 8.740 \times 10^{-4} T^2 - 5.044 \times 10^{-7} T^3 \quad (8)$$

where T is temperature (°C) and V_ϕ is partial molar volume of CO_2 in water (cm^3/mol).

Previously, two models for estimating the pure water density were introduced. Using these models, it is possible to estimate the density alteration while CO_2 is added to the system.

3.4. CO_2–$CaCl_2$–H_2O Density

As was mentioned previously, Bachu and Adams [24] proposed a model based on apparent partial molar volume that can be estimated by Garcia's correlation [25]. They also studied different methods to consider the effect of salt on the solution density and proposed Equation (9). This makes it possible to use Equation (7) for more general cases, including CO_2 in brines.

$$V_\phi^b \rho_b = V_\phi \rho_w \quad (9)$$

where ρ_b is density of brine and V_ϕ^b is partial molar volume of CO_2 in brine.

Bando et al. [23] extended the model previously proposed by Teng et al. [16] based on experimental measurements of density of electrolyte solution of NaCl–H_2O with addition of CO_2 for CO_2–H_2O system. They proposed Equation (10) to model more general cases of CO_2 in aqueous chloride solutions.

$$\rho_{aq} = \rho_b + 1.96 \times 10^{-1} x_{CO_2} + 1.54 \times 10 x_{CO_2}^2 \quad (10)$$

where ρ_{aq} is density of electrolyte solution containing CO_2 (g/cm^3) and x_{CO_2} is mole fraction of CO_2 in the solution.

We developed a new correlation based on the experimental data generated in this study (Equation (11)) to calculate density changes of $CaCl_2$ solution with addition of CO_2:

$$\rho_{aq} = \rho_b + 2.271 \times 10^{-1} x_{CO_2} + 1.6129 \times 10^{2} x_{CO_2}^{2} \quad (11)$$

The deviation of different model estimates from the experimental measurements of this study is discussed in Section 4.4.

4. Results and Discussion

In this section, we first presented results from experimental investigation of density measurements for 0, 1.91, and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2 at 328.15 to 375.15 °K and 68.9 to 206.8 Bar. Then, various models proposed for estimation of density of $CaCl_2$ solution were examined using experimental data published by Al Ghafari et al. [30] to find the best model. Then, we used the experimental data generated in this study to estimate density of CO_2–H_2O to identify the most appropriate existing model for this purpose. Finally, we used the experimental data from the current study to develop a new model for estimation of CO_2–$CaCl_2$–H_2O density.

4.1. Experimental Results

The results of experimental work conducted in this study for estimation of density of pure H_2O, saturated with CO_2 at 328.15 °K, are depicted in Figure 4. As shown in Figure 4, experimental measurements in this study are compared with those published by Hebach et al. [21]. Hebach et al. [21] measured density of pure water saturated with CO_2 at 322.85 °K and 331.8 °K. Although the experimental conditions are not the same, this comparison confirms the accuracy of the experimental technique used in this study. Density of CO_2–H_2O system measured at different P-T conditions of this study and molalities of 0, 1.91, and 4.85 mol/kg-$CaCl_2$ are listed in Table 2. These data show the trend of density change for 1.91 and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2, with changing P-T conditions.

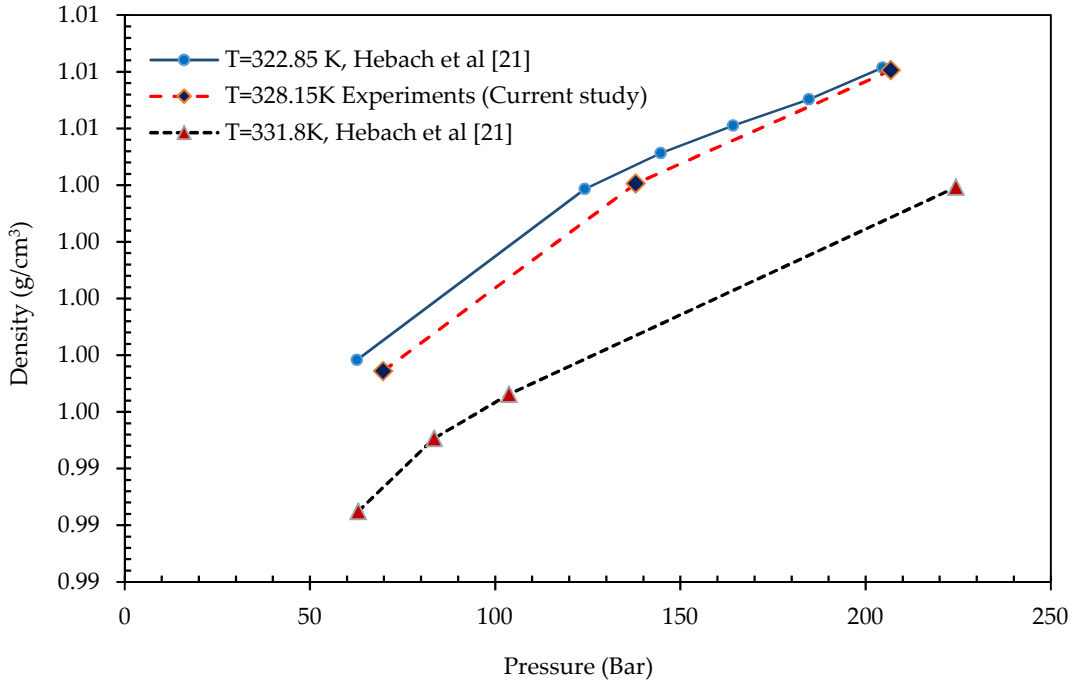


Figure 4. Comparison of experimental measurements of density of pure H_2O saturated with CO_2 versus pressure from current study with data reported by Hebach et al. [21].

Addition of CO_2 to pure H_2O increases the solution density [22,24]. Moreover, measured data in the current study indicate that density of $CaCl_2$ solution saturated with CO_2 increases with an increase in pressure, as shown in Figure 4 and Table 2. Furthermore, density of 1.91 mol/kg $CaCl_2$ solution saturated with CO_2 measured at 68.9 and 206.8 Bar is plotted versus temperature in Figure 5. As one can see from Figure 5, density of this system decreases with an increase in temperature. This result is consistent with observations made by some previous studies [21,32,33].

Table 2. Results from measurement of density of pure H_2O saturated with CO_2 in P-T conditions of current study and molalities of 0, 1.91, and 4.85 mol/kg $CaCl_2$.

Temperature(°K)	Pressure (Bar)	Liquid Density (g/cm^3), Molality = 0	Liquid Density (g/cm^3); Molality = 1.91 mol/kg-$CaCl_2$	Liquid Density (g/cm^3); Molality = 4.85 mol/kg-$CaCl_2$
328.15	68.9	0.9975	1.1710	1.3250
	137.9	1.0040		1.3450
	206.8	1.0080	1.1770	1.3650
351.65	68.9	0.9790		1.3130
	137.9		1.1565	
	206.8	0.9921		1.3610
368.15	68.9	0.9662		1.3080
	206.8	0.9815		1.3540
375.15	68.9		1.1410	
368.15	137.9	0.9600		1.3420
375.15	206.8		1.1450	

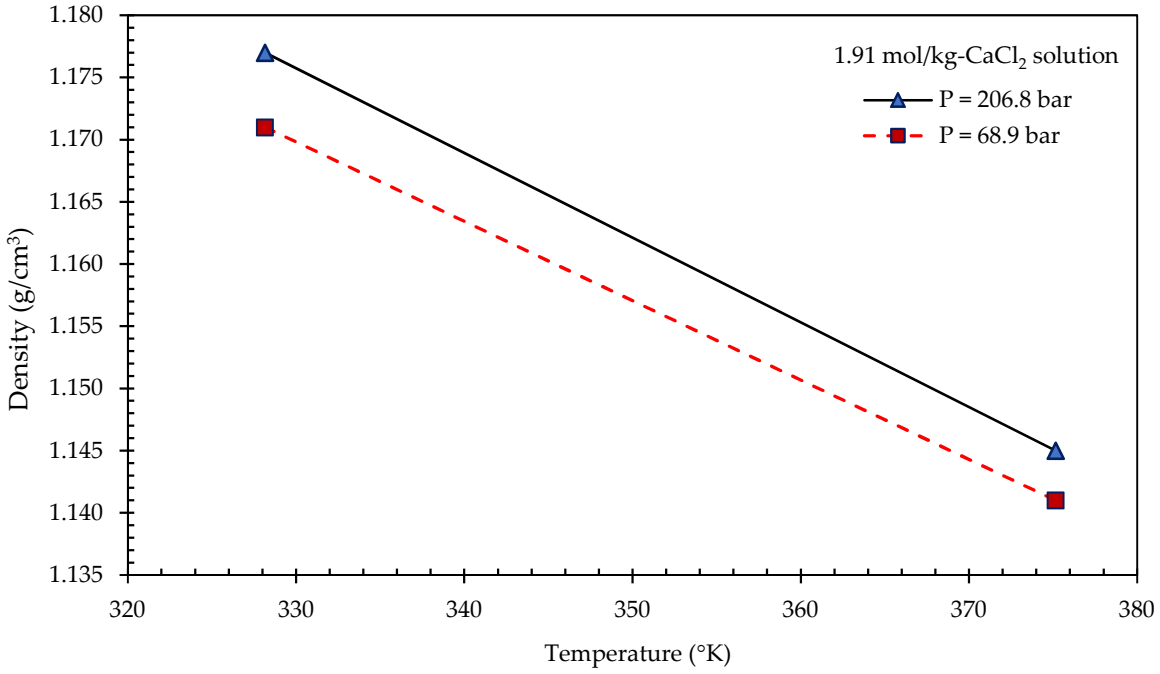


Figure 5. Experimental measurements of the density of a 1.91 mol/kg $CaCl_2$ solution saturated with CO_2 at 68.9 and 206.8 Bar versus temperature.

The density of aqueous solution saturated with CO_2 increases with an increase in $CaCl_2$ solution concentration. Figure 6 demonstrates this trend for pure H_2O and different $CaCl_2$ solutions at 328.15 °K and 68.9–206.8 Bar. $CaCl_2$ solution concentration is the most effective parameter on density of the solution. This is also in harmony with previously reported research by some previous studies [13,24,25,33,34].

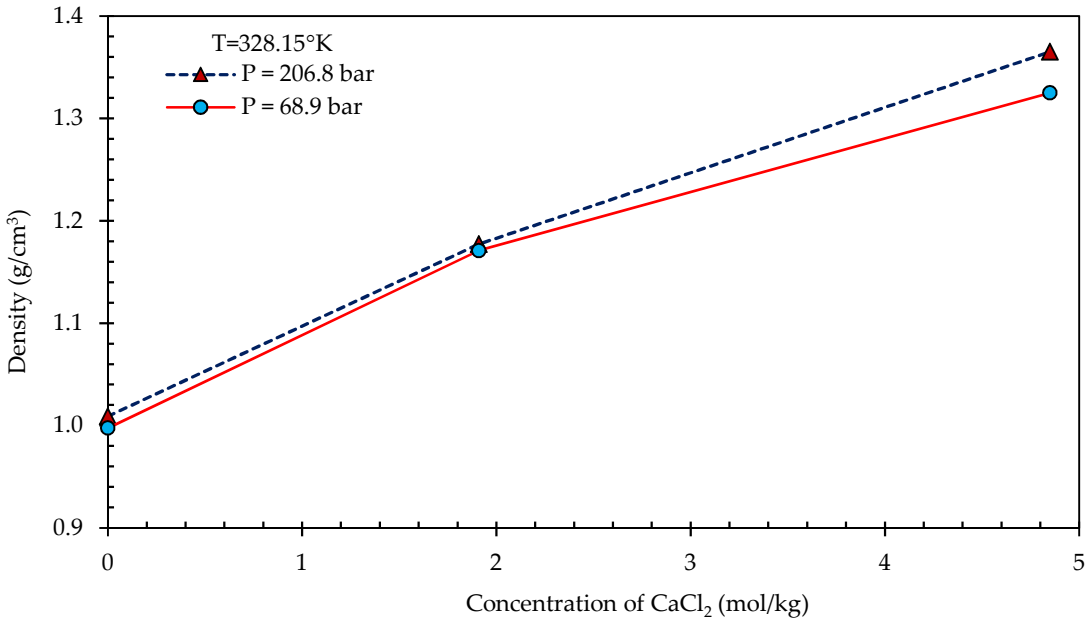
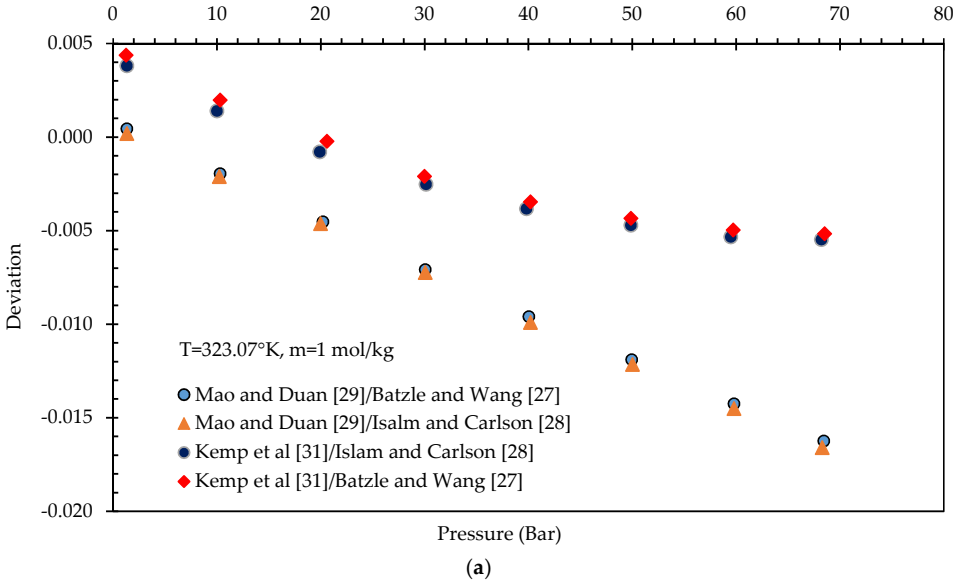


Figure 6. Experimental measurements of the density of pure H_2O and $CaCl_2$ solutions saturated with CO_2 at 328.15 °K and 68.9–206.8 Bar and versus $CaCl_2$ concentration.

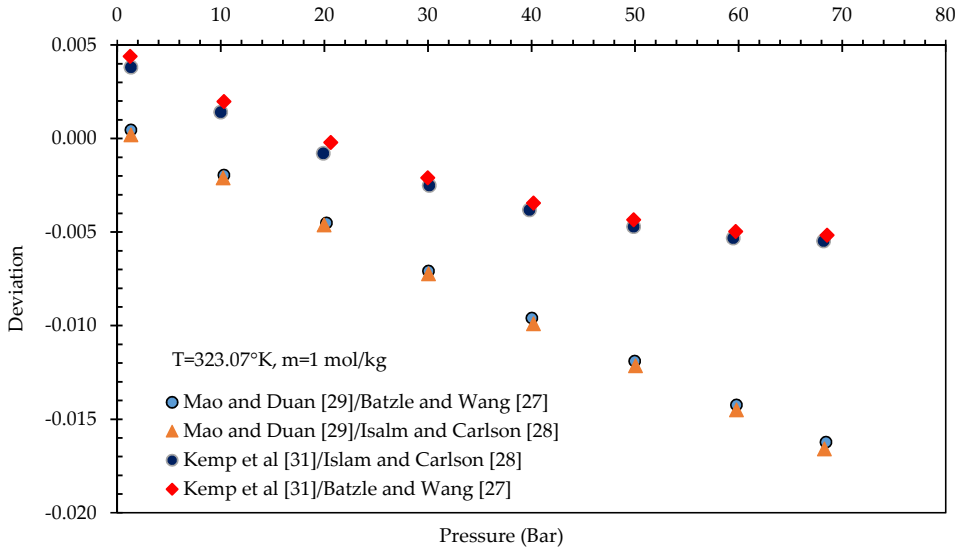
4.2. $CaCl_2$ Solution Density

To identify the best model for estimation of density of $CaCl_2$–H_2O under typical reservoir P-T conditions, predictions from models presented by Kemp et al. (1989) [31] and Mao and Duan [29] are compared with experimental measurements reported by Al Ghafri et al. [30]. Al Ghafri et al. [30] measured density of 1–6 mol/kg aqueous $CaCl_2$ solutions in P-T ranges of 298.15–477 °K and 10.5–689 Bar, respectively. Different models for pure H_2O and $CaCl_2$ solution density are used here to find the best one with minimum deviation from experimental measurements. Deviations of model estimations from experimental measurements ($\rho_{calc} - \rho_{exp}$) are compared in the desired temperature range of the current study (323.07–372.99 °K), as illustrated in Figure 7.



(**a**)

Figure 7. *Cont.*



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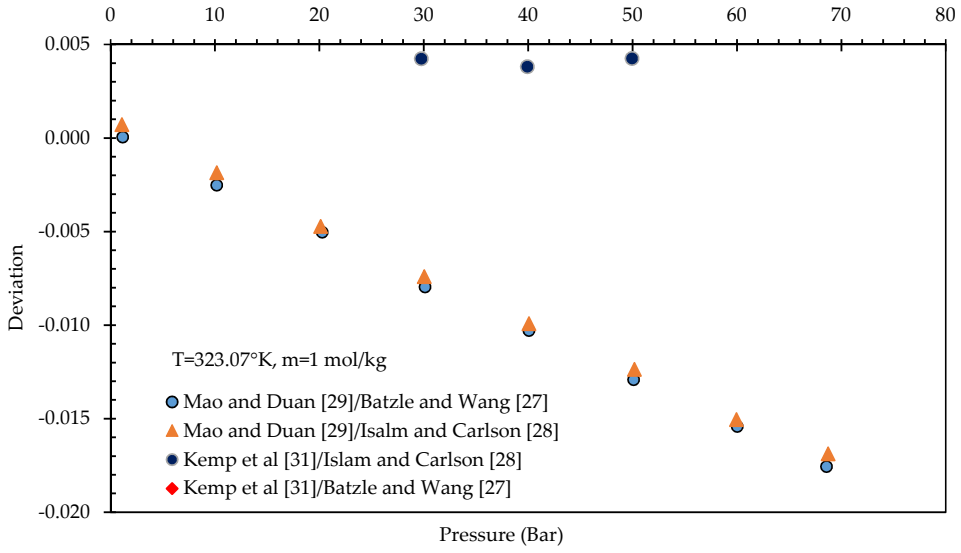

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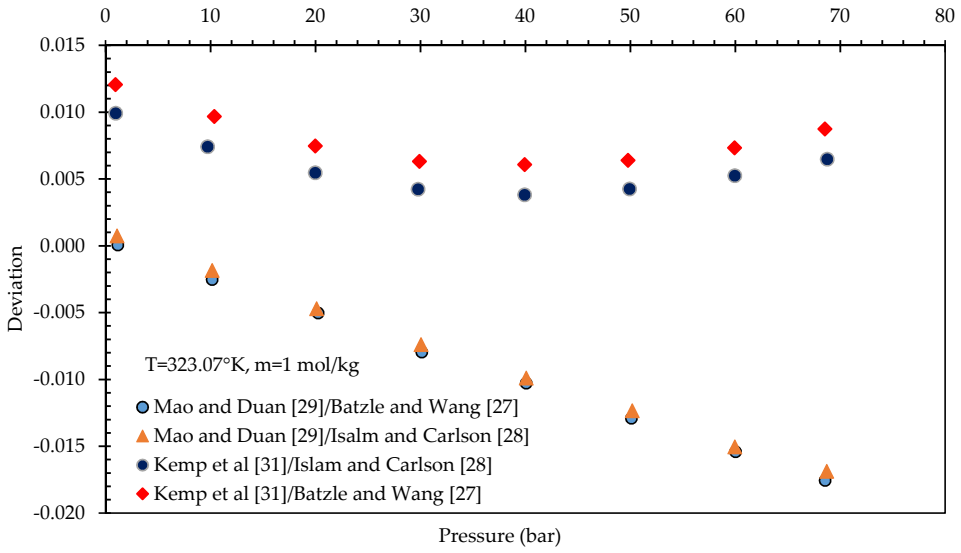

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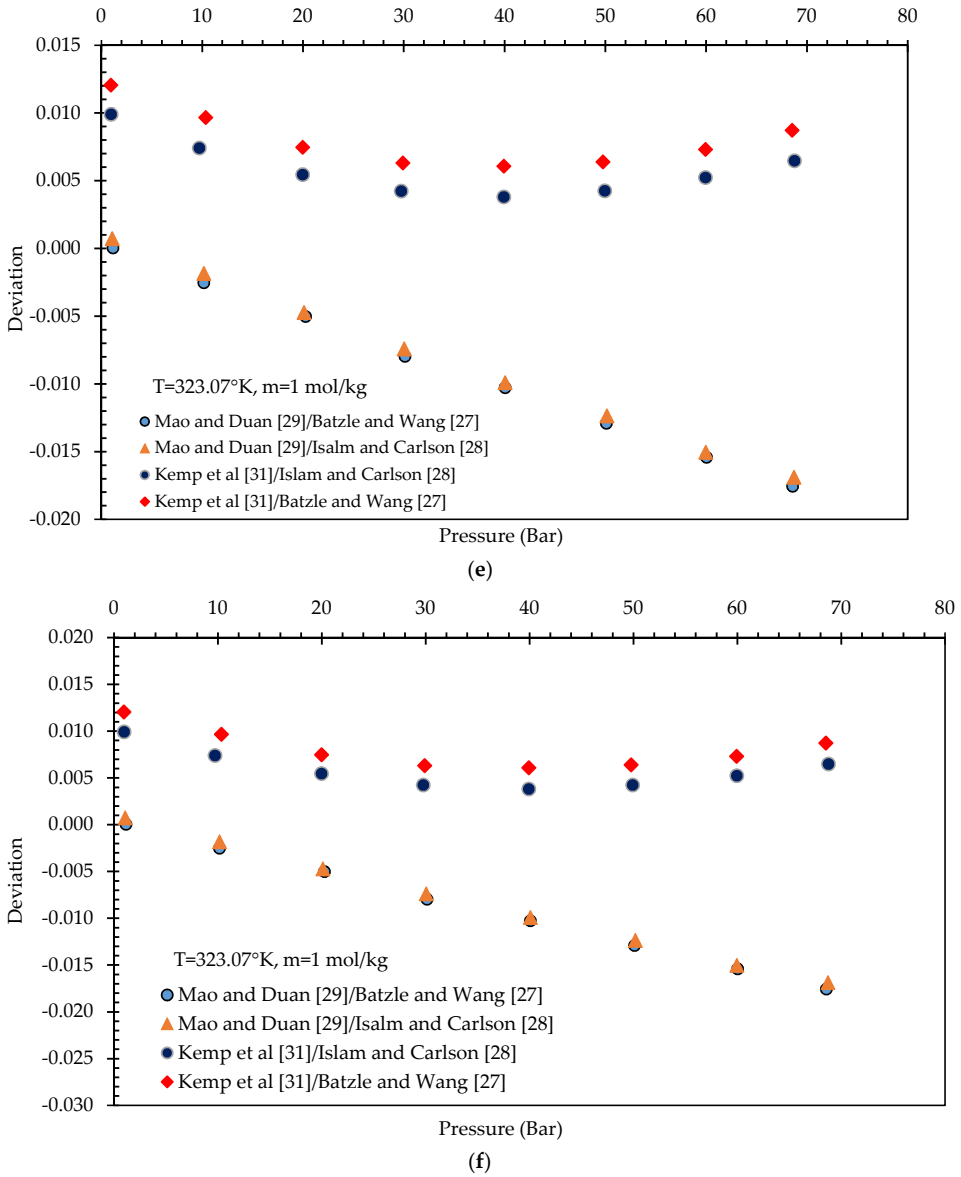


Figure 7. The deviation of various model estimates from experimental measurements of Al Ghafri et al. [30] at different temperature and $CaCl_2$ solution molalities versus pressure: (**a**) T = 323.07 °K, m = 1 mol/kg; (**b**) T = 323.07 °K, m = 6 mol/kg; (**c**) T = 348.04 °K, m = 1 mol/kg; (**d**) T = 348.04 °K, m = 6 mol/kg; (**e**) T = 372.99 °K, m = 1 mol/kg; (**f**) T = 372.99 °K, m = 6 mol/kg.

While the model proposed by Mao and Duan [29] underestimates density of $CaCl_2$ solution in all of the examined P-T conditions, the model proposed by Kemp et al. [31] overestimates the density of solutions with higher salinities for high P-T ranges. In other words, there are some conditions in which the deviation of estimates by Kemp et al. [31] tend towards zero. Moreover, in all of the cases, estimations of Kemp et al. [31] are more accurate than those of Mao and Duan [29]. It should be noted that Mao and Duan [29] recommended their model to be used with pure H_2O densities from IAPWS97. These deviations can be attributed to the approximations made by either pure H_2O or $CaCl_2$ solution density models.

To compare model estimates, average absolute deviations (AAD) and maximum absolute deviations (MAD) of model estimates from experimental measurements are defined as Equations (12) and (13), respectively.

$$\mathrm{AAD} = \left(\left|\rho_{exp} - \rho_{calc}\right| / \rho_{exp}\right) / \mathrm{N} \tag{12}$$

$$\text{MAD} = \text{Max}\left(\left|\rho_{exp} - \rho_{calc}\right| / \rho_{exp}\right) \quad (13)$$

where ρ_{exp} is density measured experimentally, ρ_{calc} is calculated density, and N is number of data.

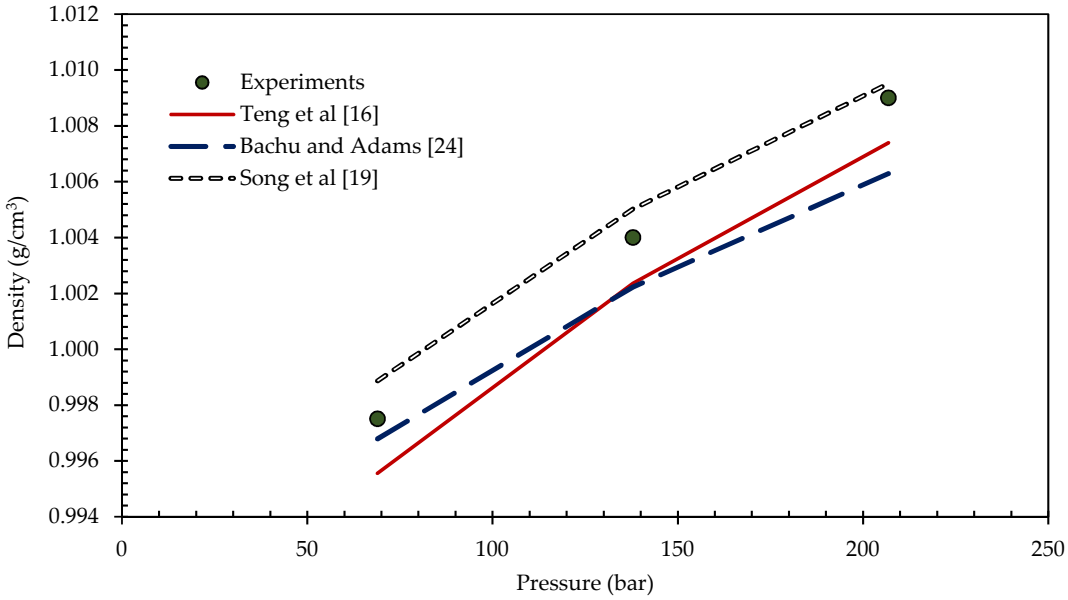
Table 3 shows the average and maximum absolute deviations of density predictions by these two models with the experimental measurements of Al Ghafri et al. [30], which are consistent with reservoir conditions. It should be noted that these models require an estimation of pure H_2O density. Hence, water density is estimated by correlations previously introduced in this article. The AAD and MAD values shown in Table 3 also confirm that the model presented by Kemp et al. [31] performs relatively better than the model proposed by Mao and Duan [29]. In addition, the pure H_2O densities estimated by Islam and Carlson [28] show less deviation from the experimental aqueous $CaCl_2$ solutions.

Table 3. Deviation of various model estimations for the $CaCl_2$–H_2O system from the experimental data measured by Al Ghafri et al. [30]. AAD is average absolute deviations and MAD is maximum absolute deviations of model (see below) estimates from experimental measurements conducted in current study.

Models for Density Estimation of Pure Water	Deviations	Models for Density Estimation of Brine	
		Kemp et al. [31]	Mao and Duan [29]
Batzle and Wang [27]	AAD	0.0089	0.0151
	MAD	0.0304	0.0504
Islam and Carlson [28]	AAD	0.0077	0.0143
	MAD	0.0349	0.0389

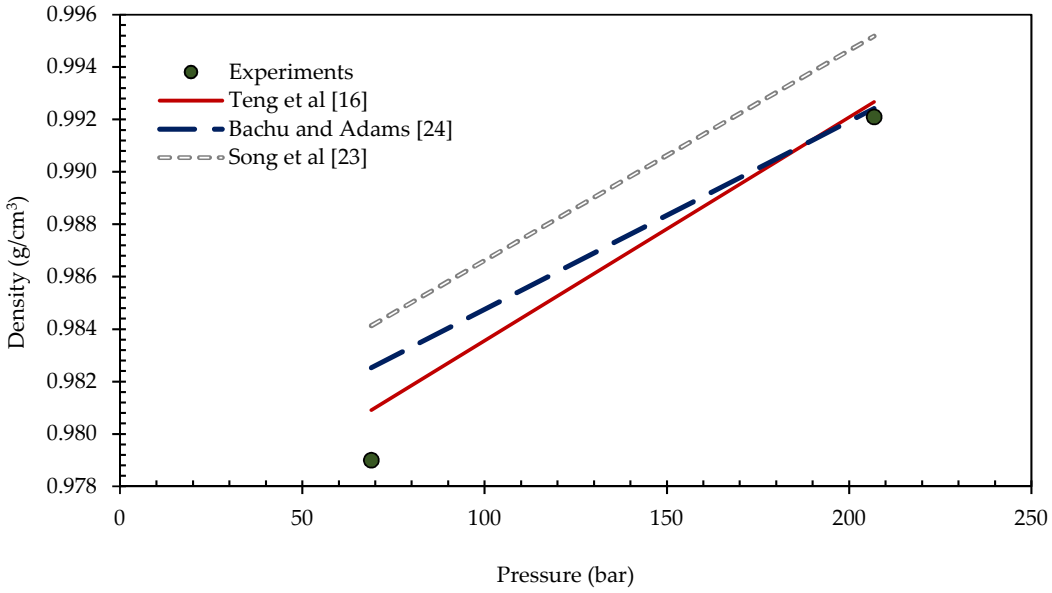
4.3. CO_2–H_2O Density

Using experimental data from the current study, the density of pure H_2O saturated with CO_2, three models presented as Equations (5)–(7) are compared at different temperatures, as presented in Figure 8. It should be emphasized that based on the previous results, the pure H_2O density is estimated by the model proposed by Islam and Carlson [28].

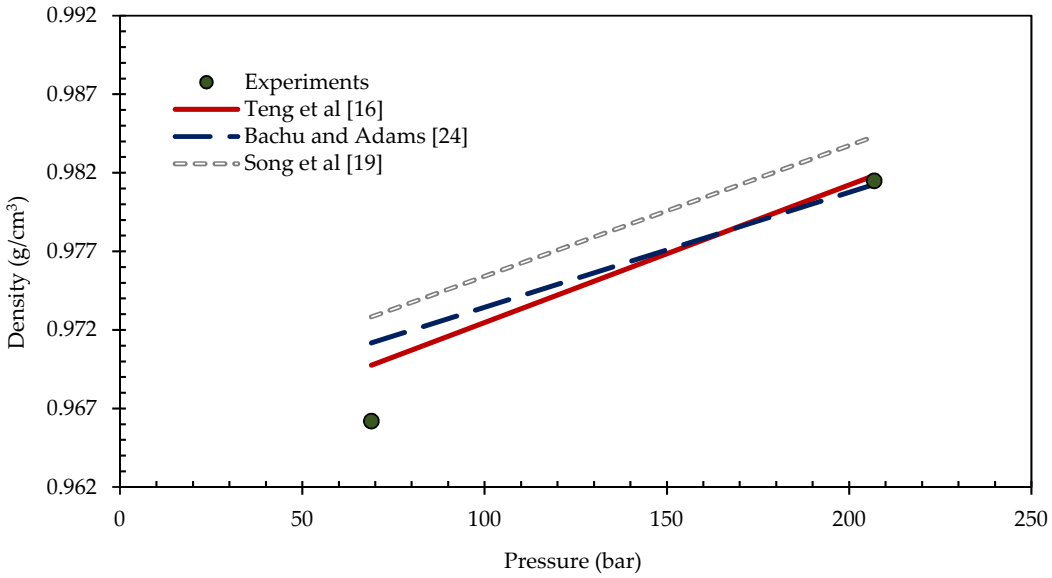


(**a**) Pure Water, T = 328.15 °K

Figure 8. *Cont.*



(**b**) Pure Water, T = 351.65 °K



(**c**) Pure Water, T = 368.15 °K

Figure 8. A comparison of experimental data from this study and three different model estimations for density of pure H_2O saturated with CO_2 at (**a**) 328.15 °K, (**b**) 351.65 °K, and (**c**) 368.15 °K.

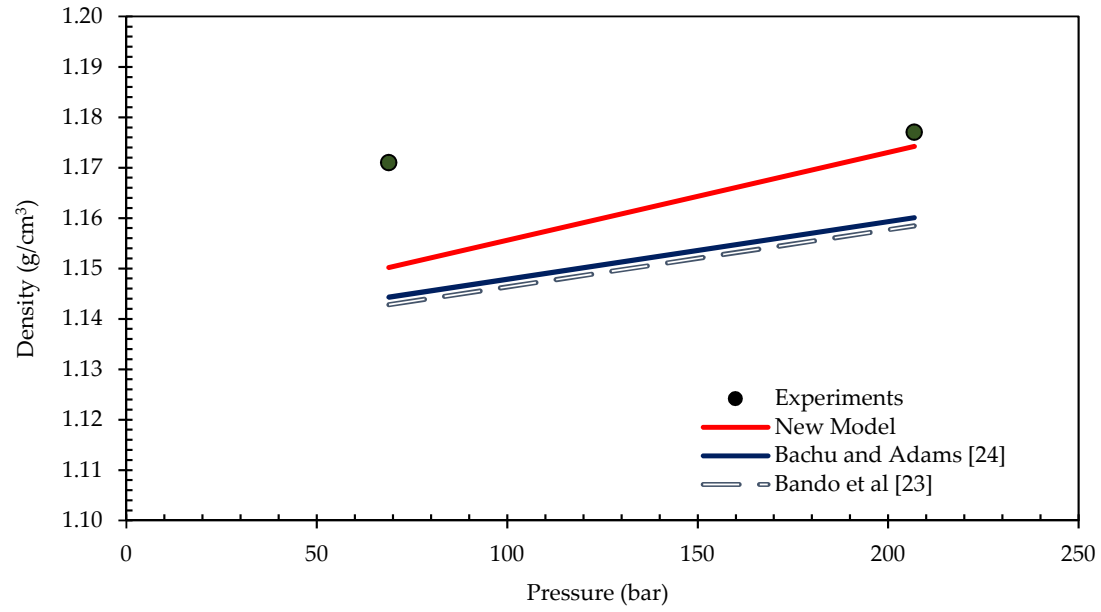
The average and maximum absolute deviations of the predictions are listed in Table 4. As can be observed from Figure 8, as well as from the AAD and MAD values presented in Table 4, the correlation proposed by Teng et al. [16] with pure water density estimation from the model proposed by Islam and Carlson [28] results in the best estimation.

Table 4. Comparison of experimental data from this study with estimations from three different models for pure H_2O saturated with CO_2.

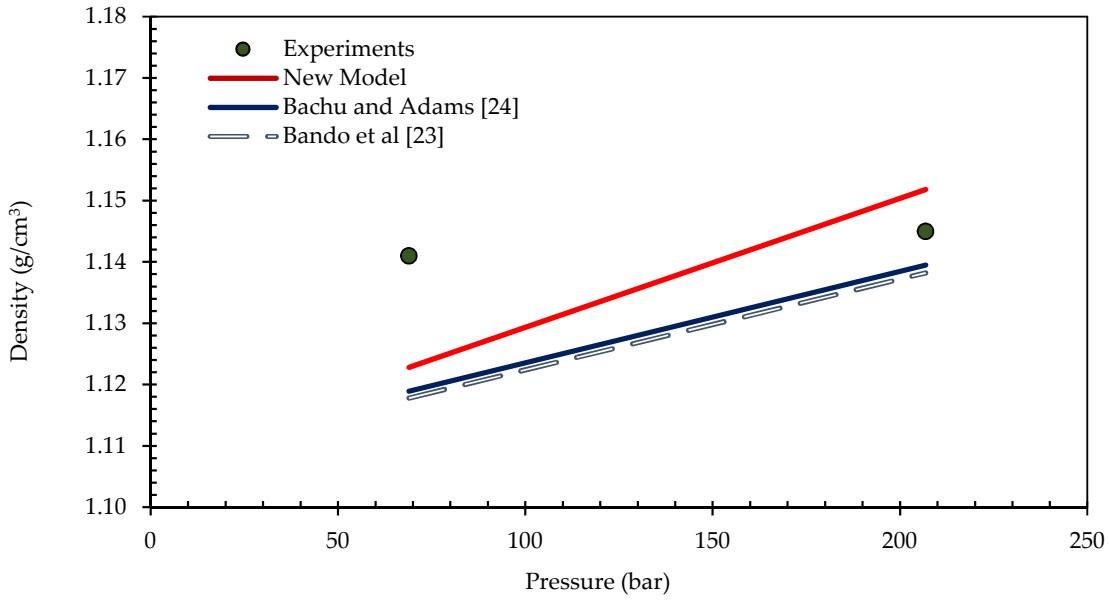
Deviations	Models for Density Estimation of CO_2 in Pure Water		
	Teng et al. [16]	Bachu and Adams (2003) [24] and Garcia [25]	Song et al. [19]
AAD	0.0016	0.0020	0.0032
MAD	0.0037	0.0051	0.0069

4.4. CO_2–$CaCl_2$–H_2O Density

We used the experimental data generated in this study to develop a new model for estimation of density of the CO_2–$CaCl_2$–H_2O $CaCl_2$ system (Equation (11)). Data from experimental measurements from this study and model estimates by Bachu and Adams [24], Bando et al. [23], and also the new model we proposed for prediction of CO_2–$CaCl_2$–H_2O density for 1.91 and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2, are compared in Figures 9 and 10. It should be noted that to predict density of the CO_2–$CaCl_2$–H_2O system, it is required to estimate density of $CaCl_2$–H_2O in advance. Moreover, estimation of density of $CaCl_2$–H_2O requires estimation of density of pure H_2O density. Based on investigations of this study (Sections 4.2 and 4.3), these estimates are obtained using Kemp et al. [31] and Islam and Carlson [28] to calculate $CaCl_2$ solution and pure H_2O densities, respectively.

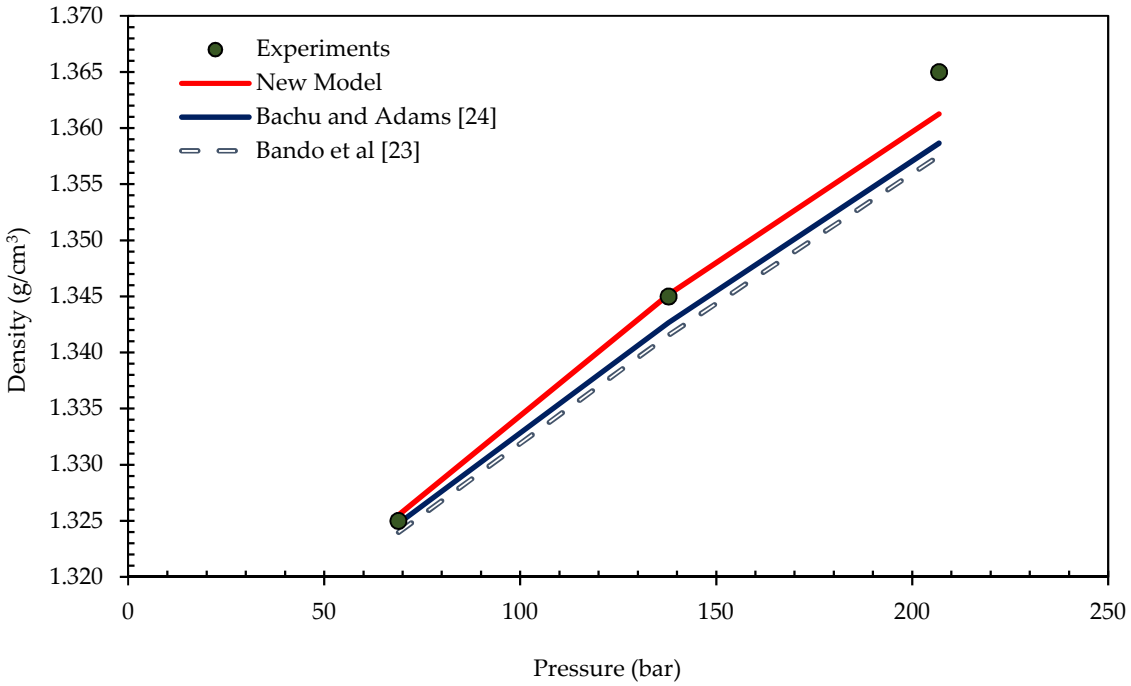


(**a**) 1.91 mol/kg $CaCl_2$ solution, T = 328.15 °K

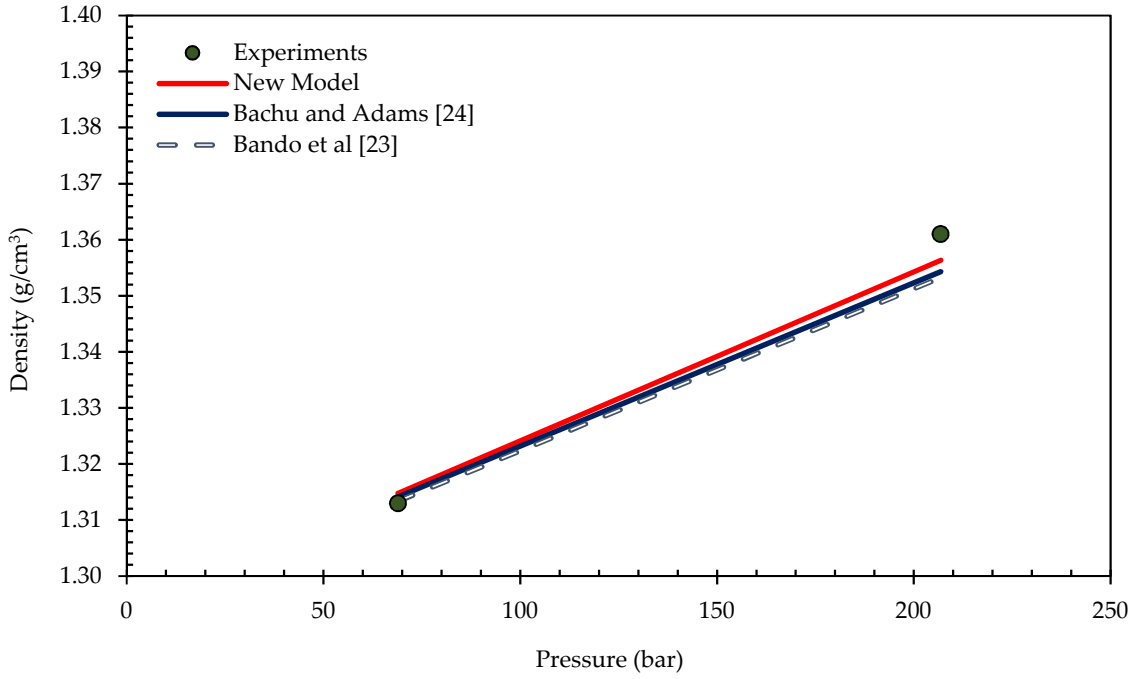


(**b**) 1.91 mol/kg $CaCl_2$ solution, T = 375.15 °K

Figure 9. A comparison of experimentally measured and different model estimations for density of a 1.91 mol/kg-$CaCl_2$ solution saturated with CO_2 at (**a**) 328.15 °K and (**b**) 375.15 °K.

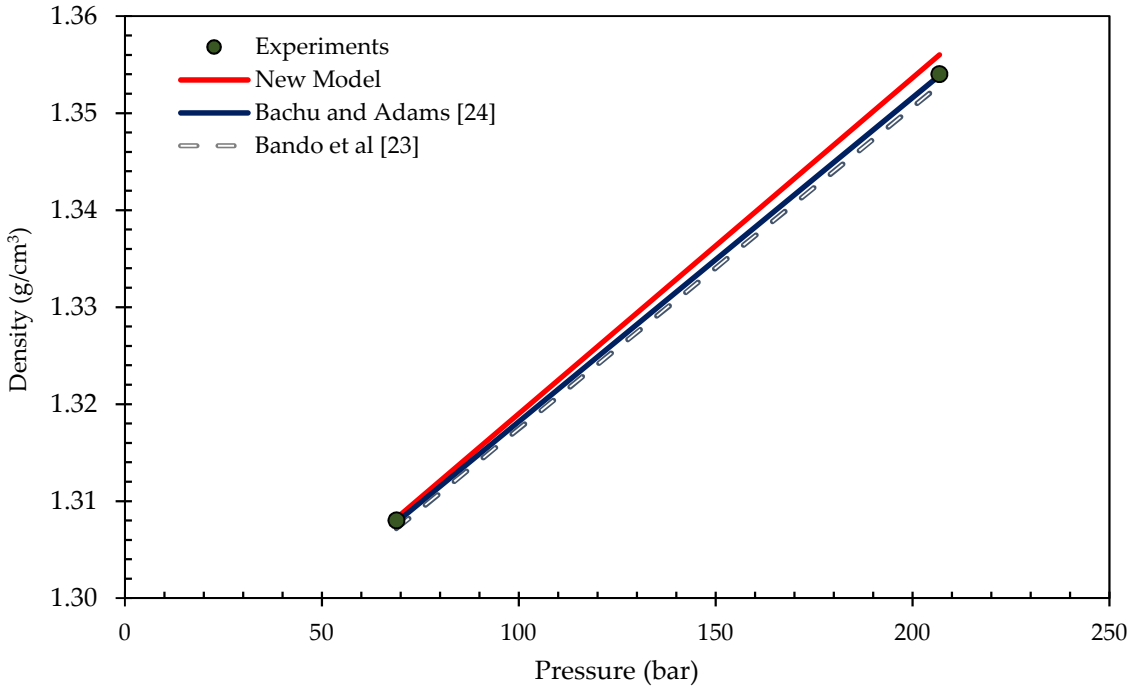


(**a**) 4.85 mol/kg $CaCl_2$ solution, T = 328.15 °K



(**b**) 4.85 mol/kg $CaCl_2$ solution, T = 351.65 °K

Figure 10. *Cont.*



(**c**) 4.85 mol/kg $CaCl_2$ solution, T = 368.15 °K

Figure 10. A comparison of experimental data and different model estimations for the density of a 4.85 mol/kg $CaCl_2$ solution saturated with CO_2 at (**a**) 328.15 °K, (**b**) 351.65 °K, and (**c**) 368.15 °K.

Figures 9 and 10 demonstrate the improvement in the model estimates by the new model developed in this study in comparison with some previous models. Moreover, the estimate deviations for different models, including the new model, are listed in Table 5. Comparing the deviations reported in Table 5 shows that the minimum deviation between predictions and experimental data belongs to the new model developed in this study for estimation of density alteration of $CaCl_2$ solutions due to addition of CO_2. The average and maximum absolute deviation between experiments and the estimates are 0.0047 and 0.0036, respectively. The average absolute deviation of the new model is 34% and 41% lower than the models previously proposed by Bachu and Adams [24] and Bando et al. [23], respectively.

Table 5. Comparison of various model estimations for $CaCl_2$ solutions saturated with CO_2 to experimental data from the current study and the new model proposed in this study.

Deviations	Models for Density Estimation of CO_2 in $CaCl_2$ Solution		
	Bachu and Adams [24] and Garcia [25]	Bando et al. [23]	New Model
AAD	0.0072	0.0080	0.0047
MAD	0.0228	0.0241	0.0177

Based on experimental investigations in this study and examination of different models proposed in the literature using the obtained experimental data, the correlation proposed by Teng et al. [16] and the model proposed by Islam and Carlson [28] are the best available models for estimation of density of pure H_2O saturated with CO_2 and density of pure H_2O, respectively (CO_2–H_2O system). In addition, for the CO_2–$CaCl_2$–H_2O system, the model proposed by Kemp et al. [31] for estimation of density of $CaCl_2$ solution and the model proposed by Islam and Carlson [28] for pure H_2O density estimation gives the best estimates with least deviations.

In petroleum engineering applications, $CaCl_2$ solutions are usually subject to CO_2 addition. The method proposed in this study can be recommended for estimation of density of $CaCl_2$ solutions

in the ternary system of CO_2–$CaCl_2$–H_2O. The new model can be applied in various areas such as geological CO_2 sequestration to evaluate capacity of saline aquifers for CO_2 storage, as well as for a more accurate simulation of CO_2 sequestration. Moreover, it can be used to further current understanding of physics of matrix acidizing in limestone reservoirs such as interaction between rock and the CO_2–$CaCl_2$–H_2O system.

5. Conclusions

Accurate estimation of changes in density of CO_2–pure H_2O and $CaCl_2$–H_2O systems is of paramount importance in areas such as matrix acidizing in limestone reservoirs as a well stimulation technique, as well as geological sequestration of CO_2 in saline aquifers. In this paper, density of 0, 1.91, and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2 at 328.15 to 375.15 °K and 68.9 to 206.8 Bar were measured through laboratory experiments. Then, a new model was developed to estimate the density of the $CaCl_2$ solutions containing CO_2 based on the experiments conducted in this study. Based on the experimental and modeling works conducted in this study the following five main conclusions can be drawn:

1. An experimental apparatus was designed and fabricated to measure density of 0, 1.91, and 4.85 mol/kg $CaCl_2$ solutions saturated with CO_2 at 328.15 to 375.15 °K and 68.9 to 206.8 Bar. The experimental data showed that solution density increases with addition of CO_2. The solution density also increases with increase in $CaCl_2$ solution concentration, increase in pressure, and decrease in temperature. However, the effect of $CaCl_2$ solution concentration on density alteration was notable compared with the effect of pressure and temperature.
2. $CaCl_2$ solution density estimated by different models was compared with the experimental data from the current study. The comparison shows that minimum errors belong to the models proposed by Islam and Carlson [28] and Kemp et al. [31] for pure H_2O and $CaCl_2$ solution, respectively.
3. The models proposed by Teng et al. [16] and Islam and Carlson [28] are the best available models for estimation of density of pure H_2O saturated with CO_2 and density of pure H_2O, respectively (CO_2–H_2O system).
4. We developed a new model for estimation of density of the CO_2–$CaCl_2$–H_2O $CaCl_2$ system (Equation (11)) based on the experimental data generated in this study. Comparing the deviations between the experimental data and the new model and the models proposed by Bachu and Adams [24] and Bando et al. [23] showed that the new model performs 34% and 41% better than these two models, respectively. For the new model, the average and maximum absolute deviation between experiments and the estimates are 0.0047 and 0.0036, respectively.
5. The new model can be applied in various areas such as geological CO_2 sequestration to evaluate capacity of saline aquifers for CO_2 storage, as well as for a more accurate simulation of CO_2 sequestration. Moreover, it can be used to further understand physics of matrix acidizing in limestone reservoirs such as interaction between rock and the CO_2–$CaCl_2$–H_2O system.

Author Contributions: A.B. conducted the experiments and analyzed the results. P.P. was the main supervisor of the research, contributed in analysis of the results, and wrote initial draft of the manuscript. A.S. contributed in analysis and discussion of the results, and reviewing and editing of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The authors would like to thank editors and two anonymous reviewers for their constructive comments that helped the authors to enhance overall quality of the manuscript.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Gomez, J.N. Design, Set-Up and Testing of a Matrix Acidizing Apparatus. Master's Thesis, Texas A&M University, College Station, TX, USA, 2006.

2. Umer Shafiq, M.; Ben Mahmud, H.K.; Rezaee, R.; Testamanti, N. Investigation of changing pore topology and porosity during matrix acidizing using different chelating agents. *IOP Conf. Ser. Mater. Sci. Eng.* **2017**. [CrossRef]
3. Bastami, A.; Pourafshary, P. Development of a new model for carbonate matrix acidizing to consider the effects of spent acid. *ASME J. Energy Resour. Technol.* **2016**, *138*. [CrossRef]
4. Dubacq, B.; Bickle, M.J.; Evans, K.A. An activity model for phase equilibria in the H_2O–CO_2–NaCl system. *Geochim. Cosmochim. Acta* **2013**, *110*, 229–252. [CrossRef]
5. Iglauer, S. Dissolution trapping of carbon dioxide in reservoir formation brine—A carbon storage mechanism. In *Mass Transfer*; InTech: Rijeka, Croatia, 2011.
6. Mohamed, I.; He, J.; Nasr-El-Din, H.A. Effect of brine composition on CO_2/limestone rock interactions during CO_2 sequestration. *JPSR* **2013**, *2*, 14–26.
7. Hassanzadeh, H.; Pooladi-Darvish, M.; Elsharkawy, A.M.; Keith, D.W.; Leonenko, Y. Predicting PVT data for CO_2–brine mixtures for black-oil simulation of CO_2 geological storage. *Int. J. Greenh. Gas Control* **2008**, *2*, 65–77. [CrossRef]
8. Ghomian, Y.; Pope, G.A.; Sepehrnoori, K. Reservoir simulation of CO_2 sequestration pilot in Frio brine formation, USA Gulf Coast. *Energy* **2008**, *33*, 1055–1067. [CrossRef]
9. Savioli, G.B.; Santos, J.E. Modeling of CO_2 storage in aquifers. *J. Phys. Conf. Ser.* **2011**, *296*, 012021. [CrossRef]
10. Tabasinejad, F.; Barzin, Y.; Moore, R.; Mehta, S.; Van Fraassen, K.; Rushing, J.; Newsham, K. Water/CO_2 system at high pressure and temperature conditions—Measurement and modeling of density in equilibrium liquid and vapor phases. In Proceedings of the EUROPEC/EAGE Annual Conference and Exhibition, Barcelona, Spain, 14–17 June 2010.
11. Goodarzi, S.; Settari, A.; Keith, D. Geomechanical modeling for CO_2 storage in Nisku aquifer in Wabamun Lake area in Canada. *Int. J. Greenh. Gas Control* **2012**, *10*, 113–122. [CrossRef]
12. Ziabakhsh-Ganji, Z.; Kooi, H. An equation of state for thermodynamic equilibrium of gas mixtures and brines to allow simulation of the effects of impurities in subsurface CO_2 storage. *Int. J. Greenh. Gas Control* **2012**, *11S*, 21–34. [CrossRef]
13. Nighswander, J.A.; Kalogerakis, N.; Mehrotra, A.K. Solubilities of carbon dioxide in water and 1 wt.% sodium chloride solution at pressures up to 10 MPa and temperatures from 80 to 200 °C. *J. Chem. Eng. Data* **1989**, *34*, 355–360. [CrossRef]
14. King, M.B.; Mubarak, A.; Kim, J.D.; Bott, T.R. The mutual solubilities of water with supercritical and liquid carbon dioxides. *J. Supercrit. Fluids* **1992**, *5*, 296–302. [CrossRef]
15. Fenghour, A.; Wakeham, W.A.; Watson, J.T.R. Densities of (water + carbon dioxide) in the temperature range 415 K to 700 °K and pressures up to 35 MPa. *J. Chem. Thermodyn.* **1996**, *28*, 433–446. [CrossRef]
16. Teng, H.; Yamasaki, A.; Chun, M.K.; Lee, H. Solubility of liquid CO_2 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. *J. Chem. Thermodyn.* **1997**, *29*, 1301–1310. [CrossRef]
17. Yaginuma, R.; Sato, Y.; Kodama, D.; Tanaka, H.; Kato, M. Saturated densities of carbon dioxide + water mixture at 304.1 K and pressures to 10 MPa. *J. Jpn. Inst. Energy* **2000**, *79*, 144–146. [CrossRef]
18. Tegetmeier, A.; Dittmar, D.; Fredenhagen, A.; Eggers, R. Density and volume of water and triglyceride mixtures in contact with carbon dioxide. *Chem. Eng. Process* **2000**, *39*, 399–405. [CrossRef]
19. Song, Y.; Nishio, M.; Chen, B.; Someya, S.; Ohsumi, T. Measurement on CO_2 solution density by optical technology. *J. Vis.* **2003**, *6*, 41–51. [CrossRef]
20. Li, Z.; Dong, M.; Li, S.; Dai, L. Densities and solubilities for binary systems of carbon dioxide + water and carbon dioxide + brine at 59 °C and pressures to 29 MPa. *J. Chem. Eng. Data* **2004**, *49*, 1026–1031. [CrossRef]
21. Hebach, A.; Oberhof, A.; Dahmen, N. Density of water + carbon dioxide at elevated pressures: Measurements and correlation. *J. Chem. Eng. Data* **2004**, *49*, 950–953. [CrossRef]
22. Song, Y.; Jian, W.; Zhang, Y.; Yang, M.; Zhao, J.; Liu, W.; Shen, Y. Density measurement and PC-SAFT/tPC-PSAFT modeling of the CO_2 + H_2O System over a wide temperature range. *J. Chem. Eng. Data* **2014**, *59*, 1400–1410. [CrossRef]
23. Bando, S.; Takemura, F.; Nishio, M.; Hihara, E.; Akai, M. Viscosity of aqueous NaCl solutions with dissolved CO_2 at (30 to 60) °C and (10 to 20) MPa. *J. Chem. Eng. Data* **2004**, *49*, 1328–1332. [CrossRef]
24. Bachu, S.; Adams, J.J. Sequestration of CO_2 in geological media in response to climate change: Capacity of deep saline aquifers to sequester CO_2 in solution. *Energy Convers. Manag.* **2003**, *44*, 3151–3175. [CrossRef]

25. Garcia, J.E. *Density of Aqueous Solutions of CO_2*; Report LBNL-49023, Lawrence Berkeley National Laboratory: Berkeley, CA, USA, 2001.
26. Bastami, A.; Allahgholi, M.; Pourafshary, P. Experimental and modelling study of the solubility of CO_2 in various $CaCl_2$ solutions at different temperatures and pressures. *Pet. Sci.* **2014**, *11*, 569–577. [CrossRef]
27. Batzle, M.; Wang, Z. Seismic properties of pore fluids. *Geophysics* **1992**, *57*, 1396–1408. [CrossRef]
28. Islam, A.W.; Carlson, E.S. Viscosity models and effects of dissolved CO_2. *Energy Fuels* **2012**, *26*, 5330–5336. [CrossRef]
29. Mao, S.; Duan, Z. The P,V,T,X properties of binary aqueous chloride solutions up to T = 573 °K and 100 MPa. *J. Chem. Thermodyn.* **2008**, *40*, 1046–1063. [CrossRef]
30. Al Ghafri, S.; Maitland, G.C.; Trusler, J.M. Densities of aqueous $MgCl_2$ (aq), $CaCl_2$ (aq), KI (aq), NaCl (aq), KCl (aq), $AlCl_3$ (aq), and (0.964 NaCl + 0.136 KCl)(aq) at temperatures between (283 and 472) °K, pressures up to 68.5 MPa, and Molalities up to 6 mol·kg^{-1}. *J. Chem. Eng. Data* **2012**, *57*, 1288–1304. [CrossRef]
31. Kemp, N.P.; Thomas, D.C.; Atkinson, G.; Atkinson, B.L. Density modeling for brines as a function of compositions temperature and pressure. *SPE Prod. Eng.* **1989**, *4*, 394–400. [CrossRef]
32. Ji, X.; Tan, S.P.; Adidharma, H.; Radosz, M. SAFT1-RPM approximation extended to phase equilibria and densities of CO_2–H_2O and CO_2–H_2O–NaCl systems. *Ind. Eng. Chem. Res.* **2005**, *44*, 8419–8427. [CrossRef]
33. Islam, A.W.; Carlson, E.S. A fully non-iterative technique for phase equilibrium and density calculations of CO_2 + brine system and an equation for CO_2. *JPSE* **2014**, *115*, 31–37. [CrossRef]
34. Zhang, Y.; Jian, W.; Zhan, Y.; Song, Y.; Yang, M.; Zhao, J.; Shen, Y. Density measurement and equal density temperature of CO_2 + brine from Dagang—Formation from 313 to 363 °K. *Korean J. Chem. Eng.* **2015**, *32*, 141–148. [CrossRef]