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# Measurement of Solubility of $CO_2$ in NaCl, $CaCl_2$, $MgCl_2$ and $MgCl_2$ + $CaCl_2$ Brines at Temperatures from 298 to 373 K and Pressures up to 20 MPa Using the Potentiometric Titration Method

**Bo Liu [1], Barham Sabir Mahmood [2], Erfan Mohammadian [1,3,*], Abbas Khaksar Manshad [4], Nor Roslina Rosli [5,*] and Mehdi Ostadhassan [1]**

1 Key Laboratory of Continental Shale Hydrocarbon Accumulation and Efficient Development, Ministry of Education, Northeast Petroleum University, Daqing 163318, China; liubo@nepu.edu.cn (B.L.); mehdi.ostadhassan@nepu.edu.cn (M.O.)
2 Department of Petroleum, Faculty of Engineering, Koya University, Koya KOY45, Kurdistan Region—F.R., Iraq; barham.sabir@koyauniversity.org
3 Department of Petroleum and Natural Gas Engineering, Cyprus International University, Via Mersin 10, Haspolat-Nicosia 99258, Turkish Republic of Northern Cyprus, Turkey
4 Department of Petroleum Engineering, Abadan Faculty of Petroleum Engineering, Petroleum University of Technology (PUT), Abadan, Iran; akmanshad113@gmail.com
5 School of Chemical Engineering, College of Engineering, Universiti Teknologi MARA, Shah Alam 40450, Selangor, Malaysia
* Correspondence: erfan.m@nepu.edu.cn or erfan.723@gmail.com (E.M.); nroslina@uitm.edu.my (N.R.R.); Tel.: +90-5338803246 (E.M.); +60-194882109 (N.R.R.)



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**Abstract:** Understanding the carbon dioxide ($CO_2$) solubility in formation brines is of great importance to several industrial applications, including $CO_2$ sequestration and some $CO_2$ capture technologies, as well as $CO_2$-based enhanced hydrocarbon recovery methods. Despite years of study, there are few literature data on $CO_2$ solubility for the low salinity range. Thus, in this study, the solubility of $CO_2$ in distilled water and aqueous ionic solutions of NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$ were obtained in a low salinity range (0–15,000 ppm) at temperatures from 298–373 K and pressures up to 20 MPa using an accurate and unconventional method called potentiometric titration. An experimental data set of 553 data points was collected using this method. The results of the experiments demonstrate that increasing pressure increases the solubility of $CO_2$ in various brines, whereas increasing temperature and salinity reduces the solubility. The role of different ions in changing the solubility is elaborated through a detailed discussion on the salting-out effect of different ionic solutions. To verify the experimental results of this research, the solubility points obtained by the potentiometric titration method were compared to some of the well-established experimental and analytical data from the literature and a very good agreement with those was obtained.

**Keywords:** $CO_2$ solubility; $CO_2$ sequestration; ionic liquids; potentiometric titration; aqueous solutions

## 1. Introduction

It is unanimously accepted that global warming and its dire consequences have become a serious problem for the whole world. Carbon dioxide ($CO_2$), which accounts for over 62% of all greenhouse gases, has a significant impact on global warming [1]. The primary source of $CO_2$ emissions is anthropogenic activities, as well as deforestation due to land clearing and a number of production and resource extraction processes [2]. The use of fossil fuels as the main source of energy increases the level of $CO_2$ in the atmosphere. According to Apadula et al. [3], $CO_2$ concentration in the atmosphere gradually increases with the growth rate of $2.05 \pm 0.03$ ppm/year. The key mechanism for mitigating the greenhouse effect is to considerably lower $CO_2$ emissions into the atmosphere. Various methods have been proposed to reduce $CO_2$ concentration in the atmosphere, such as sequestration of $CO_2$ in subsurface formations (mature hydrocarbon reservoirs, coal beds and aquifers), injection to oceans and $CO_2$ capture via mineral carbonation [4]. Among these options, deep saline aquifers are seen as promising storage sites for $CO_2$, as they can serve as large storage capacities and are common throughout the world. The technological and economic feasibility of $CO_2$ sequestration in aquifers is proven via a number of experimental and theoretical studies. However, the detailed mechanisms of sequestration of $CO_2$ to aquifer parts of mature hydrocarbon files and saline aquifers are not yet well established. Consequently, many uncertainties remain in terms of the efficiency of different $CO_2$ sequestration methods, as well as the safety of the operation due to the relatively high risk of leakage. The phase behavior of $CO_2$ in contact with the aqueous phase and the solubility of $CO_2$ in the aqueous phase are very important for assessing the effectiveness of this method. Moreover, the influence of reservoir conditions, such as reservoir pressure and temperature, brine composition and salinity, on $CO_2$ dissolution are some of the key factors that must be carefully evaluated when planning any $CO_2$ sequestration project [5]. In addition, the solubility of $CO_2$ in formation brines is of great importance for the application of various $CO_2$-based enhanced oil recovery (EOR) techniques. Accurate measurement of the solubility of $CO_2$ in brine helps to more accurately predict the amount of $CO_2$ available to interact with and mobilize reservoir oil [6]. There are many experimental studies on the solubility of carbon dioxide in deionized water in the literature. The measurement of the solubility in aqueous solutions of NaCl, $MgCl_2$ and $CaCl_2$ is also considered in some of the previous studies [7,8]. However, experimental data for the combination of aqueous salt solutions under conditions of interest for $CO_2$ sequestration are scarce. Table 1 provides a summary of previous experimental studies on the solubility of $CO_2$ in various brines.

Carroll et al. [7] comprehensively studied the solubility of $CO_2$ in water in the low-pressure range. They regressed Henry's constant equation on the experimental dataset from their previous studies. Later, numerous experimental studies on the solubility of $CO_2$ in pure water, aqueous solutions and seawater were carried out [9–14]. Prutton and Savage [15] carried out a detailed study on the solubility of $CO_2$ brines saturated with $CaCl_2$ in a wide range of thermodynamic conditions of salinity, temperature and pressure. However, their results were limited to a maximum temperature of 393 K. Malinin [16] studied the solubility of $CO_2$ in $CaCl_2$-saturated brines at temperatures above those encountered under conditions of interest for $CO_2$ injection/sequestration; in addition, all data provided by this author are limited to one salt molality (1 mol.kg$^{-1}$). Malinin and Saveleva [17] and Malinin and Kurovskaya [18] studied the solubility of $CO_2$ in an aqueous solution of $CaCl_2$ throughout a wide temperature and salinity range, but all tests were conducted at a low pressure, 4.795 MPa. Liu et al. [19] studied the solubility of $CO_2$ in $CaCl_2$ solutions at low temperatures (318 K) and Bastami et al. [20] studied the solubility of $CO_2$ in $CaCl_2$ solutions with two different salinities (1.9 and 4.8 mol.kg$^{-1}$), at temperatures up to 375 K. Zhao et al. [21] investigated $CO_2$ solubility in 0.33–2 mol.kg$^{-1}$ NaCl brine at temperatures of 323, 373 and 423 K, but only at a pressure of 15 MPa. A volumetric technique was utilized to test solubility in all three studies.

Apart from the experimental approaches, various theoretical methods were used to estimate the solubility of $CO_2$ at different conditions. Gilbert et al. [22] estimated $CO_2$ solubility in Bravo Dome and two other brines using a different correlation. Based on Pitzer's electrolyte theory, Shi and Mao [23] constructed a model to estimate $CO_2$ solubility in aqueous NaCl. Venkatraman et al. [24] proposed a method for estimating the solubility of $CO_2$ in various salts, including NaCl, $CaCl_2$ and KCl. Menad et al. [25] implemented a neural network with a radial basis function that was improved using various optimization algorithms to determine the solubility of $CO_2$ in brine. Mohammadian et al. [26] accurately estimated $CO_2$ solubility in NaCl and distilled brine using a data-driven approach (extreme learning machine). At temperatures as high as 473 K and pressures as high as 50 MPa, Tong et al. [27] developed a synthetic approach based on the quantitative determination of solvent masses and the visual observation of phase transitions. In a mixed NaCl/KCl brine, $CO_2$ solubility data are shown at 14 points of state, 36 points in $CaCl_2$ and 38 points in $MgCl_2$. The findings greatly broaden the range of conditions in which $CO_2$ solubility in these brines may be determined (temperature, pressure and molality). Furthermore, the results demonstrate that $CO_2$ solubility in $CaCl_2$ and $MgCl_2$ brines of the same molarity are, in fact, very close. Drummond [28] experimentally measured numerous $CO_2$ solubilities in NaCl-saturated brines. The latter is among the most complete experimental database of solubility; however, since several presumptions were used to calculate the solubility, the accuracy of the data is dubious.

The majority of previous studies on $CO_2$ solubility in literature assumed NaCl is the only constituent of formation brines. However, there are many brine formations around the world in which a considerable number of other salts, such as $MgCl_2$ and $CaCl_2$, can be found [22,27]. Furthermore, despite years of prior research on $CO_2$ solubility in ionic liquids over a wide range of pressures, temperatures and salinity (see Table 1), there are still research gaps that need to be filled. While a wide range of salinity has been explored in the literature, evidence on solubility in the low salinity region is scarce, for example, in the range from 0 ppm to 15,000 ppm (from 0 to 0.258 mol.kg$^{-1}$) brine salinity. The Sabah basin, off the coast of Peninsular Malaysia, contains such geological formations, with a mean salinity of roughly 10,000 ppm (0.17 mol.kg$^{-1}$) [29]. As a result, one of the goals of this study is to develop a study on solubility applicable to the injection of $CO_2$ into low salinity subsurface formations.

This study uses an unconventional solubility measurement method, i.e., potentiometric titration, to determine the solubility of $CO_2$ in brine. The technique described above is typical in chemical engineering, although it is rarely employed in research on $CO_2$ sequestration/injection into subsurface formations. Furthermore, because there is a scarcity of data in the literature on $CO_2$ solubility in brines with low salinity, in this study, the solubility of $CO_2$ was computed in brines saturated with NaCl, $CaCl_2$, $MgCl_2$ and $MgCl_2$ + $CaCl_2$ in the low salinity range of 0–1.5 wt.%. The salting-out effect, which is a measure of decreasing solubility by increasing salinity, is studied in depth. Although the findings of the current study are mainly aimed at $CO_2$ sequestration projects, such as $CO_2$ injection into subsurface formation, the results could be of importance for other applications, such as $CO_2$ capture technologies [30], $CO_2$ mineral carbonation [31] and food industry [32].

**Table 1.** Experimental data available in the literature on the solubility of $CO_2$ in deionized water and aqueous solutions of single and mixed salts.

| Temperature (K) | Pressure (Mpa) | Aqueous Phase | Experiment Method | Ref. |
|---|---|---|---|---|
| 298–448 | Up to 18 | Deionized water | Designed new analytical apparatus | [33] |
| 283–363 | Up to 13 | Deionized water | Developed high pressure cell; cubic-plus-association and the RKSA-Infochem EOS were used to estimate $CO_2$ solubility | [34] |
| | | Single salt aqueous solutions | | |
| 323–373 | Up to 20 | NaCl solution | Designed new customized mixing unit; measuring heat of mixing of a supercritical gas was used to estimate $CO_2$ solubility | [35] |
| 323.15–423.15 | Up to 15 | NaCl solution | New PVT cell designed; activity coefficient osmotic coefficients were estimated from Pitzer's model to accurately measure $CO_2$ solubility | [21] |
| 323.15–423.15 | Up to 20 | NaCl solution | A simple analysis method was developed to obtain solubility points at different pressures and temperatures | [36] |
| 323.15–423.15 | Up to 18 | NaCl solution | Designed new analytical apparatus; asymmetric $(\gamma - \varphi)$ approach was used to model the phase behavior of the two systems, with the Peng–Robinson equation of state and the electrolyte NRTL solution model | [10] |
| 303–333 | 10–20 | NaCl solution | The solubility was estimated by measuring the mass of the sample and the pressure of the dissolved gas; an equation was developed to predict $CO_2$ fraction in solution as a function of temperature, pressure and mass fraction | [10] |
| 323–413 | 5–40 | NaCl solution | High-pressure PVT apparatus was designed; two models were used in the Eclipse simulator—the correlations of Chang et al. and the Søreide and Whitson EoS model | [37] |
| 333.15–373.15 | Up to 25 | NaCl solution | Unconventional potentiometric titration method to determine the solubility of $CO_2$ | [4] |
| 333.15 | Up to 40 | NaCl solution | Titration method to determine the solubility of $CO_2$ | [6] |
| 308–424 | Up to 40 | $CaCl_2$ solution | Designed new analytical apparatus | [27] |
| 328.15–375.15 | 6.89–20.68 | $CaCl_2$ solution | High-pressure cylinder used to measure $CO_2$ solubility; the modified model was developed by refitting interaction parameters | [20] |
| 323–423 | 15 | $CaCl_2$ solution | A high-pressure cylinder was used to measure $CO_2$ solubility; the fugacity-activity procedure was used for modeling and extended to take into account the effect of different types of salts on the solubility of $CO_2$ at different temperatures, pressures and salt concentrations | [21] |
| 333.15 | Up to 40 | $CaCl_2$ solution | Titration method to determine the solubility of $CO_2$ | [6] |
| 308–424 | Up to 40 | $MgCl_2$ solution | Designed new analytical apparatus | [22] |

**Table 1.** *Cont.*

| Temperature (K) | Pressure (Mpa) | Aqueous Phase | Experiment Method | Ref. |
|---|---|---|---|---|
| | | Mixed salts aqueous solutions | | |
| 308–408 | Up to 40 | $Na^+$, $Ca^{2+}$, $Mg^{2+}$, $Cl^-$, $HCO^{3-}$, $Fe^{2+}$, $SO_4^{2-}$ | Apparatus based on the static approach was prepared; Duan model and e PR–HV model were used to predict $CO_2$ solubility | [38] |
| 308–328 | Up to 16 | NaCl + KCl + $CaCl_2$ | High-pressure cylinder used to measure $CO_2$ solubility; solubility was obtained from the amount of liquid sample and $CO_2$ in the sample. | [19] |
| 308–424 | Up to 40 | $CaCl_2$ + $MgCl_2$ | Designed new analytical apparatus | [27] |
| 332 | 29 | $Ca^2$+, $Mg^{2+}$, $Na^+$, $K^+$, $Fe^{2+}$, $Cl^-$, $SO_4^{2-}$ | PVT apparatus was designed; a correlation in the literature was used to predict the solubility of $CO_2$; a simple method for determining the density of aqueous solutions of $CO_2$ is recommended. | [39] |
| 268–298 | 1.0–4.5 | NaCl + $MgCl_2$ + $MgSO_4$ + $CaCl_2$ + KCl + $NaHCO_3$ + NaBr | Distilled the $CO_2$ out of the sample, absorbed it in an excess of standard $Ba(OH)_2$ and back-titrate the excess base | [40] |

RKSA, Redlich Kwong-Soave equations of state; PVT, Pressure volume temperature; NRTL, Non-random two-liquid model; PR–HV, Peng–Robinson and Huron–Vidal equation of state.

## 2. Materials and Methods

### *2.1. Materials*

SIGTM provided $CO_2$ (purity > 99.9%), which was used in all of the experiments. The brines of salinity and composition were made with distilled and deionized water (Milli-Q filter) with a resistance of 18.20 ohms. Systerm$^{TM}$ provided NaCl, $MgCl_2$ and $CaCl_2$ with a mass fraction purity of 0.99. No further purification or alternation was performed on the chemicals. NaOH and HCL were used with a purity of 99.7 and were purchased from Emsure$^{TM}$. The reactor was made of stainless steel with a pressure rating of 45 MPa and a temperature rating of 400 K. It also had sufficient resistivity towards corrosive materials it might have come in contact with during the experiments.

### *2.2. Experimental Methods*

Figure 1 depicts a schematic of the experimental setup used in this investigation. A Teledyne ISCO pump, a $CO_2$ bottle and a 0.1 L autoclave reactor with a magnetic stirrer were the key components. An electric heater was used to keep the reactor warm. A dip tube was attached to a floating piston sampler made locally and powered by a med$^{TM}$ syringe pump. An immersion tube was used to sample the $CO_2$-saturated saline solution. An ISCO pump regulated the pressure in each experiment. The reactor was equipped with a temperature jacket with an accuracy of 273.25 K according to the instructions for use of the device. Despite the 0.85 cm thickness of the reactor's base, a proper "connection" between the magnetic stirrer and the stirrer ball was accomplished, resulting in a well-mixed solution. The brine was poured into the reactor and warmed to the desired temperatures. $CO_2$ was then supplied at the desired pressure into a warmed reactor containing 70 mL of brine. After that, the reactor's inlet and outlet valves were closed and the solution was stirred for 3 h until it achieved equilibrium. Equilibration times have been observed to range from 10 min to 24 h in previous studies [41]. Thereafter, the bottom valve in the reactor was gently opened to minimize the pressure change in the reactor. An immersion tube was used to transport a sample of $CO_2$-saturated brine from the reactor to the sampling chamber, which had a floating piston. As soon as the sample entered the chamber, it reacted with the 0.5 M NaOH solution, filling half of the chamber.

The sampling cylinder was half-filled with brine that was later removed to let the $CO_2$ saturated sample from the reactor be mixed with the NaOH solution via a syringe pump. Because there was an abundance of NaOH in the solution, it dissolved all types of carbon particles and converted them to carbonates, resulting in no bubble gas [41]. The sample was then titrated with hydrochloric acid (HCl) until it reached the equivalency points. Once the endpoint of the reaction was reached, the volume of titrant was measured and the solubility of $CO_2$ was calculated using Equation (1):

$$C_a = \frac{C_t \times V_t \times N}{M_a} \tag{1}$$

where $C_a$ is the analyte concentration (solubility of $CO_2$) in the brine (in mol.kg$^{-1}$), $C_t$ is the titrant concentration (in mol.L$^{-1}$), $V_t$ is the volume of titrant (mL), N is the molar ratio of analyte and reactant from a balanced chemical equation and $M_a$ is the mass of the sample to be titrated (grams). The advantage of utilizing the solution mass rather than the solution volume $V_a$, as has been performed in many earlier research studies, is that the mass of the solution is not affected by temperature or pressure. As a result, the calculation of solubility is less ambiguous. The titrant was (0.5 M) HCl, which was utilized to react in a 5 mL sample. The pH of the sample was determined as a function of the titrant volume given and the titration was maintained until the pH reached values below 2; plotting the derivative of HCl volume versus pH yielded equivalence points. In addition to the technical simplicity, another benefit of this method compared to previous methods by which the solubility is measured is that the preservation of the samples inhibits the loss of $CO_2$ because of the degassing during the depressurization phase. Moreover, in contrast to previous research studies, the potentiometric method, unlike a number of previous methods, does not depend on any additional parameters, such as fugacity, density, or volatility, to be able to estimate solubility accurately.

To ensure repeatability and accuracy of the results, several experiments were repeated 3 times. The errors in the measurements were found to be 0.9–7.8%. As expected, the highest error occurred with the measurements near atmospheric pressure (0.1 MPa), regardless of the temperature, salinity and type of brine. The errors were markedly lower when the pressure in the experiments exceeded 0.2 MPa. The reason for this phenomenon was that the very low values of $CO_2$ solubilities close to atmospheric pressure were in the order of a thousandth of mol/kg, as compared to solubility values at higher pressures. Therefore, these low values could not be accurately detected using the experimental method used in this study. It is noteworthy that the focus of our study was the solubility of $CO_2$ in subsurface formations; in those scenarios, $CO_2$ is often injected at high pressures, hence it is in liquid or supercritical fluid state [42]. Therefore, near-atmospheric measurements are of a little significance for the aforementioned applications.

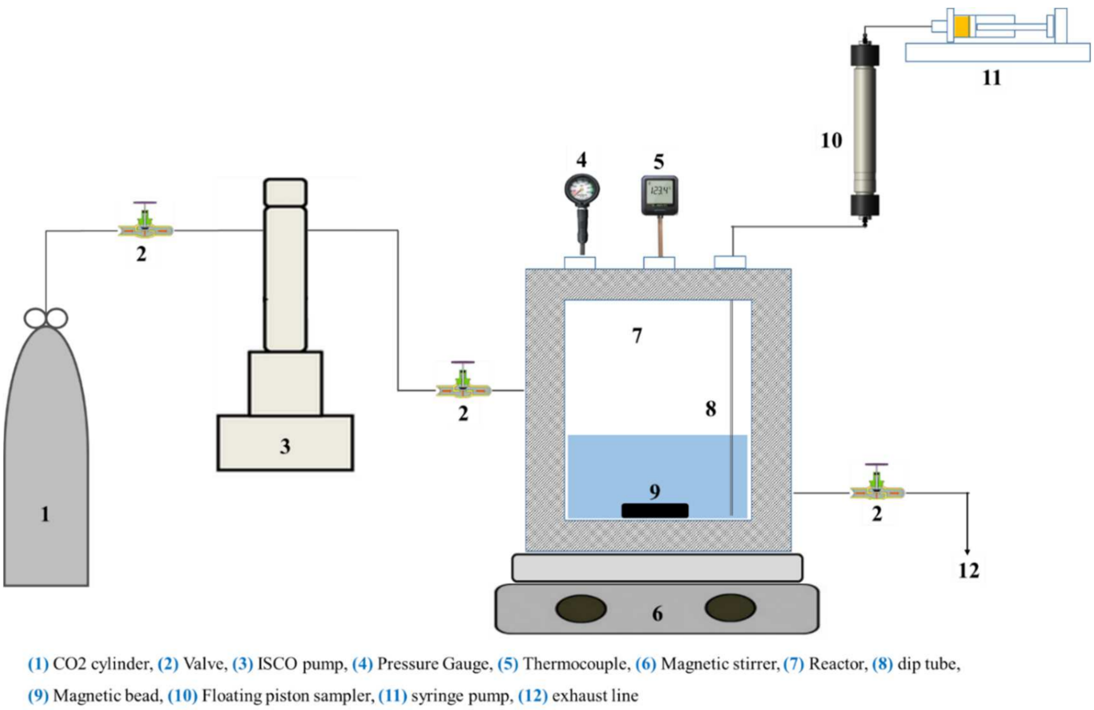



**Figure 1.** The experimental setup used for solubility measurements.

## 3. Results

Despite the fact that there have been several investigations on $CO_2$ solubility in various liquids, evidence in the low salinity range is limited. As a result, the impact of pressure change on $CO_2$ solubility was investigated under a variety of conditions in the current study. The experiments were carried out at pressures ranging from 1 to 20 MPa and temperatures ranging from 298 to 373 K. Furthermore, the experiments were carried out in a saline solution of different values of salinity (0–15,000 ppm) to confirm the reliability of the results under conditions more representative of $CO_2$ injection to subsurface formations (aquifers and hydrocarbon reservoirs). Likewise, the solubility of $CO_2$ in distilled water was tested under identical temperature and pressure conditions (1–20 MPa, 298–373 K). The outliers in the solubility databank, i.e., data with unusually high or low values, were identified through analyzing the z-score of the data points. The data points with unusually high or low values were treated as outliers and hence removed from the database using the z-score method that was applied with SPSS 18TM. The abnormal solubility data points were mostly caused by the rapid opening of the sampling valve, which resulted in a significant pressure decrease in the solution and subsequent supercritical $CO_2$ breakthrough.

### *3.1. Impacts of Pressure and Temperature on the Solubility*

$CO_2$ solubility in distilled water, NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$ is shown in Figure 2 in four different temperature series, namely, 298, 333, 353 and 373 K, respectively. It can be seen, from the figures, that increasing the pressure increased the solubility of $CO_2$ in the brine, irrespective of the type of ionic solution and temperature. In addition, it is apparent, from the figures, that the pressure dependence of carbon dioxide decreased with increasing the pressure in all temperature series. However, in this study, the points at which the solubility would become entirely unresponsive to pressure were not observed. The same effect (pressure insensitivity at higher pressures) was reported for pressure around 30 MPa by previous researchers who used different solubility measurement methods at different temperatures, pressure and salinities [11,27]; however, as the highest point of solubility measurement in this study was 20 MPa, the point of pressure insensitivity was not observed.

The effect of pressure on solubility can be expressed using Henry's law of solubility (partial pressures) [43]. According to Henry's Law, the partial pressure of the gas above the solution determines the solubility of the gas in the water. Because the concentration of molecules in the gas phase increases as pressure increases, the concentration of dissolved gas molecules in the solution at equilibrium also increases. When a gas is introduced to a system that is primarily made up of brine (solvent), some of the gas molecules collide with the liquid's surface and dissolve. When the concentration of dissolved gas molecules rises to the point where the rate at which gas molecules escape into the gas phase equals the rate at which it dissolves, dynamic equilibrium is reached. As the gas pressure rises, the amount of gas molecules per unit volume rises, increasing the rate at which gas molecules collide with the liquid's surface and dissolve. The concentration of dissolved gas rises as more gas molecules dissolve at higher pressures, until a new dynamic equilibrium is reached [43].

When it comes to the effect of temperature, it can be seen that, as the temperature rose, the solubility decreased. $CO_2$ solubility in NaCl is 1.421 mol kg$^{-1}$ at 10.33 MPa and 298 K, whereas it is 1.037 mol kg$^{-1}$, 0.877 mol kg$^{-1}$ and 0.788 mol kg$^{-1}$ at the same pressure and 353 K, 353 K and 373 K, respectively. In other words, there is a decrease in solubility of 27%, 38% and 44.54% as the temperature rises to 333 K, 353 K and 373 K from the initial value of 298 K. Previous researchers have also reported a decrease in the solubility with the increase in the temperature [12,44,45]. Le Chatelier's law could explain the reduction in solubility at higher temperatures. $CO_2$ dissolves in brine due to the interactions of the molecules of solute with those of solvents. The process of dissolving $CO_2$ in brine is exothermic ($\Delta$H reaction < 0), which implies that heat is produced as new attractive contacts arise as a result of the dissolution process [35]. According to the principle of Le Chatelier, if the system is heated, since this is an exothermic reaction, the system shifts towards the reactant's side to neutralize the applied stress, which is the rise in the temperature. The kinetic energy of a system increases as the temperature rises. As the temperature rises, this causes a more rapid motion among the molecules and the breakage of intermolecular bonds, allowing molecules to escape to the gas phase from the solution [46]. As a result, independently from pressure, type of ion in the brine, or brine salinity, increasing the temperature decreased the solubility in this set of experiments.

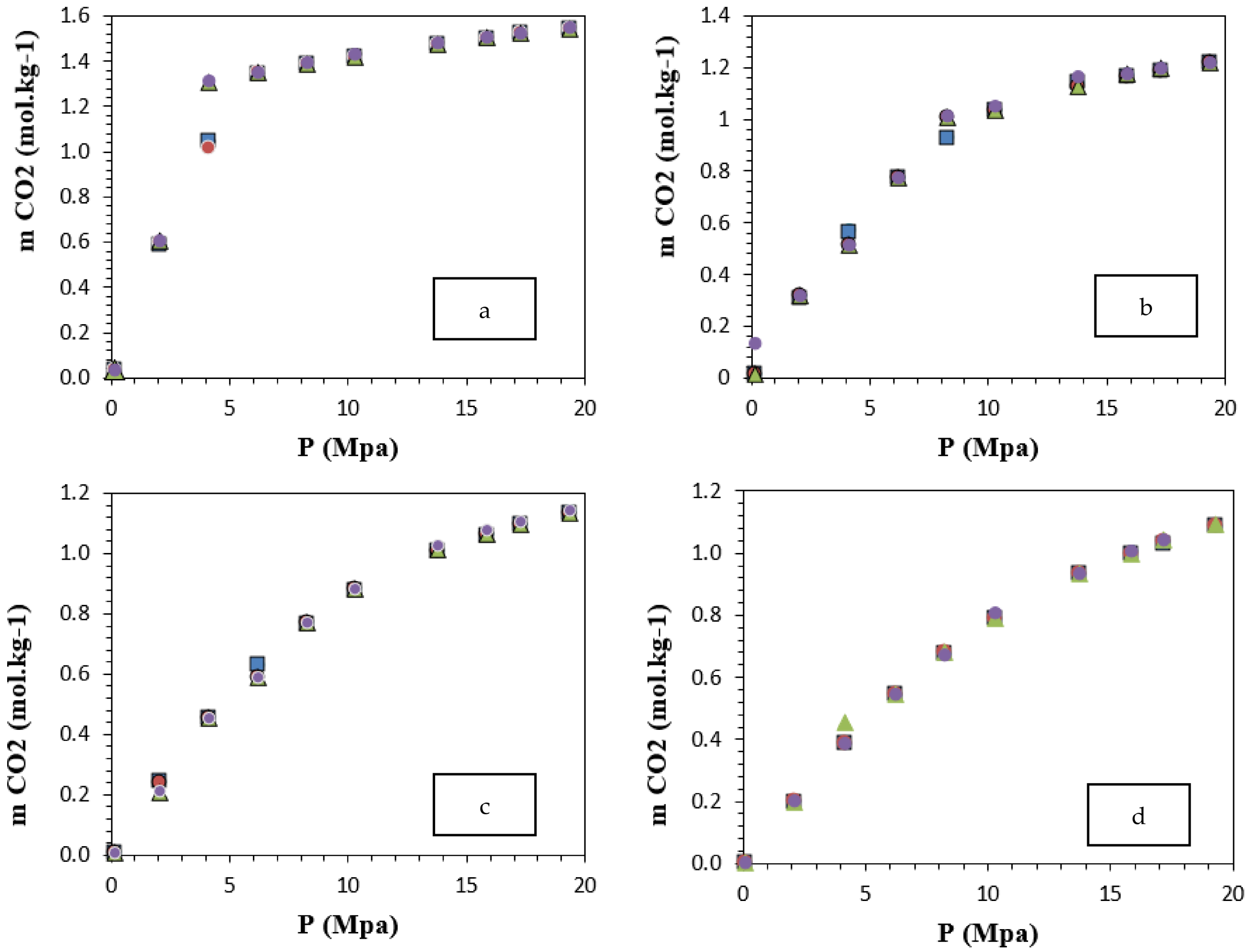



**Figure 2.** Solubility of carbon dioxide in (•)distilled water and 1000 ppm of (■) NaCl, (•) $MgCl_2$, (▲) $CaCl_2$ and (•) $MgCl_2$ + $CaCl_2$ at (**a**) 298 °K, (**b**) 333 °K, (**d**) 353 °K and (**d**) 373 °K versus pressure.

### *3.2. Effects of Salinity on $CO_2$ Solubility*

The solubility of $CO_2$ versus pressures at 0, 1000, 10,000 and 15,000 ppm in NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$ solutions at 298 K is shown in Figure 3. Figure 3 shows the reduction in $CO_2$ solubility in formation brine as the salinity increased at various pressures and temperatures for all types of aqueous solutions employed in the current study. The solubility of $CO_2$ decreased by 1% with an increase in the salinity from 0 to 1000 ppm for brine solutions in the experiments conducted in this work, while a decrease in the solubility of 3–6% was found with a factor of 10 increase in brine concentration (from 1000 to 10,000 ppm). Moreover, increasing the brine concentration from 10,000 to 15,000 ppm resulted in a 4–5% decrease in $CO_2$ solubility. The range of reduction in solubility as the salinity increased is in line with those reported in the literature when pressure and temperature were set in the same range of this study [6,25,47].

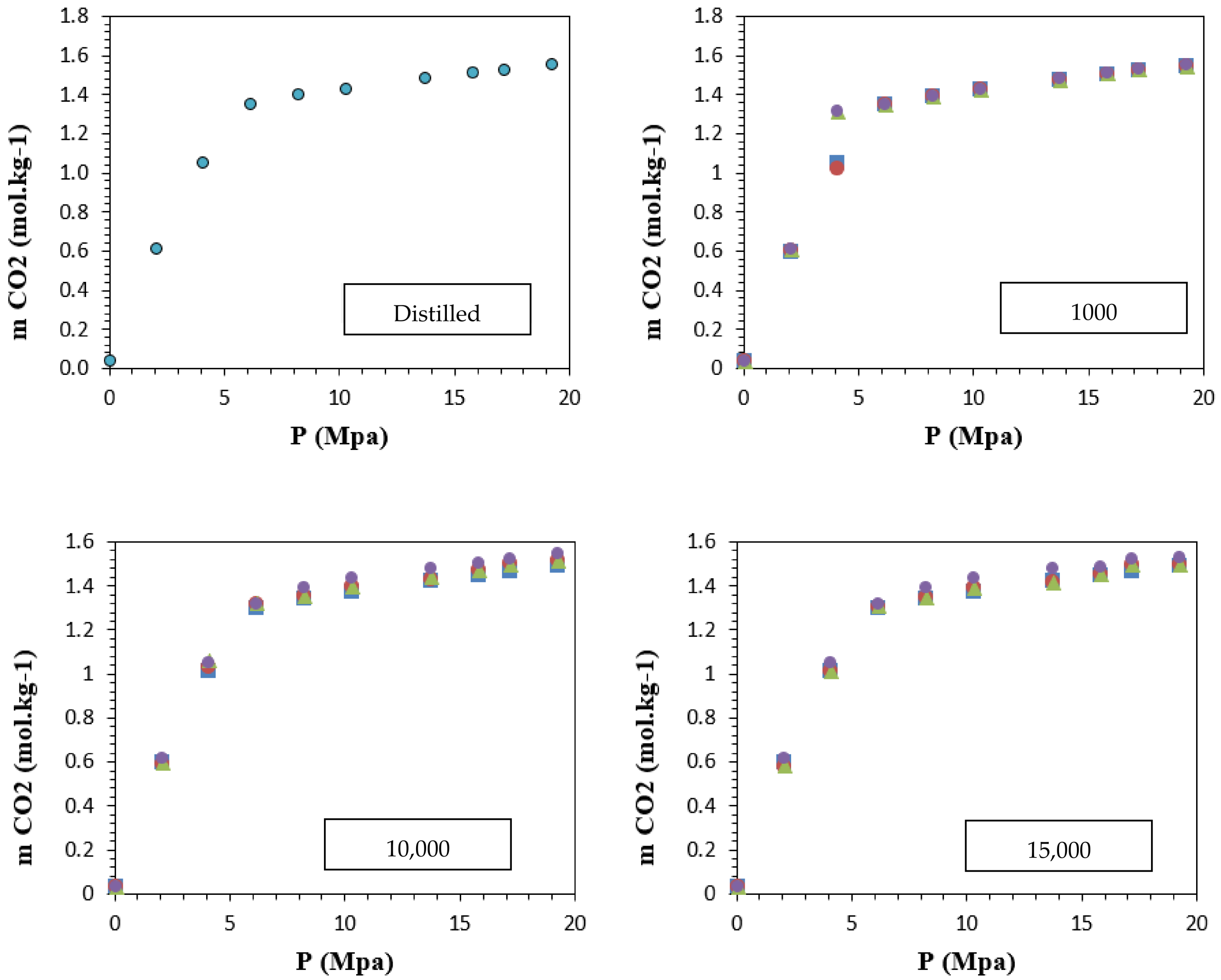



**Figure 3.** Solubility of carbon dioxide in distilled water and various salinity of (■) NaCl, (•) $MgCl_2$, (▲) $CaCl_2$ and (•) $MgCl_2$ + $CaCl_2$ at 298 °K versus pressure.

The decrease in the solubility can be explained by the fact that when salt ions such as NaCl, $MgCl_2$ and $CaCl_2$ are added to water, they bind water molecules to "solvates", leaving less water for $CO_2$ to adhere to. In other words, the presence of water molecules in the solvation of ions significantly lowers $CO_2$ molecules' weak attraction to water/brine and displaces dissolved $CO_2$ from polar water. When solutes such as NaCl, $MgCl_2$ and $CaCl_2$ (or any combination of them) are present, the solubility of $CO_2$ in brine is greatly impacted. In reality, because of the enhanced salting-out effect, the solubility reduces as the salinity rises (the salting-out effect is discussed in detail in the next part of the results). Similar results can be observed in the previous studies in which different solubility measurement methods (such as depressurization) were used to measure $CO_2$ solubility in brines which were significantly more saline than the brine used in this study [37,45].

### *3.3. Salting-Out Effect*

As the concentration of dissolved solids in the brine rises, the salting-out effect reduces $CO_2$ solubility in aqueous solutions (in this case, brine). The effect is significant because it aids in quantifying the decrease in $CO_2$ solubility as salinity rises. Studies on the hydration of ions and the interaction of ions with water molecules have shown that, at a high density, smaller ions tend to bind the molecules of water more effectively, while larger ions with a low charge density bind the water molecules weakly [48,49]. Therefore, high charge density ions have a robust impact on the structure of the water, which governs the ability of the brine to dissolve higher amounts of $CO_2$. The experiments show that, if two single-salt aqueous solutions have the same electrolyte type and share the same anion (e.g., $Cl^-$), the cation with a higher charge density (smaller radius and grater charge) has a greater salting-out effect on dissolved $CO_2$ than the cation with a lower charge density (larger radius and lower charge). For instance, $Mg^{2+}$ has a charge density that is a little higher than that of $Ca^{2+}$ (they have the same charge number, but $Mg^{2+}$ has a smaller radius than $Ca^{2+}$) [50]; hence, the amount of $CO_2$ dissolved in aqueous $MgCl_2$ is less than that in aqueous $CaCl_2$ at the same ionic strength. The solubility of $CO_2$ in an aqueous solution of NaCl follows a similar pattern. Because $Na^+$ has a lower charge density than $Mg^{2+}$, $CO_2$ is substantially more soluble in aqueous NaCl solutions than aqueous $MgCl_2$ solutions [21].

Figure 4 depicts the salting out effect in NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$ solutions with concentrations ranging from 1000 to 15,000 ppm, at pressures ranging from 1 to 20 MPa and temperatures of 298 K. Equation (2) was used to calculate the percentage of salting-out effect (S-O%).

$$S - O\ (\%) = \left[\frac{x_{Dw} - x_b}{x_{Dw}}\right] 100 \tag{2}$$

where S-O (%) is the salting out percentage, $x_{Dw}$ is $CO_2$ solubility in distilled water and $x_b$ is $CO_2$ solubility in any brine. Figure 4 shows that, at a 1000 ppm salinity, there was no substantial change in solubility. As a result, in low-salinity brine, the salting-out effect is insignificant. The salting-out effect, on the other hand, increased as the concentration of solids in the brine rose. The maximum percentage of S-O is found in the 15,000-ppm data series, where the effect reached 6–9% for all solutions at lower pressures, whereas the lowest percentage of S-O is found in brine with a concentration of 1000 ppm, where S-O fluctuated between 0.25% and 0.65%. This result is in line with the findings of Tong et al. [27], who found that increasing the temperature enhances the salting-out effect, while increasing the pressure tends to diminish it.

### 3.4. Comparison of Experimental Results with Previous Studies

The $CO_2$ solubility data points obtained using the potentiometric titration method were compared with literature data obtained well-established methods under similar conditions to examine the accuracy of the findings of the experimental method used in this study, even though the data points obtained under the same conditions of pressure, temperature and, specifically, salinity (low salinity range) were very limited. As shown in Figure 5, the experimental results of this study are in good agreement with those obtained in previous studies using more common solubility measurement methods, such as depressurization or combinations [37] and depressurization [39] methods. In Figure 5, the solid lines indicate a regression line drawn based on the data obtained in the current study and error bars indicate a 5% difference from the experimental data of this study.

The data points obtained by Duan and Sun [12] and Li et al. [39] were measured at 323 K and 332 K, respectively. The difference among the results obtained in this study, Duan and Sun's and Lee et al.'s, is most likely due to the difference in the experimental temperature in our study, which was 333 K vs. 323 K and 332 K in Duan and Sun and Li et al., respectively. Furthermore, as shown in Figure 5, comparing the measurement data from this investigation with the data from Cruz et al. [6] supports the accuracy of the solubility points obtained in this work. As a result, the potentiometric titration method produces reliable results and could be used as an alternative to some of the previous complex and often expensive methods required to accurately measure $CO_2$ solubility in a condition representative of $CO_2$ injection/sequestration to subsurface geological formations, such as aquifers and mature hydrocarbon fields.

There is a scarcity of experimental data in a similar range of pressure, temperature, salinity and composition, making it impossible to compare the findings of this work with other studies. For two $MgCl_2$ and $CaCl_2$ brines, Figure 6 shows a comparison of the solubility results from this study with solubility estimates from Duan and Sun's (2003) theoretical model. Figure 7 also illustrates the parity-plot at the same conditions of pressure, temperature, salinity and brine type. The solubility values between the two models are almost perfectly in agreement in both brines, with a coefficient of correlation of more than 99% ($R^2 > 0.99$).

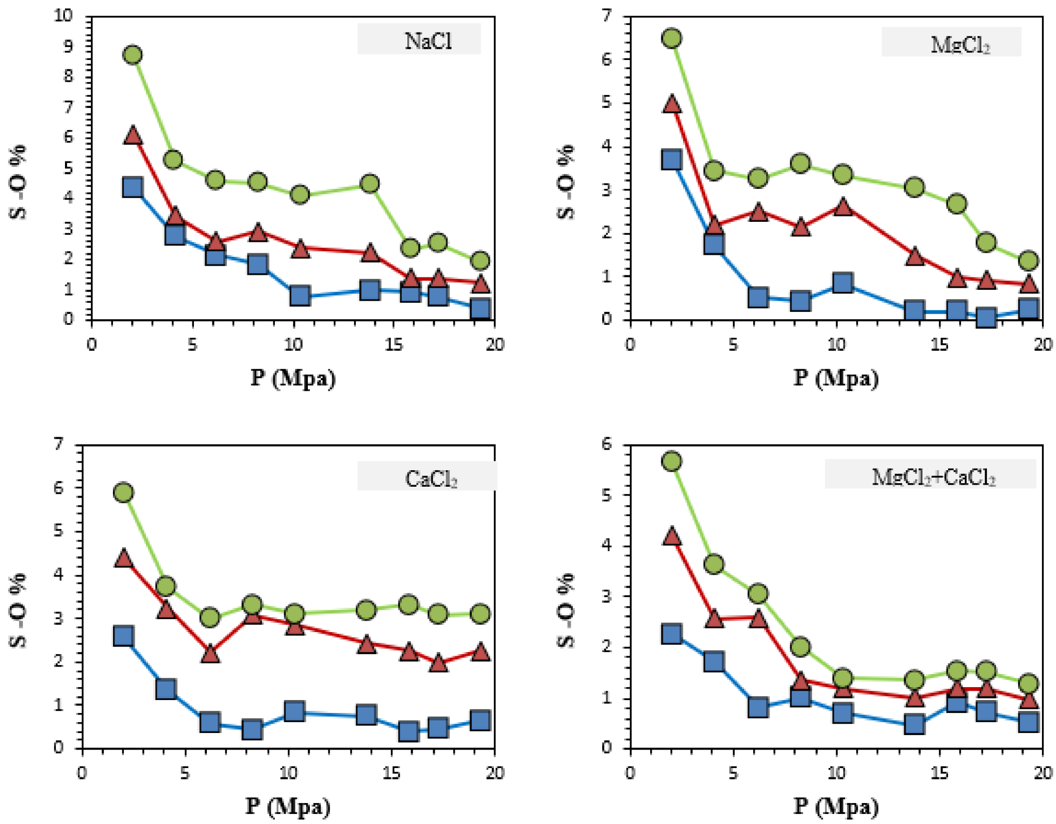



**Figure 4.** Salting-out effect of NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$ brine of (■) 1000 ppm, (▲) 10,000 ppm and (●) 15,000 ppm at 298 °K versus pressure.

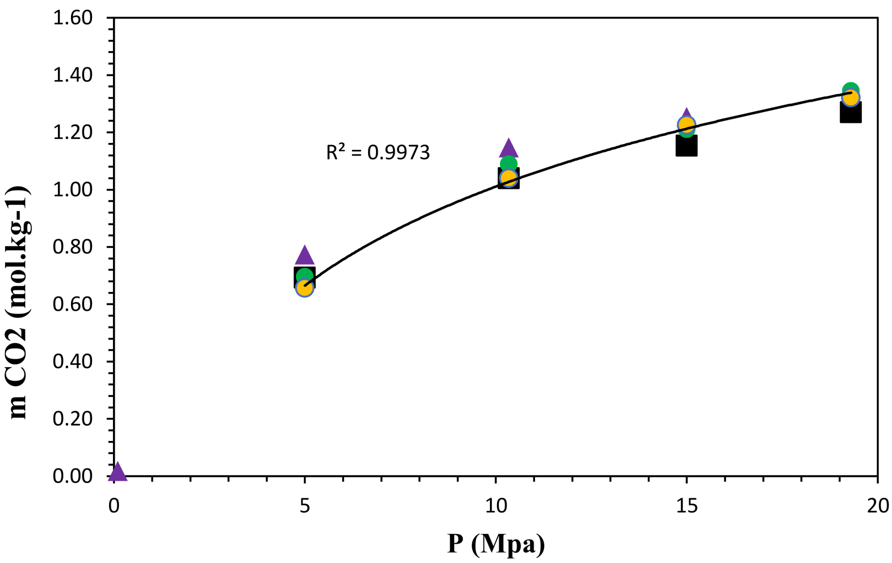
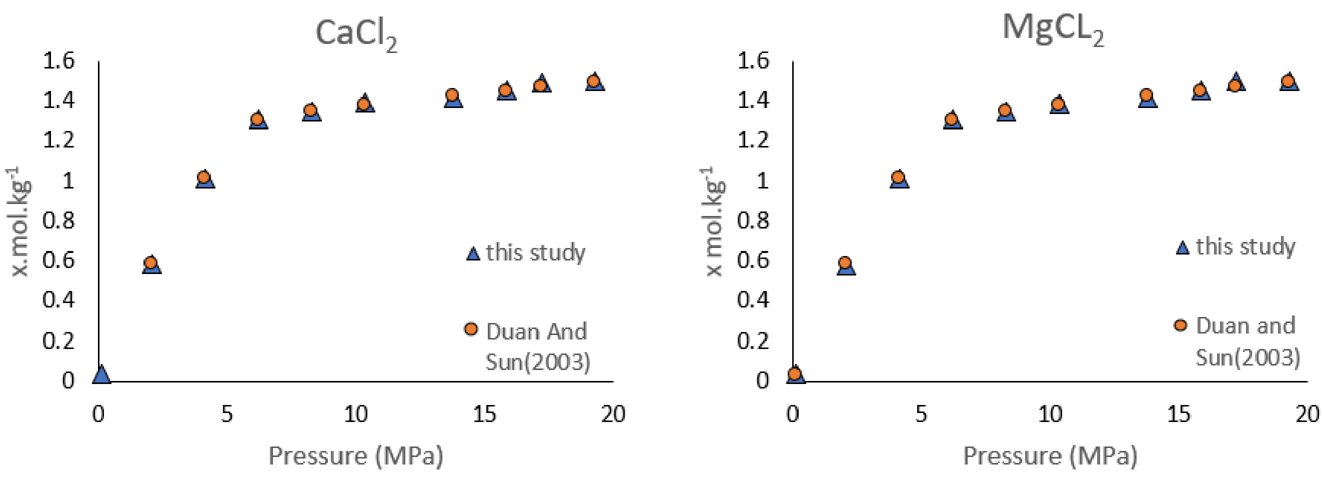
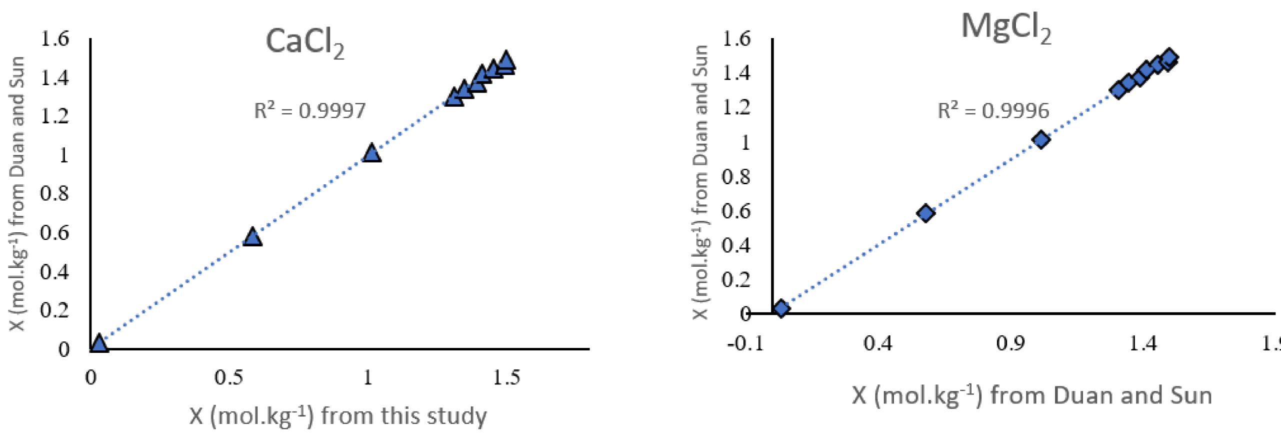



**Figure 5.** Comparison of the results of this study for $CO_2$ solubility (●) with the results of Lara et al. [6] (■), Duan and Sun [11] (▲) and Li et al. [39] (●) in distilled water (zero salinity) at 333 °K. The solid line represents the regression line fitted from the current solubility study.




(**a**) (**b**)

**Figure 6.** Comparison of Solubility of $CO_2$ in (**a**) $CaCl_2$ brine and (**b**) $MgCl_2$ at 298 °K.




(a) (b)

**Figure 7.** Parity-plots of solubility values obtained for $CaCl_2$ (**a**) and $MgCl_2$ (**b**) brines of this study and those obtained from Duan and Sun (2003) models.

### *3.5. Field Implications and Recommendations for Further Studies*

The impacts of pressure, temperature, salinity and brine composition are elaborated in the previous sections of this study. In geological formations, the salinity increases with depth. Since the solubility reduces with the increase in the salinity (irrespective of the type of salt), it can therefore be concluded that, in deeper geological formations, the contribution of the solubility mechanism weakens. Therefore, from point of view of $CO_2$ solubility mechanisms, shallower formations, or depositories with low salinities (such as hydrocarbon fields in the Sabah basin, offshore Sabah, Malaysia) would be more suitable for $CO_2$ sequestration, as larger amounts of $CO_2$ can be rendered immobile using the solubility mechanism. With regards to temperature, as shown in this study, the increase in temperature reduces the solubility of $CO_2$ in brine. Hence, it could be concluded, although only from the point of view of pressure, that deeper formations are more suitable, as the effects of temperature and salinity render the solubility mechanism less effective. The effect of pressure, on the other hand, is favorable on the solubility mechanisms. Hence, quantification of the impact of each parameter on the solubility needs to be conducted to find the optimum depth for sequestration. On the other hand, for enhanced oil recovery (EOR) applications, lower solubility of $CO_2$ in formation brines is more favorable for

$CO_2$-based EOR methods, as the amount of available $CO_2$ to interact with and eventually mobilize the residual oil is higher. Hence, it is recommended, for future studies, to address this issue by proposing a selection criterion for $CO_2$ sequestration, $CO_2$ injection and a combination of the two.

Moreover, in most studies focusing on $CO_2$ sequestration, $CO_2$ is considered to be 100% pure. This, however, is not often the case for practical scenarios in which $CO_2$ could be stemmed from different industries (such as gasification, post-combustion $CO_2$ capture, sour gas processing, or even recycled $CO_2$ from EOR operations) [51]. Moreover, it is not uncommon for natural $CO_2$ from subsurface formation to have associated gases. The $CO_2$ stream may contain several impurities, such as $H_2S$, $N_2$, Ar, etc. [51], and it might be economically and technically viable to consider $CO_2$ injection with no further purification. Therefore, it would be of great industrial importance to be able to study the solubility of $CO_2$ stream containing impurities, so that a more realistic estimation of the solubility mechanisms and, ultimately, sequestration efficiency can be made.

## 4. Conclusions

Using potentiometric titration, 553 data points of $CO_2$ solubility in various brines (NaCl, $MgCl_2$, $CaCl_2$ and $MgCl_2$ + $CaCl_2$) were obtained at temperatures ranging from 298 to 373 K and pressures up to 20 MPa. In comparison with earlier traditional procedures, the new method is shown to be reproducible and accurate. The findings are in good accord with those of prior studies at the same pressure, temperature, salinity and brine composition ranges (salt type). In terms of pressure, independently from the salinity of the brine composition, it is obvious that increasing the pressure increases $CO_2$ solubility in aqueous solutions. However, the pressure dependence of solubility decreased with the increase in the pressure, although, in this study, the point at which the solubility becomes completely independent from the pressure was not detected. The temperature has a reverse effect on the solubility; as the temperature increased, the solubility was significantly reduced, regardless of the salinity and the composition of the brine. Finally, increasing salinity also negatively affects solubility, though, at a low salinity, the effect was not so noticeable. However, the solubility decreased by over 6% as the salinity of brine increased from 0 to 15,000 ppm. Moreover, the effect of the presence of divalent and monovalent ions in brine is here discussed in detail with reference to the salting-out effect. Under the same conditions of pressure and temperature, both ion charge and ion radius were found to be influential factors in the solubility of $CO_2$ in brine. Lastly, the comparison of the experimental results obtained from the potentiometric titration method, as an unconventional method, with those of more conventional and well-established methods from the literature proved the method to be accurate and reliable.

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**Author Contributions:** Conceptualization, formal analysis, methodology, project administration, supervision, visualization and writing (original draft, review and editing), E.M.; data curation, formal analysis, visualization and software, B.S.M., A.K.M. and B.L.; supervision, validation, writing (review and editing), N.R.R. and M.O. All authors have read and agreed to the published version of the manuscript.

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