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Experimental Measurements of CO_2 Solubility in Aqueous $MgCl_2$ Solution at Temperature between 323.15 and 423.15 K and Pressure up to 20 MPa

ABSTRACT

Experimental CO_2 solubility data in brine at high temperatures and pressures are important for CO_2 capture and storage (CCS) applications. Many data has been acquired in single-salt aqueous solutions such as NaCl, $CaCl_2$ and Na_2SO_4. CO_2 solubility data in aqueous solutions containing $MgCl_2$ are extremely scarce. In this work, new experimental data of CO_2 solubility in $MgCl_2$ solutions were acquired. Thirty-three experimental points of CO_2 solubility have been reported in an original range of pressure (1.5 to 20 MPa), temperature (323.15, 373.15 and 423.15 K) and salinity (1, 3 and 5 mol/kg). Measurements were made using the potentiometric titration method. Results show that the CO_2 solubility increases with the evolution of pressure and decreases with the evolution of $MgCl_2$ concentrations. A discussion about the salting-out effect on $MgCl_2$ solutions is made, and a comparison is proposed on the same effect in aqueous systems containing calcium chloride.

INTRODUCTION

CO_2 capture and storage (CCS) in deep geological formations is an alternative for reducing the concentration of CO_2 in the atmosphere and combating the effects of global warming[1–3]. Knowledge about the solubility of carbon dioxide in aqueous electrolyte solutions is extremely important for CCS[4–7]. The deep aquifers suitable for CO_2 storage are in the temperature range between 313-423 K, with salinity ranging from 35,000 mg/L to more than 300,000 mg/L, containing mainly Cl^- and Na^+, with variable amounts of K^+, Mg^{2+} and Ca^{2+}[8,9]. Geochemical models could predict CO_2 solubility according to the temperature, pressure and composition of the aquifers[6,10–12]. However, experimental solubility points are required to reinforce their databases.

CO_2 solubility in single-salt aqueous solutions such as NaCl, $CaCl_2$ and Na_2SO_4 under CCS conditions is well documented[13–18]. The CO_2-H_2O-NaCl is the most investigated system, more than 1500 solubility points for pressure up 140 MPa, temperature comprises between 273.15-723.15 K and a molality up to 6 mol/kg have been published[4,13,17,19–25]. As far as the CO_2-H_2O-Na_2SO_4 system is concerned, to our knowledge 450 solubility points are available in the literature for pressure up to 20 MPa, a temperature range of 288.15-423.15 K and a molality 0.1-2.7 mol/kg[18,26–32]. The CO_2-H_2O-$CaCl_2$ system has been investigated as well: more than 450 points were collected. On the other hand, the literature regarding the CO_2-H_2O-$MgCl_2$ is practically scarce. Experimental studies in $MgCl_2$ solutions at high temperature, pressure and salinity are reduced to Zhao et al[33] and Tong et al[34]. However some formation brines of Na-Ca-Cl type such as Weyburn (Li et al[35] and Poulain et al[15]) or Mt Simon (Zhao et al[31] and Poulain et al[15]) contain magnesium (up to 0.049 mol/kg) as well. The acquisition of CO_2 solubility data in magnesium chloride solutions close to saturation, despite the fact that natural formations reported in the literature have concentrations between 0.05 and 0.26 mol/kg[8,9,31,36], are important in order to improve the database for geochemical models. Indeed, the optimisation

of the numerical codes on a wide concentration range (up to salt saturation) increases their robustness and limits convergence issues when ionic strength of the solutions augments. Moreover, the extension of the concentration range allows the use of the codes for other application cases like industrial waters having high Mg contents. This highlights the need to collect CO_2 solubility points for this system.

This study aims at acquire experimental data on CO_2 solubility in aqueous $MgCl_2$ solutions over a wide temperature range [323.15-423.15 K], pressures up to 20 MPa and in three different salt concentrations [1, 3 and 5 mol/kg]. Solubility is measured using the potentiometric titration method as used by dos Santos et al[18]. A discussion of the salting-out effect is also proposed, comparing to the systems containing $CaCl_2$ studied by Messabeb et al[14].

LITERATURE REVIEW

The solubility of carbon dioxide in single-salts systems has been widely studied over the years. However, with regard to the CO_2-H_2O-$MgCl_2$ system, experimental data are scarce. Six studies are reported in Table 1. Regarding the studies at high pressure, this number drops by half. Only three studies reported CO_2 solubility data at pressures other than atmospheric conditions; and at temperatures from 373.15 K, only two studies.

Table 1. Published CO_2 Solubility Data for $MgCl_2$ Solutions.

Authors	Year	Temperature (K)	Pressure (MPa)	m_{MgCl_2} (mol/kg)[a]	Analysis method
Kobe and Williams[26]	1935	298.15	0.10446	3.151	Analytical: volumetry
Yasunish and Yoshida[37]	1979	288.15-308.15	0.101325	0.356-3.967	Analytical: volumetry

He and Morse[38]	1993	273.15-363.15	0.0985-0.1006	0.1-5.0	Analytical: gas chromatography
Tong et al.[34]	2013	309.58-424.49	1.25-34.93	1.0-5.0	Synthetic: bubble point
Zhao et al.[33]	2015b	323-423	15	0.333-2	Analytical: volumetry
Jacob and Saylor[8]	2016	297	2.76-17.23	0.4-2	Analytical: Coulometric titration

[a]Molalities are expressed in moles per kilogram of water.

Kobe and Williams[26], Yasunish and Yoshida[37] and He and Morse[38] concentrated their work under atmospheric pressure and a limited temperature range up to 363.15 K.

It was only in the 2000s that studies on pressures above atmospheric pressure began to appear. Tong et al[34] measured the solubility of CO_2 in magnesium chloride solutions using the synthetic method of determining the bubble point by visual observation. The reactor is made in Hastelloy C276 and has a set of sapphire windows for the observations. Through this method, there is no need for a sampling process. The determination of solubility is determined at a fixed temperature from the known amounts of CO_2 and salt solution initially introduced into the visualization cell. Through this technique, Tong et al[34] published more than thirty-five solubility points for the CO_2-H_2O-$MgCl_2$ system.

In 2015, Zhao et al[33] acquired new data on CO_2 solubility in $MgCl_2$ solutions between 0.33-2 mol/kg, at 323.15, 373.15 and 423.15 K, however at a single pressure, at 15 MPa. The volumetric analytical method was used and eighteen points were published. In the volumetric analysis, the liquid phase containing the dissolved gases must be sampled and decompressed,

with degassing; the dissolved gases pass from the liquid phase to the gas phase. Thus, the volume of the gas is measured and converted to the number of moles by an equation of state.

Jacob and Saylor[8] measured the amount of CO_2 dissolved following acidification of the sample with $HClO_4$, trapping with an ethanol amine solution and analyzed it by coulometric titration. CO_2 dissolved in a cathode solution reacts with the ethanolamine solution to form a strong acid that causes the color of the indicator to fade. The titration return the solution to its original color. The sample CO_2 is titrated and the mass recorded in micrograms. Their study was performed only at 297 K, investigating the solubility at pressures between 2.76-17.23 MPa and at two concentrations of salt, 0.4 and 2 mol/kg.

MATERIALS AND METHODS

Chemicals products.

The names of the compounds, their respective CAS registration numbers, as well as the source and purity of the chemicals used in our work are summarized in Table 2.

Table 2. Characteristics of the Chemical Compounds Used in this Study.

Chemical name	Formula	N° CAS	Source	Purity
Carbon dioxide	CO_2	124-38-9	Air Liquide	99.7 %wt
Magnesium chloride hexahydrate	$MgCl_2.6H_2O$	7791-18-6	VWR	100% wt
Sodium hydroxide	NaOH	1310-73-2	Fisher Scientific	46/51 %wt
Hydrochloric acid	HCl	7647-01-0	VWR	0.1 ± 2 % mol/L
Pure water	H_2O	7732-18-5	Barnstead	18.2 MΩ.cm

			Smart2Pure system

The supplier states all purities values.

Apparatus Description and Operating Procedure

The acquisition of new CO_2 solubility data is carried out on an experimental laboratory pilot, consisting mainly of an autoclave with a volume of 1 L thermostatically controlled in Hastelloy C276 (the experimental pilot scheme is shown in Figure 1). It can operate at temperatures between 293.15 and 473.15 K. CO_2 loading in the autoclave is performed using a thermostated volumetric pump (Top Industrie PMHP 200-200), which could operate, for a pressure up to 20 MPa and offers automatic pressure compensation after each sampling. Once pressure and temperature are reached, agitation is maintained for about an hour (minimum) to ensure thermodynamic equilibrium. The solubility of CO_2 in the brine is determined by means of an acid-base titration: a sample of solution is taken from the reactor by means of a syringe, initially containing a solution of sodium hydroxide. The sodium hydroxide solution is in excess to ensure that all the degassed CO_2 is captured and still dissolved in the liquid phase. Then, the amount of CO_2 dissolved in the aqueous solution is determined by acid titration. Details on the CO_2 solubility measuring technique and the reactor description can be found in dos Santos et al.[18] The experimental CO_2 solubility results at a pressure range between 1.5-20 MPa and temperatures from 323.15 to 423.15 K in aqueous $MgCl_2$ solutions at the ionic strength up to 15 mol/kg are listed in Table 3.

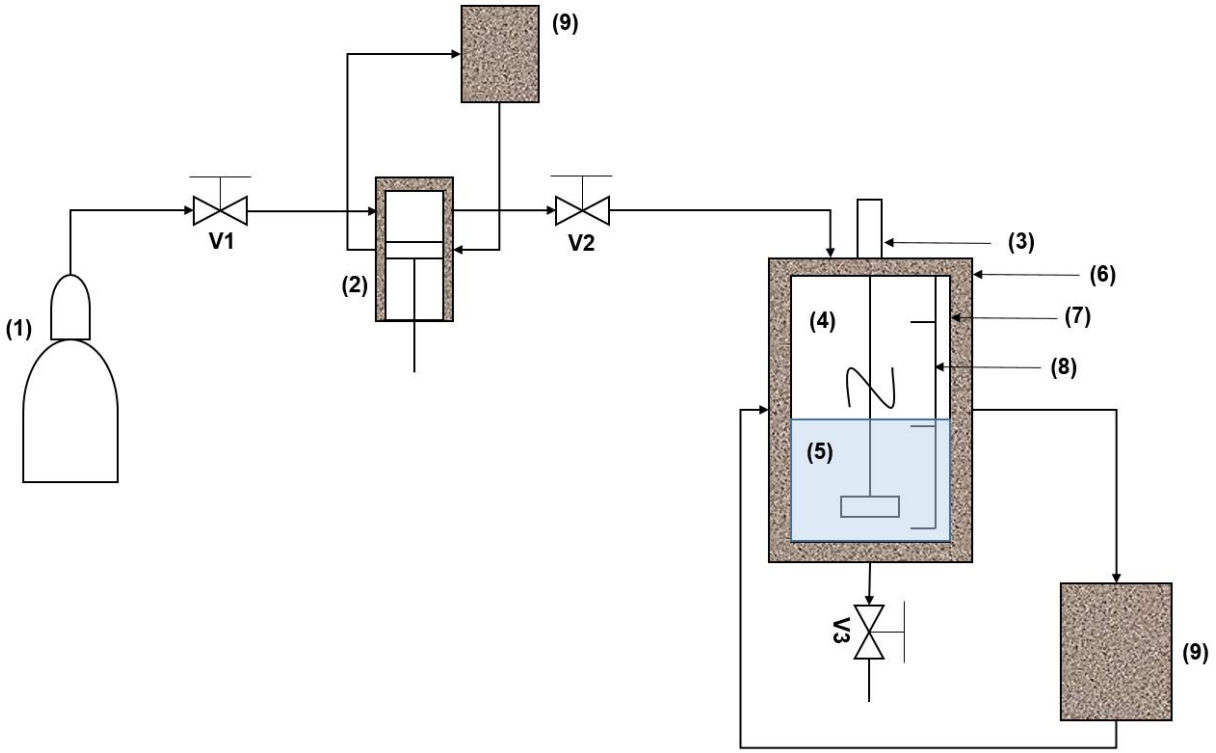


Figure 1. Scheme of the experimental cell. (1) CO_2 bottle; (2) thermostatic volumetric pump; (3) stirrer; (4) gas phase; (5) aqueous phase; (6) autoclave in Hastelloy C276; (7) double jacket; (8) thermocouples; and (9) thermostatic baths (from dos Santos et al.[18]).

Analysis

During the sampling process, a NaOH solution is used to retain the CO_2 released from the sample, as well as the amount of gas still dissolved in the liquid phase, thus converting CO_2 and HCO^{3-} into CO_3^{2-} ions according to reactions (1) and (2). Then, the determination of the quantity of carbon dioxide contained into the syringe is performed by titration using a hydrochloric acid solution (HCl) thanks to an automatic titration unit from SI Analytics (TitroLine 7800).

$$CO_{2(g)} + 2\,OH^-_{(aq)} \leftrightarrow \quad CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \qquad \textbf{(1)}$$

$$HCO_3^-{}_{(aq)} + OH^-_{(aq)} \leftrightarrow \quad CO_3^{2-}{}_{(aq)} + H_2O_{(l)} \qquad \textbf{(2)}$$

Because of the high pH, part of the dissolved magnesium in contact with the hydroxide ions reacts to form magnesium hydroxide, according to the equation (3). In aqueous systems

containing $MgCl_2$-NaOH, Mažuranić et al[39] showed that Mg^{2+} species is by far the predominant species in equilibrium with the solid phase $Mg(OH)_2$, thus forming small amounts of solid in the solution. Despite the little amount of solid, the initial NaOH concentration is calibrated in order to the excess sodium hydroxide must be sufficient to ensure reactions (1), (2) and (3):

$$MgCl_{2(aq)} + 2\,NaOH_{(aq)} \rightarrow Mg(OH)_{2(s)} + 2\,NaCl_{(aq)} \quad \textbf{(3)}$$

From the titration curve, three equivalence points can be detected, showed in the Figure 2 adapted from the previous paper (dos Santos et al.[18]).

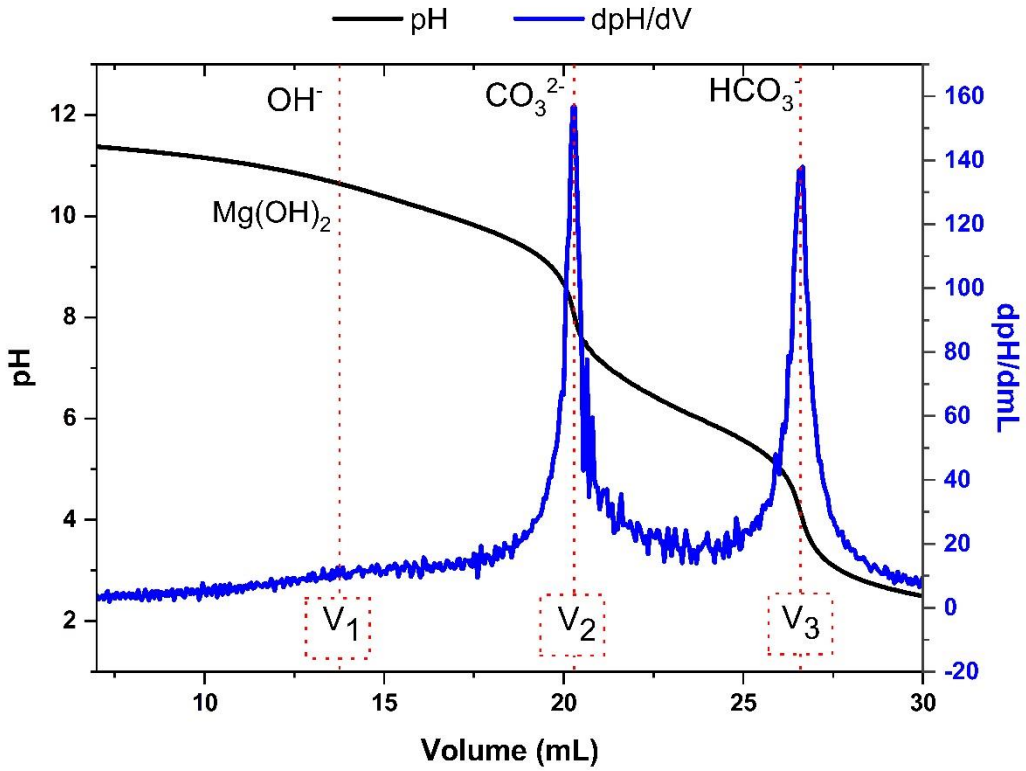


Figure 2. Curve of pH and pH derivative depending on the volume of added acid obtained from titration (adapted from dos Santos et al[18]).

The first equivalence point (V_1) corresponds to the dissolution of $Mg(OH)_2$ and the neutralization of the excess of NaOH in the sample, as shown in reaction (4). Although it is not always visible, the equivalence point V_1 is not used for the determination of the CO_2 solubility.

The second equivalence point (V_2) corresponds to the neutralization of CO_3^{2-} into HCO_3^-, according to reaction (5). Finally, the V_3 equivalence point corresponds to the transformation of HCO_3^- into H_2CO_3 (or $CO_{2(aq)}$).

$$OH^-_{(aq)} + H^+_{(aq)} \leftrightarrow H_2O_{(l)} \quad \textbf{(4)}$$

$$CO_3^{2-}{}_{(aq)} + H^+_{(aq)} \leftrightarrow HCO_3^-{}_{(aq)} \quad \textbf{(5)}$$

$$HCO_3^-{}_{(aq)} + H^+_{(aq)} \leftrightarrow H_2CO_{3(aq)} \quad \textbf{(6)}$$

Then, the amount of moles of CO_2 can be determined and checked according to the following expression:

$$\eta_{CO_2} = \eta_{CO_3^{2-}} = \eta_{HCO_3^-} = \frac{C_{HCl}\,(V_3 - V_2)}{1000} \quad \textbf{(7)}$$

The results reported in this work are the average of five successive titrations performed under each set of equilibrium conditions. Four validation criteria are used to validate the solubility points. For further information, one car refers to a previous publication (dos Santos et al.[18]).

Experimental Uncertainty

The experimental uncertainty of the present work was evaluated by the analysis of variances (ANOVA) that consists of a statistical method based on repeatability and reproducibility experiments. The principle of the ANOVA methodology was applied and discussed in a previous paper (dos Santos et al[18]). The repeatability and reproducibility experiments were performed at 373.15 K, 10 MPa and at 1 mol of $MgCl_2$ per kilogram of water. The uncertainty was obtained from the analysis of 3 different experiments (evaluation of reproducibility) performed under the same conditions with 5 titrations for each experiment (evaluation of repeatability). The average experimental uncertainty obtained from the ANOVA

calculations is equal to 1.76%. The coverage factor is derived from the Student's distribution for two degrees of freedom and a 95% confidence level.

EXPERIMENTAL RESULTS

Validation of experimental protocol with the CO_2-H_2O-$MgCl_2$ system

As shown previously, the amount of points in the literature of CO_2 solubility in aqueous $MgCl_2$ solutions is scarce, using only four analysis methods (Table 1). Since the potentiometric titration method is used for the first time for this chemical system, it must be validated. Thus, the CO_2 solubility in aqueous $MgCl_2$ solution at 1 mol/kg and at 373.15 K in the pressure range between 1.5 and 20 MPa was studied to validate the apparatus and experimental procedure. These conditions are selected because our results can be compared with data available in the literature[33,34] (Figure 3).

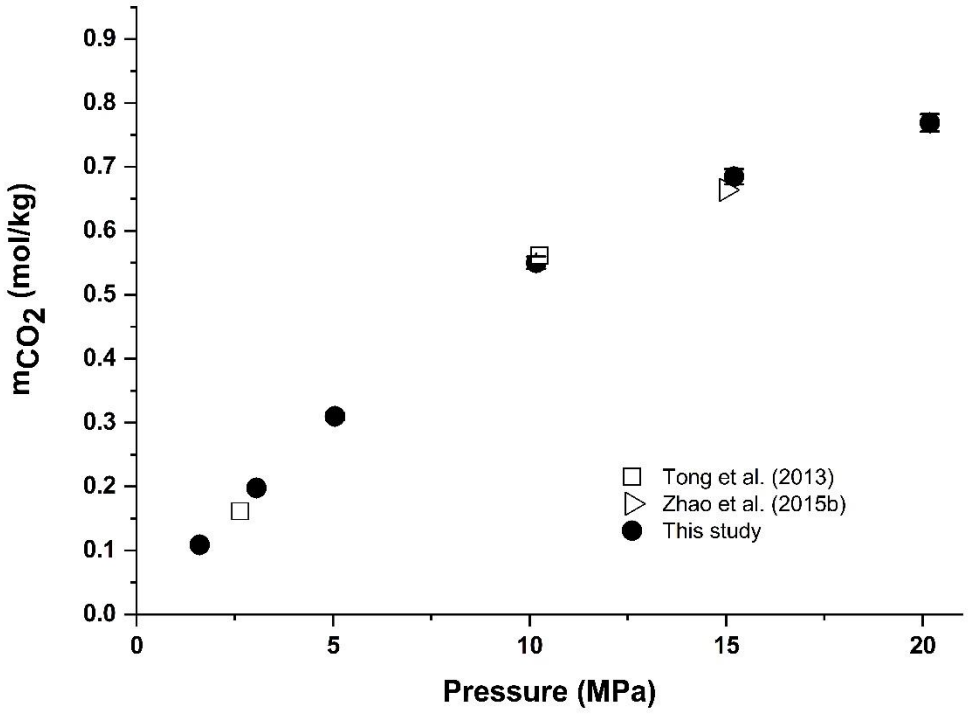


Figure 3. Solubility of carbon dioxide in a 1 mol $MgCl_2$·kg H_2O^{-1} solution at 373.15 K up to 20 MPa: this study and previous studies[33,34].

Figure 3 shows a good agreement between our results and the data in the literature. We obtained consistent results with Tong et al[34] at 10 MPa (2 % of difference) and Zhao et al[33] at 15 MPa (3.03 % of difference). In particular, it means that the potential reaction of Mg^{2+} with OH^- (Equation 3) does not influence the acid titration.

In this way, the analytical method is therefore validated for the carbon dioxide solubility results for aqueous magnesium chloride systems.

Data acquisition on the CO_2-H_2O-$MgCl_2$ system at high salinity

The results of CO_2 solubility for the CO_2-H_2O-$MgCl_2$ system were obtained at three salinities, 1, 3 and 5 mol/kg and four different temperatures, 323.15 K, 373.15 K and 423.15 K,

at a pressure range between 1.5 MPa and 20 MPa. All experimental data are reported in Table 3.

Table 3. Experimental Data of CO_2 Solubility in Magnesium Chloride Solutions at 323.15, 373.15, and 423.15 K.

m_{MgCl_2} (mol/kg)[a,b]	Temperature (K)[a]	Pressure (MPa)[a]	m_{CO_2} (mol/kg)[b]	$u(m_{CO_2})$ (mol/kg)[c]
1	323.15	1.60	0.188	0.003
		3.03	0.338	0.006
		5.11	0.527	0.009
		10.14	0.777	0.014
		15.04	0.840	0.015
		20.13	0.899	0.016
1	373.15	1.60	0.109	0.002
		3.05	0.198	0.003
		5.04	0.310	0.005
		10.17	0.550	0.010
		15.20	0.685	0.012
		20.18	0.769	0.014
1	423.15	2.98	0.140	0.002
		4.97	0.237	0.004
		10.11	0.453	0.008
		15.08	0.619	0.011
		20.02	0.753	0.013
3	323.15	5.03	0.303	0.005

		10.3	0.417	0.007
		15.08	0.462	0.008
		20.01	0.494	0.009
3	373.15	5.05	0.180	0.003
		10.12	0.299	0.005
		15.34	0.382	0.007
		20.29	0.420	0.007
3	423.15	5.06	0.132	0.002
		10.15	0.241	0.004
		15.27	0.324	0.006
		20.20	0.394	0.007
5	323.15	5.08	0.190	0.003
		10.01	0.258	0.005
		15.16	0.282	0.005
		20.29	0.323	0.006

[a]Standard uncertainties u are u(T) = 0.06 K, u(P) = 0.03 MPa and $u(m_{MgCl_2})$ = 0.001 mol/kg.

[b]Relative uncertainties u_r are $u_r(m_{CO_2})$ = 0.0176. Molalities are expressed in moles per kilogram of water. [c]$u(m_{CO_2}) = 0.0176 \cdot m_{CO_2}$ mol/kg.

Table 3 reports thirty-three points of solubility generated during the present work, where twenty-seven points are new to different conditions of T-P-m_{salt}. Still analyzing Table 3, the CO_2 solubility decreases with increasing temperature and salinity, a behavior opposite to the pressure. The increase in pressure allows the CO_2 to dissolve in greater amounts in the liquid phase. Figures 4-6 compare all the experimental points for the CO_2-H_2O-$MgCl_2$ system available at 323.15 K, 373.15 K and 423.15 K, respectively. The T-P-m_{salt} ranges presented here have not been studied so far, as shown in the isotherms present in the figures.

At 323.15 K, fourteen solubility points were obtained, thirteen of which are completely new to the literature. Only one point at 15 MPa and 1 mol/kg $MgCl_2$ solution was previously studied with a difference of less than 1 % from Zhao et al[33]. Figure 4 shows that the solubility of CO_2 increases with increasing pressure, and shows the opposite behavior when increasing the concentration, the solubility decreases.

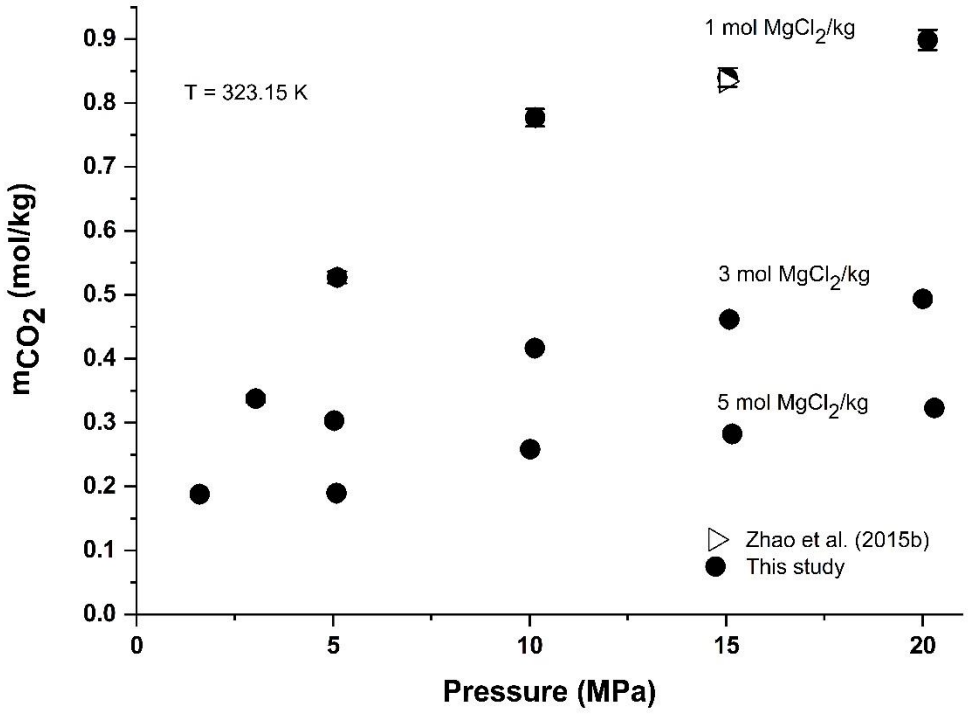


Figure 4. Solubility of carbon dioxide in a 1, 3 and 5 mol $MgCl_2 \cdot kg\ H_2O^{-1}$ solution at 323.15 K up to 20 MPa: this study and previous studies[33].

Figure 5 shows the isotherms obtained at 373.15 K à 1 and 3 mol/kg. The results at 1 mol/kg were previously discussed for validation of the experimental protocol. At 3 mol/kg, the solubility points are consistent with those presented by Tong et al[34]. Comparing CO_2 solubility points of this study to those of Tong et al[34] at 5 MPa and 15 MPa, the differences are of 2.2 % and 6.7 %, respectively.

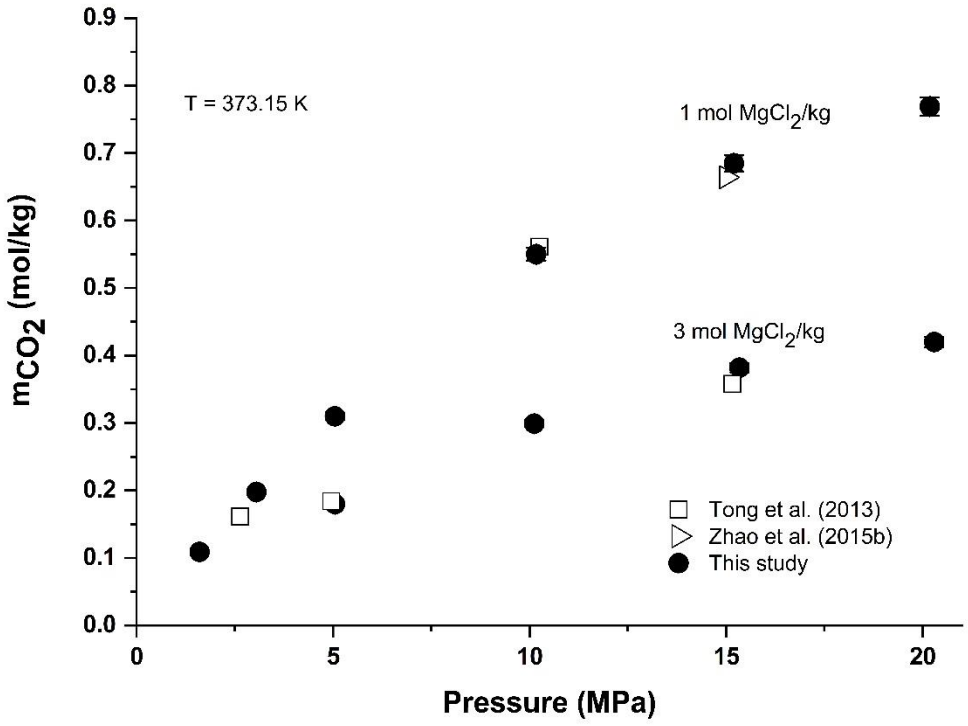


Figure 5. Solubility of carbon dioxide in a 1 and 3 mol $MgCl_2 \cdot kg\ H_2O^{-1}$ solution at 373.15 K up to 20 MPa: this study and previous studies[33,34].

At 423.15 K, as seen for 373.15 K, the set of data obtained in this study is in agreement with the experimental data available in the literature. At 1 mol/kg and 15 MPa, a slight deviation of 0.2 % is observed between the solubility point of this study and the one of Zhao et al[33]. At 20 MPa and 1 mol/kg, this deviation is of 2.17 % between the solubility points of this study and the one of Tong et al[34]. At 3 mol/kg, although there are no directly comparable data, there is a good agreement with the data published by Tong et al[34].

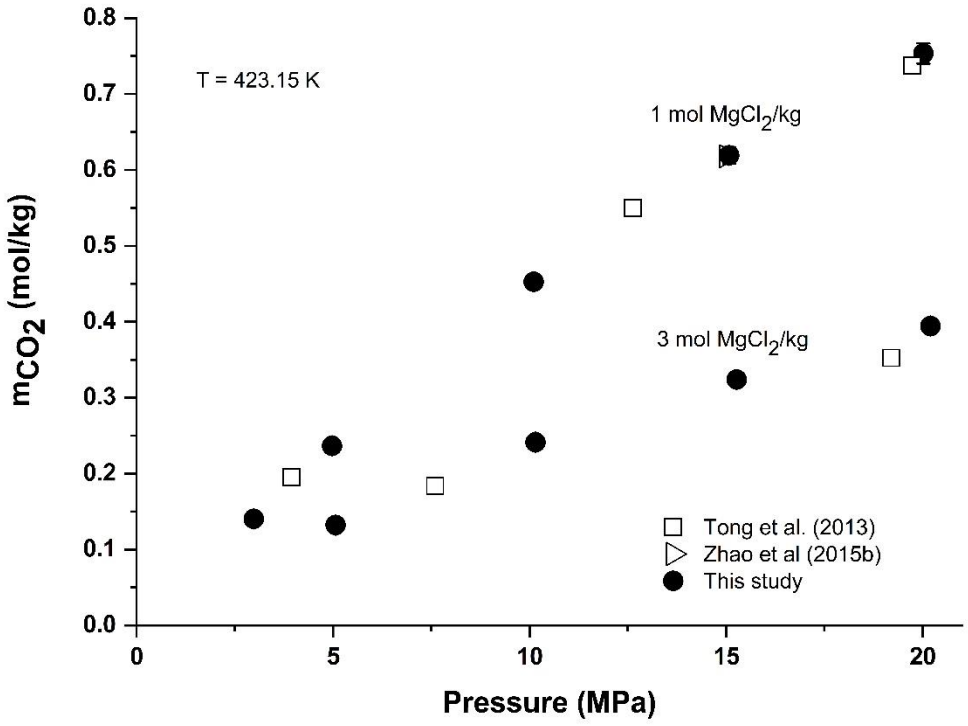


Figure 6. Solubility of carbon dioxide in a 1 and 3 mol $MgCl_2 \cdot kg\ H_2O^{-1}$ solution at 423.15 K up to 20 MPa: this study and previous studies[33,34].

DISCUSSIONS

Salting-out effect in the CO_2-H_2O-$MgCl_2$ system

Several studies on brines bringing discussions about the salting-out effect have been published. Koschel et al[40] and Mohammadian et al[41] defined the salting-out effect as the calculation of the relative difference between the solubility of CO_2 in saline solutions and the solubility of CO_2 in pure water under the same conditions of temperature and pressure. The use of this definition, represented in the following equation, was used and discussed by Messabeb et al[14], Lara Cruz et al[17] and dos Santos et al[18] as well for NaCl, $CaCl_2$ and Na_2SO_4 systems.

$$SO_{\%} = \frac{100 \times (m^0 - m)}{m^0} \quad \textbf{(8)}$$

Where m^0 is the carbon dioxide solubility in water and m is the CO_2 solubility in the brine at the same conditions of temperature and pressure. m^0 and m are expressed in terms of molality.

Table 4 shows the average values calculated for the salting-out effect and the standard uncertainties for the salting-out effect for the CO_2-H_2O-$MgCl_2$ system. The standard uncertainties values are calculated by propagating CO_2 solubility uncertainty in pure water and in the solution containing magnesium chloride. The calculation procedure is described in the paper of dos Santos et al.[18] and is discussed by Lara Cruz et al[17].

Table 4. The Average Values of Salting-Out Effect and the Calculated Standard Uncertainties for salting-out effect in Magnesium Chloride Solutions at 323.15, 373.15, and 423.15 K.

m_{CO_2} (mol/kg)	Temperature (K)	$\overline{SO_{\%}}$	$\overline{u_{SO_{\%}}}$
1	323.15	33.56	1.99
	373.15	33.02	2.01
	423.15	37.23	1.90
3	323.15	62.68	1.14
	373.15	62.75	1.14
	423.15	66.61	1.02
5	323.15	76.56	0.72

Figure 7 shows the salting-out effect calculated for the three salinities (1, 3 and 5mol/kg) in the CO_2-H_2O-$MgCl_2$ system. Table 4 and Figure 7 highlight that temperature and pressure have very little influence on the salting-out effect. On the other hand, the molality of salt has a strong influence on the solubility of carbon dioxide, consequently on the $SO_{\%}$ results. At 1 mol $MgCl_2$/kg, the salting-out effect varies between 33 and 37 %, while at 3 mol/kg the values increase, reaching between 62 and 66 %. Near $MgCl_2$ saturation, at 5 mol/kg, only one isotherm was generated (at 323.15 K), results show that the salting-out effect is 76.6 %.

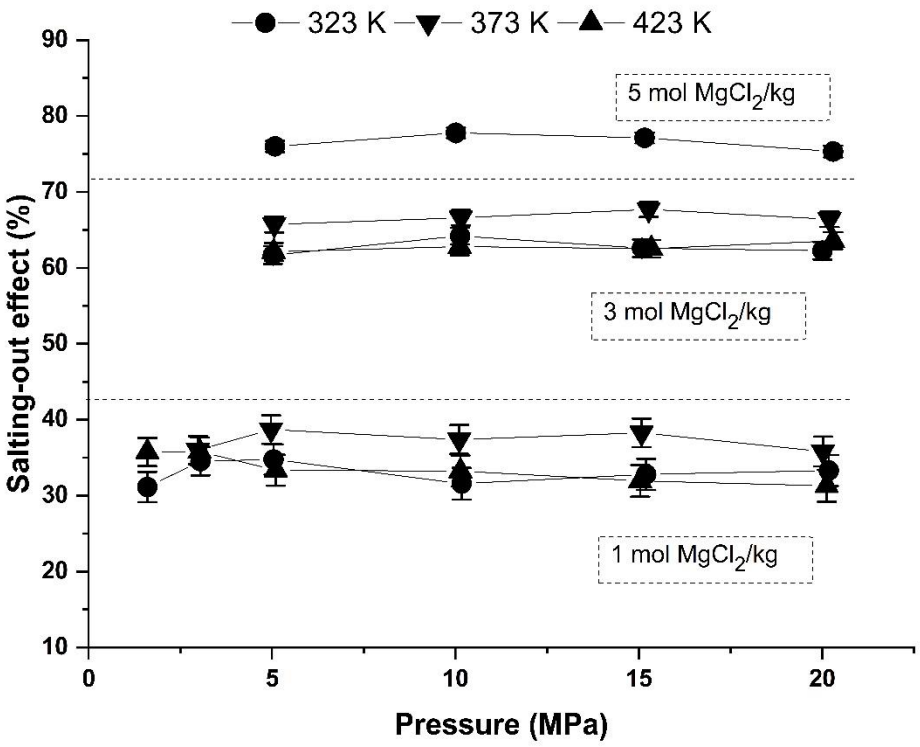


Figure 7. Evolution of the salting-out effect due to the presence of magnesium chloride as a function of molality, temperature and pressure.

Salting-out effect in the CO_2-H_2O-$MgCl_2$ and CO_2-H_2O-$CaCl_2$ systems

Salting-out effect for the systems CO_2-H_2O-$MgCl_2$ and CO_2-H_2O-$CaCl_2$ were compared to evaluate the influence of cations (Ca^{2+} and Mg^{2+}). Messabeb et al[14] published eighteen

solubility points of CO_2 in $CaCl_2$-aqueous solutions distributed between three molalities 1, 3 and 6 mol/kg. Figure 8 presents the salting-out effect for this system. Comparing Figures 7 and 8, one can observe that at 1 mol of salt/kg, the salting-out-effect is of 30-35 % for $CaCl_2$ and of 33-37 % for $MgCl_2$. At 3 mol/kg, it is of 60-65 % for $CaCl_2$ and 62-67 % for $MgCl_2$. Even though they are not directly comparable because they have different molalities - 6 mol $CaCl_2$/kg and 5 mol $MgCl_2$/kg, it is possible to notice that close to the saturation of the salt, the salting-out effect is higher. Both results, on average, are greater than 75 %.

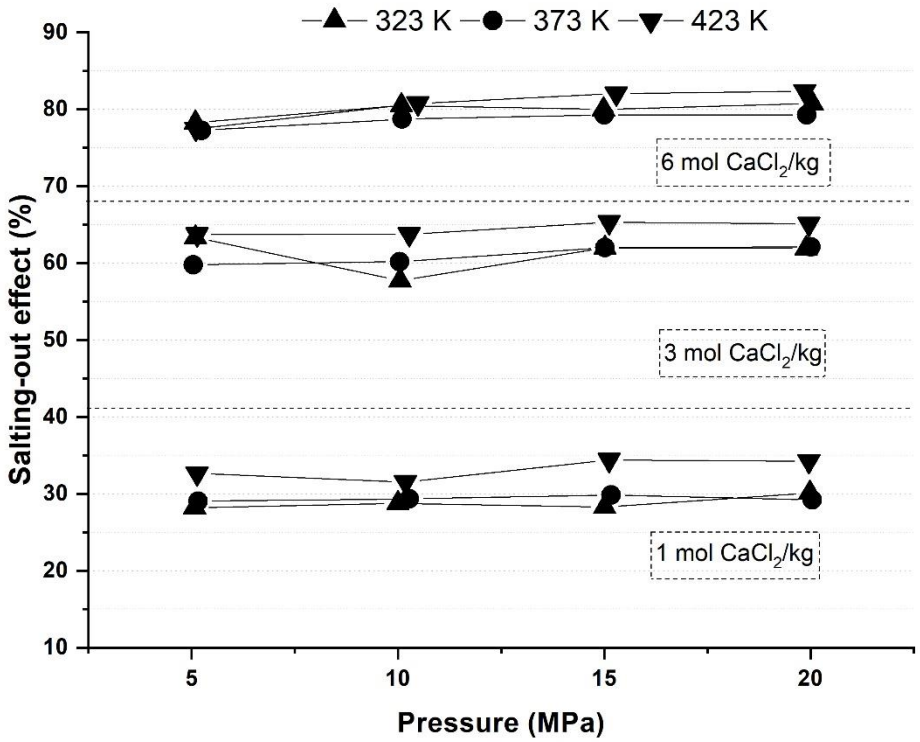


Figure 8. Comparison of the salting-out effect in the CO_2-H_2O-$CaCl_2$ system (Messabeb et al.[14]).

The similarity regarding the salting-out effect of the two systems was highlighted previously by Tong et al[34] concluding that in addition to its salinities, the charge of the ion is an important parameters in the thermodynamic equilibrium. Zhao et al[33] describe that ion-water

molecule interactions govern the behavior of CO_2 solubility in aqueous saline solutions. In the case of Mg^{2+} and Ca^{2+}, they have very similar properties (Alkaline Earth metals, similar electronic structure and same charge). In solution with chloride ions, in the configuration 1 cation-2 anions, their properties do not differ, this probably explains the similarity between solubility values, and consequently in the results of the salting-out effect.

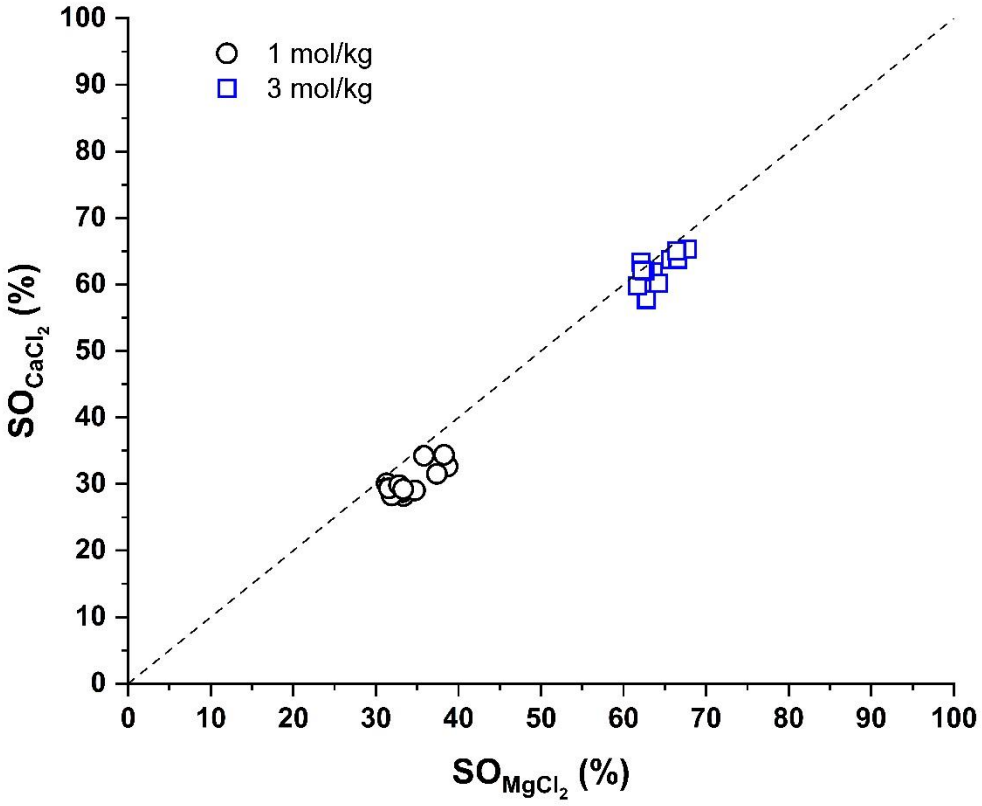


Figure 9. Comparison of salting-out effect between CO_2-H_2O-$CaCl_2$[14] and CO_2-H_2O-$MgCl_2$ systems at 1 and 3 mol/kg.

In addition, Zhao et al.[33] observed that the CO_2 solubility in aqueous $CaCl_2$ solutions is slightly higher than in aqueous solutions containing $MgCl_2$. Consequently, the salting-out effect is slightly lower for CO_2-H_2O-$CaCl_2$ systems. Zhao et al[33] describes that the charge density of Mg^{2+} is slightly higher than that of Ca^{2+} because despite the same charge number, Mg^{2+} has a smaller radius than Ca^{2+}. This slight difference results in Mg^{2+} being able to solvate more

molecules of water, leaving fewer molecules available to dissolve CO_2 than in an aqueous solution of $CaCl_2$ with the same ionic strength (ion hydration and ion-water molecule interactions[42,43]). Figure 9 directly compares the salting-out effect values between the CO_2-H_2O-$CaCl_2$ and CO_2-H_2O-$MgCl_2$ systems at 1 and 3 mol/kg. Despite the proximity of the $SO_{\%}$ values for both systems, see that the points are close to the dotted line, the $SO_{\%}$ values tend slightly towards $MgCl_2$, going in the same direction observed by Tong et al[34] and Zhao et al[33].

CONCLUSIONS

Carbon dioxide solubility was evaluated in aqueous solutions containing $MgCl_2$ at pressures up to 20 MPa, at temperatures of 323.15 K, 373.15 K and at 423.15 K and at salt concentrations of 1, 3 and 5 mol/kg. The analysis by pH-metric titration was used for the first time to study the CO_2-H_2O-$MgCl_2$ system. Our experimental results showed to be in agreement with the literature data.

The ANOVA method allowed us to quantify the experimental uncertainty of the study. Our experimental solubility data presented an uncertainty of 1.76 % obtained from repeatability and reproducibility experiment with ANOVA calculations. This study reports thirty-three new solubility points for CO_2 magnesium chloride solutions.

The salting-out effect was also calculated for our studied conditions. It has been shown that temperature and pressure have almost no influence on the results. On the contrary, the increase in salt concentration implies an increase in the salting-out effect - between 33-37 % at 1 mol/kg, 62-66 % at 3 mol/kg and 76 % at 5 mol/kg. A comparison of the salting-out effect with the CO_2-H_2O-$CaCl_2$ system was also investigated which highlights that whatever the cation is (Ca^{2+} or Mg^{2+}), the salting-out-effect is nearly the same for these two chlorinated systems.

This work enriches the amount of experimental CO_2 solubility data, aiming to help in the development of CO_2 storage technology. We saw that, just like $CaCl_2$, systems containing $MgCl_2$ can strongly influence the amount of CO_2 dissolved in aqueous solutions, consequently, in the gas storage capacity. And these experimental data can also be used to improve thermodynamic models that have parameters based on experimental data.

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Notes

The authors declare no competing financial interest.

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