

Experimental Measurements of Carbon Dioxide Solubility in Na–Ca–K–Cl Solutions at High Temperatures and Pressures up to 20 MPa

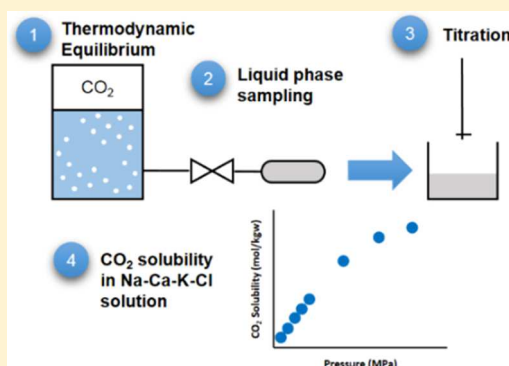
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ABSTRACT: Experimental CO₂ solubility data in brine at high pressures and high temperatures are needed in different technologies such as carbon dioxide storage or geothermal process. A lot of data have been acquired in single-salt solutions, whereas data for mixed-salt solutions remain scarce. In this study, new carbon dioxide solubility data in salt solutions have been measured. Two synthetic brines have been studied at 323, 373, and 423 K from 1 to 20 MPa. The brine 1 is composed of a mixture of NaCl and CaCl₂ and the brine 2 is made from a mixture of NaCl, CaCl₂, and KCl. Measurements have been carried out by conductimetric titration. In this study, 6 isotherms presenting 48 new solubility data have been reported. These results have been obtained in an original range of temperature, pressure, and salinity. In these conditions of temperature and pressure, we verified that an increase of the temperature or the salinity involves a decrease of the CO₂ solubility. On the other hand, an increase of the pressure implies an increase of the CO₂ solubility. Then, the obtained results were compared with the values calculated using PhreeSCALE and PSUCO₂ models. The comparison between experimental and calculated values revealed a good agreement.



■ INTRODUCTION

Geothermal energy is the exploitation of the heat provided by the earth. There is a growing interest for this renewable energy. In the case of France, a ministerial decree dated of April 2016 plans to multiply by 4 the heat production, thanks to geothermal energy by 2023.¹ For few years, several projects have been carried out more precisely in the Upper Rhine Graben.² It is essential to have good knowledge of the fluid behavior to better design the equipment to reduce the installation costs. It is also important to prevent the installation from corrosion. The choice of appropriate material remains complicated due to the composition of water (brine), the levels of both temperatures and pressures, and the presence of carbon dioxide dissolved. Indeed, carbon dioxide is the main acid gas present in the Upper Rhine Graben, and its solubility is dependent on the temperature, pressure, and composition of the brine. Consequently, models allowing an estimation of carbon dioxide solubility in brines are required. Several models have been previously developed that can calculate CO₂ solubility in the brines.^{3–8} All model parameters are fitted from the experimental data. Experimental measurements of carbon dioxide solubility in the brines are therefore essential.

Due to the recent investigations on carbon storage, much data of carbon dioxide solubility in pure water^{9–16} and single-salt solutions (NaCl,^{12,15–19} CaCl₂,^{13,20–22} KCl,^{12,21,23} etc.)

have been acquired in large range of temperatures, pressures, and molalities. Nevertheless, data for multiple-salt solutions remain scarce.^{6,11,13,24–28} The composition of the Upper Rhine Graben water is provided by Sanjuan et al. It is classified as Na–Ca–Cl type with a total dissolved solids (TDS) of approximately 90 g/L. The brine also contains potassium cation in smaller quantity.²

The aim of this work is to acquire new experimental measurements of carbon dioxide solubility in mixed-salt solutions of composition close to those encountered in the Upper Rhine Graben at 323, 373, and 423 K and pressures from 1 up to 20 MPa.

■ LITERATURE REVIEW

Carbon dioxide solubility has been widely studied in single-salt solutions at different temperatures, pressures, and molalities.^{12,13,15–23} On the other hand, studies related to the measurement of CO₂ solubility in Na–Ca–K–Cl solutions are scarce. Few experimental studies investigated the CO₂–H₂O–NaCl–CaCl₂ and CO₂–H₂O–NaCl–CaCl₂–KCl systems in the range of temperature from 323 to 423 K with pressure up

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to 20 MPa and a TDS of around 90 g/L.^{6,11,25} Compositions and operating conditions of those investigations are presented in Table 1.

In 2004, Li et al.²⁵ measured the solubility of CO₂ in the Weyburn formation at 332 K between 1.76 and 20.87 MPa. This formation water has a complex composition, but the main species are sodium ion Na⁺ at 1.2 mol/kgw, calcium ion Ca²⁺ at 0.05 mol/kgw, and chloride ion Cl⁻ at 1.4 mol/kgw.

Another study published in 2011 by Liu et al.¹¹ presented the results of CO₂ measurements in solutions containing (NaCl + CaCl₂) and (NaCl + CaCl₂ + KCl). For the system CO₂-H₂O-NaCl-CaCl₂, results were obtained at 318 K and at pressures from 2.46 to 16.02 MPa. The concentrations of NaCl and CaCl₂ in the mixture were, respectively, 0.95 and 0.5 mol/kgw. Concerning the second system CO₂-H₂O-NaCl-CaCl₂-KCl, data have been acquired at three temperatures from 308 to 328 K and pressures up to 15 MPa. Three systems of three different compositions have been studied.

More recently, Zhao et al.²⁶ acquired new solubility data of CO₂ in two synthetic brines between 323 and 423 K at pressures from 10 to 17.5 MPa. The first synthetic brine is a mixture of a lot of salts, but mainly NaCl and CaCl₂ at 1.1 and 0.14 mol/kgw. The second synthetic brine is only composed of NaCl at 1.06 and CaCl₂ at 0.22 mol/kgw. These solubility data obtained from synthetic water have been compared to the data obtained in the natural water of Mt Simon. This brine is mainly constituted of 0.96 mol/kgw NaCl and 0.16 mol/kgw CaCl₂. The measurements were achieved at 328 K between 5 and 20 MPa.

MATERIALS AND METHODS

Chemicals. Air liquid provides carbon dioxide (CAS no. 124-38-9) at 99.7% purity. Pure water (resistivity of 18.2 MΩ cm) is obtained by a Smart2Pure system. The sodium chloride salt (NaCl, 99%, CAS no. 7647-14-5), the calcium chloride salt (CaCl₂, 96%, CAS no. 10043-52-4), and the potassium chloride salt (KCl, 99%, CAS no. 7447-40-7) are provided by Acros Organics. The solution of sodium hydroxide used for the sampling step is prepared from a 46/51% wt solution of NaOH provided by ThermoFisher. Hydrochloric acid (CAS no. 7647-01-0) 0.1 mol/L ± 0.2% from VWR is used as the titrant agent.

Apparatus. The experimental apparatus used to obtain the thermodynamic equilibrium is displayed in Figure 1. It is composed of a Hastelloy C-276 autoclave of 1000 cm³, which can operate from 293.15 to 423.15 K and at maximum pressure of 20 MPa. The temperature of the cell is controlled and regulated by a thermostated bath (Lauda Proline RP 845 C). The circulation of a heat carrier fluid through the double jacket allowed to control the temperature of the cell. The temperature is measured by three platinum probes (PT100) located at three different places in the cell (gaseous phase, interface gas/liquid, and aqueous phase). The accuracy of the temperature probes is ±0.1 K. Carbon dioxide is loaded into the reactor by a thermostated volumetric pump (Top Industrie PMHP 200-200). Valve 2 is located between the pump and the cell and allows the pressure compensation during the sampling process. The pressure is measured by a pressure transducer (PA 33X) provided by Keller at an accuracy of ±0.15% of the full scale. The stirring of the gaseous phase is assured by a four-blade impeller. The stirring of the liquid phase carried out by a Rushton turbine. The device is protected by two rupture disks.

Table 1. Operating Conditions and Brine Composition of the Previous Studies and This Study for the Measurements of CO₂ Solubility in Na-Ca-K-Cl Salt Solutions

authors	year	T (K)	P (MPa)	number of data	studied brine	composition of water (mol/kgw)									
						Na ⁺	Ca ²⁺	K ⁺	Mg ²⁺	Cl ⁻	SO ₄ ²⁻	Sr ²⁺	Br ⁻	S ²⁻	
Li et al. ²⁵	2004	332	1.76–20.87	6	Weyburn (formation brine)	1.212	0.047	0.011	0.022	1.420	0.038				
Liu et al. ¹¹	2011	318	2.46–16.02	8	synthetic brine	0.95	0.5			1.45					
		308–328	2.06–15.85	24	synthetic brine	0.3	0.158	0.235		0.693					
		308–328	2.37–15.68	24	synthetic brine	0.633	0.367	0.497		1.497					
		308–328	2.06–15.85	24	synthetic brine	0.952	0.501	0.746		2.199					
Zhao et al. ²⁶	2015	323–423	10–17.5	12	PR1 (synthetic brine)	1.097	0.137	0.019	0.054	1.465	0.017	0.002	0.004		
		323–423	10–17.5	12	PR2 (synthetic brine)	1.060	0.217			1.495					
		328	5.05–20.07	4	Mt Simon (formation brine)	0.96	0.162	0.017	0.049	1.364	0.015	0.002	0.003	0.017	
this study	2018	323–423	1–20	24	brine 1 (synthetic brine)	1.2	0.2			1.6					
		323–423	1–20	24	brine 2 (synthetic brine)	1.2	0.2	0.1		1.7					

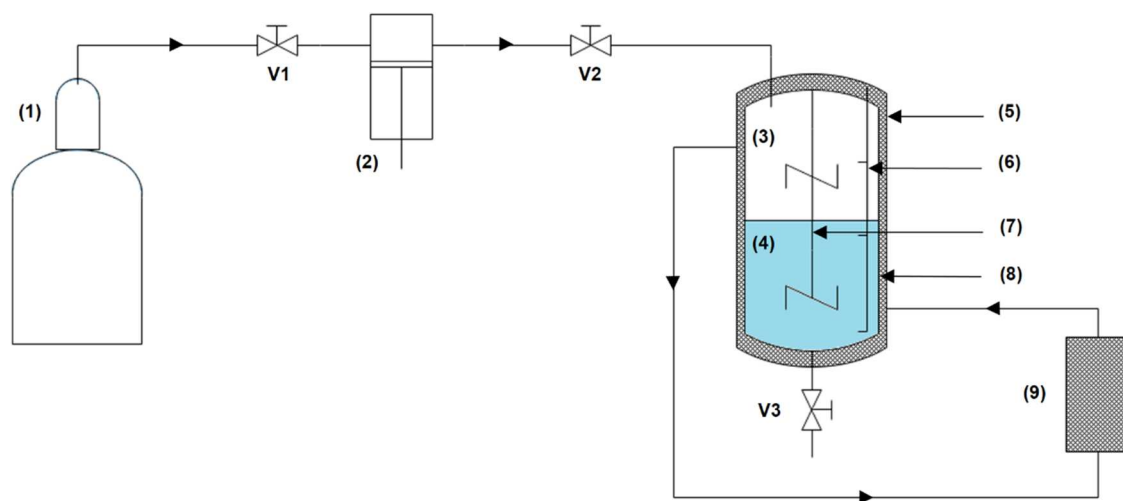
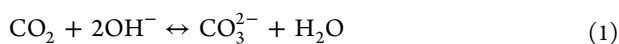


Figure 1. Scheme of the experimental device. (1) CO₂ bottle; (2) thermostated volumetric pump; (3) gas phase; (4) brine; (5) autoclave in Hastelloy C-276; (6) temperature probes; (7) stirrer; (8) double jacket; and (9) thermostated bath.

Weights less than 210 g are measured with an electronic balance from Denver Instrument (TP-214) with an accuracy of ± 0.1 mg. For the higher weights, a balance from Denver Instrument (MXX-2001) with an accuracy of ± 0.1 g is used.

The titration is realized by an automatic titrator (Titroline 800 from SI Analytics) using a pH electrode (A 162 2 M DIN ID—SI Analytics) and a conductivity electrode (LF 413T IDS—SI Analytics).

Operating Procedure. Before any experimentation, the vacuum is made in the autoclave and lines. Then, the synthetic brine is introduced into the cell. In this study, two synthetic brines were prepared. Their composition were chosen from the Upper Rhine Graben brine composition. The composition of the brines are given in Table 1. The brines are prepared by dissolving the desired quantity of salt in ultrapure water. Once the temperature reached the desired value, the valve between the high-pressure pump and the equilibrium cell is opened to load carbon dioxide (V2 on Figure 1). A heavy stirring (800 rpm) improves the carbon dioxide dissolution in the aqueous phase to reach an equilibrium faster. The sampling process consists in connecting a syringe of NaOH to the cell and withdrawing a sample of liquid phase. This trapping method is realized at atmospheric pressure. When the sample is withdrawn of the equilibrium at high pressure, a flash occurs in the syringe leading in two phases (gaseous rich in carbon dioxide and aqueous). The CO₂ in the gas phase is redissolved in the aqueous phase by homogenization. A reaction, presented in eq 1, between CO₂ dissolved and hydroxide ions occurs to form carbonate ions CO₃²⁻, which immediately react with calcium ions to precipitate calcium carbonate CaCO₃ as shown in eq 2.



At the end of the sampling process, a mixture of liquid and solid phases is present in the syringe. The content of the syringe is then analyzed.

Analysis. The measurements of carbon dioxide solubility in brine are realized by a conductimetric titration coupled with pH measurements. This method was developed in a previous

work.²² A 0.1 mol/L of hydrochloric acid solution is used as a titrant.

Two equivalent volumes are identified by the changes of slopes on the conductivity curve presented in Figure 2. This

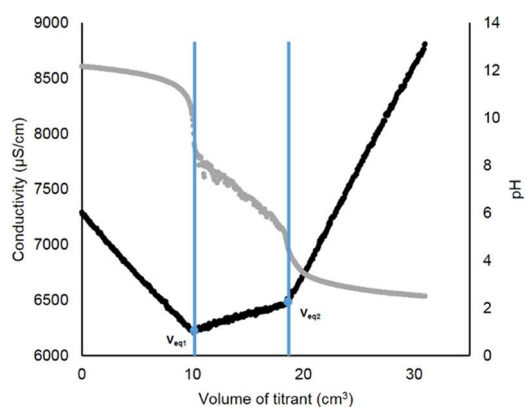


Figure 2. Conductivity (black curve) and pH (gray curve) graphs obtained from titration.

curve is composed of three parts, highlighting the evolution of the system during the titration. The pH curve is not used for the determination of the equivalent point due to the instability of the pH during the dissociation of the precipitate. Nevertheless, it is useful to confirm the reliability of the conductimetric titration, verifying that the two end points occur at the good pH value.

The first part characterized by a decrease of conductivity corresponds to the neutralization of the excess of soda in the sample according to eq 3. The first equivalent point is encountered at the end of this step, where the pH value is around 9.



Then, the addition of acid titrant leads to the dissociation of the carbonate precipitate. This is indicated by the second part of the graph, where the conductivity of the solution slightly increases. The second end point is reached when the precipitate is totally dissociated following the reaction of eq 4 and occurs at pH of around 4.

Table 2. Experimental CO₂ Solubility Measured in the Synthetic Brines

T/K ^a	brine 1			brine 2		
	P/MPa ^a	m(CO ₂) mol/kgw	error (mol/kgw) ^b	P/MPa	m(CO ₂) mol/kgw	error (mol/kgw) ^b
323	1.01	0.1342	0.0018	1.00	0.1305	0.0069
	2.01	0.2570	0.0038	2.01	0.2667	0.0032
	3.03	0.3773	0.0093	3.01	0.3758	0.0099
	4.02	0.4905	0.0097	3.99	0.5003	0.0155
	4.98	0.5783	0.0173	5.00	0.5865	0.0100
	9.92	0.8800	0.0292	10.02	0.8630	0.0317
	15.03	0.9591	0.0093	15.03	0.9057	0.0122
	19.93	1.0061	0.0093	19.97	0.9851	0.0197
373	1.05	0.0740	0.0049	1.03	0.0696	0.0020
	2.01	0.1420	0.0009	2.05	0.1511	0.0008
	3.02	0.2172	0.0028	3.02	0.2156	0.0016
	4.02	0.2801	0.0061	4.04	0.2840	0.0051
	5.09	0.3549	0.0071	5.09	0.3523	0.0097
	10.04	0.6281	0.0118	10.09	0.6036	0.0164
	15.10	0.8023	0.0113	15.09	0.7739	0.0301
	19.91	0.8710	0.0238	19.91	0.8640	0.0209
423	1.04	0.0370	0.0018	1.04	0.0372	0.0010
	1.94	0.0925	0.0012	2.00	0.0966	0.0020
	3.04	0.1566	0.0063	3.01	0.1595	0.0026
	4.09	0.2287	0.0057	4.05	0.2199	0.0036
	5.09	0.2820	0.0046	5.12	0.2804	0.0048
	10.08	0.5250	0.0100	10.08	0.5204	0.0206
	15.12	0.7208	0.0210	15.02	0.7152	0.0168
	19.91	0.8694	0.0140	19.92	0.8517	0.0136

^aStandard uncertainties are $u(T) = 0.06$ K and $u(P) = 0.03$ MPa. ^bEstimated from eq 6.

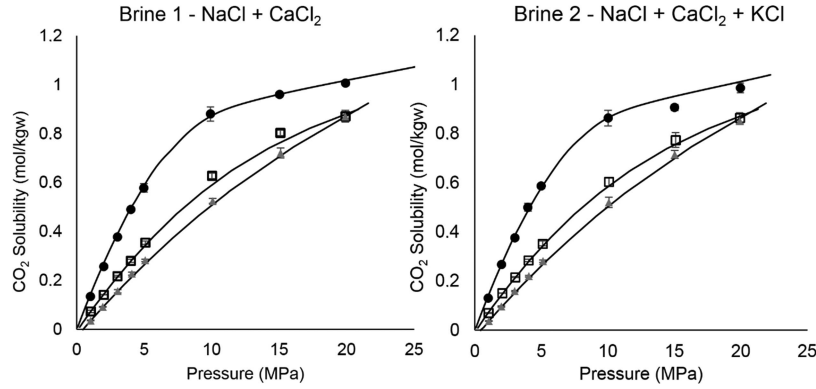
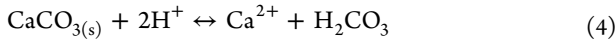


Figure 3. Experimental CO₂ solubility measurements obtained in this study in the two synthetic brines at 323 (●), 373 (□), and 423 K (silver triangle up solid) and up to 20 MPa.



The third part of the conductivity curve shows a clear increase. It is due to the addition of excess acid in the solution.

By knowing these two equivalent volumes, the amount of carbon dioxide in the aqueous phase can be determined with eq 5.

$$n_{\text{CO}_2} = n_{\text{CO}_3^{2-}} = n_{\text{CaCO}_3} = \frac{C_{\text{HCl}} \cdot (V_{\text{eq2}} - V_{\text{eq1}})}{2} \quad (5)$$

At each condition of temperature and pressure, five samples were withdrawn. The carbon dioxide solubility results from the average of these five measurements.

The uncertainty of each point is determined with a standard deviation. This is a statistic error that measures the deviation of each measurement compared to the average considering that

the values represent only part of the population. It is calculated with eq 6, where x is the solubility measurement of a given experiment, \bar{x} is the average of all measurements realized, and n is the number of experiments.

$$\text{error} = \sqrt{\frac{\sum (x - \bar{x})^2}{n - 1}} \quad (6)$$

RESULTS AND DISCUSSION

Experimental Solubility Data. In the present work, the carbon dioxide solubility was measured in two brines at three different temperatures 323, 373, and 423 K and from 1 to 20 MPa. The composition of the Upper Rhine Graben water considered as the reference has been reported by Sanjuan et al.² The two synthetic brines prepared are composed of the

main species (Na^+ , Ca^{2+} , K^+ , and Cl^-) present in the formation water. The brine 1 is a mixture of NaCl and CaCl_2 , respectively, at 1.2 and 0.2 mol/kgw. The second brine is composed of NaCl , CaCl_2 , and KCl at 1.2, 0.2, and 0.1 mol/kgw, respectively. These compositions are reported in Table 1.

The solubility data of carbon dioxide in these brines are listed in Table 2 and the isotherms are presented in Figure 3.

The results show the decrease of carbon dioxide solubility with the increase of temperature. At a given pressure, for example, around 5 MPa, the solubility decreases from 0.5783 to 0.2820 mol/kgw between 323 and 423 K. It represents a diminution of approximately 51% of the solubility. Nevertheless, we can observe a dimming of this effect at higher pressure, especially when it exceeds 10 MPa. Indeed, at 20 MPa, the solubility drops from 1.0061 to 0.8694 mol/kgw between 323 and 423 K, i.e., the solubility is reduced of 14%.

An increase of pressure leads to a better solubilization of carbon dioxide in the aqueous phase. For instance, at 323 K, the solubility of CO_2 in the brine 1 increases from 0.1342 to 0.8800 mol/kgw when the pressure rises from 1.01 to 9.92 MPa. It means that the solubility is multiplied by 6.6 when the pressure goes up by 10 MPa. However, this increase of CO_2 solubility with the pressure is attenuated when it exceeds 10 MPa. Indeed, the values of CO_2 solubility vary from 0.8800 mol/kgw at 9.92 MPa to 1.0061 mol/kgw at 19.93 MPa. The factor of solubility increase is reduced to 1.1 for a rise of pressure to 10 MPa.

The carbon dioxide solubility diminishes with the increase of the concentration of salts in the solution. In fact, in the brine 1, the CO_2 solubility is higher than that in the brine 2, since the latter has the same concentration of NaCl and CaCl_2 salts as the former but also contains KCl at 0.1 mol/kgw. Nevertheless, this decrease in solubility is very low in this study due the small amount of potassium chloride added in the second synthetic brine.

These obtained results cannot be directly compared to the literature because of the difference of the operating conditions of temperature or water composition. Nevertheless, we can observe trends in Figure 4. For instance, around 323 K, the

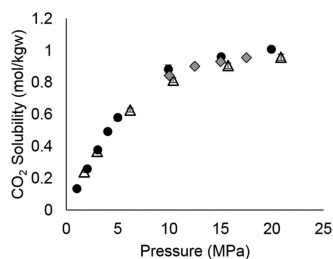


Figure 4. Observed trends between this study with the brine 1 (●) at 323 K and the previous studies of Li et al. (Δ) at 332 K and Zhao et al. with PR1 synthetic brine (silver tilted square solid) at 323 K.

solubility values obtained by Li et al. are slightly lower than the results of this study. This observation is consistent, since the temperature of the study of Li et al. is higher (332 K) than that of this study. Moreover, the complex composition of the Weyburn formation with a lot of salts also participate in reducing the CO_2 solubility.²⁵

Furthermore, we can notice that data acquired by Zhao et al. are also inferior to our data. This trend could be explained by the more complex composition of the brine of Zhao et al.²⁶

Higher is the concentration of salts, lower is the carbon dioxide solubility.

Comparison between Our Experimental Data and Calculated Values. The experimental data obtained in this study were compared with the values obtained using PhreeSCALE.^{29,30} Developments of PhreeSCALE is based on PHREEQC-V3,³¹ which is a geoscience software used to compute, among others, liquid–vapor equilibrium. In these software, the solubility of gas CO_2 is computed by Appelo et al.³¹

$$m_{\text{CO}_2} = \frac{P_{\text{CO}_2} \phi_{\text{CO}_2}}{\gamma_{\text{CO}_2}} K_{\text{H}} \exp\left(\frac{-V_{\text{m,CO}_2}(P - P_0)}{RT}\right) \frac{m_0}{P_0} \quad (7)$$

K_{H} is the Henry's constant, P is the pressure, ϕ is the fugacity coefficient, γ is the activity coefficient, $V_{\text{m,CO}_2}$ is molar volume of CO_2 , m is the molality, R is the ideal gas constant, and T is the temperature. The subscript 0 represents the standard state, P_0 is equal to 1 atm, and m_0 to 1 mol/kg.

The molar of CO_2 , $V_{\text{m,CO}_2}$ is computed using the Helgeson–Kirkham–Flowers models.³²

The Henry's constant corresponds to the equilibrium of the following reaction



Values of equilibrium constant are provided by Plummer and Busenberg.³³ The fugacity coefficient is computed using the Peng–Robinson equation of state. The activity of the coefficient of CO_2 is computed using the Pitzer model (equations are implemented in PhreeSCALE). Pitzer model is a semiempirical model used to compute the liquid-phase properties (water activity, activity coefficient, etc.). This model depends on the temperature, the molality of the species, and their interactions. The details of the equations can be found in the article published by Pitzer in 1991.³⁴

The interactions parameters for the Na–K–Ca–Cl systems are provided by Lach et al.³⁵ The interaction parameters $\text{CO}_2\text{-X}$ are those provided by the database Pitzer.dat distributed by PHREEQC-V3. Using the interactions parameters available in the literature, we can compute the solubility of CO_2 in different brines.

The experimental obtained data were also compared to the PSUCO2 model recently developed by Zhao et al.^{6,15,21} This model has been chosen because we already compare our experimental data to those obtained by these authors. Moreover, the PSUCO2 model is available on the Internet.³⁶

In Figure 5, we compare the experimental values and the predicted values. The values calculated by PhreeSCALE and PSUCO2 model represent correctly the data obtained. The maximum deviation between the experimental and the calculated values is around 10%.

CONCLUSIONS

The use of a simple analysis method developed in our previous paper allowed to obtain 48 new solubility points at three different temperatures and up to 20 MPa in two synthetic brines. The first brine was a mixture of NaCl and CaCl_2 , whereas the second one contains KCl as well. These new data have been acquired in a novel range of temperature, pressure, and salinity. These experimental data will be useful to test the models and better understand the phase behavior between CO_2 and salt solutions. From the results, we can conclude that

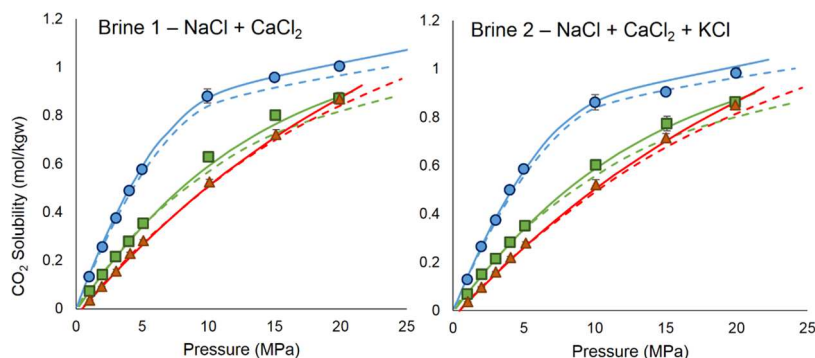


Figure 5. Comparison between experimental data obtained in the two synthetic brines at 323 (●), 373 (■), and 423 K (▲) up to 20 MPa and predicted CO₂ solubility obtained with PhreeSCALE (solid line) and PSUCO2 model (dashed line).

in the range of temperature and pressure of this study (1) an increase in pressure leads to a better dissolution of carbon dioxide in an aqueous salt solution; (2) the CO₂ solubility decreases when the temperature increases; and (3) the increase of the salinity of the brine involves a diminution of the gas solubility in the liquid phase. The obtained results have been compared to the values calculated with PhreeSCALE using the interaction parameters described in a previous paper and the PSUCO2 model. This comparison shows that the calculated values are in good agreement with the experimental data without the need for optimization.

The device and the analysis method will be used for further investigating the liquid–vapor equilibrium. One of the main prospect of this work is to study material corrosion in these environments (high pressure, high temperature, and brines) to determine the most appropriate material for geothermal equipment.

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Notes

The authors declare no competing financial interest.

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