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Experimental measurements and modelling of thermodynamic properties of NaCl-CaCl₂ aqueous solutions up to high temperatures and CO₂ pressures

Arnault Lassin¹, Pedro Felipe dos Santos², Marion Ducouso², Pierre Cézac², Laurent André^{1,3}

¹ BRGM, 3 avenue C. Guillemin, 45060 Orléans, France

² Université de Pau et des Pays de l'Adour, E2S UPPA, LaTEP, Pau, France

³ Université d'Orléans, CNRS, BRGM, ISTO UMR 7327, 45071 Orléans, France

a.lassin@brgm.fr

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ABSTRACT

Geothermal energy currently uses hot deep brines. However, their exploitation can raise issues specifically due to their high salinity and the variations of temperature and pressure during their pumping. Main disorders are the potential degassing of fluids, including CO₂, but also the precipitation of minerals in the facilities (production/injection wells, heat exchangers...) involving expensive maintenance works.

The chemical and physical properties of the geothermal fluids are key control factors, determining the heat-carrying potential for energy transfer over the lifetime of the well. An improved understanding of the properties of these fluids is therefore necessary to avoid exploitation issues as mentioned above, and even optimize site developments and operations. Additionally, the future for exploration, prediction and utilization of novel geothermal technologies – namely enhanced geothermal systems and supercritical resources – is intimately tied to the understanding of the physical and chemical properties of the reservoir fluids.

The REFLECT project aims to improve the accuracy and consistency of key thermodynamic and kinetic input data in order to optimize sustainable geothermal reservoir management, power and heat production and reinjection strategies. Geochemical modelling, which relies on the measurement of high quality data, is one of the numerical approaches needed to reach this goal.

In a first step, published laboratory measurements were collected to estimate the properties of saline chloride fluids (NaCl and CaCl₂) containing dissolved CO₂. A focus was made on properties such as CO₂ solubility for medium temperature brines up to 473.15 K.

In parallel to data collection, a modelling work was set-up to calculate these fluid properties using the specific tool named PhreeSCALE. Relying on the Pitzer

equations, it is able to compute thermal and volumetric properties of aqueous solutions such as heat capacity or density of the geothermal fluids.

The methodology relies on successive steps that include the estimation of Pitzer's interaction parameters for the CaCl₂-H₂O, CaCl₂-NaCl-H₂O, and CaCl₂-NaCl-CO₂-H₂O systems to reproduce literature data. The model applies from 298.15 up to 473.15 K, and to elevated pressures.

1. INTRODUCTION

Geothermal energy currently uses hot deep brines. However, their exploitation can raise issues specifically due to their high salinity and the variations of temperature and pressure during their pumping. Main disorders are the potential degassing of fluids including CO₂, but also the development of scaling in the facilities (production/injection wells, heat exchangers...) involving expensive maintenance works (Eroini, 2011; Boch et al., 2017; Todd and Blumle, 2022).

Moreover, these processes are interrelated since the degassing of CO₂ is generally concomitant with water evaporation, pressure and temperature decrease during heat extraction operations (Alt-Epping et al., 2013). The chemical disturbances induced by the outgassing (increase of concentrations and of pH) strongly favour mineral precipitation, and thus scaling (Thomas and Gudmundsson, 1989; Benoit, 1989; Simmons and Christenson, 1994). It is therefore of major interest to develop a sound knowledge of CO₂ solubility in hot and pressurized brines. The REFLECT project (<https://www.reflect-h2020.eu/>) aims to improve the accuracy and consistency of key thermodynamic and kinetic input data in order to optimize sustainable geothermal reservoir management, power and heat production and reinjection strategies. More specifically and in line with the scaling issues, one objective of the project is to improve the modelling capacity to predict CO₂ degassing in the facility.

Because of the environmental issues related to the climate change resulting (at least partly) from human activity, the exploitation of the underground as a source of decarbonated energy, or as a large volume to store permanently waste gases (e.g., CO₂) or temporarily energy vectors (natural gas, hydrogen, heat), has regained much interest (Kelemen et al., 2019; Zivar et al., 2021; Mahon et al., 2022). The knowledge developed in these domains can be beneficial to geothermal energy. This is particularly true for experimental CO₂ solubility data in brines, acquired in the context of the carbon capture and underground storage technology (CCUS) (Carvalho et al., 2015; Mohammadian et al., 2015; Chabab et al., 2019).

In this context, various chemical systems have been studied until recently and are now well known (dos Santos et al., 2021a, 2021b, 2020; Messabeb et al., 2017, 2016; Poulain et al., 2019; and references therein). However, many chemical systems still need to be investigated or their description improved. As an additional contribution to these developments, the present work focuses on the CaCl₂-NaCl-CO₂-H₂O system. It relies on the collection of bibliographic CO₂ solubility data and on their numerical exploitation to develop a robust geochemical model with predictive capabilities.

2. BACKGROUND AND METHOD

2.1 Collection of experimental CO₂ solubility data

In order to study the CaCl₂-NaCl-CO₂-H₂O system, focus must be made on the simpler CaCl₂-CO₂-H₂O and NaCl-CO₂-H₂O systems first. The latter is already well known (see the extensive experimental data collection by dos Santos et al., 2021b) and described with dedicated models (dos Santos et al., 2021b; Duan et al., 2006; Shi and Mao, 2017; Zhao et al., 2015). The former is a little less known, despite some thermodynamic models have been developed (Appelo, 2015; Bastami et al., 2014; Shi and Mao, 2017; Springer et al., 2012; Zhao et al., 2015). New experimental CO₂ solubility data in CaCl₂ synthetic brines have been acquired since (Lara Cruz et al., 2021; Messabeb et al., 2017; Poulain et al., 2019). They cover ranges of pressures and temperatures that are complementary to previously published data. Indeed, they either extend the pressure and salinity ranges or refine the pressure intervals between measurements (see below). In summary, the temperature, pressure and CaCl₂ concentration values covered by all published CO₂ solubility data range between 293 and 424 K, 0.1 and 40 MPa, and 0 and 6.3 mol·kg⁻¹, respectively. Some inconsistencies can be noticed among all these sets of data and, in some occasions, within datasets from same authors. More specifically, Prutton and Savage (1945) indicate experimental uncertainties of 3%, but when compared with other datasets, discrepancies of up to 20% can be found. Bastami et al. (2014) do not provide any indication on their uncertainties, which complicates the comparison with other datasets and models. Tong et al. (2013) and Liborio (2017) also reported experimental errors of up to 10 and 15% in their

respective datasets. Consequently, a lower weight was given to these datasets while developing the geochemical model for the CaCl₂-CO₂-H₂O system.

Experimental CO₂ solubility data for the CaCl₂-NaCl-CO₂-H₂O system were essentially acquired by Lara Cruz et al. (2021), Liu et al. (2011), Poulain et al. (2019), Zhao et al. (2015a), representing almost 70 data points. The temperature, pressure, NaCl and CaCl₂ concentration values covered by these data range between 318 and 453 K, 1.2 and 40 MPa, 0.95 and 2.99 mol·kg⁻¹, and 0.2 and 0.67 mol·kg⁻¹, respectively.

2.2 Numerical modelling

Thermodynamic equilibrium between the CO₂-rich phase and the aqueous solution in the autoclave can be described according to the equality of the chemical potential of CO₂ in the two phases. This results in the following equation that corresponds to Henry's law (Appelo et al., 2014):

$$m_{CO_2} = \frac{\varphi_{CO_2}^{vap} \times P \times y_{CO_2}}{\gamma_{CO_2}^m} \times K_H \times \exp\left(-\frac{V_{m,CO_2}(P-P_0)}{RT}\right) \times \frac{m_0}{P_0} \quad [1]$$

m_{CO_2} is the molality of aqueous CO₂ (mol·kg⁻¹), $\varphi_{CO_2}^{vap}$ is the fugacity coefficient of CO₂ in the gas (or supercritical) phase (unitless), P is the total gas pressure (Pa), y_{CO_2} is the mole fraction of CO₂ in the gas phase (unitless), $\gamma_{CO_2}^m$ is the activity coefficient of aqueous CO₂ (unitless), K_H (unitless) is the Henry's law constant for the dissolution reaction of CO₂(g) into CO₂⁰, V_{m,CO_2} is the partial molar volume of aqueous CO₂ (m³·mol⁻¹), P_0 is the reference pressure (= 10⁵ Pa), R is the ideal gas constant (= 8.31446 J·mol⁻¹·K⁻¹), T is the absolute temperature (K) and m_0 is the reference molality (= 1 mol·kg⁻¹).

m_{CO_2} and y_{CO_2} are the unknowns of equation [1], P and T are constraints, V_{m,CO_2} is described by the HKF equation of state for aqueous species (Helgeson et al., 1981; Tanger and Helgeson, 1988), $\varphi_{CO_2}^{vap}$ is determined by the Peng-Robinson equation of state, $\gamma_{CO_2}^m$ is computed according to the Pitzer equations. More details about the latter equations can be found in Pitzer (1991). More specifically, the activity coefficient of aqueous CO₂ can be expressed as follows (dos Santos et al., 2021b):

$$\ln(\gamma_{CO_2}^m) = 2m_{CO_2}\lambda_{CO_2,CO_2} + \sum_{c=1}^{n_c} 2m_c\lambda_{CO_2,c} + \sum_{a=1}^{n_a} 2m_a\lambda_{CO_2,a} + \sum_{c=1}^{n_c} \sum_{a=1}^{n_a} m_c m_a \zeta_{CO_2,c,a} \quad [2]$$

λ_{CO_2,CO_2} , $\lambda_{CO_2,c}$, $\lambda_{CO_2,a}$ are binary Pitzer interaction parameters between two molecules of CO₂⁰, one molecule of CO₂⁰ and a cation c , and one molecule of CO₂⁰ and an anion a , respectively. $\zeta_{CO_2,c,a}$ is a ternary Pitzer interaction parameter between one molecule of CO₂⁰, a cation c and an anion a . n_c and n_a are the number of different cations and anions in the solution, respectively. As the Pitzer equation are semi-empirical, these specific interaction parameters cannot be determined *a priori* and must be fitted using

experimental data, like gas solubility in brines amongst others.

In the present work, geochemical calculations are done at thermodynamic equilibrium using the PhreeSCALE software (Lach et al., 2016). It results from an evolution of PhreeqC (Parkhurst and Appelo, 2013), a software that is widely used in the geochemical modelling community. The Pitzer equations that are implemented in these two calculation codes can handle partial dissociation of electrolytes but are limited to ionic strength-dependent virial contributions of second order. Compared to PhreeqC, PhreeSCALE includes a more rigorous treatment of the partial derivatives of the Pitzer equations of the excess Gibbs free energy of the solutes. Consistent thermal and volumetric properties of aqueous solutions such as heat capacity or density of geothermal fluid can be calculated too.

To fit the specific interaction parameters involving CO_2^0 , an additional numerical tool named PEST (Doherty, 2004) is used in combination with PhreeSCALE. Starting from an initial set of interaction parameter values, PEST launches PhreeSCALE, which computes the concentration of dissolved CO_2 . PEST then compares the results to the experimental values. As long as convergence criterion is not met, PEST suggests a new set of parameter values and launches PhreeSCALE again. When the convergence criterion is met, the fitting procedure stops and the last set of parameters proposed by PEST is saved.

The development of a consistent thermodynamic database is a long term process, and thus necessarily incremental. Therefore, the procedure above must be applied based on pre-existing models for the investigated brines. In the present work, we use the chemical model recently developed by Lassin et al. (submitted) for the $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ system, and the one developed by (dos Santos et al., 2021b) for the $\text{CO}_2\text{-NaCl-H}_2\text{O}$ system. Indeed, the models mentioned previously (section 2.1) mostly apply to the solubility of CO_2 in simple binary brines, while the objective here is to consider a mixture of brines whose description is not a straightforward addition of two models for binary brines.

The model of Lassin et al. (submitted) for the $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ system is based on the Pitzer equations and includes the partial dissociation of the CaCl_2 electrolyte. The standard partial molar properties of the aqueous species involved (namely, Ca^{2+} , Cl^- , CaCl^+ , and CaCl_2^0) are described according to the HKF equation of state (Sverjensky et al., 1997). The model is able to describe the osmotic coefficient of the CaCl_2 aqueous brines and salt solubility up to 523 K. It is also able to describe salt solubility in the $\text{NaCl-CaCl}_2\text{-H}_2\text{O}$ system over the whole range of mixture ratios, at least up to 403 K (experimental solubility data not available at higher temperatures). Moreover, the models of Lassin et al. (submitted) and dos Santos et al. (2021b) are consistent with each other since they both include the interaction parameters of Lach et al. (2017) for the $\text{NaCl-H}_2\text{O}$ system.

3. RESULTS AND DISCUSSION

3.1 CO_2 solubility in the $\text{CaCl}_2\text{-H}_2\text{O}$ binary system

Only two new specific binary interaction parameters involving the CO_2^0 aqueous species were found necessary to describe CO_2 solubility in CaCl_2 and $(\text{NaCl} + \text{CaCl}_2)$ brines, up to 6 M CaCl_2 , 40 MPa of CO_2 and 423 K. These parameters, namely $\lambda_{\text{CO}_2,\text{Ca}^{2+}}$ and $\lambda_{\text{CO}_2,\text{CaCl}^+}$ are temperature dependent, according to the following equation:

$$\lambda_{\text{CO}_2,c}(T) = A + BT + C/T \quad [3]$$

The corresponding coefficients are given in Table 1.

Table 1: Coefficients for the temperature function [3] of the $\text{CO}_2^0\text{-Ca}^{2+}$ and $\text{CO}_2^0\text{-CaCl}^+$ specific interaction parameters.

Parameter	A	$B \times 10^3$	C
$\lambda_{\text{CO}_2,\text{Ca}^{2+}}$	1.45781	-1.44809	-258.144
$\lambda_{\text{CO}_2,\text{CaCl}^+}$	-4.05504	5.83521	708.627

Results are plotted in Figure 1 for the solubility of CO_2 in CaCl_2 binary aqueous solution as a function of CO_2 pressure, and at various CaCl_2 concentrations and temperatures. For each condition, errors σ were calculated according to the following equation (Christov and Møller, 2004), and reported in Table 2:

$$\sigma = \sqrt{\frac{\sum (m_{\text{CO}_2,\text{exp}} - m_{\text{CO}_2,\text{calc}})^2}{N}} \quad [4]$$

where $m_{\text{CO}_2,\text{exp}}$ and $m_{\text{CO}_2,\text{calc}}$ are the experimental and calculated molalities of dissolved CO_2 , respectively, at a given condition of CaCl_2 concentration, pressure and temperature. The sum covers all conditions of pressure at a given temperature and CaCl_2 concentration, represented by N data points.

Table 2: Errors σ between experimental and calculated CO_2 solubility in CaCl_2 brines, for each condition of temperature and CaCl_2 concentration.

Temperature (K)	CaCl_2 ($\text{mol} \cdot \text{kg}^{-1}$)	Number of data points N	Error σ
323	1	11	0.015
	3	4	0.013
	6	4	0.013
373	1	30	0.043
	3	7	0.035
	6	5	0.009
423	1	17	0.022
	3	8	0.032
	6	4	0.011

Figure 1 and Table 2 show that the model satisfactorily describes the experimental data within their dispersion intervals, between 323 and 423 K, and up to 6 M CaCl_2 . Beyond the pressure values investigated experimentally, the calculated CO_2 solubility smoothly increases, demonstrating the numerical stability of the

model and suggesting extrapolation capabilities with respect to pressure, temperature and salinity.

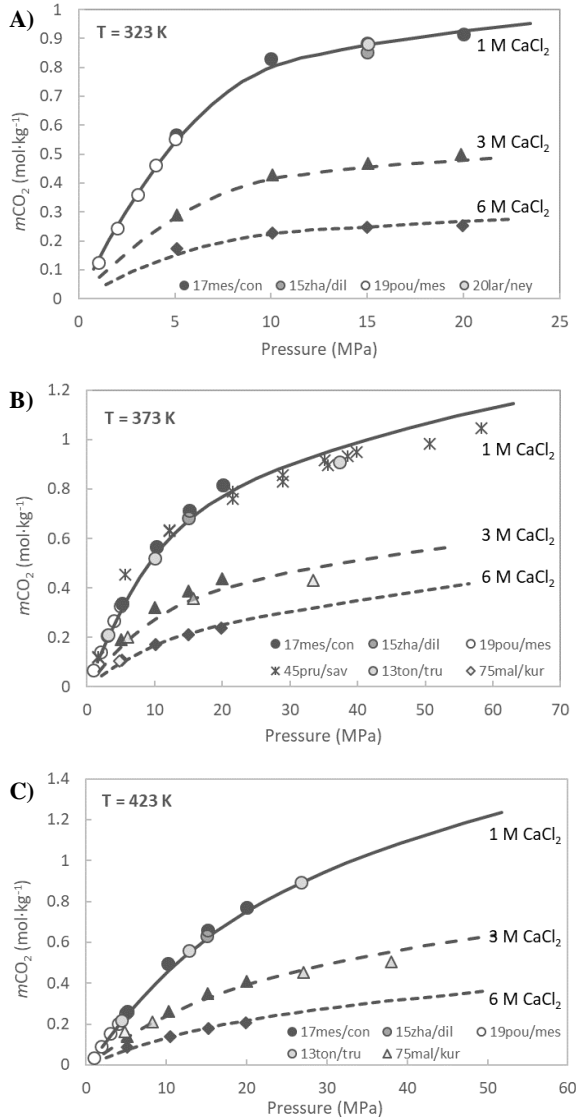


Figure 1: CO₂ solubility in CaCl₂ aqueous brines as a function of pressure, for various CaCl₂ concentrations, at A) 323 K, B) 373 K, and C) 423 K. Symbols: experimental data (45pru/sav = Prutton and Savage, 1945; 75mal/kur = Malinin and Kurovskaya, 1975; 15zha/dil = Zhao et al., 2015; 13ton/tru = Tong et al., 2013; 17mes/con = Messabeb et al., 2017; 19pou/mes = Poulain et al., 2019; 20lar/ney = Lara Cruz et al., 2021). Lines: model (this work).

3.2 CO₂ solubility in the ternary NaCl-CaCl₂-H₂O system

Results obtained for the solubility of CO₂ in (CaCl₂ + NaCl) aqueous brines are plotted in Figure 2. Errors σ are reported in Table 3. They show that the calculated solubility of CO₂ can reproduce satisfactorily the

experimental data using only binary CO₂-cation interaction parameters (where cation = Na⁺, Ca²⁺ or CaCl⁺). Note that the set of Pitzer interaction parameters proposed by dos Santos et al. (2021b) and used in the present study, can describe the solubility of CO₂ in NaCl brines up to 473 K. Therefore, it is not surprising that our model is able to describe the solubility of CO₂ in the (NaCl + CaCl₂) aqueous mixture at 423 K.

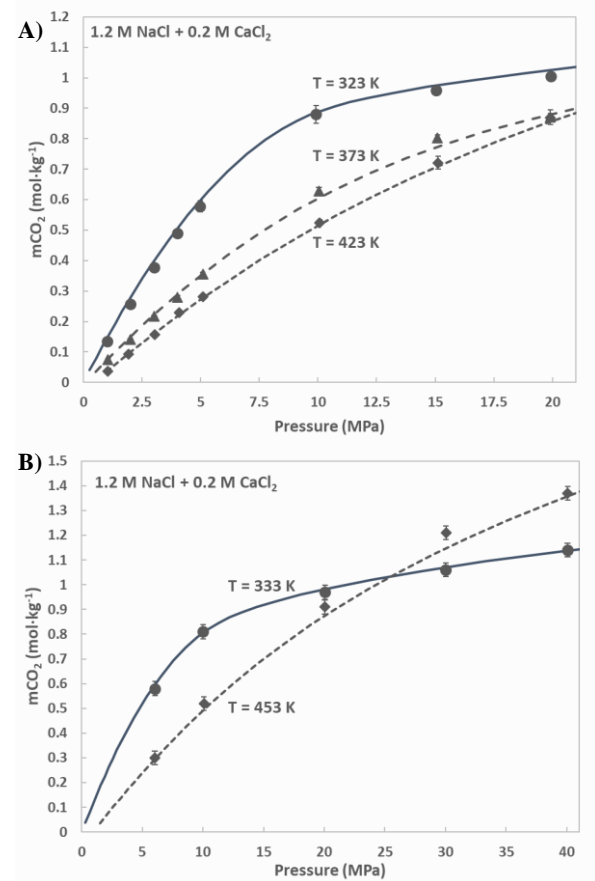


Figure 2: CO₂ solubility in (NaCl + CaCl₂) aqueous brines as a function of pressure, at A) 323, 373, and 423 K, and B) 333 and 453 K. Symbols: experimental data, A) Poulain et al. (2019), B) Lara Cruz et al. (2021). Lines: model (this work).

Table 3: Errors σ between experimental and calculated CO₂ solubility in (NaCl + CaCl₂) brines, for each condition of temperature.

Temperature (K)	Number of data points N	Error σ
323	8	0.022
333	5	0.018
373	8	0.016
423	8	0.035
453	5	0.086

These encouraging results make it possible, by means of geochemical modelling, exploring the solubility of CO₂ in extended (NaCl + CaCl₂) aqueous mixtures. Thus, a parametric study was done considering the whole range of compositions for the $x\text{NaCl} + (0.5-x/2)\text{CaCl}_2$ mixture, where $0 < x < 1$, for three total Cl concentration (i.e., 1.6, 3.6 and 6 mol·kg⁻¹), three temperatures (i.e., 323, 373, and 423 K), and two CO₂ fugacity values (i.e., 5 and 15 MPa).

The latter constraint is a convenient way to set the concentration of dissolved CO₂. Indeed, according to Henry's law and because the chloride content is constant when the mole fraction x of Na varies from 1 to 0, the molality of dissolved CO₂ is proportional to its fugacity in the CO₂-rich phase. Thus, the effect of the brine mixture composition on the calculated equilibrium pressure can be compared for different salinities. Results are plotted in Figure 3.

They suggest that whatever the temperature and the chloride concentration, the composition of the NaCl+CaCl₂ mixture does not affect the pressure required to equilibrate the system with a CO₂ fugacity of 5 MPa. At higher CO₂ fugacity, namely 15 MPa, the calculated equilibrium pressure varies with the chemical composition of the brine mixture. This variation is more pronounced at high salinity with large Na proportions, and lower temperatures. In these conditions, increasing Ca (at the expense of Na) increases the pressure required to equilibrate with the CO₂ fugacity (Figure 3-A). In other words, the presence of Ca in the brine has a salting-out effect on CO₂. This effect can be reversed at high temperature and high salinity: the equilibrium pressure slightly decreases when small quantities of Ca replace Na at 423 K (Figure 3-C). At higher Ca content (c.a. 5 mol.%), the salting-in effect of Ca stops and turns to a salting-out effect.

3. CONCLUSIONS

A new set of specific interaction parameters has been developed to describe the solubility of CO₂ in CaCl₂ + NaCl aqueous brines according to a geochemical model based on the HKF and Pitzer equations. The model is valid for CaCl₂ concentrations up to 6 M, temperatures up to 453 K and pressures up to 40 MPa.

Predictive calculations using this model suggest that, at high pressure, low temperature and high NaCl concentration, the presence of CaCl₂ in the mixture increases the salting-out effect of the brine, event at low Ca/Na ratios.

An extension of the model to larger chemical systems may help describing the behaviour of brines that are more representative of the fluids involved in geothermal exploitation plants.

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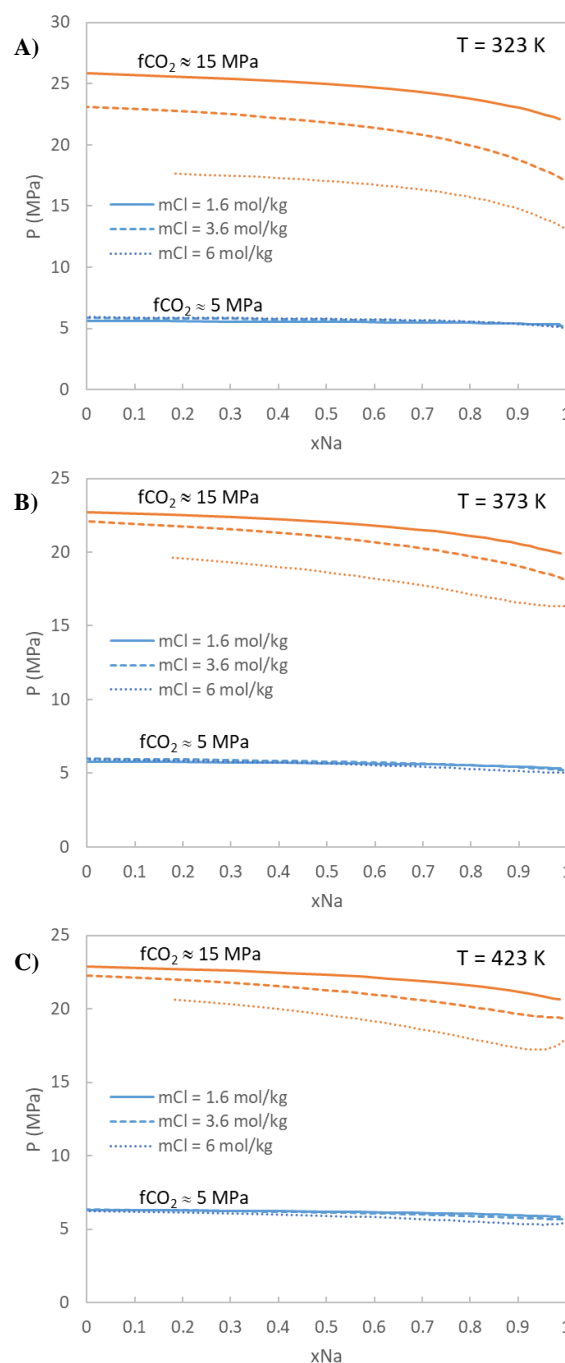


Figure 3: Predicted CO₂ solubility in (NaCl + CaCl₂) aqueous brines as a function of Na mole fraction, for Cl molality of 1.6, 3.6 and 6 M, CO₂ fugacity of 5 and 15 MPa, at A) 323, B) 373, and C) 423 K.

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